CARBON CAPTURE PROGRAM R&D

COMPENDIUM of CARBON CAPTURE TECHNOLOGY

2024

U.S. Department of ENERGY
NATIONAL ENERGY TECHNOLOGY LABORATORY

DISCLAIMER

TABLE OF CONTENTS

OVERVIEW

The U.S. Department of Energy's (DOE) Office of Fossil Energy and Carbon Management (FECM) administers a comprehensive, multi-pronged approach for carbon management by developing both point source carbon capture and carbon dioxide removal technologies. When coupled with secure geologic carbon storage or carbon dioxide (CO_2) conversion into long-lasting products, these technologies will support the United States in achieving ambitious goals for a greenhouse gas (GHG)-neutral economy by 2050, a carbon-pollution-free power sector by 2035, and a 50% reduction from 2005 levels in economy-wide net GHG pollution by 2030.

DOE's National Energy Technology Laboratory (NETL) manages both the Point Source Carbon Capture and Carbon Dioxide Removal Programs. NETL is progressing research and development (R&D) of advanced CO_2 capture technologies for fossil fuel-based power generation and industrial sources and carbon dioxide removal co-located with low-carbon energy sources.

The Point Source Carbon Capture Program is developing the next generation of advanced CO_2 capture concepts and accelerating commercially deployable solutions that can be applied to a wide spectrum of CO_2 emissions sources. The deployment of point source carbon capture technologies will decarbonize existing infrastructure in the power and industrial sectors, including hydrogen, ethanol, cement, and steel production facilities.

The Carbon Dioxide Removal Program is fostering R&D focused on direct air capture (DAC), biomass carbon removal and storage (BiCRS), and enhanced mineralization, with emerging research in ocean-based carbon dioxide removal. Carbon dioxide removal technologies remove CO_2 that has accumulated in the atmosphere and oceans and durably stores it in geologic, bio-based, and ocean reservoirs, or in value-added products, to create negative emissions. This wide array of approaches will help achieve gigaton-scale CO_2 removal by 2050 and support DOE's Carbon Negative Shot goal to remove CO_2 from the atmosphere and geologically store it for less than $100/net tonne CO_2-equivalent (CO_2e) for at least 100 years.

The Carbon Capture Technology Compendium is compiled biannually to provide a technical summary of CO_2 capture technology R&D sponsored by DOE/NETL's Point Source Carbon Capture and Carbon Dioxide Removal Programs. The current Compendium presents 145 projects in a single document, all of which were active at some point between October 1, 2021, and October 1, 2023.

The Compendium is organized into three main sections. The first section covers research performed by NETL's Research and Innovation Center (RIC). The second section includes projects managed under the Point Source Carbon Capture Program, organized in subsections based on the application of the technologies (i.e., post-combustion capture and pre-combustion capture from both power generation and industrial sources). The third and final section includes projects managed under the Carbon Dioxide Removal Program, organized in subsections based on the application of the technologies (i.e., DAC, BiCRS, and enhanced mineralization).

Each subsection is arranged by the ending scale of the current R&D effort, from front-end engineering design (FEED) and pre-FEED, to large- and small-scale pilot testing (Technology Readiness Level [TRL] 6–7), to conceptual engineering and materials design at bench and laboratory scale (TRL 2–5). Finally, within the set of projects for each ending scale, the projects are organized by key technology—solvents, sorbents, membranes, electrochemical, hybrid, novel concepts, or enabling technologies.

CARBON CAPTURE TECHNOLOGY SHEETS

Research and Innovation Center Technologies

Carbon Capture Simulation for Industry Impact (CCSI²)

primary project goal

The Carbon Capture Simulation for Industry Impact (CCSI²) project is designed to use the computational tools and models developed under the Carbon Capture Simulation Initiative (CCSI) in partnership with industry to accelerate and de-risk the scale-up of new and innovative carbon capture technology. CCSI² operates in conjunction with and in support of the Department of Energy (DOE) Fossil Energy and Carbon Management's (FECM's) Point Source Carbon Capture Program to focus on advancing promising technologies.

technical goals

- Provide support for new and existing carbon capture technology programs.
- Apply computational methodologies that can support FECM funded point source capture demonstrations/pilots, through quantification of uncertainty, development of high-fidelity models, and assisting in the development of optimal test plans to maximize value of data generated.
- Deploy CCSI² model library/modeling hierarchy for development and/or enhancement of high-fidelity flexible process models to improve predictive capability for process scale-up and design for FECM funded projects.
- Investigate and model amine emissions, applying machine learning where appropriate, at a pilot facility such as Technology Centre Mongstad.

technical content

The CCSI² project teams execute fundamental analysis, modeling, and optimization of carbon capture technology by working closely with Federal program management and industry partners. With the objective of maximizing the value of FECM funded projects, the CCSI² team has been tasked to: efficiently identify data collection needs; computationally and experimentally characterize carbon capture materials; design, optimize, and prototype devices and processes; and fully propagate uncertainty in model predictions for complete perspective on results accuracy. The team has historically assisted the Carbon Capture Program and technology developers by providing:

- Detailed understanding of capture materials through system performance subject to parametric uncertainty
- Designs for high performance and intensified unit operations
- Synthesis of processes optimized for novel materials
- Characterization of dynamic system behavior
- More informed design, operating, and control decisions
- Optimized processes under uncertainty

project focus:

Carbon Capture Simulation for Industry Impact

participant:

National Energy Technology Laboratory–Research and Innovation Center

project number:

PSCC-MYRP Goal 1

predecessor projects:

2018 CCSI² FWP–1022422
2020 CCSI² FWP–1022422
2022 CCSI² FWP–1022422

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partners:

Los Alamos National Laboratory; Lawrence Berkeley National Laboratory; Pacific Northwest National Laboratory; Lawrence Livermore National Laboratory; West Virginia University; University of Texas-Austin; University of Toledo; University of Notre Dame; University of Pittsburgh; Carnegie Mellon University

- Intelligent Sequential Design of Experiments (SDoE) at all technology readiness levels (TRLs) for model refinement, system optimization, and acceleration of deployment
- Machine Learning (ML) frameworks to reduce computational time
- Support for the Framework for Optimization and Quantification of Uncertainty and Surrogates (FOQUS) which will centralize and integrate computational capabilities critical to the Carbon Capture Program and CCSI^2 mission.

CCSI^2 is led by the National Energy Technology Laboratory (NETL) and leverages DOE national laboratories' unique strengths that support modeling and simulation. In full pursuit of the CCSI^2 vision, this project integrates the modeling and simulation capabilities at NETL and complements them with essential, world-class expertise at Lawrence Berkeley National Laboratory (LBNL), Lawrence Livermore National Laboratory (LLNL), Los Alamos National Laboratory (LANL), and Pacific Northwest National Laboratory (PNNL) in its core National Laboratory consortium.

Objective 1 — Stakeholder and Program Support

Stakeholder Engagement and Coordination

CCSI^2 has benefitted since its origin in CCSI from active engagement with industry and academic stakeholders who have continually reviewed and made recommendations on program content and emphasis, participated in training and early product testing and evaluation, and created a continuous pipeline of productive end uses that bring the promise of CCSI into practical application. Stakeholder Engagement continues and evolves toward greater and more valuable applications of CCSI^2 in ensuring the optimal deployment of future energy technology and process systems.

Software Development and Release Management

The research team facilitated the development and public release of CCSI^2 tools, supporting and educating users and developers alike so that they can maximize utility found in their use of the platform while also synthesizing user feedback to inform roadmaps for new releases. The team continues the open-source development of the existing CCSI^2 toolset, primarily the FOQUS application and related components. Additionally, the research team developes and deploys mechanisms by which user questions, expectations, and feedback can be addressed and incorporated into current and future development of the platform. The team continually evaluates these technologies for their effectiveness over the lifetime of the project.

Objective 2 — Point Source Capture Power Generation Pilot Support

TCM Pilot Project Support

The Technology Centre Mongstad (TCM) in Norway is one of the world's largest facilities for testing CO_2 capture technologies (12 MWe scale). CCSI^2 has collaborated with TCM in previous projects, including a test campaign for aqueous MEA solvent in which sequential design of experiments (SDoE) was implemented to guide collection of data to enable reduction of model uncertainty. CCSI^2 and TCM also collaborated on the development of a process model for the CESAR1 solvent system [aqueous blend of 27 wt% 2-amino-2-methyl-1-propanol (AMP) and 13 wt% piperazine (PZ)]. This model was validated with a set of steady-state data for a natural gas-based combined cycle turbine flue gas (~3.5 vol% CO_2). TCM is planning a new test campaign for CESAR1 solvent and has expressed interest in collaborating with CCSI^2 to implement SDoE strategies to maximize our understanding of the CESAR1 technology in the limited test time available. The test campaign is expected to occur in 2025 with a timeline of 3-4 months.

EPRI EEMPA Pilot Support

CCSI^2 helps to integrate performance projections for solvent characterization, using data from bench-scale column experiments, and advancing fundamental modeling capabilities for pilot scale, used to increase the value of FECM investment in pilot and full-scale demonstrations. Furthermore, future work will also focus on leveraging the integrated modeling capability to target characteristics for novel solvent formulations for further improvement of capture performance and cost.

RTI GEN2 NAS Pilot Support

RTI developed a novel Generation 2 Non-Aqueous Solvent (GEN2NAS) solvent as an advanced, next generation, post-combustion capture technology, and their current work is focused on identifying candidate solvent mixtures (combinations of amines and diluents) that represent promising improvements over their existing NAS technology. The two chosen candidate systems will be evaluated through experimental data collection, and the selected GEN2NAS system will be tested at bench scale. One candidate system has already been identified, and it shows significantly lower vapor pressure than the first-generation NAS system and MEA. Moreover, the GEN2NAS is expected to achieve CO_2 capture levels up to 97% with specific reboiler duty in the range of 2.1 – 2.5 GJ/tonne CO_2 and lower the cost of capture for NGCC plants by 40% in comparison with existing technologies. CCSI^2 will perform rigorous process model development, including rotating packed beds for use in place of traditional absorber columns. The work will also extend CCSI^2's capabilities in solvent-based CO_2 capture modeling, uncertainty quantification, and sequential design of experiments for supporting experimentation.

UKy/Nucor Steel Plant Capture Pilot Support

The UKy, solvent-based, carbon capture process has been demonstrated to reduce solvent regeneration energy 20–30% while reducing recirculation rate of the solvent by 30–45%, with a lower degradation compared to MEA. The capture process will be demonstrated on Nucor Steel Gallatin treating electric arc furnace in which the evolved gas has a low CO_2 concentration of ~1.5 vol% with low SO_2 and water concentrations. CCSI^2 is providing computational modeling, optimization, and UQ support to the upcoming test campaign at Nucor Steel.

US Steel Membrane Capture Pilot Support

NETL developed high performance polymeric materials for use in industrial carbon dioxide separations with excellent properties, including: (1) high CO_2 permeability and CO_2/N_2 selectivity, (2) good film forming properties, (3) high flexibility and mechanical strength, and (4) stability with water and common flue gas contaminants.

In separately funded work, NETL designed and constructed a test apparatus that will measure properties of a membrane module when used on a slipstream from the waste gas of a US Steel blast furnace for steel manufacturing. Leveraging this apparatus CCSI^2 will implement their computational toolset to evaluate the performance of the membrane module and to develop an optimized plan to test the technology as part of an integrated carbon capture system in a steel manufacturing process.

Honeywell Piperazine Pilot Support

UT-Austin is commercializing Piperazine based CO_2 capture with the Advanced Stripper (PZAS) process. Piperazine (PZ) reacts quickly with CO_2, is resistant to oxidation, and can be used with stripping at 5 bar. The advanced stripper reduces energy use by 10 to 20% over a simple stripper. This technology has been included in a license from UT-Austin to Honeywell UOP. CCSI^2 will continue to optimize and publish modeling results with PZAS that can be used as a representative case study to evaluate against other second-generation amine scrubbing technologies.

OSU Facilitated Transport Membrane Pilot Support

The Ohio State University (OSU) developed high-performance facilitated transport membranes for industrial carbon dioxide separations. Small pilot tests suggest these materials possess a remarkable combination of CO_2 permeability and CO_2/N_2 selectivity. OSU received funding from the Office of Fossil Energy and Carbon Management to conduct two large pilot demonstrations. The first was for flue gas from Holcim US's cement plant in Holly Hill, South Carolina. The second was for flue gas from the NGCC power plant located at the Wyoming Integrated Test Center in Gillette, Wyoming. The CCSI^2 team provides pilot support through the development and execution of a statistical design of experiments (SDoE) which will be used to evaluate parameters of a membrane performance module and guide development of integrated carbon capture systems.

High Capture Modeling and Verification

In preparation for the increased need for understanding and optimizing the cost of deep decarbonization of point source and industrial sectors, the CCSI^2 team extended the existing carbon capture technology modeling frameworks to capture rates greater than 95% for solvent-based capture systems such as MEA and CESAR1. CCSI^2 efforts include: economic model development, uncertainty quantification, analysis of multiple system configurations, investigation of hybrid solvent sorbent processes, reduced technical risk, and process intensification. This will increase understanding and preparedness for developing test plans to validate and scale-up capture technologies implementing higher capture rates.

Technical Risk Reduction

CCSI^2 computational approaches reduce risks of commercializing carbon capture technology by executing proven methods for process development and improvement rooted in computational- and model-based methods from statistics, applied mathematics, and industrial engineering. Two powerful approaches advanced by this subtask include Sequential Design of Experiments (SDoE) and Robust Optimization (RO). SDoE will maximize the value of data generated during pilot testing to answer operational questions and reduce variability, uncertainty, and risk. RO will identify optimal system settings that are robust to changes across a feasible operating regime. Together SDoE and RO benefit technology developers by providing cost-effective strategies to collect pilot data, refine models, and satisfy performance and safety constraints while managing uncertainty to meet developers' objectives.

Objective 3 Pilot Data and Modeling Validation

CCSI^2 conducts detailed review of process models and test plans developed by program participants funded through PSC Funding Opportunity Announcements. This activity will help ensure that extramural projects maximize the value of their data generation efforts and provide the developers with more thorough validation of their models.

technology advantages

- CCSI^2 provides process and economic modeling support, optimization, and UQ to help guide testing.
- CCSI^2 optimization techniques determine optimal set points of CO_2 capture processes.
- CCSI^2's uncertainty analysis and quantification framework is used to guide the development and planning of R&D to maximize understanding at practical scales and to optimize solvent-based processes.
- The CCSI^2 team engages carbon capture technology developers for direct and widespread support of priority interests of the Carbon Capture Program with the aim to fully understand and exploit the unique behavior of recently developed transformational carbon capture materials and equipment.
- CCSI^2 improves technical understanding of CO_2 system operation in ways that will serve to guide R&D required for an increasingly dynamic electrical grid evolving to incorporate more intermittent renewables.
- CCSI^2 is constantly developing a more comprehensive understanding of CO_2 capture technology for applications including natural gas and industrial sources, at deeper levels of decarbonization.
- CCSI^2 expertise is versatile and can extend to analogous issues, e.g. direct air capture.

R&D challenges

- Fundamental challenges to obtaining competitive cost goals: mass transfer rates; carbon capture energy requirements; and optimization of system/equipment design, operation, and of the experiments required to generate data to sufficiently characterize them.
- Modeling the fundamental, multi-physics and coupled hydrodynamic behavior of solvent based CO_2 capture processes is exceedingly complex. For example, the accurate prediction of interfacial area resulting from interactions between solvents and contactor packing can be challenging yet is crucial for optimizing the design and operation solvent based CCS systems, without unnecessary overdesign.
- In dynamic processes, process operation and disturbances can fluctuate which presents challenges determining optimal process set-points to reach the test-campaigns objectives.

- As dimensionality of design and operational choices grow, it becomes more difficult to fully explore the intended design space. Therefore, there is a growing need to generate enough computational efficiency and experimental data to validate models across the range of ever-increasing choices.

status

- CCSI^2 provides quarterly releases of FOQUS version; support for the software continues to fix bugs and add capabilities directly supporting the analysis needs of the Carbon Capture Program.
- CCSI^2 completed an optimization of an integrated cement plant with MEA carbon capture process.
- Multiple collaborations between CCSI^2 and industrial organizations focused on demonstration of novel CO_2 capture technologies at Norway's Technology Centre Mongstad (TCM), one of the world's largest venues for testing capture technologies (~ 12 MWe).
- Collaboration between RTI and CCSI^2 on multi-scale modeling of non-aqueous solvent system (NAS).
- Leveraged SDoE to guide NAS test campaign at TCM and focused on demonstrating high levels of CO_2 capture with low solvent emissions and regeneration energy requirement.
- CCSI^2 also provided large pilot support for Membrane Technology Research (MTR) by developing a 1D model for the MTR flat sheet membrane with non-uniform channel heights.
- SDoE performed with commercial nitrogen membrane model to demonstrate the potential for stochastic parameter estimation.

available reports/technical papers/presentations

CCSI Toolset: *https://github.com/CCSI-Toolset/*.

CCSI Toolset suite of computational models for carbon capture equipment and design processes. *https://github.com/CCSI-Toolset*

Michael Matuszewski, "Carbon Capture Simulation for Industry Impact (CCSI^2)," Cement & Lime Decarbonization Workshop, July 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CLD_Matuszewski.pdf*

Joshua Morgan, "CCSI^2 Process Modeling and Optimization Highlights," 2022 Carbon Management Project Review Meeting, Pittsburgh, PA, August 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_PSC17_Morgan.pdf*

"Overview of Carbon Capture Simulation for Industry Impact (CCSI^2) Project," presented by Michael Matuszewski, 2021 Carbon Management and Oil and Gas Research Project Review Meeting, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Matuszweski.pdf*.

"CCSI^2 Brief: Computational Support for the Carbon Capture Program," presented by Benjamin Omell, DOE-NETL's 2020 Integrated Project Review Meeting, October 2020. *https://netl.doe.gov/sites/default/files/netl-file/20VPRCC_Omell.pdf*.

"CCSI^2 Project Overview," presented by Michael Matuszewski, 2018 NETL CO_2 Capture Technology Project Review Meeting, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/M-Matuszewski-CCSI2-Capture-Impact-Simulation.pdf*.

"CCSI^2 and Toolset Support Program Overview and Toolset Introduction," presented by Michael Matuszewski, 2017 NETL CO_2 Capture Technology Project Review Meeting, August 2017. *https://netl.doe.gov/sites/default/files/event-proceedings/2017/co2%20capture/3-Wednesday/M-Matuszewski-CCSI2-Program-Overview.pdf*.

Point Source Carbon Capture Systems Analysis

primary project goal

The National Energy Technology Laboratory's Research and Innovation Center (NETL-RIC) will develop tools, benchmarks and guidelines that will aid the Point Source Carbon Capture Program in the evaluation and characterization of flexible, near-zero emissions power production and decarbonized industrial processes.

technical goals

- Identify, develop and validate targets for programmatic performance of capture technologies based upon detailed economic analysis.
- Technical risk reduction by reducing impacts of uncertainty in design and deployment of power and industrial carbon capture demonstrations.
- Develop an interactive data platform aligned to support the Point Source Carbon Capture Program and enable one-stop access to authoritative, priority data resources and enabling visualization and exploratory capabilities through the Office of Fossil Energy and Carbon Management (FECM)/NETL Energy Data eXchange® (EDX) disCO2ver virtual data system for public and private stakeholders.
- Provide technical expertise and support for program activities.
- Work in concert with other U.S. Department of Energy (DOE) offices to develop holistic models and strategies for the decarbonization of industrial systems by leveraging their work on the base industrial process and alternatives to electrify or otherwise decarbonize processes without carbon capture.
- Provide unbiased technical reports to establish baseline analysis and scaling guidelines, create economic targets for new carbon capture technologies, and provide accurate and reliable information that can help inform decision-making and better serve the needs of the public.
- Develop in-depth market and systems analysis to project future deployments of program research and development (R&D) in economic models and the Energy Market Forum (EMF).

technical content

NETL-RIC performs a variety of analyses that support DOE-FECM's Point Source Carbon Capture Program's vision of demonstrating carbon capture on power and industrial scales with reliable carbon storage that will lead to commercially viable options for a decarbonized economy by 2050. These include techno-economic analysis (TEA) screening of new carbon capture technologies, systems design, goals and metrics development, and market analyses. These activities provide predictions on the cost and technical viability of carbon capture technologies for both in-house NETL-RIC projects and extramural projects, as well as provide an unbiased analysis to inform the Point Source Carbon Capture Program.

project focus:

Point Source Carbon Capture Systems Analysis

participant:

National Energy Technology Laboratory–Research and Innovation Center

project number:

PSCC-MYRP Goal 2

predecessor projects:

2022 Carbon Capture FWP

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partners:

LANL; LBNL; PNNL; LLNL; ORNL; West Virginia University; University of Texas-Austin; University of Toledo; University of Notre Dame; University of Pittsburgh; Carnegie Mellon University

The NETL-RIC systems analysis efforts support all four Point Source Carbon Capture Program focus areas:

- Focus Area 1: Enabling Point Source Carbon Capture Power Demonstrations: Technology development to support successful demonstration of retrofit carbon capture and storage (CCS) projects at electricity generation facilities.
- Focus Area 2: Point Source Carbon Capture Power: Net-Zero, Flex Power: Technology development of flexible carbon capture with high capture efficiency to enable Net-Zero Power Demonstration projects.
- Focus Area 3: Enabling Point Source Capture (PSC)-Industrial Demonstrations: Technology development to support successful demonstration of retrofit CCS projects at industrial facilities.
- Focus Area 4: PSC Industrial: Integrated Low-Carbon Industrial Processes Coupled with Carbon Capture: Technology development for integrated decarbonized industrial processes coupled with transformational carbon capture technologies to enable Net-Zero Industrial Demonstration projects.

NETL-RIC is developing new methods to provide foundational analytical support that ties accomplishments in the laboratory to results in real-world systems. Benchmark TEA, LCA and process designs will form the basis of comparison for technologies funded for front-end engineering design (FEED) studies and pilot-scale testing of power and industrial carbon capture systems, providing analytical support for all Point Source Carbon Capture Program focus areas.

Important new areas to be evaluated include alternate decarbonization pathways for industrial sources to aid in the development and evaluation of hybrid systems, as well as the establishment of a knowledge base for the cost and performance of non-CCS-based industrial sources for market comparisons.

technology advantages

- Provide critical review of extramural TEA, LCA and FEED studies for the Point Source Carbon Capture Program.
- Market assessment to develop representative operational profiles and market-based goals for future R&D efforts.
- Techno-economic baseline cases for cement and other industrial processes will help improve design scenarios for industrial partners.
- Enable semi-automated data integration and processing for near-real-time spatio-temporal analytics, which will support nationwide capture activities, including support for cost modeling and supply chain optimization opportunities.
- The update to the Carbon Capture Retrofit Database, including new flexible sources and CCS calculations, will provide screening-level, unit-specific costs of capture based on actual plant operational data.

R&D challenges

- Matching real-time and flexible operation scenarios with specific industrial applications (e.g., cement, iron/steel, pulp/paper, etc.) and power application processes.
- Certain industry-specific trace contaminants in the exhaust gases may be difficult to capture in models with the capture technology applied.
- Changes to energy models require significant specialized expertise in both coding and data development. These changes must be optimized so that the total run time of the models is not significantly increased, and so that inclusion of the new capabilities does not hinder the optimization routines of the models.

status

The capture systems analysis group at DOE-NETL has several activities planned for the near future, including:

- Complete and publish a summary paper based on results from power plant FEED studies.

- Launch the EDX data repository for program data management for power and industrial pilots and FEED projects.
- Develop an analysis report for a flexible power plant with carbon dioxide (CO_2) capture evaluated under load-following in fully dynamic modes.
- Finalize the cement baseline process model for the entire plant evaluation, including an LCA.
- Develop the steel/iron baseline process model for the entire plant evaluation, including an LCA.
- Complete a summary paper on industrial pre-FEEDs/FEEDs, pending availability of public FEED reports.
- Develop petrochemical, pulp and paper, glass, and lime decarbonization pathway baseline process models for entire plant evaluation, including an LCA.
- Develop market-based tools to aid in understanding deployment scenarios and employment impacts.
- Update the Carbon Capture Retrofit Database to include new flexible sources and CCS calculations.

available reports/technical papers/presentations

NETL Energy Analysis Website: *https://netl.doe.gov/ea/about*.

Hackett, Gregory, "Representation of Fossil Power Generation Technologies in NREL's Annual Technology Baseline," 2023 USAEE/IAEE North American Conference, Chicago, Illinois, November 2023.

Cvetic, P., Buchheit, K., Kuehn, N., Zoelle, A., Woods, M., Hackett, G., & Fout, T., "Natural Gas Combined Cycle (NGCC) Power Plants with Carbon Capture and Exhaust Gas Recycle (EGR)," Department of Energy, NETL, Pittsburgh, PA, October 16, 2023. DOI: *https://doi.org/10.2172/2251495*.

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S. Hughes and P. Cvetic, "Analysis of Carbon Capture Retrofits for Cement Plants," National Energy Technology Laboratory, Pittsburgh, March 31, 2023. *https://doi.org/10.2172/1970135*.

Roussanaly, S., Rubin, E. S., van der Spek, M., Booras, G., Berghout, N., Fout, T., Garcia, M., Gardarsdottir, S., Kuncheekanna, V. N., Matuszewski, M., McCoy, S., Morgan, J., Nazir, S. M., & Ramirez, A., "Towards Improved Guidelines for Cost Evaluation of Carbon Capture and Storage," White Paper on Point Source Carbon Capture April 2021.*https://netl.doe.gov/projects/files/TowardsImprovedGuidelinesforCostEvaluationofCarbonCaptureandStorage_042921.pdf*.

Mobile Emissions Monitoring

primary project goal

The National Energy Technology Laboratory's Research and Innovation Center (NETL-RIC) is developing tools to monitor and quantify amine capture media degradation and non-CO_2 secondary air emissions from point source carbon capture (PSCC) systems, as well as tools that can support long term operations and can potentially decrease cost and improve reliability of PSC systems.

technical goals

- Develop methodologies and tools for mobile air emissions monitoring units.
- Develop in-situ sensors to detected real-time amine (solvent) degradation.
- Develop a mobile amine degradation analysis unit.
- Develop validated methodology for accelerated evaluation capture media performance degradation (leading to secondary air emissions).
- Identify, develop, and validate targets for programmatic performance for capture technologies based upon detailed economic analysis.

technical content

Application of CO_2 capture on an industrial or power system will require low levels of incoming SO_2 and NOx, particularly if amine-based solvents are used. Criteria pollutant emissions of such systems equipped with carbon capture are likely to be lower than an identical system without carbon capture and storage (CCS). However, the degradation of capture media during operations may result in the formation and emission of capture media byproducts, such as nitrosamines and nitramine for amine-based solvents.

The objective is to develop toolsets that can be used to monitor and quantify capture media degradation and concomitant air emissions. While initial focus is on solvent amine-based capture media, with appropriate extensions the methods, frameworks, and tools can be applicable to other types of capture media. Coupled together the toolsets, along with the Carbon Capture Simulation for Industry Impact (CCSI^2) predictive capability, the products will provide for a deep understanding of capture media degradation and potential non-CO_2 secondary air emissions. The data generated can be used to support Office of Fossil Energy and Carbon Management (FECM) and Office of Clean Energy Demonstrations (OCED) activities on characterization and quantification of secondary emissions, including model development.

The tools will be utilized and deployed at pilots and demonstrations to assist technology developers and advance PSCC technologies. An aim is to develop standardized test methodologies. It's government-owned, government-operated status uniquely positions NETL to generate and provide unbiased information on amine degradation and secondary air emissions.

project focus:

Non-CO_2 Secondary Emissions Monitoring

participant:

National Energy Technology Laboratory–Research and Innovation Center

project number:

PSCC-MYRP Goal 3

predecessor projects:

n/a

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partners:

n/a

Mobile Air Emission Unit

NETL-RIC will develop advanced technologies to monitor, characterize and quantify non-CO_2 secondary air emissions (such as nitrosamine) from PSCC systems due to degradation of solvent (amine) based capture media through deployment of a mobile air emissions testing laboratory at power and industrial retrofit pilots and demonstrations. The effort will investigate measurement, reporting, and verification (MRV) for PSCC applied to power generation and industrial systems and leverage NETL expertise and capabilities with air monitoring and analytical chemistry to design, construct, and commission a mobile air monitoring laboratory to measure amine degradation products in air emission from PSCC systems. The program also plans to establish collaborations with other organizations such as the National Carbon Capture Center (NCCC), Stanford University, University of Oslo, SINTEF, and other test centers. The mobile emissions laboratory will be deployed at FECM (and OCED) power and industrial pilots and demonstrations to assist developers with characterizing and quantifying non-CO_2 secondary air emissions during pilot testing.

Mobile Amine Degradation Analysis Units

NETL-RIC will develop advanced technologies to monitor, characterize and quantify amine degradation through deployment of a mobile amine degradation analysis unit at power and industrial retrofit pilots and demonstrations. These units will provide developers information to evaluate carbon capture material degradation pathways and products. The program will leverage existing NETL expertise and capabilities with analytical chemistry and materials characterization to design, construct, and commission a mobile amine degradation unit that can provide information on the change of amine chemistry and structure during PSCC systems operation. The mobile amine degradation analysis unit will be deployed at FECM (and OCED) power and industrial pilots and demonstrations to assist developers with characterizing amine (solvent) degradation.

In-Situ Sensors for Real Time Monitoring of Solvent Capture Media Degradation

NETL-RIC will develop advanced technologies for in-situ, real-time measurement of the degradation of amine solvent-based carbon capture media for deployment at power and industrial retrofit demonstrations. Coupling the data generated on amine degradation with other on-line process sensors (such as temperature) will provide insight on amine performance and degradation, as well as inform optimal operations based on real-time sensor data. The project will develop, lab test and field test optical fiber sensors for amine degradation and CO_2 monitoring, which can be designed to include ammonia and nitrosamine sensing. In addition, laser-induced breakdown spectroscopy (LIBS) will be prototyped and field tested for trace metals detection from flue gas. New novel sensors will also be developed for highly sensitive monitoring of toxic nitrosamines, nitramines, and other byproducts. Researchers will utilize the mobile amine degradation laboratory (when available) to validate sensor performance during field trials and use artificial intelligence/machine learning models to predict amine degradation and inform optimal operations based on real-time sensor data. The sensors will be deployed at FECM (and OCED) power and industrial pilots and demonstrations to assist developers with in-situ, real-time monitoring of amine solvents.

Validated Methodology for Accelerated Evaluation of Capture Media Degradation – SOLVENT HALT (Highly Accelerated Life Testing)

NETL-RIC will advance evaluation of capture media by developing a validated method to assess media degradation that leads to non-CO_2 secondary air emissions. The methodology will be comprehensive and incorporate service conditions to predict degradation in a wide range of applications (e.g., power generation, industrial, continuous, and flexible operations). This will afford PSCC technology developers a standard and the ability to rapidly assess capture media durability for use in power and industrial applications. The initial focus is on amine solvents, however if successful, the methodology and framework could be extended to other media. Researchers will use artificial intelligence/machine learning and targeted laboratory experiments (with physics-based simulations to fill gaps), to understand degradation mechanisms in capture media to establish and validate a methodology/framework for accelerated prediction of capture media degradation leading to non-CO_2 secondary air emissions at conditions representative of service. R&D efforts will leverage CCSI^2, Institute for Design of Advanced Energy Systems (IDAES), and other existing NETL simulation tools when appropriate, leverage research by others, establish collaborations with other organizations, such as SINTEF, use data available in the literature, available results from tests at NCCC, or other similar test centers utilizing slip streams, and available results from the pilots and NETL for further validation of the methodology framework. The methodology will be made available to validate CCSI^2 predictive capability for emissions.

technology advantages

- Enable real-time emissions measuring (e.g., nitrogen containing emissions, HAPs, aerosols) at pilots and demonstrations.
- Enable real-time in-situ liquid phase measurement of degradation products from amine solvent based capture media and products at PSCC pilots and demonstrations.
- Help understand amine degradation that leads to air emissions.

R&D challenges

- Developing qualitative calibration procedures for sensors that are representative of the relevant industrial environment.
- Identifying unknown species and impurities that are present under real industrial loaded conditions.
- Ongoing adjustment and revision of procedures and developed methodologies for monitoring and qualifying emissions.

status

The mobile emissions monitoring group at DOE-NETL have received their emissions monitoring equipment (isokinetic sampling and time of flight mass spectrometer) in September 2024. Researchers are currently developing sampling and calibration procedures for known degradation products and setting up in house testing apparatus. The mobile lab trailer design phase is complete and is being constructed by DES in South Carolina. The field testing of optical fiber sensors is currently being conducted at NCCC.

available reports/technical papers/presentations

N/A

Membrane Capture Media Development

primary project goal

The National Energy Technology Laboratory's Research and Innovation Center (NETL-RIC) is developing transformational NETL-developed membranes for industrial point source carbon capture (PSCC) applications. Previously, RIC has demonstrated a new rubbery polymer, thin film composite membrane that is designed to separate CO_2/N_2 for industrial retrofit applications. The membrane features gas separation performance that exceeds commercially available membranes, with stable long-term performance in the presence of humidity, and thus is attractive for industrial PSCC applications.

technical goals

- Complete activities (e.g., construct test skid, scale-up, etc.) necessary to conduct a field test of NETL membranes for CO_2 removal in an industrial retrofit application such as steel manufacturing.
- Demonstrate the effectives of NETL's new rubbery polymer, thin-film composite (TFC) membrane CO_2 removal in an industrial retrofit application by completing a field test at a steel manufacturing plant.
- Based on the results of the field trial, identify and develop materials with improved performance characteristics.
- Evaluate the long-term degradation characteristics of membranes with improved performance in flexible operating conditions.
- Prepare new material for an industrial field test.

technical content

This objective of this project is to support the development of integrated low-carbon industrial processes coupled with carbon capture by maturing and transferring NETL carbon capture membrane technology to industry. Efforts will focus on scale-up and validation for industrial carbon capture applications. Initial emphasis is on the upcoming field testing of an NETL membrane at a steel plant, with further development aimed at increasing scale and evaluation under flexible industrial conditions.

Research efforts will demonstrate the effectiveness of NETL's new rubbery polymer, thin film composite membrane for industrial PSCC applications. This goal will be supported by a suite of activities to prove the viability of novel carbon capture systems utilizing transformational capture media. The overall approach technology will progress from a technology readiness level (TRL) of 3/4 (laboratory demonstration) to a TRL of 5/6 (field demonstration) by scaling up carbon capture systems and evaluating long term degradation characteristics. Industrial partners will be identified for hosting field sites and for technology transfer.

project focus:

Membranes with CO_2 or H_2 Selectivity

participant:

National Energy Technology Laboratory–Research and Innovation Center

project number:

PSCC-MYRP – Goal 4

predecessor project:

2022 Carbon Capture FWP

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partners:

N/A

- Computational fluid dynamics (CFD) coupled with 3-D printing NETL will be used to scale up this membrane material and design flat sheet membrane modules.
- An extended field test representing an order of magnitude increase in scale will be conducted at an industrial (steel manufacturing) plant to demonstrate the scalability and stability of the membrane in actual waste gas with contaminants.
- Long term performance evaluation will be conducted on this class of membranes under steady state operation as well as cyclic flexible operation.

The NETL-RIC research team is pushing the limits of membrane materials design to achieve the overall goals of reducing the energy penalty and cost of CO_2 separation relative to conventional technologies. The team is utilizing their unique experience in fabrication and experimental work coupled with computational tools to optimize membrane design to have higher performance and directly compete with the best performing CO_2/N_2 separation membranes in the state of the art. In addition, the NETL-RIC team is working to develop test modules for model validation toward a better fundamental understanding of membrane module design.

Substrate / Gutter Layer Development and Roll-to-Roll Fabrication

CO_2 capture using TFC membranes (Figure 1) relies on selective materials with high CO_2/N_2 separation performance, excellent thin film forming ability, low material cost, and more importantly, non-aging properties. A rubbery polymer blend with high ether oxygen content and high molecular weight (MW) can meet all these requirements. Specifically, ether oxygens provide high CO_2/N_2 separation properties, polymers in rubbery state are resistant to physical aging, and high MW promotes thin film formation due to a large amount of chain entanglements. The membrane support and gutter layer of a TFC also need to have the right characteristics to mechanically support the thin selective layer while presenting minimal resistance to gas transport. Excessive pore size of the support requires a thicker gutter layer to compensate, leading to poor performing TFCs. NETL has successfully developed high performance selective materials (i.e., cross-linked rubbery blend of poly(dimethylsiloxane) [PDMS]-methoxyethoxyethoxyphosphazene [MEEP]) for CO_2/N_2 separation, highly permeable gutter layer coatings, and novel flat-sheet membrane. These developed materials, membranes, and the associated fabrication techniques, if combined, can lead to TFCs among the CO_2/N_2 separation membranes available. Thus, there is strong motivation to pursue high permeance rubbery blended TFC membranes for industrial CO_2 capture.

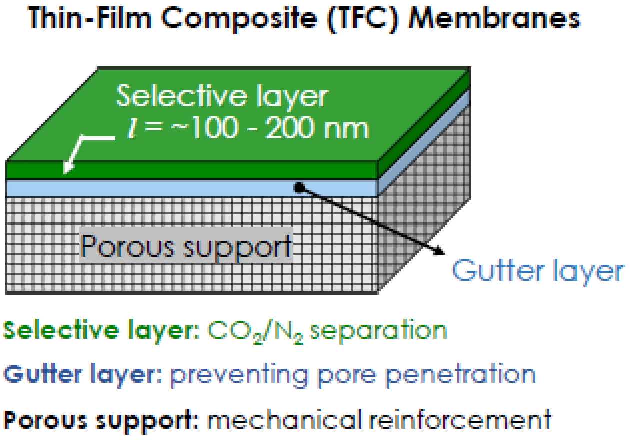
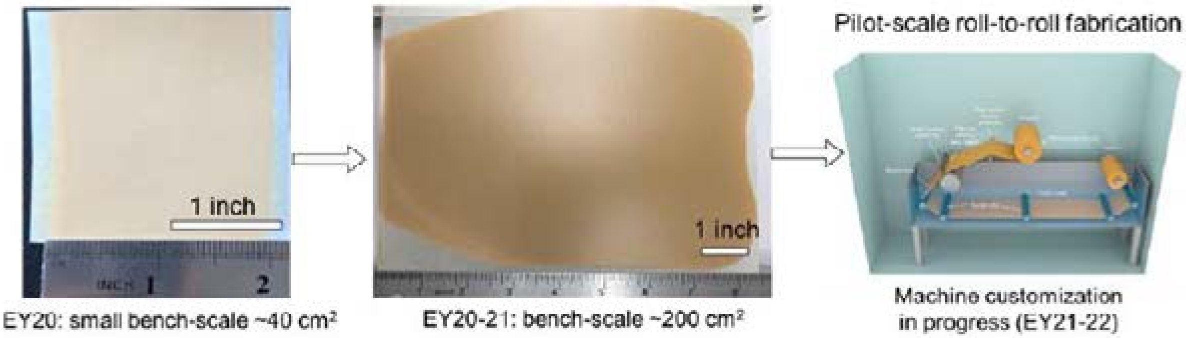


Figure 1: Thin-Film Composite (TFC) Membranes

NETL worked on scale-up fabrications of PDMS-MEEP TFCs from a coupon-size (1–10 cm^2) to a bench-scale (approximately 100 cm^2) by using scalable coating methods like knife casting and wire-wound rod coating. Knife-cast 100-cm^2 TFCs with uniform coatings have been achieved with some minor defects as indicated by the varying selectivity of 14–37 obtained over different sampling areas. To further scale up TFC fabrications, NETL identified a suitable roll-to-roll (R2R) polymer coating machine (Figure 2 and Figure 3) that was manufactured by Yasui Seiki after performing a successful membrane coating test run in Yasui Seiki's facility in Bloomington, Indiana. The coating machine, after its installation and shakedown, was able to apply PDMS gutter layer and PDMS-MEEP selective layer coatings at 30-cm-wide in an R2R process.



EY20: small bench-scale ~40 cm²

EY20-21: bench-scale ~200 cm²

Machine customization in progress (EY21-22)

Figure 2: Scale-up approach for polybenzimidazole (PBI) membrane supports: from hand-cast bench-scale membranes (40–200 cm^2) to R2R machine casting pilot-scale membranes (30 cm by 10 m).

Figure 3: A photograph of NETL's R2R membrane casting machine with the inset showing a 30-cm-wide PBI membrane support produced by the machine.

Module Development

NETL has previously deployed an automated membrane testing skid (Figure 4) at the National Carbon Capture Center (NCCC), which delivers conditioned flue gas from the E. C. Gaston Plant to be processed in a laboratory-scale membrane module. This skid was successfully operated with minimal attendance for more than 5,000 hours, with fully automated flow regulation and gas chromatography (GC) analysis. The main benefit of this skid was to make available flue gas testing data for membranes at a scale not normally available for actual flue gas testing. Specifically, it was designed to test post-combustion membranes up to around 10 cm^2 in scale. This work has been described in a peer-reviewed publication in the Journal of Membrane Science 542 (2017) p 217-225.

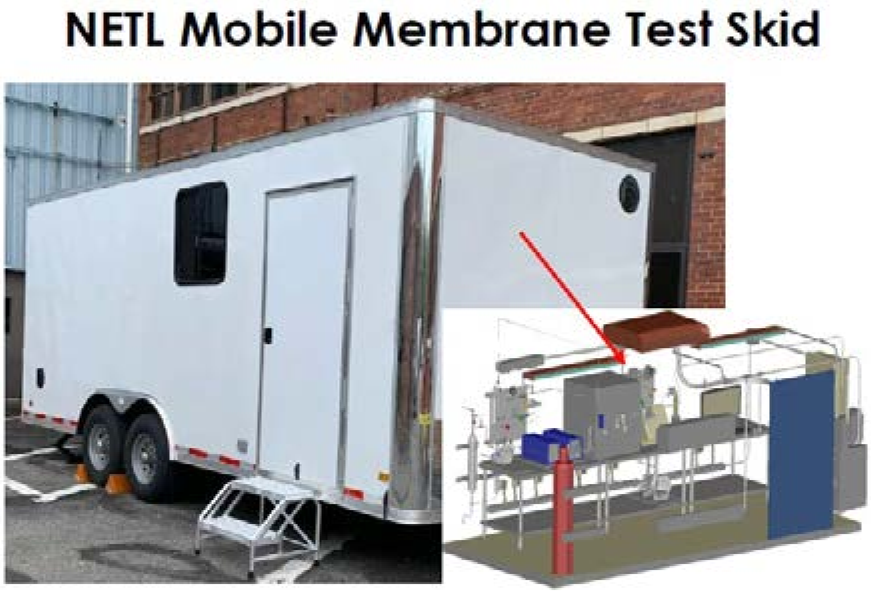


Figure 4: NETL Mobile Membrane Test Skid

Due to the difference in scale and testing procedure from the NCCC skid, a new skid was constructed at NETL. The experience gained from prior NCCC testing was incorporated to make sure the new skid has similar or superior automation, accessibility, and robustness as the NCCC skid. The new skid will operate using the isobaric (constant pressure) principle but, unlike the NCCC skid, will use a permeate vacuum condition instead of a sweep gas to enable testing of a higher membrane area. There will be no gas pre-treatment on the facility side, which could adversely impact the sensitive electronic instrumentation. Gas conditioning, including humidification/dehumidification, will be incorporated into the skid as appropriate following consultations with the host company personnel.

Testing at U.S. Steel

NETL is collaborating with U.S. Steel for a field test using blast furnace waste gas (>20% CO_2) at the U.S. Steel Edgar Thomson Plant. In preparation for the field demonstration, NETL performed gas permeation measurements on the PDMS-MEEP TFC membranes using gas mixtures of 20–30% CO_2/80–70% N_2, which represent characteristic emissions from steel mills. A plate-and-frame module enclosing 900 cm^2 membranes will be field tested at a commercial steel mill. One to three (1–3) membrane modules will be tested for 1,000 hours each to ensure repetition of data. To support the mixed-gas testing, plate-and-frame membrane modules with a favorable flow pattern inside will be customized to reduce the concentration polarization effect that negatively affects separation properties of high permeance membranes. 3D printing integrated with computational fluid dynamics (CFD) simulation will be employed to design and optimize the plate-and-frame membrane modules.

Test Cell Development

Recently, NETL researchers discovered traditional cells are not ideal for high-permeance membrane testing. The problem is the mixed-gas CO_2 permeance and selectivity can be >30% lower than their pure-gas values of >2000 GPU high-permeance membranes because traditional circular permeation cells have inefficient flow patterns and stagnant zones. A better cell design for mixed-gas measurement can increase both the selectivity ratio and the permeance ratio for membranes previously measured using the old design. NETL has successfully used their 3D-printing technology to design minicells which significantly enhanced the permeance and selectivity ratios.

technology advantages

Rubbery Membrane

- High-permeance and CO_2/N_2 selectivity TFC membranes, stable under high-humidity conditions and common flue gas contaminants, and resistant to physical aging, providing performance stability.

Membrane Test Unit

- NETL's membrane technology leads to reduced cost of CO_2 capture.

R&D challenges

Rubbery Membrane

- Scaling up the membrane support production and selective layer coating in a continuous roll-to-roll process.
- Designing and producing multi-leaf plate-and-frame modules with ideal flow patterns that can minimize membrane concentration polarization.
- Packing TFC membranes into membrane modules without affecting the integrity of TFCs.
- Evaluating the TFCs in high gas flowrates under industrial gas stream environments with moistures and contaminants.

Membrane Test Unit

- Feed gas streams from an industrial site will have different contaminants and higher levels of particulates than previous testing at NCCC with no facility-side pre-treatment, which could result in unanticipated or premature failure of research equipment on the test unit.
- The anticipated scale for membrane testing is greater than previously performed at NETL or NCCC, necessitating new modules and testing techniques.

status

Rubbery Membrane

A plate-and-frame module enclosing 900-cm^2 membranes is currently being field-tested at a commercial steel mill. One to three membrane modules are being tested for 1,000 hours each to ensure replication of data.

Membrane Test Unit

The preliminary engineering design documents of the membrane permeance test unit are completed. The preliminary design documentation included a process flow diagram and an equipment list. Negotiations with U.S. Steel led to a nondisclosure agreement (NDA) being finalized and signed for testing at the Edgar Thomson plant. A site visit by NETL personnel was made to ascertain a specific testing site location and available utilities. Construction of the membrane permeance test unit is currently under way.

available reports/technical papers

Lingxiang Zhu, "Highly Permeable Thin Film Composite Membranes of Rubbery Polymer Blends for CO_2 Capture," 2023 FECM / NETL Carbon Management Research Project Review Meeting, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC31_Zhu.pdf*.

Lingxiang Zhu, "Highly Permeable Thin Film Composite Membranes of Rubbery Polymer Blends for CO_2 Capture," 2022 Carbon Management Project Review Meeting, August 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_PSC18_Zhu.pdf*.

Zhu, L.; Kusuma, V.; Hopkinson, D., "Highly Permeable Thin Film Composite Membranes of Rubbery Polymer Blends for CO_2 Capture." 2021 DOE/NETL Carbon Management and Oil & Gas Research Project Review Meeting. Point Source

Carbon Capture – Lab, Bench, and Pilot-Scale Research. August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Zhu.pdf*.

Systems Analysis and Modeling for Carbon Dioxide Removal Technologies

primary project goal

The National Energy Technology Laboratory's Research and Innovation Center (NETL-RIC) is developing new methods to provide foundational analytical support that forms a framework for assessing the real-world operational viability of technologies undergoing research and development (R&D) in carbon dioxide removal (CDR). To better understand operational and technical limitations, NETL is focused on developing unbiased and consistent approaches to critical analyses for CDR technologies, including life cycle analysis (LCA); techno-economic analysis (TEA); monitoring, reporting and verification (MRV); and process modeling.

technical goals

- Develop and assess goals and metrics for the U.S. Department of Energy's (DOE) CDR Program by setting protocols and standards for evaluating the cost, performance and environmental impact of technology within the program.
- Conduct process, cost and life cycle analyses for multiple carbon capture pathways and specific extramural projects.
- Develop tools for dissemination to researchers and technology developers to aid in TEA studies.
- Deepen the understanding of the various CDR approaches to guide future development and inform project selection.
- Evaluate technologies with a unique lack of bias to consistently assess the viability of a range of CDR approaches.

technical content

Since CDR is a relatively new carbon capture approach, systems analyses are critical to establishing realistic expectations and estimates for technology costs upon commercialization. It is also important to evaluate proposed solutions on a common basis for comparison to each other and to determine the net effect of different technologies on the environment. As such, Goals 1 and 2 are focused on evaluating LCA, TEA, MRV and process modeling for CDR technologies to form a consistent basis that technology developers can rely on to perform accurate assessments of their technologies. This can then help evaluate the role of direct air capture (DAC) and other carbon-negative solutions within the larger suite of deployable tools to decarbonize the U.S. electricity sector.

Goal 1 — Create Protocols for TEA, LCA and MRV

Previous work in these analyses (TEA, LCA and MRV) followed the basis established for the DOE Carbon Conversion Program that allowed LCAs to be

project focus:

Carbon Dioxide Removal Systems Analysis

participant:

National Energy Technology Laboratory–Research and Innovation Center

project number:

CDR-MYRP Goals 1 and 2

predecessor project:

2023 Carbon Capture FWP

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partners:

N/A

standardized for comparisons among DOE-funded projects. The LCA team generated a bioenergy with carbon capture and storage (BECCS) baseline model and report, as well as a DAC LCA manuscript. Efforts continued to update the DAC guidance document in order to stay up to date with the progression of these technologies, including changing public perception, and additional work has been applied to the BECCS Biomass Supply Screening Tool to ensure its quality for broader use.

Recently, the focus of LCA work has expanded to include more novel technologies, including marine CDR and enhanced weathering/mineralization. Studies are aimed at ensuring the program has a good baseline understanding of the ability of these technologies to capture and store carbon dioxide (CO_2) and is aware of potential environmental tradeoffs. Initial explorations of enhanced weatherization and marine CDR included a literature review and an assessment of the role of MRV and how LCAs can inform MRV requirements. These can be critical in determining the additionality of carbon removals, which form the basis for carbon removal credits.

Goal 1 is also focused on identifying the most promising CDR technology pathways and attributes in terms of costs. Focus is placed on establishing realistic expectations and estimates for technology costs upon commercialization, so that R&D can be focused on the parameters that highly affect the overall technology cost. Information that ties accomplishments in the laboratory to results in real-world systems enables R&D to progress at lower costs and with greater stakeholder confidence. This type of information is also required to perform a TEA to evaluate if performance data (from laboratory- to pilot-scale testing) provides progress toward program goals or sets targets for the performance data based upon the results of a TEA. Previous work focused on the evaluation of several of the most prominent and well-studied approaches to CDR, with breakdowns of the estimated costs for the solvent- and sorbent-based studies, is shown in Figure 1.

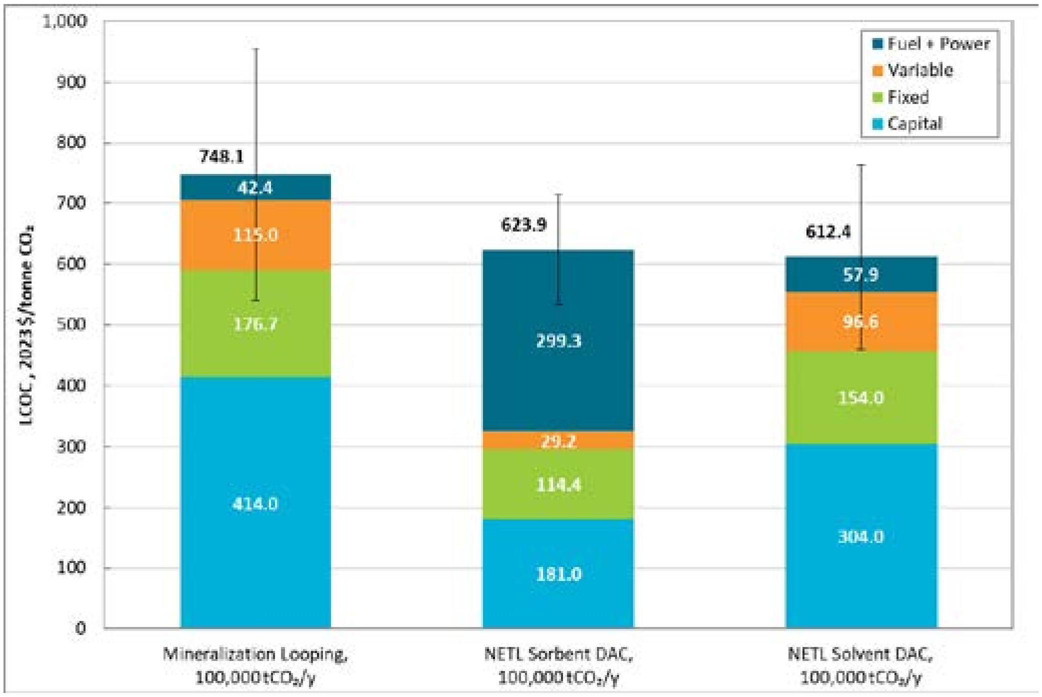

Figure 1: The TEAs performed by RIC focused on three of the most prominent DAC technologies currently, estimating costs based on process modeling and the most accurate cost information available.

Work has focused on continuing the development of the NETL DAC models to include systems operating with alternative energy sources (i.e., solar, thermal, geothermal, etc.). An additional case study on a system using mineralization looping was performed to allow for broader comparison to the solvent- and sorbent-based DAC cases. Results from this study are summarized in the center (sorbent) and right (solvent) bars of Figure 1. Work was also performed under this goal to develop a guidance document for the performance of TEAs on DAC technologies based upon prior guidance documents developed for capture retrofits and carbon conversion.

TEA work expanded to include additional approaches to CDR, including marine CDR and enhanced weatherization/mineralization processes. A literature review and a case matrix were developed for each of these studies.

The marine CDR study focused on electrochemical separation of CO_2 removal with multiple separation approaches and equipment considered and compared. Limited data was obtainable for these emerging technology pathways, so the completed case studies are still subject to further refining as more usable data can be shared by technology developers in the field.

There is a specific focus within the Office of Fossil Energy and Carbon Management (FECM) on transparent and communicative approaches to enable true removal of CO_2 to enable appropriate tracking of progress toward the Carbon Negative Shot goal. This includes designing, testing and implementing rigorous and easy-to-use analysis and MRV approaches to validate quantitative measures of CDR. The development and implementation of a rigorous and comprehensive MRV framework, similar to those for TEA and LCA, will be critical for novel CDR approaches, which will benefit from guidance from NETL to achieve this goal. The team will provide updates to existing case studies, baselines and best practices, and guideline documents. NETL can also assist in first-of-a-kind MRV and LCA on small-scale pilot CDR facilities/projects that arise from funding opportunities. NETL will, when possible, make use of efforts discussed in Goals 5 and 6 of the CDR Multiyear Research Plan (MYRP) to validate portions of the TEA, LCA and MRV studies.

Goal 2 — Assess the Viability of Process Approaches Based on Technical and Systemic Limitations

As a related goal, NETL aims to understand the appropriate investment amounts and topic areas needed to optimize the impact of R&D dollars. To better understand this, processes must be evaluated to determine the potential marginal cost benefits of breakthrough component approaches. These approaches may include novel regeneration methods, improved contactor design and capture medium development. Performing this effectively can provide a path to commercialization for cutting-edge technologies while also identifying insurmountable physical and technological hurdles. NETL will also develop fundamental process models and perform computational fluid dynamics (CFD) simulations for base-level evaluation of novel CDR technologies. The results will then be used to evaluate these systems in terms of cost, life cycle emissions, market potential and MRV needs.

Under this goal, NETL will also provide benefits through the use of Carbon Capture Simulation for Industry Impact ($CCSI^2$)/Institute for the Design of Advanced Energy Systems (IDAES) to validate performance assumptions made for DAC hubs and pilots in partnership with the Office of Clean Energy Demonstrations (OCED). Furthermore, the performance data from DAC hubs projects and projects awarded from DOE’s Commercial DAC Technology Prize Competition will be used to update TEA and LCA results and CFD modeling and provide insights into technology scaling. NETL work on this goal will be in tandem with developments in Goals 3, 4 and 5 of the CDR MYRP to validate portions of the analyses.

technology advantages

- TEA and LCA expertise in advanced power systems and carbon capture, including engineers and analysts who have conducted hundreds of detailed studies of advanced power generation technologies, frequently paired with carbon capture.
- Access to an extensive set of equipment cost and performance data, including that used in the “Cost Performance Baseline for Fossil Energy Plants” volumes.
- Extensive set of references to ensure high-quality, consistent, comparable analyses results, including the Quality Guidelines for Energy Systems Studies (QGESS) and Systems Engineering and Analysis (SE&A) Guidelines.

R&D challenges

- The expansion of CDR to include novel approaches with widely varying process configurations and removal mechanisms requires the development of new models for CDR technologies and the exercise of these models to develop baseline cases for CDR technologies while aiming to meet ambitious FECM cost goals.

- While the International Organization for Standardization (ISO) guidance exists for performing LCAs, the decisions that must be made within that framework are not always straightforward, particularly when trying to prescribe an approach that will be applicable to all the potential projects that will use that guidance.

status

Development of TEA, LCA and process models is ongoing. A detailed process engineering and cost analysis of microwave-assisted DAC technology is complete. Recent LCA and TEA studies for enhanced mineralization and marine CDR are nearing completion while aiming to incorporate more real-world data into the models to enhance their applicability. Case studies of DAC technologies are being developed into a viable baseline study that can serve as the basis/benchmarks for protocol development.

available reports/technical papers

Hackett, G. "NETL Techno-Economic Analysis," Western Regional Carbon Conversion Procurement Grant Program Workshop, September 2022. *https://netl.doe.gov/sites/default/files/2022-09/5.%20Hackett%20-%20Techno-Economic%20Analysis%20091322.pdf*.

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J. Valentine, A. Zoelle, "Direct Air Capture Case Studies: Sorbent System," National Energy Technology Laboratory, Pittsburgh, PA, July 8, 2022. *https://www.netl.doe.gov/energy-analysis/details?id=d5860604-fbc7-44bb-a756-76db47d8b85a*.

Valentine, J., Zoelle A., Homsy, S., Mantripragada, H., Kilstofte, A., Sturdivan, M., Steutermann, M., and Fout, T. "Direct Air Capture Case Studies: Solvent System," National Energy Technology Laboratory, August 2022. https://netl.doe.gov/energy-analysis/details?id=36385f18-3eaa-4f96-9983-6e2b607f6987.

Stauff, N.E., et al. "Assessment of Nuclear Energy to Support Negative Emission Technologies" U.S. Department of Energy, September 2023. *https://fuelcycleoptions.inl.gov/SiteAssets/SitePages/Home/Nuclear_to_support_NET_final.pdf*.

Measurement of Pollutant Emissions from CDR Technology

primary project goal

The National Energy Technology Laboratory's Research and Innovation Center (NETL-RIC) is committed to advancing the U.S. Department of Energy's (DOE) understanding of co-benefits and disbenefits across carbon dioxide removal (CDR) and carbon management technologies and aims to robustly address air quality impacts of direct air capture (DAC) technology and other CDR technologies. This research goal focuses on the use of experiments and computational studies that can help quantify amine sorbent degradation, identify mechanisms of degradation in DAC technologies, and provide critical information necessary to enable the reduction or avoidance of DAC-related emission of pollutants.

technical goals

- Perform analytical measurements to quantify and characterize the degradation of amine sorbents used for DAC.
- Carry out first principles calculations to elucidate the mechanisms of degradation pathways for common aminated sorbent materials.
- Design and implement techniques and infrastructure for trace pollutant quantification at the DAC Center.
- Design and validate accelerating aging protocols to allow for rapid characterization of the stability of novel amine DAC sorbents.

technical content

Goal 3 — Develop and Validate Methods for Quantitative Prediction and Measurement of Pollutant Emissions and Secondary Pollutant Capture by CDR Technology

CDR is an emerging field of carbon management that is addressing several key knowledge gaps in addition to the development of specific individual technologies. These include the treatment of pollutants in DAC systems, addressing both absorption of pollutants from the atmosphere and secondary emissions from the DAC systems themselves. Goal 3 is focused on quantifying and characterizing the degradation of DAC materials as a key aspect of understanding the full impact of DAC deployment. NETL is working to ensure that the development of DAC technologies does not harm communities and may even result in environmental improvement of air and water quality. DAC developers are increasingly aware of problems posed by amine degradation of DAC sorbents, which shortens the lifetime of sorbents, driving up the cost of the technology while possibly releasing degradation products such as ammonia or

project focus:

Carbon Dioxide Removal Process Emissions

participant:

National Energy Technology Laboratory–Research and Innovation Center

project number:

CDR-MYRP Goal 3

predecessor project:

N/A

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N/A

organic nitrogen compounds into the environment. Amine degradation is a critical issue in point-source capture (PSC) systems as well, so efforts under the PSC Multiyear Research Plan (MYRP) will be complementary to and cooperative with this objective.

Many DAC sorbent materials contain amine functionalities that effectively bind with carbon dioxide (CO_2) molecules, but can show oxidative and/or thermal degradation when subjected to heat in the presence of oxygen. The rate at which different materials degrade and release amine emissions can affect the full impact of DAC deployment on communities. A combination of analytical chemistry and first principles computational chemistry approaches will be used to determine and model likely mechanisms of amine degradation on an amine-functionalized polymer sorbent. Testing will be performed in analytical laboratories at NETL as well as at NETL's DAC Center. The results of experiments will inform computational work to enable generalized insight into the degradation pathways. Data from both experimental and computational work will be further refined to allow for longer-term predictions of amine degradation following the validation of short-term empirical measurements, which will be key to determine environmental metrics of commercial deployment of these technologies. These accelerated aging protocols will then be tested at the DAC Center or in NETL's analytical laboratories.

Initial work is focused on completing analytical measurements of degradation and initiating first principles calculations to identify intermediates and products of at least one major degradation reaction pathway. Then, the team will design and implement techniques and infrastructure for trace pollutant quantification at the DAC Center and measure trace emissions from multiple technologies undergoing testing at the DAC Center. Finally, the focus will be on developing an accelerated aging protocol for predicting the long-term degradation of aminated materials, followed by extended validation testing.

technology advantages

- NETL has access to a suite of data science/analytics and modeling for energy innovation and application, as well as computational infrastructure, including WATT, Joule, Wafer-scale, and the Energy Data eXchange.
- NETL is uniquely positioned to serve as an unbiased resource to make consistent predictive toolsets available to technology developers without favoring any one technology.

R&D challenges

- A variety of types of DAC materials are composed of different amine-containing reactive groups that may undergo different degradation mechanisms depending on conditions.

status

Under Goal 3, analytical measurements of degradation and first principles calculations to identify intermediates and products of major degradation reaction pathways were initiated. Future work is focused on trace pollutant quantification at the DAC Center, along with infrastructure and techniques for testing and validation. An accelerated aging protocol for predicting the long-term degradation of aminated materials will be created and validated.

available reports/technical papers

None.

A National Testbed for High-Quality Performance Testing and Analysis of Emerging DAC Technologies

primary project goal

The National Energy Technology Laboratory's Research and Innovation Center (NETL-RIC) is constructing a new testing center for direct air capture (DAC) technologies, called the NETL DAC Center, at its site in Pittsburgh, Pennsylvania. The center will provide a consistent means of testing DAC technologies in an unbiased manner across a variety of scales and climate conditions. Testing will be aided by computational tools that enhance the testing procedure and provide insight into deployment options.

technical goals

- Build a first-of-a-kind test facility dedicated to DAC technologies available to technology developers seeking unbiased performance testing.
- Allow for simulation of realistic conditions across multiple technology scales and environmental parameters.
- Develop computational tool sets to allow for smooth operation of test facilities, suggest most efficient testing approach, and project optimal conditions for deployment.

technical content

In 2022, NETL received $20 million in funding for the development of a novel testing facility capable of assessing DAC technologies at various states of maturity at the laboratory site in Pittsburgh, Pennsylvania. The DAC Center operates in a similar manner to the National Carbon Capture Center (NCCC), which is focused on point-source capture technologies. The facility is designed to allow for partnership with technology developers to assess their novel DAC technologies in a consistent manner that assures performance in potential future environments. The major aim of this work is to help developers understand the impact of climate and economic conditions on deployment of their technologies in locations around the United States. Construction on the site began in 2023, with a focus on the smaller-scale test systems, with full operations planned for 2025.

The DAC Center has the following three scales at which testing can be carried out, represented by the renderings in Figure 1:

- Material Scale: Designed for novel material assessments at approximately 0.1 kg carbon dioxide (CO_2)/day. These tests are focused on material properties

project focus:

DAC Testing Facility

participant:

National Energy Technology Laboratory–Research and Innovation Center

project number:

CDR-MYRP Goals 4

predecessor project:

N/A

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partners:

N/A

and longevity and are able to accommodate a variety of different material forms, including granular, fiber and structured materials.

- Module Scale: Integrated reactor systems at approximately 4 kg CO_2/day. These tests are focused on module capture and flow measurements. This equipment can accommodate not only a variety of form factors, including granular solids, fiber mats and monoliths, but it can also allow for unconventional regeneration methods, such as Joule heating or microwaves.
- Prototype Scale: Bays for developer-built skids at approximately 30 kg CO_2/day. This testing focuses on testing small pilot-scale prototype DAC units. The equipment can test up to 3,000 standard cubic feet of air per minute and includes connections to utilities such as steam, electricity and cooling water.

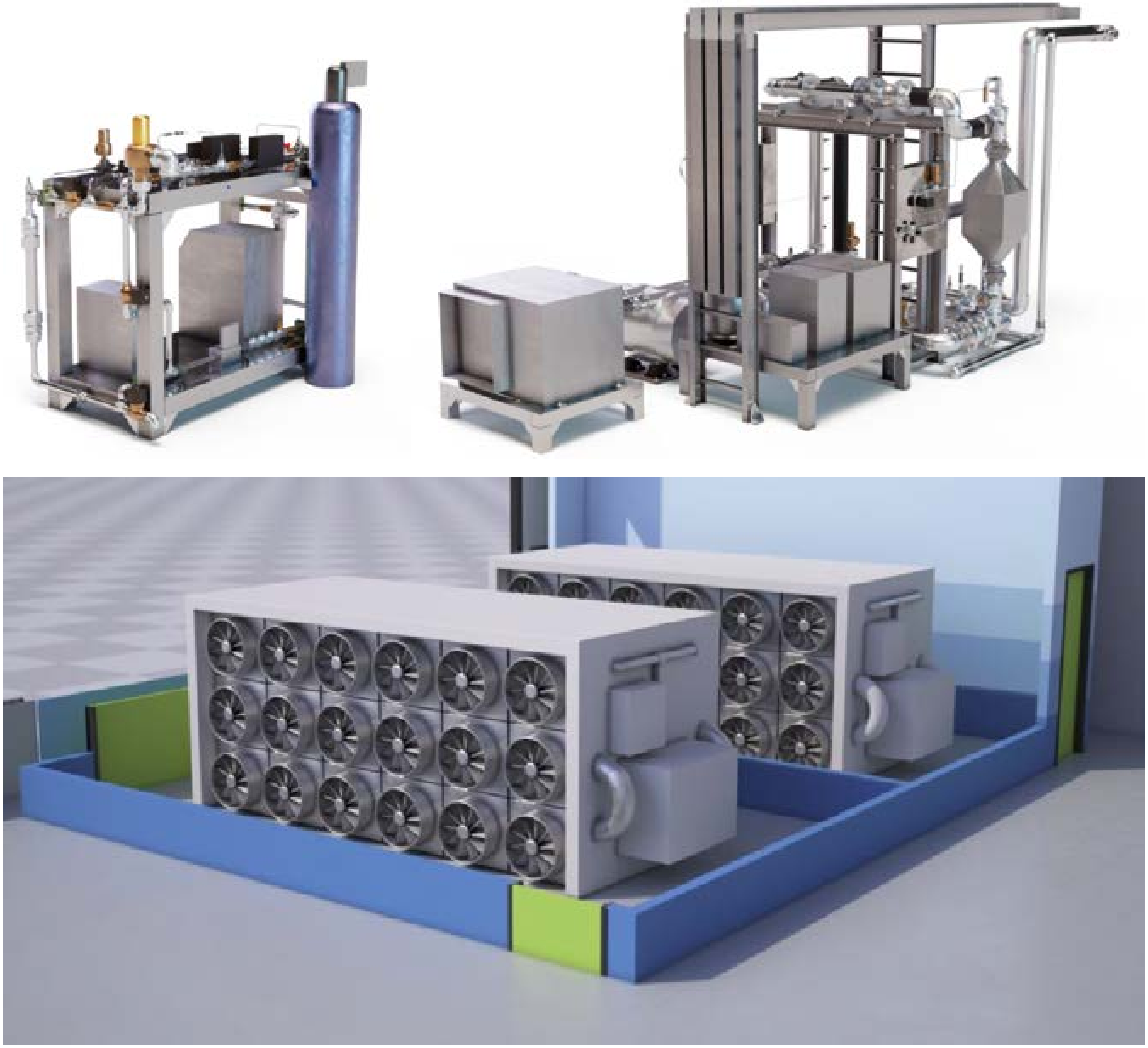

Figure 1: Renderings of the three scales of testing at the NETL DAC Center: Material Scale (top-left), Module Scale (top-right) and Prototype Scale (bottom).

Computational tools will be integrated with the DAC Center to enhance the value of the testing that developers carry out. Computational models across a range of scales will be optimized under different carbon-constrained scenarios. Analysis of design-of-experiments will provide recommended testing conditions for each technology, and a cyber-physical interface to be designed for the facility will allow for the fine tuning of environmental conditions and energy availability situations for DAC materials of interest. This simulation work can aid not only technology developers testing at the DAC Center site, but also other Office of Fossil Energy and Carbon Management (FECM) project technologies that are being tested elsewhere. Participants performing testing at NETL will also have access to NETL's suite of experts for various complementary analyses, including techno-economic analysis, life cycle analysis, and process optimization through the use of computational fluid dynamics programs.

While the prototype-scale test site is being constructed, work is ongoing for the smaller scales to ensure that clients are able to test technologies effectively. Validation of select sorbents will be a first step toward establishing the validity of the DAC Center, which is critical to attain an expanded client base for this testing. The DAC Center is poised to provide the maximum benefit to its customers while establishing a "gold standard" of performance testing for DAC materials.

technology advantages

- The DAC Center provides a versatile tool that can verify technologies under a wide variety of climate and air quality conditions that may be difficult to fully evaluate elsewhere.
- Equipment is appropriate to perform rigorous testing at a wide range of technology scales.
- Computational tools can allow for simulation of energy availability conditions and optimization of deployment environments.

R&D challenges

- Building first-of-a-kind testing facility necessitates adaptability during unforeseen challenges.
- Accurate validation is required to attract future users of the facilities.

status

NETL has constructed and validated testing for units at the material scale. Customers have begun to bring their developed materials to the NETL DAC Center for performance testing. The prototype-scale test system is currently under construction. Validation of the prediction tool set capabilities will then be carried out for a representative sorbent to establish consistency. Full capabilities are expected to be available to potential customers in 2025.

available reports/technical papers

NETL DAC Center Fact Sheet. *https://netl.doe.gov/sites/default/files/2024-03/R-D235%20-%20NETL%20Direct%20Air%20Capture%20DAC%20Center.pdf*.

A Comprehensive Roadmap to Development, Technology Transfer and Commercialization for CDR Technology

primary project goal

The National Energy Technology Laboratory's Research and Innovation Center (NETL-RIC) is working to develop next-generation carbon dioxide removal (CDR) technologies. Novel sorbent materials are being studied at the laboratory level to advance their viability toward commercial development, which requires establishment of connections with industrial partners to realize these goals. A major focus of this goal is to establish pathways for external technologies and those developed at NETL to achieve eventual commercial deployment.

technical goals

- Develop NETL technologies through laboratory research beginning from various scales of development.
- Collaborate with industrial partners to enable further technology readiness advancement toward potential commercial deployment.
- Determine pathways for emerging CDR technologies to progress toward commercialization that are applicable to a broad range of externally developed technologies.

technical content

A suite of CDR technologies are currently in research stages of development, with hurdles existing to reach commercialization. Despite research proving the advantages of more novel technologies, only the first-generation technologies, which are primarily amine-based direct air capture (DAC) systems, have reached deployment scale. It is critical to better understand the challenges the new advanced technologies face to achieve demonstration and commercial market viability. Thus, under this task, NETL is focused on creating technology development base case studies that can be applied to emerging CDR technologies. A focus of this work will be on developing novel amine porous solid sorbent technologies at NETL, across a range of starting technology readiness levels (TRLs), in collaboration with industrial partners to progress the technologies toward maturity. This will address key knowledge gaps to help accelerate CDR technology and establish a technology pipeline that will aid in advancing toward U.S. Department of Energy's (DOE) Carbon Negative Shot goals.

project focus:

Carbon Dioxide Removal Materials, Process, and Scale-up

participant:

National Energy Technology Laboratory–Research and Innovation Center

project number:

CDR-MYRP Goal 5

predecessor project:

2023 Carbon Capture FWP

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partners:

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There are two low-TRL research projects ongoing under Goal 5. The first is focused on developing computational methods for accurate screening of gas sorption and diffusion in metal organic framework (MOF) materials, as well as to aid in their design and synthesis. NETL completed a large screening study of MOF materials, calculating gas sorption and diffusion in more than 100,000 MOF materials and more than 1 million mixed matrix materials (by combination with experimental results for polymers), and ranked them based on their individual estimated costs of carbon capture. In most studies of gas sorption in MOFs, the MOF atoms are held fixed to simplify the calculations. NETL researchers further developed computational software to allow for including the effect of MOF atom movement, leading to more accurate calculations of key parameters of carbon dioxide (CO_2) sorption. NETL researchers are currently developing machine learning model potentials to further improve the accuracy of predictions for CO_2 sorption in MOFs. The most promising simulated MOFs may be used in synthesis tasks under this goal.

The other low-TRL thrust is focused on introducing porosity in a covalently bonded amine polymer material via water soluble crosslinkers. This sorbent, based on commercial polymer and mesoporous fillers, combines a high molecular weight amine functionalized polymer and crosslinkers to introduce porosity. This generates a material with high mechanical strength and a high number of adsorptive amine sites that can also be processed into various form factors, including solid fibers, electro-spun fibers, flat sheets, etc., without a need for additional processing steps or another material. The result is a robust DAC material with rapid, high-capacity CO_2 capture and no amine leaching. A diagram of the sorbent components of polymer and filler is shown in Figure 1. While this material is still in the early stages of development, a report of invention and publication have recently been submitted, laying the groundwork for the creation of a licensable material and collaborative work with commercial partners.

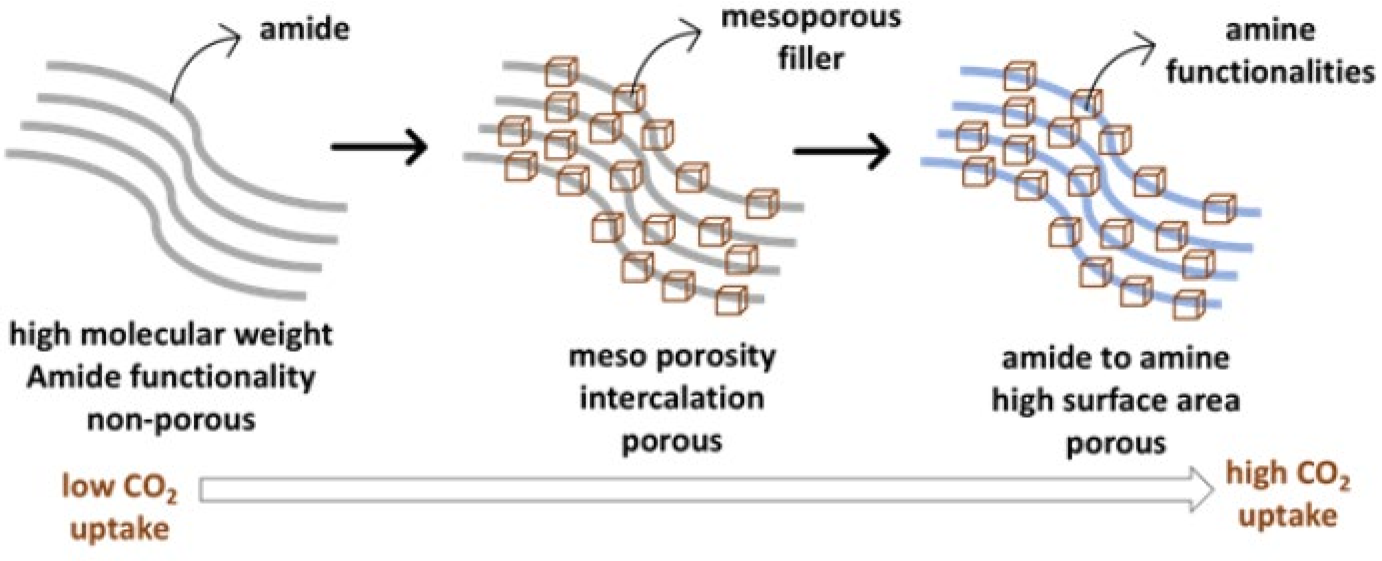

Figure 1: Illustrative representation of the novel polymeric sorbent design emphasizing the poly(N-vinylformamide) with a high density of amine sites and the filler material with high mesoporosity.

Middle-Stage Technologies

Three middle-stage TRL areas of research exist under this goal, including one focused on the development of a viable polymeric sorbent technology that combines desirable performance characteristics of state-of-the-art DAC materials with the added benefits of improved processability. This sorbent overcomes challenges facing DAC materials that show promising absorptive performance as powders but need to be incorporated into a structured form to be utilized successfully in a real DAC process. This modification of sorbents in powder form to structured form requires additional materials such as binders, which can decrease working capacities and provide barriers to heat and mass transfer, worsening the kinetics of adsorption and desorption. NETL researchers have developed the PIM-1-AO amine polymer, with the reaction mechanism shown in Figure 2, that displays promising properties, such as high surface area, permanent microporosity, uniform pore size distribution, and high chemical and thermal stability. A selection of amines such as diethylenetriamine (DETA), tris(2-aminoethyl)amine (TAEA) and tris(3-aminopropyl)amine (TAPA) have been incorporated into the material. The material is based on a polymer of intrinsic porosity (PIM-1), which provides a porous and stable structure. Modification of the PIM-1 by the amidoxime functional group creates a tethering point that tightly holds amine groups and renders the polymer soluble, which allows for the sorbent to be shaped into forms amenable for CO_2 capture from ambient air. These polymers also offer chemical stability; high CO_2 uptake; fast kinetics; and the possibility to be shaped into any desired contactor geometry, such as hollow fibers or porous mats. At NETL, this material has been formulated as a porous fiber, an electrospun mat, a hand-cast flat sheet and a machine-cast flat sheet. NETL is partnering with several industrial partners, investigating various strategies for formulating the PIM-1-AO-amine material into DAC contactors of various types. The team also plans to investigate the incorporation of porous sorbent particles (such as amine-functionalized MOFs) into the shapeable polymer material. Following testing under realistic DAC conditions, the most promising PIM-1-AO amine formulations are being fashioned into a small DAC contactor to be tested at the DAC Test Center in the near future.

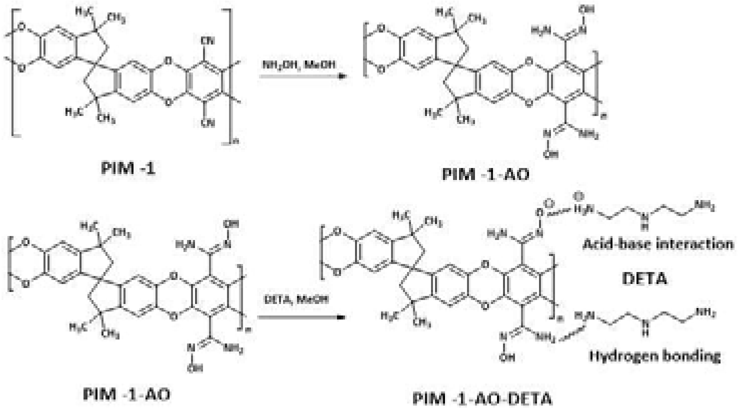

Figure 2: Reaction scheme and preparation of PIM-1-AO-DETA sorbent.

A second mid-TRL research area is focused on designing and optimizing novel DAC reactors through NETL's simulation-based engineering (SBE) capabilities. The simulation work uses small-scale experiments to validate the modeling approach and to help guide the design and optimization process with well-characterized, small-scale physical models. The models serve as platforms for system optimization and could incorporate technologies for advanced manufacturing and process intensification. These computational tools are used to analyze novel reactors to study air flow and interaction with various polymer sorbent bed geometries, and to predict the effect of different reactor geometries, temperature zones, pressure differentials, gas velocity field gradients, and other reactor characteristics on device performance. This research is aimed at developing, validating and demonstrating the application of computational fluid dynamics (CFD) models to DAC system design and optimization. Validated CFD models and simulation-based optimization serve as key steps toward eventual commercial-scale design and optimization.

A third mid-level TRL area of research is focused on developing a multiscale modeling framework that can provide high-fidelity process-scale models with accurate predictions of performance at larger scales. Work follows the successes of scale-up modeling for point-source capture technologies using the Carbon Capture Simulation for Industry Impact ($CCSI^2$) tool set. This task helps to determine and guide technology development of the polymeric sorbent and the DAC process developed at NETL through the development of rigorous, optimized processes and to understand the impact of physical property models on the predictability of the process, guiding data collection efforts to improve performance predictions at process scale. These modeling tools and framework will be used to better incorporate learnings to direct testing at the NETL DAC Center, targeting conditions that will have the largest impact in reducing technical risk.

Late-Stage Technologies

DAC technologies require novel materials that have high uptake capacities, rapid and energy efficient regeneration, durability, and scalability to have an impact at larger scales. Advanced technologies must utilize promising materials and work them into form factors that allow for continued high performance while allowing them to be amenable to larger-scale processing. One example of a technology developed at NETL that is nearing commercial stage is a scalable flat-sheet-supported amine CO_2 sorbent, which is referred to as fibrous amine-functionalized matrix (FAM). This sorbent is based on the impregnation of functional materials into a porous glass fiber flat sheet to form free-standing sheets amenable to incorporation into structured gas-solid contactors. In this work, these advanced materials are incorporated into a flat-sheet-based sorbent that can offer high mechanical strength, low pressure drop and efficient heat transfer for ambient air carbon capture. Other advantages include its ease in collecting material for transport and disposal, the lack of amine emissions, and short contact times that lead to faster cycling and smaller equipment.

A diagram showing the synthesis processes for both the drip-coat method, used at smaller scales, and the spray-coat method, to be used at larger scales, is shown in Figure 3. In this research, an optimized formula is incorporated into flat-sheet substrates, using heat to crosslink the fibers containing the amine sorbents. The sorbent and substrate selected were tested under realistic DAC conditions to ensure high performance with a scalable form factor, with successful performance results. Ongoing work is focused on sorbent characterization, performance assessment and reactor design. Researchers aim to establish FAM sorbent performance under authentic DAC conditions at laboratory scale and construct a lab-scale reactor module based on optimal conditions to move this toward a scaled-up product. NETL is currently working in collaboration with industrial companies to pursue further scale-up to a potential marketable product.

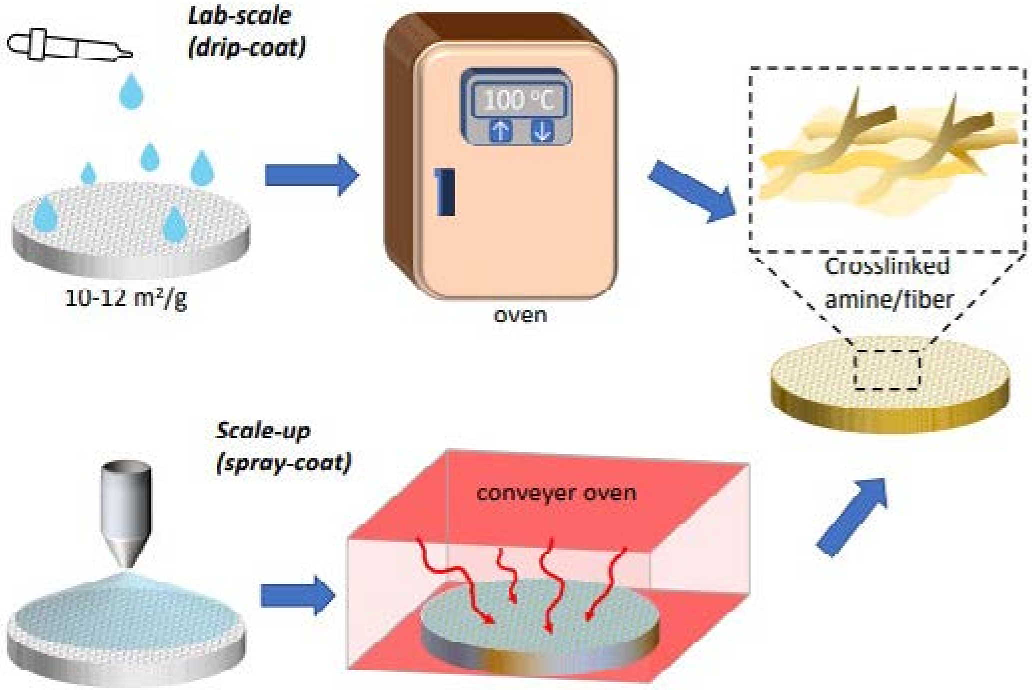

Figure 3: Overview of drip-coat and spray-coat methods for synthesis of FAM sorbent materials.

Commercialization Approach

Through historic investment in technology development for carbon capture, NETL has evolved an integrated development approach that leverages diverse capabilities — including computational material design, synthesis, fabrication, CFD, advanced process design/optimization, and techno-economic analysis (TEA)/life cycle analysis (LCA) — to collaboratively create technologies that address programmatic goals. This approach has generated a pipeline of sorbent-based technologies for DAC at varying stages of development. Improved materials that address the critical needs for improved performance, scale up and commercialization can substantially accelerate progress toward the DOE Carbon Negative Shot goal, but more effective methods of interaction are needed between material developers and companies seeking to deploy DAC technology. To address this issue, NETL is expanding its collaborative process of technology development to include commercialization partners at all stages of the process. Partners involved in the commercialization of DAC technology will be brought into the development process using the pipeline technologies as test cases. Leveraging these experiences, it will be possible to construct a roadmap for joint development and technology commercialization in the DAC space.

technology advantages

- NETL is working with a suite of technologies that span a range of TRLs, allowing for a wide variety of learning experiences in how collaboration with industry in the progression of these technologies may occur.
- NETL is uniquely positioned to perform work to determine the challenges and most effective pathways for technologies to reach commercialization and make this information widely available to developers of emerging CDR technology.

R&D challenges

- CDR deployment is currently limited to a few technologies that represent the early generations of research, as there are numerous pitfalls with advancing novel technologies to commercial readiness.
- Commercialization relies on the connections with industrial partners with resources and expertise that are outside of laboratory research.

status

Technologies being developed by NETL researchers are at various stages in their technology readiness. In each case, efforts are ongoing to continue to scale-up the technologies while collaborating with industrial partners who can aid in the progression toward marketable products.

available reports/technical papers

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Tiwari, S., et al. “Computational Screening & Design of Alkylamine-Functionalized Polymer Sorbents.” 2023 Carbon Management Project Review Meeting. *https://www.osti.gov/biblio/1997459*.

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Wang, Q., et al. “Direct Air Capture of CO_2 Using a Robust Synthesized Fibrous Amine-Functionalized Matrix (FAM) Sorbent.” *Energy Analysis | netl.doe.gov*.

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Budhathoki, S. et al. "High-throughput computational prediction of the cost of carbon capture using mixed matrix membranes." 2018. *https://doi.org/10.1039/C8EE02582G*.

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Develop, Validate and Deploy a Computational and Procedural Toolset for Measurement and Verification of Mineralization Storage Durability

primary project goal

The National Energy Technology Laboratory's Research and Innovation Center (NETL-RIC) is developing a novel tool to objectively assess storage durability of novel carbon dioxide removal (CDR) technologies. The goal of this effort is to develop a transparent, science-informed computational framework to objectively quantify and compare the durability of CDR approaches for a variety of candidate pathways over a range of relevant conditions. The computational approach will be validated with results from available third-party field demonstrations to ensure their accuracy and usefulness to quantify storage durability.

technical goals

- Establish a conceptual basis and develop a computational tool to quantitatively forecast and verify storage durability of proposed mineralization pathways, in the context of process uncertainties.
- Test, refine and validate the mineralization storage durability tool using representative, hypothetical CDR mineralization scenarios and available data from third-party pilot tests.

technical content

Goal 6 — Develop, Validate and Deploy a Transparent, Defensible, Computational and Procedural Tool for Measurement and Verification of CDR Mineralization Storage Durability

CDR is an emerging field of carbon management referring to a suite of approaches with potential to remove carbon dioxide (CO_2) from the atmosphere, to address emissions from the hardest to decarbonize sectors — like agriculture and transportation — and to eventually remove legacy CO_2 emissions from the atmosphere. Candidate CDR approaches include direct air capture (DAC) coupled to durable storage, soil carbon storage, biomass carbon removal and storage, enhanced mineralization, ocean-based CDR, and afforestation/reforestation. For mineralization approaches, there is a critical need to better understand how durable CO_2 storage truly is to properly assess

project focus:
CDR Durability

participant:
National Energy Technology Laboratory–Research and Innovation Center

project number:
CDR-MYRP Goal 6

predecessor project:
N/A

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partners:
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the greenhouse gas emissions reductions that can be claimed. As such, Goal 6 is focused on developing a quantitative, science-based tool to credibly estimate and validate CO_2 removal durability.

NETL will develop a computational tool to quantify storage permanence for CO_2 mineralization processes — a critical element of establishing the viability of novel, net-negative CDR approaches. The team will develop and apply computational tools that can accurately predict and assess mineralization durability. These models will be developed and further refined in coordination with third-party field studies using observed data to evaluate concordance with durability forecasts and to assess the effectiveness of the toolsets.

The team will first aim to establish the key system features, processes and parameters relevant to evaluating CDR durability — including mineralization pathways, process elements, system boundaries, relevant scales and timeframes, and governing physical-chemical attributes (kinetics, thermodynamics, mass transfer constraints, etc.). A computational model capable of linking these parameters at various scales and process complexities will be developed. Following the building of this framework, a user interface will be created that incorporates functionality for scenario and parameter definition, simulation execution, sensitivity and uncertainty analysis, and results visualization and interpretation. This tool will be validated through comparing forecasts of durability with empirical data from select field tests for a variety of mineralization pathways — in collaboration with CDR stakeholders.

Research to quantify CDR durability is intended to complement those of CDR Multiyear Research Plan (MYRP) Goals 1, 2, 3 and 5, and contribute to the overarching goal of developing best practices for measurement, reporting and verification (MRV) of CDR technologies.

technology advantages

- NETL has access to a suite of data science/analytics and modeling for energy innovation and application, as well as computational infrastructure, including WATT, Joule, Wafer-scale, and the Energy Data eXchange.
- NETL is uniquely positioned to serve as an unbiased resource to make consistent predictive toolsets available to technology developers without favoring any one technology.

R&D challenges

- A variety of types of candidate mineralization pathways have been proposed and developing a coherent, defensible conceptual and computational framework to evaluate CDR durability for all pathways is technically challenging.
- Many of the proposed mineralization pathways involve interaction with open natural systems; approaches to estimate mineralization reaction rates/efficiencies and reactant/product disposition in these systems is uncertain and characterizing durability will require appropriate representation of these uncertainties.
- Validation of CDR durability will require identification of appropriate measures and availability of quality datasets from field demonstrations and commercial-scale activities.

status

The effort to design a conceptual framework to estimate and validate CDR mineralization durability has been initiated. Forthcoming work will focus on developing a prototype computational tool for preliminary testing and evaluation.

available reports/technical papers

None.

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CARBON CAPTURE TECHNOLOGY SHEETS

Point Source Carbon Capture

CO_2 Capture at Louisville Gas & Electric Cane Run Natural Gas Combined Cycle Power Plant

primary project goal

Electric Power Research Institute (EPRI) and partners are conducting a front-end engineering design study (FEED) for the University of Kentucky (UKy) solvent-agnostic low-cost carbon dioxide (CO_2) capture process retrofitted to the Louisville Gas & Electric and Kentucky Utilities (LG&E-KU) Cane Run Generating Station Unit 7 (CR7), a 640-megawatt (MW) natural gas combined cycle (NGCC) power generation unit, a PPL facility, to capture 95% of approximately 1.7 million tonnes per year (tpy) CO_2.

technical goals

- Complete a FEED study of an integrated aqueous CO_2 capture system at the LG&E-KU CR7 NGCC power generation unit.
- Prepare a detailed engineering design, construction, and operation plan, including a design basis; process design package; cost estimate; analysis of CO_2 transportation and long-duration storage options; and separate analyses on the business case, life cycle, environmental health and safety (EH&S), environmental justice, and economic revitalization and job creation.

technical content

EPRI, UKy, Bechtel, and PPL Corporation (via LG&E and KU) are conducting a FEED study for capture of greater than 95% of the CO_2 from unit CR7 in Jefferson County, Kentucky (Figure 1). This unit is representative of power plants in the Midwest and Midsouth of the United States where intermittent renewable power and geographical storage for CO_2 is limited. An optimized aqueous amine absorption capture process developed by UKy will be applied to the CR7. The UKy process can accommodate any solvent (i.e., it's solvent-independent), but the project will use UKy's aqueous primary amine solvent. The projected cost is \$49.0/tonne CO_2 (2018 dollars), at 95% CO_2 capture from CR7, a 640-MW NGCC commissioned in 2015 and located in an economically and environmentally distressed region in urban Louisville, Kentucky. Carbon dioxide storage to the north of the CR facility along the Ohio River corridor will be carefully considered, including options for interim transportation by barge to the Gulf Coast via Ohio River then Mississippi River until a pipeline infrastructure is in place.

program area:
Point Source Carbon Capture

ending scale:
FEED

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Solvent-based Carbon Capture at NGCC Plant

participant:
Electric Power Research Institute (EPRI)

project number:
FE0032223

predecessor projects:
N/A

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partners:
All4 Inc.; Bechtel National Inc.; Louisville Gas & Electric and Kentucky Utilities, PPL companies; University of Kentucky Research Foundation; University of Michigan; Vogt Power International

start date:
12.22.2022

percent complete:
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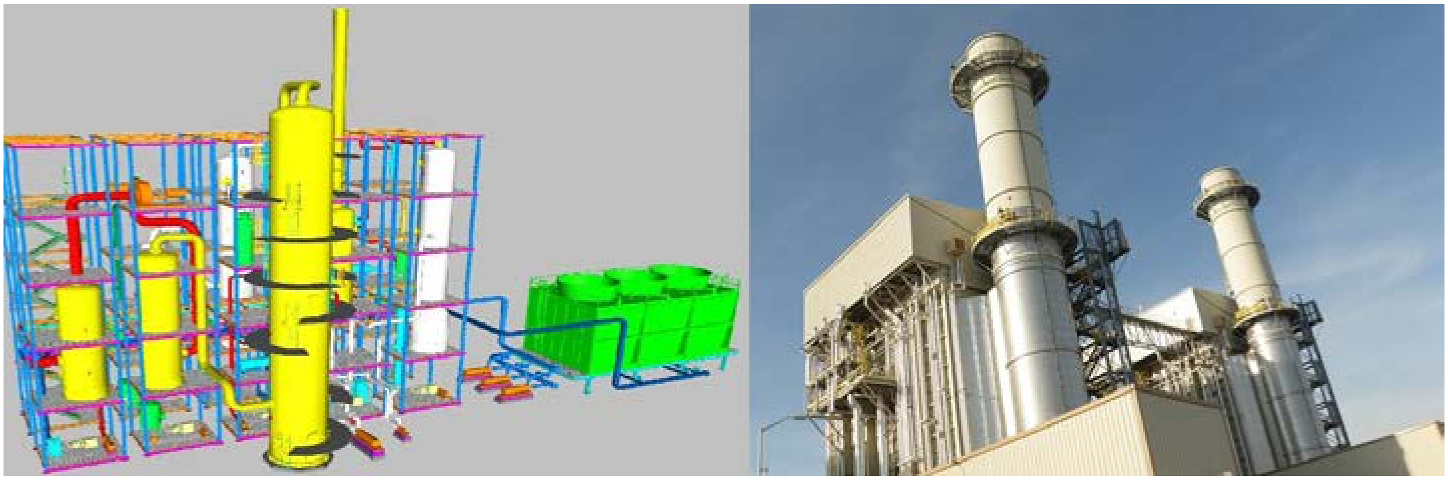

Figure 1: Conceptualized carbon capture plant (left) for the Cane Run #7 NGCC power generation unit at LG&E-KU, a PPL facility.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	g/mol	<90, amine	<90, amine
Normal Boiling Point	°C	160	160
Normal Freezing Point	°C	2	2
Vapor Pressure @ 15°C	bar	0.0007	0.0007
Manufacturing Cost for Solvent	$/kg	6 (estimated in 2023)	6 (estimated in 2023)
Working Solution			
Concentration	kg/kg	<0.45	<0.45
Specific Gravity (15°C/15°C)	-	~1.01	~1.01
Specific Heat Capacity @ STP	kJ/kg-K	3.5	3.5
Viscosity @ STP	cP	4.3	4.3
Absorption			
Pressure	bar	1	1
Temperature	°C	33-55	33-55
Equilibrium CO_2 Loading	mol/mol	2.3	2.5
Heat of Absorption	kJ/mol CO_2	55-6	55-60
Solution Viscosity	cP	3-5	3-5
Desorption			
Pressure	bar	1.6-2.2	1.6-2.2
Temperature	°C	117-120	117-120
Equilibrium CO_2 Loading	mol/mol	1.1-1.4	1.1-1.4
Heat of Desorption	kJ/mol CO_2	55-60	55-60
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	>95/>99.9/1.65	
Absorber Pressure Drop	in WC	<15	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Based on evaluation of historic data from 2019 to 2022, the design flue gas condition leaving the heat recovery steam generator (HRSG), wet basis, is chosen as:

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
15 psia	202.6 °F	3.81	10.96	73.23	12.00	--	--	9

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The UKy solvent is an aqueous solution of a hindered primary amine. A carbamate species is formed upon CO_2 absorption. In a CO_2 capture absorber, the absorption rate, **R**, as a function of temperature, T, and carbon loading, **C/N**, can be expressed as: $R(T, C/N) = k_G \cdot a \cdot (P_{CO2} – P^*_{CO2})$ where k_G is mass transfer coefficient, **a** is effective wetted surface area, and $(P_{CO2} – P^*_{CO2})$ is the driving force, the difference in the partial pressure of CO_2 in liquid from the gas. Significant increase in **R**, via k_G and **a**, and corresponding reduction of capital cost comes from the mass transfer enhancement of the aqueous system compared to any second-generation technology because there is an order of magnitude greater effective wetted surface area in the top of the absorber.

Solvent Contaminant Resistance – UKy analysis shows the solvent is more resistant to degradation, a 40–50% improvement than 30 wt% MEA. Accumulation of metals within the solvent is expected to be equivalent to that within 30 wt% MEA.

Solvent Foaming Tendency – UKy small pilot CO_2 capture unit operations do not show significant frothing concern with the UKy solvent.

Flue Gas Pretreatment Requirements – When applied to natural gas-fired flue gas, no pretreatment is required. The solvent used is a hindered primary amine and is not known to form stable nitrosamine species, therefore no additional nitrogen oxide (NO_X) removal is anticipated. No additional moisture removal required, as it is for ionic liquids.

Solvent Makeup Requirements – Two factors contributing to solvent makeup rate are degradation and emission. UKy analysis shows the solvent has degradation rates less than 30 wt% MEA and when the UKy-developed solvent recovery technology is applied, the solvent emission will be about 0.5 parts per million (ppm) or less. The anticipated solvent makeup rate is less than 0.6 kg/tonne CO_2 captured for routine transition state operation by following external load change for power generation. However, the anticipated solvent makeup rate could be less than 0.3 kg/tonne CO_2 captured for industrial applications that are routinely operated at near-steady state.

Waste Streams Generated – The waste streams of the UKy post-combustion CO_2 capture process are the same as any other post-combustion CO_2 capture process. There will be a reclaimer waste stream from the solvent loop.

Process Design Concept – The preliminary general layout for the CO_2 capture process is shown over an aerial view of the Cane Run Generating Station, a PPL facility, Figure 2. The circles marked by the "A" are the proposed locations for the absorber columns. The blue rectangle marked by the "B" will house the balance of plant for the project. The circle marked by the "C "is the proposed location of the stripper tower. Location of the absorbers in very close proximity to the stack allows for elimination of a booster fan in UKy technology by greatly reducing the flue gas path pressure drop and therefore operating and capital costs.

Figure 2: Preliminary general layout of major CO_2 capture unit equipment.

The block flow diagram (BFD) in Figure 3 contains the components and configuration to be used in the carbon capture island for Cane Run Generating Station Unit 7. Two absorption trains and one solvent regeneration train are assumed. The flue gas enters through the direct contact cooler (DCC), moves through the absorber from the bottom, moves through the absorber filled with lean solvent, exits the top of the absorber, moves to the water wash, and then ultimately through the stack. Cooling water cycles through the DCC associated with each absorber. Plant water is sent directly to the water wash. Rich solvent leaves the absorber and is sent through heat recovery exchangers to the stripper. The lean solvent exits the stripper and cycles back to the absorber through the same set of heat exchangers. The CO_2 removed from the rich solvent in the stripper exits overhead and is sent to the CO_2 compressor train.

Staged solvent feeds into the absorber and stripper increases CO_2 capture rate while lowering solvent degradation and energy requirement. In the absorber, most of the solvent with a higher carbon loading is fed to the middle of the column, capturing most of the CO_2, while a smaller amount of solvent at a lean carbon loading is fed to the top as a polishing step, capturing the remaining CO_2. The absorber temperature profile is controlled through the feed stream temperatures, as in the case of intercooling, to enhance the absorption driving force, which results in an effective, short column. The rich solvent is split into two streams prior to entering the stripper: a warm stream is introduced at the top of the stripper at lower temperature and the remaining rich solvent is introduced in the middle of the column at higher temperature to minimize the overhead stream H_2O/CO_2 content and reduce the required regeneration energy. Heat is recovered from three sources: (1) the stripper overhead condenser heat is used to heat the rich solvent, (2) the inter-stage coolers of CO_2 the compressor are used to heat the rich solvent, and (3) reboiler condensate sensible heat is used to preheat a portion of the rich solvent to be fed to the stripper. Each further reduces the reboiler specific duty and cooling tower duty, and improves overall plant efficiency. The UKy-developed, machine learning-based feed-forward process control strategy continuously and automatically minimizes steam extraction while meeting external load changes and maintaining the target CO_2 capture.

As shown in Figure 3, taking advantage of NGCC positive pressure HRSG exhaust, the flue gas enters the carbon capture unit at a lower temperature than for case B31B (NGCC with CCS) from the 2019 National Energy Technology Laboratory (NETL) bituminous baseline report Rev 4, eliminating the need for a blower and reducing the cooling duty. As shown in, Figure 3 the flue gas is then cooled by co-current, downward, in-duct direct contact cooling before entering the bottom of the absorber where 95+% of the CO_2 is captured with staged solvent feeds. Treated flue gas exits the top of the absorber through the water wash section, achieving emissions of less than 0.8 ppm amine entrainment and aerosols. The rich solvent is fed to the stripper at two points over structured packing to minimize the $H_2O:CO_2$ vapor ratio at stripper exhaust. In the stripper, most of the solvent is regenerated to a higher lean loading and a smaller amount of solvent is regenerated to a lower lean loading required for the high capture efficiency, thus minimizing degradation and energy consumption associated with the deeper stripping. A typical rich solvent loading (2.3–2.5 mol C/kg soln) is maintained to keep the regeneration energy low under the UKy rich split arrangement. Together, these unique features of the UKy CO_2 capture system lower the reboiler specific duty to approximately 1,060 British thermal units (Btu)/lb CO_2. Minimizing energy consumption through heat recovery also decreases cooling water duty.

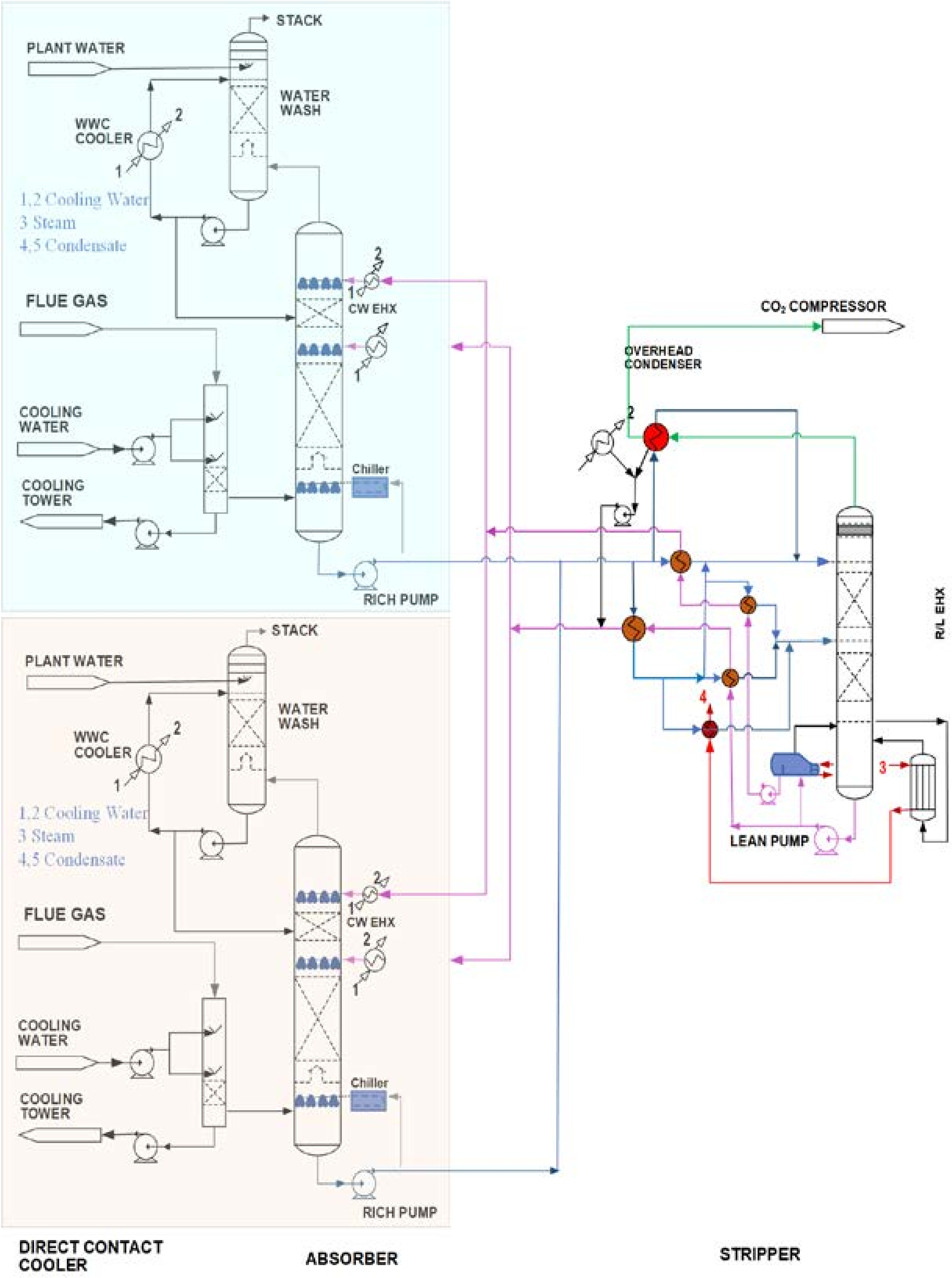

Figure 3: BFD for UKy CO_2 capture process applied to Cand Run Generating Station Unit 7, patent protected.

TABLE 2: PRELIMINARY POWER PLANT CARBON CAPTURE ECONOMICS AT 95% CO_2 CAPTURE EFFICIENCY, COMPARED TO 2019 B31B AT 90% CO_2 CAPTURE EFFICIENCY

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	2018$/tonne CO_2	$49.00	$49.00
Capital Cost	2018$/MWhr	18	18
Variable Cost	2018$/MWhr	5.6	5.6
Cost of Electricity (Excluding Transportation & Storage)	2018$/MWhr	61.1	61.1

Following U.S. Department of Energy (DOE)/NETL guidelines, Rev 4, and using knowledge gained on the equipment cost, the ratio among the bare erected cost, total plant cost, and equipment and material costs from the techno-economic analysis (TEA) issued by Trimeric for another UKy DOE/NETL project (DE-FE0031604), a preliminary TEA was conducted using the UKy CO_2 capture process and solvent. However, this is not a direct comparison due to the lack of details associated with the proprietary Cansolv process on the system's equipment specifications, sizing, methodology, and auxiliary power calculation. Even with 95% CO_2 capture efficiency, the overall plant efficiency is maintained at 48.0%, slightly higher than 47.7% of 2019 B31B. While the net power output is nearly maintained, significant capital cost reduction—28.1% for overall plant, 55.9% for the CO_2 removal system—can be achieved for UKy technology compared to 2019 B31B. The contribution of capital investment to cost of electricity with 95% CO_2 capture is reduced by 28.1% from $25 (90% capture) to $18.0/megawatt-hour (MWhr). The expected cost of CO_2 capture excluding transportation and storage is reduced by 39%, from $79.7 (90% capture) to $48.7/tonne CO_2 captured.

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Capital Cost – Projected capital expenditures in dollars per unit of energy produced.

Variable Cost – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – The values provided in the table are based on the reference plant provided by NETL for the TEA, found in the "Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity" report Revision 4, September 24, 2019, $2018.

Scale of Validation of Technology Used in TEA – The Aspen Plus® model used for the TEA has been validated with experimental data from the UKy 0.7-megawatt-electric (MWe) engineering-scale CO_2 capture unit.

technology advantages

- The absorber height is minimized by maximizing the liquid/gas contact area, temperature control, and discretized packing.
- High CO_2 capture efficiency is achieved with a split lean absorber feed, with most of the CO_2 being captured by the lower feed at a higher rich loading and the remaining CO_2 captured by the upper feed at a leaner rich loading.
- Solvent degradation is minimized by regenerating only a small amount of the solvent to the low lean loading required for the high CO_2 capture efficiency.
- Energy consumption is minimized through novel heat recovery strategy and a split rich feed to the stripper, which also reduces the CO_2 content in the stripper overhead stream and decreases the cooling water duty.
- The CO_2 capture technology is completely integrated with the gas turbine, heat recovery steam generator, and CO_2 compressors, to eliminate the need for a flue gas blower and recover waste heat.

R&D challenges

- Long-duration CO_2 storage capacity may not be located near enough to the CO_2 capture site for favorable economics.

status

The initial engineering design for the facility incorporating the UKy solvent-based CO_2 capture system at 95% CO_2 capture has been completed.

Lessons learned include the following:

- Increasing the backpressure on the gas turbine may be a possible mechanism to eliminate the flue gas blower, saving capital and operating cost while increasing availability.
- Optimization of the steam extraction point from the NGCC unit requires full HRSG and steam turbine models.

available reports/technical papers/presentations

Berger, Adam H., CO_2 Capture at Louisville Gas and Electric Cane Run Natural Gas Combined Cycle Power Plant, 2024 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh PA, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_PSCC_5_Berger.pdf.*

Berger, Adam H., CO_2 Capture at Louisville Gas and Electric Cane Run Natural Gas Combined Cycle Power Plant, 2023 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh PA, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC28_Berger.pdf*.

Berger, Adam H., CO_2 Capture at Louisville Gas and Electric Cane Run Natural Gas Combined Cycle Power Plant, Project Kickoff Meeting, Pittsburgh PA, January 2023. *https://netl.doe.gov/projects/plp-download.aspx?id=14613&filename=CO2+Capture+at+Louisville+Gas+and+Electric+Cane+Run+Natural+Gas+Combined+Cycle+Power+Plant.pdf*.

Polk Power Station Natural Gas Combined Cycle Carbon Capture Front-End Engineering and Design Study

primary project goal

The Tampa Electric Company (TEC), with ION Clean Energy Inc. (ION), Sargent & Lundy LLC (S&L), and other partners, is preparing a front-end engineering design (FEED) study for the retrofit ION's post-combustion carbon dioxide (CO_2) capture technology at the Polk Power Station (PK) natural gas combined cycle (NGCC) plant – Unit 2 (PK2).

technical goals

- Complete a FEED study and cost estimate (AACE Class 3: -20% to +30%) for a commercial-scale CO_2 capture facility retrofitted onto the existing Polk Power Station Unit 2 NGCC.
- Complete a techno-economic analysis (TEA) and life cycle analysis (LCA) of the integrated CO_2 capture system.

technical content

TEC and partners are conducting a FEED study of retrofitting ION's post-combustion CO_2 capture technology at the 1,190-megawatt (MW) NGCC Polk Power Station Unit 2 located in Mulberry, Florida. The Polk site has many features that make it an ideal candidate for applying post-combustion carbon capture, including favorable geology for onsite large-scale storage of CO_2. The system will be designed to achieve 95% capture efficiency and resulting in approximately 3 million tonnes of CO_2 captured per year. It will utilize ION's transformational solvent (ICE-31), which has been developed and demonstrated by ION to be able to achieve a minimum of 95% CO_2 capture with exceptional long-term stability in NGCC environments.

The objective of the project is to design a cost-effective system that maintains the necessary flexibility of a dispatch-based generating asset, pushes the boundaries of scalability upward, maximizes energy efficiency, and utilizes a transformational solvent. During the proposed FEED study, the project team will apply its extensive knowledge base for the purpose of designing a CO_2 capture facility that best fits the commercial needs of TEC. The results of the FEED study will have broad applicability for the U.S. generation fleet as the combustion turbines installed at Polk are the most widely deployed in the United States and the generating system in which Polk operates has a significant portion of non-dispatchable renewable energy that will increase in the future. This FEED study will demonstrate how a large and critical unit can be equipped with carbon capture and storage (CCS) to operate within and support a decarbonized electric grid in the future.

program area:

Point Source Carbon Capture

ending scale:

FEED

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

Solvent-Based Carbon Capture at NGCC Plant

participant:

Tampa Electric Company

project number:

FE0032224

predecessor projects:

N/A

NETL project manager:

Carl P. Laird
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principal investigator:

Nathan Kirkconnell
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partners:

Ernst & Young LLP; GE Energy Management Services Inc.; ION Clean Energy Inc.; Kiewit Engineering Group Inc.; Koch Specialty Plant Services LLC; S&ME Inc.; Sargent and Lundy; Siemens Energy Inc.; Strategic Staffing Solutions (S3); Vogt Power International

start date:

03.01.2023

percent complete:

67%

Figure 1. Concept rendering of proposed project at Polk Power Station Unit 2.

technology advantages

- Greater than 10% reduction in energy penalties, which is a key factor in limiting the process impact on the cost of electricity (COE).
- High solvent capacity for CO_2 reduces operating expense (OPEX), further limiting impact on COE.
- Reduced water content in the solvent, which has economic and technical benefits.
- Faster solvent kinetics that reduces absorber size for similar capture performance as the base case.
- Revolutionary stability against oxidation minimizes solvent degradation and emissions.

R&D challenges

- Difficulty with integrated system design.
- Challenges with space requirements for the CO_2 capture system.

status

The FEED study is underway for retrofitting ION's post-combustion CO_2 capture technology at the 1,190-MW NGCC Polk Power Station. The project basis of design was finalized, FEED engineering completed, capital cost estimate input received, constructability review completed, and site plan finalized.

available reports/technical papers/presentations

Kirkconnell, Nathan, FEED Study for Carbon Capture System Polk Unit 2 NGCC, 2024 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_PSCC_5_Dilport.pdf*.

Kirkconnell, Nathan, FEED Study for Carbon Capture System Polk Unit 2 NGCC, 2023 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC28_Dilport.pdf*.

Kirkconnell, Nathan, FEED Study for Carbon Capture System Polk Unit 2 NGCC, Project Kickoff Meeting, Pittsburgh, PA, April 2023.

Front-End Engineering Design for a CO_2 Capture System at Calpine's Delta Energy Center

primary project goal

ION Clean Energy is performing a front-end engineering design (FEED) study for a solvent-based carbon dioxide (CO_2) capture system to be retrofitted onto Calpine's Delta Energy Center (DEC), an existing natural gas combined cycle (NGCC) power station located in Pittsburg, California. The design effort utilizes ION's water-lean ICE-21 solvent that has been proven at large pilot scale with natural gas flue gas.

technical goals

- Develop the overall project design basis and criteria with respect to integration with the base plant and the balance of plant (BOP) scope.
- Generate the design documents required for the carbon capture island, including process flow diagrams, equipment lists, and a refined set of requirements; conduct a preliminary design review with stakeholders.
- Complete detailed design activities, including the creation of detailed equipment lists, detailed controls description, emissions and effluent list, capture system process and instrumentation diagrams, and an equipment layout plan; conduct a critical design review.
- Complete the design work for the BOP activities that are necessary to tie in the carbon capture island to the generating station; develop general arrangement drawings and a preliminary 3D model.
- Produce the system-level engineering packages needed to support the critical design review, including the system-level heat and water balances.
- Conduct a train configuration and unit cycling study; steam and power sourcing study; cooling water and optimization study; water and wastewater treatment study; reliability, availability and maintenance analysis; hazard and operability review; and constructability review.
- Generate a comprehensive estimate of the cost of capture.

technical content

ION's CO_2 capture technology is based on the use of a water-lean solvent (ICE-21) with low viscosity, fast kinetics and high working capacity. The ICE-21 solvent technology has been operated successfully at bench scale and small and large pilot scales, exhibiting improvements in regeneration energetics, emissions, solvent make-ups rates and material compatibilities. Through pilot testing, ION has confirmed its understanding of process improvements and analytics to enable successful operation of its solvent at lower liquid/gas circulation rates, packing heights and regeneration energies. ION has implemented additional process

program area:

Point Source Carbon Capture

ending scale:

FEED

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

Solvent-Based Capture from NGCC Flue Gas

participant:

ION Clean Energy Inc.

project number:

FE0032149

predecessor projects:

Calpine California CCUS Holdings LLC; Sargent & Lundy; Koch Engineered Solutions; Siemens Energy; Kiewit; Toshiba America Energy System; Hamon-Deltak

NETL project manager:

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principal investigator:

Andrew Awtry
ION Clean Energy Inc.
andrew.awtry@ioncleanenergy.com

partners:

none

start date:

02.01.2022

percent complete:

85%

improvements, including solvent split-stream integration, compression heat recovery and water use minimization, resulting in a significant reduction in energy penalty compared to other advanced amine solvents. ION's solvent outperformed baseline solvent monoethanolamine (MEA) with respect to energy usage, degradation rate, material compatibility and solvent emissions when tested with natural gas flue gas at the Technology Centre Mongstad (TCM) large-scale testing center. Test results also validated ION's ProTreat process model, which is used to simulate a commercial-scale plant capture system.

ION's preliminary design for the DEC CO_2 capture island incorporates two trains to remove 95% of the CO_2 from the flue gas, while still being able to support maximum turndown conditions. The system is designed to capture 2.4 million tonnes of CO_2 per year at the expected capacity factor. The process flow diagram of a typical ION solvent-based CO_2 capture facility is shown in Figure 1.

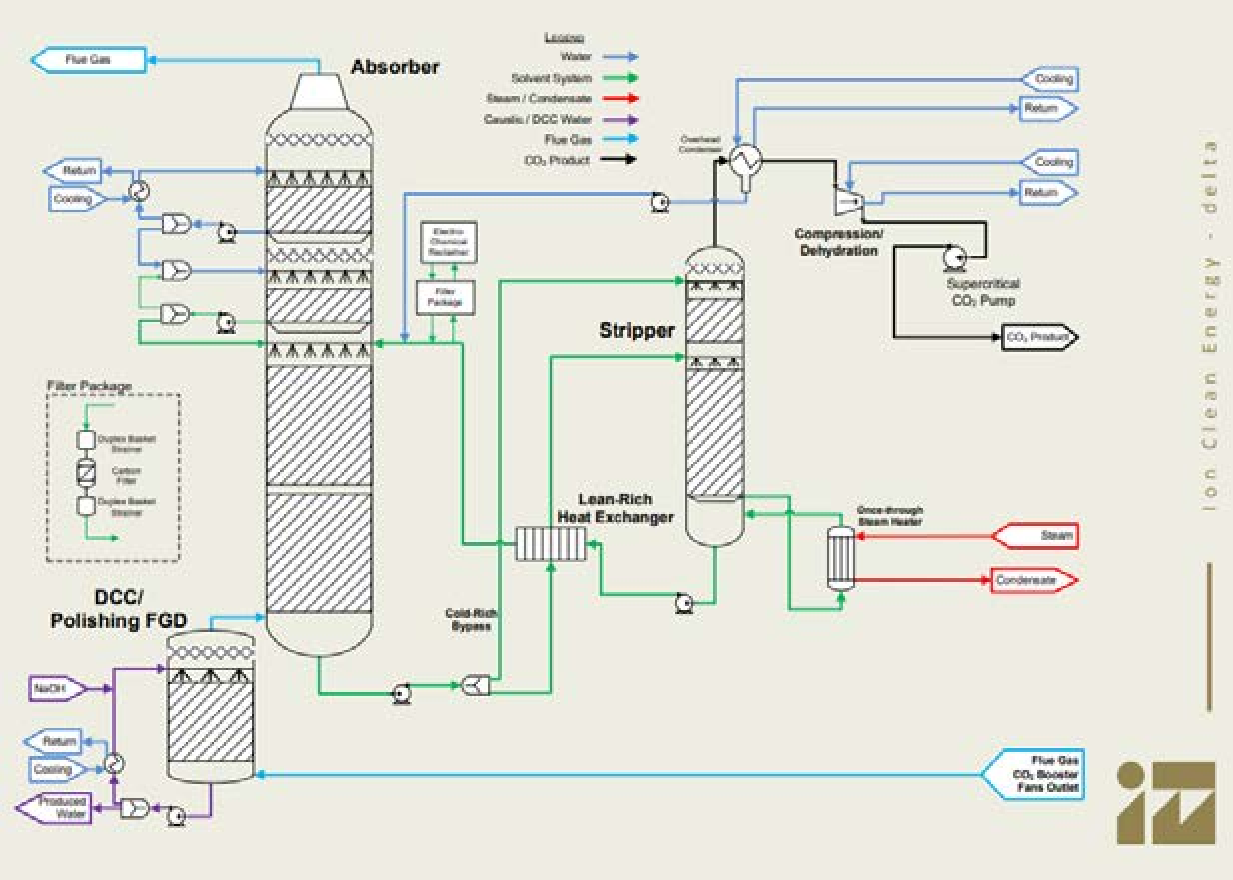

Figure 1: Process flow diagram of ION's solvent-based CO_2 capture technology.

DEC is an 857-megawatt (MW) NGCC power plant located in the Pittsburg-Antioch industrial area, northeast of San Francisco, California. The power block at DEC consists of three natural gas turbines, three heat recovery steam generators and a single steam turbine. Makeup water for the base plant is provided by the Delta Diablo Sanitary District and the direct contact cooler blowdown. The major process equipment and BOP systems needed for a complete CO_2 capture facility require a sizable footprint. The DEC plant sits on a property with sufficient available land located adjacent to allow the CO_2 capture system to be installed near the unit. DEC is also in close proximity to a number of CO_2 point sources, including an additional Calpine NGCC facility, Los Medanos Energy Center (LMEC). ION is designing a pilot system to be installed at LMEC that will have the same process design as the pilot for DEC. The test campaign at LMEC includes testing of both the ICE-21 solvent and the next-generation ICE-31 solvent (DE-FE0031950) to determine how the solvent technology responds to Calpine's specific operating profile, and the learnings will be used to inform the DEC FEED study.

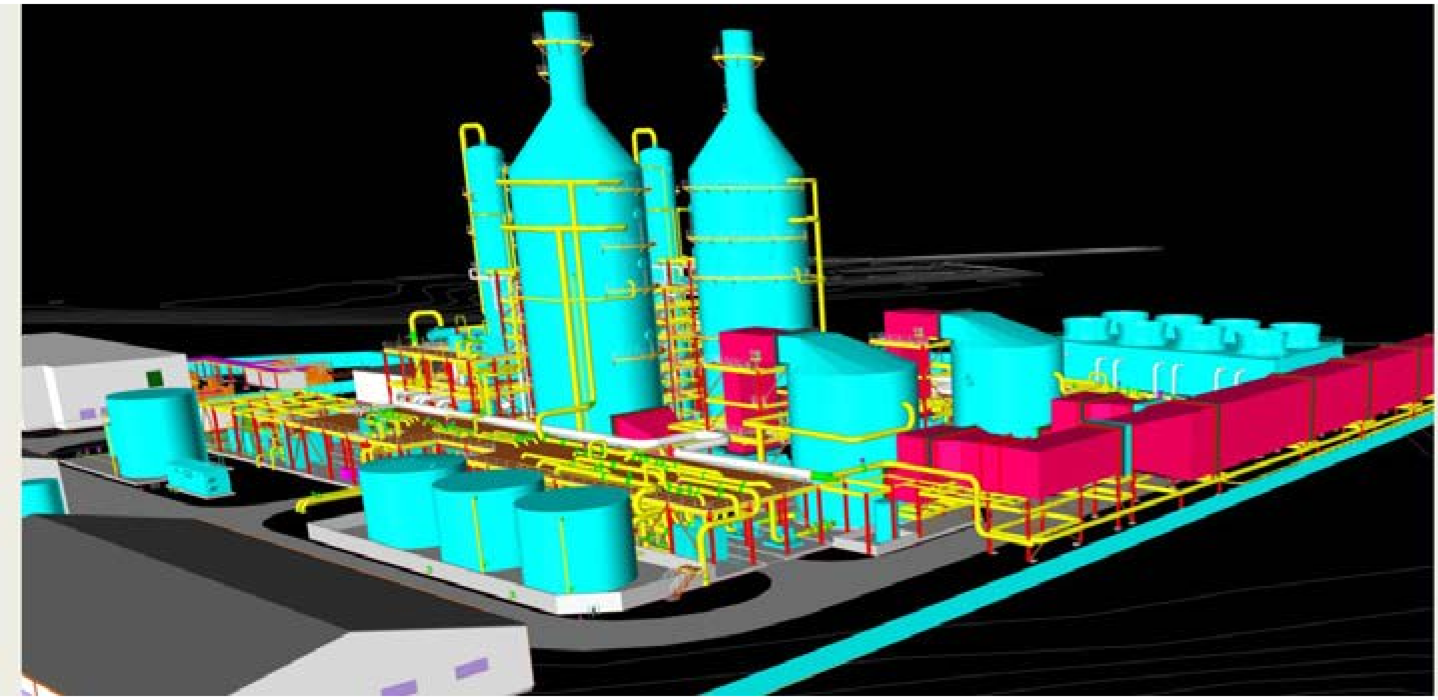

Figure 2: Carbon capture system.

The engineering design is being performed based on a level consistent with an AACE Class 3 estimate with an accuracy of -20% to 30% for the capital cost estimate.

The solvent and process parameters are provided in Table 1.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	85 – 150	85 – 150
Normal Boiling Point	°C	160 – 230	160 – 230
Normal Freezing Point	°C	-20	-20
Vapor Pressure @ 15°C	bar	<0.0008	<0.0008
Manufacturing Cost for Solvent	$/kg	—	—
Working Solution			
Concentration	kg/kg	0.6 – 0.85	0.6 – 0.85
Specific Gravity (15°C/15°C)	-	1.05 – 1.1	1.05 – 1.1
Specific Heat Capacity @ STP	kJ/kg-K	3.2	3.2
Viscosity @ STP	cP	<10	<10
Absorption			
Pressure	bar	0.03 – 0.05	0.03 – 0.05
Temperature	°C	20 – 60	20 – 60
Equilibrium CO_2 Loading	mol/mol	2.5 – 3.0	2.5 – 3.0
Heat of Absorption	kJ/mol CO_2	-1,300 to -1,600	-1,300 to -1,600
Solution Viscosity	cP	<15	<15
Desorption			
Pressure	bar	0.2 – 0.4	0.2 – 0.4
Temperature	°C	110 – 135	110 – 135
Equilibrium CO_2 Loading	mol/mol	0.05 – 0.20	0.05 – 0.20

Heat of Desorption	kJ/mol CO_2	1,500 – 1,900	1,500 – 1,900

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
inWC	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.5	205	3.9	13.0	70.5	11.4	0.8		<2.5

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical absorption/desorption of CO_2 to/from working solution.

Solvent Contaminant Resistance – Extremely stable towards oxygen (O_2).

Solvent Foaming Tendency – No issues (more than 3,000 hours experience).

Flue Gas Pretreatment Requirements – As for any stable amine-based solvent.

Solvent Make-Up Requirements – Aimed at less than 0.10 kg/tCO_2.

Waste Streams Generated – Similar profile but estimated to be less than other stable amine-based solvents.

Process Design Concept – Flowsheet/block flow diagram, if not included above.

technology advantages

- Reduced steam requirements for solvent regeneration, high solvent capacity, lower solvent replacement rates due to improved solvent stability and advanced operational control, and lower pump duties due to reduced solvent flow rates lead to a reduction in operating expenses (OPEX).
- Fast solvent kinetics allow for a smaller absorber column with less packing, leading to capital expenditures (CAPEX) savings.
- The activities proposed will result in a Class 3 FEED for the integration of a large-scale carbon capture system onto an existing NGCC power station.
- The DEC capture facility design will be standardized so that it can be readily scaled and optimized to capture CO_2 from other Calpine NGCC facilities.

R&D challenges

- Steam sourcing.

status

The BOP and carbon capture island piping and instrumentation diagrams (P&IDs), along with equipment lists, drawings and 3D model, were finalized. The project team also finalized the life cycle analysis (LCA), techno-economic analysis (TEA), business case analysis, revitalization and job creation outcomes analysis, and environmental justice analysis. A cost estimate, including the cost of CO_2 capture, was completed and the final FEED report is underway.

available reports/technical papers/presentations

Awtry, A. "Project Delta (FE0032149): Front-End Engineering and Design for a CO_2 Capture System at Calpine's Delta Energy Center", Presented at the 2024 FECM/NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_PSCC_5_Awtry.pdf*.

Awtry, A. "Project Delta (FE0032149): Front-End Engineering and Design for a CO_2 Capture System at Calpine's Delta Energy Center", Presented at the 2023 FECM/NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC28_Awtry.pdf*.

Awtry, A. "Project Delta, DE-FE0032149: Front-End Engineering and Design for a CO_2 Capture System at Calpine's Delta Energy Center", Project Kickoff Meeting, June 2022. *https://netl.doe.gov/projects/files/Front-End%20Engineering%20and%20Design%20for%20a%20CO2%20Capture%20System%20at%20Calpine%e2%80%99s%20Delta%20%20Energy%20Center.pdf*.

Project Diamond Vault Carbon Capture Front-End Engineering Design Study

primary project goal

Louisiana Economic Development Department (LED) is performing a front-end engineering design (FEED) study for the installation of an amine-based solvent carbon dioxide (CO_2) capture system at a coal power plant. The Diamond Vault project is anticipated to reduce the plant's CO_2 emissions by 95% by storing the CO_2 in geologic features.

technical goals

- Develop CO_2 capture island engineering and design package.
- Conduct preliminary steam and electric sourcing and cooling water option studies.
- Conduct risk, life cycle, business case, and environmental health and safety analyses.
- Develop capital and operations and maintenance cost estimates that cover both carbon capture process and balance of plant scope.
- Show proof of concept that a proprietary amine-based solvent CO_2 capture process can be economically applied on a large-scale coal/petcoke electric generating unit.

technical content

LED is conducting a pre-FEED and FEED study of the installation of an amine-based CO_2 capture process in Cleco Power's Madison Unit 3 (MU3) coal power plant in Baton Rouge, Louisiana. MU3 is located near geology that can be used for storing CO_2. This will minimize the costs associated with CO_2 transport, improving overall project economics.

MU3 has a 600-megawatt (MW) boiler with a circulating fluidized bed (CFB). It is fueled by 70% petcoke (a waste product of oil refining) and 30% Illinois basin coal. Its existing air quality control systems (AQCS) include a circulating dry scrubber (CDS), a selective noncatalytic reduction (SNCR), and a fabric filter for sulfur dioxide (SO_2), nitrogen oxide (NO_X) and particulate matter.

The FEED study will be performed in three phases: (i) an initial feasibility phase that defines the project and establishes preliminary costs; (ii) a pre-FEED phase based on the feasibility phase results to further refine the project and preliminary costs; and (iii) a FEED phase that will be a continuation of the pre-FEED phase with a construction contractor to develop a final cost estimate for the project and make the project execution-ready.

program area:
Point Source Carbon Capture

ending scale:
FEED

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Diamond Vault FEED Study

participant:
Louisiana Economic Development Department

project number:
FE0032165

predecessor projects:
N/A

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Louisiana Economic Development Department
robert.abboud@la.gov

partners:
Mitsubishi Heavy Industries; Cleco Power LLC; Sargent & Lundy; Black & Veatch; https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_PSCC_6_Bordelon.pdfConstruction Contractor TBD

start date:
04.01.2023

percent complete:

The study includes the development of process flow diagrams, piping and instrument diagrams, heat and material balances, plot plans, arrangement drawings, equipment lists, and one-line diagrams. The balance of plant engineering design includes specifications for utilities such as compression; cooling water; waste treatment; and the sources of energy, electricity and/or steam necessary to power the capture process. Civil and structural engineering tasks are incorporated throughout the design to support the estimates. The overall project capital cost estimate will be consistent with an AACE International Class 2 cost estimate (approximate accuracy of -15% to +20%) based on the CO_2 capture and balance of plant design packages, site-specific labor rates, project-specific considerations, and the selected contracting approach. The team will also complete analyses of the life cycle greenhouse gas emissions, business case, technology environmental health and safety risks, environmental justice, and economic revitalization and job creation outcomes of implementing the project.

Figure 1: Cleco Power's Madison Unit 3 power plant.

technology advantages

- Project Diamond Vault is anticipated to reduce MU3's CO_2 emissions by 95% by storing the CO_2 in geologic features underneath Brame Energy Center.
- A first-of-a-kind installation that will serve as an example for other coal facilities considering the adoption of carbon capture technology.

R&D challenges

- The location of the carbon capture island was moved to minimize impacts to base facility operations.
- Equipment sparing for the final design basis and turn down had to be changed from the original feasibility study.
- Additional controls needed to be evaluated based on stack test results.

status

LED, with selected vendor Mitsubishi Heavy Industries America, decided to locate the carbon capture system island adjacent to the MU3 stack to minimize ductwork and utility routing and operations disruption. The design was finalized following stack testing.

available reports/technical papers/presentations

Bordelon, M., Cleco Power, *"Project Diamond Vault Carbon Capture FEED Study,"* 2024 FECM / NETL Carbon Management Research Project Review Meeting, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_PSCC_6_Bordelon.pdf*.

Bordelon, M., Cleco Power, *"Project Diamond Vault Carbon Capture FEED Study,"* 2023 FECM / NETL Carbon Management Research Project Review Meeting, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC31_Bordelon.pdf*.

Abboud, R., Louisiana Department of Economic Development, and Bordelon, M., Cleco Power, "Project Diamond Vault Carbon Capture Front End Engineering Design Study," Project Kickoff Meeting, July 2023. *https://netl.doe.gov/projects/files/Project%20Diamond%20Vault%20Carbon%20Capture%20Front%20End%20Engineering%20Design%20Study.pdf*.

Retrofittable Advanced Combined Cycle Integration for Flexible Decarbonized Generation

primary project goal

General Electric Gas Power (GEGP), in collaboration with Linde Inc., Kiewit Engineering Group Inc., and Southern Company Services, conducted a front-end engineering design (FEED) study for a "Generation 2" amine-based post-combustion carbon capture system integrated with an existing natural gas combined cycle (NGCC) power plant, designed to capture carbon dioxide (CO_2) emissions with at least 95% efficiency.

technical goals

- Select the NGCC power plant/carbon capture system interfaces to minimize integrated performance loss and advance to 95% from previous 90% CO_2 capture FEED studies, and investigate the impact of exhaust gas recirculation (EGR) on reducing capture cost.
- Complete detailed heat and mass balances, piping and instrumentation diagrams (P&IDs), piping layouts, electrical design, and all other details needed to define the capital/operating costs to support plant-level construction.
- Perform a techno-economic analysis (TEA) and life cycle analysis (LCA); complete environmental, health, and safety (EH&S) and hazard and operability (HAZOP) reviews of the capture system design; and perform sensitivity studies of CO_2 capture from 90% to as high as 99%.

technical content

The FEED study focused on a commercial-scale carbon capture plant installed at an existing F-Class NGCC site. GEGP anticipates a high level of system integration that is low-cost, highly efficient, and scalable to other commercial sites.

This is accomplished through advancements in three aligned technology elements:

- Element 1: Amine-based carbon capture with efficiency advanced from 90–95% ("Generation 2").
- Element 2: Comprehensive NGCC/capture system integration with advanced plant-level controls.
- Element 3: EGR technology applied to the gas turbine.

Among the options for post-combustion CO_2 capture from NGCC power plants, liquid solvent-based technologies are currently the most attractive for large-scale commercial application in terms of cost, performance, reliability, and Technology Readiness Level (TRL). However, several challenges still exist for solvent-based

program area:

Point Source Carbon Capture

ending scale:

FEED

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

FEED Study on Amine-Based Solvent Technology Retrofit to NGCC Plant

participant:

General Electric Gas Power (GEGP)

project number:

FE0032131

predecessor projects:

N/A

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partners:

Linde Inc.; Kiewit Engineering Group Inc.; Southern Company Services

start date:

02.11.2022

percent complete:

100%

technologies. Solvent stability and degradation add to plant operating expenses (OPEX), creating further headwinds in the face of this critical infrastructure development. Offering a superior solution that addresses all these challenges, the Linde-BASF aqueous amine solvent-based carbon capture technology provides the optimal synergy of solvent performance and innovative engineering design that minimizes the cost and risk implications of CO_2 capture when deployed at commercial scale. The Linde-BASF technology is based on a typical lean-rich solvent absorption/regeneration cycle for CO_2 capture, but leverages several key innovative features for both solvent and process optimization. A schematic of the Linde-BASF process, including process improvements, are shown in Figure 1.

Linde and BASF have jointly developed and demonstrated advanced CO_2 capture capabilities since 2007. BASF's early solvent development efforts resulted in the formulation of new, next-generation solvents, such as OASE® blue. Linde has improved process design, with CO_2 capture from low-pressure sources, and demonstrated longer stability and a lower solvent circulation rate that further reduces the cost of CO_2 capture from NGCC plants.

The key process components of the Linde-BASF technology are all at TRL 6. This includes absorber/stripper columns, heat exchangers and reboiler, stripper heat integration/recovery, emissions control, and the OASE blue solvent. The TRL 6 is also supported by experimental data, including Linde-modeled external heat integration for carbon capture process (2012); pilot testing (1.5-megawatt-electric [MWe] scale) on coal-fired flue gas in Wilsonville, Alabama, with up to 95% capture efficiency (2014-2016); flue gas aerosol reduction process options tested at Niederaussem for OASE blue solvent (2015); and successful engineering-scale testing of components on 0.45-MWe NGCC-based exhaust gas (2016).

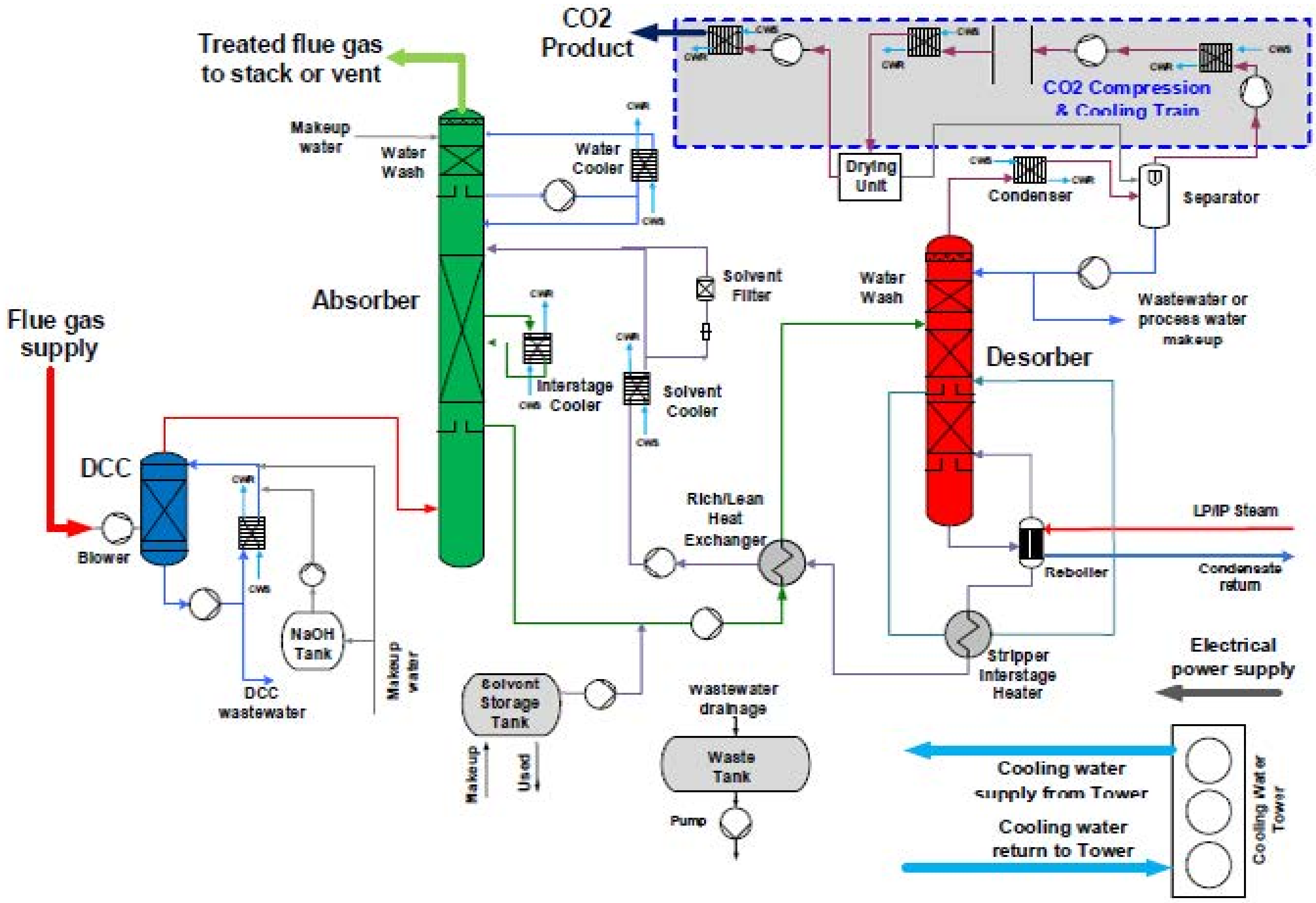

Figure 1: Linde-BASF carbon capture technology.

Description of NGCC Integration

The second element is an NGCC plant-level integration. GEGP has successfully executed gas turbine/combined cycle FEED-related studies for power generation and chemical process industries and oil and gas customers for many years. Examples include application of the first reheat bottoming cycle design, along with the introduction of the F-Class gas turbine, and similar customer plant FEED studies, with its steam-cooled H-Class gas turbine in its early application. GEGP has also been involved with combined cycle power island system designs for integrated gasification combined cycle (IGCC) plants. Examples include the first coal demonstration project in the United States and, more recently, a full-scale IGCC plant in the United States that includes future carbon capture capability. As the complexity of the cycle increases, the need for advanced controls is more critical. With the close dependency of the carbon capture system on the NGCC plant, and vice versa, the need for adaptive, closed-loop, model-based control becomes crucial to maintaining flexible, reliable, and stable operation. This is particularly important during transients caused by changing load or ambient pressure and temperature. The project is identifying and developing key system configurations to enable reliable operation of the NGCC and carbon capture systems, as well as defining a plant operating philosophy to be used by the gas turbine and plant control systems. An optimal configuration includes processes for managing stable and reliable capture system operation at reduced NGCC plant load and NGCC starting/loading. This comprehensive approach yields a more robust solution compared to a piece-meal approach of separate controls for the gas turbine, steam turbine, and carbon capture system. This element also focuses on identifying the optimal location of steam extraction from the existing NGCC power plants, as well as the technically and commercially feasible modifications that should be made to both the steam turbine and the heat recovery steam generator (HRSG) to allow the large steam supply to the carbon capture system. An operability assessment is performed to identify recommended locations of alternate steam supply to allow stable NGCC/carbon capture system operation across a wide range of ambient conditions and plant load demand, including operability of the steam turbine. The second element is at TRL 9, as other equally complicated integration technologies employing advanced controls and bottoming cycle optimization, such as IGCC, have been designed and operated successfully.

Description of Exhaust Gas Recirculation

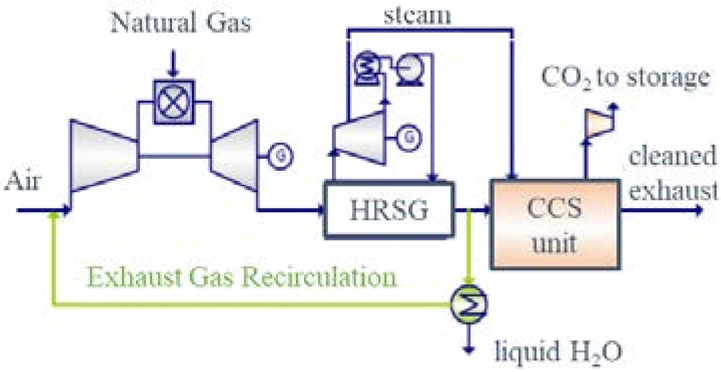

Figure 2: Exhaust gas recirculation.

The third element is the addition of EGR (Figure 2) at the Plant Barry host site located in Bucks Alabama. EGR is a viable and promising option to (a) reduce the exhaust gas flow to the carbon capture system, resulting in cost reductions, and (b) increase the CO_2 concentration in the exhaust gas, resulting in increased capture rate. GEGP has extensively studied EGR since 2006 and anticipates that EGR may be needed to practically achieve carbon capture efficiencies greater than 95%. In 2008, GEGP performed TRL 6-level EGR testing of an F-Class combustor that is the same pre-mixer combustion configuration as that at the Plant Barry host site. These tests confirmed the feasibility of using GEGP's F-Class dry low nitrogen oxide (DLN) combustors in low oxygen conditions with EGR levels up to 30%, potentially up to 40% and higher. These tests also verified that EGR provides increased CO_2 concentrations (>8% CO_2) and reduced nitrogen oxide (NO_X) emissions. These TRL 6-level test results are directly applicable to the Plant Barry FEED study. GEGP is also considering the use of commercially available gas turbine inlet air chilling in the EGR loop for improved plant output. Furthermore, GEGP investigated higher levels of EGR, up to and including Stoichiometric EGR (SEGR) in 2012.

The project begins with various conceptual designs, with a down select leading to a single NGCC/carbon capture and storage (CCS) configuration. The project focuses on system operability to include startup, shutdown, and a range of outputs and loads, which is critical to enable NGCC plants with CO_2 capture to complement renewable power sources.

The project concludes with a detailed design, assessment of technical viability across a real-world plant operating profile, TEA and LCA, and a business case assessment.

technology advantages

- Identifies carbon capture system integration and operation risks and recommends solutions to eliminate or manage the risks.

R&D challenges

- Identifying the optimal location of steam extraction from the existing NGCC power plants.
- A large amount of condensation formation occurs in the "compressor inlet casing entry to the IGV inlet" region, due to temperature depression resulting from the high flow acceleration in this region.

status

This project was completed on March 31, 2024. The FEED study was completed.

available reports/technical papers/presentations

Sholes, J., "Retrofittable Advanced Combined Cycle Integration for Flexible Decarbonized Generation," Final Technical Report, June 2024. *https://www.osti.gov/biblio/2377996*.

Sholes, J., "Retrofittable Advanced Combined Cycle Integration for Flexible Decarbonized Generation," 2023 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC28_Sholes.pdf*.

Sholes, J., "Retrofittable Advanced Combined Cycle Integration for Flexible Decarbonized Generation," 2022 Carbon Management Project Review Meeting, Pittsburgh, PA, August 2022.

Sholes, J., "Retrofittable Advanced Combined Cycle Integration for Flexible Decarbonized Generation," Project kickoff meeting presentation, March 2022.

Deer Park Energy Center Natural Gas Combined Cycle Carbon Capture System Front-End Engineering Design Study

primary project goal

Calpine Texas CCUS Holdings LLC teamed up with Electricore Inc. to conduct a front-end engineering design (FEED) study on a modular, commercial-scale, post-combustion carbon capture (PCC) system to capture 95% of the total carbon dioxide (CO_2) emissions (5 million tonnes per annum [MTPA]) from the flue gas generated at Calpine's Deer Park Energy Center (DPEC) — a natural gas combined cycle (NGCC) power plant located in Deer Park, Texas.

technical goals

- Perform a FEED study for installing a 5 MTPA PCC system at Calpine's Deer Park Energy Center in Texas.
- Complete an AACE Class 3 cost estimate to define the levelized cost of carbon abatement (LCCA) and the sensitivity of which relative to the carbon capture rate.
- Design the carbon capture system to be scalable to Calpine's largest NGCC plants to allow for rapid commercialization.

technical content

DPEC in Texas was the site chosen for the FEED study. DPEC was selected based on the results of a comprehensive pre-FEED and preliminary TEA study across most of Calpine's fleet spanning multiple states. Each facility was ranked numerically based on several parameters relative to the impact on LCCA (in \$/tonne of CO_2). Parameters considered were proximity to a CO_2 sink and cost of offtake, hub effects/transportation infrastructure availability, market feasibility of low-carbon power, water availability, facility performance, and steam demand. From this study, DPEC was considered to be the most suitable facility for the FEED.

The PCC system selected was Shell's CANSOLV amine technology, as it has been tested at commercial scale for the capture of CO_2 from coal flue gas streams and exhibits low parasitic energy consumption, fast kinetics and extremely low volatility. A schematic of the CANSOLV system is shown in Figure 1.

The goal of the project was to decrease the average cost of carbon capture, utilization and storage (CCUS) to \$30/tonne of CO_2 or less and to improve the thermal efficiency of PCC systems treating flue gas from NGCC systems. In addition, the system was designed to be scalable to the rest of Calpine's fleet to promote rapid commercialization. The results of the project define employment benefits from the creation of clean energy power plant jobs in focus-area

program area:
Point Source Carbon Capture

ending scale:
FEED

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Shell CANSOLV Process for CO_2 Capture from NGCC Plants

participant:
Calpine Texas CCUS Holdings LLC

project number:
FE0032137

predecessor projects:
none

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partners:
Electricore Inc.; Black & Veatch; Shell Corporation; Sargent & Lundy; Siemens; University of Houston; Toshiba; The Resource Company

start date:
02.01.2022

percent complete:
100%

communities and help to address legacy environmental justice issues in the American southwest. The project team prepared commercial assessments, including a business case analysis; techno-economic analysis (TEA); life cycle analysis (LCA); and environmental, health, and safety (EH&S) risk assessment. Additionally, the project evaluated public policy considerations, including an environmental justice Analysis and an economic revitalization and job creation outcomes analysis.

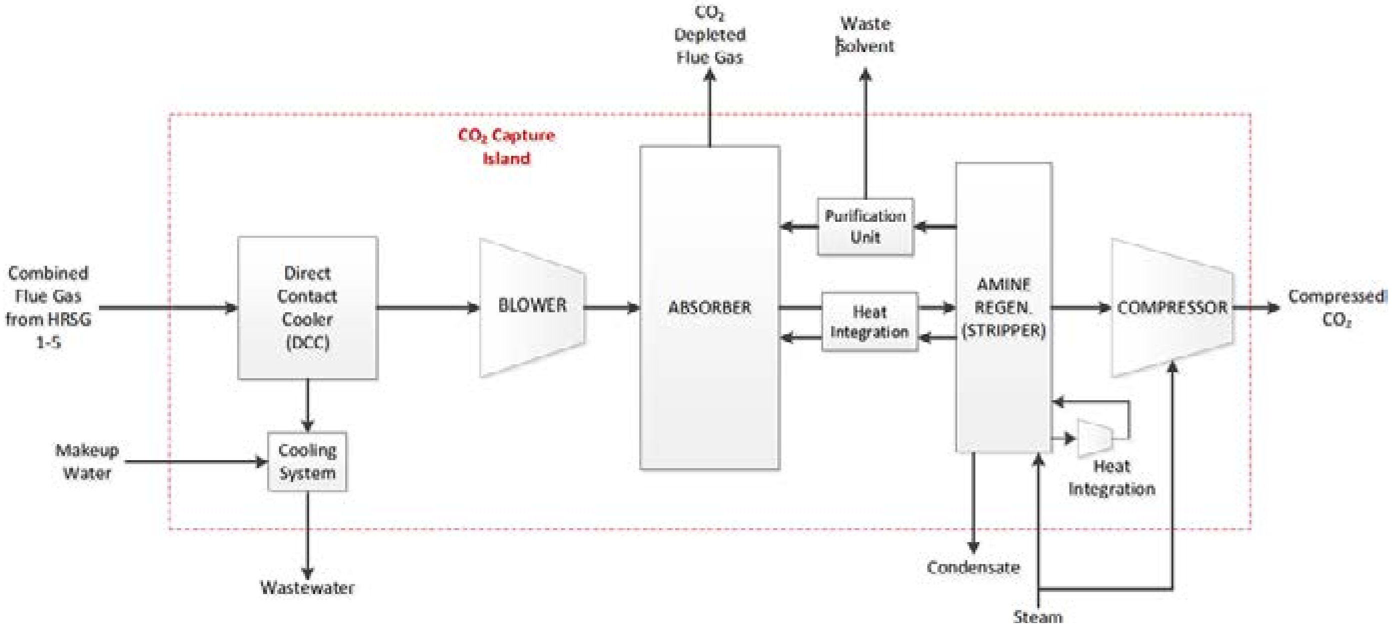

Figure 1: Shell CANSOLV process.

The Deer Park facility was chosen based on several factors: (1) high existing capacity factor, (2) large carbon emissions volumes, (3) high steam generation capability compared to maximum load, (4) proximity to existing infrastructure (water, pipelines, storage sites, etc.), and (5) proximity to other carbon sources. With regards to water usage, the DPEC site is a combined heating and power (CHP) plant — there is a significant amount of excess steam available for carbon capture and storage (CCS). This also makes the site suitable for a duct burning scheme, enabling high-temperature, high-pressure steam availability to drive the capture process, limiting impacts to the intermediate- and low-pressure steam turbines. Meanwhile, a back pressure turbine was installed to recover potential lost work output. Finally, the steam turbine assembly was used to drive the main CO_2 compressor, reducing net auxiliary loads and thus improving overall efficiency.

The final TEA of the project is summarized in Table 1.

TABLE 1: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	$/tonne CO_2	101	30
Cost of Carbon Avoided	$/tonne CO_2	-	—
Capital Expenditures	$/MWhr	-	—
Operating Expenditures	$/MWhr	-	—
Cost of Electricity	$/MWhr	-	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – The analysis was based on Case 12 in "Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity, Rev. 2."

Scale of Validation of Technology Used in TEA – The analysis was based on pilot-scale testing.

technology advantages

- Low volatile organic compound (VOC) emissions.
- More energy efficient than comparable technologies (Selexol, Rectisol, etc.).
- High capture rate (95%).

R&D challenges

- Limiting impact to the efficiency of the NGCC plant.
- Optimizing cost of carbon abatement.
- Determining the optimal flue gas cooling option.

status

- The project was completed on November 30, 2023. A final report is pending.

available reports/technical papers/presentations

Herman, C., 2023, "Deer Park Energy Center NGCC Carbon Capture System FEED Study." *Presented at the 2023 FECM/NETL Carbon Management Research Project Review Meeting.* Pittsburgh, PA. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC28_Herman.pdf*.

Herman, C., 2022, "Deer Park Energy Center NGCC Carbon Capture System FEED Study." Project Kickoff Meeting. *https://netl.doe.gov/projects/files/Deer%20Park%20Energy%20Center%20Natural%20Gas%20Combined%20Cycle%20Carbon%20Capture%20System%20Front-End%20Engineering%20Design%20Study.pdf*.

Front-End Engineering and Design: Project Tundra Carbon Capture System

primary project goal

Minnkota Power Cooperative performed a front-end engineering and design (FEED) study to install a post-combustion carbon dioxide (CO_2) capture system at Square Butte Electric Cooperative's Milton R. Young Station, Unit 2 (MRY2), located near Center, North Dakota. Based on the results of pre-FEED studies of two leading commercial-ready carbon capture technologies, Fluor's Econamine FG Plus^{SM} (EFG+) technology was selected for installation.

technical goals

- Complete a FEED study for constructing the carbon capture system at MRY2, including balance of plant (BOP).
- Address final challenges to implementing CO_2 capture with studies to optimize plant efficiency.
- Finalize a permitting strategy for the overall project.
- Evaluate environmental, health, and safety (EH&S) concerns and mitigation approaches.
- Conduct a hazard and operability (HAZOP) review.
- Complete a FEED-level cost estimate and construction schedule.

technical content

Minnkota completed a FEED study on the addition of Fluor's EFG+ technology to an existing power plant fueled by North Dakota lignite to deliver the engineering and design work needed to demonstrate the feasibility of a next-generation carbon capture system technology at world-scale. The FEED comprises a broader effort led by Minnkota, titled Project Tundra, which is an initiative to build the world's largest carbon capture facility in North Dakota and to implement carbon capture, utilization, and storage (CCUS) to preserve the use of lignite, support the CO_2 enhanced oil recovery (EOR) industry, and revitalize legacy oil fields.

The project team substantiated the economics and engineering supporting the business case for construction and operation of Fluor's EFG+ technology to capture 12,978 short tons/day (11,773 tonnes/day) by removing 90% of the CO_2 available from the processed flue gas streams (including the 477 megawatt MRY2 and the three natural gas boilers providing the steam supply for operation of the capture system).

Fluor's EFG+ technology is an advanced amine-based process tailored for removal of CO_2 from low-pressure, high-oxygen-containing flue gas (up to 15 vol%) and has been used in 30 commercial plants worldwide to process flue gases derived from

program area:

Point Source Carbon Capture

ending scale:

FEED

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

Econamine FG Plus Retrofit to Coal-Fired Power Plant

participant:

Minnkota Power Cooperative Inc.

project number:

FE0031845

predecessor project:

N/A

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partners:

Fluor Enterprises Inc.; Burns & McDonnell; David Greeson Consulting; Hunt International Energy Services; ND Industrial Commission; UNDEERC; Golder Associates; AECOM; Square Butte Electric Cooperative

start date:

10.01.2019

percent complete:

100%

a variety of fuels. The basic plant configuration consists of a two-stage direct contact cooler (DCC) for flue gas cooling and sulfur dioxide (SO_2) removal, an absorber, a regenerator, and a compression and dehydration system to generate pipeline-ready CO_2, as shown in Figure 1. As the conditioned flue gas flows up the absorber, CO_2 is chemically absorbed into a circulating solvent stream flowing down the column. The CO_2-loaded solvent is then pumped from the bottom of the absorber, through a heat recovery exchanger where it is heated against hot CO_2-lean solvent, and into the top of the regenerator. As the solvent flows down the regenerator, it is contacted by steam, which strips the CO_2 from the solvent, producing an overhead mixture of steam and CO_2. The steam/CO_2 product is cooled, and the steam is condensed and separated from the CO_2 product. Hot CO_2-lean solvent from the bottom of the regenerator is pumped back through the heat recovery exchanger where it is cooled against the cold CO_2-loaded solvent before being returned to the top of the absorber.

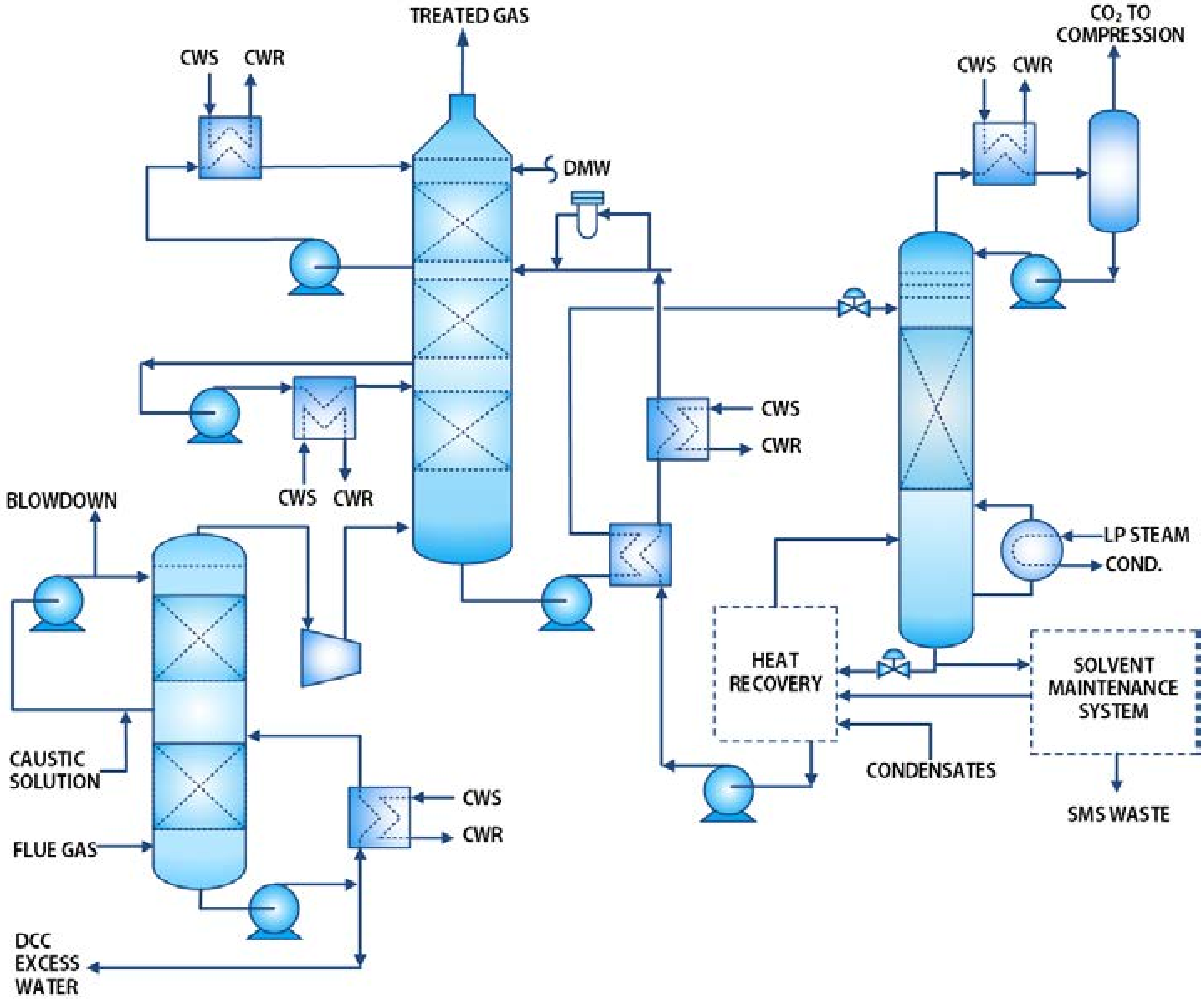

Figure 1: Schematic of Fluor's EFG+ CO_2 capture technology.

Advancements to progress the technology beyond the current state-of-the-art include steam cycle integration with advanced heat recovery to improve energy efficiency; methods for removing aerosols and a unique solvent maintenance system to minimize solvent degradation, thereby improving the environmental and cost profile; design of the world's largest capture facility (3.6 million tonnes/year, a twofold increase over any other facility) to capture greater economies of scale; optimization for cold climate performance; and establishment of the lowest levelized cost of capture attempted at world-scale.

Experience gained from Fluor's EFG+ demonstration plant in Wilhelmshaven, Germany, which captures 70 tonnes of CO_2 per day from a coal-fired power plant, has enabled Fluor to make significant improvements to the process. Some of the unique features of the process design include:

- The EFG+ solvent is a proprietary formulation of primary amines with a regeneration steam requirement 30% lower than generic monoethanolamine (MEA).
- Fluor's patented two-stage DCC treats the flue gas in two sections, cooling the flue gas to harvest quality combustion knock-out water and removing SO_2 to single-digit part per million (ppm) levels.
- Fluor's patented absorber intercooling technology removes heat of absorption to increase the CO_2 carrying capacity of the solvent, reducing the net steam demand of the EFG+ process by 3–5%.
- A lean solvent heat recovery and integration system that lowers the external regeneration steam demand for the reboiler and reduces the total solvent regeneration energy requirement by approximately 10–15%.
- Minimized pressure drop in absorber due to advanced design of internals and packing in the DCC and absorber, thereby reducing the blower power by approximately 65% compared to conventional carbon capture plants.
- A solvent maintenance system (SMS) to remove heat-stable salts (HSSs) and other non-volatile degradation products to maintain solvent hygiene and performance.

The project team previously conducted a pre-FEED study to determine constructability, tie-in locations, preliminary pipe routings and interfaces, electrical interconnections, equipment specifications, capture system power requirements, geotechnical details, and control design. These components formed the basis of the full FEED study, which resulted in the following multidisciplinary design package:

- A FEED study report along with an electronic 3D model in SmartPlant® 3D.
- Material takeoffs (MTOs) exported from the 3D model for large-bore pipe lengths, fittings, flanges, valves, raceway, cables, and instrumentation; structural steel and concrete takeoffs developed from structural design software and sketches.
- An optimized general arrangement drawing.
- A tie-in list and location plan, with input from construction specialists during the detailed design phase; updates to process and instrumentation diagrams (P&IDs) with tie-in information.
- Detailed specifications for the major equipment packages.
- A Level 2 Process Hazard Analysis (i.e., HAZOP) report utilizing the overall P&IDs.
- A steam supply design.
- A fire protection study in accordance with National Fire Protection Agency codes and standards.
- An instrument control list with inputs and outputs and distributed control system (DCS) points, including cost specifications for all major instrument and control packages.
- Exploratory excavation plans and specifications to verify that proposed foundation and subsurface facilities are clear of obstructions.
- Preliminary foundation sketches to support equipment and ancillaries required for FEED cost estimates.
- Preliminary architectural drawings and sketches to support a cost specification for pre-engineered buildings and heating, ventilation, and air conditioning (HVAC), and obtaining budgetary quotes to support the FEED cost estimate.

Based on the pre-FEED study, a \$50/tonne 45Q tax credit for CO_2 storage or a \$35/tonne 45Q tax credit for EOR, plus projected CO_2 sales to oil companies for EOR operations, provides enough revenue to cover the capital, return on capital, and plant's operating costs, while yielding a near 10% return to tax equity. In addition, the cost of capture is expected to be \$49/tonne CO_2, which is a 20% reduction from the cost of CO_2 capture at the Petra Nova facility, the U.S.'s first commercial post-combustion carbon capture system at a coal-fired power plant. The FEED study is the next step in verifying and optimizing these costs and projections to reflect the higher level of engineering and design and cost-estimating certainty. The overall economic results of the FEED study are shown in Table 1.

For the BOP items, operating cost estimates will be developed through detailed studies involving Fluor, owner's engineer Burns & McDonnell, and Minnkota. Both the operating and capital costs for an EFG+ plant are dependent on a number of variables, including, but not limited to, plant location, site conditions, plant capacity, final configuration, modularization versus field erected, flue gas conditions, air versus water cooling, and cost of utilities such as steam and electricity.

Although the EFG+ technology and the chemistry of the process are the same regardless of scale, the process equipment in the EFG+ process must be designed to ensure that the EFG+ chemistry occurs efficiently. Specifically, the scale-up challenge is construction of large-diameter columns and achieving good gas/liquid distribution in the packing.

As part of the pre-FEED, the team evaluated natural gas-fired auxiliary boiler and steam turbine extraction scenarios. Early stages of the FEED study will choose which steam source will be utilized.

In addition to removing approximately 3.6 million tonnes per year of CO_2, the carbon capture facility installed at MRY2 is designed to remove approximately 2,200 tonnes of SO_2 annually. However, significant concentrations of alkali-derived aerosols have been measured at MRY2 during previous studies, which can impact both amine solvent emissions and degradation rates. Also, solvent emissions from the absorber may include ppm levels of amine and degradation byproducts in the form of ammonia and aldehydes. The combination of the aldehydes/amine may constitute a new major source of VOCs, which requires a Title V permit under the Clean Air Act. In the FEED, Fluor evaluated the cost-effectiveness of solutions for removal of aerosols upstream of the absorber, thereby eliminating/mitigating the challenge of aerosol-exacerbated emissions of amine from the absorber. Preliminary air dispersion modeling was performed in the pre-FEED study to determine appropriate stack height, parameters, and location. In order to confirm that the site would not exceed National Ambient Air Quality Standards (NAAQS), an additional air dispersion model was required using the final FEED study parameters, emissions, and layout.

An SMS was also included in the EFG+ plant design for MRY2 to maintain favorable solvent purity and produce a small waste effluent stream that was collected and periodically hauled offsite for disposal. Furthermore, by maintaining low impurity levels in the solvent, undesired VOC emissions were reduced dramatically.

Wastewater produced by the EFG+ plant includes blowdown from the DCC (knock-out water and SO_2 scrubbing solution). The condensed water vapor from cooled flue gas is of high quality and can be used as cooling water makeup at MRY2 after minor treatment. After investigating the compatibility of existing MRY Station wastewater treatment, Minnkota concluded that disposal via a Class I injection well is the likely method of disposal for some of the effluents. The FEED study included design and costing of a Class I well. The proposed changes required the MRY2 plant to modify its National Pollutant Discharge Elimination System (NPDES) permit for industrial wastewater discharges.

Any plant constructed in North Dakota requires a winterization plan, as temperatures can reach to -40°C or less. Through the pre-FEED effort, the project team identified best practices for ensuring the plant remains efficient and operational during the winter months, including specifications for building foundation depth, insulation and material specifications, cold process startup/shutdown, and buried fluid lines.

Flue Gas Assumptions – Unless noted, average flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
13.7	140	10.29	21.28	61.96	5.66	0.79	41.8	149.4

Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The absorption of CO_2 is a chemical reaction.

Solvent Contaminant Resistance – The solvent has very good resistance to contaminants in the flue gas aided by the solvent maintenance system.

Solvent Foaming Tendency – None.

Flue Gas Pretreatment Requirements – SO_2 removal and temperature control is required prior to the absorber.

Waste Streams Generated – Solvent maintenance system waste, water treatment waste, and cooling tower blowdown.

Process Design Concept – Flowsheet/block flow diagram shown above in Figure 1.

Proposed Module Design – Will be determined based on results of a logistics/route study.

TABLE 1: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Value
Cost of Carbon Captured	$/tonne CO_2	$80.60
Capital Expenditures	$/tonne CO_2	$57.89
Operating Expenditures	$/MWhr	$20.57
Cost of Electricity	$/MWhr	$30.00

Data used:

- Average annual operating expenses (OPEX) for carbon capture system = $20.57/tonne (unescalated 2021 dollars).
- Average annual CO_2 captured and avoided = 3,652,600 tonnes.
- Capital expenses (CAPEX) to place the capture system into service = $1.938 billion.
- Megawatt-electric (MWe) of treated flue gas = 530 MWe.
- Total OPEX over 20-year life of project = $1.502 billion (unescalated 2021 dollars).
- Host power plant trailing three-year average (2019–2021) cost of electricity (operations, maintenance, and fuel) = $30/megawatt-hour (MWh) (unescalated 2021 dollars).
- The project is a stand-alone processor of flue gas and pays for all services and energy at market rates such that the economics of the host power plant are not impacted by the installation and operation of the project. This is key to ensure the continued merit order dispatch of the host power plant in the Midcontinent Independent System Operator (MISO) market.

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – For this FEED study, the data are based on a specific plant – Minnkota Power Cooperative Milton R. Young Station.

Scale of Validation of Technology Used in TEA – While a formal TEA has not been completed, the economics are based on a full FEED study of a 530-MWe sized capture system, which is a scale up from the pilot scale tests at Technology Centre Mongstad.

Qualifying Information or Assumptions:

- Annual combined (host + carbon capture and storage [CCS]) capacity factor = 85%.
- All costs and production estimates are based on CO_2 delivered to the fence line of the CCS dehydrated and compressed to 1,500 pounds per square inch (psi) (i.e., “pipeline quality” ready for shipment).
- Transport and storage of CO_2 is not included in these numbers.

technology advantages

- Advanced solvent formulation with high CO_2 capacity and high absorption rate.
- Low pressure-drop packing in DCC and absorber has the potential to lower the power consumption for the blower by 65%.
- Large diameter column design for absorber and DCC reduces the number of absorption trains required, thereby lowering capital costs.
- Novel absorber intercooler configuration increases solvent loading and lowers the overall solvent circulation rate, further reducing power consumption and solvent loss.
- A lean solvent heat recovery and integration system that reduces the steam demand for solvent regeneration by 10–15%.
- Fluor’s proprietary SMS lowers overall solvent loss and makeup.
- Advanced reclaiming technology significantly reduces reclaimer waste.

R&D challenges

- Lignite coal-based flue gases, such as that produced at MRY2, contain alkali-derived aerosols and particulate matter that can have a detrimental impact on both amine solvent emissions and degradation rates.
- Integration into an existing facility poses many operating and plant layout challenges.
- Maintaining a proper water balance for the facility becomes a challenge.

status

The project concluded on June 30, 2023. The project team developed an optimized design manual of the carbon capture system, including analyses for integrating the carbon capture system with the plant’s steam cycle or utilizing natural gas-fired auxiliary boilers. The gas-fired boilers were selected as the basis for the FEED study. The capture facility was increased in size to accommodate the flue gas from the gas-fired boilers, resulting in the ability to remove approximately 3.65 million tonnes of CO_2 versus the pre-FEED levels of 3.6. The boilers also allowed for additional flexibility in the operation by allowing a tie to the MRY1 unit flue gas duct for operation when MRY2 is offline. The results show that the total capital cost of the project would be $1.938 billion USD. The total cost of capture, transportation, and storage was estimated to be $80.60/tonne, as a “breakeven CO_2 emissions penalty.” Due to the high capture cost, the team concluded that the scenario where natural gas boilers provide the energy for running the capture plant is more expensive than the previous pre-FEED study’s scenario where extracted steam was used. The team plans on re-exploring the steam extraction scenario in a future study.

available reports/technical papers/presentations

Pfau, G.; Wolf, D.; Laudal, D.; Bleth, C.; Greeson, D., 2023, "Front-End Engineering and Design: Project Tundra Carbon Capture System." *Final Technical Report.* Minnkota Power Cooperative, Inc., Grand Forks, ND. Report No. DOE-MINNKOTAPOWER-31845. *https://www.osti.gov/biblio/1987837*.

Pfau, G., 2023, "Front-End Engineering & Design: Project Tundra Carbon Capture System," Closeout Meeting, May 2023. *https://netl.doe.gov/projects/files/Front-End%20Engineering%20and%20Design%20Project%20Tundra%20Carbon%20Capture%20System.pdf*.

Pfau, G., 2021, "Front-End Engineering & Design: Project Tundra Carbon Capture System," presented at the 2021 NETL Carbon Management and Oil and Gas Research Project Review Meeting - Integrated CCUS Projects and FEED Studies. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CCUS_Pfau.pdf*.

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Pfau, G., 2019, "Front-End Engineering & Design: Project Tundra Carbon Capture System," DOE Kickoff Meeting. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10890&filename=Front-End+Engineering+%26+Design%3a+Project+Tundra+Carbon+Capture+System.pdf*.

Commercial Carbon Capture Design and Costing: Part Two (C3DC2)

primary project goal

ION Clean Energy Inc. (ION), Nebraska Public Power District (NPPD), and their partners conducted a front-end engineering design (FEED) study for a water-lean solvent (ICE-21)-based carbon capture system designed for retrofit onto Unit 2 of NPPD's Gerald Gentleman Station (GGS2), a 700-megawatt (MW) coal-fired power station located in Western Nebraska.

technical goals

- Conduct a FEED study for a commercial-scale CO_2 capture system retrofitted onto an existing coal-fueled Rankine cycle power station.
- Decarbonize as much of Unit 2 as possible utilizing ION's ICE-21 solvent technology.
- Investigate biomass co-firing.
- Leverage prior experience gained through U.S. Department of Energy (DOE) project award FE0031595, which conducted a design and costing study for a 300-MW slipstream carbon capture system for GGS2.

technical content

The project team designed the capture system and produced a capital cost estimate that would cover both the engineering design for the carbon capture process and the balance of plant. The engineering design was performed at a level consistent with an Association for the Advancement of Cost Engineering (AACE) Class 2 estimate, which would result in a capital cost accuracy range of -15 to +20%. The FEED study was based off of an integrated design at NPPD's Gerald Gentleman Station's Unit 2, which would utilize a two-unit, 350-MW train design for the CO_2 capture system. The project will utilize ION's ICE-21 solvent technology using a carbon capture process comparable to a standard temperature-swing chemical absorption scheme (such as monoethanolamine [MEA]), with the following key differences in design:

- Cold-rich bypass to control stripper temperature and reduce required heating steam.
- Optimized lean/rich cross exchanger (LRXC) design.
- Sulfur dioxide (SO_2) polishing via sodium hydroxide (NaOH) to reduce total sulfur emissions.
- Optimized CO_2 compressor selection.

A schematic of the CO_2 capture process is shown in Figure 1.

program area:
Point Source Carbon Capture

ending scale:
FEED

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Water-Lean Solvent Technology Retrofit to Coal-Fired Power Plant

participant:
ION Clean Energy Inc.

project number:
FE0031840

predecessor project:
FE0031595

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ION Clean Energy Inc.
erik.meuleman@ioncleanenergy.com

partners:
Nebraska Public Power District; Sargent & Lundy; Koch Modular Process Systems; Siemens

start date:
10.01.2019

percent complete:
100%

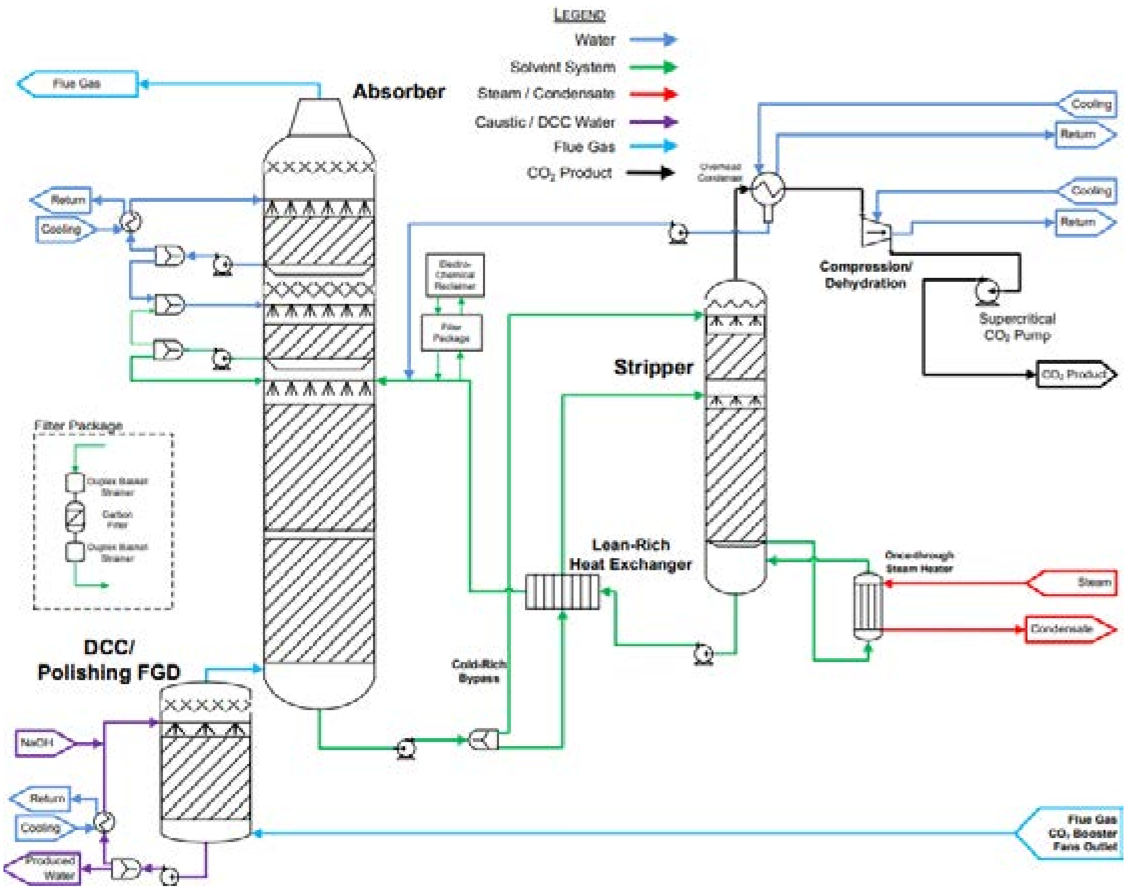


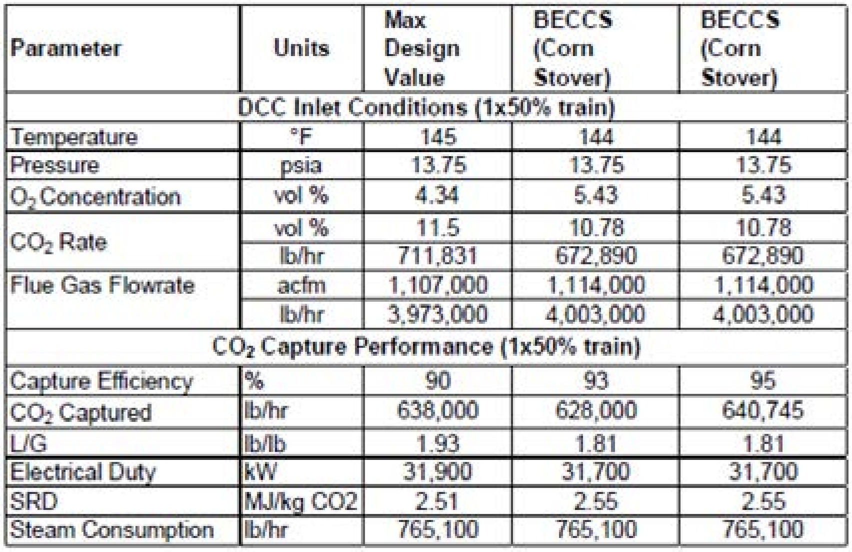
Figure 1: Carbon capture system design.

The FEED study produced process flow diagrams; utility flow diagrams; piping and instrument diagrams; heat and material balances; a 3D model; plot plans; final layout drawings; complete engineered process and utility equipment lists; one-line diagrams for electrical, electrical equipment, and motor schedules; vendor quotations; detailed project execution plans; and resourcing and workforce plans developed by the project team. Balance of plant engineering design included specifications for utilities, such as compression, cooling water, and waste treatment, as well as the sources of electricity and steam necessary to power the capture process. Civil and structural engineering tasks were also incorporated throughout the design to include the proper stormwater runoff and spill containment, as well as geological assessments to support foundation design.

The team conducted a series of studies and investigations to aid in the design of the carbon capture facility, including steam sourcing, cooling water system, solvent materials compatibility, wastewater treatment, permitting and regulatory review, reagent handling, constructability review, overpressure relief, and project execution and operations management planning.

In addition, the project team incorporated a sensitivity study for biomass using corn stover pellets (bioenergy with carbon capture and storage [BECCS]) to assess the potential for net-zero or net-negative carbon emissions. The pellets were delivered by truck to a retrofitted gasifier unit. The syngas produced by the gasifier was then used to co-feed the coal boiler. The CO_2 capture performance results of this study are shown in Table 1, where the as-designed CO_2 capture facility would result in a 93% capture rate of CO_2 in the BECCS case but could be increased to 95% capture with the addition of more plates in the LRXC.

TABLE 1: BECCS PERFORMANCE RESULTS



Parameter	Units	Max Design Value	BECCS (Corn Stover)	BECCS (Corn Stover)
DCC Inlet Conditions (1x50% train)				
Temperature	°F	145	144	144
Pressure	psia	13.75	13.75	13.75
O_2 Concentration	vol %	4.34	5.43	5.43
CO_2 Rate	vol %	11.5	10.78	10.78
	lb/hr	711,831	672,890	672,890
Flue Gas Flowrate	acfm	1,107,000	1,114,000	1,114,000
	lb/hr	3,973,000	4,003,000	4,003,000
CO_2 Capture Performance (1x50% train)				
Capture Efficiency	%	90	93	95
CO_2 Captured	lb/hr	638,000	628,000	640,745
L/G	lb/lb	1.93	1.81	1.81
Electrical Duty	kW	31,900	31,700	31,700
SRD	MJ/kg CO2	2.51	2.55	2.55
Steam Consumption	lb/hr	765,100	765,100	765,100

The final report summarized project results from the FEED study, including a systems and benefits analysis, summarized the results from the technical and economic feasibility analysis of scale-up, and made recommendations for future research and development (R&D). The operating parameters of the capture system's design is given in Table 2.

TABLE 2: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Design Value
Molecular Weight	mol^{-1}	75–95
Normal Boiling Point	°C	150–210
Normal Freezing Point	°C	-15–2
Vapor Pressure @ 15°C	bar	1-2 x 10^4
Manufacturing Cost for Solvent	$/kg	Proprietary
Working Solution		
Concentration	kg/kg	0.6–0.85
Specific Gravity (15°C/15°C)	—	0.9–1.2
Specific Heat Capacity @ STP	kJ/kg-K	2–3
Viscosity @ STP	cP	<5
Absorption		
Pressure	bar	1.0–1.15
Temperature	°C	20–50
Equilibrium CO_2 Loading	mol/mol	0.4–1.0
Heat of Absorption	kJ/mol CO_2	50–100
Solution Viscosity	cP	<20
Desorption		
Pressure	bar	1.1–1.8
Temperature	°C	80–150
Equilibrium CO_2 Loading	mol/mol	0.01–0.40
Heat of Desorption	kJ/mol CO_2	50–100

Finally, Table 3 shows the accomplished economic performance data from the study and the comparison with previously established R&D targets.

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

LRXC – Lean/Rich Cross Exchanger. A heat exchanger that connects the lean and rich solvent streams that further cools the lean solvent while heating the rich solvent, increasing absorption and desorption efficiencies.

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – Estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.7	150	10.5	20.5	66.4	5.3	0.80	15	150

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The physico-chemical properties of ION's solvent system allow for a unique mechanism that combines fast kinetics with low energy consumption.

Solvent Contaminant Resistance – Sulfur oxides (SO_X) and nitrogen oxides (NO_X), other than nitric oxide (NO), are absorbed into the solvent and lower the carrying capacity of CO_2. Oxidative and thermal degradation are manageable. To date, ION's solvent system has not been limited by contaminant concentration.

Solvent Foaming Tendency – No foaming issues have been seen during either of ION's solvent pilot test campaigns.

Flue Gas Pretreatment Requirements – It is preferred that the flue gas be saturated with water vapor and can include any concentration of CO_2. Pretreatment to levels of SO_X less than 10 to 30 parts per million (ppm) (spikes are manageable) and NO_X less than 100 to 200 ppm is also favored.

Solvent Makeup Requirements – Proprietary.

Waste Streams Generated – Proprietary.

Process Design Concept – ION's solvent-based process steps include pre-scrubbing to remove SO_X, several other gases, and most of the particles; a direct contact cooling unit to control the inlet flue gas temperature and humidity; an absorber consisting of a packed column with counter-flow for removal of CO_2 into the proprietary solvent; and water wash to remove solvent droplets and vapors from the exhaust gas. Following the absorption step, the final unit operation is a regenerator to produce the CO_2, recover the solvent, and recycle the solvent back to the absorber.

Finally, Table 3 shows the accomplished economic performance data from the study and the comparison with previously established R&D targets.

TABLE 3: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	34.97	30.00
Capital Expenditures	\$/MWhr	22.80	21.00
Operating Expenditures	\$/MWhr	14.03	12.00
Increase in Cost of Electricity	\$/MWhr	36.83	33.00

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Increase in Cost of Electricity – Projected additional cost of electricity per unit of energy produced under expected operating conditions for the addition of CO_2 capture process.

technology advantages

As part of the FEED study, the proprietary ION ICE-21 solvent technology was utilized. Relative to aqueous MEA technology and other commercial capture systems, ION's ICE-21 solvent technology offers the following benefits to lower operating and capital costs for CO_2 capture:

- Reduction in regeneration energy requirements.
- Higher CO_2 loading capacities.
- Reduced corrosion and solvent losses.
- Faster absorption kinetics.
- Less water used by the process.

The carbon capture plant was designed to take full advantage of these benefits, which resulted in a smaller physical plant, reduced energy requirements, less solvent degradation, lower emissions, and lower capital costs relative to systems built with the DOE Bituminous Baseline Study case benchmark solvents.

R&D challenges

In the project, ION looked to optimize the operating costs versus the capital costs, which were defined by some design basis decisions such as sparing philosophy, process robustness, and maintenance.

status

The project was completed on October 31, 2022. The results show that the process with 10% biomass syngas feed can achieve a 98% overall reduction in CO_2 emissions compared to a fully coal-powered plant without carbon capture and storage (CCS). More than 100% net reduction (carbon-negative) can be achieved through a higher packing factor in the absorber and stripper columns and a more optimized LRXC.

available reports/technical papers/presentations

Awtry, A., 2023, "Design and Costing of ION's CO_2 Capture Plant Retrofitted to a 700 MW Coal-Fired Power Plant." Final Technical Report, March 2023. *https://www.osti.gov/servlets/purl/1963720/*.

Awtry, A., 2021, "Design and Costing of ION's CO_2 Capture Plant Retrofitted to a 700 MW Coal-Fired Power Plant." Presented at the 2021 NETL CO_2 Capture Technology Project Review Meeting, August 3, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CCUS_Awtry.pdf*.

Awtry, A., 2020, "Design and Costing of ION's CO_2 Capture Plant Retrofitted to a 700 MW Coal-Fired Power Plant." Presented at the 2020 NETL CO_2 Capture Technology Project Review Meeting, August 18, 2020. *https://netl.doe.gov/sites/default/files/netl-file/20CCUS_Awtry.pdf*.

Awtry, A., Meuleman, E., Atcheson, J., "Commercial Carbon Capture Design & Costing: Part Two," NETL Project Kickoff Meeting, December 5, 2019. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10866&filename=Commercial+Carbon+Capture+Design+and+Costing%3a+Part+Two+(C3DC2).pdf*.

Large-Scale Commercial Carbon Capture Retrofit of the San Juan Generating Station

primary project goal

The overall goal of this project was to perform a front-end engineering design (FEED) study for the retrofit of the San Juan Generating Station (SJGS) with post-combustion carbon capture. The FEED study documented the initial engineering and cost estimates for the retrofit project, including the levelized cost of carbon capture on an existing plant, and provided estimates of the technical and economic viability of extending the life of the existing SJGS coal-fired power plant through the installation of Mitsubishi Heavy Industries' (MHI) Kansai Mitsubishi Carbon Dioxide Recovery (KM CDR) Process™ carbon dioxide (CO_2) capture technology.

technical goals

- Complete preliminary engineering and design work to support developing a detailed cost estimate for the cost of retrofitting CO_2 capture at SJGS.
- Perform multiple feasibility and design studies based on project-specific details in preparation for developing engineering deliverables. These studies will help define the scope of the retrofit project, based on project-specific decisions, technology-specific performance, site-specific requirements, and client-specific needs.
- Once the scope has been defined, detailed design will commence for the CO_2 capture system and its integration with the existing facility. Various design and engineering deliverables will be developed that will help define commodity quantities, equipment specifications, and labor effort required to execute the project.

technical content

Enchant and its partners performed a FEED study for retrofitting the host site with an advanced amine-based carbon capture technology. The FEED study was performed for 847 megawatts electric (MWe; Units 1 and 4 at SJGS in Waterflow, New Mexico). The coal was supplied by the adjacent mine, San Juan Coal Company, owned by Westmoreland Holdings. The original contract was set to expire on June 30, 2022; however, San Juan Coal offered SJGS a new contract in support of the plant's continued operation under decarbonization. Both operating units are equipped with state-of-the-art environmental controls that meet or exceed government-permitted levels of emissions for nitrogen oxide (NO_X), sulfur dioxide (SO_2), particulate matter (PM), and mercury (Hg), making the unit carbon capture-ready from an emissions perspective.

Work on this FEED study produced detailed engineering designs, costing, and timelines for the construction. It also designated permitting agencies and

program area:

Point Source Carbon Capture

ending scale:

FEED

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

Amine-Based KM CDR Process Retrofit to Coal-Fired Power Plant

participant:

Enchant Energy LLC

project number:

FE0031843

NETL project manager:

Carl Laird
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ccrane@enchantenergy.com

partners:

City of Farmington; Mitsubishi Heavy Industries America Inc.; Mitsubishi Heavy Industries Engineering Ltd.; Sargent and Lundy LLC; Navigant Consulting; EJM Associates LLC; Baker Tilly Virchow Krause LLP

start date:

10.15.2019

percent complete:

100%

timelines in order to execute the follow-on build-and-operate project. Lessons learned during the FEED study were documented to assist in future large-scale capture retrofit projects at coal-fired power plants.

SJGS Units 1 and 4 are already equipped with environment control equipment, including wet flue gas desulfurization (WFGD) for SO_2 control, fabric filter baghouses for PM control, and selective noncatalytic reduction (SNCR) for NO_X control. MHIA's amine-based carbon capture technology will remove 95% of the CO_2 from the flue gas, resulting in 20,026 tonnes per day (MTD) of CO_2 removed. At an 85% capacity factor, a total of 6,212,980 metric tons per year of CO_2 will be produced and transported from SJGS to either the Kinder Morgan Cortez CO_2 pipeline or Class VI storage wells. The site boundary pressure was set at an estimated 2,800 pounds per square inch gauge (psig) to account for the required injection pressures at the Cortez pipeline and storage wells, as well as the estimated pressure loss through the transport pipeline. Compression of the CO_2 extracted from the flue gas is accomplished by the combination of CO_2 compressors and CO_2 pumps. Existing SJGS Unit 1 and 4 flue gas operating data, along with recent stack testing results and future coal seam projections, were used to establish the flue gas design basis for the design of MHIA's carbon capture system. Electric power to support the new carbon capture system will be sourced from the existing SJGS Unit 1 and 4 generators. Water supply and wastewater studies were conducted to determine the available capacity and impact to SJGS. Makeup water to SJGS is sourced from the San Juan River, and it was determined there is sufficient water to support the additional makeup water required for carbon capture. The additional waste produced from the carbon capture system will primarily be treated by the existing wastewater treatment system. Safety was a primary consideration in the design of the carbon capture system. A hazard and operability (HAZOP) review was conducted to identify potential risks and mitigating safety measures that should be implemented into the design. The results from the HAZOP review were incorporated in the detailed design phase of the project.

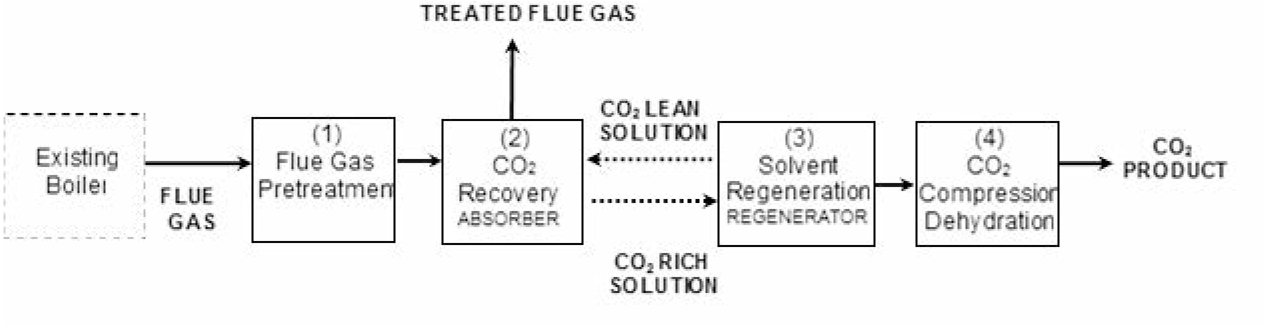

Figure 1: Block flow diagram of the CO_2 recovery plant.

The KM CDR Process has the following key features: (1) demonstrated performance on a large-scale (240 MWe); (2) high-performing amine solvent KS-1™ (high absorption capacity, low steam consumption, high resistance to oxidation and thermal degradation); and (3) key process technologies, such as an amine emission reduction system, solvent degradation reduction, automatic load adjustment control system, and amine purification system.

The CO_2 recovery facility consists of four main sections, as shown in Figure 1: (1) flue gas pretreatment, (2) CO_2 recovery, (3) solvent regeneration, and (4) CO_2 compression and dehydration. In flue gas pretreatment, the flue gas temperature is cooled in the flue gas quencher by direct contact with circulation water. The circulation water is injected with caustic soda to reduce the amount of SO_2 in the flue gas entering the amine system. A flue gas blower is installed downstream of the flue gas quencher to overcome the pressure drop across the flue gas quencher and the CO_2 absorber.

Figure 2 shows the process flow diagram for the CO_2 recovery and solvent regeneration steps. In CO_2 recovery, the cooled flue gas from the flue gas quencher is introduced at the bottom of the CO_2 absorber. The flue gas moves upward through the packing while the CO_2-lean solvent is supplied at the top of the absorption section where it flows down onto the packing. The flue gas contacts with the solvent on the surface of the packing, where 95% of the CO_2 in the flue gas is absorbed by the solvent. The CO_2-rich solvent from the bottom of the CO_2 absorber is sent to the regenerator. The CO_2-lean flue gas exits the absorption section of the CO_2 absorber and enters the flue gas washing section of the CO_2 absorber. The flue gas contacts with circulating water to reduce the carryover amine that is emitted from the top of the CO_2 absorber.

In solvent regeneration, cool-rich solvent is heated by the hot-lean solvent extracted from the bottom of the regenerator in a heat exchanger. The pre-heated rich solvent is then introduced at the top of the regenerator column and flows down over the packing, where it contacts with stripping steam. As it flows down the column, the rich solvent releases captured CO_2 and is regenerated back into lean solvent. The steam in the regenerator is produced by the reboiler, where low-pressure steam is used to heat the lean solvent. The lean solvent is then cooled to the optimum absorption temperature before being recycled back to the CO_2 absorber.

The overhead vapor leaving the regenerator is cooled, and the condensed liquid from this unit is then returned to the system. In CO_2 compression and dehydration, CO_2 is compressed through a multi-stage gas compressor. Treatment such as oxygen (O_2) removal or dehydration may be necessary to meet pipeline and storage guidelines.

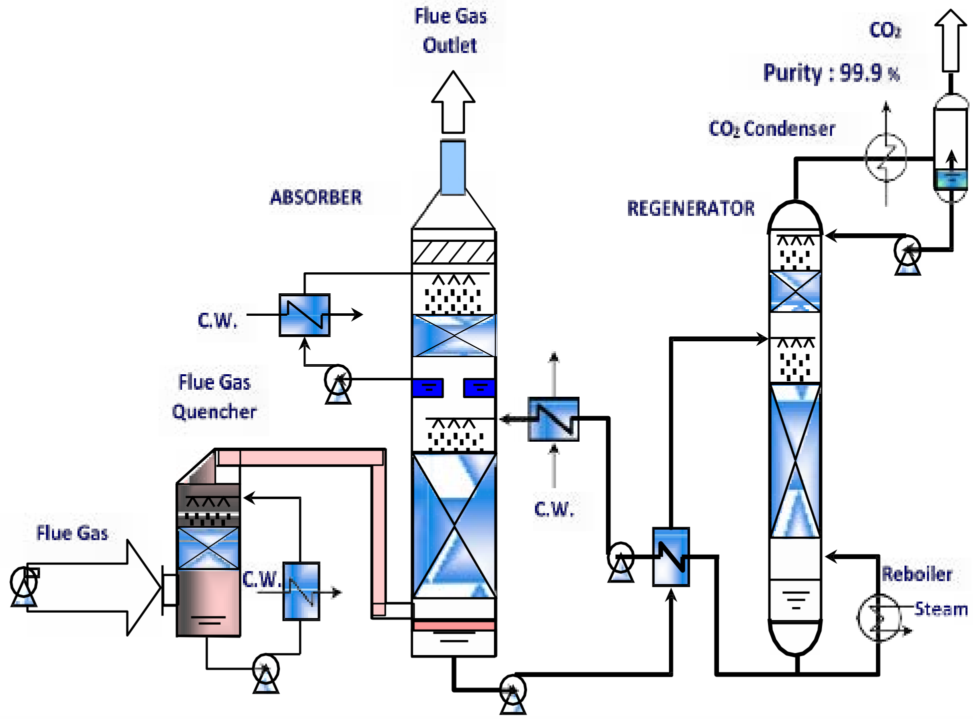

Figure 2: Carbon capture basic process flow diagram.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Design Value
Molecular Weight	mol^{-1}	proprietary data
Normal Boiling Point	°C	proprietary data
Normal Freezing Point	°C	proprietary data
Vapor Pressure @ 15°C	bar	proprietary data
Manufacturing Cost for Solvent	$/kg	proprietary data
Working Solution		
Concentration	kg/kg	proprietary data
Specific Gravity (15°C/15°C)	-	proprietary data
Specific Heat Capacity @ STP	kJ/kg-K	proprietary data
Viscosity @ STP	cP	proprietary data
Absorption		
Pressure	bar	proprietary data
Temperature	°C	proprietary data
Equilibrium CO_2 Loading	mol/mol	proprietary data

Heat of Absorption	kJ/mol CO_2	proprietary data
Solution Viscosity	cP	proprietary data
Desorption		
Pressure	bar	proprietary data
Temperature	°C	proprietary data
Equilibrium CO_2 Loading	mol/mol	proprietary data
Heat of Desorption	kJ/mol CO_2	proprietary data
Module Design		
Flue Gas Flowrate	kg/hr	5,650,894
CO_2 Recovery, Purity, and Pressure	%/ %/ barg	95% / >95 mol% dry* / 193†
Absorber Pressure Drop	bar	proprietary data
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	proprietary data

* Pipeline requirement.

† Facility fence-line pressure requirement, downstream of CO_2 pumps.

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – Estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD unit (wet basis) used in the FEED study design basis should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
11.97	127	9.93	17.16	66.91	5.98	—	19.2	106

Chemical/Physical Solvent Mechanism – Chemical absorption

Solvent Contaminant Resistance – Low solvent degradation.

Solvent Foaming Tendency – Ordinary.

Flue Gas Pretreatment Requirements – Desulfurization.

Solvent Makeup Requirements – Periodically.

Waste Streams Generated – Reclaimed waste.

Process Design Concept – Block flow/process flow diagrams shown in Figures 1 and 2.

Proposed Module Design – Partial Module Design.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Target Value ($2019) [1] (@ 85% Capacity Factor)
Total Project Cost	$	1,295,280,000
Capital Annualization Factor	--	0.1243
Annualized Capital Cost	$/yr	161,000,000
Annual O&M Cost	$/yr	99,939,000
Total Annual Cost	$/yr	260,939,000
CO_2 Captured	mmscfd	312.45
Annual CO_2 Captured	tonnes	6,000,000
Cost of Carbon Captured	$/tonne	43.49

[1] Note that target values are based on the pre-feasibility study performed prior to the DOE award (July 2019) as the project team has not finished capital and O&M cost development deliverables.

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Calculations Basis – The economic calculation performed for the pre-feasibility study utilized many similar references as the Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity report Rev 2 and 3, including similar annualization factor for high-risk capital investment and 85% referenced capacity factor. Overall economics were developed using AACE Class 5 accuracy for retrofitting the existing San Juan Generating Station Units 1 and 4. For all calculation basis information, refer to the publicly available study "Enchant Energy, San Juan Generating Station – Units 1 & 4, CO_2 Capture Pre-Feasibility Study, FINAL."

Scale of Validation of Technology Used in TEA – Costs were developed using publicly available cost information for commercially available amine-based solvent systems scaled for the size and characteristics of the SJGS facility. For information regarding capital cost development, refer to the publicly available study "Enchant Energy, San Juan Generating Station – Units 1 & 4, CO_2 Capture Pre-Feasibility Study, FINAL."

Qualifying Information or Assumptions – Information prepared during the pre-feasibility study was not prepared in conjunction with MHI for the KM-CDR™ Process. Costing was based on 90% capture for the flue gas design basis provided in the pre-feasibility report, not herein. For all assumptions used to develop these costs, refer to the publicly available study "Enchant Energy, San Juan Generating Station – Units 1 & 4, CO_2 Capture Pre-Feasibility Study, FINAL."

technology advantages

- FEED studies for carbon capture systems at this site will provide the U.S. Department of Energy (DOE) with a more detailed understanding of carbon capture costs in a commercial application, thereby enabling DOE to better design its research and development (R&D) program to reduce those costs for similar carbon capture technologies being developed in its R&D portfolio.
- This FEED study could lead to the largest carbon capture project in the world, and with its 95% CO_2 capture rate, it could be the lowest-emitting CO_2-per-MWh large-scale, fossil-fueled power plant.
- Adding carbon capture technology will allow SJGS to meet and exceed the stringent CO_2 emissions standards of the New Mexico Energy Transition Act and will also allow for electricity sales delivered across the west, including into California under its stringent decarbonization standards.

R&D challenges

- To deploy the post-combustion amine technology on coal-fired gas while adequately managing accumulation of impurities in the exhaust without excessive cost.
- Ensuring reliable operation over a long period at large scale.

status

The project was completed on September 30, 2022. The results of the FEED study show that the projected capital cost of the installation is $1.55 billion based on pricing through May 31, 2022. The projected operation and maintenance (O&M) cost on an annual basis is $171 million. The resulting cost of capture for SJGS is projected to be $46.7/tonne of CO_2 removed. The resulting net total electric power output from SJGS Units 1 and 4 after carbon capture addition is expected to be 482 MW (a net loss of 365 MW, or 43% of total power output).

available reports/technical papers/presentations

Crane, C., 2022, "Large-Scale Commercial Carbon Capture Retrofit of the San Juan Generating Station." *Final Technical Report.* Enchant Energy LLC. Report No. DOE-ENCHANT-31843. *https://www.osti.gov/servlets/purl/1889997*.

Selch, J. & Mandelstam, 2020, "Large-Scale Commercial Carbon Capture Retrofit of the San Juan Generating Station," DOE Project Kickoff Meeting. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10879&filename=Large-Scale+Commercial++Carbon+Capture+Retrofit+of+the++San+Juan+Generating+Station.pdf*.

Selch, J. & Mandelstam, 2020, "Large-Scale Commercial Carbon Capture Retrofit of the San Juan Generating Station," *Proceedings of the 2020 Carbon Capture Project Review Meeting*. *https://netl.doe.gov/sites/default/files/netl-file/20CCUS_Selch.pdf*.

Adair, H.; Crane, C.; Mandelstam, 2021, "Update on Large-Scale Commercial Carbon Capture Retrofit of the San Juan Generating Station," *Proceedings of the 2021 NETL Carbon Management and Oil and Gas Research Project Review Meeting*. Integrated CCUS Projects and FEED Studies. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CCUS_Mandelstam.pdf*.

Full-Scale FEED Study for Retrofitting the Prairie State Generating Station with an 816-MWe Capture Plant Using Mitsubishi Heavy Industries America Post-Combustion CO_2 Capture Technology

primary project goal

The University of Illinois Urbana-Champaign and its partners performed a front-end engineering design (FEED) study to retrofit the Prairie State Generation Company's (PSGC) coal-fired power station with post-combustion carbon capture. The University of Illinois Urbana-Champaign and the project team produced a FEED study that used Mitsubishi Heavy Industries' (MHI) Advanced Kansai Mitsubishi Carbon Dioxide Recovery (KM CDR) Process™ to retrofit one of PSGC's two generating units (approximately 816 megawatt-electric [MWe]) in Marissa, Illinois. If built, it would become the largest post-combustion carbon dioxide (CO_2) capture plant in the world.

technical goals

- Complete preliminary engineering and design work to support developing a detailed cost estimate for the cost of retrofitting CO_2 capture at PSGC.
- Perform feasibility and design studies in preparation for developing engineering deliverables.
- Perform a detailed design of the complete capture system integrated with the host site plant alongside a complete techno-economic analysis (TEA) and performance analysis.

technical content

The overall project goal was a full FEED study on a carbon capture system for Unit #2 (816 MWe) at the PSGC Energy Campus in Marissa, Illinois, based upon the KM CDR Process CO_2 capture technology from MHI. This capture technology represents the current state-of-the-art and employs an improved solvent from that used at the 240-MWe Petra Nova capture plant in Thompsons, Texas. The capture technology was scaled-up to 816 MWe.

This FEED study produced detailed engineering designs, cost estimation, and timelines for the construction. It also designated permitting agencies and timelines in order to execute the follow-on build and operation of the project. Lessons learned during the FEED study were documented to assist in future large-scale capture retrofit projects at coal-fired power plants.

program area:
Point Source Carbon Capture

ending scale:
FEED

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Amine-based Advanced KM CDR Process Retrofit to Coal-Fired Power Plant

participant:
University of Illinois Urbana-Champaign

project number:
FE0031841

NETL project manager:
Carl Laird
carl.laird@netl.doe.gov

principal investigator:
Kevin O'Brien
University of Illinois at Urbana-Champaign
kcobrien@illinois.edu

partners:
Mitsubishi Heavy Industries Ltd.; Prairie State Generating Company; Kiewit Engineering Group Inc.; Sargent & Lundy

start date:
10.01.2019

percent complete:
100%

Parameter Descriptions:

Chemical/Physical Solvent Mechanism – KS-21 is an amine-based solvent that reacts selectively with CO_2.

Solvent Contaminant Resistance – KS-21 has a higher resistance to forming heat-stable salts (HSSs) formed from the reactions between amine and impurities than standard monoethanolamine (MEA). Impurities still need to be removed by solvent reclaiming, otherwise the CO_2 capture performance becomes degraded.

Solvent Foaming Tendency – Amine-based solvents can be oxidized by the oxygen contained in the flue gas and results in accumulation of HSSs, which would cause foaming of the solvent.

Flue Gas Pretreatment – The KM CDR Process utilizes a flue gas quencher to remove any residual sulfur oxide (SO_X), nitrogen oxide (NO_X), and particulate matters (PM) from the incoming flue gas. These impurities can lead to an increase in the amine consumption rate through degradation and emissions.

Solvent Make-Up Requirements – The replenishment of solvent due to operational losses caused by the impact of the contaminants in the coal-fired flue gas.

Proposed Module Design – The modular design not only reduces the cost, but also improves the fabrication quality and productivity. In this study, the onsite labor hours for the flue gas quencher and the CO_2 absorber were reduced by 71% by applying modularized towers in the Advanced KM CDR Process compared to conventional design. Reduction for actual projects will depend on site logistics and other factors.

The KM CDR Process is an improvement upon MHI's original KM CDR Process and is an amine-based CO_2 capture process that uses a newly developed solvent known as KS-21. The CO_2 capture system can recover 95% of the CO_2 from the flue gas and compress and treat the CO_2 to adequate pipeline conditions.

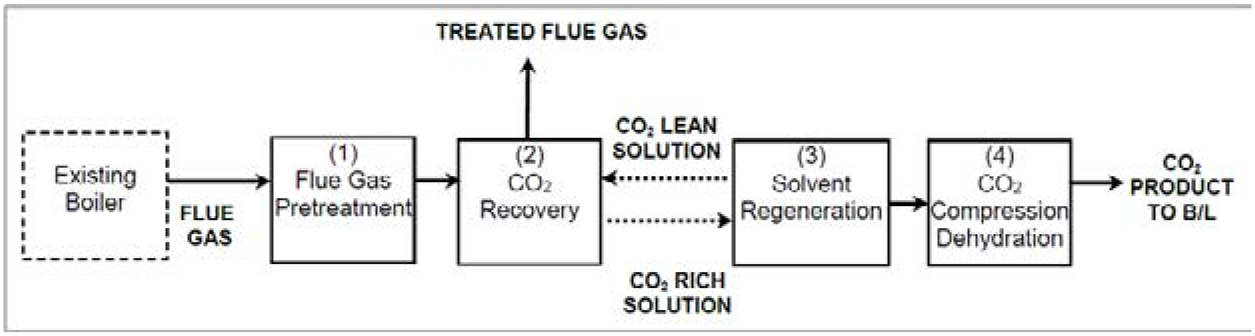

Figure 1: Block flow diagram of the CO_2 recovery plant.

The CO_2 recovery facility consists of four main sections, as shown in Figure 1: (1) flue gas pretreatment, (2) CO_2 recovery, (3) solvent regeneration, and (4) CO_2 compression and dehydration. In flue gas pretreatment, the flue gas temperature is cooled in the flue gas quencher by direct contact with circulation water. The circulation water is injected with caustic soda to reduce the amount of sulfur dioxide (SO_2) in the flue gas entering the amine system. A flue gas blower is installed downstream of the flue gas quencher to overcome the pressure drop across the flue gas quencher and the CO_2 absorber.

Figure 2 shows the process flow diagram for the CO_2 recovery and solvent regeneration steps. In CO_2 recovery, the cooled flue gas from the flue gas quencher is introduced at the bottom of the CO_2 absorber. The flue gas moves upward through the packing while the CO_2-lean solvent is supplied at the top of the absorption section where it flows down onto the packing. The flue gas contacts with the solvent on the surface of the packing, where at least 95% of the CO_2 in the flue gas is absorbed by the solvent. The CO_2-rich solvent from the bottom of the CO_2 absorber is sent to the regenerator. The CO_2-lean flue gas exits the absorption section of the CO_2 absorber and enters the flue gas washing section of the CO_2 absorber. The flue gas contacts with circulating water to reduce the carryover amine that is emitted from the top of the CO_2 absorber.

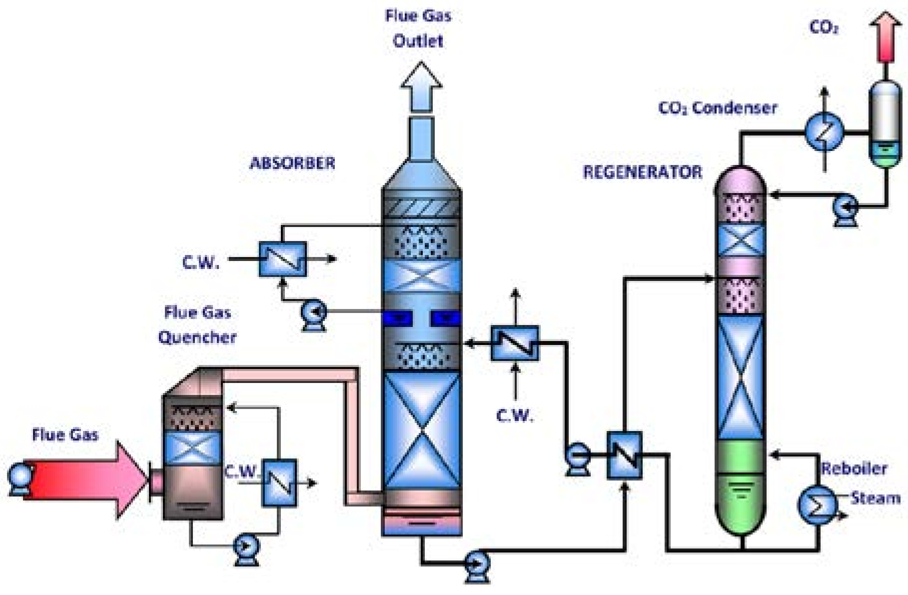

Figure 2: Carbon capture basic process flow diagram.

In solvent regeneration, cool rich solvent is heated by the hot lean solvent extracted from the bottom of the regenerator in a heat exchanger. The pre-heated rich solvent is then introduced at the top of the regenerator column and flows down over the packing, where it contacts with stripping steam. As it flows down the column, the rich solvent releases captured CO_2 and is regenerated back into lean solvent. The steam in the regenerator is produced by the reboiler, where low-pressure steam is used to heat the lean solvent. The lean solvent is then cooled to the optimum absorption temperature before being recycled back to the CO_2 absorber.

The overhead vapor leaving the regenerator is cooled, and the condensed liquid from this unit is then returned to the system. In CO_2 compression and dehydration, CO_2 is compressed through a multi-stage gas compressor. Treatment such as oxygen (O_2) removal or dehydration may be necessary to meet pipeline and storage guidelines. The economics of the overall process are shown in Table 1.

TABLE 1: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current Project Value	Target Project Value
Cost of Carbon Captured	\$/tonne CO_2	43.42	45
Cost of Carbon Avoided	\$/tonne CO_2	54.29	—
Capital Expenditures	\$/MWhr	24.5	—
Operating Expenditures	\$/MWhr	27.3	—
Cost of Electricity	\$/MWhr	N/A	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – Includes costs incurred during the construction phase and throughout the life of the project, including costs to finance the project through construction and debt service through the operation of the plant. Calculation methodology follows NETL-PUB-2263B "Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity" (Rev. 4), with capital expenditure and operational expenditure costs developed during the FEED study implemented where available. Cost of Electricity (COE) calculations are not considered as the new CO_2 capture facility is not a source of power.

Scale of Validation of Technology Used in TEA – Large-scale capture retrofit (816 MWe).

Qualifying Information or Assumptions –

- Included in cost calculations:
  - Capital costs developed during the FEED study.
  - Operating costs developed during the FEED study.
  - Owner costs.
  - 90% capacity factor.
  - Fixed charge rate: 0.0661.[†]
- Not included in cost calculations:
  - Taxes.
  - Insurance on operating facility.
  - CO_2 Transport & Storage (T&S) costs.
  - Site-specific costs.*
  - Costs associated with construction or operation of the existing PSGC coal-fired power station.

* Capital cost has been normalized by removing $155 million of site-specific costs to allow for comparison to generic cost assessments (e.g., 15-mile pipeline routing cooling tower blowdown to an outfall structure).

Land, permitting costs, legal fees, owners engineer costs, owner contingency, and financing costs are approximated as 10% of total project cost. NETL-PUB-22580 "Cost Estimation Methodology for NETL Assessments of Power Plant Performance" (February 2021) indicates 17.7% (15% + 2.7%) as typical, based on an engineering, procurement, construction, and management (EPCM) model and including FEED study costs; 10% used due to engineering, procurement, and construction (EPC) being the expected delivery model (labor/material risk already carried in contractor cost) and the project having already completed the FEED study.

[†] The financial structure for debt-to-equity split, cost of debt, and return on equity (ROE) is based on a real rates financial structure for investor-owned utility from NETL-PUB-22580 "Cost Estimation Methodology for NETL Assessments of Power Plant Performance" (February 2021). Spending nominally distributed over the four-year capital expenditure period (10%/40%/30%/20%).

technology advantages

- Used an improved, newly developed proprietary solvent known as KS-21. This solvent's properties translate into reduced capital costs.
  - Less volatility, which reduced the height of the water wash section of the CO_2 absorber, lowering capital cost.
  - Improved thermal stability, allowing the regenerator to be operated at a higher pressure and temperature, thereby reducing the equipment size and the power consumption for CO_2 compression, resulting in lowering operating and capital costs.
  - More resistance to oxidative degeneration, which reduces solvent loss.
  - Lower heat of absorption, which allows higher circulation rate and therefore slightly less steam consumption.
- Can recover 95% of the CO_2 from the flue gas and compress and treat the CO_2 to adequate pipeline conditions.
- The capture system was scaled up using multiple trains so that it could be standardized and modularized, and so that the overall project cost could be reduced.

R&D challenges

- Deploying the post-combustion amine technology on coal-fired gas while adequately managing accumulation of impurities in the exhaust without excessive cost.
- Ensuring reliable operation over a long period at large-scale (17,000–23,000 tonnes per day).

status

The FEED study was completed on June 30, 2022. Reports were completed and submitted during the duration of the project, including the design basis document, utility requirements, detailed engineering document, hazard and operability (HAZOP) review, watershed impact report, constructability review, cost assessment, and regulatory and permitting pathway/analysis reports. The overall cost of capture (not including transport and storage cost) was found to be \$43.42/tonne CO_2.

available reports/technical papers/presentations

O'Brien, K. et al., 2022, "Full-scale FEED Study for Retrofitting the Prairie State Generating Station with an 816 MWe Capture Plant using Mitsubishi Heavy Industries Post-Combustion CO2 Capture Technology." *Final Technical Report.* University of Illinois at Urbana-Champaign. Report No. DOE-UIUC-0031841-01. *https://www.osti.gov/biblio/1879443*.

"Full-Scale FEED Study for a 816 MWe Capture Plant at the Prairie State Generating Company Using Mitsubishi Heavy Industries of America Technology," November 13, 2019. Presented by Kevin O'Brien, University of Illinois, NETL Project Kickoff Meeting. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10869&filename=Full-Scale+FEED+Study+For+a+816+MWe+Capture+Plant+at+the+Prairie+State+Generating+Company+Using+Mitsubishi+Heavy+Industries+of+America+Technology.pptx*.

"Full-Scale FEED Study for a 816 MWe Capture Plant at the Prairie State Generating Company Using Mitsubishi Heavy Industries of America Technology," August 17, 2020. Presented by Kevin O'Brien, University of Illinois, 2020 NETL Project Review Meeting - CCUS Integrated Projects. *https://netl.doe.gov/sites/default/files/netl-file/20CCUS_OBrien.pdf*.

"Full-Scale FEED Study for a 816 MWe Capture Plant at the Prairie State Generating Company Using Mitsubishi Heavy Industries of America Technology," August 2, 2021, Presented by Kevin O'Brien and Jason Dietsch, University of Illinois, 2021 NETL Carbon Management Research Project Review Meeting. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CCUS_OBrien.pdf*.

"Full-Scale FEED Study for a 816 MWe Capture Plant at the Prairie State Generating Company Using Mitsubishi Heavy Industries of America Technology" January 5, 2022. Presented by Kevin O'Brien, University of Illinois, Final Project Briefing. *https://www.netl.doe.gov/projects/plp-download.aspx?id=12602&filename=Full-Scale+FEED+Study+for+a+816+MWe+Capture+Plant+at+the+Prairie+State+Generating+Company+Using+Mitsubishi+Heavy+Industries+of+America+Technology.pdf*.

Piperazine Advanced Stripper Front-End Engineering Design

primary project goal

The University of Texas at Austin (UT-Austin) performed a front-end engineering design (FEED) study of the piperazine advanced stripper (PZAS) process for carbon dioxide (CO_2) capture from the natural gas combined cycle (NGCC) power plant at Golden Spread Electric Cooperative's (GSEC) Mustang Station in Denver City, Texas.

technical goals

- Develop a comprehensive estimate for the total installed cost of PZAS with CO_2 compression on an NGCC power plant.
- Provide cost details to be used in the economic optimization of the process features of PZAS and other second-generation amine scrubbing processes.
- Provide the host site and cost-share partners with the information necessary to determine whether a commercial project to capture and use CO_2 for enhanced oil recovery (EOR) can be justified.
- Provide the U.S. Department of Energy (DOE) with a more detailed understanding of carbon capture costs in a commercial application.

technical content

The PZAS process is a second-generation amine scrubbing process with advanced solvent regeneration for post-combustion CO_2 capture. Figure 1 shows the flow and operating conditions for PZAS as tested at the National Carbon Capture Center (NCCC) pilot plant and reflects the final design for Mustang Station. The NGCC at Mustang Station is comprised of a combined cycle facility, which consists of two gas turbines with two heat recovery steam generators (HRSGs) and a steam turbine with a total rating of 464 megawatts-electric (MWe).

The system uses a 5 molal piperazine (PZ) solvent that absorbs CO_2 two and half times faster than 30 wt% monoethanolamine (MEA), requiring only 25 feet of absorber packing height to achieve 90% CO_2 removal. Flue gas from the NGCC is contacted with PZ solvent at a lean loading of 0.20 mol CO_2/gram-equivalent PZ to remove 90% of the CO_2. The hot flue gas leaving the HRSG is cooled in the bottom section of the absorber by recirculation of rich solvent through an exchanger using air cooling, mostly eliminating the temperature bulge of the absorber. Gas leaving the middle section of the absorber is contacted with air-cooled wash water in the top section of structured packing.

Rich PZ solvent is pumped through the cold cross-exchanger, the hot cross-exchanger, and the steam heater to the sump of the stripper. A fraction of the rich solvent (5 to 10%) is heated in the cold bypass exchanger. A fraction of the warm rich solvent (20 to 40%) is bypassed at its bubble point after the cold cross-exchanger. The two bypass streams are combined and fed to the top of the

program area:
Point Source Carbon Capture

ending scale:
FEED

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Piperazine Solvent with Advanced Stripper Retrofit to NGCC

participant:
University of Texas at Austin

project number:
FE0031844

predecessor project:
FE0005654

NETL project manager:
Krista Hill
krista.hill@netl.doe.gov

principal investigator:
Gary T. Rochelle
The University of Texas at Austin
gtr@che.utexas.edu

partners:
AECOM; Trimeric Corporation

start date:
10.01.2019

percent complete:
100%

stripper. The flows of the bypassed streams are optimized to minimize the steam duty. Heat is recovered from the hot lean solvent as it is returned through the hot cross-exchanger and the cold cross-exchanger and then further cooled in the trim cooler. The stripper sump is maintained at 150°C and 6.3 bar(a). Vapor from the stripper sump flows through two sections of random packing. Heat is recovered from the vapor leaving the stripper in the cold bypass exchanger. The CO_2 product is further cooled in a condenser and the water is separated and returned to the absorber water wash. The advanced stripper configuration results in a heat duty of 2.4 gigajoules (GJ)/tonne CO_2, compared to values of 2.4 to 2.7 GJ/tonne CO_2 for six other solvents tested at NCCC with the simple stripper under coal and NGCC operations. The improvement in energy performance is achieved through use of the cold rich bypass and warm rich bypass streams in the advanced stripper configuration.

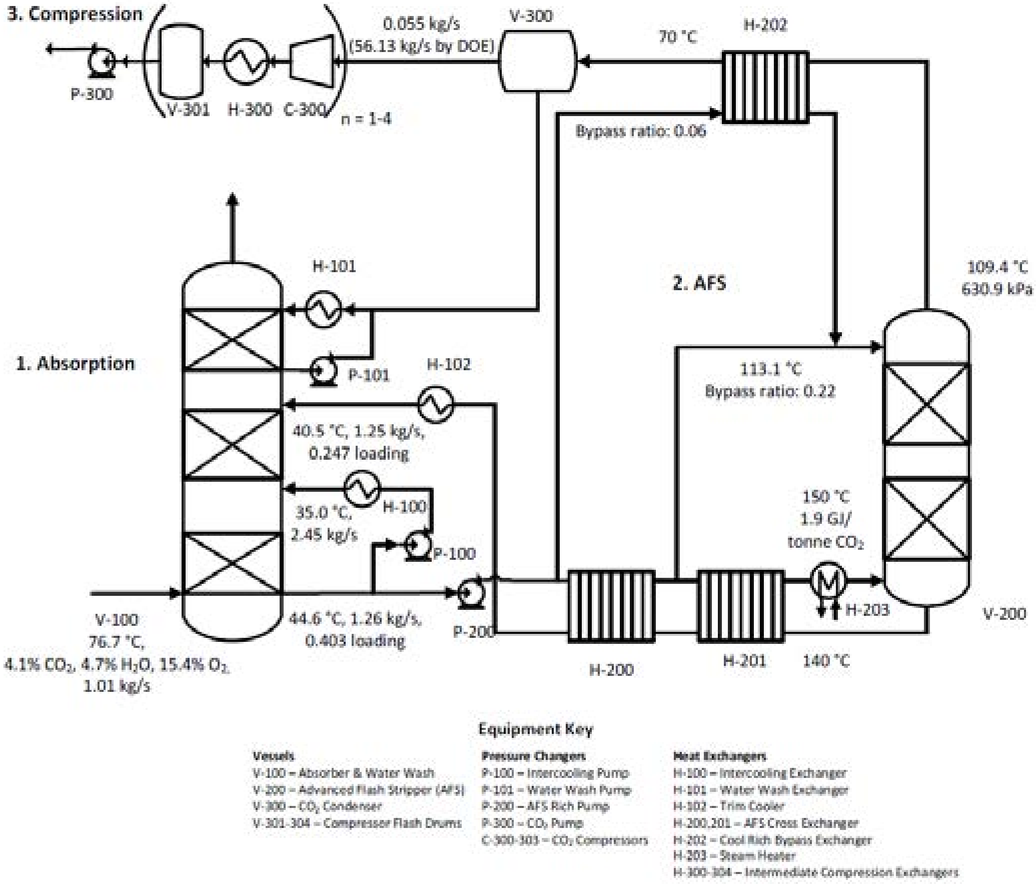

Figure 1: PZAS process flowsheet.

The PZAS process has evolved from bench-scale experiments to pilot-scale test campaigns, including testing at UT-Austin's Separations Research Program (SRP) pilot plant using simulated coal and natural gas flue gas and testing at NCCC using flue gas derived from fossil fuels at both coal and NGCC conditions. Previous testing confirmed that a 5 molal PZ solution is superior to an 8 molal solution of PZ. The reduced viscosity of 5 molal PZ results in an enhanced CO_2 absorption rate in the absorber and improved heat transfer performance in the cross-exchanger, reducing the heat duty in the advanced flash stripper (AFS) steam heater. Combining the 5 molal PZ solvent with the AFS may decrease the cost of CO_2 capture to less than $40/tonne.

The details of the techno-economic analysis (TEA) that was prepared for the PZAS process in the previous DOE-funded project, DE-FE0005654, were utilized to determine equipment sizes and to develop an approximate capital cost estimate for installing PZAS at Mustang Station. The PZAS process is estimated to require a capital investment roughly two-thirds that of other second-generation amine scrubbing processes, which is largely attributable to a significant decrease in absorber column size and modest decrease in stripper column size.

As part of the FEED study, the project team developed detailed estimates for these direct capital cost components and provided a more accurate estimate of total plant costs for a PZAS installation at Mustang Station. The resulting estimates were used to arrive at a more accurate Lang factor for developing future cost estimates for carbon capture on NGCC plants. The project team interfaced directly with vendors to obtain detailed design and cost estimates for individual pieces of equipment for a full-scale capture facility. Operating costs were estimated based on PZAS experience at the NCCC pilot plant and the resulting TEA. Parasitic loads were calculated based on developed thermodynamic properties of PZAS and the design of heat exchangers and other equipment requiring either electricity or steam energy. An appropriate source of steam will be identified that results in maximum efficiency. The FEED also examined the benefits and economics of integrating CO_2 captured from a power station directly into an existing CO_2 pipeline network and possibly direct use by local CO_2-EOR end-users in the area. The economics data is shown in Table 2.

Definitions:

Bar(a) – Unit used to indicate absolute pressure, where the reference pressure is absolute zero (i.e., not taking into account atmospheric pressure).

Molal Concentration (Molality) – The amount (in moles) of solute, divided by the mass (in kilograms) of the solvent.

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The reaction of PZ with CO_2 involves formation of the following four PZ species:

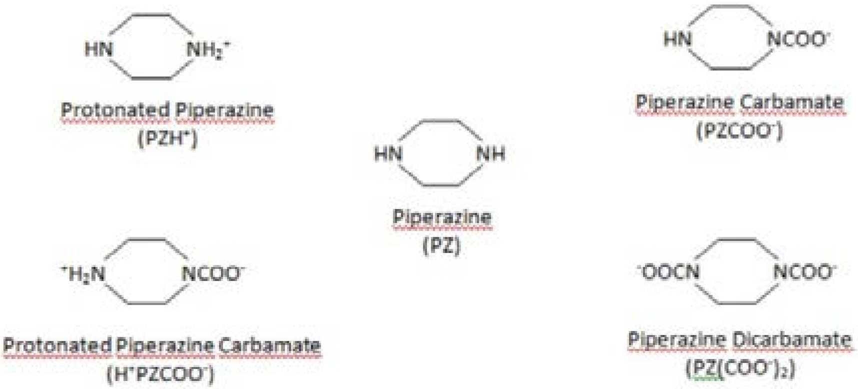

Figure 2: Molecular structure of piperazine species.

These reactions are as follows:

1. $PZH^+ + H_2O \leftrightarrow PZ + H_3O^+$
2. $PZ + CO_2 + H_2O \leftrightarrow PZCOO^- + H_3O^+$
3. $H_2O + H^+PZCOO^- \leftrightarrow H_3O^+ + PZCOO^-$
4. $PZCOO^- + CO_2 + H_2O \leftrightarrow PZ(COO^-)_2 + H_3O^+$

TABLE 1: EQUILIBRIUM CONSTANTS FOR ABOVE REACTIONS

Eq. No	Equilibrium Constant	In K = A + B/T + C InT		
		A	B	C
1	$K_1 = \frac{x_{PZ} x_{H3O+}}{x_{H2O} x_{PZH+}}$	-11.91	-4,351	—

2	$K_2 = \frac{x_{H3O+}x_{PZCOO-}}{x_{PZ}x_{CO2}x_{H2O}}$	-29.31	5,615	—
3	$K_3 = \frac{x_{H3O+}x_{PZCOO-}}{x_{H+PZCOO-}x_{H2O}}$	-8.21	-5,286	—
4	$K_4 = \frac{x_{H3O+}x_{PZ(COO-)2}}{x_{PZCOO-}x_{CO2}x_{H2O}}$	-30.78	5,615	—

This speciation and solubility model has been used to predict the partial pressure of CO_2 and mole fraction of species in solution as a function of PZ loading; the results show a good match between the model and the experimental data.

Solvent Contaminant Resistance – 5 molal PZ is thermally stable at 150°C with negligible oxidative degradation. The total amine loss is estimated to be 0.5% per week when stripping at 150°C. At 135°C, the estimated total amine loss of PZ is 0.3%, as compared to 3.0% in the case of an MEA solvent. PZ forms nitrosamines and other nitro products with nitrogen dioxide (NO_2). Both pilot-scale flue gas testing and bench-scale testing have confirmed that nitrosamines decompose at temperatures of 150°C and greater.

Solvent Foaming Tendency – Pilot plant tests of PZ with two different sources of coal-fired flue gas and with air/CO_2 have experienced no persistent problems with foaming. However, bench-scale experiments have shown the possibility for PZ to foam under certain conditions (e.g., after undergoing oxidative degradation).

Solvent Makeup Requirements – Including an estimate for additional amine lost in the reclaiming process, the required makeup rate is estimated to be less than 0.5 kg PZ per metric ton of CO_2 captured for PZ regenerated at 150°C. The estimated makeup rate for 30 wt% MEA at 120°C is approximately 2.0 kg/MT CO_2.

Waste Streams Generated – The major amine solid/liquid waste streams come from reclaimer waste. There could be fugitive liquid amine emissions, which can be controlled by incorporating seamless valves, rupture disks, closed-loop ventilation systems, pumps with dual mechanical seals, minimum welds, and correct gasket material selection. Due to the low fly ash concentration of natural gas combustion gas, the heavy metal concentration in the solvent is not expected to trigger a hazardous waste classification with this technology. Measurement of PZ emissions from the NCCC pilot plant with NGCC conditions have established that the PZAS process will produce less than 0.3 ppm PZ in the clean flue gas.

Process Design Concept – Flowsheet/block flow diagram shown above in Figure 1.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD (wet basis) should be assumed as:

		Composition						
		vol%					ppmv	
Pressure	**Temperature**	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.7 psia	135°F	4.3	17.25	66.44	14	0.80	0	15

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value
Cost of Carbon Captured	\$/tonne CO_2	105
Cost of Carbon Avoided	\$/tonne CO_2	—
Capital Expenditures	\$/MWhr	—
Operating Expenditures	\$/MWhr	—
Cost of Electricity	\$/MWhr	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

technology advantages

As compared to conventional amine solvents, the advantages of PZ are:

- Faster CO_2 absorption rate, higher working capacity, higher thermal stability, and less oxidative degradation—all of which point toward 10 to 20% less energy use.
- Advanced stripper configuration minimizes steam heater heat duty required for regeneration, limiting equipment sizes for major process equipment.
- Elevated regeneration pressure eliminates two initial stages of CO_2 compression, resulting in capital cost savings.
- High absorption rate leads to smaller absorber size, reducing capital cost.
- PZ is resistant to oxidative degradation in the absorber.
- Five molal PZ is less corrosive than MEA at typical absorber temperatures, allowing less expensive and more readily available materials of construction to be used.
- No direct contact coolers are required.

R&D challenges

- Mitigation of oxidative degradation of the solvent will likely require continuous thermal reclaiming.

status

The project was completed on June 30, 2022. The results of the FEED demonstrated a capital cost of $725 million, resulting in a total cost of capture of $105/tonne of CO_2. The project team identified several opportunities for improving overall plant performance and costs, including steam extraction from the existing steam turbine, additional absorber packing for improved CO_2 removal, and higher exchanger area to reduce natural gas consumption.

available reports/technical papers/presentations

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Front-End Engineering Design of Linde-BASF Advanced Post-Combustion CO_2 Capture Technology at a Southern Company Natural Gas-Fired Power Plant

primary project goal

Southern Company Services Inc. conducted a front-end engineering design (FEED) study for a carbon dioxide (CO_2) capture system based on Linde-BASF's aqueous amine solvent-based technology installed at an existing Southern Company natural gas-fired combined cycle (NGCC) power plant.

technical goals

- Select an NGCC generating plant as the host site for the FEED study based on a set of defined criteria (performance of the gas turbines, availability of space to house a carbon capture system, availability of utilities to support the system, suitability of the surrounding geology for enhanced oil recovery [EOR] or storage).
- Produce a design basis for the carbon capture system based on the specific site requirements, including flue gas composition, environmental requirements, and requirements for modularization.
- Complete a conceptual design package for the process area of the post-combustion capture plant and assess the logistics for solvent delivery required for a commercial-scale carbon capture plant.
- Complete design packages for mechanical, electrical, structural, instrumentation and control, and facilities engineering and assess the cost and logistics for constructability and site security.
- Utilize the cost and schedule estimates of equipment vendors and contractors to derive a total project cost and schedule estimate within ±15% error.

technical content

Linde and BASF have jointly developed, optimized, and tested an advanced post-combustion CO_2 capture technology since 2007. The Linde-BASF technology for capturing CO_2 from flue gas using the BASF OASE® blue solvent is a mature technology that has been tested in two pilot plants with different flue gas sources, covering a wide variety of flue gas compositions and impurities. The Linde-BASF aqueous amine solvent-based post-combustion CO_2 capture technology provides a solution for key challenges encountered by solvent-based carbon capture

program area:

Point Source Carbon Capture

ending scale:

FEED

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

Linde-BASF Amine Solvent-Based Technology Retrofit to NGCC Plant

participant:

Southern Company Services Inc.

project number:

FE0031847

predecessor projects:

N/A

NETL project manager:

Andrew O'Palko
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principal investigator:

Landon Lunsford
Southern Company
LDLUNSFO@southernco.com

partners:

Linde Gas North America LLC; BASF; Linde Engineering Dresden

start date:

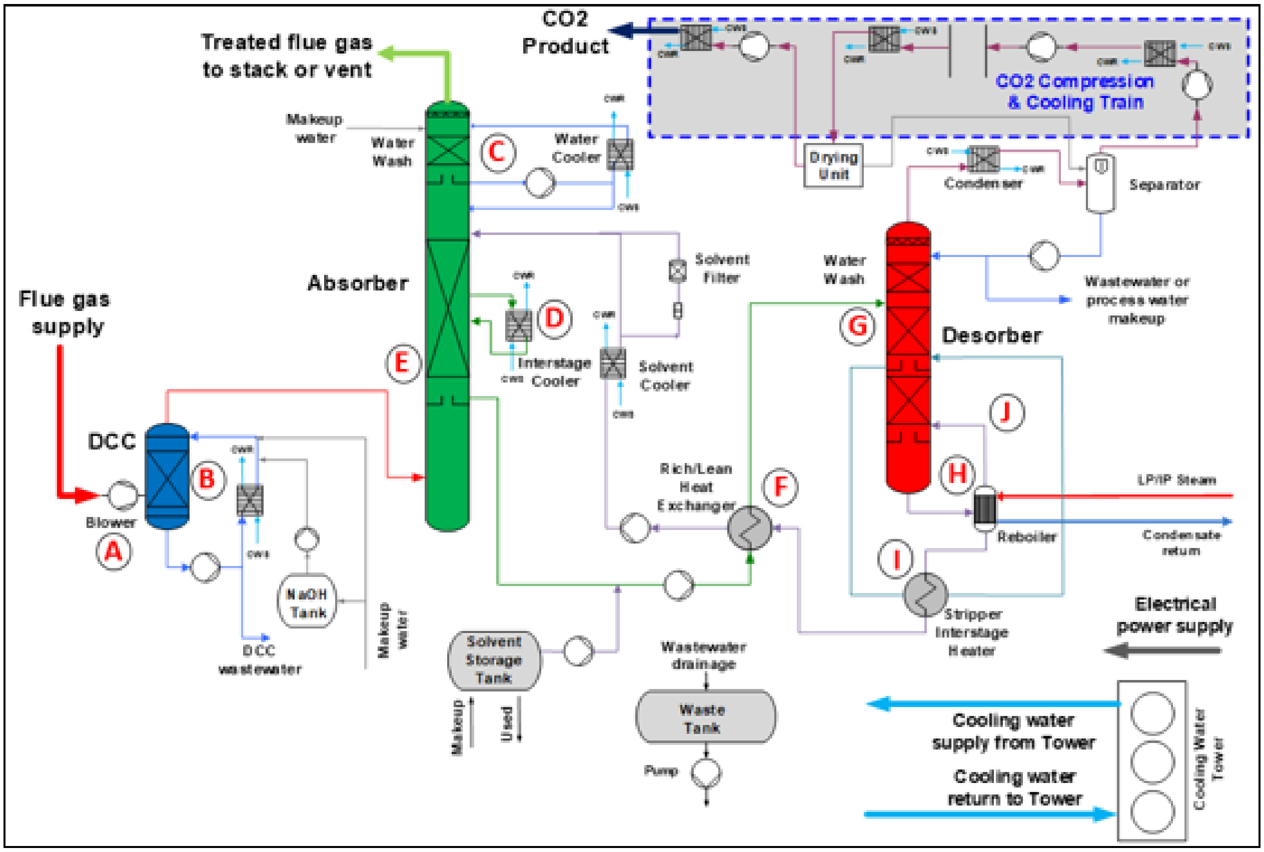
01.29.2020

percent complete:

100%

technologies, which include relatively high capital costs, significant parasitic energy requirements, and solvent stability and degradation issues.

The technology is based on a typical lean-rich solvent absorption/regeneration cycle for CO_2 capture but leverages several key innovative features for both solvent and process optimization to reduce the cost of CO_2 capture from NGCC plants. The optimized properties of the OASE® blue solvent led to capital and operating cost reduction due to efficient CO_2 capture from low pressure sources through favorable reaction kinetics and reduced reboiler steam energy consumption; better stability than monoethanolamine (MEA); and a lower solvent circulation rate. In addition to advances in solvent design, Linde has achieved significant improvements in process design, as outlined in Figure 1.



A. Flue gas blower provides sufficient pressure to overcome pressure drop across the direct contact cooler (DCC)/pre-scrubber and absorber. The blower location can be adjusted to minimize cost based on arrangement of equipment and piping at the NGCC site.
B. Integrated DCC/pre-scrubber to reduce sulfur oxides (SO_X) content below 5 parts per million (ppm) and simultaneously cool the flue gas stream to ~35–40°C.
C. Innovative and patented water wash section at the top of the column to reduce amine losses, even in the presence of aerosols. Dry bed configuration helps mitigate aerosol-driven amine losses.
D. A gravity-driven inter-stage cooler for the absorber that eliminates the need for a pump and related controls.
E. High-capacity structured packing reduces the absorber diameter, thereby enabling a larger single-train plant construction and greatly reduced capital costs.
F. Solvent-based heat exchanger designed to operate over a wide range of temperature approaches, which provides the opportunity to optimize the performance and capital cost trade-off.
G. Regenerator designed for operation at pressures up to 3.4 bara significantly reduces CO_2 compression energy and eliminates the bulky first stage of the CO_2 compressor, resulting in capital cost savings.
H. Innovative plate and frame design of the reboiler minimizes thermal degradation of solvent and provides for a lower solvent inventory and faster dynamics to respond to flue gas load and composition changes.
I. Stripper Inter-Stage Heater (SIH) enhances energy-efficient CO_2 stripping from the solvent by recovering heat from the lean solvent to provide intermediate reboil, thereby reducing energy consumption of solvent regeneration.
J. Variations of the stripper-reboiler flashing configuration, which are being evaluated to further minimize solvent regeneration energy.

Figure 1: Process flow diagram of Linde-BASF OASE® blue post-combustion CO_2 capture technology.

A development timeline of the Linde-BASF technology is shown in Figure 2. Previous testing of a 0.45-MWe dry lignite-fired pilot plant incorporating the Linde-BASF technology has shown that the OASE® blue solvent is more stable than MEA after 2,500 hours of testing. The process was also previously tested at 1.5-MWe-scale at the National Carbon Capture Center (NCCC) under the U.S. Department of Energy (DOE)-funded project DE-FE0007453, validating solvent stability and revealing a cyclic capacity 20% higher than MEA and regenerator steam consumption 25% lower than MEA. These results confirmed the ability of this technology to be cost-effective, energy efficient, and compact.

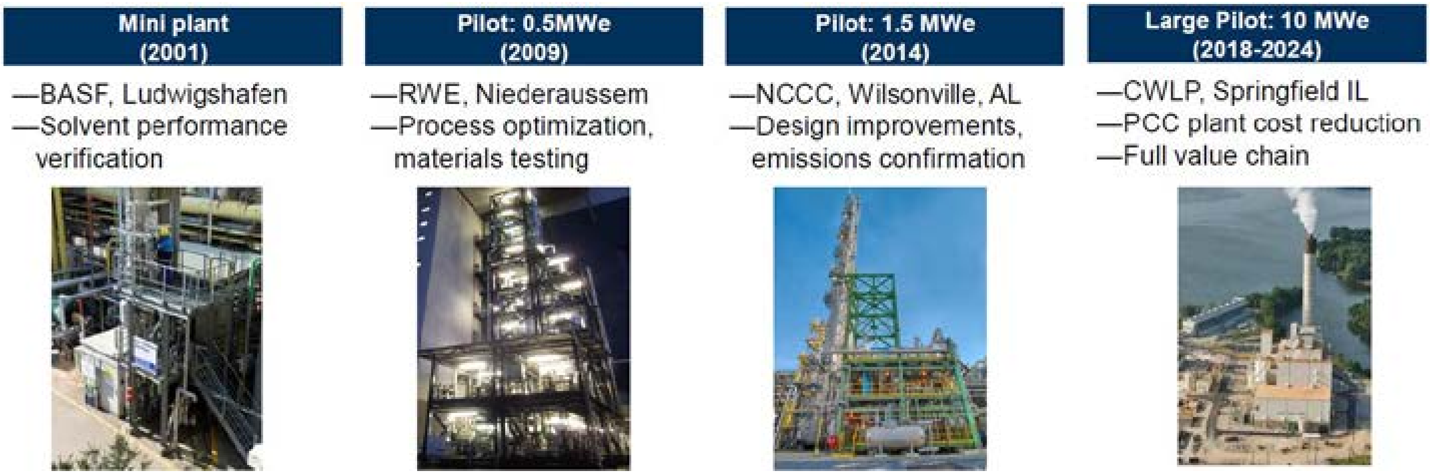


Figure 2: Linde-BASF post-combustion CO_2 capture technology development.

Milestones achieved thus far for the Linde-BASF post-combustion CO_2 capture technology applied to NGCC flue gas conditions are outlined in Figure 3. These include testing on an NGCC flue gas composition at the 0.45-MWe pilot-scale in Niederaussem, Germany; completion of a detailed FEED study on CO_2 capture from a 510-MWe NGCC power plant in 2011; and completion of a pre-FEED study for CO_2 capture at a 480-MWe NGCC power plant in 2018.

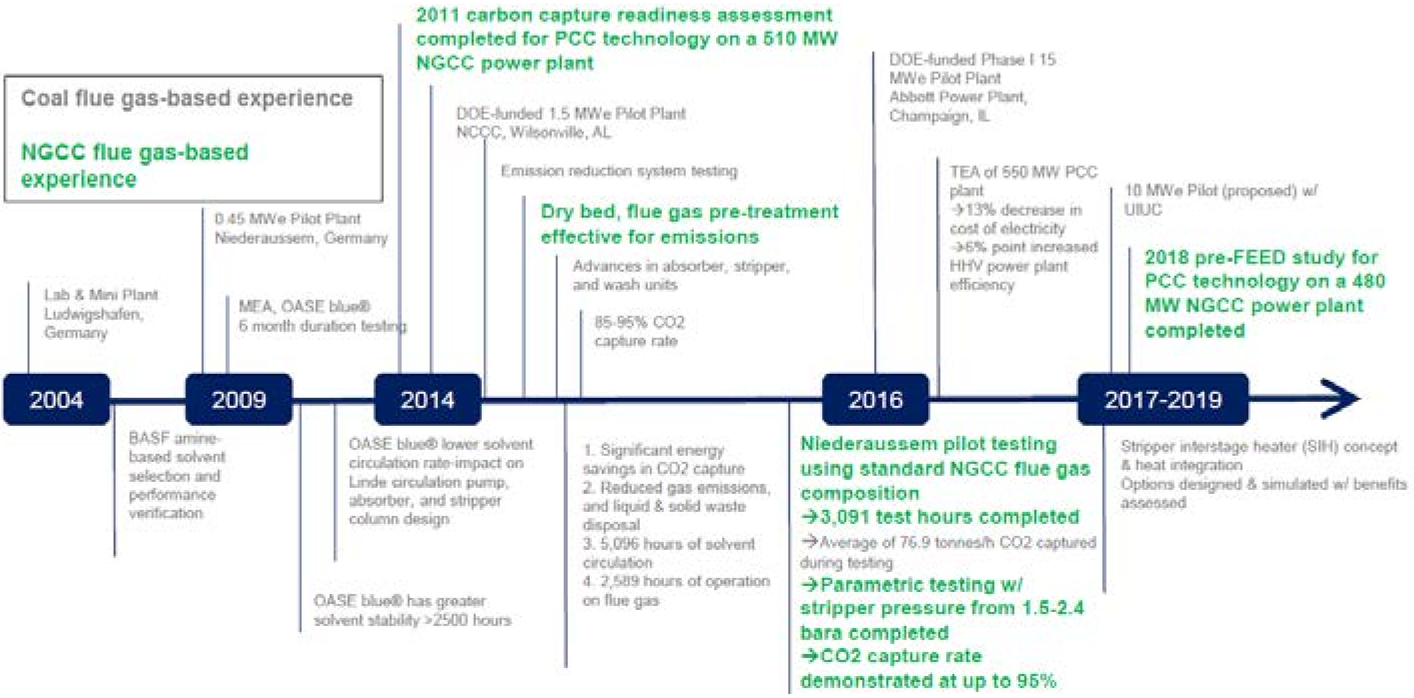


Figure 3: Milestones achieved by Linde-BASF post-combustion CO_2 capture technology.

The general approach for the FEED follows the methodology described in Figure 4, and the operating parameters of the system are shown in Table 1.

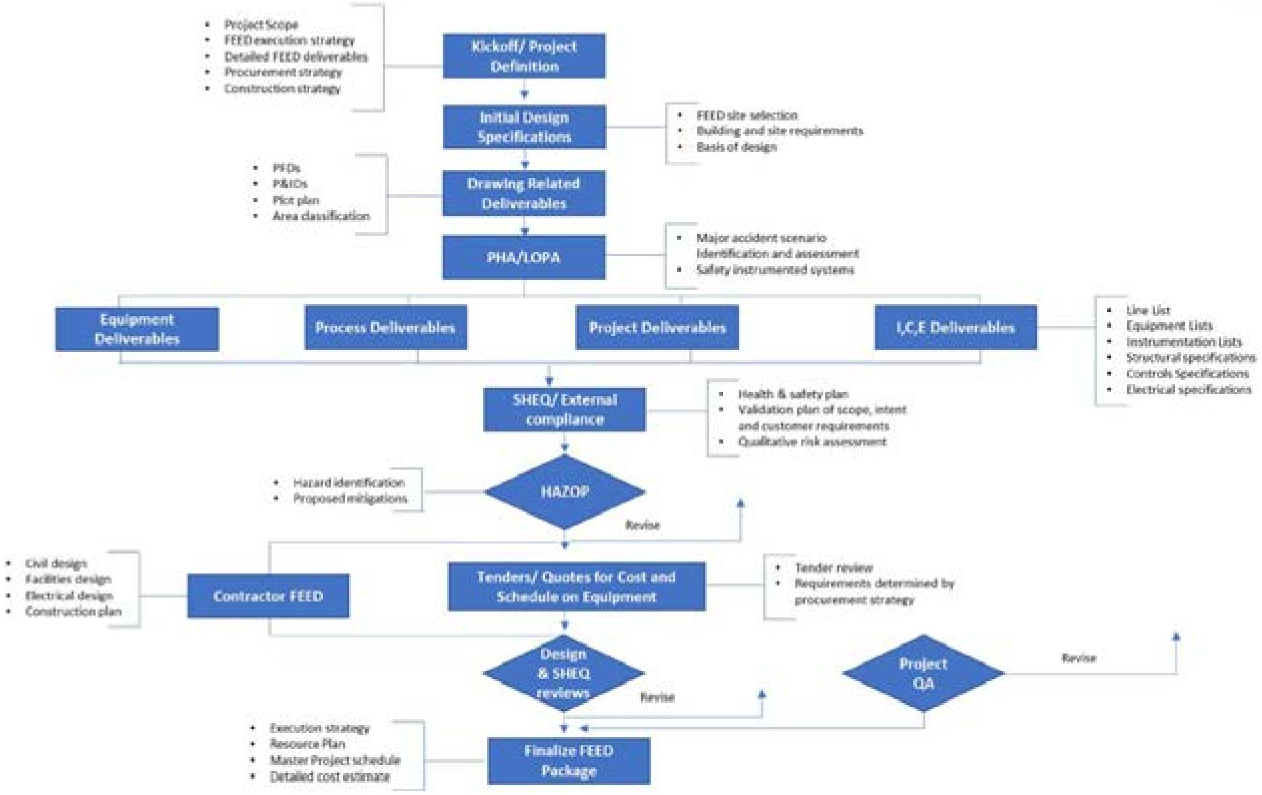


Figure 4: FEED approach.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Design Value
Molecular Weight	mol^{-1}	proprietary
Normal Boiling Point	°C	proprietary
Normal Freezing Point	°C	-5 to 25
Vapor Pressure @ 15°C	bar(a)	proprietary
Manufacturing Cost for Solvent	$/kg	proprietary
Working Solution		
Concentration	kg/kg	proprietary
Specific Gravity (15°C/15°C)	-	1.0 – 1.2
Specific Heat Capacity @ STP	kJ/kg-K	proprietary
Viscosity @ STP	cP	1.5 – 7.0
Absorption		
Pressure	bar(a)	0.9 – 1.1
Temperature	°C	30 – 60
Equilibrium CO_2 Loading	mol/mol	proprietary
Heat of Absorption	kJ/mol CO_2	proprietary
Solution Viscosity	cP	1.5 – 7

Desorption		
Pressure	bar(a)	1.6 – 3.4
Temperature	°C	125 – 140
Equilibrium CO_2 Loading	mol/mol	proprietary
Heat of Desorption	kJ/mol CO_2	proprietary
Module Design		
Flue Gas Flowrate	kg/hr	Designed for >375 MWe slipstream
CO_2 Recovery, Purity, and Pressure	% / % / bar	90%, >99.9% (dry), 3.4 bar(a)
Absorber Pressure Drop	bar	proprietary
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	proprietary

Process designs that reduce the energy required for solvent regeneration through heat recovery integration are being optimized as part of the FEED study. Waste heat sources at the NGCC-fired host site can be leveraged to reduce the parasitic steam consumption of the CO_2 capture system and reduce the negative impact of the capture plant on power plant steam cycle efficiency or net electrical power generation. Sources include: (1) supplemental low- to medium-pressure steam from the power plant steam cycle in the range of 5–6 bara not currently used for electricity production can be redirected for use in the post-combustion CO_2 capture plant reboiler; (2) waste heat recovered from the hot flue gas upstream of the CO_2 capture plant after the heat recovery steam generator (HRSG) can be used to pre-heat CO_2-rich solvent entering the stripper column; or (3) external steam generation can reduce the steam input from the power plant. In addition, process optimization within the post-combustion CO_2 capture plant itself, including lean vapor compression (LVC) involving flashing of the CO_2-lean solution at the bottom of the stripper and redirecting the vapor after compression back to the bottom of the stripper, is an option that can substantially reduce the reboiler steam consumption for NGCC-fired CO_2 capture down to 2.4 gigajoules (GJ)/tonne CO_2 based on past FEED studies conducted for large Linde-BASF post-combustion CO_2 capture plants.

Linde has conducted extensive research on the management of flue gas aerosol particles that contribute to amine losses through the treated gas exiting the absorber, including both literature studies and aerosol measurements taken during testing of the Linde-BASF post-combustion CO_2 capture technology at NCCC. Experimentally, Linde has determined that if aerosol concentrations are less than 10^7 particles/cm^3 for particles ranging from 70–200 nanometer (nm) in diameter, there is no need for pre-treatment beyond a direct contact cooler (DCC)/pre-scrubber and dry bed wash section in the absorber to manage the aerosols. Aerosol concentrations are expected to be much lower for NGCC-derived flue gas than for coal-fired flue gas; therefore, typical emissions control measures have been integrated into the Linde-BASF CO_2 capture plant design.

Two Southern Company host sites are being evaluated in the first phase of the FEED study: Alabama Power Company's Plant Barry (Units 6 and 7), located in Bucks, Alabama, and Mississippi Power Company's Plant Daniel (Units 3 and 4), located in Moss Point, Mississippi. Each of the gas-fired combined cycle units (Units 6 and 7 at Plant Barry and Units 3 and 4 at Plant Daniel) produce a nominal 525 MWe (net). For either host site, equipment and operating modifications in the combined cycle to increase CO_2 concentration in the flue gas is a primary focus of the FEED study to minimize carbon capture costs. Cooling water capacity at both combined cycle plants is limited; therefore, evaluations of new cooling tower capacity versus air cooling are being performed in the FEED. For each site, steam supply to the carbon capture process may be available via extraction from the steam turbine, but the overall impact on the HRSG, steam cycle, and steam turbine is being evaluated during the FEED to determine the cost impact of extraction versus alternate steam production from a package boiler or cogeneration unit.

The FEED will provide a financial indicator of the costs of installation at an actual domestic NGCC power plant site and potentially illustrates that this capture system can be employed at operating commercial coal-fired power plants. The commercial FEED will provide a realistic framework for NGCC power plants to be built CO_2 capture-ready or to retrofit existing NGCC plants with an economical CO_2 capture system.

Definitions:

Bar(a) – Unit used to indicate absolute pressure, where the reference pressure is absolute zero (i.e., not taking into account atmospheric pressure).

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the HRSG unit (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.8	231	4	9	74	12	1	0.08	2

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Carbon dioxide in the flue gas chemically binds to the OASE® blue aqueous amine-based solvent via an exothermic absorption step and this chemical bond is broken in the endothermic desorption step via heat provided by steam in the reboiler of the regenerator column, generating pure CO_2.

Solvent Contaminant Resistance – The OASE® blue solvent is highly resistant against many contaminants in the flue gas, as shown in both parametric and long-term continuous tests (see Electric Power Research Institute [EPRI] report[1] for additional information).

Solvent Foaming Tendency – During the pilot plant operations, although anti-foaming injection was included in the design, its use was not found necessary.

Flue Gas Pretreatment Requirements – The pretreatment requirement includes reducing sulfur oxide (SO_X) in the flue gas to 2 to 5 parts per million (ppm) in order to limit solvent degradation and is implemented in a DCC in conjunction with flue gas cooling, typically by adding appropriate amount of sodium hydroxide corresponding to the SO_X present in the flue gas.

Solvent Makeup Requirements – The OASE® blue solvent makeup rate is determined by the sum of the amine losses in the treated gas leaving the absorber column and the rate of solvent degradation during operation over time. Low makeup rates were observed during long-term testing well below an operationally manageable threshold. Low solvent makeup is expected at scale when processing flue gas from power plants with a baghouse filter for particulate removal or with upstream flue gas pretreatment for aerosol mitigation.

Waste Streams Generated – The main waste liquid stream is from the DCC where SO_X and nitrogen oxide (NO_X) are removed; this stream is typically handled in the power plant wastewater treatment facility. A small amount of solid waste is removed using an activated carbon filter and mechanical cartridge filter that are replaced at regular intervals. Since the solvent degradation observed in the pilot testing is small, no solvent reclamation unit is envisioned in the large scale.

Process Design Concept – Flowsheet/process flow diagram shown in Figure 1.

Proposed Module Design – Free standing absorber and stripper columns will be tied into a modularized process skid. There will be associated containers for electrical equipment, analytical equipment, and process control.

technology advantages

- Exhibits a lower solvent circulation rate, reduced reboiler steam energy consumption compared to process using MEA solvent, reduced absorber diameter due to high efficiency packing, and lower downstream CO_2 compression cost due to the ability to operate at higher desorber pressures.
- BASF is the producer of the OASE® blue solvent and the owner of the solvent technology. A major global player in the chemical industry, BASF has the capabilities to reliably produce and supply the OASE® blue solvent in sufficient volumes needed for commercialization, thereby enabling application at scale by avoiding issues related to solvent manufacturing for large-scale commercial plants.
- The Southern Company-Linde-BASF partnership combines the necessary capabilities and experience to deliver the complete CO_2 capture technology value chain from solvent production to full-scale CO_2 capture plant engineering, procurement, and construction (EPC); commercial deployment; and long-term, continuous operations.

R&D challenges

- Carryover and emissions of amines and amine degradation products.
- Handling large volumes of process condensate from DCC.
- Disposal of spent activated carbon and filters can generate solid waste management issues.
- Designing for low liquid/gas ratios caused by lower CO_2 concentration in natural gas flue gas may result in below-target CO_2 capture rate and/or vapor and liquid maldistribution.
- Equipment scale-up associated with large vapor flows due to low CO_2 concentration.
- Engineering the liquid hydraulics and gas distribution in large manifolds needed for multiple absorbers.

- Integration of post-combustion CO_2 capture plant with host site.

status

The project was completed on June 30, 2022. The FEED results determined a total as-spent capital cost (excluding financing costs) of $752.2 million USD. The project team selected Plant Daniel (525 MWe) in Mississippi as the host site for the FEED study employing the Linde-BASF CO_2 capture technology. The basic design and engineering reports were completed with heat and material balances, process flow diagrams, preliminary process and instrumentation diagrams, and a steam source study. In addition, the final report included a hazard and operability study (HAZOP) study as part of the design package.

available reports/technical papers/presentations

Lunsford, L.; Krishnamurthy, K.; Jarmus, D.; Nichols, J.; Caroll, J.; Palmer, A.; Brown, C.; Powell, S.; Chu, B., 2022, "Front End Engineering Design of Linde-BASF Advanced Post-Combustion CO_2 Capture Technology at a Southern Company Natural Gas-Fired Power Plant." *Final Technical Report.* Southern Company Services, Inc. Birmingham, AL. Report No. DOE-SCS-31847. *https://www.osti.gov/biblio/1890156*.

Lunsford, L., 2021, "Front End Engineering Design of Linde-BASF Advanced Post-Combustion CO_2 Capture Technology at a Southern Company Natural Gas-Fired Power Plant," presented at the 2021 NETL Carbon Management and Oil and Gas Research Project Review Meeting - Integrated CCUS Projects and FEED Studies. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CCUS_Lunsford.pdf*.

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Moser, P., Schmidt, S., Stahl, K., Vorberg, G., Lozano, G., Stoffregen, T., Rösler, F., 2014, "Demonstrating Emission Reduction – Results from the Post-combustion Capture Pilot Plant at Niederaussem," *Proceedings of the 12th Annual International Conference on Greenhouse Gas Control Technologies*. Energy Procedia. Issue 63, pp. 902-910. *https://www.sciencedirect.com/science/article/pii/S1876610214019158*.

Moser, P., Schmidt, S., Wallus, S., Ginsberg, T., Sieder, G., Clausen, I., Garcia Palacios, J., Stoffregen, T., Mihailowitsch, D., 2013, "Enhancement and Long-Term Testing of Optimised Post-Combustion Capture Technology – Results of the Second Phase of the Testing Programme at the Niederaussem Pilot Plant," *Proceedings of the 11th Annual International*

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references

[1] BASF-Linde Post Combustion Carbon Capture Pilot Plant at the National Carbon Capture Center, 2016 Test Campaign Results, EPRI, February 2017.

Front-End Engineering Design Study for Retrofit Post-Combustion Carbon Capture on a Natural Gas Combined Cycle Power Plant

primary project goal

Electric Power Research Institute (EPRI) and its partners Fluor Corporation and California Resources Corporation (CRC) conducted a front-end engineering design (FEED) study to determine the technical and economic feasibility of a retrofit, post-combustion carbon capture technology on a commercially operating, natural gas-fired combined cycle (NGCC) power plant.

technical goals

- Conduct a FEED study for 75% overall capture (90% capture on 83% slipstream) at CRC's 550-megawatt-electric (MWe) NGCC Elk Hills Power Plant (EHPP) using Fluor's proprietary Econamine FG Plus^{SM} (EFG+) aqueous amine technology.
- Capture 4,000 tonnes of carbon dioxide (CO_2) per day that will be used by CRC for enhanced oil recovery (EOR) in fields adjacent to the power plant.

technical content

The FEED study examined the cost and engineering requirements for installing a plant to capture CO_2 produced by the 550-MWe NGCC unit located in the Elk Hills Oil Field in Kern County, California. Fluor is the design engineering contractor and Fluor's EFG+ technology is used for the carbon capture system design. CRC is the owner and operator of the host site, EHPP. Fluor's EFG+ technology is a post-combustion CO_2 capture technology with proven process for removal of CO_2 from flue gases, with the CO_2 product used for EOR and other applications.

The FEED study deliverables included a design basis, process flow diagrams, piping and instrument diagrams, equipment datasheets, a plot plan, bulk material takeoffs, and a capital cost estimate. For the design basis of the FEED study, the details include: consolidated historic performance and run history of the power plant; an evaluation of various operating scenarios and conditions; the results from flue gas testing and validation studies of solvent performance through FEED; historic construction details from surrounding facilities to incorporate site requirements; review and optimization of energy use and waste streams; and an evaluation of construction practices and contracting strategies to optimize the cost, schedule, and risks. A block flow schematic of the capture system is shown in Figure 1.

program area:
Point Source Carbon Capture

ending scale:
FEED

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
FEED Study to Retrofit NGCC Plant with Econamine FG Plus^{SM} Capture Technology

participant:
Electric Power Research Institute, Inc.

project number:
FE0031842

NETL project manager:
Carl Laird
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principal investigator:
Abhoyjit Bhown
EPRI
abhown@epri.com

partners:
Fluor Corporation; California Resources Corporation

start date:
10.01.2019

percent complete:
100%

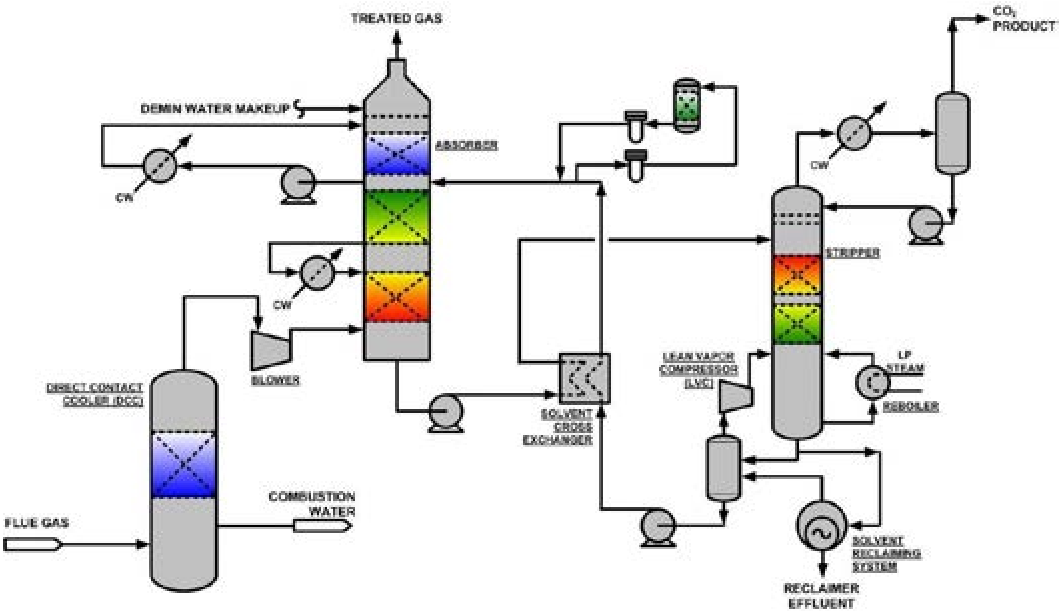

Figure 1: Simplified schematic of Fluor Corporation's Econamine FG Plus™ CO_2 capture process.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the NGCC unit (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.5	205	4.54	9.30	72.95	12.34	0.88	0.7	1.7

Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The absorption of CO_2 is by chemical reaction.

Solvent Contaminant Resistance – The solvent has high resistance to contaminants in the flue gas due to the solvent maintenance system's ability to maintain the solvent in pristine condition.

Solvent Foaming Tendency – None.

Flue Gas Pretreatment Requirements – None.

Solvent Makeup Requirements – 0.42 kg/tonne CO_2.

Waste Streams Generated – Solvent maintenance system waste.

Process Design Concept – Flowsheet/block flow diagram shown in Figure 1.

Proposed Module Design – To be prepared after logistics/route study.

technology advantages

- FEED studies for carbon capture systems at actual sites such as this will provide the U.S. Department of Energy (DOE) with a more detailed understanding of carbon capture costs in a commercial application, thereby enabling DOE to better design its research and development (R&D) program to reduce those costs for similar carbon capture technologies being developed in its R&D portfolio.

- This FEED study could lead to the world's first commercial deployment of carbon capture on a natural gas-fired power plant and could be duplicated at other power plants across the world.
- Fluor's latest version of its EFG+ technology has several key features, including enhanced solvent formulation that has a high resistance to degradation, reduced amine circulation rate, a solvent maintenance system that keeps the solvent in pristine condition, low waste production, very low absorber vent emissions, and load-following capability. These features are proven on both gas turbine exhaust and coal flue gas. The enhanced dual-cell column and absorber design enables a large flue gas throughput, which reduces capital costs.

R&D challenges

- Targeting not just operating expenses, but also capital expenses in this FEED study to minimize the overall cost of CO_2 capture via utilization of various technology and process synergies.
- Optimizing cooling water usage as California and the Bakersfield area's ongoing challenge of water availability for power production.

status

The project was completed on February 28, 2022. The final FEED study package was completed and submitted to the National Energy Technology Laboratory (NETL). Design activities completed include process modeling, heat and material balances, process and utility flow diagrams, piping and instrumentation diagrams, equipment sizing and selection, process hazard analysis, cause and effect diagrams, plot plan, electrical load list, 3D model development, and capital and operating cost estimates.

available reports/technical papers/presentations

Bhown, A.S., 2022, "Front-End Engineering Design Study for Retrofit Post-Combustion Carbon Capture on a Natural Gas Combined Cycle Power Plant." *Final Technical Report.* Electric Power Research Institute. Report No. DOE-EPRI-31842. *https://www.osti.gov/biblio/1867616*.

Bhown, A.S., 2021, "Front-End Engineering Design Study for Retrofit Post-Combustion Carbon Capture on a Natural Gas Combined Cycle Power Plant," Proceedings of the 2021 NETL Carbon Management and Oil and Gas Research Project Review Meeting - Integrated CCUS Projects and FEED Studies. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CCUS_Bhown.pdf*.

Bhown, A.S., 2020, "Front-End Engineering Design Study for Retrofit Post-Combustion Carbon Capture on a Natural Gas Combined Cycle Power Plant," Proceedings of the 2020 NETL Project Review Meeting - CCUS Integrated Projects. *https://netl.doe.gov/sites/default/files/netl-file/20CCUS_Bhown.pdf*.

Bhown, A.S., 2019, "Front-End Engineering Design Study for Retrofit Post-Combustion Carbon Capture on a Natural Gas Combined Cycle Power Plant," DOE Project Kickoff Meeting. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10875&filename=Front-End+Engineering+Design+Study+for+Retrofit+Post-Combustion+Carbon+Capture+on+a+Natural+Gas+Combined+Cycle+Power+Plant.pdf*.

Front-End Engineering Design Study for a Carbon Capture Plant Retrofit to a Natural Gas-Fired Gas Turbine Combined Cycle Power Plant

primary project goal

Bechtel National Inc. has performed a front-end engineering design (FEED) study for a carbon capture and compression plant retrofit to an existing natural gas-fired combined cycle (NGCC) power plant located in Texas. The capture plant is based on conventional technology comprising a non-proprietary aqueous solvent, monoethanolamine (MEA), an absorber-stripper cycle, and multi-stage centrifugal compressors.

technical goals

- Develop a project design basis to provide general project requirements that apply to the specific plant site, ambient conditions, fuel feedstock and flue gas characteristics, environmental requirements, and modularization design requirements.
- Develop process engineering documents for constructing the carbon capture system, including block flow diagrams, heat and mass balance diagrams, process flow diagrams for major components, piping and instrumentation diagrams, and a water balance diagram.
- Conduct a preliminary hazard and operability (HAZOP) study and produce a report to document the results.
- Develop civil, structural, mechanical, electrical, and control systems engineering design packages.
- Develop a layout and design package that includes process plant arrangement drawings and piping and instrumentation diagrams.
- Summarize expected emissions and waste streams.
- Review various contracting and purchasing options for procuring a new process system and perform a constructability review to identify construction access, lay-down areas, and sequencing of construction work.
- Develop an overall project capital cost estimate within a ±15% accuracy.
- Prepare a final FEED study package that is available for public use.

technical content

Bechtel executed a FEED study on retrofitting an existing NGCC power plant with an amine-based post-combustion carbon capture plant. The prospective end use for the captured carbon dioxide (CO_2) is enhanced oil recovery (EOR). Bechtel has

program area:

Point Source Carbon Capture

ending scale:

FEED

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

Amine-Based Solvent Technology Retrofit to NGCC Plant

participant:

Bechtel National Inc.

project number:

FE0031848

predecessor projects:

N/A

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partners:

Electric Power Research Institute Inc.; Nexant

start date:

10.01.2019

percent complete:

100%

developed a technology readiness level (TRL) 9 carbon capture, utilization, and storage (CCUS) concept for retrofitting an existing NGCC with mature and field-proven technology and equipment. Figure 1 illustrates a simplified process flow diagram of a conventional absorber-stripper scrubbing system with a non-proprietary solvent such as MEA.

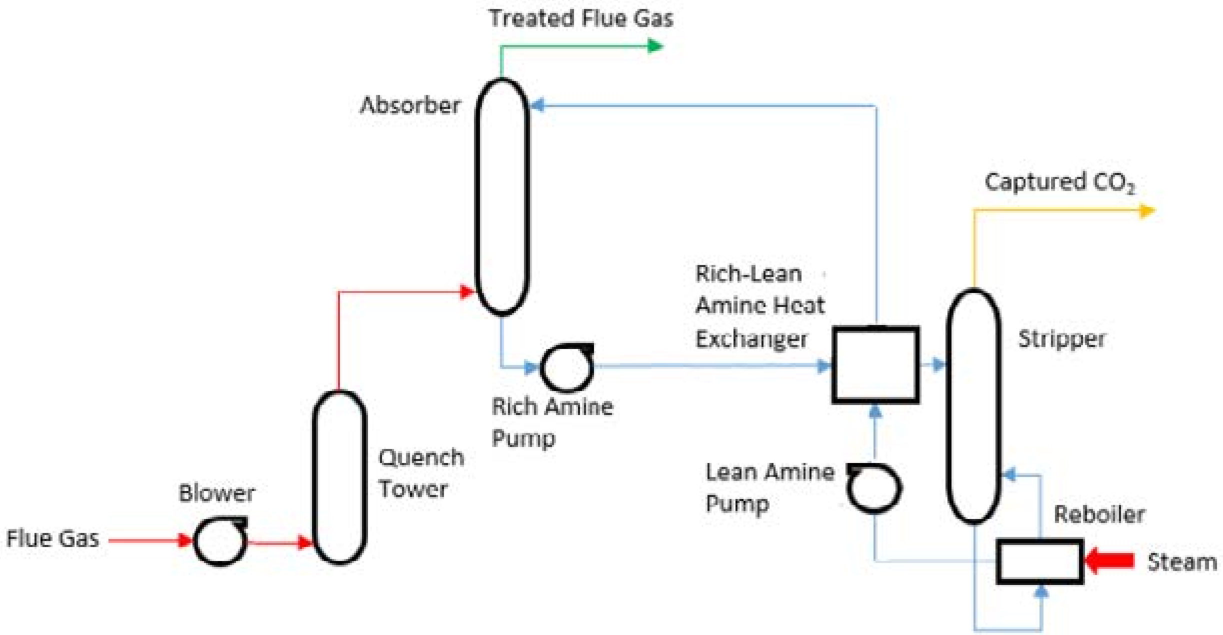

Figure 1: Generic simplified flowsheet for amine-based CO_2 capture from flue gas.

Bechtel has applied an "open access" and "open technology" methodology to the process and physical design of the facilities and the solvent used in the technology. An "open access" technology approach denotes that the owner/operators of a post-combustion carbon capture plant are in full control of the technology used in the plant. The post-combustion carbon capture hardware can be procured by competitive tendering against a non-proprietary specification, similar to conventional power plants. This allows the owner/operators to specify the post-combustion carbon capture plant hardware and solvent selection based on the latest published technology and operating experience. "Open access" technology utilizes a generic, non-proprietary solvent that is readily purchased on the open market from chemical manufacturers at a relatively low cost. These features facilitate lower capital and operating expenses and avoid royalty payments and technical restrictions associated with the use of proprietary system designs and solvent selection. The operating parameters of the system are shown in Table 1.

The host site selected for the FEED study is the Sherman Generating Station, a 2x2x1 NGCC located in Sherman, Texas. The 758-megawatt-electric (MWe) power plant built by Bechtel is powered by two Siemens F class gas turbines. The selection of the site has several advantages, including:

- The NGCC plant was built by Bechtel; therefore, key project personnel have access to all design documents and are familiar with the facility.
- The plant includes F class gas turbines, a state-of-the-art technology.
- The location of the host plant is near oil-bearing formations favorable for EOR operation.

Lessons learned and experience gained from earlier FEED and FEED verification studies performed by Bechtel were used as a basis for this FEED study. Bechtel prepared a FEED verification in 2015 under the direction of Shell for a proposed carbon capture retrofit to gas turbine Unit 13 at the Peterhead Power Station in Scotland. In 2009, Bechtel performed a FEED study for a CO_2 capture and compression facility designed to capture 85% of the CO_2 emissions from a 420-MWe gas-fired power plant in Norway. Both a proprietary solvent and MEA were used as bases of design. The plants involved in both FEED studies employ Siemens gas turbines, similar to the gas turbines in the Sherman facility; thus, much of the engineering work has already been completed by Bechtel for flue gas conditions very similar to the host site in Texas. Bechtel's FEED report is based on these past design reports.

The major deliverable of this completed FEED study is a design package that includes the following topic areas: flue gas blower and quench, CO_2 absorption, semi-lean amine system, CO_2 stripping and heat integration, CO_2 compression and drying, CO_2 pumping and dense phase transfer, amine reclaiming, and amine storage. It was found in this case study that the baseline CO_2 capture cost is \$114.50/tCO_2 (when including both annualized capital and annual operations/maintenance), that the energy penalty on the powerplant is 67.3 MW, that the average forgone electricity revenue is equivalent to \$13/tCO_2 captured, and that a pilot testing program should be used to resolve design uncertainties (such as amine degradation rates). A summary of the economics are given in Table 2.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Design Value
Molecular Weight	mol^{-1}	61.08
Normal Boiling Point	°C	170
Normal Freezing Point	°C	10.3
Vapor Pressure @ 15°C	bar	<1
Manufacturing Cost for Solvent	\$/kg	1 – 2
Working Solution		
Concentration	kg/kg	35
Specific Gravity (15°C/15°C)	—	1.02
Specific Heat Capacity @ STP	kJ/kg-K	3.6
Viscosity @ STP	cP	4
Absorption		
Pressure	bar	1.089
Temperature	°C	53.5
Equilibrium CO_2 Loading	mol/mol	0.4 – 0.49
Heat of Absorption	kJ/mol CO_2	TBD
Solution Viscosity	cP	2.56
Desorption		
Pressure	bar	2.31
Temperature	°C	130.8
Equilibrium CO_2 Loading	mol/mol	0.22 – 0.25
Heat of Desorption	kJ/mol CO_2	TBD
Module Design		
Flue Gas Flowrate	kg/hr	2.53×10^6
CO_2 Recovery, Purity, and Pressure	% / % / bar	80-90 / 99.0+ / 200
Absorber Pressure Drop	bar	0.076
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	TBD

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.038 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical natural gas fired combined cycle power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 3.82 %. Therefore, the partial pressure of CO_2 is roughly 0.0382 atm or 0.0387 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the heat recovery steam generator (HRSG) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.5	194	3.82	7.74	74.78	12.81	0.85	-	2

Parameter Descriptions:

Flue Gas Pretreatment Requirements – Flue gas is cooled to approximately 50°C before entering absorber towers through a fogging system that reduces temperature and saturates flue gas with water.

Solvent Makeup Requirements – Detailed in the FEED report.

Chemical/Physical Solvent Mechanism – The chemical/physical solvent mechanism is primarily controlled by the solubility and alkalinity characteristics of the amine. MEA is fully water soluble and exhibits high alkalinity. MEA's low molecular weight permits higher solution capacity and its low boiling point allows higher recovery during reclamation of contaminated solution. Carbon dioxide solubility in MEA solutions is relatively high. Regeneration of MEA solutions is accomplished at reasonable temperatures with moderate heat input. Further discussion is included in the FEED report.

Solvent Contaminant Resistance – Detailed in the FEED report.

Solvent Foaming Tendency – Detailed in the FEED report.

Waste Streams Generated – MEA and ammonia emissions from the absorber are reasonable and are defined in the FEED report. Liquid and solid wastes from solvent maintenance and reclaiming is defined in the FEED report.

Process Design Concept – The process overview under normal operation consists of the following systems:

- Flue gas diversion—The flue gas is directed from the existing stack to the plant.
- Flue gas cooling—The flue gas as supplied is too hot to process efficiently in the absorber and is cooled to its saturation temperature before entering the absorber.
- CO_2 absorption—Parallel absorbers use an amine solution to remove the CO_2 from the flue gas.
- Heat integration—Heat is recovered from internal streams to enhance plant energy efficiency.
- CO_2 stripping—The amine is regenerated for reuse by liberating the CO_2 from the amine solution.
- CO_2 compression and drying—The CO_2 is compressed, dried, further compressed, and liquefied to meet the CO_2 specifications.
- Amine reclamation—Heat stable salts (HSS) and degradation/oxidation products are removed from the amine solution.
- Amine storage—Fresh amine and lean amine are stored and injected into the absorption system to maintain the amine solution concentration.

Proposed Module Design – Detailed in the FEED report.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	114.50	114.50
Cost of Carbon Avoided	\$/tonne CO_2	136.50	136.50
Capital Expenditures	\$/MWhr	32.43	32.43
Operating Expenditures	\$/MWhr	11.50	11.50
Cost of Electricity	\$/MWhr	63.93	63.93[1]

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions

Calculations Basis – Data are based on Panda Power's Sherman Natural Gas-Fired Combined Cycle Power Plant located in Texas.

Scale of Validation of Technology Used in TEA: This study used the ProMax® process simulation software to develop the mass and energy balances for the design energy case. The Carbon Capture Simulation Initiative (CCSI) Toolset (by the National Energy Technology Laboratory [NETL]) was also applied to compare results using the ASPEN Plus simulation package. Results from the two modelling tools were evaluated to identify uncertainties. Because of those modelling uncertainties, pilot plant testing was recommended before proceeding to full-scale plant design.

Costs were based on actual costs from quotes for full-scale facility and costs for construction.

MEA has been extensively piloted at the National Carbon Capture Center (NCCC) in Alabama and at Test Center Mongstad in Norway.

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[1] Assumed cost of electricity is \$20.00 per MWh without carbon capture.

Qualifying Information or Assumptions:

Capital cost estimate based on worldwide sourcing.

Costs are specific to the Sherman, Texas, site.

Estimate includes builders risk insurance and general liability.

Operating hours per year: 5,000.

Level of operation: 420 MW equivalent.

Average value of reduced electricity sales to the Electric Reliability Council of Texas (ERCOT): $25/MWhr.

Electricity sales reduction: 67.3 MW.

technology advantages

- Use of generic solvent avoids restrictions and costs associated with proprietary solvents.
- An "open access" and "open technology" approach can accelerate CCUS deployment and reduce the costs of CCUS by facilitating efficient know-how exchange and competition within the fleet of plants that may be built over the next five to 10 years.
- "Open access" and "open technology" full-scale plants can facilitate the progression of post-combustion capture systems currently at TRL 9 to achieve a commercial readiness index of 6 within 10 years or less.
- Bechtel has extensive experience in carbon capture studies, plus detailed design, construction, and operation of NGCC power plants and CO_2 capture plants, including involvement in several previous FEED studies on CO_2 capture retrofits to NGCC plants.

R&D challenges

- Steam extraction complexity.
- Confirmation of carbon capture simulation software accuracy for generic amine solutions at high solvent strengths.

status

The project was completed on January 31, 2022. The project team has developed final engineering documents that include block flow diagrams, process flow diagrams, heat and mass balances, water balance diagrams, piping and instrument diagrams, and summary equipment specifications. Engineering design packages were prepared for civil, structural, mechanical, electrical, automation, and environmental systems. The results showed an overall capital cost of $477 million USD for the retrofit, with a bassline cost of capture of $114.50 per tonne of CO_2.

available reports/technical papers/presentations

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Commercial-Scale Front-End Engineering Design Study for Membrane Technology and Research's Membrane Carbon Dioxide Capture Process

primary project goal

Membrane Technology and Research Inc. (MTR) conducted a front-end engineering design (FEED) study for a membrane-based carbon dioxide (CO_2) capture system installed at Basin Electric's 400-megawatt-electric (MWe) Dry Fork Station power plant in Gillette, Wyoming. The project builds on prior work in advancing MTR's membrane capture technology through small pilot testing and a pre-FEED study.

technical goals

- Complete FEED study of MTR capture process applied to the 400-MWe Dry Fork Station.
- Complete an environmental review of full-scale MTR membrane capture at Dry Fork Station.
- Provide a path to commercialization (detailed costs and construction plan) for a full-scale membrane capture plant based on actual equipment costs with a reliability of ±15%.

technical content

The project team performed a FEED study of MTR's membrane CO_2 capture technology applied at commercial-scale as the next step in the development of the process, after the successful completion of small pilot testing and execution of a full-scale pre-FEED study. The study included an estimate of the cost and performance of a first-of-its-kind commercial-scale membrane capture plant and a plan for its construction. The plant was designed to capture approximately 5,600 tonnes per day (TPD) of CO_2 (approximately 2.0 million tonnes/year of CO_2), representing 70% of the Dry Fork Station power plant's CO_2 emissions. The system incorporates the innovative high-performance Polaris™ membrane packaged in low-pressure-drop membrane modules. Earlier research has shown that the MTR process has the potential to capture CO_2 from coal-fired flue gas at the U.S. Department of Energy (DOE) capture cost target of less than $40/tonne CO_2.

A preliminary process flow diagram of the membrane capture process examined in the FEED study is shown in Figure 1.

program area:
Point Source Carbon Capture

ending scale:
FEED

application:
Post-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Polaris™ Polymeric Membrane-Based Process Retrofit to Coal Plant

participant:
Membrane Technology and Research Inc.

project number:
FE0031846

predecessor projects:
FE0026414, DE-NT0005312, FC26-07NT43085, FE0005795, FE0007553, FE0013118

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partners:
Sargent & Lundy (S&L); Basin Electric; Trimeric Corporation; Electric Power Research Institute (EPRI); Carbon Management Strategies (CMS)

start date:
10.01.2019

percent complete:
100%

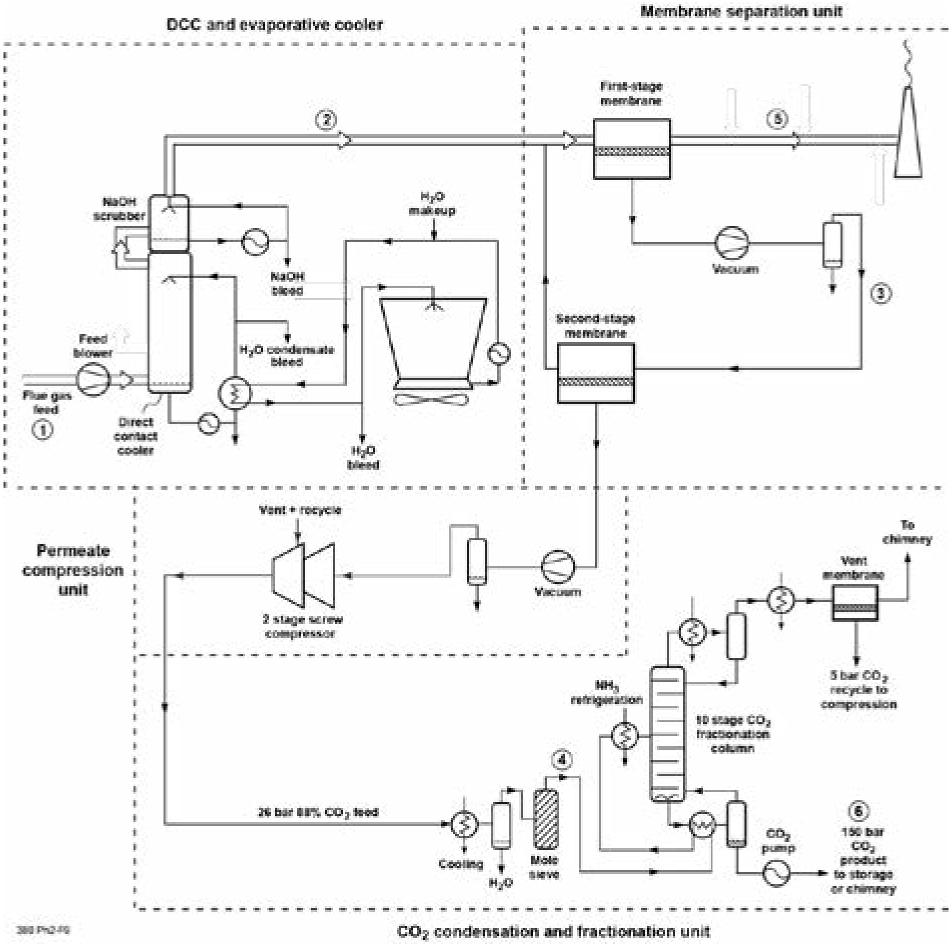

Figure 1: Preliminary design for full-scale membrane capture plant.

Compared to other industrial membrane applications, the main challenge of membrane technology for post-combustion CO_2 capture is the low partial pressure of CO_2 in flue gas, resulting in a large membrane area being required due to the small driving force for separation. MTR has developed two innovations that address this problem:

- A new class of membranes called Polaris that exhibit 10 times the CO_2 permeance of conventional gas separation membranes, leading to a large decrease in required membrane area and reduced capital cost.
- A low-pressure-drop, low-cost membrane module design. The pressure differentials, and therefore the energy required, to circulate gas through the module is a fraction of that measured in conventional modules.

Single-stage membrane designs are unable to produce high-purity CO_2 combined with high CO_2 capture rates because the system performance is limited by the small pressure ratio across the membrane. MTR's multi-stage membrane process design (Figure 2) addresses the pressure ratio constraint to efficiently capture 50 to 75% of the CO_2 in flue gas. First, the combustion flue gas enters a primary capture module, which produces a permeate containing ~55 to 60% CO_2. This gas is then treated by a second membrane stage to further enrich the CO_2 stream to greater than 85% CO_2. The CO_2-rich permeate from the second-stage module is dehydrated and compressed.

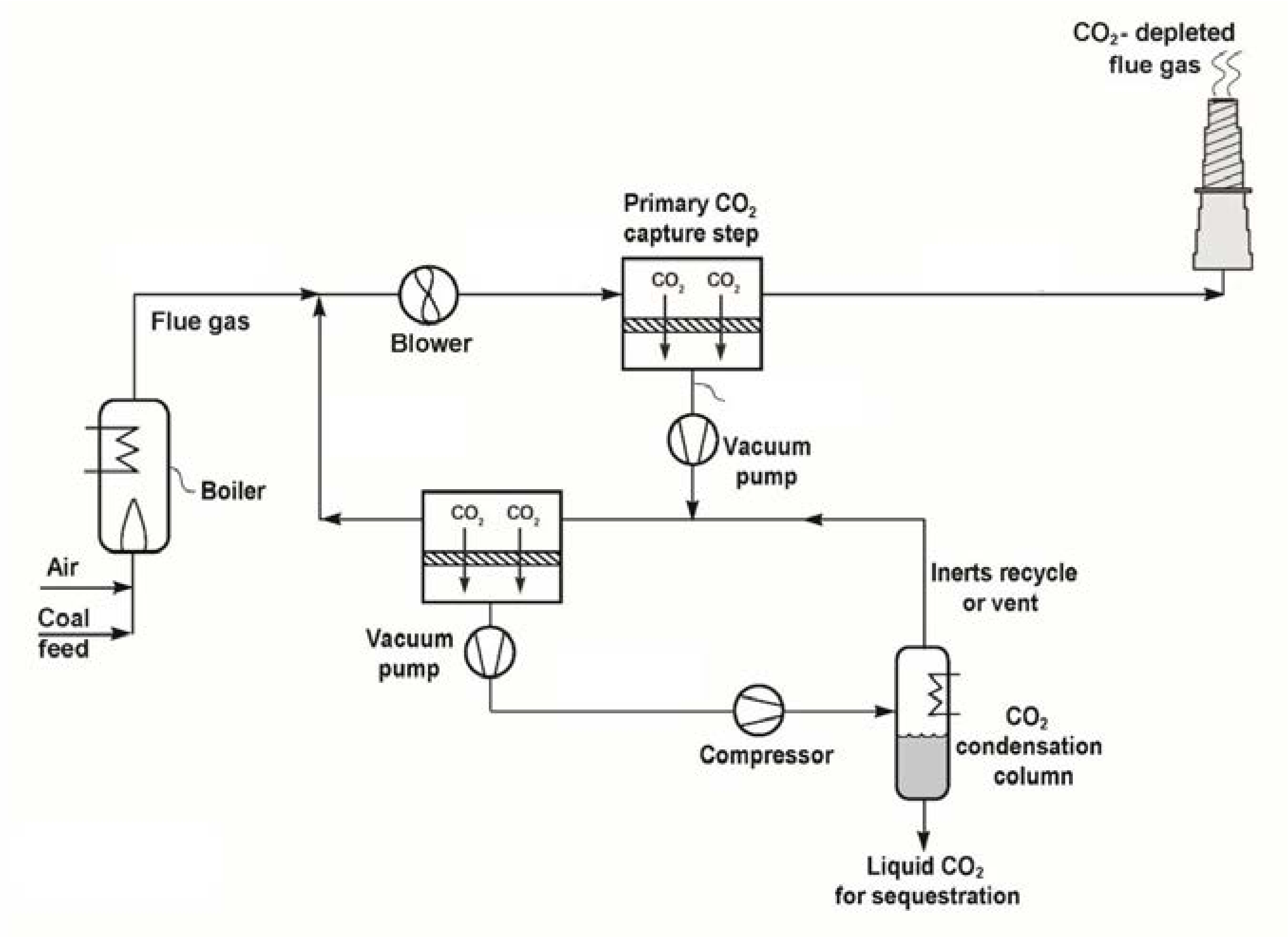

Figure 2: MTR CO_2 capture process.

MTR's Polaris membrane was first developed in a previous DOE-funded project, DE-NT43085. Polaris exhibits high CO_2 permeance and high CO_2/nitrogen (N_2) selectivity for post-combustion flue gas applications. The thin-film composite membrane utilizes hydrophilic polymers. Commercial Polaris membranes offer a step-change improvement over typical commercial CO_2-selective membranes used for natural gas treatment, with an average CO_2 permeance of 1,000 gas permeation units (GPU) and a CO_2/N_2 selectivity of 50. Recent studies have improved membrane performance, demonstrating a CO_2 permeance of 3,000 GPU at lab-scale. The combination of these membranes with novel module and process innovations greatly reduces the projected cost of CO_2 capture.

Membranes packed into spiral-wound modules are widely used in commercial membrane installations today. Spiral-wound modules are robust, resistant to fouling, and economical; they are used in 95% of the reverse osmosis (RO) desalination industry and more than 70% of the membrane market for CO_2 removal from natural gas. Figure 3 shows the general design features of a spiral-wound membrane module. The module consists of a permeate collection tube with a spiral formation of permeate spacers and feed spacers, which allow the flue gas and separated CO_2 to flow through the device. The process parameters for the Polaris membranes in a spiral-wound module configuration are shown in Table 1.

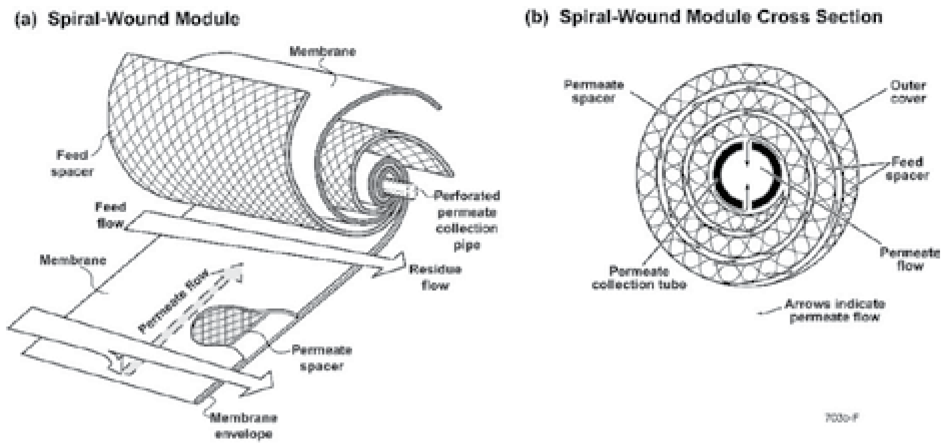

Figure 3: Schematic diagram of a spiral-wound membrane module.

TABLE 1: MEMBRANE PROCESS PARAMETERS IN SPIRAL-WOUND MODULE CONFIGURATION

Materials Properties	Units	Design Value
Materials of Fabrication for Selective Layer	—	proprietary polymer
Materials of Fabrication for Support Layer	—	proprietary polymer
Nominal Thickness of Selective Layer	µm	<1
Membrane Geometry	—	spiral
Max Trans-Membrane Pressure	bar	70
Hours Tested without Significant Degradation	—	11,000
Manufacturing Cost for Membrane Material	$\$/m^2$	10
Membrane Performance		
Temperature	°C	30
CO_2 Pressure Normalized Flux	gpu or equivalent	1,000
CO_2/H_2O Selectivity	—	0.3
CO_2/N_2 Selectivity	—	30
CO_2/SO_2 Selectivity	—	0.5
Type of Measurement	—	Mixed gas
Module Design		
Flow Arrangement	—	crossflow and countercurrent
Packing Density	m^2/m^3	1,000
Shell-Side Fluid	—	N/A
Flue Gas Flow rate	kg/hr	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90% / >96% / 140
Pressure-Drops Shell/Tube Side	bar	0.1
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{m^2}$	50

Under a previous DOE-funded project, DE-FE0005795, a membrane skid designed to capture 1 tonne of CO_2 per day from a 7,000-standard-m^3/day (250,000 standard cubic feet per day [scfd]) flue gas slipstream was installed and tested at the National Carbon Capture Center (NCCC; Figure 4). The skid held up to eight (four crossflow and four countercurrent sweep), 8-inch-diameter Polaris membrane modules. The system accumulated more than 11,000 hours of operation with flue gas testing spiral-wound modules in both steps of the MTR process: a capture step operating with permeate vacuum and a selective-recycle step that uses air sweep to provide driving force for CO_2 removal. The test demonstrated membrane operation in commercial-scale modules and determined typical membrane lifetimes under coal combustion flue gas operating conditions.

Figure 4: Membrane skid used for 1-TPD bench-scale slipstream testing at NCCC.

Scale-up of the Polaris capture system from the 1-TPD bench-scale unit to a 20-TPD small pilot system using commercial-scale membrane components was also completed in FE0005795. The 20-TPD system is a two-level design, with membrane modules located on the upper level, and all rotating and associated equipment on the lower level. Like the 1-TPD unit, the 20-TPD unit was designed for slipstream operation at NCCC and is shown in Figure 5.

Figure 5: 20-TPD small pilot system installed at NCCC.

Pilot-scale operation of the previous 1-MWe (20-TPD) membrane CO_2 capture system, integrated with a Babcock & Wilcox (B&W) 0.6-MWe coal-fired research boiler, was performed in the DOE-funded project DE-FE0026414 to determine how various membrane parameters impact the performance of a boiler system. Operation of the integrated membrane-boiler system involves the recycling of CO_2-laden air back to B&W's boiler via a countercurrent sweep membrane. A modest reduction in boiler efficiency due to recycled CO_2 was measured (1.8%) at 90% capture, showing that the selective-recycle process is feasible and the impact on boiler performance is relatively small.

While previous tests have shown that recycle to the boiler is feasible, operation at ~70%+ capture without recycle is often of interest, because it offers lower capture costs and still reduces coal plant emissions to less than that of a natural gas power plant. Therefore, the current FEED study focuses on a two-stage membrane system that captures 70% of the CO_2 in the flue gas without selective recycle and concentrates the gas to about 85% CO_2. A CO_2 purification unit is then used to produce greater than 99% CO_2 at 150 bar. For the full-scale capture plant, container-sized skids will be used as the basic modular building block. An evaluation of the most efficient arrangement of the membrane capture skids is being conducted in the FEED study.

MTR applied an alternative approach to membrane packing to develop planar modules optimized for low-pressure operation. Testing of the small pilot-scale 20-TPD system at NCCC and B&W incorporated this novel large-area membrane module designed by MTR in project DE-FE0007553. A single planar membrane module element has the equivalent membrane area of five 8-inch spiral-wound membrane modules. Figure 6 shows the plate-and-frame module design. The simple, straight flow path of the new module design results in a pressure-drop that is almost four times lower than that measured for the spiral-wound module, as shown in Figure 7, resulting in energy and cost savings. At full-scale, this reduced pressure-drop represents about a 10-MWe savings in fan power. The planar module skids are projected to cost $50/m^2 of membrane at full commercialization stage. Process parameters for the Polaris membranes in a planar module configuration are shown in Table 2.

Figure 6: Prototype plate-and-frame module during testing at NCCC.

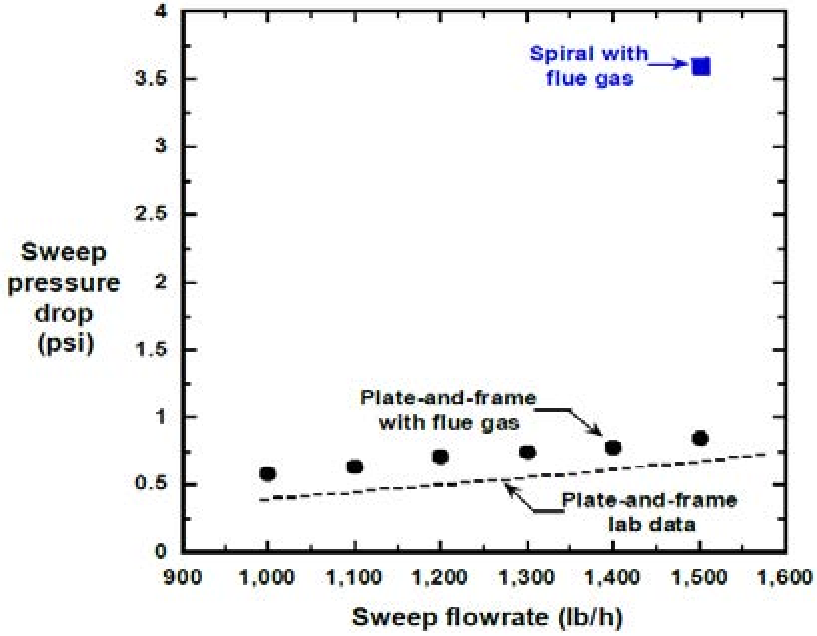

Figure 7: Measured pressure-drop in plate-and-frame module, compared to spiral-wound module.

TABLE 2: MEMBRANE PROCESS PARAMETERS IN PLATE-AND-FRAME MODULE CONFIGURATION

Materials Properties	Units	Design Value
Materials of Fabrication for Selective Layer	—	proprietary polymer
Materials of Fabrication for Support Layer	—	proprietary polymer
Nominal Thickness of Selective Layer	µm	<1
Membrane Geometry	—	plate-and-frame
Max Trans-Membrane Pressure	bar	2
Hours Tested without Significant Degradation	—	1,500
Manufacturing Cost for Membrane Material	$\$/m^2$	30
Membrane Performance		
Temperature	°C	30
CO_2 Pressure Normalized Flux	gpu or equivalent	1,700
CO_2/H_2O Selectivity	—	0.5
CO_2/N_2 Selectivity	—	30
CO_2/SO_2 Selectivity	—	0.5
Type of Measurement	—	Mixed gas
Module Design		
Flow Arrangement	—	crossflow, partial countercurrent
Packing Density	m^2/m^3	1,000
Shell-Side Fluid	—	N/A
Flue Gas Flow rate	kg/hr	
CO_2 Recovery, Purity, and Pressure	%/%/bar	70% / >96% / 150
Pressure-Drops Shell/Tube Side	bar	0.1
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{m^2}$	50

Definitions:

Membrane Geometry – Flat discs or sheets, hollow-fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed- or pure-gas measurements; target permeance and selectivities should be for mixture of gases found in desulfurized flue gas.

Flow Arrangement – Typical gas separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Membrane Permeation Mechanism – Permeation through the Polaris membrane occurs by the passive solution-diffusion mechanism.

Contaminant Resistance – The membranes are known to be unaffected by water (H_2O), oxygen (O_2), and sulfur dioxide (SO_2). The effect of trace contaminants, such as Hg, arsenic, etc., was examined in the field tests at NCCC and no major issues were found.

Flue Gas Pretreatment Requirements – The greatest concern of species present in flue gas is that particulate matter will foul the membranes, reducing module lifetimes. The field tests at NCCC treated post-FGD flue gas, and in extended testing (more than 13,000 hours), fouling was not a significant issue.

Membrane Replacement Requirements – The target membrane module lifetime is three years, which is at the conservative end of the typical industrial gas separation module lifetime of three to five years.

Waste Streams Generated – The membrane process will recover greater than 95% of the H_2O in flue gas as liquid. The quality of this H_2O and its potential to be reused in the plant will be studied in future work.

Process Design Concept – See Figure 1.

Further improvements to the membrane module design to reduce fabrication costs resulted in a module prototype based on injection-molded, fiber-reinforced thermoplastics. The modules are designed to fit one on top of another to create a module stack, which is placed on a container-sized skid, as shown in Figure 8. The large membrane capture system will consist of multiple container-sized membrane module skids that will be prefabricated using advanced, high-volume manufacturing and shipped to the plant site. This approach minimizes expensive site assembly and installation work and enhances fabrication quality. The FEED study is evaluating and quantifying savings based on the modular construction approach.

Figure 8: Containerized plate-and-frame membrane module stacks.

MTR also previously evaluated a hybrid membrane-absorption process system combining Polaris membranes and an amine solvent-based capture system under DOE-funded project DE-FE0013118. The integrated system combines MTR's plate-and-frame sweep module with a CO_2 capture system developed by the University of Texas at Austin (UT-Austin) that uses a piperazine (PZ) solvent and advanced high-temperature/high-pressure regeneration. This hybrid design requires significantly less membrane area for a two-step CO_2 capture process, compared to MTR's all-membrane process. In the hybrid design, MTR's Polaris membrane recycle stage enriches flue gas from ~13 to ~20% CO_2 and a 5 molal PZ advanced flash stripper with cold-rich bypass is optimized to take advantage of the higher CO_2 concentration. Both series and parallel configurations were considered with the hybrid design, as shown in Figure 9. Process modeling of MTR's plate-and-frame skid integrated with UT-Austin's Separations Research Program (SRP) 0.1-MWe pilot plant showed that a hybrid-parallel configuration offers a lower cost of capture than the series configuration. However, the benefits of a hybrid system do not outweigh the costs. The estimated economics data, including cost of capture, is shown in Table 3.

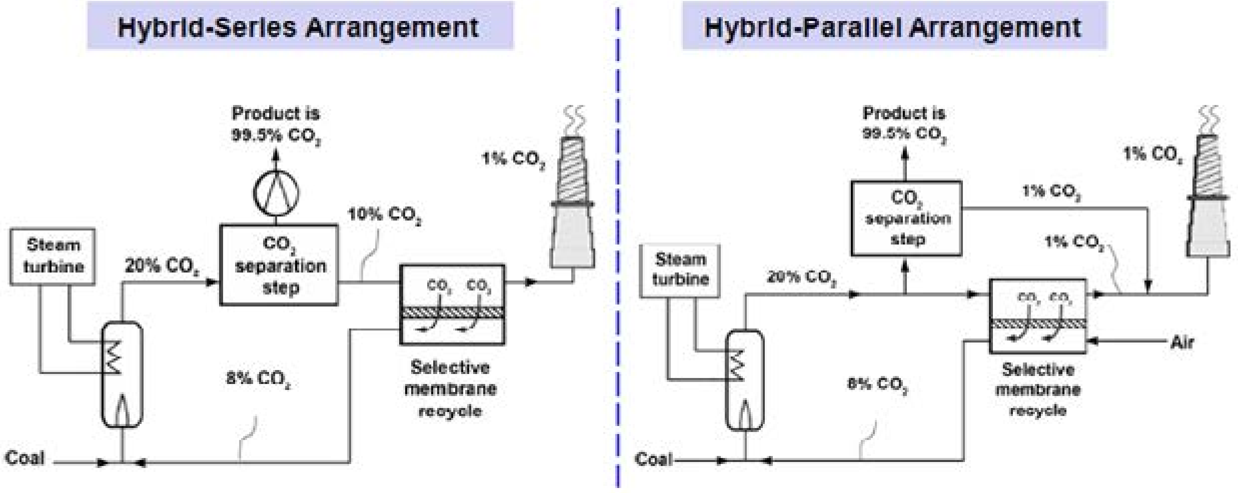

Figure 9: Two hybrid configurations for membrane-absorption CO_2 capture process.

TABLE 3: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	54	43
Cost of Carbon Avoided	\$/tonne CO_2	n/a	n/a
Capital Expenditures	\$/MWhr	18.4	23.9
Operating Expenditures	\$/MWhr	25.9	22.2
Cost of Electricity	\$/kWhr	0.05	0.05

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

MTR is also currently working on three additional DOE-sponsored projects related to this study. DE-FE0031587 is a three-phase project for the design, construction, and operation of a large-scale pilot system to treat 10 MWe of flue gas at Wyoming's Integrated Test Center, with support from Basin Electric's Dry Fork Station power plant. The Phase I feasibility program and the Phase II FEED study are complete and the project is now in Phase III. The National Environmental Policy Act (NEPA) review and Environmental Information Volume (EIV) that were completed in Phase I can be leveraged in this FEED project. The second project recently completed (DE-FE0031589) is a pre-FEED study led by the Electric Power Research Institute (EPRI), in collaboration with MTR, Nexant, and Bechtel, to evaluate a full-scale (640-MWe) membrane capture technology applied to Duke Energy's East Bend Station. The general configuration from the pre-FEED capture plant design is being used as the starting point for the Dry Fork Station FEED study. In project DE-FE0031591, MTR and its partners are scaling-up the next-generation Polaris membranes and modules to a final form optimized for commercial use, and validating their performance in an engineering-scale field test at Technology Centre Mongstad.

The Dry Fork Station power plant is an ideal location for installation of a membrane CO_2 capture system due to:

- High CO_2 content (~15% on dry basis) in the flue gas increases efficiency of membrane capture system.
- Cool, dry climate allows cooling water operation at ~25°C, resulting in an energy savings of 25 MWe/tonne of CO_2 captured.
- Dry Fork Station generates electricity at a low cost, which is important for a capture process powered only by electricity.
- CO_2 utilization opportunities with nearby oil fields and CO_2 pipeline.

technology advantages

- The Polaris membranes developed are more than 10 times more permeable to CO_2 than conventional membranes, which reduce the required membrane area and capital costs.
- A membrane system does not contain any chemical reactions or moving parts, making it simple to operate and maintain.
- The membrane material has a high tolerance to wet acid gases and is inert to O_2.
- The membrane system has a flexible footprint and low energy cost.

- The membrane capture system can recover water from flue gas.
- The use of an existing air stream to generate a CO_2 partial-pressure gradient in the countercurrent sweep membrane stage reduces the need for compressors or vacuum pumps, thus reducing the overall energy cost.
- The recycled CO_2 from the air sweep to the boiler increases the CO_2 partial-pressure driving force for separation in the initial CO_2 separation step (either membrane or absorption/stripper unit), reducing total system cost.

R&D challenges

- Uncertainty in vacuum pumps and compression equipment efficiency and stability treating flue gas.
- Potential performance problems with the CO_2 purification equipment.
- Scale-up of advanced Polaris membranes that exhibit a CO_2 permeance of 3,000 GPU to reduce the capital cost of the membrane system.

status

The project was completed on June 30, 2022. The project team finished a complete FEED study of the carbon capture retrofit at Dry Fork Station. The study included a hazard and operability (HAZOP) analysis, a constructability survey, and a techno-economic analysis (TEA). The team performed all balance of plant (BOP) engineering and design work, developed technical specifications/datasheets used to solicit budgetary quotes, and prepared a detailed engineering deliverables package. The results show that the MTR membrane system can achieve an overall cost of capture of about \$38.50/tonne of CO_2.

available reports/technical papers/presentations

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Large Pilot Testing of Linde-BASF Advanced Post-Combustion Carbon Dioxide Capture Technology at a Coal-Fired Power Plant

primary project goal

The University of Illinois is designing, constructing, and operating a 10 megawatt-electric (MWe) carbon capture system based on the Linde-BASF advanced amine-based post-combustion capture technology at a coal-fired power plant, specifically City Water, Light, and Power's (CWLP) Dallman Unit 4 in Springfield, Illinois.

technical goals

The project workplan consists of three phases and the project is currently in Phase III. The Phase III objectives are to:

- Complete construction and installation of the 10-MWe carbon capture system.
- Complete parametric and steady state testing.
- Complete a full techno-economic analysis (TEA).
- Perform a risk factor analysis.

technical content

The Linde-BASF advanced CO_2 capture process incorporating BASF's novel amine-based solvent, OASE® blue, with Linde's process and engineering innovations allows for a significant increase in energy efficiency and reduced cost for CO_2 recovery from coal-based power plants. The project consisted of three phases:

- Phase I was a feasibility study of the initial engineering design, including National Environmental Policy Act (NEPA) issues and host site selection.
- Phase II was a full front-end engineering design (FEED) study showing predicted plant performance.
- Phase III (current) will consist of procuring additional equipment, constructing the actual plant, and performing live testing.

program area:

Point Source Carbon Capture

ending scale:

Large Pilot

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

Linde-BASF CO_2 Capture Process for Coal-Fired Power Plants

participant:

University of Illinois at Urbana-Champaign

project number:

FE0031581

Predecessor projects:

FE0026588
FE0007453

NETL project manager:

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partners:

Linde; Affiliated Construction Services; Affiliated Engineers Inc.; Visage Energy; BASF Corporation; City Water, Light, and Power

start date:

04.04.2018

percent complete:

70%

In addition to a reduction in regeneration energy and a lower solvent circulation rate enabled by the BASF solvent, Linde has achieved significant improvements in process design, as shown in Figure 1, featuring an advanced stripper inter-stage heater design to optimize heat recovery in the process. This results in lower capital and operating costs for the CO_2 capture system. The Linde-BASF technology addresses all the major challenges for solvent-based carbon capture, including: (1) high specific energy for regeneration, (2) lack of stability due to thermal and oxidative degradation, (3) increased corrosiveness with increased CO_2 loading, and (4) lack of tolerance to impurities from coal combustion products. The design parameters for the solvent are shown in Table 1.

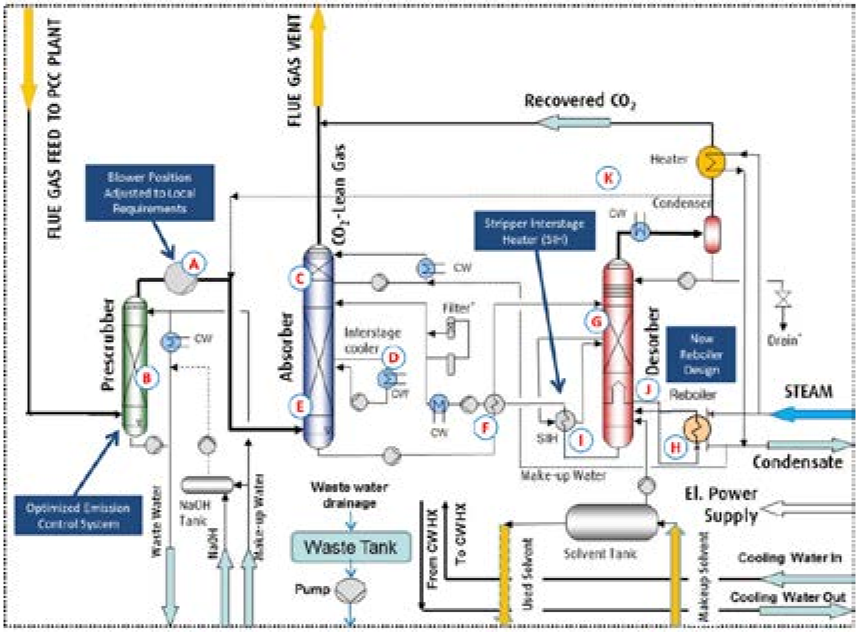

Figure 1: Large pilot process configuration for Linde-BASF technology with Highlighted design improvements.

A. Flue gas blower provides enough pressure to overcome the pressure drop across the pre-scrubber and absorber.

B. Integrated pre-scrubber and direct contact cooler to reduce SO_X content below 5 ppm and simultaneously cool the flue gas stream to ~35–40°C.

C. Innovative and patented water wash section at the top of the column to reduce amine losses, even in the presence of aerosols.

D. A gravity-driven inter-stage cooler for the absorber that eliminates the pump and the controls.

E. High-capacity structured packing reduces the absorber diameter, thereby enabling a larger single-train plant construction.

F. Solvent-based heat exchanger designed to operate over a wide range of temperature approaches, which provides the opportunity to optimize the performance and capital cost trade-off.

G. Regenerator designed for operation at pressures up to 3.4 bar(a), significantly reduces CO_2 compression energy and eliminates the bulky first stage of the CO_2 compressor train, resulting in capital cost savings.

H. Innovative plate and frame design of the reboiler minimizes thermal degradation of solvent and provides for a lower solvent inventory and faster dynamics to respond to power plant load changes.

I. Stripper Inter-Stage Heater (SIH) enhances energy-efficient CO_2 stripping from the solvent by recovering heat from the lean solvent to provide intermediate reboil, thereby reducing energy consumption of solvent regeneration.

J. Variations of the stripper-reboiler flashing configuration, which are being evaluated for an ultimate reduction of solvent regeneration energy.

K. Optional CO_2 recycle stream, provided to evaluate the effect of plant loading and variable CO_2 concentration in the flue gas on overall energy consumption, and to limit the effects of power plant loading on flue gas CO_2 mol% fluctuations.

Previous testing of a 0.45-MWe pilot plant incorporating the Linde-BASF technology and utilizing lignite-fired power plant flue gas has shown that the OASE blue solvent is stable, with little degradation observed over 55,000 hours, whereas the reference monoethanolamine (MEA) solvent started to degrade appreciably under the same conditions after 2,000 hours. The Linde-BASF CO_2 capture process was also previously tested at 1.5-MWe-scale at NCCC under project DE-FE0007453, supported by the U.S. Department of Energy (DOE). The study validated solvent stability and demonstrated a cyclic capacity 20% higher than MEA and regenerator steam consumption 25% lower than MEA. These results confirmed the ability of this technology to be cost-effective, energy efficient, and compact. This project leverages work done previously through a DOE Phase I grant (DE-FE0026588), in which a 15-MWe pilot plant of the Linde-BASF advanced CO_2 capture technology was designed to be integrated with the University of Illinois' Abbott Power Plant on the campus of the University of Illinois at Urbana-Champaign (UIUC), with the goal of capturing approximately 300 tonnes per day (tpd) of CO_2 at a 90% capture rate. The 15-MWe pilot project aimed to optimize the process at larger scale and gather performance data under realistic conditions to enable a robust commercial design. Phase I of the project resulted in the completion of a preliminary plant design with basic engineering and cost estimates; establishment of permitting needs; identification of approaches to address environmental, health, and safety concerns related to pilot plant installation and operation; and completion of a detailed TEA, demonstrating that the implementation of Phase II (Detailed Design, Construction, and Operation) of the project is feasible. The project also established strategies for workforce development for the operation and maintenance of carbon capture systems based on the Linde-BASF technology that are retrofitted to existing power plants.

The initial design and costing of the 10-MWe capture plant for installation at the selected host site (City Water, Light, and Power [CWLP] coal-fired power plant in Springfield, Illinois) was based on the estimate for the 15-MWe pilot in the previous DOE-funded project and established industry-scaling factors. The capture system will be installed in the Dallman 4 unit, which is a nominal 200-MWe pulverized coal-fired unit that became operational in 2009. The unit employs a Foster Wheeler front and rear wall-fired pulverized coal boiler equipped with low-nitrogen oxide (NO_X) burners; a selective catalytic reduction (SCR) unit for NO_X removal; a hydrated lime injection (HLI) system for sulfur trioxide (SO_3) removal; a fabric baghouse to capture particles; a flue gas desulfurization (FGD) system to mitigate sulfur dioxide (SO_2) emissions; and a wet electrostatic precipitator (ESP) to remove liquid droplets, such as sulfuric acid mist. For the 10-MWe capture pilot, a slipstream of flue gas from the Dallman 4 unit will be utilized as a feed gas for CO_2 capture.

A summary of the expected economics results is shown in Table 2. Based on results from small pilot studies and the TEA, the technology will achieve high CO_2 capture (≥90%) and generate high-purity (>99.9%) captured CO_2 in a cost-effective manner. The results indicated that when the proposed advanced Linde-BASF technology is integrated with a 650-MWe net supercritical pulverized coal power plant, there will be an increase in power plant efficiency of approximately 1.2 percentage points, a nominal 12.6% reduction in COE, and 26.3% reduction in cost of CO_2 capture ($/MT) compared to the latest DOE/National Energy Technology Laboratory (NETL) base case (Case B12B reference, listed under "Current R&D Value" in Table 2).

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	proprietary	proprietary
Normal Boiling Point	°C	proprietary	proprietary
Normal Freezing Point	°C	proprietary	proprietary
Vapor Pressure @ 15°C	bar(a)	proprietary	proprietary
Manufacturing Cost for Solvent	$/kg	—	—
Working Solution			
Concentration	kg/kg	proprietary	proprietary
Specific Gravity (15°C/15°C)	—	proprietary	proprietary
Specific Heat Capacity @ STP	kJ/kg-K	proprietary	proprietary
Viscosity @ STP	cP	proprietary	proprietary
Absorption			
Pressure	bar(a)	1.0	0.9-1.1
Temperature	°C	30-70	30-60
Equilibrium CO_2 Loading	mol/mol	proprietary	proprietary
Heat of Absorption	kJ/mol CO_2	proprietary	proprietary
Solution Viscosity	cP	proprietary	proprietary
Desorption			
Pressure	bar(a)	1.6-3.4	1.6-3.4
Temperature	°C	124-140	124-140
Equilibrium CO_2 Loading	mol/mol	proprietary	proprietary
Heat of Desorption	kJ/mol CO_2	proprietary	proprietary
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	LB1 Case: 2,718,270	SIH Case: 2,674,784
CO_2 Recovery, Purity, and Pressure	% / % / bar(a)	90%, 99.98% (dry), 3.4 bar(a)	90%, 99.98% (dry), 3.4 bar(a)
Absorber Pressure Drop	bar	0.1	

Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	proprietary

Definitions:

Bar(a) – Unit used to indicate absolute pressure, where the reference pressure is absolute zero, i.e., not taking into account atmospheric pressure.

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – “Current” is market price of chemical, if applicable; “Target” is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		mol%					ppmv	
psig	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
0	135	9.8	17	67	5.3	0.80	34	30

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Carbon dioxide in the flue gas chemically binds to the OASE blue aqueous amine-based solvent via an exothermic absorption step and this chemical bond is broken in the endothermic desorption step via heat provided by steam in the reboiler of the regenerator column, generating pure CO_2.

Solvent Contaminant Resistance – The OASE blue solvent is highly resistant against many contaminants in the flue gas, as shown in both parametric and long-term continuous tests (see Electric Power Research Institute [EPRI] report[1] for additional information).

Solvent Foaming Tendency – During the pilot plant operation, although anti-foaming injection was included in the design, its use was not found necessary.

Flue Gas Pretreatment Requirements – The pretreatment requirement includes reducing sulfur oxide (SO_X) in the flue gas to 2 to 5 parts per million (ppm) in order to limit solvent degradation and is implemented in a direct contact cooler in conjunction with flue gas cooling, typically by adding appropriate amount of sodium hydroxide corresponding to the SO_X present in the flue gas.

Solvent Makeup Requirements – The OASE Blue solvent makeup rate is determined by the sum of the amine losses in the treated gas leaving the absorber column and the rate of solvent degradation during operation over time. Low makeup rates were observed during long-term testing well below an operationally manageable threshold. Low solvent makeup is expected at scale when processing flue gas from power plants with a baghouse filter for particulate removal or with upstream flue gas pretreatment for aerosol mitigation.

Waste Streams Generated – The main waste liquid stream is from the direct contact cooler where SO_X and NO_X are removed; this stream will go through an oxygenation treatment that converts sulfite and bisulfite compounds into sulfate compounds prior to being discharged to the local sanitary district. A small amount of solid waste is removed using an activated carbon filter and mechanical cartridge filter that are replaced at regular intervals. Since the solvent degradation observed in the pilot testing is small, no solvent reclamation unit is envisioned in the large scale.

Process Design Concept – See Figure 1.

Proposed Module Design – Free standing absorber and stripper columns will be tied into a modularized process skid. There will be associated containers for electrical equipment, analytical equipment, and process control.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value (NETL Case B12B)	Target R&D Value
Cost of Carbon Captured	$/megatonne CO_2	$55.60	$41.01
Cost of Carbon Avoided	$/megatonne CO_2	n/a	n/a
Capital Expenditures	$/MWhr	$50.98	$40.18
Operating Expenditures	$/MWhr	$54.24	$50.70
Cost of Electricity	$/MWhr	$114.12	$99.78

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

technology advantages

- Significant reduction in specific regeneration steam consumption (24–40% lower), electrical power (14–26% lower), and cooling water duty (32–43% lower) compared to a reference MEA plant.

- Increased higher heating value efficiency (HHV) for power production (up to ~32.7% efficiency) and lower thermal load compared to a reference MEA plant (28.4% efficiency) due to a combination of advanced solvent and process improvements, including integrated pre-scrubber and direct contact cooler, downstream gas blower, higher desorber pressure, and interstage gravity-flow cooler.
- The total plant costs are ~20% lower compared to a reference MEA plant, with significantly lower post-combustion capture plant capital costs.
- The Linde-BASF technology is readily scalable to large capacities with a single-train system, offering the potential to further reduce costs by utilizing economies of scale.
- BASF is the producer of the OASE Blue solvent and the owner of the solvent technology. A major global player in the chemical industry, BASF has the capabilities to reliably produce and supply the OASE blue solvent in sufficient volumes needed for commercialization, thereby enabling application at scale by avoiding issues related to solvent manufacturing for large-scale commercial plants.
- The Linde-BASF partnership combines the necessary capabilities and experience to deliver the complete CO_2 capture technology value chain from solvent production to full-scale CO_2 capture plant EPC, commercial deployment, and long-term, continuous operations.

R&D challenges

- Scale-up of absorber column at low cost, maintaining uniform vapor and liquid distribution.
- Optimizing operation of the stripper to reduce steam utilization and increase energy efficiency of the CO_2 capture process using advanced stripper configurations and stripper inter-stage heating.
- Managing flue gas impurities and aerosol formation to reduce amine losses.
- Testing of new process units for energy optimization.
- Integration with operations at the CWLP host site.

status

Phase III is currently underway. All equipment procurement and foundational work is complete. In addition, outside the battery limit (OSBL) construction and module fabrication is nearing completion.

available reports/technical papers/presentations

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Engineering-Scale Testing of Transformational Non-Aqueous Solvent-Based Carbon Dioxide Capture Process at Technology Centre Mongstad

primary project goal

Research Triangle Institute (RTI) is developing and testing, at large pilot scale, a non-aqueous solvent (NAS; i.e., water-lean solvent) carbon dioxide (CO_2) capture process to confirm the potential to reduce the parasitic energy penalty associated with the capture of CO_2 from flue gas; demonstrate the long-term process operational reliability at static and dynamic conditions; and verify the solvent degradation rate, emissions, solvent loss, and corrosion characteristics of the solvent at engineering scale.

technical goals

- Evaluate water-lean solvent degradation and material compatibility.
- Measure water-lean solvent performance over static and dynamic operating conditions.
- Design/procure water-lean solvent-specific components for implementation in the host site facility.
- Perform large pilot testing with NAS at TCM facility.
- Confirm a reduction in parasitic energy penalty to less than 2.6 gigajoules (GJ)/tonne CO_2 captured.
- Complete a techno-economic analysis (TEA).

technical content

RTI is advancing the development of a water-lean solvent-based CO_2 capture process that was previously developed and tested at lab- and bench-scale (~10 kilowatts [kW]) with simulated flue gas under the U.S. Department of Energy (DOE)-funded project FE0013865 and with real flue gas under FE0026466. Water-lean solvents have the potential to significantly reduce the cost of CO_2 capture from coal-fired flue gas when compared to first-generation aqueous amine-based solvent processes by reducing the energy required for solvent regeneration. RTI's water-lean solvent is a hydrophobic, sterically hindered, carbamate-forming amine with low-water solubility solubilized in a diluent having low vapor pressure and low viscosity. It is characterized by low heats of absorption and generation of high CO_2 partial pressures at low temperatures and has the potential to reduce the regeneration energy to less than 2.1 GJ/tonne CO_2. The overall reboiler heat

program area:
Point Source Carbon Capture

ending scale:
Large Pilot

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Water-Lean Solvent for Coal-Fired Flue Gas

participant:
Research Triangle Institute

project number:
FE0031590

predecessor projects:
FE0026466
FE0013865

NETL project manager:
Mariah Young
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principal investigator:
Marty Lail
Research Triangle Institute
mlail@rti.org

partners:
Technology Centre Mongstad (TCM); Electric Power Research Institute Inc.

start date:
08.08.2018

percent complete:
95%

duty, or thermal regeneration energy, is made up of the sensible heat, heat of vaporization of water, and heat of absorption. The heat of vaporization, due to the lack of water, is significantly less for water-lean solvents than for aqueous amine-based processes. Also, water-lean solvents overcome the foaming issues that are often associated with aqueous solvents, as shown in Figure 1. RTI's CO_2-rich water-lean solvent has a viscosity of less than 30 cP and is non-foaming.

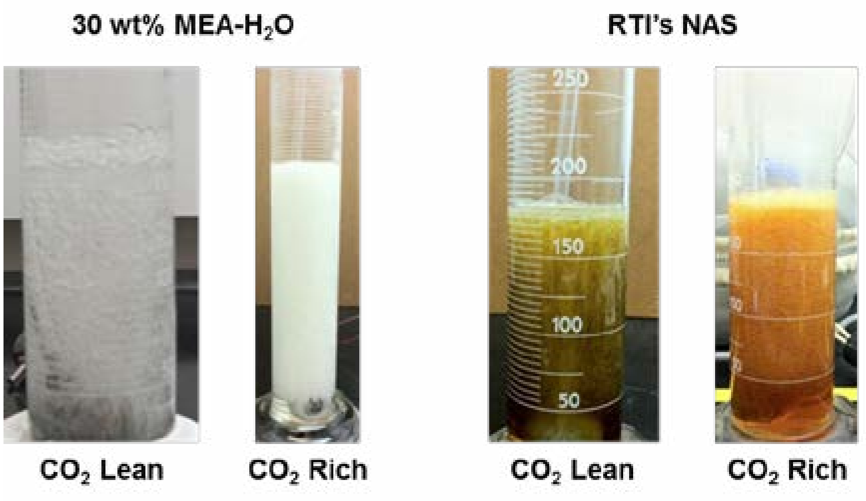

Figure 1: Comparison of foaming in aqueous and RTI's water-lean solvents.

The NAS CO_2 capture process includes a solvent regenerator design specifically for water-lean solvents that combines heat delivery and gas release in a single-step process unit to maintain lower regeneration temperatures. The process, as shown in Figure 2, is like conventional solvent scrubbing systems with key novel design features:

- NAS solvent recovery and wash section—similar to water washing, but water-lean solvents have low water-solubility.
- Solvent regenerator—lack of low-boiling component (conventional reboilers are not applicable).

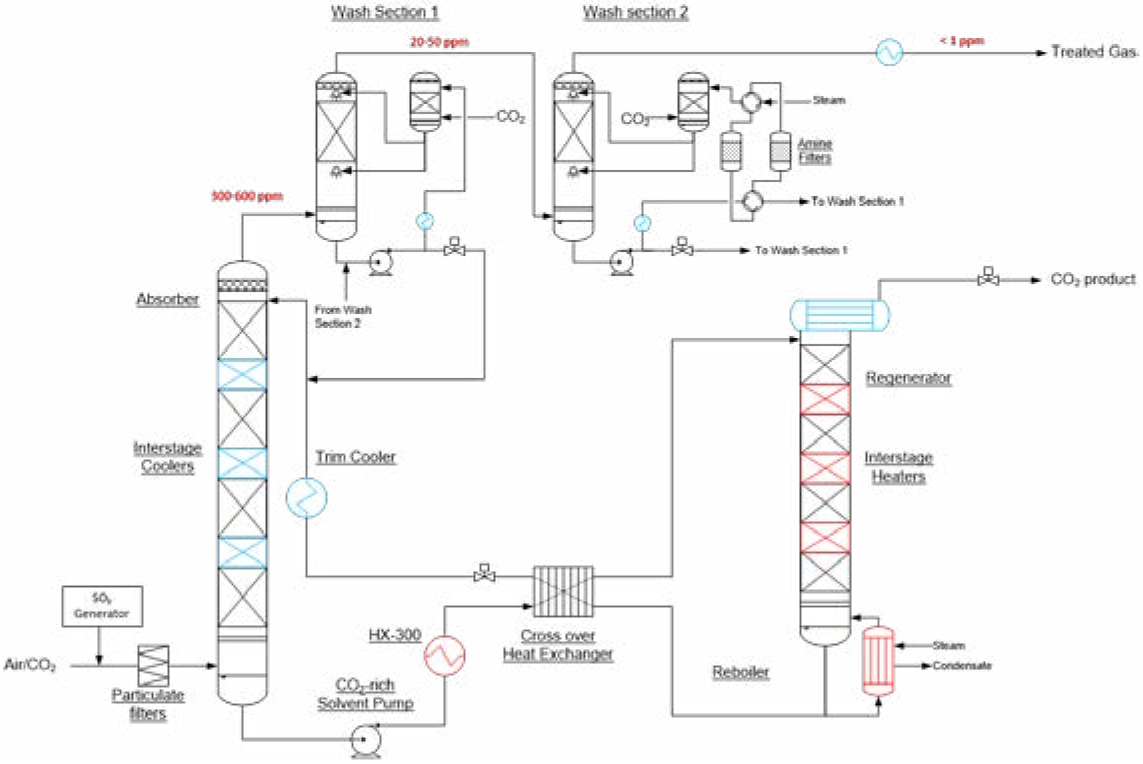

Figure 2: NAS CO_2 capture process diagram.

Under DOE-funded project DE-FE0026466, RTI used the bench-scale test unit (up to 60 kW) at SINTEF's Tiller plant to experimentally show that the water-lean solvent can achieve 90% CO_2 capture and generating a high-purity CO_2 product (greater than 95% CO_2), as well as to evaluate the effectiveness of the developed NAS recovery/wash section and solvent regenerator design. Bench-scale testing at SINTEF's Tiller plant was first performed using the monoethanolamine (MEA) control and the water-lean solvent in an unmodified configuration of the test unit. Baseline testing of the water-lean solvent using propane and coal-fired flue gas was performed over a period of approximately four months, showing a CO_2 capture rate of approximately 90%. Heat stable salts (HSS) and metals analyses were used to determine the solvent stability and corrosion. The HSS level was relatively constant and low during the test campaign. The results also indicate that the corrosion rate of NAS is quite low and stable, confirming previous test results that showed much lower corrosion rate for NAS as compared with MEA.

As the CO_2 capture system at Tiller was designed specifically to achieve the optimum performance for an aqueous-based solvent, it is not an ideal setup to realize the energy reduction benefit by using the water-lean solvent. Based on the knowledge acquired throughout the testing in RTI's gas absorption system (BsGAS) with various process configurations, the following modifications (Figure 3) to the existing absorption system at the Tiller plant were made:

- Addition of two interstage coolers between existing sections of packing in the absorber.
- Replacement of three existing packing sections in the regenerator column with three new sections consisting of an electric/steam heating portion located at the top-half of the section and a high surface area packing portion located at the bottom-half of the section.
- Expansion of lean-rich heat exchanger by adding a second crossover plate-and-frame heat exchanger in series.
- Addition of coal-fired burner.
- Rich solvent preheater installed at regenerator inlet.
- Addition of an acid wash/water wash section.

Result Highlights:

- Interstage heaters: 2.19 (all) to 2.86 (none) GJ/tonne-CO_2
- Interstage coolers: 2.19 (all) to 3.23 (none) GJ/tonne-CO_2
- The use of preheater (HX-305) lowers the SRD

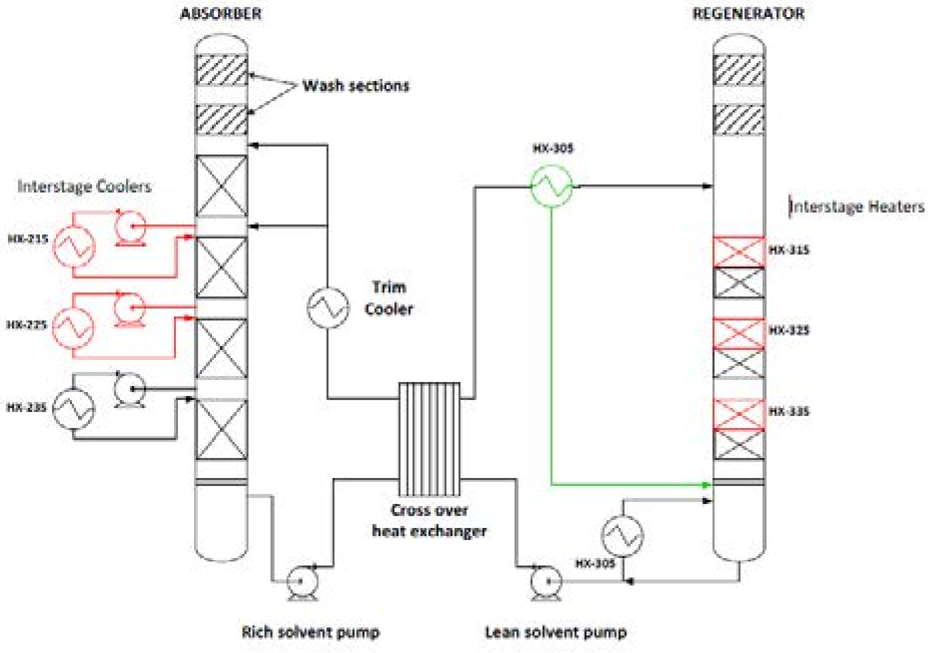

Figure 3: Design improvements for NAS-based process.

The solvent formulation was also refined to increase CO_2 loading and working capacity and to reduce the reboiler heat duty required for solvent regeneration. The improved formulation (NAS-5) results in an increase in CO_2 working capacity from ~0.45 mol_{CO2}/mol_{amine} to ~0.48 mol_{CO2}/mol_{amine}, , and is expected to reduce the reboiler heat duty by decreasing the liquid/gas (L/G) ratios and the heat of absorption at higher temperatures. Through testing in RTI's bench-scale BsGAS, it was found to be advantageous to use two interstage coolers in the absorber column (with one at the bottom and one at the top) to achieve a heat duty near 2 MJ/kg-CO_2. The coolers play an essential role in lowering the temperature in the absorber column to maintain a high CO_2 loading in the solvent. A wash column was added to RTI's BsGAS to allow for testing different conditions to reduce amine losses for the technology, demonstrating that the wash section could effectively remove 92–93% of the amine emissions from the absorber. The process parameters of the solvent are shown in Table 1.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	95–115**	99
Normal Boiling Point	°C	185–243**	200
Normal Freezing Point	°C	(-6 to -24)**	-9.15
Vapor Pressure @ 15°C	bar	4.47e–4**	4.47e–4
Manufacturing Cost for Solvent	$/kg	14	5
Working Solution			
Concentration	kg/kg	0.5–0.6*	0.55
Specific Gravity (15°C/15°C)	-	0.9–1.035*	1.035
Specific Heat Capacity @ STP	kJ/kg-K	2.78*	2.78
Viscosity @ STP	cP	4.38–4.7*	4.7
Absorption			
Pressure	bar	0.133*	0.133
Temperature	°C	35–45*	38
Equilibrium CO_2 Loading	mol/mol	2.04–2.22*	2.04
Heat of Absorption	kJ/kg CO_2	1,700–2,000*	1,931
Solution Viscosity	cP	4–30*	28
Desorption			
Pressure	bar	2–7.8*	2
Temperature	°C	90–110*	105
Equilibrium CO_2 Loading	mol/mol	0.45–1.13*	0.45
Heat of Desorption	kJ/kg CO_2	2,100*	2,045

* Experimentally measured data.

** Calculated data for different concentrations and conditions using standard mixing rules from pure components data.

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

		Composition						
		vol%					ppmv	
Pressure psia	Temperature °F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical.

Solvent Contaminant Resistance – More resistant than MEA to sulfur oxides (SO_X) and nitrogen oxides (NO_X).

Solvent Foaming Tendency – Less foaming than aqueous amine solvent.

Flue Gas Pretreatment Requirements – Temperature adjustment and SO_X control.

Solvent Makeup Requirements – 0.2–0.5 kg/tonne CO_2.

Waste Streams Generated – None.

Process Design Concept – See Figure 2.

Following the installation of the NAS-specific components into the Tiller plant, including a new particulate filter, updated coal-burner control software, additional absorber intercoolers, additional water wash section, regenerative "inter-heaters," and one additional crossflow heat exchanger, parametric testing was performed with NAS-5 to allow optimal operating conditions to be identified and long-term testing to be completed. Test results showed an average CO_2 capture rate of 90% and the lowest reboiler heat duty obtained was 2.3 GJ/tonne CO_2 when the rich solvent pre-heater was used.

Additional baseline testing of the new water-lean solvent formulation was performed at the National Carbon Capture Center (NCCC) to investigate solvent degradation, corrosion, and emissions using the Slipstream Solvent Test Unit (SSTU) with long-term exposure to coal-derived flue gas from the Gaston Power Plant in Wilsonville, Alabama. The NCCC system was operated for 580 hours with flue gas with intermittent delays. The effects of flue gas velocity, CO_2 capture efficiency, and aerosols on amine emissions were studied during the test campaign. Preliminary testing has indicated that the water-lean solvent displays minimal corrosion; therefore, the materials of construction for some of the equipment could be replaced with lower cost options. A TEA and environmental, health, and safety (EH&S) assessment of the NAS process based on test data obtained from SINTEF's Tiller plant and from the SSTU at NCCC show that the NAS technology has the potential to meet DOE's $40/tonne CO_2 capture target when it is fully developed and poses little EH&S risk.

In RTI's current DOE-funded project, engineering-scale tests are being performed using the existing large pilot infrastructure at the Technology Centre Mongstad (TCM) in Norway. The test campaign includes baseline testing with the water-lean solvent in TCM's 12-megawatt-electric (MWe) pilot plant in the configuration designed for aqueous-amine solvents, a hardware revamp of the plant to implement NAS-specific components, and follow-on NAS testing under optimized conditions. Based on the findings realized during the evaluation of RTI's BsGAS and SINTEF's Tiller plant under various process configurations, the following modifications to the existing system at TCM are being made:

- Addition of one interstage cooler between existing sections of packing in the absorber.
- Higher capacity pump in the thermosyphon reboiler for efficient regeneration.
- Adjustment of water wash flue gas inlet to maintain volume during operation.

In addition, strategies for reducing the amine emissions to less than 1 part per million (ppm) are being implemented to meet TCM's emissions requirements, including modifying the existing water wash section of the TCM unit, lowering the gas flow rate, and adding an intercooler to the absorber. Large pilot-scale test results will be used to demonstrate the applicability of the water-lean solvent as a drop-in replacement solvent in conventional capture systems and the process scalability and commercial potential of RTI's transformational NAS CO_2 capture process for pulverized coal power plants.

Included in this study is a TEA. The economic data for the current integrated power plant with CO_2 capture is shown in Table 2.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	43.3	43.3
Cost of Carbon Avoided	\$/tonne CO_2	59.2	59.2
Capital Expenditures	\$/MWhr	62.4	62.4
Operating Expenditures	\$/MWhr	25.7	25.7
Cost of Electricity	\$/MWhr	80.95	80.95

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

technology advantages

- Low water solubility.
- Reduced regeneration energy.
- High solvent regeneration pressure at low regeneration temperatures, such that desorbed CO_2 can go directly to second stage of compression.
- Favorable thermodynamics.
    - Low heat of absorption.
    - High working capacity based on vapor-liquid equilibrium (VLE).
- Excellent thermal and oxidative stability; no formation of HSS.

- Low vapor pressure (less than 0.3 kPa [40°C], less than 10 ppm emissions in treated flue gas).
- Low conductivity; low corrosion rates.
- Low oxygen solubility.

R&D challenges

- Implementation of NAS-specific components into host site facility.
- Effective control of water content in both the rich and lean water-lean solvent solution to minimize regeneration energy required.
- Minimizing the rise in absorber temperature.
- Operating TCM plant within emissions requirements.
- Obtaining sufficient heat exchange for optimal performance.
- Improving the working capacity of the solvent.
- Solvent emissions control.

status

Testing was completed. The TEA for the project has been completed, including an uncertainty quantification and impacts from solvent recovery, corrosion, and full integration with the power plant.

available reports/technical papers/presentations

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Large Pilot Testing of the MTR Membrane Post-Combustion CO_2 Capture Process

primary project goal

Membrane Technology and Research Inc. (MTR) is designing, building, and operating a 150-tonne-per-day (TPD) large pilot membrane-based post-combustion carbon dioxide (CO_2) capture system at the Wyoming Integrated Test Center (WITC) in Gillette, Wyoming.

technical goals

- Complete an initial Environmental Information Volume (EIV) and a preliminary design of the pilot system.
- Complete the permitting process and National Environmental Policy Act (NEPA) documentation.
- Complete design work, site preparations, and construction of the 150-TPD membrane system.
- Install and operate the large pilot system at the host site.
- Update the techno-economic analysis (TEA).

technical content

MTR has developed a new class of membranes, called Polaris™, that have 10 times the CO_2 permeance of conventional gas separation membranes. A tenfold increase in permeance leads to a tenfold decrease in the required membrane area, which substantially reduces the capital cost and footprint of the capture system. These membranes, along with innovative process modifications, address challenges for post-combustion carbon capture.

Over the past decade, MTR has worked with the U.S. Department of Energy (DOE) to develop these innovations into a cost-effective CO_2 capture process. As a result of these successes, the technology was scaled-up to a 20-TPD (1-megawatt-electric [MWe]) small pilot system that was operated in slipstream tests at the National Carbon Capture Center (NCCC). These activities have brought the MTR technology to the point where it is ready for large pilot evaluation. The large pilot system being built in this project is based on the fully validated Gen-1 Polaris membranes. This membrane has been scaled-up to commercial production quantities. In addition to successful use for CO_2 capture in field tests at the NCCC and Babcock & Wilcox Enterprises Inc. (B&W), the Polaris Gen-1 membrane has been used in commercial natural gas and refinery membrane applications. The pilot membrane system features containerized module skids that represent the final commercial-scale membrane form factor. The plate-and-frame modules, as shown in Figure 1, are designed for high-volume manufacturing, resulting in

program area:

Point Source Carbon Capture

ending scale:

Large Pilot

application:

Post-Combustion Power Generation PSC

key technology:

Membranes

project focus:

Large Pilot Testing of Polymer Membrane System

participant:

Membrane Technology and Research Inc.

project number:

FE0031587

predecessor projects:

FE0026414; FE0007553; FE0005795

NETL project manager:

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principal investigators:

Richard Baker/Brice Freeman
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brice.freeman@mtrinc.com

partners:

WITC; Sargent & Lundy; Trimeric Corporation; Graycor

start date:

04.01.2018

percent complete:

70%

dramatic cost reductions, and are compatible for all post-combustion carbon capture applications.

Figure 1: Plate-and-frame membrane module.

A simplified version of the process to be used in the pilot plant is shown in the block diagram in Figure 2. The large pilot unit is designed to capture approximately 70% of the CO_2 content (150 TPD) from a 10-MWe slipstream of flue gas provided by WITC. This range of partial capture using membranes offers the lowest cost of capture ($/tonne CO_2). The flue gas to be delivered to the unit is at 85°C and contains 12.7% CO_2 and 18% water on average. A blower is used to increase the flue gas pressure to 1.2 bar absolute. The flue gas is then cooled in a direct contact cooler (DCC). A dedicated evaporative cooling tower will produce the cooling water required for the DCC and the various vacuum and compression intercoolers and aftercoolers. The DCC reduces the water content of the gas to 1.5% and increases the CO_2 content to approximately 15%.

The gas leaving the DCC then enters the first-stage membrane modules. The membranes partition the gas into a CO_2-enriched permeate (approximately 50% CO_2) and a CO_2-depleted vent gas (approximately 4% CO_2). The CO_2-depleted flue gas is vented to the atmosphere via a dedicated stack.

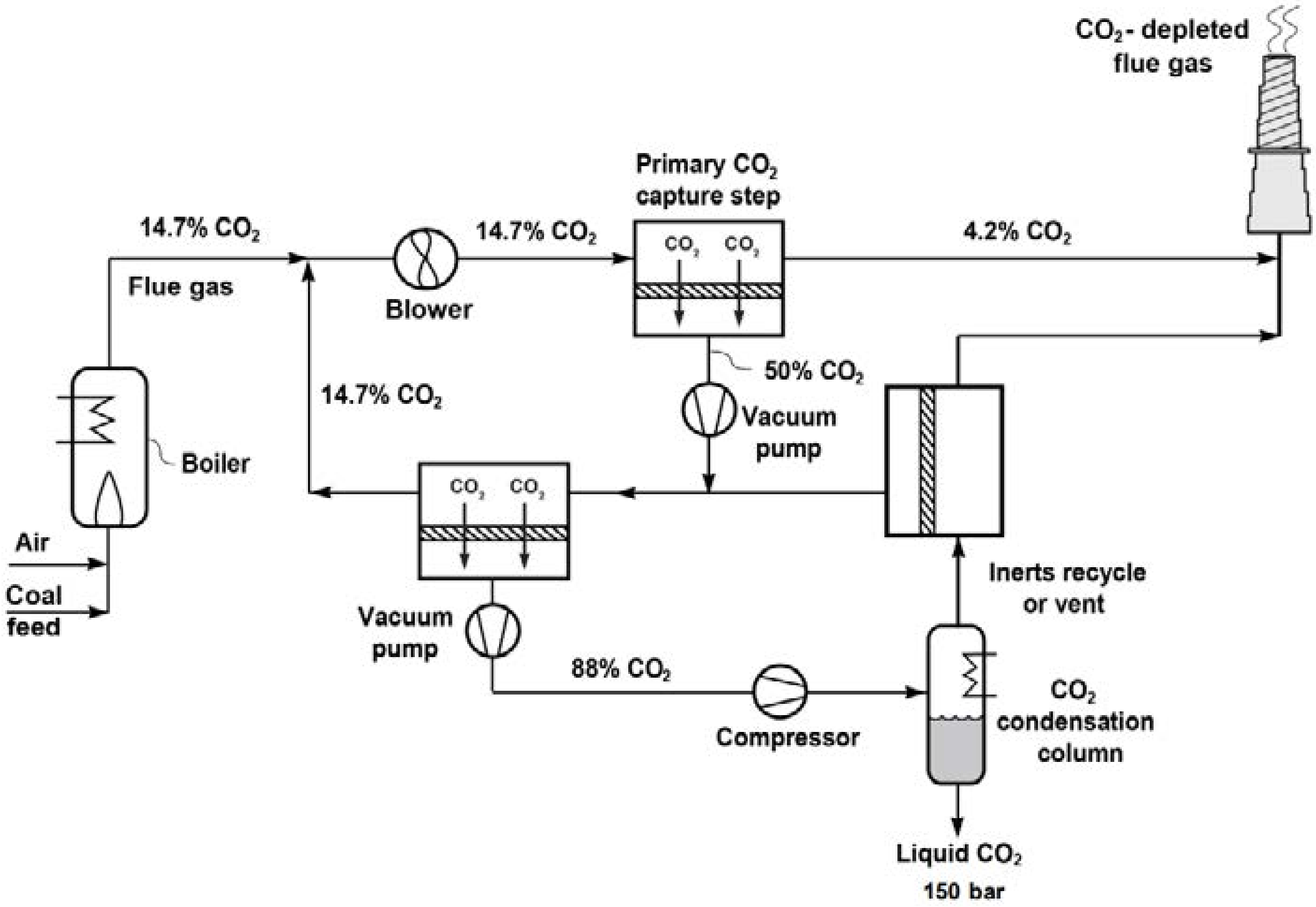

Figure 2: Simplified block diagram of the MTR large pilot CO_2 capture plant to be built.

The driving force for CO_2 permeation is provided by a vacuum pump, which pulls to about 0.1 bar absolute pressure on the permeate-side of the membrane. From the discharge of the vacuum pump, the CO_2-enriched permeate is compressed to about 1.1 bar and sent to a second-stage membrane, which further enriches the gas to approximately 85% CO_2. The second-stage membrane unit is much smaller than the first one and uses a vacuum pump to provide driving force.

The twice-enriched permeate gas from the second membrane stage is compressed to 25 bar. Some of the water in the gas is removed in the inter-stage cooler of the compressor. Most of the water that remains is removed from the compressed gas by cooling to 5°C. A molecular sieve drier is then used to produce bone-dry gas. The dry gas is passed to a low-temperature distillation unit to provide high-purity CO_2. The liquid CO_2 is then pumped to 153 bar as required for enhanced oil recovery (EOR) or storage.

A model of the 150-TPD large pilot membrane skid is shown in Figure 3. The membranes are housed in low-pressure-drop plate-and-frame modules, which reduce cost and increase packing density. There are eight modules per stack and six stacks per container skid. The skids are stacked two high, with a total of six containers for the large pilot (five skids for first-stage membrane separation and one skid for second-stage membrane separation). This will be the final form factor for this membrane CO_2 capture technology. The membrane portion of the capture plant has a compact footprint, processing 10 MWe of flue gas in an area of approximately 100 by 100 feet, with a maximum height of 30 feet.

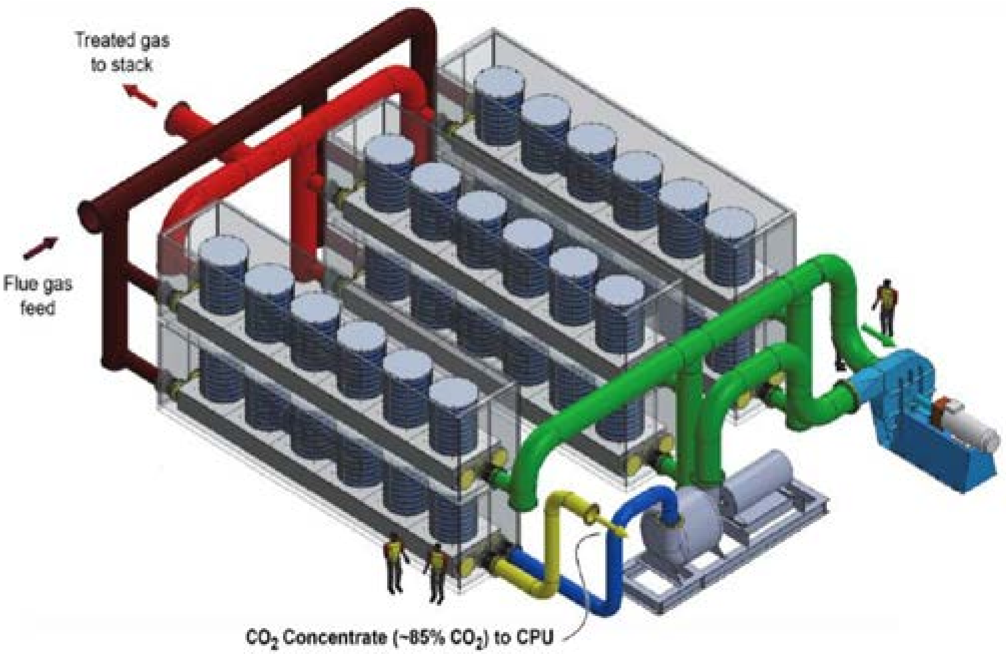

Figure 3: Preliminary general arrangement drawing of the 150-TPD large pilot system to be installed at WITC.

Figure 4: Preparation for equipment installation.

WITC is providing the test site for the Phase II and Phase III programs. WITC is located in Gillette, Wyoming, adjacent to the Basin Electric Dry Fork 420-MWe coal power plant. Basin Electric will supply the project with the equivalent of 10 MWe of flue gas. Duct work and fans to deliver flue gas to the test site are in place. Power and water necessary for the project have also been installed. The membrane unit will recover approximately 70% of the CO_2 content of this gas, or approximately 150 TPD. At full-scale, a 70% reduction in CO_2 emissions would bring the remaining CO_2 emissions of a coal power plant to below that of an equivalent-sized natural gas power plant.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	proprietary polymer	
Materials of Fabrication for Support Layer	—	proprietary polymer	
Nominal Thickness of Selective Layer	µm	<1	<1
Membrane Geometry	—	flat sheet	flat sheet
Max Trans-Membrane Pressure	bar	1.1	1.1
Hours Tested without Significant Degradation	—	11,000 h	11,000 h
Manufacturing Cost for Membrane Material (Module and Skid)	\$/m^2	50-100	50-100
Membrane Performance			
Temperature	°C	30	30
CO_2 Pressure Normalized Flux	GPU or equivalent	1,000	2,000
CO_2/H_2O Selectivity	—	0.3	0.3
CO_2/N_2 Selectivity	—	50	50
CO_2/SO_2 Selectivity	—	0.5	0.5
Type of Measurement	—	flue gas	flue gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	plate-and-frame	
Packing Density	m^2/m^3	1,000	
Shell-Side Fluid	—	N/A	
Flue Gas Flowrate	tons/hr	70.31	
CO_2 Recovery, Purity, and Pressure	%/%/bar	70-75%, 99%, 153 bar	
Pressure Drops Shell/Tube Side	bar	feed: 0.05/sweep: 0.025	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow-fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure-gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Permeation occurs by a passive, solution-diffusion process. Permeation driving force through the first-stage membrane module is provided by a vacuum pump, which pulls to about 0.1 bar absolute pressure on the permeate-side of the membrane. The second-stage membrane unit is much smaller than the first one, and also uses a vacuum pump to provide driving force.

Contaminant Resistance – The membranes are known to be unaffected by water (H_2O), oxygen (O_2), and sulfur dioxide (SO_2). The effect of trace contaminants, such as Hg, etc., is unknown.

Flue Gas Pretreatment Requirements – Testing at the NCCC showed no additional pretreatment was required downstream of a wet flue gas desulfurization (FGD).

Membrane Replacement Requirements – Greater than three-year membrane lifetime.

Waste Streams Generated – The membrane process will recover greater than 95% of the H_2O in flue gas as liquid. The quality of this H_2O and its potential to be reused in the plant will be studied in future work.

technology advantages

- The process does not use any hazardous chemicals. No new emission streams are produced.
- The membranes developed are 10 times more permeable to CO_2 than conventional membranes, which reduce the required membrane area and capital costs.
- A membrane system does not contain any chemical reactions or moving parts, making it simple to operate and maintain.
- The system is compact and modular.
- The two-stage membrane design allows for high-purity CO_2 combined with high capture rates.
- The low-pressure-drop modules reduce parasitic energy.
- The system is very efficient at partial capture (50 to approximately 70%).

R&D challenges

- There is a risk that the membranes may be less stable at large scale than anticipated.
- Efficiency of vacuum pumps and compression equipment.

status

MTR completed an EIV, FEED study, and NEPA documentation for the construction and large pilot testing of the MTR membrane post-combustion CO_2 capture process. The overall design of the 150-TPD large pilot plant was finalized, including a detailed 3D model for construction. Membrane modules have been fabricated and tested and are prepared for stacking. Fabrication of the 53-foot shipping containers and module stack base units has been initiated.

available reports/technical papers/presentations

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Scale-Up and Testing of Advanced Polaris Membrane CO_2 Capture Technology

primary project goal

Membrane Technology and Research Inc. (MTR) designed, built, and operated an advanced Polaris™ membrane carbon dioxide (CO_2) capture system at the Technology Centre Mongstad (TCM) using actual flue gas from a refinery catalytic cracker, which simulates coal flue gas. This test system was used to validate recent membrane technology advancements and mitigate risk in future scale-up activities. Successful completion of this project signifies readiness to proceed to the next step—testing a larger proof-of-concept advanced membrane system on the scale of 10–25 megawatts-electric (MWe).

technical goals

- Design the membrane test system and complete host site preparations.
- Fabricate commercial-scale membranes and low-pressure-drop membrane modules.
- Fabricate a membrane test system skid, with membrane modules incorporated into skid, and install system at TCM.
- Conduct a minimum six-month field test, including three months of steady-state operation and parametric tests that focus on verifying system performance at partial capture rates that minimize capture costs.
- Evaluate optimal integration of advanced compression into the membrane capture process, including cost estimates.
- Complete a techno-economic analysis (TEA) and environmental, health, and safety (EH&S) assessment of the membrane capture technology.

technical content

In this project, no additional membrane development was required. A previously validated second-generation (Gen-2) membrane was scaled-up to commercial manufacturing roll-to-roll equipment. This production scale-up process produces cost savings through bulk materials usage and application of automated manufacturing equipment.

The goal of this project was to scale-up advanced Polaris Gen-2 membranes and modules to a final form optimized for commercial use, and to validate their transformational potential in an engineering-scale field test at TCM. This program expands on work conducted by MTR over the past decade with DOE support to develop efficient membrane CO_2 capture technology. This effort has produced the MTR Polaris class of membranes and a patented selective recycle process design that lowers the cost of capture.

program area:

Point Source Carbon Capture

ending scale:

Large Pilot

application:

Post-Combustion Power Generation PSC

key technology:

Membranes

project focus:

Polymeric Membranes for CO_2 Capture from Coal-Fired Power Plants

participant:

Membrane Technology and Research, Inc.

project number:

FE0031591

predecessor projects:

FE0005795
FE0026414

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partners:

Technology Centre Mongstad; Dresser-Rand; Trimeric Corporation; WorleyParsons/Advisian

start date:

08.01.2018

percent complete:

100%

Over the course of this development effort, key improvements made included higher-permeance membranes, low-pressure-drop modules, and a process design that optimizes the efficiency of capture.

The Polaris Gen-2 membranes have demonstrated 70% higher CO_2 removal capacity compared to the original membrane in bench-scale tests at the National Carbon Capture Center (NCCC) (Figure 1). They were packaged into new modules designed for low-pressure flue gas treatment. Prototypes of these modules have been validated in prior field trials that confirm large energy and cost savings. Assemblies of these modules were fitted into a standard container that represents the final form factor for this technology, with future commercial systems simply utilizing large numbers of this modular repeat unit.

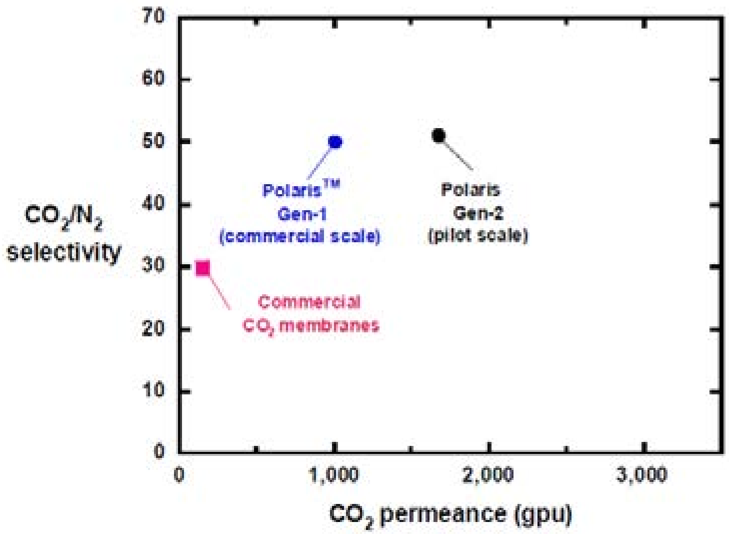

Figure 1: A CO_2/N_2 trade-off plot showing data for two generations of MTR Polaris membrane. Data are pure-gas values at room temperature.

These step-change material and device advances were incorporated into a system design that takes advantage of the inherent efficiency of membranes for bulk separations. Capture costs can be minimized by operating at partial capture rates (50–80%), while still reducing coal plant CO_2 emissions to that of a gas-fired power plant or less. The pairing of Polaris Gen-2 membrane technology with advanced CO_2 compression technology could lead to lower capital costs and energy use for the process. This technology combination was previously featured in the DOE Pathways Study as an attractive way to reach future cost targets.

In addition to an advanced membrane material, this project also utilizes a new type of low-pressure-drop module. This plate-and-frame module, in addition to its relatively compact size, had about four times lower pressure-drop as prior spiral modules during field testing at NCCC under the same conditions (Figure 2), resulting in large energy savings.

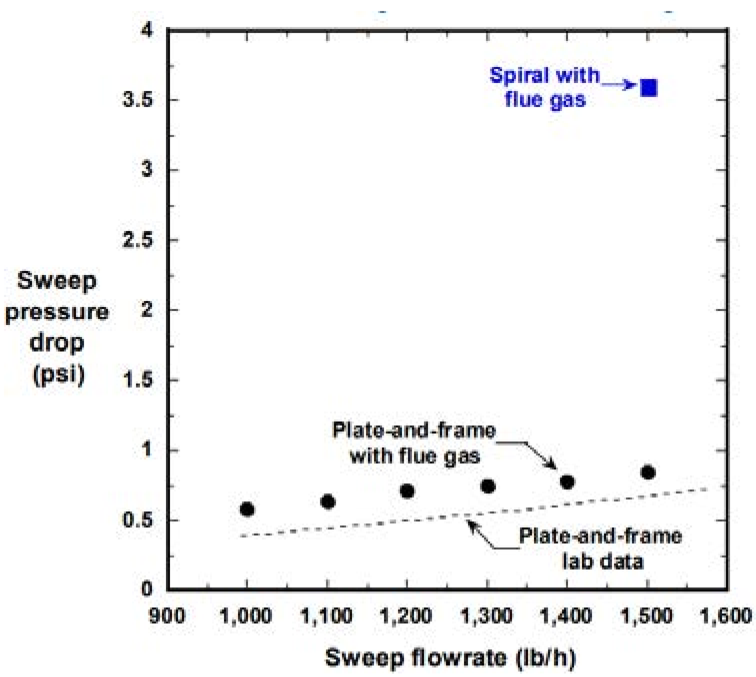

Figure 2: Difference in pressure-drop between spiral and plate-and-frame modules in NCCC field tests.

To reduce the cost of the membrane modules, MTR plans to fabricate them from structural plastics. During this project, a mold flow analysis was completed for the new module design. With this analysis, any issues with the mold design can be identified prior to actual fabrication of the mold and the molding company can determine how to operate their machinery with the MTR mold. Various process parameters were profiled and optimized, including temperature, pressure, number of gates, and gate locations.

Using the mold flow analysis, MTR, along with the domestic mold fabricator and custom plastics injection molding companies, finalized a mold design. A detailed drawing of the new planar stack containing eight membrane modules is shown in Figure 3. The process parameters for these membranes are shown in Table 1.

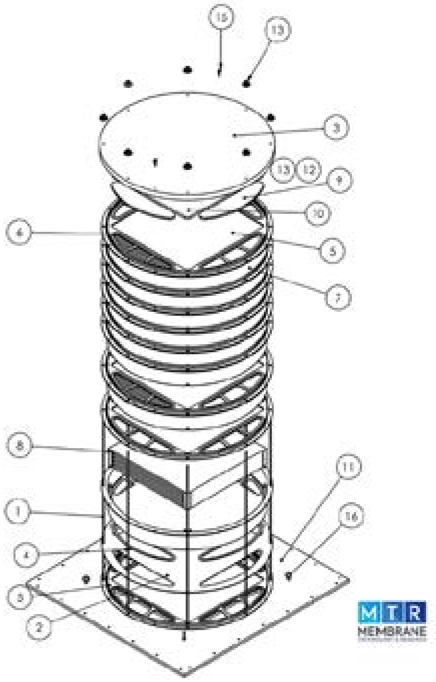

Figure 3: Detailed drawing of a membrane module stack containing eight membrane modules.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	proprietary polymer	
Materials of Fabrication for Support Layer	—	proprietary polymer	
Nominal Thickness of Selective Layer	µm	<1	<1
Membrane Geometry	—	flat sheet	flat sheet
Max Trans-Membrane Pressure	bar	70	70
Hours Tested without Significant Degradation	—	>11,000 (real coal)	>13,000 (real and simulated coal)
Manufacturing Cost for Membrane Material	$/m^2	50	20
Membrane Performance			
Temperature	°C	30	30
CO_2 Pressure Normalized Flux	GPU or equivalent	1,700	1,700
CO_2/H_2O Selectivity	—	0.3	0.3
CO_2/N_2 Selectivity	—	50	50
CO_2/SO_2 Selectivity	—	0.5	0.5
Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	plate-and-frame (crossflow and countercurrent)	
Packing Density	m^2/m^3	1,000	
Shell-Side Fluid	—	N/A	
Flue Gas Flow rate	kg/hr	2,676	
CO_2 Recovery, Purity, and Pressure	%/%/bar	75, >85, 1 (test system conditions)	
Pressure Drops Shell/Tube Side	bar	feed: <0.05/sweep: 0.05	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464 × 10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Figure 4 shows a simple process flow diagram for the MTR engineering-scale system installed at TCM. A slipstream of flue gas is sent to the membrane system (stream 1). After passing through a feed blower, the flue gas (stream 2) goes to the first membrane step, where a vacuum on the permeate is used to remove CO_2. The membrane permeate (stream 4) is sent to a second-stage CO_2 purification unit (stream 5). Some of this purified CO_2 can be routed through a spillback line (stream 9) to the front of the membrane system to increase the concentration of CO_2 in the feed from 13 to ~20%. In this way, the feed to the membrane system will mimic the fully integrated case without having to recycle CO_2 to the boiler. With this spillback option, the 20% CO_2 membrane feed contains about 1 MWe worth of CO_2. The partially treated flue gas that leaves the first membrane step (stream 3) is then sent to the sweep membrane unit. Air (stream 6) flows on the permeate-side of these membranes and removes additional CO_2 from the flue gas. The CO_2-enriched air (stream 7) would be sent to the boiler in integrated operation, but here it is just vented after analysis. Finally, the cleaned flue gas (stream 5) flows to the stack.

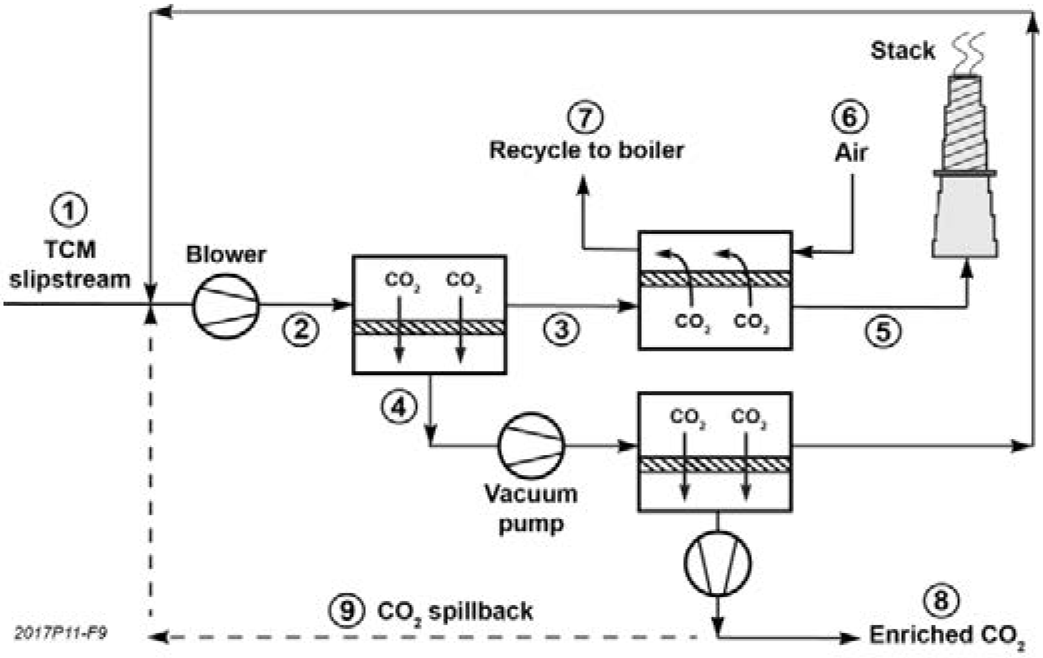

Figure 4: Simplified process flow diagram for the MTR skid operating at TCM.

Finally, the economics data for the developed membranes is shown in Table 2.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	54	43
Cost of Carbon Avoided	\$/tonne CO_2	97	80
Capital Expenditures	\$/MWhr	23.9	18.4
Operating Expenditures	\$/MWhr	25.9	22.2
Cost of Electricity	\$/MWhr	50	50

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Permeation through the Polaris membrane occurs by the passive solution-diffusion mechanism.

Contaminant Resistance – The membranes are known to be unaffected by water (H_2O), oxygen (O_2), and sulfur dioxide (SO_2). The effect of trace contaminants, such as Hg, arsenic, etc., is still under investigation. Polaris modules exposed to coal-fired fuel gas at NCCC for more than a year had no reduction in performance.

Flue Gas Pretreatment Requirements – When placed downstream of existing power plant flue gas emission treatment unit operations to remove particulates (nitrogen oxide [NO_X] and SO_2). The MTR Polaris post-combustion CO_2 capture membrane process design does not require additional pretreatment.

Membrane Replacement Requirements – MTR has installed hundreds of commercial membrane systems in the petrochemical, refinery, and natural gas industries over the past 30 years. The membrane module lifetime is estimated to be three years, which is at the conservative end of the typical industrial gas separation module lifetime of three to five years.

Waste Streams Generated – The MTR capture process will produce a dry, CO_2-depleted flue gas stream routed to the stack and a liquid stream containing much of the moisture in the flue gas (because the MTR membrane captures water as well as CO_2). Prior studies have determined that this water can be recycled to existing flue gas desulfurization (FGD) blowdown wastewater treatment.

technology advantages

- Polaris Gen-2 membranes have a CO_2 permeance approximately 70% higher than Gen-1 and nearly 20 times that of conventional membranes.
- There are no hazardous chemicals or emissions in the membrane process.
- The plate-and-frame membrane module minimizes pressure-drop.
- A simple system allows for low-cost partial capture, while a novel two-step design efficiently captures CO_2 at high removal rates.
- The CO_2 recycle increases feed concentration, reducing membrane area and energy requirements.
- High turndown and rapid response to dynamic conditions are possible.
- The membrane module stack reduces module space and cost, which translates into additional cost savings in the system due to reduced ductwork and system complexity.

R&D challenges

- Optimizing CO_2 capture rate to minimize capture cost.
- Long-term stability of Gen-2 membranes.
- High-permeance membrane is required to lower capital cost.
- Pressure-drops must be minimized to reduce energy losses.
- Balance of plant equipment cost and efficiency, particularly for rotating equipment, are critical to system performance.
- Scale-up and integration issues (and operational complications from multiple vacuum pumps and valves, and complicated ductwork in multiple flow banks) likely given the large number of membranes needed to service a 550-MWe plant.

status

The project has concluded. The capture system was tested using a range of capture rates of up to 90% (average of 70%). The results showed that the MTR membrane can achieve similar cost results to the DOE Volume 1 Case B12B (supercritical Rankine cycle with CO_2 capture). Cost metrics can be improved further with higher CO_2 mass flow rate, less stringent purity requirements, and direct improvements to the membrane.

available reports/technical papers/presentations

Merkel, T., et al. "Scale-Up and Testing of Advanced Polaris Membrane CO_2 Capture Technology," Final Project Report. August 2023. *https://www.osti.gov/servlets/purl/1995006*.

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Engineering-Scale Test of a Water-Lean Solvent for Post-Combustion Capture

primary project goal

Electric Power Research Institute (EPRI) is conducting engineering-scale testing of a novel water-lean solvent to achieve 90% recovery of carbon dioxide (CO_2) while requiring reboiler duties ≤2.3 GJ/tonne CO_2 for post-combustion capture of CO_2 from coal- and natural gas-derived flue gas.

technical goals

- Develop a cost-effective method for synthesizing sufficient quantities of solvent to perform a 0.5-megawatt-electric (MWe)-scale test at the National Carbon Capture Center (NCCC) in Wilsonville, Alabama, while evaluating process modifications needed to optimally operate the solvent process.
- Manufacture the solvent and implement equipment modifications at the NCCC.
- Conduct test campaigns with both coal and natural gas flue gas sources and perform techno-economic analyses (TEAs) and an environmental, health, and safety (EH&S) risk assessment assuming full-scale deployment of the solvent and process at power plants.

technical content

EPRI is scaling-up and testing the EEMPA solvent, a water-lean single-amine solvent developed by Pacific Northwest National Laboratory (PNNL), comprised of more than 90 wt.% N-(2-ethoxyethyl)-3-morpholinopropan-1-amine. The 0.5-MWe-scale testing is being conducted at the NCCC's Pilot Solvent Test Unit (PSTU). This project will verify that EEMPA can capture CO_2 with heat duties lower than advanced aqueous amine solvents, and with low degradation rates when exposed to real flue gas. The tests also serve as a demonstration of the use of plastic packing, which could reduce the capital cost of post-combustion capture processes. Knowledge gained from these tests may also benefit other solvent systems.

In Phase I of the project, activities include development of a cheaper solvent synthesis route ($10/kg cost target) and identification and contracting of a solvent manufacturer, test facility process model development, host site planning, and initial TEA and EH&S risk assessment. Phase II activities comprise the manufacture of the solvent (~2,000 gallons) and modification of the PSTU equipment for the engineering-scale test. Raw material procurement, solvent manufacturing, and quality assurance will be performed, and solvent product will be delivered to the test facility. Equipment procurement, permitting, and construction will be completed. A test plan will also be developed. Phase III activities include test facility commissioning, separate test campaigns on coal and natural gas flue gases, performance and emissions data collection, data reduction and analysis, and test

program area:
Point Source Carbon Capture

ending scale:
Small Pilot

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Water-Lean Solvent for Coal and Natural Gas Applications

participant:
Electric Power Research Institute

project number:
FE0031945

predecessor project:
FWP-70924

NETL project manager:
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principal investigator:
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jswisher@epri.com

partners:
Pacific Northwest National Laboratory; RTI International; Paul M. Mathias Consulting LLC; Gradient; Worley; Southern Company Services

start date:
10.01.2020

percent complete:
75%

facility demobilization and solvent removal. The project will conclude with the completion of a final TEA, a final EH&S risk assessment, and an update of the Technology Maturation Plan (TMP).

EEMPA (Figure 1) is formulated as a water-lean single-amine solvent, consisting of less than 10 wt.% water. The major advantage of a water-lean solvent is lower water vaporization during the solvent regeneration step, especially compared to the aqueous amines.

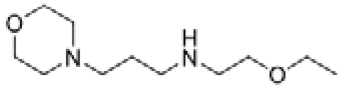

Figure 1: Chemical structure of EEMPA.

This solvent was developed through detailed analysis of hydrogen bonds at the molecular level and their influence on the solvent's viscosity. The selection over hydrogen bond orientation and strength resulted in the development of a derivative that is greater than 90% lower in viscosity than the reference compound. The low regeneration temperature of EEMPA provides a solvent system with potential for a minimal temperature swing between absorption and regeneration cycles.

In previous lab- and bench-scale testing, EEMPA achieved a 90% capture rate with low specific reboiler duties. The favorable thermal performance is attributable to the low water content (around 2 wt.% or less) and a shift in the ionic character of the solvent with higher temperature, disfavoring the CO_2-bound ionic species. Specific reboiler duties down to 2.0 GJ/tonne CO_2 have been observed in experiments. Cost-optimal designs for coal indicate 2.34 GJ/tonne is achievable.

Although EEMPA is formulated without the water of conventional CO_2 capture solvents, it can be used within a conventional solvent scrubbing process design using packed absorption and stripping columns (Figure 2). High viscosity can be an issue for some water-lean candidates; however, EEMPA has demonstrated only modest increases in the viscosity upon uptake of CO_2 (<12 cP at 40°C, 0.22 mol CO_2/mol EEMPA) and mass transfer coefficients are comparable to other solvents. EEMPA can use conventional "simple" stripper designs, but because of the nature of its thermodynamic properties, it may be able to take advantage of alternative designs with simpler construction and lower capital costs. Some of these improvements will be tested at the NCCC.

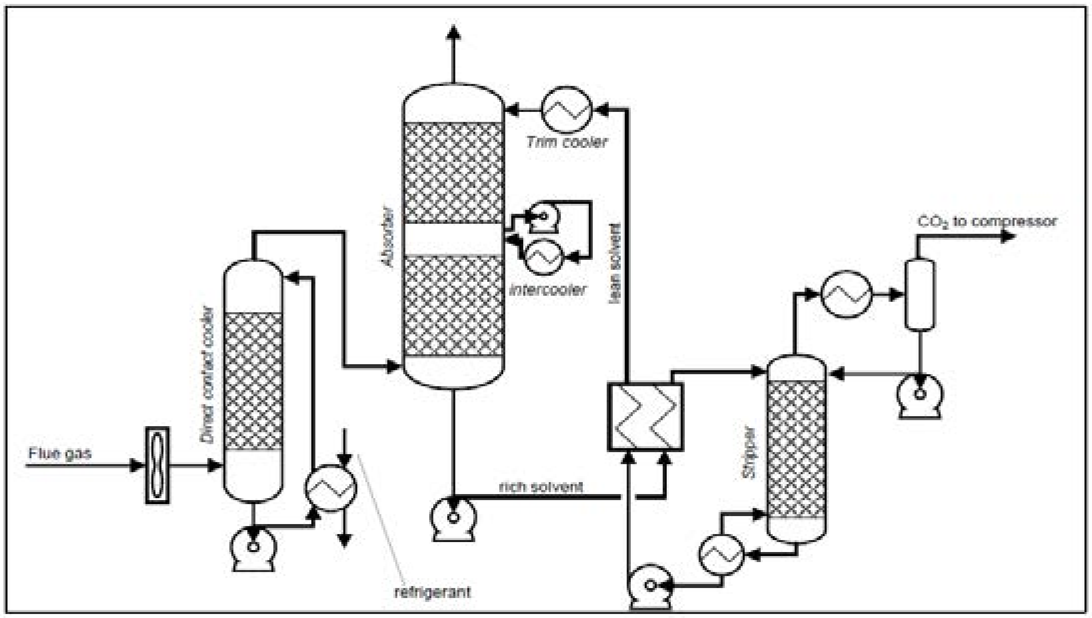

Figure 2: Process flowsheet using a simple stripper arrangement for EEMPA.

Modeling and TEA studies have also estimated 17% lower total equivalent work and 14% lower costs than the National Energy Technology Laboratory's (NETL's) Baseline Study Case B12B (Cansolv), and costs as low as \$39.4/tonne CO_2 in 2018 pricing basis.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	216.3	—
Normal Boiling Point	°C	181.0	—
Normal Freezing Point	°C	<0	—
Vapor Pressure @ 15°C	bar	5E-5	—
Manufacturing Cost for Solvent	\$/kg	13	10
Working Solution			
Concentration	kg/kg	0.98 (hydrated)	—
Specific Gravity (15°C/15°C)	-	0.94	—
Specific Heat Capacity @ STP	kJ/kg-K	1.97	—
Viscosity @ 15°C	cP	12	—
Absorption			
Pressure	bar	1	—
Temperature	°C	45	—
Equilibrium CO_2 Loading	mol/mol	0.225	—
Heat of Absorption	kJ/mol CO_2	75	—
Solution Viscosity	cP	25	—
Desorption			
Pressure	bar	1.8	—
Temperature	°C	118	—
Equilibrium CO_2 Loading	mol/mol	0.045	—
Heat of Desorption	kJ/mol CO_2	75	—

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of inorganic salt and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., a monoethanolamine [MEA]-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical.

Solvent Contaminant Resistance – EEMPA appears to be relatively stable toward oxidative and thermal degradation and hydrolysis in the absence of steel, while sulfur oxide (SO_X) and nitrogen oxide (NO_X) form heat-stable salts.

Solvent Foaming Tendency – EEMPA showed no evidence of foaming during 40 continuous hours of testing with simulated flue gas.

Flue Gas Pretreatment Requirements – It is assumed that a pre-scrubber will be used to reduce sulfur dioxide (SO_2) and NO_X to about 5 parts per million (ppm) and 50 ppm, respectively.

Solvent Makeup Requirements – Solvent makeup rates are expected to be at worst comparable to 5M MEA, though preliminary degradation studies indicate higher chemical durability of EEMPA under absorber and stripper conditions.

Waste Streams Generated – Sulfur oxides and NO_X form heat-stable salts, which will need treatment to recover EEMPA in a working process. Preliminary results indicate the addition of polarity-swing assisted regeneration can facilitate regeneration of heat-stable salts, releasing NO_X and SO_X from EEMPA at 60°C and 130°C, respectively.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	39.4	37.9
Cost of Carbon Avoided	\$/tonne CO_2	60.2	58.3
Capital Expenditures	\$/MW	4,231,000	4,231,000
Operating Expenditures	\$/MWhr	28.4	27.2
Cost of Electricity	\$/MWhr	105.7	104.4

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per MW of power generation capacity.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced. Operating costs include both variable operating cost and fixed operating costs at an 85% capacity factor.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – Values presented are based on a new build supercritical pulverized coal plant with EEMPA-based post-combustion capture at 90% recovery of CO_2. The base power plant design and TEA referenced Cases B12A/B12B provided by NETL, found in Revision 4 of the "Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity" report (https://www.netl.doe.gov/energy-analysis/details?id=3745).

Scale of Validation of Technology Used in TEA – The models used to perform the TEA were validated with large bench-scale testing of the solvent in an integrated continuous flow system.

Qualifying Information or Assumptions – The capture process was a "simple stripping" design with a conventional packed regenerator column and steam-driven reboiler.

technology advantages

- Significantly lower regeneration energy compared to aqueous amines.
- Single-component, miscible in water.
- Low viscosity gain upon reaction with CO_2.
- Low surface tension.
- Compatible with potentially cheaper materials of construction (e.g., plastics).
- Low corrosivity.
- Good thermal and chemical stability.
- Potential for advanced heat integration and regeneration steps that could save costs (e.g., flash regeneration).

R&D challenges

- Potentially costly, and large-scale production yet to be demonstrated.
- Imposes need for careful control of the process water balance.

status

The project team completed a preliminary hazard and operability (HAZOP)/Design Hazard Review (DHR) exercise in June 2022. A safety datasheet for EEMPA was also prepared. Based on the data, the team selected a viable synthesis route for the solvent. Solvent was manufactured and sent to NCCC. Testing of the solvent at the NCCC is planned to begin in summer 2024.

available reports/technical papers/presentations

"Engineering-Scale Test of a Water-Lean Solvent for Post-Combustion Capture," 2024 NETL Carbon Management Research Project Review Meeting, August 7, 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_PSCC_7_Swisher.pdf*

"Engineering-Scale Test of a Water-Lean Solvent for Post-Combustion Capture," 2023 NETL Carbon Management Research Project Review Meeting, August 29, 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC29_Swisher.pdf*

"Engineering-Scale Test of a Water-Lean Solvent for Post-Combustion Capture," 2022 NETL Carbon Management Research Project Review Meeting, August 17, 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_PSC17_Bhown.pdf*

"Engineering-Scale Test of a Water-Lean Solvent for Post-Combustion Capture," 2021 NETL Carbon Management Research Project Review Meeting, August 12, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Swisher.pdf*.

"Engineering-Scale Test of a Water-Lean Solvent for Post-Combustion Capture," DOE Project Kickoff Meeting, April 12, 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11031&filename=Engineering-Scale+Test+of+a+Water-Lean+Solvent+for+Post-Combustion+Capture.pdf*.

"Low-Viscosity, Water-Lean CO_2BOLs with Polarity-Swing Assisted Regeneration," NETL CO_2 Capture Technology Meeting, August 13, 2018. *https://www.netl.doe.gov/sites/default/files/event-proceedings/2018/co2%20capture/monday/D-Heldebrant-PNNL-Polarity-Swing-Regeneration.pdf*.

"Low-Viscosity, Water-Lean CO_2BOLs with Polarity-Swing Assisted Regeneration," DOE Project Kickoff Meeting, September 15, 2017. *https://www.netl.doe.gov/sites/default/files/netl-file/FWP-70924-PNNL-DOCCSS-kickoff.pdf*.

D. Malhotra, D. C. Cantu, P. K. Koech, D. J. Heldebrant, A. Karkamkar, F. Zheng, M. D. Bearden, R. Rousseau, and V. A. Glezakou, "Directed Hydrogen Bond Placement: Low Viscosity Amine Solvents for CO_2 Capture." ACS Sustainable Chem. Eng., (2019), 7 (8), pp 7535–7542.

D. Malhotra, J. P. Page, M. E. Bowden, A. Karkamkar, D. J. Heldebrant, V. A. Glezakou, R. Rousseau, P. K. Koech. "Phase change aminopyridines as carbon dioxide capture solvents." Ind. Eng. Chem. Res., (2017), 56, (26), 7534-7540.

D. Malhotra, P. K. Koech, D. J. Heldebrant, D. C. Cantu, F. Zheng, V. A. Glezakou, R. Rousseau, "Reinventing design principles for developing low-viscosity carbon dioxide binding organic liquids (CO_2BOLs) for flue gas clean up." ChemSusChem. (2017), 10, 636 –642.

Engineering-Scale Demonstration of Transformational Solvent on NGCC Flue Gas

primary project goal

ION Clean Energy Inc. (ION) is empirically validating the capital and operating costs for ION's ICE-31 solvent on a 1-megawatt-electric (MWe) slipstream of flue gas from Calpine's Los Medanos Energy Center (LMEC), a commercially dispatched natural gas combined cycle (NGCC) power plant. To accomplish this, the project team is designing, constructing, and operating an engineering-scale carbon dioxide (CO_2) capture pilot that will capture 10 tonnes per day (tpd) of CO_2.

technical goals

- Validate process models on NGCC flue gas over a range of capture efficiencies (up to 99%).
- Demonstrate the solvent stability of the ICE-31 technology over a long-term operational period to determine true long-term operating costs, including solvent makeup, reclaiming, and disposal.
- Demonstrate expected capital cost on NGCC flue gas as compared to baseline technologies.
- Establish true long-term operating costs, including solvent makeup, reclaiming, and disposal.
- Perform an environmental, health, and safety (EH&S) assessment and a techno-economic assessment (TEA).

technical content

The 1-MWe CO_2 capture pilot project leverages the benefits of ION's innovative ICE-31 solvent technology to reduce the levelized cost of electricity while limiting CO_2 emissions from natural gas-fired power plants. The project builds on ION's lab-, bench-, and small pilot-scale testing of solvent technologies and serves as a vital step of piloting a process with actual NGCC flue gas to further validate this technology's expected suitability for future commercial-scale deployment.

In a previous screening of both commercially available amines and designer amines, ION identified the water-lean amine-based solvent technology ICE-31. ICE-31 exhibits superior regeneration energy, working capacity, kinetics, material compatibility, stability under both oxidative and thermally challenging environments, and a minimal environmental impact.

program area:

Point Source Carbon Capture

ending scale:

Small Pilot

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

Water-Lean Amine-Based Solvent for Natural Gas Applications

participant:

ION Clean Energy Inc.

project number:

FE0031950

predecessor project:

FE0031727

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partners:

Koch Modular Process Systems; Sargent & Lundy; Calpine Corporation

start date:

10.01.2020

percent complete:

60%

Under the previous U.S. Department of Energy (DOE)-funded project FE0031727, "Validation of Transformational CO_2 Capture Solvent Technology with Revolutionary Stability (Project Apollo)," ICE-31 was scaled up and validated at the National Carbon Capture Center's (NCCC) 0.6-MWe pilot solvent test unit on natural gas-fired boiler and coal-fired flue gas; this testing encompassed CO_2 inlet concentrations ranging from 4.4% (simulated NGCC conditions) through 13% (real coal-fired flue gas).

In this project (Project Enterprise), ION will utilize a modular design and fabrication approach to deliver the engineering-scale system that will be designed to yield a CO_2 product flow with greater than 95% purity suitable for compression and dehydration into a CO_2 pipeline. The CO_2 capture process will be optimized to take full advantage of the benefits provided by the ICE-31 solvent in combination with other process improvements, all of which are derived through a process-intensification design philosophy focused on NGCC flue gas. The benefits of this holistic approach include a smaller physical plant, reduced energy requirements, improved CO_2 product quality, less solvent degradation, lower emissions, lower water usage, less maintenance, and lower capital costs.

The long-term test campaign will include a demonstration of end-to-end process optimization; comprehensive chemical costs of the NGCC carbon capture facility; and further validation of ION's rigorous, rate-based process model on NGCC flue gas. Upon completion of this project, ION's solvent technology will be ready for commercial deployment as defined in the Technology Maturation Plan. Learnings from the completed testing under FE0031727 have provided substantial information to support ICE-31's readiness for front-end engineering design for commercial facilities and Project Enterprise seeks to confirm these results and provide any critical operating expenses (OPEX) considerations as projects move to Final Investment Decision.

ION worked with Calpine's LMEC facility to determine the best location for the 1-MWe pilot and identified an optimal location next to the cooling towers (Figure 1). The image shows the proposed location of the pilot system, as well as tie-in points for steam, electricity, cooling water, instrument air, and natural gas (if needed). Additional project team members include Koch Modular Process Systems, a commercial design and fabricator of modular CO_2 capture units who will design and supply the engineering-scale system, and Sargent & Lundy, an experienced engineering firm in the power industry who will manage all balance of plant (BOP) engineering and construction required for site preparation and installation of the pilot system.

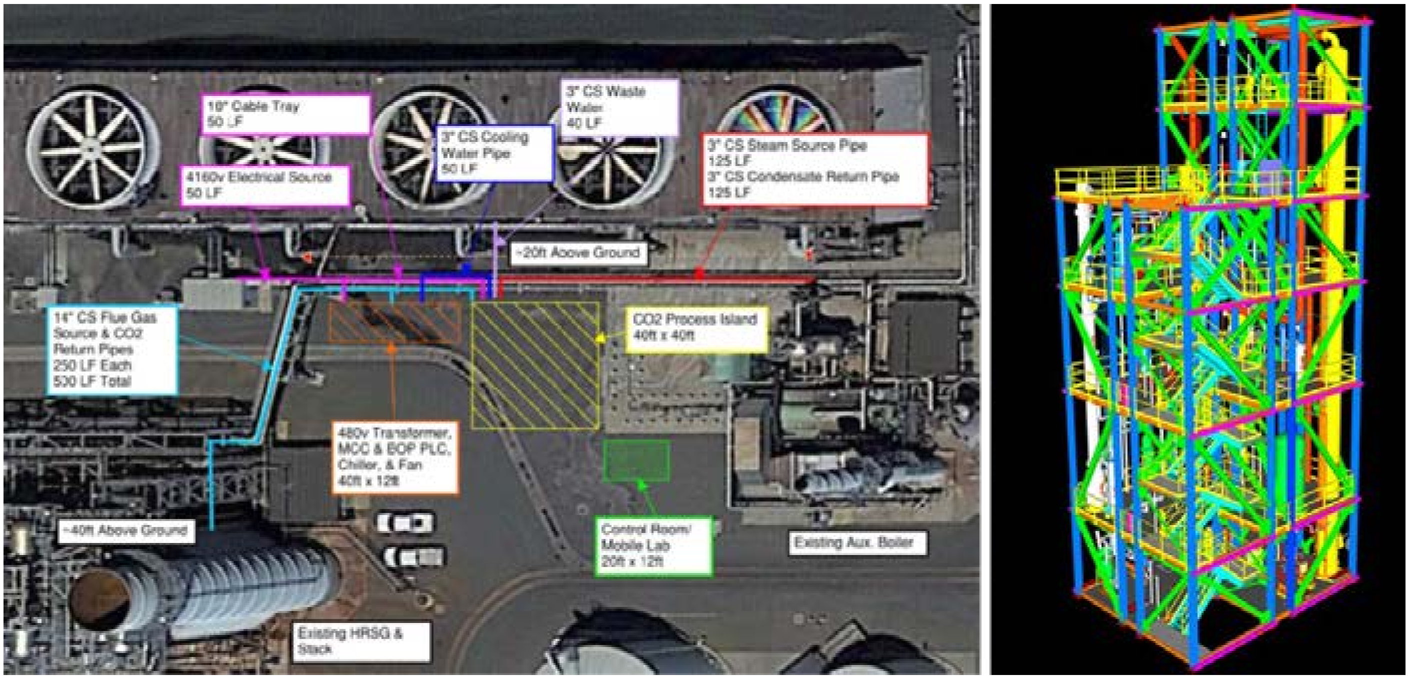

Figure 1: (Left) Overhead view of LMEC with 1,600-ft^2 (150 m^2) pilot site and required tie-ins identified. (Right) Image of the 3D model of the modular system.

Project activities will be accomplished through three phases: design, construction, and operation. The Design Phase will result in a pilot system design that has the necessary flexibility for solvent performance optimization and demonstration. The project team will design the CO_2 capture system and the BOP systems needed to support the 1-MWe pilot at the NGCC facility. A hazard and operability analysis (HAZOP) will be conducted for the pilot system, which will help shape the detailed design. The Construction Phase will realize both the CO_2 capture island and BOP designs and result in a completely assembled system. It will include procurement of necessary equipment and materials, building of the BOP and CO_2 capture systems, and development of the control software. This phase concludes with the installation of the pilot system at the site, the necessary site tie-ins, and site-acceptance testing.

The Operational Phase will commence with baseline testing using first- and second-generation solvents before parametric and long-term testing of ICE-31. The test plan will involve the same baseline parametric testing performed on the previous solvents for a direct comparison, before moving on to a long-term testing strategy to evaluate the solvent lifetime under continuous cycling of operations required to follow the NGCC system. The long-term test campaign will include demonstration of end-to-end process optimization, as well as produce comprehensive technology costs of the NGCC carbon capture facility. The purpose of this long-term testing is to evaluate the solvent performance for a long enough duration to fully understand the interactions and degradation pathways when interacting with the flue gas. This phase will conclude with the decommissioning of the plant and the reversion of the site to its prior state. The operating parameters of the ICE-31 solvent are shown in Table 1.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	80–150	100–150
Normal Boiling Point	°C	220–250	220–250
Normal Freezing Point	°C	<-15	<-20
Vapor Pressure @ 15°C	bar	<0.0001	<0.0001
Manufacturing Cost for Solvent	$/kg	Proprietary	Proprietary
Working Solution			
Concentration	kg/kg	650–800	650–800
Specific Gravity (15°C/15°C)	-	0.8–1.1	0.8–1.1
Specific Heat Capacity @ STP	kJ/kg-K	1.5–2.5	1.3–2.0
Viscosity @ STP	cP	<10	<10
Surface Tension @ STP	dyn/cm	<50	<50
Absorption			
Pressure	bar	1.0	1.0
Temperature	°C	40	40
Equilibrium CO_2 Loading	gmol CO_2/kg	0.5–1.0	0.5–1.0
Heat of Absorption	kJ/kg CO_2	-1,600 to -1,750	-1,600 to -1,750
Solution Viscosity	cP	<20	<20
Desorption			
Pressure	bar	1.5–2.0	1.5–4.5
Temperature	°C	110–125	110–140
Equilibrium CO_2 Loading	gmol CO_2/kg	0.05–0.20	0.05–0.20
Heat of Desorption	kJ/kg CO_2	<1,800	<1,800

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of inorganic salt and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization unit (FGD; wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical absorption/desorption of CO_2 to/from working solution.

Solvent Contaminant Resistance – Sulfur oxide (SO_X) and nitrogen oxide (NO_X) are manageable. Extremely stable towards oxygen (O_2).

Solvent Foaming Tendency – No issues (more than 3,000 hours experience).

Flue Gas Pretreatment Requirements – As for any stable amine-based solvent.

Solvent Makeup Requirements – Aimed at less than 0.010 kg/tCO_2.

Waste Streams Generated – Similar profile but estimated to be less than other stable amine-based solvents.

Process Design Concept – Similar to stable amine-based solvents, just a smaller footprint.

Proposed Module Design – N/A.

technology advantages

- Fast kinetics, coupled with low water content, enhances the carrying capacity and reduces regeneration energy.
- Environmentally benign (i.e., low parasitic load, near-zero emissions, and negligible solvent makeup).
- Low thermal and oxidative degradation rates result in revolutionary solvent stability, reducing solvent makeup rates and associated OPEX.
- Low specific reboiler duty (SRD) and solvent stability result in smaller capture plant equipment, reducing capital expenditure (CAPEX).
- ICE-31 solvent is currently available from commercial chemical manufacturers.

R&D challenges

- Acquiring sufficient long-term solvent performance on natural gas-fired flue gas from a commercially dispatched power station.
- Developing a robust test plan to investigate the necessary conditions required for commercial operations.

status

The complete system was fully commissioned. Both ICE-21 and ICE-31 solvents have been procured. The detailed test plan was completed. Testing is ongoing.

available reports/technical papers/presentations

Meuleman, E. and Fine, N. “ION Validation of Transformational CO_2 Capture Solvent Technology with Revolutionary Stability: Project Apollo”, *Final Technical Report*, August 2023, *https://doi.org/10.2172/1997451*.

Awtry, A., 2024, “Engineering-Scale Pilot for the Demonstration of ION’s Transformational Solvent on NGCC Flue Gas.” *Proceedings of the 2024 NETL Carbon Management Research Project Review Meeting.* *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_PSCC_7_Fine.pdf*.

Awtry, A., 2023, “Engineering-Scale Pilot for the Demonstration of ION’s Transformational Solvent on NGCC Flue Gas.” *Proceedings of the 2023 NETL Carbon Management Research Project Review Meeting.* *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC29_Awtry.pdf*.

Awtry, A., 2022, “Engineering-Scale Pilot for the Demonstration of ION’s Transformational Solvent on NGCC Flue Gas.” *Proceedings of the 2022 NETL Carbon Management Research Project Review Meeting*.

Fine, N., 2021, “Validation of Transformational CO_2 Capture Solvent Technology with Revolutionary Stability (Apollo),” *Proceedings of the 2021 NETL Carbon Management Research Project Review* Awtry, A. & Fine, N., 2020, “Engineering-Scale Demonstration of Transformational Solvent on NGCC Flue Gas (Project Enterprise),” DOE Project Kickoff Meeting. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11039&filename=Engineering-Scale+Demonstration+of+Transformational+Solvent+on+NGCC+Flue+Gas+(Project+Enterprise).pdf*.

Fine, N., 2021, “Engineering-Scale Demonstration of Transformational Solvent on NGCC Flue Gas (Project Enterprise),” *Proceedings of the 2021 NETL Carbon Management Research Project Review Meeting*, August 13, 2021. Pittsburgh, PA. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Fine_0.pdf*.

Fine, N., 2021, "Validation of Transformational CO_2 Capture Solvent Technology with Revolutionary Stability (Apollo)," *Proceedings of the 2021 NETL Carbon Management Research Project Review Meeting*. Pittsburgh, PA. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Fine.pdf*.

Engineering-Scale Demonstration of the Mixed-Salt Process for CO_2 Capture

primary project goal

SRI International (SRI) is constructing an engineering-scale pilot unit (~0.5 megawatt-electric [MWe]) to demonstrate the mixed-salt process (MSP), an advanced ammonia (NH_3) and potassium carbonate (K_2CO_3) solvent-based carbon dioxide (CO_2) capture technology developed at SRI. The pilot unit will demonstrate enhanced CO_2 capture efficiency, high loading capacity, and reduced energy consumption at engineering-scale.

technical goals

- Field-test the MSP at engineering scale to determine process operability under both dynamic and steady-state conditions using actual flue gas.
- Demonstrate that the MSP can capture CO_2 at or above 90% efficiency.
- Regenerate CO_2 with greater than 95% purity.
- Test the process with advanced heat integration for improved process efficiency and determine optimal regeneration energy requirement.
- Optimize the engineering-scale operation of the MSP to achieve high capture rate, high cyclic CO_2 loading, and high-purity CO_2 stream at high pressure.
- Evaluate solvent and water management strategies.
- Collect data to perform the detailed techno-economic analysis (TEA) of CO_2 capture process integration to a full-scale power plant.

technical content

SRI International has been developing a novel mixed-salt solvent-based technology for post-combustion CO_2 capture using a non-degradable solvent that combines readily available, inexpensive potassium and NH_3 salt solutions and employs a novel flow configuration that is optimized to improve absorption kinetics, minimize NH_3 emissions, and reduce water use compared to state-of-the-art, NH_3-based and amine technologies. The solvent and process parameters are provided in Table 1.

A singular NH_3-based process, such as chilled NH_3, has several advantages (e.g., very high CO_2 loading capacity, reduced reboiler duty due to high-pressure regeneration, and fast absorption kinetics). Challenges of this process include the need for a large water wash to reduce NH_3 emissions, requirement to chill the solvent, and energy usage for solid dissolution. A singular K_2CO_3-based process offers several advantages (e.g., no emissions, long-term industrial use, and simple permitting). However, this process has lower efficiency and CO_2 loading, as well as energy requirements for solid dissolution and vacuum water stripping. By combining these two solvent technologies, SRI capitalizes on the advantages of

program area:
Point Source Carbon Capture

ending scale:
Small Pilot

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Ammonia and Potassium Carbonate-Based Mixed Salt Solvent

participant:
SRI International

project number:
FE0031588

predecessor project:
FE0012959

NETL project manager:
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partners:
Baker Hughes (BH); OLI Systems Inc.; National Carbon Capture Center (NCCC)

start date:
07.01.2018

percent complete:
75%

each while minimizing the drawbacks. The MSP maintains the high CO_2 loading and enhanced absorption kinetics, delivering high-pressure CO_2 in a solids-free system. The rate of CO_2 absorption is enhanced by having NH_3 act as a promoter that shuttles the CO_2 to the carbonate ion in the solution across the gas/liquid interface and increases the partial pressure of CO_2 in the dissolved phase. This increases the rate of CO_2 collision with carbonate ion and results in an increase in the rate of CO_2 absorption. Furthermore, by combining the salts, the capture system experiences reduced reboiler and auxiliary electricity loads, reduced NH_3 emission, reduced water usage, and a reduced system footprint.

Taking into consideration the key advantages discussed above, the regenerator energy requirement was estimated and compared to monoethanolamine (MEA)-based and pure K_2CO_3-based processes. Figure 1 shows a significant reduction in regenerator heat requirement for the MSP. In the MSP, the sensible heat is lower than that of MEA-based technology because the MSP is operated with very high CO_2 loading and lean regeneration; thus, a lower volume of solvent is required to carry the CO_2. In addition, since the regenerator operates at a higher pressure in the MSP, the reflux ratio is very low (water $[H_2O]/CO_2$ less than 0.01); therefore, the heat of evaporation is insignificant. The heat of reaction is considerably lower for MSP compared to amine processes, leading to further reduction in reboiler heat duty. Another key difference in the MSP is that, unlike chilled NH_3 or a neat K_2CO_3-based process, the MSP is designed to operate without solids in the absorber, eliminating additional heat requirement for solid dissolution in the regenerator or heat exchangers.

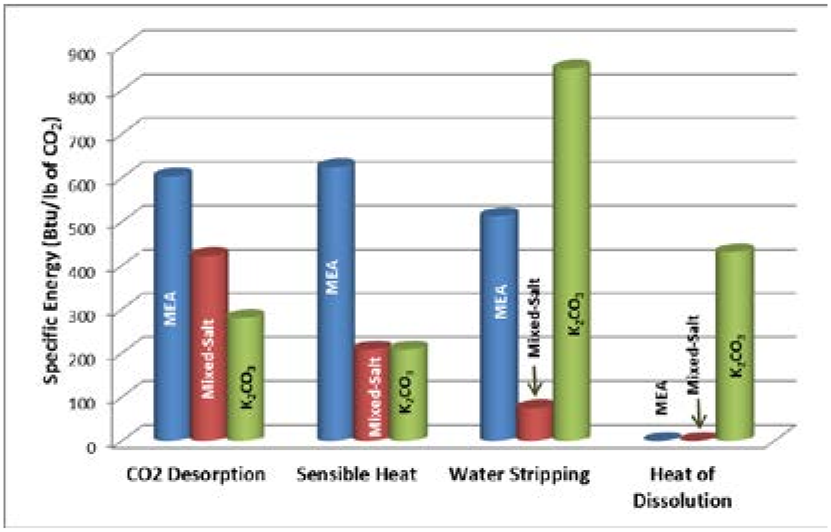

Figure 1: Estimated regenerator heat requirement for mixed-salt system with 0.2–0.6 cyclic loading of CO_2.

The MSP system, shown in Figure 2, comprises two isothermal absorbers, a multi-stage regenerator, and auxiliary equipment. The absorbers operate with different ammonia to potassium ratio (NH_3/K) solutions formulated to maximize the absorption and minimize the NH_3 loss. The absorber system is designed to integrate downstream of a flue-gas desulfurization (FGD) unit in a pulverized coal power plant. The CO_2 in the flue gas stream is absorbed in the absorber columns, which are operated with liquid recycle and heat exchangers to remove the heat of reaction and keep the solution at the optimum temperature for efficient absorption and minimum NH_3 slip. The CO_2-rich solutions from the absorbers are sent to the regenerator for CO_2 stripping and solvent regeneration. The MSP multi-stage regenerator produces two CO_2-lean salt streams with different NH_3/K ratios. These streams are drawn from a lower-middle stage and the bottom stage of the regenerator. The regenerator is operated at high-pressure, isobaric conditions, and has a temperature gradient along the height of the column. The key advantage of the MSP regenerator design is to capture the latent heat within the regenerator before the stream exits the vessel, thus generating almost dry CO_2 stream (H_2Ovap/CO_2 less than 0.2) at high pressure, reducing both operational and capital CO_2 compression costs. The overall benefit of MSP is a significant reduction in the cost of the CO_2 capture.

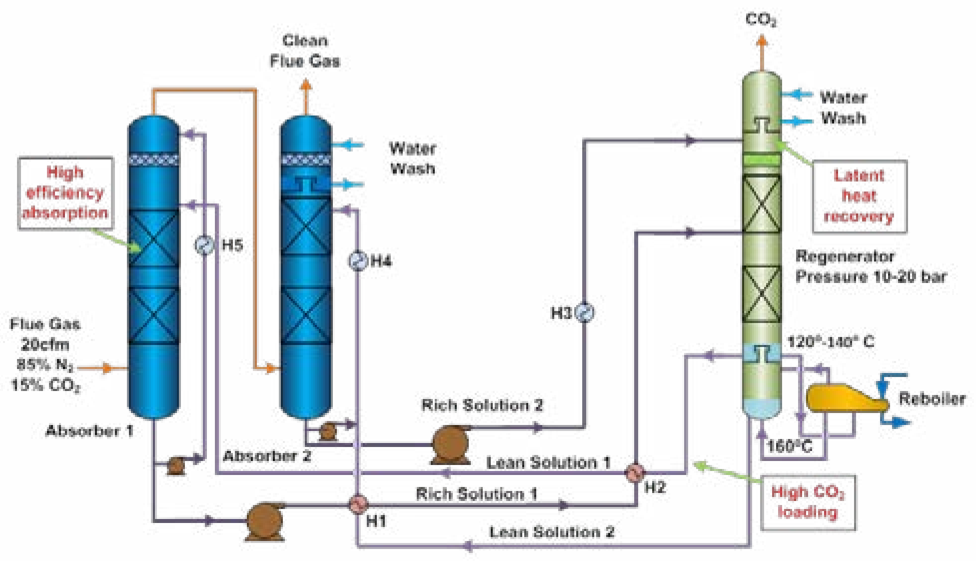

Figure 2: SRI mixed-salt simplified process diagram.

Bench-scale operation of the individual absorber and regenerator units provided optimized process parameters prior to the design and testing of the large bench-scale integrated absorber-regenerator system. The absorber was operated near ambient temperature and the regenerator was operated up to 160°C. The absorber system (Figure 3) has two absorber columns (8-inch diameter) that are designed to operate independently with different absorption solutions, and the gas stream passes through them in series. The dual absorber system operates with a high NH_3/K ratio solution in the first absorber and low NH_3/K ratio solution in the second absorber, which results in a reduction in NH_3 loss from the absorbent solution compared with a single solution approach, as shown in Figure 4. The data from the mixed-salt absorber system testing also demonstrated that it was possible to reach greater than 90% CO_2 capture even using a solution that has fairly high CO_2 loadings (e.g., in the 0.4–0.6 range).

Figure 3: Close-up view of two absorber columns.

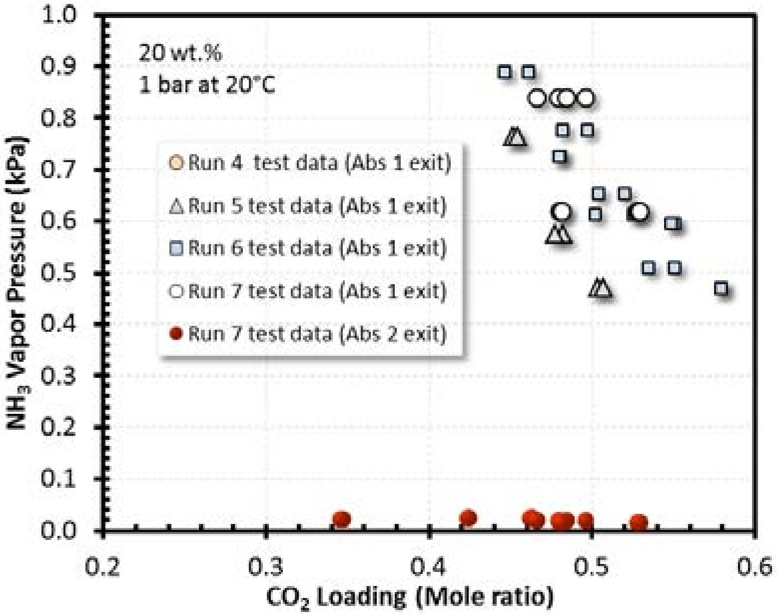

Figure 4: Measured NH_3 vapor pressure at various CO_2 loadings for tests conducted with a single absorber (Runs 4, 5, and 6) and for the test conducted with the dual absorber (Run 7).

Regenerator tests were performed with 20 and 30 wt.% mixed-salt compositions in a semi-continuous mode. Figure 5 is a photograph of the large bench-scale regenerator showing solution inlets, outlets, and heat exchangers. Figure 6 shows the number of moles of CO_2 stripped in a series of runs in the pressure ranges of 6–7 and 11–12 bar in the temperature range of 120–160°C for 20 wt% mixed-salt solutions with 0.49 CO_2 loading.

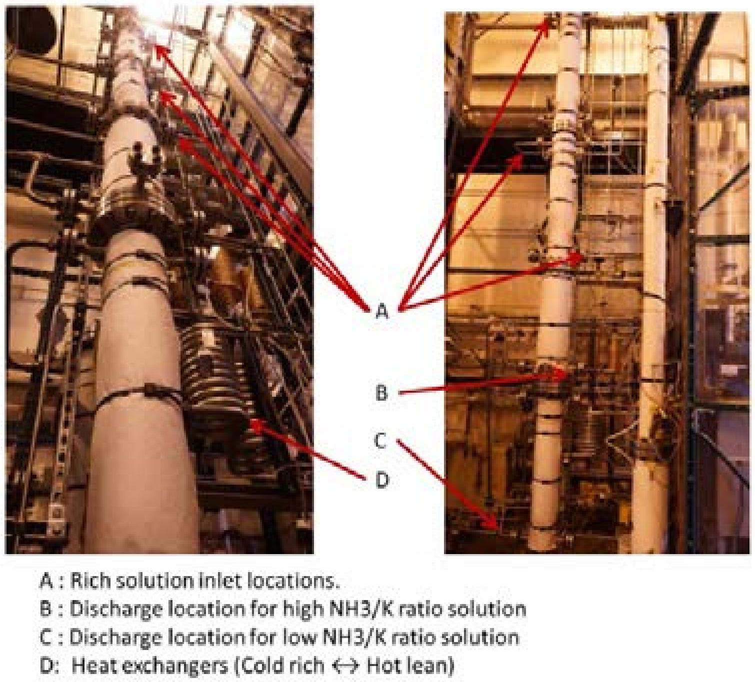

Figure 5: Large bench-scale regenerator.

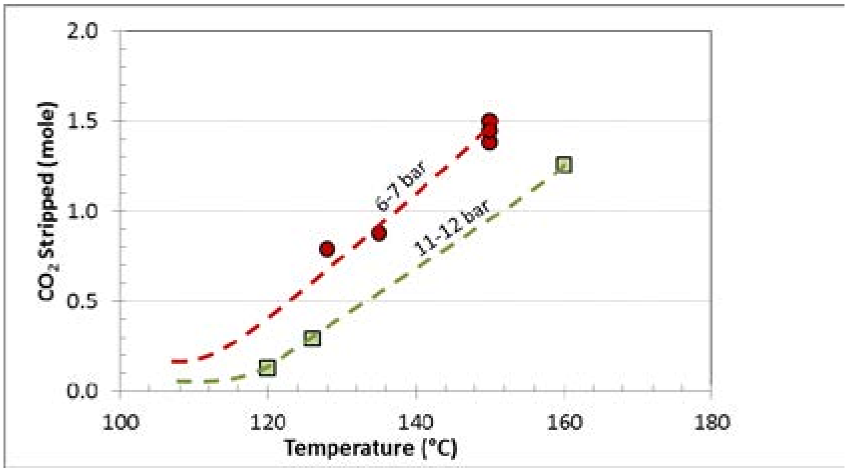

Figure 6: CO_2 stripping as a function of regeneration temperature and pressure.

The integrated bench-scale CO_2 capture and regeneration system, as depicted in Figure 2, was operated for 60 hours. The rich liquid flow from absorber 1 was split and pumped into the column at two stages with approximately 20% going to an upper stage. The rich solution from absorber 2 was cooled to approximately 15°C and pumped to the top stage of the regenerator column to reduce the NH_3 emission from the regenerator. As a polishing step, the high-pressure water wash was mounted at the very top of the regenerator such that the emitted CO_2 gas has less than 10 parts per million (ppm) NH_3 content. The lean stream with high NH_3/K ratio for absorber 1 was drawn from a lower-middle stage of the regenerator column, which was at approximately 130°C. The lean solution with low NH_3/K ratio for absorber 2 was drawn from the bottom stage of the regenerator column, and the temperature of this stage was about 160°C. The regenerator was operated under isobaric conditions with a temperature gradient, approximately 30–50°C at the top and 155–160°C at the bottom. Two main heat exchangers recovered the sensible heat from the regenerated solution to heat the incoming rich solution. The outgoing lean streams from heat exchangers were approximately 40°C, and thus they needed to be cooled to about 15–20°C before they were fed to the absorber columns. For the continuous operation of the regenerator, the input rich-solution flows and exit lean-solution flows were balanced, and the liquid levels of draw stages were carefully controlled to avoid flooding or dry-up of regenerator stages. The integrated system performed as designed with excellent absorption and regeneration cycles and demonstrated more than 90% CO_2 capture. To further decrease the NH_3 loss and water usage, two improvements were implemented in the MSP bench-scale system. Firstly, the length of absorber 2 was extended and slight modifications were made to the solvent flow recirculation. Secondly, a water wash was also installed, with larger surface area and recirculation than the original MSP design. These changes reduced the NH_3 in the absorber exit from approximately 3,000 ppm to approximately 1,000 ppm and the NH_3 in the water wash exit to less than 10 ppm. In addition, the raw water consumption was reduced by a factor of six.

A model for detailed mass-balance and heat-balance calculations for a flue gas feed equivalent to a 550-MWe coal flue gas stream was developed using OLI's Environmental Simulation Program (ESP). The model was validated using the mini-pilot experimental data. The technology was modeled for the CO_2 recovery facility, in which 90% of the CO_2 from flue gas was captured from a supercritical pulverized coal plant with a nominal net output of 550 MWe (U.S. Department of Energy [DOE] Case 11). The other fixed parameters were 99% purity of regenerated high-pressure CO_2 and less than 10 ppm NH_3 release from the capture system. The modeled flowsheet is shown in Figure 7. The flowsheet model includes a flue gas conditioning block and an NH_3 recovery block representing a complete MSP-based CO_2 capture plant.

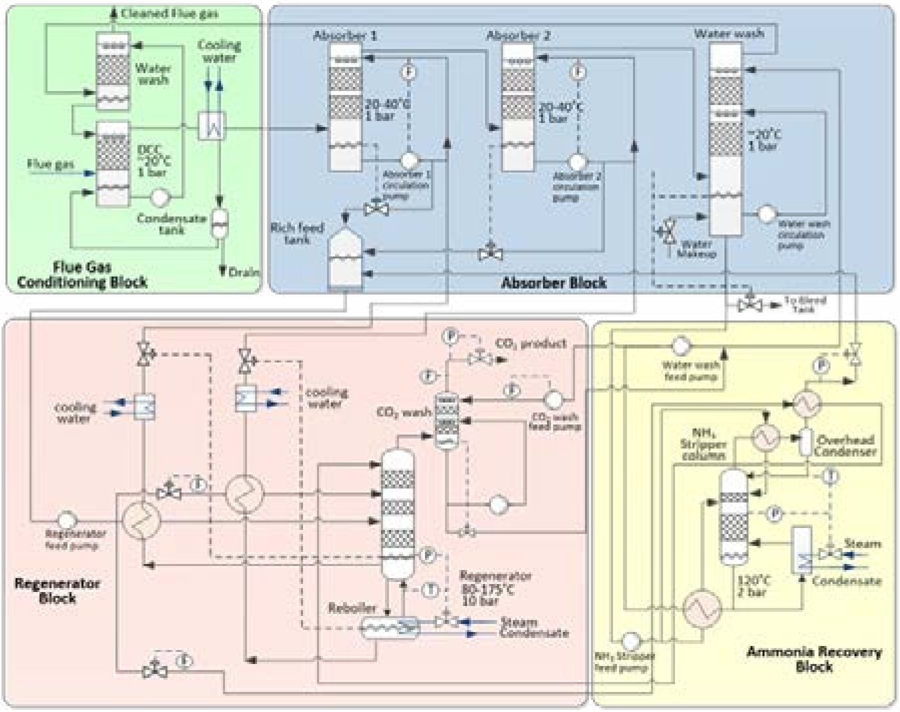

Figure 7: Process flowsheet for simulation.

The MSP captures more than 90% of the CO_2 from the incoming flue gas and regenerates this CO_2 at a pressure of 12 atmospheres. The dual-absorber process, combined with the water wash, results in NH_3 emissions of only 100 ppm in the CO_2-scrubbed flue gas stream. This is further reduced below 10 ppm in a polishing acidified water wash before release to the atmosphere. The total reboiler duty of the process, which is a combination of the regenerator reboiler duty and the NH_3 stripper reboiler duty, is 1.84 MJ/kg CO_2 captured. The study showed the technology offers much lower energy penalty than Fluor Econamine FG Plus^{SM} technology, which uses a formulation of MEA and a proprietary corrosion inhibitor to recover CO_2 from the flue gas.

Currently, a modular 0.5-MWe CO_2 capture system for engineering-scale demonstration is being built, which will be installed in the National Carbon Capture Center (NCCC). Detailed engineering and hazard and operability study (HAZOP) analysis of the plant have been completed and the modular units are being constructed at the engineering, procurement, and construction (EPC) company site. The plant installation in NCCC Bay 2 is scheduled for September 2024. Figure 8 shows a 3-D layout of the plant.

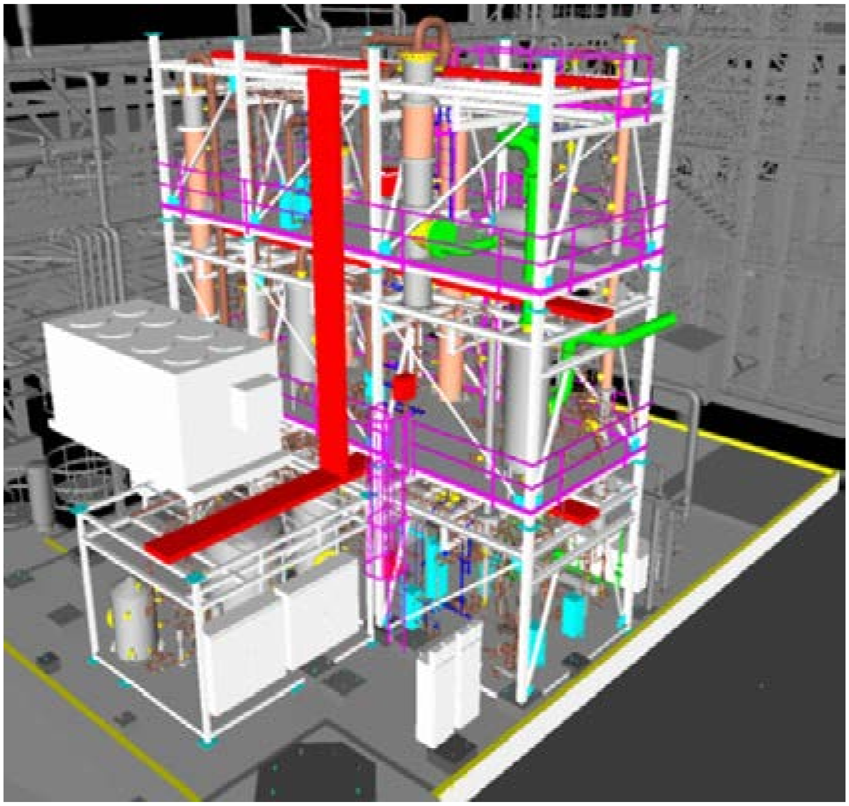

Figure 8: MSP 0.5-MWe CO_2 capture plant to be installed in NCCC Bay 2.

Testing of the large bench-scale integrated system, along with process modeling, provided information for the TEA and determined costs associated with the use of this system in a 550-MWe power plant. The cost of electricity (COE) found in the analysis of the mixed-salt technology was $127.3/MWh, yielding a reduction of 10.8% compared to the COE from the National Energy Technology Laboratory's (NETL) Case B12B of 142.8 $/MWh (from the Volume 1 report on fossil energy plants). The overall economics of the capture system are summarized in Table 2. The data in the table and the TEA will be updated upon completion of the current 0.5-MWe engineering-scale testing and parametric optimization studies.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	18	18
Normal Boiling Point	°C	100	100
Normal Freezing Point	°C	0	0
Vapor Pressure @ 15°C	bar	0.017	0.017
Manufacturing Cost for Solvent	$/kg	—	—
Working Solution			
Concentration	kg/kg	0.27-0.40	0.4
Specific Gravity (15°C/15°C)	—	1.1-1.3	1.2
Specific Heat Capacity @ STP	kJ/kg-K	2.8-3.5	3.1
Viscosity @ 15°C	cP	1.6	1.6
Absorption			
Pressure	bar	1	1
Temperature	°C	20-40	25-40
Equilibrium CO_2 Loading	mol/mol	0.6 (rich)	0.6 (rich)

Heat of Absorption	kJ/mol CO_2	1,000–1,200		<1,200
Solution Viscosity	cP	1.5-1.6		1.6
Desorption				
Pressure	bar	10-15		10
Temperature	°C	120-170		120-160
Equilibrium CO_2 Loading	mol/mol	0.2 (lean)		<0.2 (lean)
Heat of Desorption	kJ/mol CO_2	1,000-1,200		<1,200
Proposed Module Design			*(for equipment developers)*	
Flue Gas Flowrate	kg/hr		—2475	
CO_2 Recovery, Purity, and Pressure	% / % / bar	>90	>95	~12
Absorber Pressure Drop	bar		<0.1	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$		TBD	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of inorganic salt and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – In the MSP, CO_2 is captured by a chemical absorption that involves a series of ionic chemical reactions among CO_2, NH_3, K_2CO_3, and H_2O. The mechanism of CO_2 capture by chemical absorption using various chemical formulations has been studied extensively. The MSP chemistry comprises gas/liquid-phase mass transfer, followed by a series of chemical reactions in the liquid phase. The overall process chemistry can be summarized as:

$$K_2CO_3 - NH_3\text{-}xCO_2\text{-}H_2O + (y\text{-}x)\ CO_2 \leftrightarrow K_2CO_3 - NH_3\text{-}yCO_2\text{-}H_2O$$

where $y > x$

Solvent Contaminant Resistance – The solvent is expected to be resistant to several contaminants, such as sulfur oxides (SO_X) and nitrogen oxides (NO_X), nominally present in a flue gas stream. Sulfur dioxide (SO_2) reacts with the solvent, but it can be removed in the direct contact cooler section as sulfates. The resistance of the solvent to trace metals is not yet known.

Solvent Foaming Tendency – Solvent foaming tendency was not observed in the bench-scale tests.

Flue Gas Pretreatment Requirements – Unlike in an MEA system, a mixed-salt system does not require deep FGD; 200-ppm level SO_2 is acceptable.

Solvent Makeup Requirements – Mixed-salt is a mixture of NH_3 and K_2CO_3 and it is inexpensive and readily available. The loss of the solvent is expected to be less than 0.2 kg/tonne of CO_2 captured.

Waste Streams Generated – Water wash with trace ammonium sulfate from the SO_2 captured by the direct contact cooler.

Process Design Concept – See Figure 2.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	$/tonne CO_2	38	—
Cost of Carbon Avoided	$/tonne CO_2	TBD	—
Capital Expenditures	$/MWhr	57.1	—
Operating Expenditures	$/MWhr	60.3	—
Cost of Electricity	$/MWhr	127.3	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

technology advantages

- High-pressure regeneration of greater than 99% pure dry CO_2, resulting in reduced compression costs.
- Non-degradable solvent uses inexpensive, industrially available materials.
- Low NH_3 emissions using two-stage absorber approach.
- Low water usage.
- Operates with no solids in the absorber and no hazardous waste generation, low sensitivity to impurities.
- Higher efficiency compared to MEA due to low auxiliary loads, low heat of reaction (35–50 kJ/mol), low reboiler duty (~2 MJ/kg of CO_2), lack of need for stream polishing, high CO_2 loading capacity (10 wt%), and high-temperature (20–40°C) absorber operation without the need for solvent chilling.

R&D challenges

- Residual NH_3 in the exit gas stream.
- Reduction of NH_3 evaporation at higher reaction rates.
- High-pressure drop in absorber column.

status

Budget Period 3 has concluded. Budget Period 4 has been approved and is underway. The full plant is currently under construction. In addition, SRI has licensed the core MSP technology to Baker Hughes.

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Safeguarding Amines from Oxidation by Enabling Technologies

primary project goal

The University of Texas (UT) at Austin is developing technologies to safeguard amine-based carbon dioxide (CO_2) capture processes from solvent loss by oxidation. The project team is evaluating strategies to minimize amine oxidation in advanced second- and third-generation solvents caused by two of the most significant impurities: oxygen and nitrogen dioxide (NO_2). These effective technologies will reduce the cost and environmental risk of solvent-based carbon capture systems by addressing the effects of flue gas impurities on solvent loss.

technical goals

- Develop technology to overcome amine oxidation processes which includes nitrogen sparging, optimizing time and temperature with dissolved oxygen, optimizing time and temperature at the bottom of the stripper, and in the presence of adsorbed soluble iron.
- Baseline experiments will consist of gas-fired turbine conditions using 5 molar (m) piperazine and the advanced flash stripper (PZAS). Further experiments will extend this work to hydroxyl-ethyl-piperazine (HEP), the blend of amino-methyl-propanol (AMP)/PZ, and other amines.
- Test solvent oxidation mitigation methods in the lab.
- Test promising oxidation mitigation technologies at UT Austin Separations Research Program (SRP) (0.1 MWe).
- Text oxidation mitigation technologies at larger scale at National Carbon Capture Center (NCCC) at 1 MWe.
- Perform economic analysis of oxidation mitigation strategies.

technical content

The University of Texas at Austin has been developing a CO2 capture process (PZAS) using 5 m (30 wt%) PZ with the advanced flash stripper (AFS) (Figure 1). This solvent and process (PZAS) serves as the baseline for this project on solvent loss. Five molar PZ absorbs CO2 two times faster and has 1.36 times greater capacity than 30 wt% monoethanolamine (MEA). The AFS requires 15–20% less heat than a simple stripper. The PZAS system has been demonstrated at National Carbon Capture Center (NCCC) coal conditions (0.5 megawatt [MW]) and natural gas combined cycle (NGCC) conditions (0.3 MW) to require a heat duty less than 2.1 gigajoules (GJ)/tonne CO_2 removed.

The PZAS process is representative of second-generation amine scrubbing technology for CO_2 capture. It is fully published and represents a valuable case

program area:
Point Source Carbon Capture

ending scale:
Small Pilot

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Reduce Solvent Loss in Amine-Based CO_2 Capture Processes

participant:
University of Texas at Austin

project number:
FE0031861

predecessor projects:
N/A

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partners:
N/A

start date:
03.01.2020

percent complete:
93%

study with results that will be useful for proprietary second-generation processes, such as those offered by MHI and Shell/Cansolv. This technology sheet describes general approaches to minimizing oxidation and addresses the specific objectives of this project.

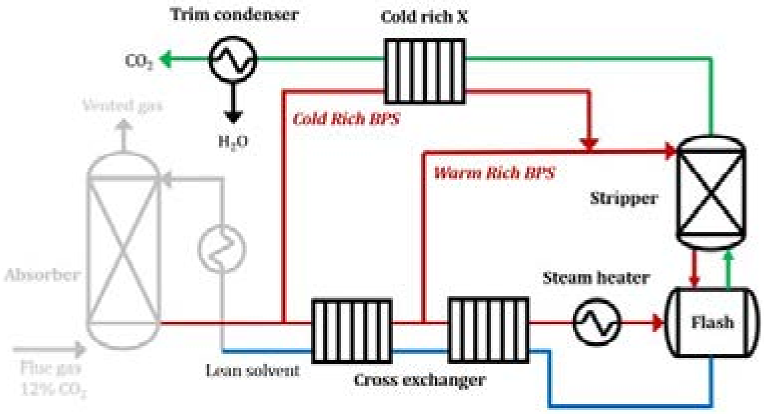

Figure 1: PZAS process.

Early bench-scale work showed that MEA, ethylenediamine, and other amines readily oxidize at 40–60°C when there is sufficient mass transfer to dissolve 0.05–0.21 bar oxygen (O_2) and some dissolved iron to initiate the free radical reaction. A necessary prerequisite for low oxidation is to select amines resistant to oxidation at 40–60°C. MHI, Shell/Cansolv, and other developers of second-generation amines have claimed that their solvents are resistant to oxidation. This project will evaluate PZ, HEP, and AMP/PZ, which have previously been shown to be resistant to oxidation.

Figure 2 shows the oxidation rate of PZ in four pilot plants as the accumulation of nitrogen degradation products. An important objective of this proposed work is to understand why there is less oxidation at the University of Texas Separations Research Program (UT-SRP) and NCCC-AFS so that those conditions can be applied to reduce oxidation at other sites, with other solvents, and with other process configurations. Four features may be responsible for low oxidation and represent opportunities that can be used commercially:

- There was no NO_2 in the flue gas at SRP and NCCC-AFS, so eliminating NO_2 may be an effective method of minimizing oxidation.
- The AFS provides flashing of the hottest solvent that removes dissolved oxygen before it reaches the maximum time and temperature in the stripper sump.
- The average residence time of hot lean solvent in the stripper sump is less than two minutes at UT-SRP and NCCC-AFS, which may minimize oxidation of amine by Fe^{+3}.
- Dissolved iron was less than 0.02 micromoles (mM) at UT-SRP and less than 0.10 parts per million (ppm) at NCCC-AFS.

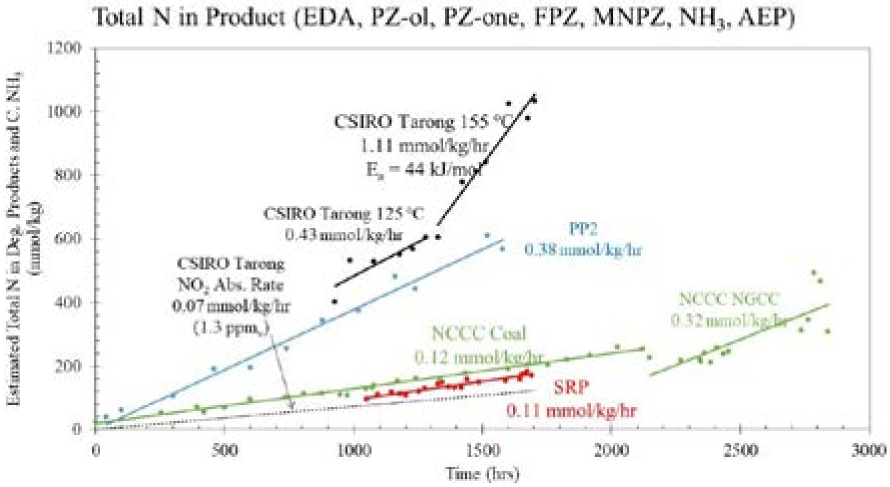

Figure 2: Total nitrogen quantified in degradation products and estimated cumulative ammonia at SRP, PP2, Tarong, and NCCC.

If an amine is resistant to oxidation at absorber conditions, rich solvent leaving the absorber sump will be saturated with oxygen at the absorber temperature (T) and PO2. When heated to stripper T in the cross exchanger, the faster kinetics at elevated T will result in oxidation in the rich line before the dissolved oxygen is removed by stripping or flashing. Researchers have demonstrated that PZ and methyldiethanolamine (MDEA)/PZ will oxidize by this mechanism.

The University of Texas at Austin has demonstrated, using bench-scale testing, that nitrogen sparging in the rich solvent can reduce oxidation by a factor of 3.5–4.5 when the rich solvent is exposed to 150°C for 30 seconds without prior stripping (Figure 3). These results also establish that oxidation requires residence time at elevated temperatures and would be negligible at absorber T. It appears that oxidation could be reduced by operating the stripper at lower temperatures.

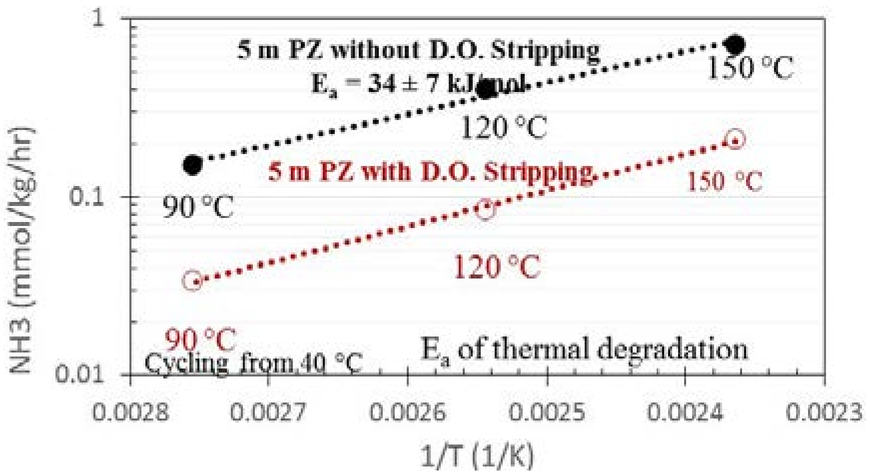

Figure 3: N_2 sparging reduces oxidation in high-temperature oxidation reactor (HTOR) by a factor 3.5–4.5. Cycling from 40°C with 0.1 mmol Fe^{+2}/kg. At 40°C absorption/40°C stripping, the ammonia (NH_3) production rate (0.025 mmol/kg-hr) would be negligible. (Nielsen, 2018)

In a pilot plant or larger-scale system, it is probable that oxidation by dissolved oxygen will occur in the hot liquid holdup between the cross exchanger and the top of the stripper where the oxygen will be removed. With a typical commercial simple stripper, the holdup in the rich feed line could be 40 sec (200 ft of pipe at 5 ft/s). However, in advanced configurations such as the AFS, the rich solvent feed can be 10–25°C colder than the stripper sump, thus reducing the oxidation rate by this mechanism, as seen at UT-SRP (Figure 2).

technology advantages

- Create environmentally friendly solvent processes for CO_2 capture.
- Safeguard second- and third-generation solvents from O_2 and NO_2 oxidation, reducing solvent degradation and extending solvent lifetime.

R&D challenges

- Using research and development (R&D) corrosion loop test results to design SRP pilot modifications for residence time tests.

status

The University of Texas at Austin developed an ultraviolet visible (UV-Vis) measurement technique as a method for evaluating metal ion (iron) species in amine solvents. Their experimental data allowed them to estimate adsorption rates and isotherms for PZ oxidation products on carbon in degraded samples. During this work, researchers learned that NO_2

pre-scrubbing was an effective way to reduce mononitrosopiperazine accumulation and that nitrogen sparging reduced the oxidation degradation products in the solvent. The project conclusions on Fe^{+2}/Fe^{+3} was the Fe^{+3} solubility in PZ varies solvent degradation from 0.02–2 mM. Carbon bed treatment reduced ammonia (NH_3) production and removed PZ degradation products at the NCCC and in HTOR. Carbon bed treatment removed 3 mM of "soluble" iron from the NCCC solvent system. All the "soluble" Fe must be removed to reduce oxidation. In addition, greater than 0.01 m PZ protects carbon steel from corrosion at the absorber temperature.

available reports/technical papers/presentations

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Chevron Natural Gas Carbon Capture Technology Testing Project

primary project goal

Chevron, partnering with Svante Technologies Inc. (Svante), Electricore Inc., Kiewit Engineering Group Inc., Kiewit Power Constructors, and Offshore Technical Services, is validating Svante's transformational VeloxoTherm™ solid sorbent carbon capture technology at engineering scale under indicative natural gas flue gas conditions at Chevron's Kern River Oil Field.

technical goals

- Complete the design, construction, commissioning, and long-term testing of an engineering-scale plant of approximately 25 tonnes per day (TPD) under steady-state and dynamic conditions at varying flue gas carbon dioxide (CO_2) concentrations (4–14%) from a once-through steam generator (OTSG).
- Conduct a techno-economic analysis (TEA) on the Svante rapid-cycle thermal swing adsorption (RC-TSA) technology as integrated into a nominal 550-megawatt (MW) (net) natural gas power plant with a comprehensive gap analysis.
- Conduct a comprehensive gap analysis.
- Complete a Technology Maturation Plan (TMP) and Environment, Health, and Safety (EH&S) Risk Assessment.

technical content

The VeloxoTherm process developed by Svante is comprised of an RC-TSA process that uses a proprietary novel metal-organic framework (MOF) sorbent material, Calgary Framework-20 (CALF-20), which is a patented architecture of structured adsorbent beds (SABs). The innovative RC-TSA process occurs inside Svante's rotary adsorption machine designed to capture CO_2 from industrial and natural gas-fired flue gas streams. SABs possess unique physical and transport properties that serve to greatly improve the performance of gas separation, enabling fast cycle times and small equipment sizes that deliver attractive capture economics. Figure 1 shows the Rotary Adsorption Machine (RAM) design at the core of the technology. Svante uses solid adsorbents that have very high surface-to-volume ratios to capture CO_2. A new class of advanced sorbent material, CALF-20, has been developed by Svante and lab-tested under DOE Cooperative Agreement No. DE-FE0031732 and field-tested in Q3-2020 at a cement plant in Vancouver, Canada.

program area:

Point Source Carbon Capture

ending scale:

Small Pilot

application:

Post-Combustion Power Generation PSC

key technology:

Sorbents

project focus:

Metal-Organic Framework-Based Sorbent

participant:

Chevron

project number:

FE0031944

predecessor projects:

N/A

NETL project manager:

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partners:

Electricore Inc.; Svante Technologies Inc.; Kiewit Engineering Group Inc.; Kiewit Power Constructors; Offshore Technical Services

start date:

10.01.2020

percent complete:

83%

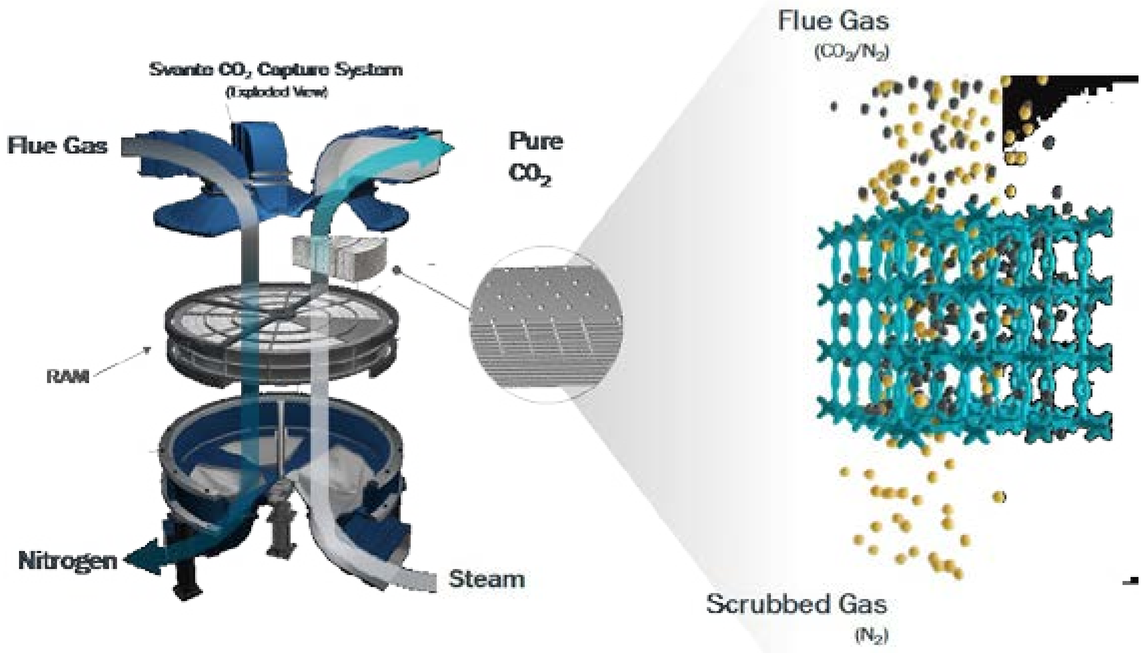

Figure 1: VeloxoTherm™ Rotary Adsorption Machine (RAM).

The sorbent material exhibits unique resistance to sulfur oxide (SO_X), nitrogen oxide (NO_X), and oxygen impurities, as well as moisture swing. Utilizing CALF-20 eliminates the need for a site nitrogen generator that is required on an amine-doped silica sorbent plant to protect the adsorbent from oxidation during conditioning steps. The VeloxoTherm process has been scaled-up to 30 TPD of CO_2 and is undergoing demonstration with flue gas derived from natural gas combustion at Cenovus in Canada using a first-generation sorbent material of amine-doped silica. In this project, the team leveraged the design and learnings from the Cenovus 30-TPD project to improve the performance and flexibility of a second-of-a-kind (SOAK) engineering-scale plant (400 Series) using CALF-20 MOF sorbent material.

The test program was performed at a feed CO_2 concentration of approximately 8% (10.5% dry basis) for normal steady-state operations, with flexibility to gather data and test equipment at a wide operating range of 4–14% CO_2 in the feed by employing an air-mixing and CO_2 product recycling system. The CO_2 product specification is at 95% purity (versus 85% in the Cenovus unit). To achieve this product purity and process flexibility, a reflux step was added to the RAM and balance of plant (BOP).

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density	kg/m^3	350-380	350-380
Bulk Density	kg/m^3	NA	NA
Average Particle Diameter	mm	0.31-0.35	0.31-0.35
Particle Void Fraction	m^3/m^3	NA	NA
Packing Density	m^2/m^3	2300-2500	2300-2500
Solid Heat Capacity @ STP	kJ/kg-K	1.4-1.6	1.4-1.6
Thermal Conductivity	W/(m-K)	0.25-0.35	0.25-0.35
Manufacturing Cost for Sorbent	$/kg	30-35	20-25
Adsorption			
Pressure	bar	1-1.1	1-1.1
Temperature	°C	50	50
Equilibrium Loading (20% CO_2)	g mol CO_2/kg	1.7-1.9	1.7-1.9
Heat of Adsorption	kJ/mol CO_2	35-38	35-38

Desorption			
Pressure	bar	0.8-1.0	0.8-1.0
Temperature	°C	120-140	120-140
Equilibrium CO_2 Loading (20% CO2)	g mol CO_2/kg	0.3-0.4	0.3-0.4
Heat of Desorption	kJ/mol CO_2	35-38	35-38
Proposed Module Design			
Flow Arrangement/Operation	—	Rapid cycle rotary valves moving bed	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90-95 95 150	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the laminated sorbent composite sheet area/filter bed volume.

Equilibrium Loading – The basis for CO_2 loadings is mass of dry sorbent measured with 20% CO_2 in N_2 mixture without moisture.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Physisorption.

Sorbent Contaminant Resistance – High oxidation resistance below 50 parts per million (ppm) SO_X and NO_X.

Sorbent Attrition and Thermal/Hydrothermal Stability – Very stable under direct steam regeneration.

Flue Gas Pretreatment Requirements – Conventional Direct Contact Cooler (DCC).

Sorbent Make-Up Requirements – A three- to five-year lifetime without bed replacement.

Waste Streams Generated – No chemicals in depleted N_2 and typical cooling water blow-down.

TABLE 2: CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	50	30
Cost of Carbon Avoided	\$/tonne CO_2	Site specific	Site specific
Capital Expenditures	\$/TPD	70,000 to 80,000	60,000 to 70,000
Operating Expenditures	\$/tonne CO_2	26 - 28	20-23

Cost of Electricity	\$/tonne CO_2	12-18	12-18

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided is site specific depending on the source of electricity and steam.

Capital Expenditures – Projected capital expenditures in dollars per tonne per day of capacity.

Operating Expenditures – Projected operating expenditures in dollars per unit of tonne of CO_2 produced including filter bed replacement and compression cost.

Cost of Electricity – Projected cost of electricity per unit of tonne of CO_2 produced for a range of price of electricity of 3.5 to 6 cents per kWh.

Scale of Validation of Technology Used in TEA – The technology numbers were validated for use in the TEA from pilot-scale data.

technology advantages

- Svante's technology can utilize regeneration steam at slight vacuum. This enables the use of low-temperature waste heat from the flue gas, compression train, and base plant, greatly reducing operating cost of the carbon capture plant.
- Svante's solid adsorption technology does not release secondary emissions or effluents that could be costly to contain and could complicate permitting of the project.
- Novel technology replaces large chemical solvent towers (conventional approach) with a single piece of compact equipment, reducing capital expenses (CAPEX) and plot space.
- Advanced sorbent material exhibits sharper temperature and pressure swing adsorption and desorption, which allows for lower energy loads and faster kinetic rates.
- The proprietary material also exhibits unique resistance to SO_X and NO_X, oxygen impurities, and moisture swings.

R&D challenges

- Engineering-scale testing and analysis.

status

Chevron's partner, Svante, completed the Preliminary TEA Summary Report and process flow diagram identifying major process equipment of a retrofit to capture CO_2 from existing NGCC power plant facilities. Svante completed an upgrade of the Rotary Seal Validation Testing (RSVS) for design validation of key parameters. A 50-day RSVS was completed. Chevron demonstration site construction, full commissioning, startup, and operator training was completed. The project demonstrated MOF sorbent scale-up capabilities (BASF manufacturing) for the larger-scale testing. Additional and complementary tests conducted at Svante confirm material properties, sorbent characterization, and slurry processability into coated laminates are meeting current specifications. Ongoing research and development (R&D) efforts include 14% indicative coal flue gas feed testing, 4% indicative NGCC flue gas testing, base performance and steady-state feed testing, and load-following and intermittence testing.

available reports/technical papers/presentations

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Sorbent-Based Post-Combustion CO_2 Slipstream Testing

primary project goal

TDA Research Inc. completed pilot-scale testing of their alkalized alumina sorbent technology for post-combustion carbon dioxide (CO_2) capture. A pilot-scale skid was designed and installed at National Carbon Capture Center (NCCC) to process coal-derived flue gas equivalent to 0.5 megawatt-electric (MWe) of power generation. Parametric and long-term steady-state testing was completed to demonstrate the effectiveness of the technology to reduce the cost of CO_2 capture and to develop scale-up conditions for the process.

technical goals

- Modify bench-scale unit to mimic proposed pilot plant configuration and conduct testing in bench unit to optimize process and collect data for pilot plant design.
- Characterize breakthrough performance and pressure drop for different sorbent pellet sizes.
- Design pilot plant unit based on developed low-cost alkalized alumina sorbent technology.
- Scale-up production of sorbent.
- Fabricate and install pilot plant unit at the NCCC.
- Perform parametric and steady-state testing on pilot plant using actual flue gas.
- Update environment, health, and safety (EH&S) study and techno-economic analysis (TEA) based on pilot plant testing results.

technical content

TDA Research Inc. designed and operated a 0.5-MWe pilot-scale process for post-combustion CO_2 capture based on their novel alkalized alumina sorbent developed previously in a U.S. Department of Energy (DOE)-funded project (DE-NT0005497). The regenerable sorbent acts as a physical adsorbent for CO_2. The CO_2 capture process runs near isothermally at around 140–150°C in both adsorption and regeneration, requiring no heating or cooling between adsorption and regeneration steps. The sorbent is regenerated with low pressure (15.5 pounds per square inch absolute [psia]) steam. The sorbent shows excellent tolerance to contaminants, including sulfur dioxide (SO_2) and nitrogen oxides (NO_X).

An overall schematic of TDA's system is shown in Figure 1, consisting of two primary components: (1) the adsorber/regenerator unit and (2) the CO_2 compression and purification unit. The process is designed for the sorbent to remove the CO_2 from the flue gas at intermediate temperature and near-ambient

program area:
Point Source Carbon Capture

ending scale:
Small Pilot

application:
Post-Combustion Power Generation PSC

key technology:
Sorbents

project focus:
Alkalized Alumina Sorbent Pilot Test

participant:
TDA Research Inc.

project number:
FE0012870

predecessor projects:
NT0005497

NETL project manager:
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partners:
University of California at Irvine; Porocel; Babcock and Wilcox; Louisiana State University; Western Research Institute; ExxonMobil; National Carbon Capture Center

start date:
02.03.2014

percent complete:
100%

pressure, and then be regenerated with low-pressure superheated steam. A multiple fixed-bed design is used, providing counter-flow contact between solids and gases, where the beds cycle between adsorption and desorption. The flue gas flows in parallel through the adsorption beds and in series across regeneration beds. This setup has several advantages over moving beds, including a simple-bed design, basic ductwork, low construction cost, and the elimination of parasitic power required to move the sorbent, all of which result in a lower overall cost than moving beds.

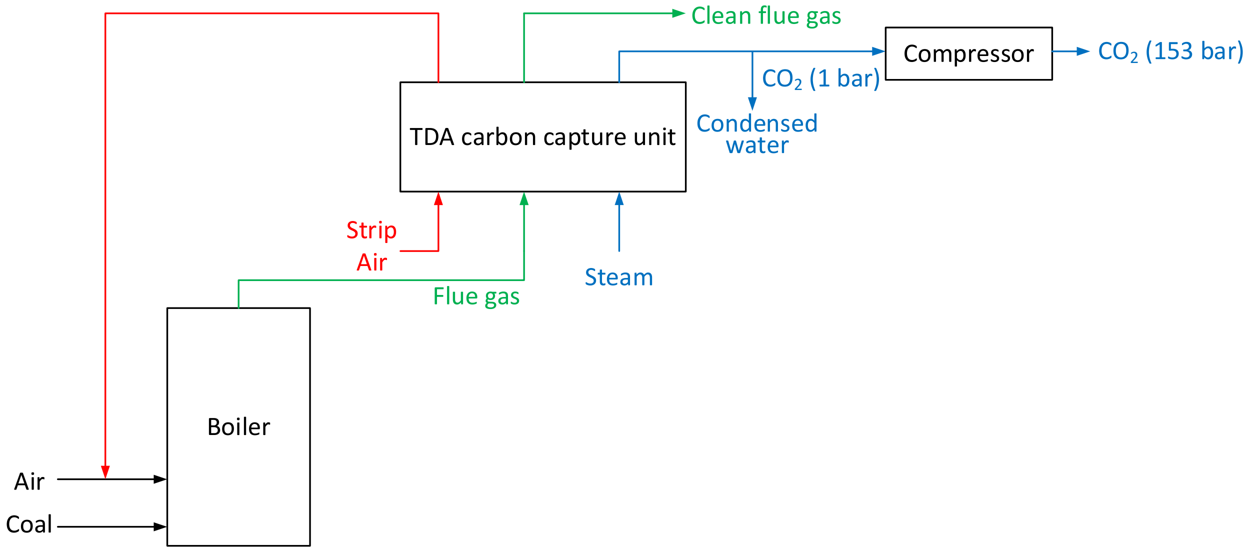

Figure 1: Block flow diagram of TDA's CO_2 capture system.

The process scheme was optimized through testing with sorbent loaded in a 10-bed bench-scale unit. Operating in steam saver (SS) mode to reduce the need for fresh regeneration steam resulted in improved capture performance. TDA evaluated several different sorbents, including commercial and customized sorbents, on the bench-scale unit to determine an optimal sorbent for testing at the NCCC.

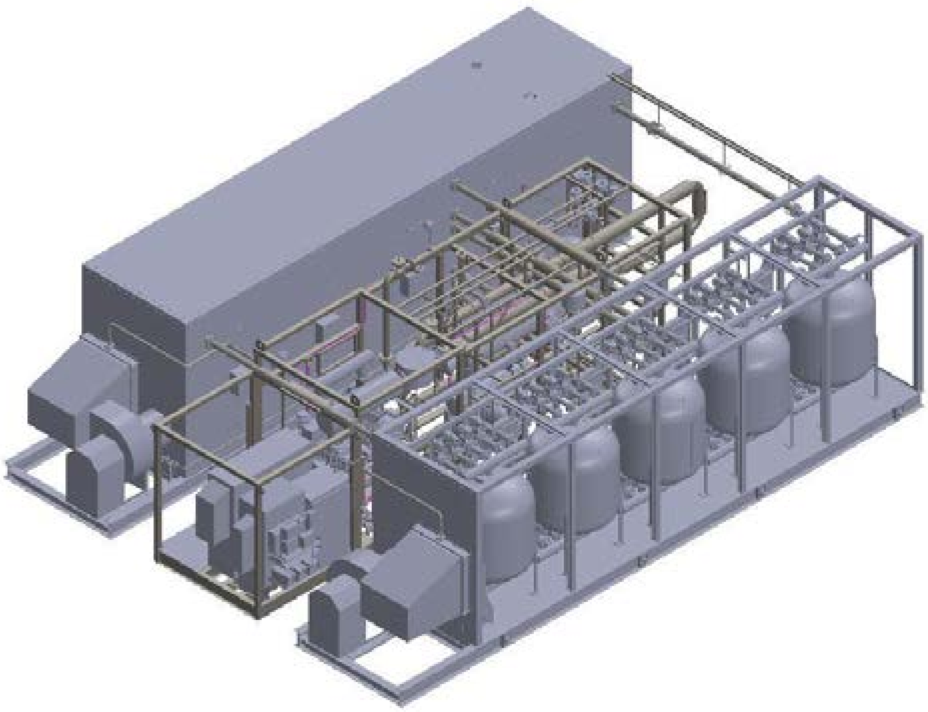

Figure 2: TDA's 0.5-MWe test skid.

The slipstream pilot plant is a 0.5-MWe skid-mounted system (shown in Figure 2) with two sorbent bed trailers, each housing five sorbent beds. Each trailer is insulated and heated to provide an isothermal environment. The adsorption/regeneration system containing multiple fixed beds with sorbent switches between adsorption, regeneration, and purge operations. The complete slipstream pilot unit includes adsorption/regeneration beds, heat exchangers, blowers, valving, and instrumentation.

Slipstream pilot unit testing under both parametric and long-term steady-state conditions using actual coal-fired and natural gas (NG) flue gases provided data and recommended operating conditions to update the TEA and EH&S assessment, as well as for definition of recommended scale-up conditions. The test results showed that TDA's process can achieve 90% capture and 95% CO_2 purity for both coal and natural gas flue gases. For a 550-MWe supercritical coal-fired power plant with CO_2 capture, the capture cost for TDA's process is $34.9/tonne CO_2 captured, which meets DOE's goal of $40/tonne and is 17.1% less than the DOE baseline Case 12.

During initial testing, the sorbent had lower performance than expected, due to manufacturing inaccuracies. As a result, TDA developed a reprocessing approach to improve the sorbent's performance. However, during a 3.5-month shutdown of the plant, the sorbent transformed to a form not effective in CO_2 capture. Therefore, TDA's sorbent was extracted and five of the beds were filled with Dynocel (a customized sorbent) and the other five beds were filled with Chlorocel (a commercial sorbent) for the remainder of the test campaign, in which a long-term (three-month) test resulted in approximately 91% CO_2 capture and ≥95% CO_2 purity for both coal and natural gas flue gases.

The sorbent and process parameters are provided in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1320	750
Bulk Density	kg/m^3	790	520
Average Particle Diameter	mm	1.5	3.175
Particle Void Fraction	m^3/m^3	0.40	0.55
Packing Density	m^2/m^3	9.4E+07	9.4E+07
Solid Heat Capacity @ STP	kJ/kg-K	0.72	0.72
Crush Strength	kg$_f$	8	8
Manufacturing Cost for Sorbent	$/kg	6.5	3
Adsorption			
Pressure	bar	1.12	1.12
Temperature	°C	140	140
Equilibrium Loading	g mol CO_2/kg	1.0	1.5
Heat of Adsorption	kJ/mol CO_2	-12.5 to -41.9	-12.5 to -41.9
Desorption			
Pressure	bar	1.17	1.17
Temperature	°C	150	150
Equilibrium CO_2 Loading	g mol CO_2/kg	0.93	1.0
Heat of Desorption	kJ/mol CO_2	12.5 to 41.9	12.5 to 41.9
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	Simulated moving bed	
Flue Gas Flowrate	kg/hr	2,273	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90 / 95 / 1.013	
Adsorber Pressure Drop	bar	0.02	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atmosphere [atm]).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated bulk manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – The sorbent is an adsorbent and is regenerated with steam.

Sorbent Contaminant Resistance – Based on extended cycling 1,500 hours with simulated flue gas with 13.8% CO_2, 104 parts per million (ppm) SO_2, 3% oxygen (O_2), and 9% water (H_2O), sorbent life was calculated to be one year with 5 ppm of SO_2. No effect of NO_X on capacity was seen after 200 cycles with 739 ppm nitric oxide (NO) and 84 ppm nitrogen dioxide (NO_2).

Sorbent Attrition and Thermal/Hydrothermal Stability – None provided.

Flue Gas Pretreatment Requirements – Flue gas should have less than 5 ppm sulfur oxides (SO_X).

Sorbent Makeup Requirements – 15% per year.

Waste Streams Generated – None known.

Process Design Concept – See Figure 1 above.

Proposed Module Design – Note the module location, as well as the pressure, temperature, and composition of the gas entering the module. TDA's CO_2 capture system is located downstream of the FGD unit. The adsorbent removes dilute

CO_2 from the flue gas (10–14% CO_2, 8–10% H_2O, less than 5 ppm SO_2) at intermediate temperature (140°C) and near-ambient pressure.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	34.90	40.0
Cost of Carbon Avoided	\$/tonne CO_2	47.65	—
Capital Expenditures	\$/MWhr	52.0	—
Operating Expenditures	\$/MWhr	40.2	—
Cost of Electricity	\$/MWhr	92.2	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – The analysis was based on Case 12 in “Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity, Rev. 2.”

Scale of Validation of Technology Used in TEA – The analysis was based on pilot-scale testing.

technology advantages

- Inexpensive, durable sorbent.
- Low-pressure (17 psia) steam for sorbent regeneration, low regeneration energy.
- Near isothermal operation.
- No heat recovery from solids required.
- Rapid adsorption/regeneration kinetics.
- Low heat of adsorption.
- Counter-current operation maximizes capture efficiency and sorbent loading.
- No secondary pollutants generated.

R&D challenges

- Minimize the parasitic demands from the sorbent system.
- Effectively produce a sorbent from low-cost raw materials with extensive regenerative life.

status

TDA Research Inc. designed and constructed a 0.5-MWe-scale pilot plant test unit and produced sufficient sorbent for testing. Parametric tests were completed with actual coal flue gas and simulated natural gas flue gas (coal flue gas diluted with air). High-purity CO_2 product (greater than 95%) was achieved by tuning a process step that diverts a small fraction of the product stream when a bed first comes onto regeneration. Long-term testing was completed, with 90% capture and 95+% CO_2 purity maintained throughout the test by adjusting operating parameters. TDA also developed a process to restore the sorbent capacity after it has been in service for a long time.

available reports/technical papers/presentations

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Yi, F. "Sorbent Based Post-Combustion CO_2 Capture Slipstream Testing," Project Final Review, July 2022. *https://netl.doe.gov/projects/plp-download.aspx?id=13713&filename=Sorbent+Based+Post-Combustion+CO2+Capture+Slipstream+Testing.pdf*.

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Engineering-Scale Design and Testing of Transformational Membrane Technology for CO_2 Capture

primary project goal

Gas Technology Institute (GTI) is advancing the Ohio State University's (OSU) transformational membrane-based carbon dioxide (CO_2) capture technology through engineering-scale testing on actual coal-derived flue gas at the Wyoming Integrated Test Center (ITC).

technical goals

- Design and build an engineering-scale CO_2 capture system using OSU's membrane in commercial-size membrane modules.
- Conduct tests on coal flue gas at ITC and demonstrate a continuous, steady-state operation for a minimum of two months. Gather the data necessary for process scale-up.
- Complete initial detailed techno-economic analysis (TEA) and detailed design of the engineering-scale system.
- Complete construction of the engineering-scale system and install it at ITC.
- Complete engineering-scale testing and analysis and achieve 95% CO_2 purity, and validate a capture cost.

technical content

The amine-containing CO_2-selective membranes developed under U.S. Department of Energy (DOE)-funded projects (FE0031731; FE0026919; FE0007632) consist of a thin selective layer coated on a polymer support and exhibit high CO_2 permeance and very high selectivity of CO2 over nitrogen (N_2). The performance is based on a facilitated transport mechanism, in which a reversible CO_2 reaction with fixed-site and mobile amine carriers enhances the CO_2/N_2 separation. OSU has developed the membrane in commercial-size—a spiral-wound membrane module shown in Figure 1. The novel CO_2-selective membranes are synthesized by formulating amine-containing polymer into a thin-film composite membrane configuration (Figure 2). The polymer selective layer, typically 100–200-nm thick, carries out the CO_2/N_2 separation. The highly gas-permeable nanoporous support layer provides the mechanical strength necessary for use in a separation module.

program area:

Point Source Carbon Capture

ending scale:

Small Pilot

application:

Post-Combustion Power Generation PSC

key technology:

Membranes

project focus:

Membrane Technology for Coal-Fired Power Plants

participant:

Gas Technology Institute

project number:

FE0031946

predecessor projects:

FE0007632; FE0026919; FE0031731

NETL project manager:

Mariah Young
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principal investigator:

Shiguang Li
Gas Technology Institute
shiguang.li@gastechnology.org

partners:

Ohio State University;
Trimeric Corporation;
Wyoming Integrated Test Center

start date:

10.01.2020

percent complete:

35%

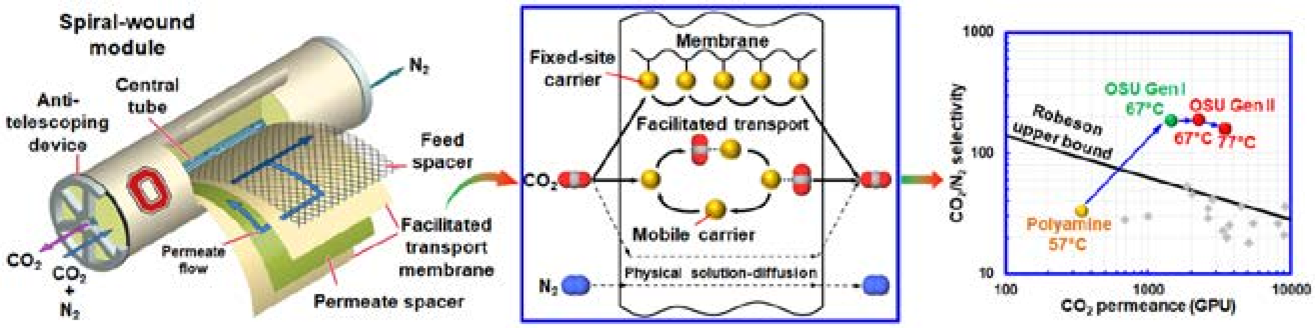

Figure 1: Diagrams of the membrane module (left), transport mechanism (middle), and performance (right).

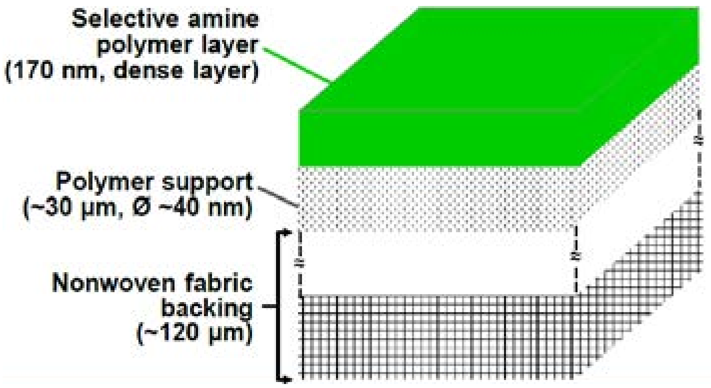

Figure 2: Schematic of the thin-film composite membrane.

In the presence of a transmembrane partial pressure difference, as illustrated in Figure 1 (middle), CO_2 molecules from the feed side dissolve in the selective layer via reaction with the amine carriers ($CO_2 + R\text{-}NH_2 + H_2O \rightleftharpoons R\text{-}NH^+ + HCO_3^-$). The reaction product (HCO_3^-) diffuses across the membrane and eventually is converted back to the CO_2 molecules via the reverse reaction and released on the low-pressure side.

The fixed-site carrier is covalently bound to the polymer, and the mobile carrier exists as nonvolatile amino acid salt. Thus, the carriers stay in the membrane. The permeation of N_2 is extremely slow due to the lack of reactive diffusion. The disparate permeation rates result in a high CO_2 permeability and a high CO_2/N_2 selectivity, which are usually more than three-fold of those shown by membranes relying on size or condensability discrimination through the solution-diffusion mechanism.

The project is to design and build a nominal 1-megawatt-electric (MWe) engineering-scale unit (approximately 20 tonnes per day [TPD]) using this transformational membrane with commercial-size modules and test it with coal-fired flue gases at ITC, located at Basin Electric Power Cooperative's Dry Fork Station, seven miles north of Gillette, Wyoming. The testing goal is to capture 60–90% CO_2 of the feed CO_2 with approximately 95% CO_2 purity. The test system will proceed in two modes—a single-stage process that is anticipated to be preferred for the lower CO_2 capture rates and an innovative retentate recycle two-stage process for the higher CO_2 capture rates (Figure 3). The data will be used in the TEA to determine the optimum configuration to meet DOE's programmatic goals.

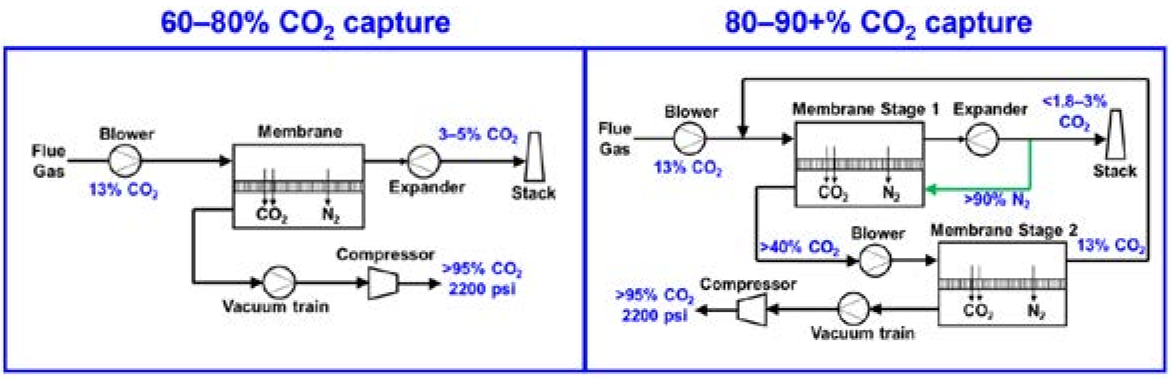

Figure 3: Flow diagrams of a one-stage membrane process to achieve 60–80% capture (left) and an innovative process to achieve >80% capture (right).

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	amine-containing polymer	
Materials of Fabrication for Support Layer	—	polyethersulfone on non-woven fabric	
Nominal Thickness of Selective Layer	nm	170	170
Membrane Geometry	—	flat sheet	flat sheet
Max Trans-Membrane Pressure	bar	4	4
Hours Tested without Significant Degradation	—	2,500	2,500
Manufacturing Cost for Membrane Material	$\$/m^2$	20	20
Membrane Performance			
Temperature	°C	77	77
CO_2 Pressure Normalized Flux	GPU or equivalent	3,500	3,500
CO_2/H_2O Selectivity	—	1	1
CO_2/N_2 Selectivity	—	160	160
Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	spiral-wound, countercurrent	
Packing Density	m^2/m^3	~2,000	
Permeate-Side Fluid	—	vacuum or retentate recycle	
Flue Gas Flowrate	ft^3/min	30.9	
CO_2 Recovery, Purity, and Pressure	%/%/bar	60–90 >95 1	
Pressure Drops Shell/Tube Side	psi/m	1.5/1.5	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{m^2}$	21.2	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-10} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD (flue gas desulfurization; wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.79 psia	135°F	12.46	14.97	68.12	3.64	0.81	42	74

Other Parameter Descriptions:

Membrane Permeation Mechanism – Facilitated transport for amine-containing selective layer.

Contaminant Resistance – Resist up to 3 parts per million volume (ppmv) sulfur dioxide (SO_2) and nitrogen dioxide (NO_2), respectively.

Flue Gas Pretreatment Requirements – Removal of particulates; SO_2 and NO_2 polishing to 3 ppmv.

Membrane Replacement Requirements – Estimated approximately four years.

Waste Streams Generated – Nitrogen with water, about 1% CO_2, and minor impurities.

Process Design Concept – Flowsheet diagrams shown in Figure 3.

Proposed Module Design – See Figure 1 (left).

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS (90% CAPTURE)

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	40.3	40.0
Capital Expenditures	\$/MWhr	19.8	20.0
Operating Expenditures	\$/MWhr	10.5	12.0
Cost of Electricity	\$/MWhr	100.5	100.4

TABLE 3: POWER PLANT CARBON CAPTURE ECONOMICS (70% CAPTURE)

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	33.6	30.0
Capital Expenditures	\$/MWhr	10.6	10.5
Operating Expenditures	\$/MWhr	6.8	7.0

Cost of Electricity	\$/MWhr	85.9	86.0

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – "Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity, Rev. 4" report (*https://www.netl.doe.gov/energy-analysis/details?id=3745*).

Scale of Validation of Technology Used in TEA – Bench-scale testing.

Qualifying Information or Assumptions – A direct contact cooler is not needed to condition the flue gas since the membrane is operated at 77°C. The purchased equipment cost for the turbo expander is \$300/kilowatt-electric (kWe) based on literature data.

technology advantages

- Simplicity of membrane design leads to low-cost membranes.
- High CO_2 selectivity due to facilitated transport mechanism.
- Sensitivity study suggests that the COE at 70% CO_2 capture can be approximately 30% less than the DOE baseline approach.

R&D challenges

- Membrane stability in the presence of high-level contaminants, such as SO_2 and nitrogen oxide (NO_X).
- Corrosion or particulates fouling of membrane system equipment.

status

OSU has demonstrated that their engineering-scale prototype membrane exhibited CO_2 permeance of 3,500 GPU and CO_2/N_2 selectivity of 160 at 77°C, consistent with the Gen II membrane performance obtained previously. The TEA based on bench-scale data suggests the membrane can achieve approximately 30% reduction in COE for a 70% CO_2 capture rate with a one-stage process compared with the DOE baseline approach and approximately \$33.6/tonne for a 90% CO_2 capture rate with an innovative two-stage process. Current efforts are focusing upon detailed engineering design of the test skid, scheduling procurement, construction, and factory-acceptance testing and site-installation planning.

available reports/technical papers/presentations

Shiguang Li, GTI Energy, Yang Han, Ohio State University, "Engineering Scale Design and Testing of Transformational Membrane Technology for CO_2 Capture," 2024 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_PSCC_7_Li.pdf*.

Shiguang Li, GTI Energy, Yang Han, Ohio State University, "Engineering Scale Design and Testing of Transformational Membrane Technology for CO_2 Capture," 2023 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC29_Li.pdf*.

Shiguang Li, GTI Energy, “Engineering Scale Design and Testing of Transformational Membrane Technology for CO_2 Capture,” 2023 Budget Period 1 Project Review Meeting, Pittsburgh, PA, October 2022.

Shiguang Li, GTI Energy, Yang Han, Ohio State University, “Engineering Scale Design and Testing of Transformational Membrane Technology for CO_2 Capture,” 2022 Carbon Management Project Review Meeting, Pittsburgh, PA, August 2022.

Shiguang Li, GTI Energy, “Engineering Scale Design and Testing of Transformational Membrane Technology for CO_2 Capture,” 2022 Project Update Meeting, Pittsburgh, PA, July 2022.

Shiguang Li, Yang Han, Winston Ho, Travis Pyrzynski, Weiwei Xu, and Howard Meyer, “Engineering Scale Design and Testing of Transformational Membrane Technology for CO_2 Capture,” NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/S-Li%2C-GTI-Transformational-Membrane-Testing.pdf*.

Shiguang Li, Yang Han, Winston Ho, Travis Pyrzynski, Weiwei Xu, Howard Meyer, and John Marion, “Engineering Scale Design and Testing of Transformational Membrane Technology for CO_2 Capture,” Project kickoff meeting presentation, Pittsburgh, PA, July 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11034&filename=Engineering+Scale+Design+and+Testing+of+Transformational+Membrane+Technology+for+CO2+Capture.pdf*.

Membrane-Sorbent Hybrid System for Post-Combustion Carbon Capture

primary project goal

TDA Research Inc. (TDA) designed and constructed a 1-megawatt-electric (MWe)-scale membrane-sorbent hybrid post-combustion carbon capture system and evaluated its operation in a long-duration field test using industrial flue gas that closely resembles coal-fired flue gas. The hybrid process consists of a polymeric membrane and low-temperature physical adsorbent to remove carbon dioxide (CO_2) from flue gas.

technical goals

- Design the 1-MWe-scale test unit.
- Fabricate the test unit.
- Install the test unit at the Technology Centre Mongstad (TCM).
- Complete a nine- to 12-month-long field test campaign at TCM using actual flue gas.
- Complete an updated techno-economic analysis (TEA) based on the field test data.

technical content

TDA designed, constructed, and operated a slipstream 1-MWe pilot-scale process for post-combustion CO_2 capture using actual flue gas. The hybrid process consists of a polymeric membrane and a low-temperature physical adsorbent. This technology is based on TDA's previously developed sorbent, and a membrane developed by Membrane Technology and Research (MTR). TDA's sorbent uses a mesoporous carbon modified with surface functional groups to remove CO_2 via physical adsorption. Carbon dioxide-surface interaction is strong enough to allow low partial pressure operation and regeneration energy is low because the CO_2 is not bonded to the sorbent. The feasibility of the hybrid sorbent-membrane system was initially proven in a prior U.S. Department of Energy (DOE)-funded project (DE-SC0011885) using coal-derived flue gas at 4-kilowatt-electric (kWe) scale, showing greater than 90% CO_2 capture and high purity.

An overall schematic of TDA's system is shown in Figure 1, consisting of two primary components: (1) the membrane unit and (2) the CO_2 adsorption unit. The membrane operates at approximately 50°C under mild vacuum, removing approximately 50% of the CO_2 and nearly all the water. The reduced vacuum pump requirements reduce power consumption and system cost. The sorbent removes the remaining CO_2 from the membrane effluent to ensure 90% carbon capture. Sorbent regeneration is facilitated using boiler feed air as a sweep gas and the CO_2-laden air after sorbent regeneration is fed to the boiler to generate a CO_2-rich

program area:
Point Source Carbon Capture

ending scale:
Small Pilot

application:
Post-Combustion Power Generation PSC

key technology:
Hybrid

project focus:
Membrane-Sorbent Hybrid System for CO_2 Capture from Coal-Fired Flue Gas

participant:
TDA Research Inc.

project number:
FE0031603

predecessor projects:
SC0011885

NETL project manager:
Andrew O'Palko
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principal investigator:
Gokhan Alptekin
TDA Research Inc.
galptekin@tda.com

partners:
Membrane Technology and Research; Technology Centre Mongstad; Gas Technology Institute; University of California Irvine

start date:
08.15.2018

percent complete:
100%

flue gas stream to increase the driving force across the membrane. The overall energy intake of the CO_2 capture process is reduced by using a hybrid membrane-sorbent configuration, while the capture efficiency is not degraded.

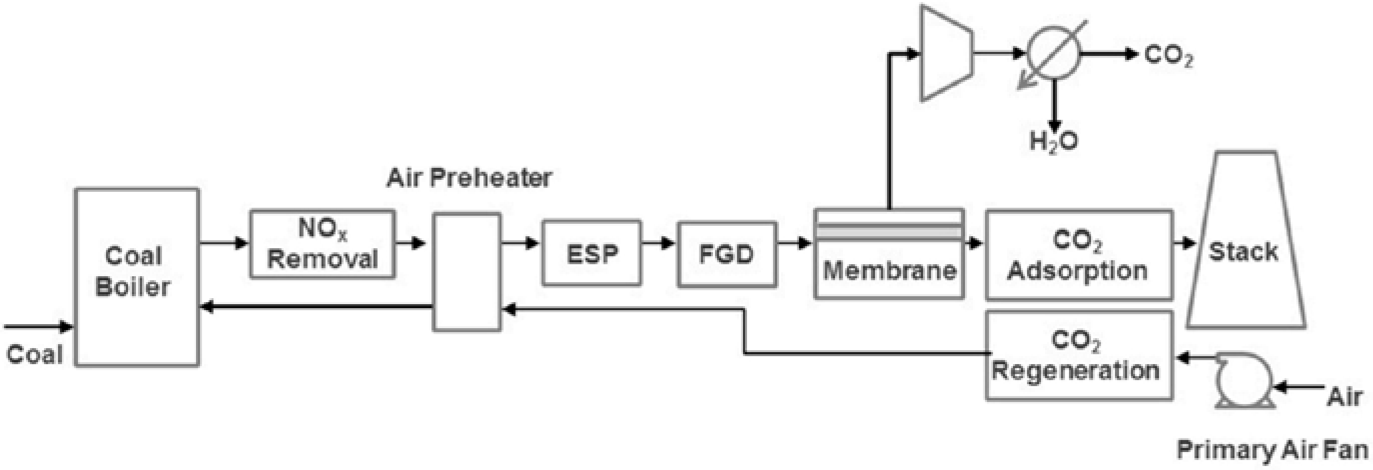

Figure 1: Flow diagram of the TDA Research hybrid membrane-sorbent CO_2 capture system.

TDA developed its modular sorbent bed concept known as the radial outflow reactor, shown in Figure 2. Two modules were used, one operating in adsorption mode and one in desorption mode, to provide continuous transfer of CO_2 into the boiler air. For the 1-MWe-scale tests at TCM, three modules were used, as shown in Figure 3, with two of the modules operating in series to show how the modular design concept works.

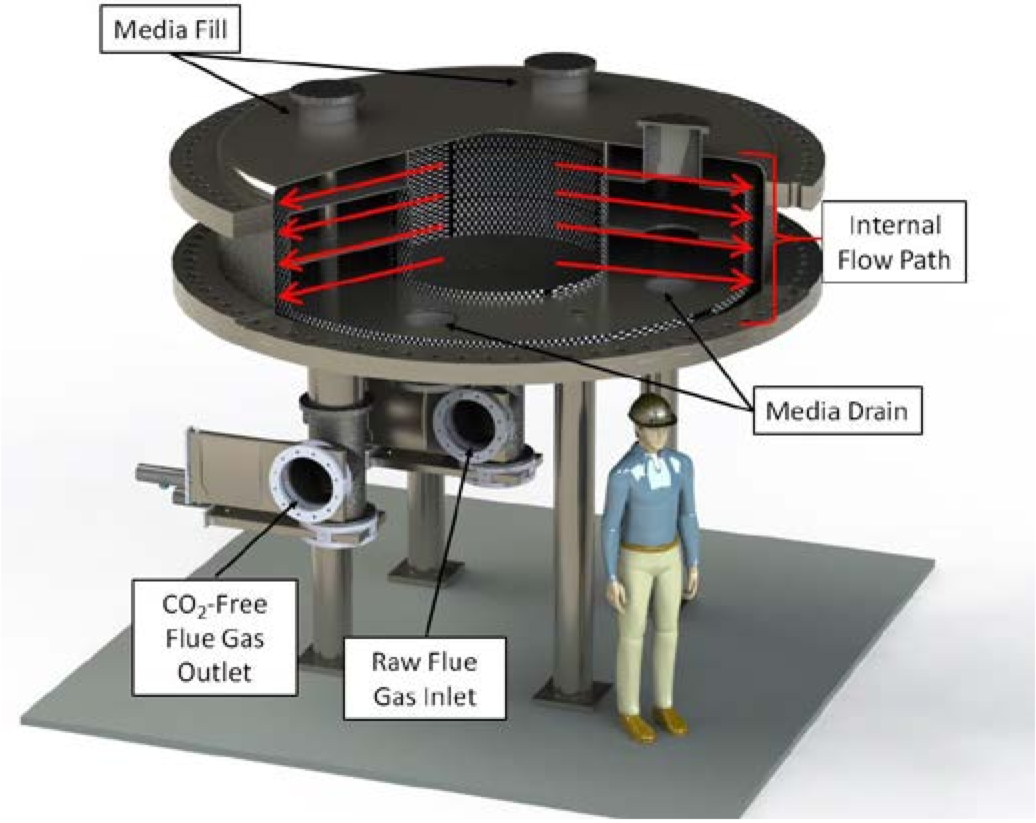

Figure 2: TDA Research's modular radial outflow reactor concept.

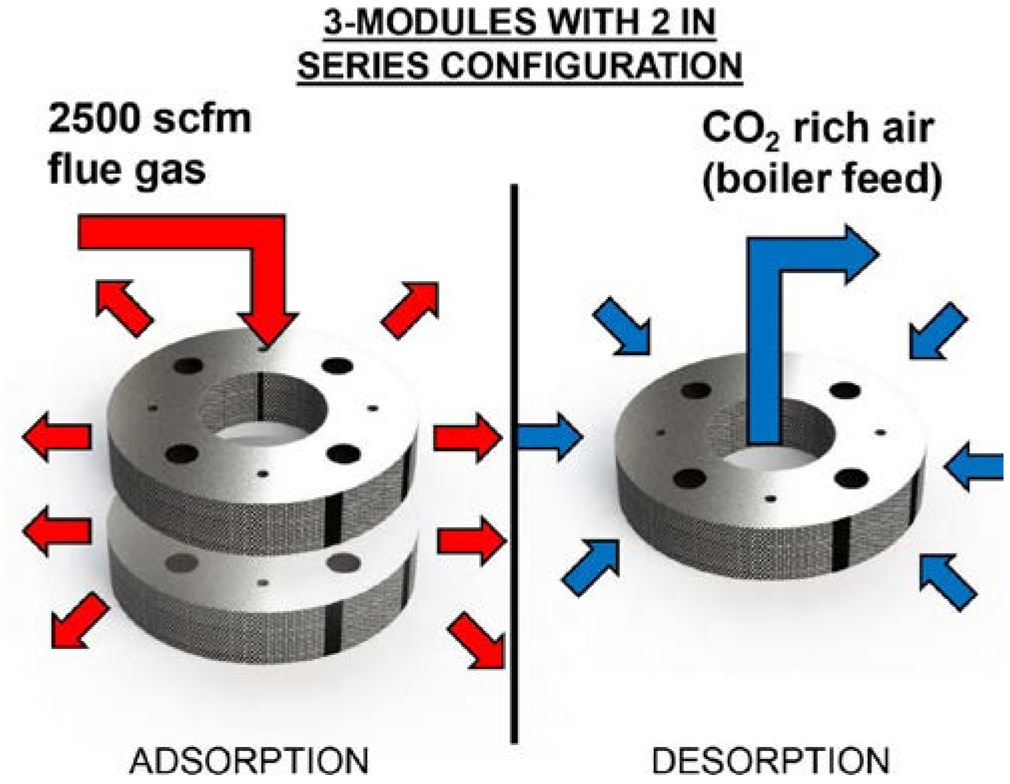

Figure 3: TDA Research 1-MWe modules.

The 1-MWe membrane-sorbent hybrid pilot test unit was designed and built to be installed for testing at TCM in Norway. A test campaign was performed using industrial flue gas that closely resembles coal-fired flue gas to evaluate the operating performance of the capture system at various conditions and to complete at least 4,000 hours of continuous operation. This testing under both parametric and steady-state conditions provides data and recommended operating conditions to update the membrane performance data and the TEA and environment, health, and safety (EH&S) analysis. The project aimed to demonstrate the novel hybrid system for reduction in carbon capture cost. The sorbent process parameters are provided in Table 1 and the membrane and process parameters are provided in Table 2.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1300	1300
Bulk Density	kg/m^3	589	589
Average Particle Diameter	mm	0.4-1.7	0.8-2.4[a]
Particle Void Fraction	m^3/m^3	0.37	0.37
Packing Density	m^2/m^3	240	240
Solid Heat Capacity @ STP	kJ/kg-K	0.93[b]	0.93[b]
Crush Strength	kg_f	—	—
Manufacturing Cost for Sorbent	$/kg	3.75	3.75
Adsorption			
Pressure	bar	1.0	1.0
Temperature	°C	30	30
Equilibrium Loading	g mol CO_2/kg	0.5	0.5
Heat of Adsorption	kJ/mol CO_2	20-30	20-30

Desorption				
Pressure	bar	1.0	1.0	
Temperature	°C	30	30	
Equilibrium CO_2 Loading	g mol CO_2/kg	0.05	0.05	
Heat of Desorption	kJ/mol CO_2	20-30	20-30	
Proposed Module Design		*(for equipment developers)*		
Flow Arrangement/Operation	—	Radial flow fixed beds		
Flue Gas Flowrate	kg/hr	TBD		
CO_2 Recovery, Purity, and Pressure$^+$	% / % / bar	N/A	N/A	N/A
Adsorber Pressure Drop	bar	<100 mbar		
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	TBD		

$^+$ Sorbent subsystem does only recirculation of CO_2 and is the secondary separation system in the hybrid configuration.

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atmosphere [atm]).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated bulk manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

		Composition						
Pressure	**Temperature**	vol%					ppmv	
psia	°F	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – U.S. Patent No. 9,120,079 B1.

Sorbent Contaminant Resistance – Sulfur oxide (SO_X) and nitrogen oxide (NO_X) tolerant up to 100 parts per million (ppm).

Sorbent Attrition and Thermal/Hydrothermal Stability – Less than 0.1% over one year.

Flue Gas Pretreatment Requirements – None.

Sorbent Makeup Requirements – Five-year replacements.

Waste Streams Generated – None.

Process Design Concept – Flowsheet/block flow diagram, included above (Figure 1).

Proposed Module Design – Radial flow fixed beds.

TABLE 2: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Proprietary Polymer	
Materials of Fabrication for Support Layer	—	Proprietary Polymer	
Nominal Thickness of Selective Layer	µm	<1	<1
Membrane Geometry	—	Thin film composite	Thin film composite
Max Trans-Membrane Pressure	bar	1.0	1.0
Hours Tested without Significant Degradation	—	11,000	3 years
Manufacturing Cost for Membrane Material	\$/m^2	—	—
Membrane Performance			
Temperature	°C	30	30
CO_2 Pressure Normalized Flux	GPU or equivalent	1,000 to 3,000	3,000
CO_2/H_2O Selectivity	—	0.25	0.25
CO_2/N_2 Selectivity	—	25-30	30
CO_2/SO_2 Selectivity	—	0.5	0.5
Type of Measurement	—	mixed	mixed
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	Partial countercurrent	
Packing Density	m^2/m^3	500 to 1,000	
Shell-Side Fluid	—	N/A	
Flue Gas Flowrate	kg/hr	TBD	
CO_2 Recovery, Purity, and Pressure$^+$	%/%/bar	90% 95% 150	
Pressure Drops Shell/Tube Side	bar	0.15	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	TBD	

$^+$ CO_2 recovery, purity, and pressure downstream of the cryogenic purification and pumping system.

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either co-current, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Membrane Permeation Mechanism – Proprietary polymeric membrane.

Contaminant Resistance – SO_X and NO_X tolerant up to 100 ppm.

Flue Gas Pretreatment Requirements – None.

Membrane Replacement Requirements – TBD.

Waste Streams Generated – None.

Process Design Concept – Flowsheet/block flow diagram, included above (Figure 1).

Proposed Module Design – Plate and frame module design for full-scale unit; spiral wound modules used in field test.

technology advantages

- Low pressure drop and high performance at the low CO_2 partial pressure in the adsorption stage.
- Efficient membrane operation due to high driving force and low cost due to mild vacuum requirements.
- Reduced capture cost while maintaining CO_2 capture performance due to the hybridization of the process.
- A preliminary TEA showed a substantial improvement in net plant efficiency (approximately F3.5% increase on higher heating value [HHV] basis) compared with the state-of-the-art amine-based CO_2 capture system.

R&D challenges

- Scaling-up the hybrid system from bench-scale to the 1-MWe system size for testing in this project.
- Assuring high membrane selectivity to get greater than 95% purity CO_2.
- Maintaining uniform flow distribution in sorbent reactor.

status

The project was completed on August 14, 2023. The results show that the membrane achieves stable performance with around 70–80% CO_2 purity, leading to an overall output purity of approximately 95% for the hybrid system. The hybrid system also reliably removes CO_2 at a rate of more than 95%. The overall system integrated with the Rankine Cycle power plant had a net plant efficiency of 30.0% and a cost of capture of \$39.1/tonne CO_2, which is 14.4% lower than the equivalent DOE reference case. If run without any CO_2 recirculation to the boiler, the cost of capture decreases to \$38/tonne, about 16.8% lower than the reference case.

available reports/technical papers/presentations

Aleptekin, G.; Jayaraman, A.; Bonnema, M.; Bruinsma, D.; Cates, M.; Cesario, M.; Gribble, D.; Gushlaw, B.; Hohman, J.; Kugler, F., 2023, “Membrane-Sorbent Hybrid System for Post-Combustion Carbon Capture.” Presented at the FECM/NETL 2023 Carbon Management Research Review Meeting. Pittsburgh, PA. August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC28_Alptekin.pdf*.

Aleptekin, G.; Jayaraman, A.; Bonnema, M.; Bruinsma, D.; Cates, M.; Cesario, M.; Gribble, D.; Gushlaw, B.; Hohman, J.; Kugler, F., 2021, “Membrane-Sorbent Hybrid System for Post-Combustion Carbon Capture.” Presented at the 2021 Carbon Management and Oil and Gas Research Project Review Meeting. DOE/NETL. Pittsburgh, PA. August 12, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Alpteken.pdf*.

Aleptekin, G.; Jayaraman, A.; Gribble, D.; Cates, M.; Hohman, J.; Kugler, F.; Bruinsma, D., 2020, “Membrane-Sorbent Hybrid System for Post-Combustion CO_2 Capture.” Presented at the DOE/NETL 2020 Carbon Capture Project Review Meeting. Pittsburgh, PA. October 7, 2020. *https://netl.doe.gov/sites/default/files/netl-file/20VPRCC_Alptekin_B.pdf*.

Alptekin, G.; Jayaraman, A.; Gribble, D.; Bonnema, M., 2018, “Membrane-Sorbent Hybrid System for Post-Combustion CO_2 Capture,” Project Kickoff Meeting Presentation, Pittsburgh, PA. October 1, 2018. *https://netl.doe.gov/projects/plp-download.aspx?id=10483&filename=Membrane-Sorbent+Hybrid+System+for+Post-Combustion+CO2+Capture.pdf.*

Alptekin, G., Jayaraman, A.; Gribble, D.; Bonnema, M., 2018, “Membrane-Sorbent Hybrid System for Post-Combustion CO_2 Capture,” Presented at the NETL 2018 CO_2 Capture Technology Meeting, Pittsburgh, PA. August 16, 2018. *https://netl.doe.gov/sites/default/files/netl-file/G-Alptekin-TDAR-Membrane-Sorbent-Hybrid.pdf*.

Dual-Loop Solution-Based Carbon Capture System for Net-Negative Carbon Dioxide Emissions with Lower Costs

primary project goal

The University of Kentucky is designing and testing a dual-loop carbon dioxide (CO_2) capture system (i.e., two solvent absorption/regeneration loops) on an existing 0.1-megawatt-thermal (MWth) bench-scale facility using natural gas-derived flue gas, augmented to match natural gas combined cycle (NGCC) CO_2 and oxygen (O_2) concentrations.

technical goals

- Design, fabricate, and research of the dual-solvent carbon capture technology.
- Determine long-term electrode and cation-exchange membrane stability, with system performance stability during load variation and energy consumption optimization.
- Complete parametric and long-term testing.
- Prepare a techno-economic analysis (TEA), life cycle analysis (LCA), and environment, health and safety (EH&S) assessment.

technical content

The project will address the technical challenge from the low-CO_2 (approximately 4 vol%) and high-O_2 (approximately 12 vol%) concentrations in NGCC flue gas, along with a very high CO_2 capture efficiency (95+%) and 20% cost reduction from NETL RC B31B in baseline report Rev. 4. The University of Kentucky (UK) proposes a dual-loop solution process to lower the capital cost (CAPEX) by an estimated 50% and offset the operating cost (OPEX) with negative CO_2 emissions and hydrogen (H_2) production. The dual-loop CO_2 capture process is also flexible to respond to rapid variation of electricity demand with increased intermittent renewable energy supplied to the grid. In addition, it is feasible for year-round operation and is geographically robust. In the proposed process, the two counter-current absorption loops had previously not been evaluated when integrated with each other in one absorber and with two regeneration unit operations. The electrochemical regeneration process, while demonstrated at the lab scale, has not been scaled to the bench. The successful development of the proposed technology will result in three major outcomes for NGCC utilities and other CO_2-emitting industries: (1) development of a cost-effective approach to achieve net-negative CO_2 emissions; (2) extending the individual key technology to a broader set of industrial flue gas streams, with mass transfer enhancement, blue hydrogen production and solvent degradation reduction; and (3) development of a method

program area:

Point Source Carbon Capture

ending scale:

Bench scale

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

Dual Solvent System, One Amine-Based with Thermally Integrated Contactor and One KOH-Based Electrochemically Regenerated with H_2 Production

participant:

University of Kentucky Research Foundation

project number:

FE0032134

predecessor projects:

N/A

NETL project manager:

Mariah Young
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partners:

EPRI; Louisville Gas & Electric and Kentucky Utilities

start date:

03.01.2022

percent complete:

62%

of load-following by maintaining the primary capture loop relatively stable for high-generation efficiency and equipment longevity and varying the CO_2 capture in the polish loop with H_2 production.

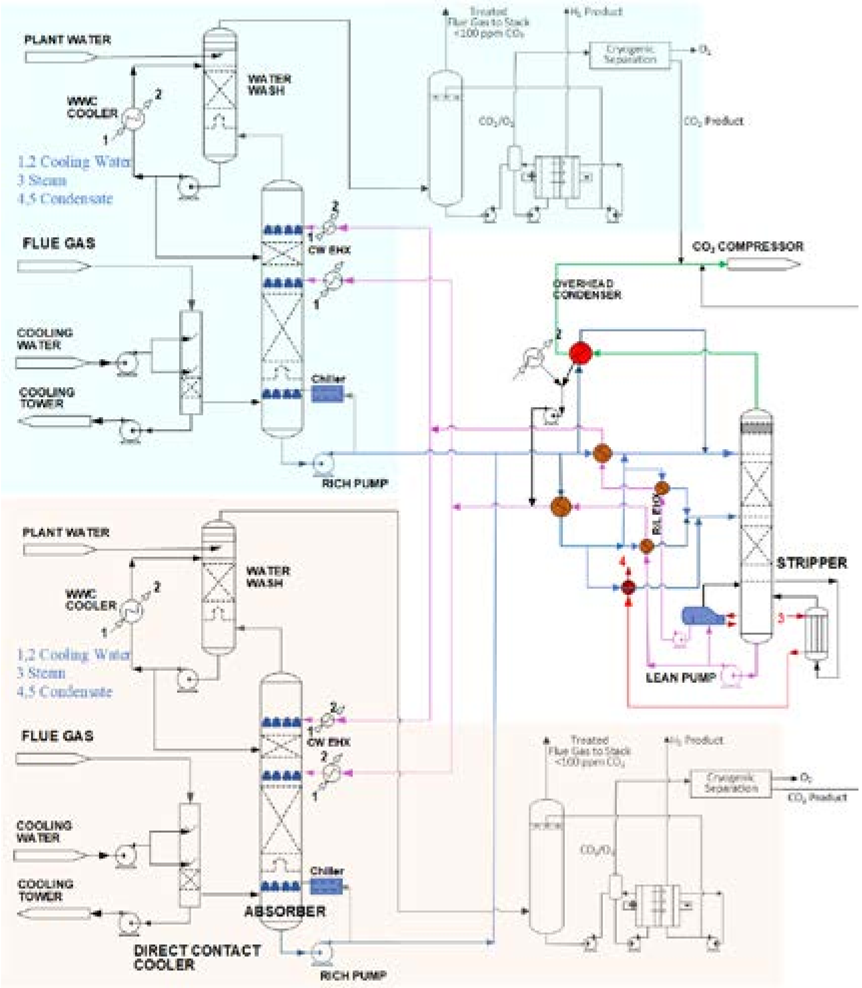

Figure 1: UK Center for Applied Energy Research (CAER) dual-loop carbon capture system for NGCC flue gas.

TABLE 1: SOLVENT PROCESS PARAMETERS

Working Solution	Units	Current R&D Value	Target R&D Value
Concentration	kg/kg	<0.45*	0.15*
Specific Gravity (15°C/15°C)	-	1.01*	1.14*
Specific Heat Capacity @ 30°C, 1 bar	kJ/kg-K	3.3#	3.5#
Viscosity @ 40°C (fresh condition, C/N=0)	cP	2.8*	1.04*
Surface Tension @ 25°C	mN/m	51 @ 25°C*	69 @ 19°C*
CO_2 Mass Transfer (K_L)	mol/s	0.003#	0.001# (dilute reaction environment)
CO_2 Reaction Rate	k	2.462E3&	3.874E3! (dilute reaction environment)
Thermal Conductivity (25°C)	W/(m·K)	0.3#	0.7#
Absorption			
Pressure	bar	1*	1*
Temperature	°C	35-55*	20-30*
Equilibrium CO_2 Loading	gmol CO_2/kg	2.3*	1.4*

Heat of Absorption	kJ/mol CO_2	65-80#	144, electric#
Solution Viscosity	cP	4.3 (rich condition)*	1.58*
Desorption			
Pressure	bar	1.6-2.2*	<2*
Temperature	°C	117-120*	30-40*
Equilibrium CO_2 Loading	gmol CO_2/kg	1.1-1.4*	0*
Heat of Desorption	kJ/mol CO_2	65-80*	144, electric*
Degradation	% Capacity Fade/Cycle	Not Applicable	Not Applicable
Solvent Makeup Rate Under Constant Dynamic Operation	—	~135%/year	Not Applicable
Known Degradation Products and Liquid-Phase Concentrations. *Total and individual concentrations depend on reclaiming*.**	—	Urea (1,300 ppm*), HEI (165 ppm*), HEMI (~2,100 ppm*), HEIA/HPMIZD (~460 ppm*), HEEDA/AME (~180 ppm*)	Not Applicable
Emissions Criteria Pollutants and Capture System/Media Secondary Emissions***	—	Total VOC ≤0.8 ppm* after water wash **At absorber exit, prior to water wash**: acetaldehyde, ~2,750 µm/m^3* formaldehyde, ~310 um/m^3* No stable nitrosamines have been observed.	No KOH emissions; no criteria pollutant emissions

Notes

* Experimental Data, #Estimated from Aspen Plus®, \$Calculated based on Vapor Liquid Equilibrium (VLE).

[&] CO_2 Reaction Rate Constant (k2 @ 15°C) (L/mol s) Henni et al. 2008.

[!] CO_2 Reaction Rate Constant (k2 @ 15°C) (L/mol s) Pinsent et al. 1956.

** See values for UK hindered primary amine solvent.

*** Total VOC <<0.8 ppm after water wash. No stable nitrosamines have been observed.

References

[&] Amr Henni, Julien Li, Paitoon Tontiwachwuthikul. Reaction Kinetics of CO_2 in Aqueous 1-Amino-2-Propanol, 3-Amino-1-Propanol, and Dimethylmonoethanolamine Solutions in the Temperature Range of 298-313 K Using the Stopped-Flow Technique. Industrial Engineering Chemical Research. Volume 47. Number 7. Pages 2213-2220. 2008.

[!] B.R.W. Pinsent, L. Pearson, F.J. W Roughton. The Kinetics of Combination of Carbon Dioxide with Hydroxide Ions. Transactions of the Faraday Society. Volume 52. Pages 1512-1520. 1956.

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine monoethanolamine [MEA] in an aqueous solution).

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.7 psia	135°F	13.17	17.25	66.44	2.34	0.80	42	74

Chemical/Physical Solvent Mechanism – The primary loop solvent is a water-lean formulation with a hindered primary amine as the absorbing component. A carbamate species is formed upon CO_2 absorption. In a CO_2 capture absorber, the absorption rate, **R**, as a function of temperature, **T**, and carbon loading, **C/N**, can be expressed as: $\mathbf{R(T, C/N) = k_G \cdot a \cdot (P_{CO2} - P^*_{CO2})}$, where $\mathbf{k_G}$ is mass transfer coefficient, **a** is effective wetted surface area, and $\mathbf{(P_{CO2} - P^*_{CO2})}$ is the driving force, the difference in the concentration of CO_2 in liquid from the gas. Significant increase in **R**, via $\mathbf{k_G}$ and **a**, and corresponding reduction of capital cost comes from the mass transfer enhancement of the proposed aqueous system compared to any second-generation technology because there is an order of magnitude greater effective wetted surface area in the top of the absorber.

Solvent Contaminant Resistance – The UK analysis shows the aqueous formulation of the solvent, containing the same amine, is more resistant to degradation, 40–50% improvement than 30 wt% MEA. Accumulation of metals within the solvent is expected to be equivalent to that within 30 wt% MEA. Degradation analysis of the water-lean formulation is part of this current effort.

Solvent Foaming Tendency – No foaming observed.

Flue Gas Pretreatment Requirements – Not applicable to NGCC flue gas, as the flue gas contains less than 5 parts per million (ppm) of sulfur dioxide (SO_2). If further SO_2 reduction is preferred, this can be done with a standard counter-current pretreatment column with a circulating solution of either of soda ash (Na_2CO_3) or sodium hydroxide (NaOH). The absorbing component of the solvent used is a hindered primary amine and does not form stable nitrosamine species, therefore no additional nitrogen oxide (NO_X) removal is required. No additional moisture removal is required either, as it is for ionic liquids.

Solvent Makeup Requirements – See Table 1.

Waste Streams Generated – The waste streams of the dual loop CO_2 capture process are the same as any other post-combustion CO_2 capture process. There will be a blowdown stream from the SO_2 pretreatment column, if applied, and a reclaimer waste stream from the solvent loop.

Process Design Concept – see Figure 1.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured, excluding T&S	\$/tonne CO_2	36.5	36.5
Cost of Carbon Avoided	\$/tonne CO_2	43.5	43.5
Capital Expenditures	\$/MWhr	18.9	18.9
Operating Expenditures	\$/MWhr	-0.7	-0.7
Cost of Electricity, excluding T&S	\$/MWhr	58.0	58.0

Definitions:

T&S – Transport & storage.

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis –

Using 2022 B31B.95 as a reference and applying both the UK post-combustion CO_2 capture unit and solvent at 95% capture efficiency and the polishing loop technology to capture the remaining 5% CO_2, significant benefits can be realized if credit is taken from CO_2 removed from air and sale of H_2 produced. The CO_2 removed from the NGCC combustion air stream is 14,590 tonne/year and this corresponds to 3740 tonne/year of H_2 produced in the polishing loop during potassium hydroxide (KOH) regeneration. For CO_2 removal, \$100/tonne CO_2 is assumed, for an annual credit of \$5.8 million, and assuming a reasonable H_2 sale price of \$8/kg for the pure, electrochemically produced H_2 stream, costs can be additionally offset by \$29.9 million annually, a 17.5% reduction in annual operating and maintenance (O&M) costs, led by the CO_2 removal and H_2 production. An additional benefit, not quantified, is that with application of both CO_2 capture loops allows the NGCC and carbon capture and storage (CCS) to be operated at relatively steady state for high overall plant thermal efficiency and increased equipment longevity by varying the polishing loop load for CO_2 capture and H_2 production. The CAPEX is reduced from \$1729/kW to \$1498/kW for net power generation, a 13% reduction compared to 2022 B31B.95, even with a 5% increase in the amount of CO_2 captured. Additionally, lower capital costs are realized from the UK post-combustion NGCC CO_2 capture process from elimination of the flue gas boost fan, direct contact cooler and associated duct work, and the column height reduction more than offsets the capital costs associated with the polishing loop electrochemical regenerator and CO_2/O_2 stream purification.

technology advantages

- Near 100% CO_2 capture.
- Lower CO_2 capture cost.
- H_2 and O_2 product streams might be sold to offset OPEX.

- Flexibility to operate with primary loop only or both loops.

R&D challenges

- Polishing loop longevity — electrochemical cell electrodes and membrane.
- Polishing loop energy consumption — electrochemical cell potential and KOH regeneration energy.
- Primary loop absorber performance — solvent distribution and temperature profile control.

status

The project team has demonstrated the performance target of achieving a 99.8% CO_2 capture rate. There was 95+% CO_2 capture in primary loop with high liquid/gas (L/G) ratio. There was less than 100 ppm CO_2 emitted after the polishing loop. There was between 85–90% CO_2 capture in the primary loop with reduced L/G ratio.

available reports/technical papers/presentations

Nikolic, Heather, "Dual-Loop Solution-Based Carbon Capture System for Net Negative Carbon Dioxide Emissions with Lower Costs," 2024 NETL BP2 Review Meeting, October 2024. *https://netl.doe.gov/projects/files/Dual-Loop%20Solution-Based%20Carbon%20Capture%20System%20for%20Net%20Negative%20Carbon%20Dioxide%20Emissions%20with%20Lower%20Costs.pdf*.

Nikolic, Heather, "Dual-Loop Solution-Based Carbon Capture System for Net Negative Carbon Dioxide Emissions with Lower Costs," 2024 Carbon Management Research Project Review Meeting, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_Posters_Nikolic.pdf*.

Nikolic, Heather, "Dual-Loop Solution-Based Carbon Capture System for Net Negative Carbon Dioxide Emissions with Lower Costs," 2023 FECM / NETL Carbon Management Research Project Review Meeting, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC29_Nikolic.pdf*.

Nikolic, Heather, "Dual-Loop Solution-Based Carbon Capture System for Net Negative Carbon Dioxide Emissions with Lower Costs," 2023 NETL BP1 Review Meeting, January 2023. *https://netl.doe.gov/projects/files/Dual-Loop%20Solution-Based%20Carbon%20Capture%20System%20for%20Net%20Negative%20Carbon%20Dioxide%20Emissions%20with%20Lower%20Costs.pdf*.

Nikolic, Heather, "Dual-Loop Solution-Based Carbon Capture System for Net Negative Carbon Dioxide Emissions with Lower Costs," 2022 NETL Kickoff Meeting, March 2022. *https://netl.doe.gov/projects/files/Dual-Loop%20Solution-Based%20Carbon%20Capture%20System%20for%20Net%20Negative%20Carbon%20Dioxide%20Emissions%20with%20Lower%20Costs.pdf*.

Nano-Confined Ionic Liquid Membrane for Greater Than or Equal to 97% CO_2 Capture from Natural Gas Combined Cycle Flue Gas

primary project goal

Gas Technology Institute (GTI), with partner State University of New York Buffalo, is developing a nano-confined ionic liquid (NCIL) membrane with high carbon dioxide (CO_2) permeance and CO_2/nitrogen (N_2) selectivity for capturing CO_2 from natural gas combined cycle (NGCC) flue gas.

technical goals

- Develop an NCIL membrane technology capturing greater than or equal to 97% CO_2 from NGCC flue gas.
- Test NCIL membranes.
- Demonstrate significant progress toward a 40% reduction in the cost of CO_2 capture versus a reference NGCC power plant.

technical content

The project aims to develop transformational membrane material (Figure 1) and a novel membrane process to provide step reductions in CO_2 capture cost for NGCC power plants and that will meet U.S. Department of Energy's (DOE) performance and cost goals. GTI has recently developed a transformational NCIL membrane that showed CO_2 permeance as high as 2,400 gas permeance unit (GPU) with a CO_2/N_2 selectivity of 2,100, which is significantly higher than state-of-the-art membranes in the Robeson plot. To overcome the issue of process pressure limitation and to use the high selectivity to the greatest extent, water vapor sweep with a counter-current flow mode is used to maximize the driving force for CO_2. The super high selectivity, as well as the counter-current flow mode, achieves greater than or equal to 95% CO_2 purity and greater than or equal to 97% CO_2 capture efficiency by a single CO_2 membrane stage for typical NGCC flue gas (~4 vol% CO_2). Most of the H_2O vapor is recovered by a highly H_2O-selective membrane and then recycled to the inlet of the permeate side of the NCIL membrane. This novel concept of process is designed without using steam from the power plant and is thus highly energy efficient.

Techno-economic analysis (TEA) based on preliminary testing data suggests this transformational membrane can achieve 97% CO_2 capture efficiency with a cost of $44.30/tonne CO_2 captured.

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Nano-confined Ionic Liquid Membrane for CO_2 Capture

participant:
Gas Technology Institute (GTI)

project number:
FE0032215

predecessor projects:
N/A

NETL project manager:
Andrew O'Palko
andrew.opalko@netl.doe.gov

principal investigator:
Shiguang Li
Gas Technology Institute
shiguang.li@gastechnology.org

partners:
State University of New York (SUNY) - Buffalo

start date:
03.01.2023

percent complete:
70%

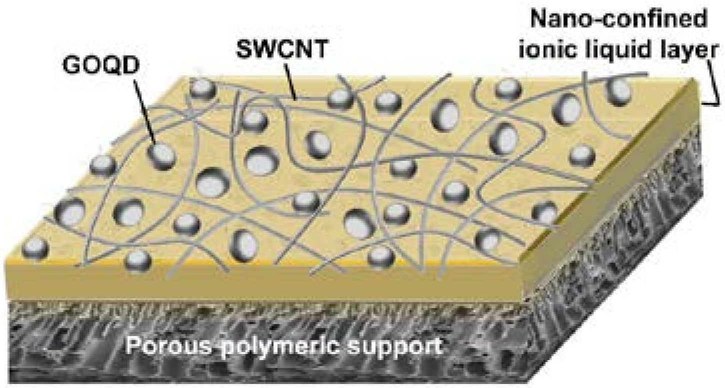

Figure 1: Schematic of GTI's NCIL membrane (GOQD - graphene oxide quantum dots; SWCNT - single-walled carbon nanotube).

technology advantages

- High CO_2/N_2 selectivity of the NCIL membrane.
- Low CO_2 capture cost.

R&D challenges

- A challenge may be that the CO_2 capacity of the ionic liquid is not sufficient for optimal NCIL membrane performance.
- Meeting CO_2 capture efficiency (greater than or equal to 97%).

status

The membrane showed CO_2 permeance as high as 2,400 GPU with a CO_2/N_2 selectivity of 2,100 for typical NGCC flue gas. When water vapor sweep was applied in the permeate side, greater than 95% CO_2 dry-basis purity and greater than 97% CO_2 capture rate was achieved with a single stage. The initial TEA indicates CO_2 capture cost of \$44.6/tonne of CO_2 captured at 95% capture, which is a 26% reduction versus DOE's reference case of \$59.9/tonne of CO_2 captured from an NGCC power plant.

available reports/technical papers/presentations

Shiguang Li, et al., "Transformational Nano-confined Ionic Liquid Membrane for Greater than or Equal to 97 Percent Carbon Dioxide Capture from Natural Gas Combined Cycle Flue Gas," 2024 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh PA, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_Posters_SLi.pdf*.

Shiguang Li, "Transformational Nano-confined Ionic Liquid Membrane for Greater than or Equal to 97 Percent Carbon Dioxide Capture from Natural Gas Combined Cycle Flue Gas, 2023 FECM / NETL Carbon Management Research Project Review Meeting," Pittsburgh PA, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC30_Li1.pdf*.

Shiguang Li, "Transformational Nano-confined Ionic Liquid Membrane for Greater than or Equal to 97 Percent Carbon Dioxide Capture from Natural Gas Combined Cycle Flue Gas," Project Kick-Off Meeting, Pittsburgh PA, April 2023. *https://netl.doe.gov/projects/files/Transformational%20Nano-confined%20Ionic%20Liquid%20Membrane%20for%20Greater%20than%20or%20Equal%20to%2097%20Percent%20Carbon%20Dioxide%20Capture%20from%20Natural%20Gas%20Combined%20Cycle%20Flue%20Gas.pdf*.

Enhancement of Carbon Capture Reactor Performance

primary project goal

The University of Kentucky (UK) Research Foundation will improve solvent/packing wettability and increase CO_2 mass transfer in the absorber column through the development of new absorber reactor components/materials for the UK heat-integrated carbon capture technology, including using advanced polymeric packings that have enhanced compatibility with newly developed high viscosity non-aqueous/water-lean solvents.

technical goals

- Develop and test absorber reactor components that increase CO_2 mass transfer for high viscous solvents through increased turbulence on the gas-liquid interface and improved solvent wetting on the packing surface.
- Demonstrate the ability to efficiency capture CO_2 at 90–97% or greater and make significant progress toward a 40% reduction in cost of capture versus the reference natural gas combined cycle (NGCC) power plant with carbon capture at the same carbon capture efficiency.
- Perform a techno-economic analysis (TEA) on the proposed technology to demonstrate decreased capital costs for NGCC capture plants at 95+% CO_2 capture efficiency.

technical content

This project proposes to develop high-efficiency absorber reactor components that can help to reduce the costs of post-combustion NGCC CO_2 capture by significantly reducing the capital cost by shortening the packing requirement through enhanced solvent wetting and improved CO_2 mass transfer using micro-structured packing to maximize the volumetric productivity of NGCC capture systems. To further enhance CO_2 mass transfer, UK is proposing the development absorber reactor packing that can enhance surface wetting and local mechanical mixing inside the absorber column to increase liquid/gas transport for faster mass transfer. This is accomplished using the inherent solvent physical properties including viscosity and surface tension coupled with packing material fabricated with unique surface structures and properties.

The packing surface sub-structures and patterns can enhance solvent wetting and destabilize the stable liquid film and bring fresh unreacted amine from the bulk to the surface interface. The improvements in CO_2 capture using these novel reactor concepts are most applicable to diffusion-controlled solvents, as opposed to kinetically controlled solvents, where the primary action is to increase the effective diffusion rate of CO_2 into the solvent through increased wetting and intra-solution turbulence on the packing surface. This impact translates to increasing the volumetric productivity of the absorber column.

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Novel Concepts

project focus:
Absorber Packing Enhancement

participant:
University of Kentucky Research Foundation

project number:
FE0032217

predecessor projects:
N/A

NETL project manager:
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principal investigator:
Jesse Thompson
University of Kentucky Research Foundation
jesse.thompson@uky.edu

partners:
Electric Power Research Institute (EPRI)

start date:
02.01.2023

percent complete:
68%

With the application of additive manufacturing, also known as 3D printing, fabrication of polymer-based packing with unique designs and surface sub-structures (Figure 1) can also result in favorable wetting profiles on the packing surfaces, leading to a significant benefit by increasing mixing and CO_2 mass transfer. One benefit of using 3D printing technology is the potential for unlimited design options together with the speed at which prototypes can be produced and tested. 3D-printed Nylon has been identified as a good candidate for use in amine absorber columns due to its physical and chemical stability after exposure to amine solvents.

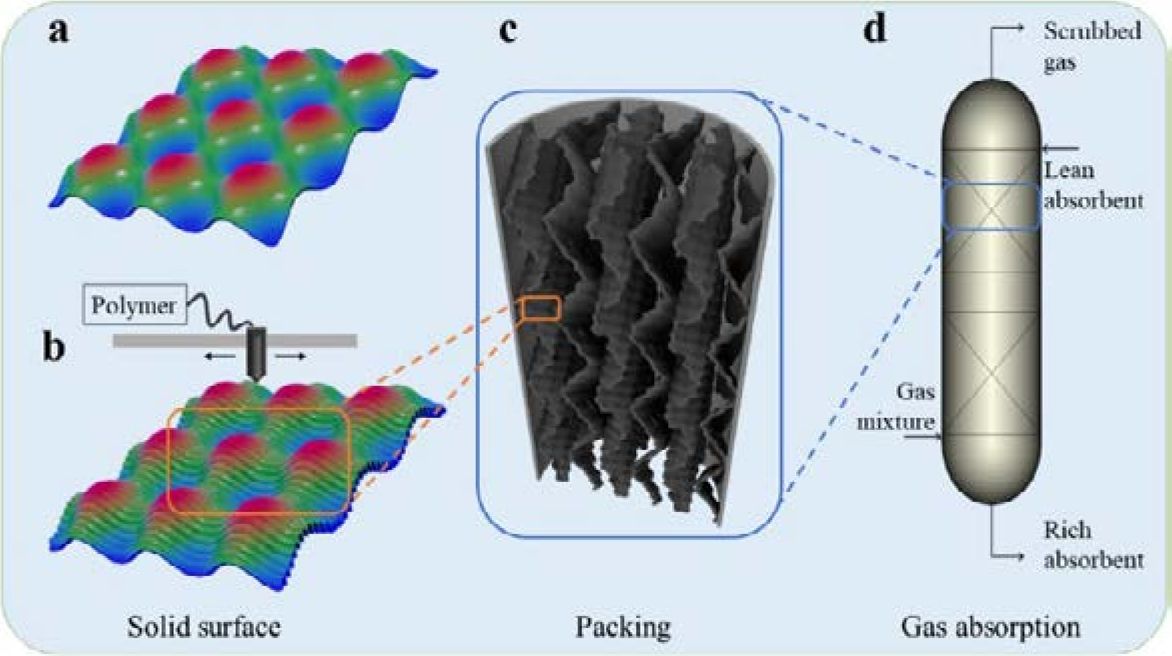

Figure 1: 3D printing of the Nylon surface with additional wavy sub-texture; (a) smooth steel surface, (b) polymer surface with sub-structure, (c) 3D-printed Nylon packing section, (d) CO_2 capture absorber column.

The successful development of the proposed technology will have a multitude of benefits to the CO_2 capture community and the public. Most importantly, this work will help the deployment and reduce the costs of post-combustion NGCC CO_2 capture technologies by at least 40% of the U.S. Department of Energy (DOE)/National Energy Technology Laboratory (NETL) NGCC reference case and promote the utilization of abundant natural gas for production of reliable electricity.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent (Amine)	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	75	75
Normal Boiling Point	°C	160	160
Normal Freezing Point	°C	0	0
Vapor Pressure @ 15°C	bar	0.0007	0.0007
Manufacturing Cost for Solvent	$/kg	6.5	6.5
Working Solution			
Concentration	kg/kg	0.45	0.45
Specific Gravity (15°C/15°C)	-	1.05	1.05
Specific Heat Capacity @ STP	kJ/kg-K	3.5	3.5
Viscosity @ STP	cP	10	10
Absorption			
Pressure	bar	1	1
Temperature	°C	40	40
Equilibrium CO_2 Loading	mol/mol	2.3	2.8

Heat of Absorption	kJ/mol CO_2	60	60
Solution Viscosity	cP	15	18
Desorption			
Pressure	bar	2	2
Temperature	°C	120	120
Equilibrium CO_2 Loading	mol/mol	1.8	2.0
Heat of Desorption	kJ/mol CO_2	55	55

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – “Current” is market price of chemical, if applicable; “Target” is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
15.27 psia	86°F	4.08	8.75	74.28	12.00	0.89	-	<100

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Carbamate formation.

Solvent Contaminant Resistance – Good resistance to oxygen.

Solvent Foaming Tendency – No foaming observed.

Flue Gas Pretreatment Requirements – Typical nitrogen oxide (NO_X) pretreatment.

Solvent Make-Up Requirements – Minimal solvent make-up expected.

Waste Streams Generated – No waste stream anticipated beyond routine reclaiming of the solvent.

Process Design Concept – Flowsheet/block flow diagram in Figure 2.

Proposed Module Design – Nylon-structured packing with surface roughness to increase solvent mixing.

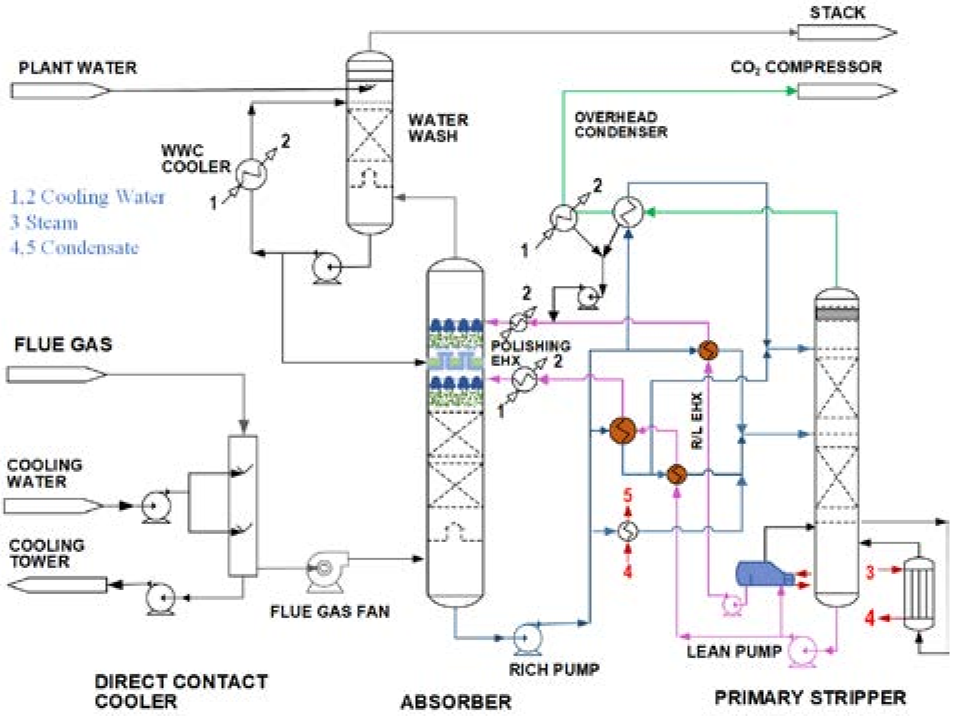

Figure 2: UK NGCC Process Design.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	54.2	36.1
Cost of Carbon Avoided	\$/tonne CO_2	73.4	44.0
Capital Expenditures	\$/MWhr	20.0	12.0
Operating Expenditures	\$/MWhr	43.8	26.3
Cost of Electricity	\$/MWhr	—	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – NGCC plant from the Case B31B in the National Energy Technology Laboratory (NETL) baseline report Revision 4a.

Scale of Validation of Technology Used in TEA – Technology Readiness Level (TRL) 3 (non-integrated bench-scale testing).

Qualifying Information or Assumptions – No qualifying assumptions were used.

technology advantages

- Operating at 40°C eliminates the cost of the direct contact cooler (DCC), and its cooling tower and balance of plant accounts for lowering the overall cost of carbon capture and storage (CCS) by 10%.
- Operating at 40°C results in nearly 35% reduction of solvent viscosity when compared to operating at 30°C.

R&D challenges

- Improving solvent properties for CO_2 uptake and release.
- Improving process and heat integration design to enhance CO_2 mass transfer in the absorber column.

status

The UK Research Foundation continued research and development (R&D) efforts using 3D-printed polymer packing and modified their design to have an additional surface sub-texture that further improves liquid turbulence on the surface translating to improved CO_2 capture rates. The project's preliminary TEA suggests that reducing the packing height by 25% through process intensification and enhancement in CO_2 mass transfer and using a lower-cost material (polymer) can result in a significant (52%) reduction in the construction cost of the absorber.

available reports/technical papers/presentations

Thompson, J., "Enhancement of Carbon Capture Reactor Performance," 2024 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh PA, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_Posters_Thompson.pdf*.

Thompson, J., "Enhancement of Carbon Capture Reactor Performance," 2023 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh PA, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC30_Thompson.pdf*.

Thompson, J., "Enhancement of Carbon Capture Reactor Performance," Kickoff Meeting, Pittsburgh PA, March 2023. *https://netl.doe.gov/projects/plp-download.aspx?id=14771&filename=Enhancement+of+Carbon+Capture++Reactor+Performance.pdf*.

Highly Efficient Regeneration Module for Carbon Capture Systems in Natural Gas Combined Cycle (NGCC) Applications

primary project goal

SRI International, in partnership with Baker Hughes, Trimeric Corporation and OLI Systems, designed, fabricated and tested at bench scale a highly efficient regeneration module capable of generating an ultra-lean solvent solution for capturing carbon dioxide (CO_2) from dilute sources, such as natural gas combined cycle (NGCC) flue gas at 95% or higher efficiency. SRI redesigned the regenerator unit of their existing large bench-scale mixed salt process (MSP) unit that includes two absorption modules and optimized the overall flow configuration for minimum energy penalty.

technical goals

- Design and model an advanced flash stripper integrated with the MSP system.
- Fabricate a stripper and other auxiliary components that can be integrated with the existing MSP bench-scale system.
- Test the integrated system using simulated flue gas (equivalent to 10 kWe).
- Perform live testing of the complete system and develop a complete techno-economic analysis (TEA).

technical content

SRI's MSP, a transformational ammonia-based CO_2 capture technology, combines two well-established conventional ammonia- and potassium-carbonate-based processes in a novel way to yield improved efficiency, decreased use of heat and electrical energy, reduced ammonia emissions, and a high-pressure CO_2 product. SRI has successfully demonstrated the MSP in a large bench-scale system with continuous integrated absorber and regenerator operation for coal-based power plant applications.

As part of a previous project (FE0012959), SRI and other partners constructed a bench-scale absorption system (shown in Figure 1) to determine the effectiveness of the MSP solvent applied to simulated coal flue gas. This study (FE0032135) aimed to fabricate and test an advanced stripper with the existing absorber system at SRI. The complete system uses a traditional temperature-swing absorption scheme using two absorber columns linked in series, as shown in Figure 2.

SRI redesigned the bottom portion of the MSP regenerator. The top section of the stripper (for CO_2) operates at 10 ± 2 bar and 120–140°C; the bottom section (for

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Advanced Regeneration for SRI's Mixed Salt Process for CO_2 Capture

participant:
SRI International

project number:
FE0032135

predecessor projects:
FE0012959

NETL project manager:
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principal investigator:
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SRI International
indira.jayaweera@sri.com

partners:
OLI Systems Inc.
Trimeric Corporation
Baker Hughes

start date:
01.14.2022

percent complete:
100%

ammonia) operates at 8 ± 2 bar and 140–160°C. The optimized design was modeled using computational fluid dynamics (CFD) in order to generate an ultra-lean solvent (approximately 0.2 CO_2 loading). The results of this model were integrated into a complete system model using the MSP flowsheet. After updating the stripper design to reflect the model results, the bench-scale system at SRI was retrofitted with the new stripper, and parametric testing was performed.

Figure 1: Bench-scale MSP system.

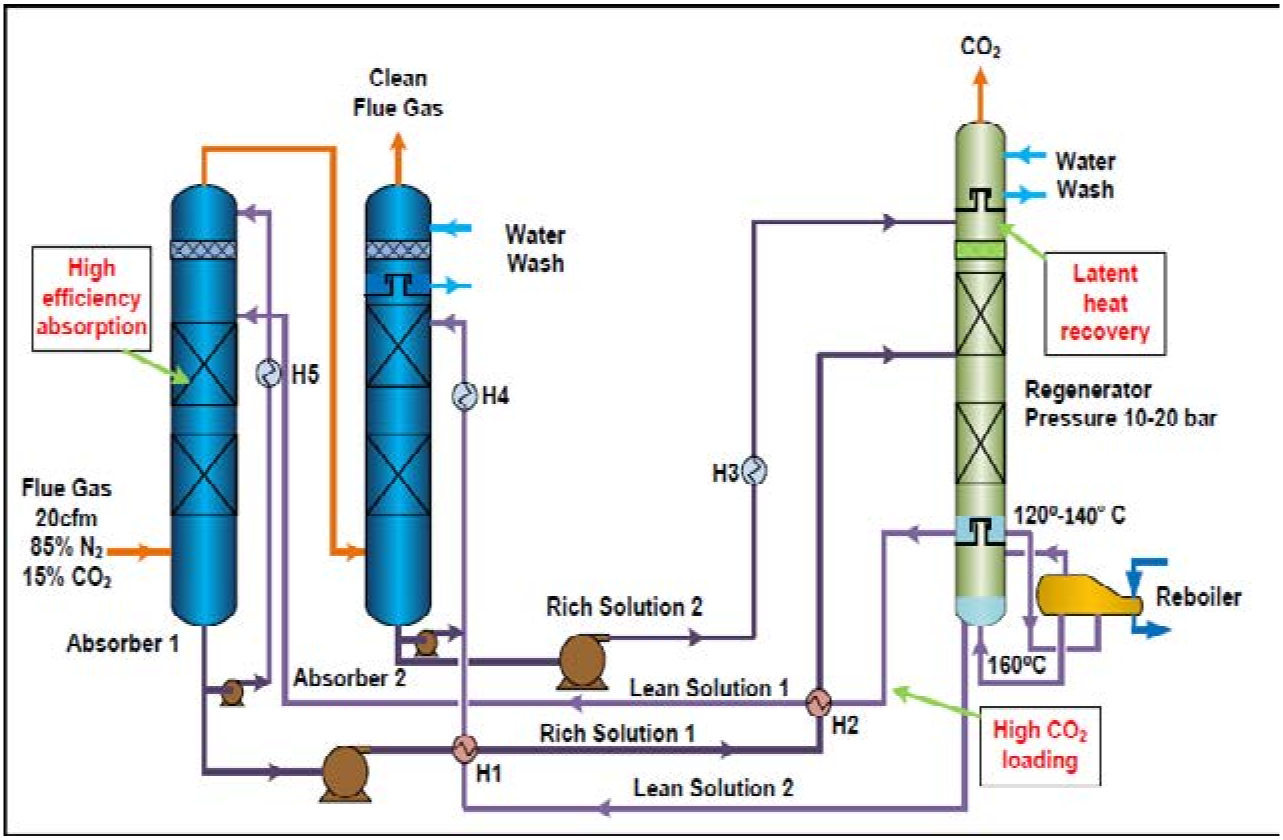

Figure 2: Block flow diagram of the MSP system.

The results of the model were compared with the equivalent U.S. Department of Energy (DOE) case from the most recent (2015) Volume 1 report for NGCC plants with carbon capture (Case B31B). After completing the hazard and operability

(HAZOP) study, full system integration and data collection began. The solvent operating parameters from this study are presented in Table 1. After completing the live tests, a TEA was prepared, with results summarized in Table 2.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	18	18
Normal Boiling Point	°C	100	100
Normal Freezing Point	°C	0	0
Vapor Pressure @ 15°C	bar	0.017	0.017
Manufacturing Cost for Solvent	$/kg	0	0
Working Solution			
Concentration	kg/kg	0.27-0.32	0.32
Specific Gravity (15°C/15°C)	-	1.37	1.37
Specific Heat Capacity @ STP	kJ/kg-K	3.2	3.2
Viscosity @ STP	cP	1.6	1.6
Absorption			
Pressure	bar	1	1
Temperature	°C	20-30	20-30
Equilibrium CO_2 Loading	mol/mol	0.4-0.5	0.5
Heat of Absorption	kJ/mol CO_2	50--70	50-70
Solution Viscosity	cP	1.5-1.8	1.5-1.8
Desorption			
Pressure	bar	>10	10-12
Temperature	°C	120-160	130-160
Equilibrium CO_2 Loading	mol/mol	0.2-0.35	0.3
Heat of Desorption	kJ/mol CO_2	50-70	50-70
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	3.93E06	
CO_2 Recovery, Purity, and Pressure	% / % / bar	95 99 12	
Absorber Pressure Drop	bar	0.06	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	—	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature and composition leaving the heat recovery steam generator (HRSG) should be assumed as (Reference: Cost and Performance Baseline for Fossil Energy Plants Volume 1. Bituminous Coal and Natural Gas to Electricity; Case B31B):

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	232	4.08	8.75	74.3	12.0	0.89	0	0

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The solvent is an ammonia and potassium carbonate mixed salt solution and is regenerated with steam.

Solvent Contaminant Resistance – Excellent.

Solvent foaming tendency – None.

Flue Gas Pretreatment Requirements – None.

Solvent Makeup Requirements – 15% per year.

Waste Streams Generated – None known.

Process Design Concept – See Figure 2.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	$/tonne CO_2	$68.9	TBD
Cost of Carbon Avoided	$/tonne CO_2	—	—
Capital Expenditures	$/MWhr	—	—
Operating Expenditures	$/MWhr	—	—
Cost of Electricity	$/MWhr	—	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – The analysis was based on Case 12 in “Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity, Rev. 2.”

Scale of Validation of Technology Used in TEA – The analysis was based on pilot-scale testing.

technology advantages

- High CO_2 loading.
- High pressure release of CO_2 (10–12 bar).
- Low energy consumption.
- Removes common acid pollutants and particulates.

R&D challenges

- Minimizing the formation of solids in the main solvent path.
- Reducing ammonia slip.
- Minimizing system power consumption.

status

The project completed on September 30, 2024. All major research efforts have concluded, and a final report is pending.

available reports/technical papers/presentations

Jayaweera, I., 2022, “Efficient Regeneration Module for Carbon Capture Systems in NGCC Applications.” *Proceedings of the 2022 Carbon Management Project Review Meeting.* Pittsburgh, PA. *https://netl.doe.gov/projects/files/Efficient%20Regeneration%20Module%20For%20Carbon%20Capture%20Systems%20In%20NGCC%20Applications.pdf*.

ROTA-CAP: An Intensified Carbon Capture System Using Rotating Packed Beds

primary project goal

Gas Technology Institute (GTI), with Clean Carbon Solutions Ltd. (CCSL), developed and tested at bench-scale a transformational carbon dioxide (CO_2) capture technology (ROTA-CAP™) using novel rotating packed-bed (RPB) absorbers and regenerators combined with an advanced solvent toward providing an economically viable carbon capture system.

technical goals

- Design, construct, and commission the ROTA-CAP equipment at GTI.
- Develop a preliminary process model and perform an initial fabrication feasibility study for commercial process.
- Test the ROTA-CAP system with simulated flue gases and natural gas burner flue gas at GTI to determine key operating parameters.
- Calibrate the process model and measure solvent carryover.
- Perform long-term reliability and operability testing at the National Carbon Capture Center (NCCC) on coal-fired flue gas.
- Verify the process model.
- Determine scale-up challenges, solvent degradation, and aerosol formation.
- Complete a high-level techno-economic analysis (TEA).

technical content

The RPB contactor design comprises a rotating disk of packing material that generates a high gravity centrifugal force, which distributes solvent radially toward the outer edge of the disk, providing a high surface area for mass transfer to occur as countercurrent flue gas contacts the solvent droplets. An integrated absorber-regenerator bench-scale test skid for the ROTA-CAP system is designed, constructed, and operated at GTI using simulated flue gas and natural gas burner flue gas to determine key operating parameters. ROTA-CAP absorber is a single-shaft, multi-rotor RPB absorber with interstage cooling. Integrated with the compact RPB regenerator, ROTA-CAP has a very small footprint for the absorber-regenerator package. See Figure 1 for a schematic of RPBs in gas-liquid contactor operation. CCSL provided an advanced solvent for the test, such as its proprietary amine-promoted buffer salt (APBS) solvent. To compare the performance of ROTA-CAP to the conventional process using commercial monoethanolamine (MEA) solvent, the team utilized the Slip Stream Test Unit (SSTU) at NCCC. See Figure 2 for a general bench-scale ROTA-CAP skid process flow diagram. Long-term (1,000-hour) stability testing of the integrated ROTA-CAP CO_2 capture system was conducted on a coal-fired flue gas slipstream at NCCC at a scale of 1

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Rotating Packed Bed with Advanced Solvent

participant:
Gas Technology Institute

project number:
FE0031630

predecessor projects:
N/A

NETL project manager:
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principal investigator:
Osman Akpolat
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partners:
Clean Carbon Solutions Ltd.; National Carbon Capture Center

start date:
10.01.2018

percent complete:
100%

tonne CO_2 per day, and the collected data were used to determine solvent degradation and aerosol formation. A simulation process model was developed for integrated RPB carbon capture systems and will be used to aid in larger-scale deployment of the ROTA-CAP technology, such as integration with coal-fired power plants. A high-level TEA of the process was performed based on experimental data and the capture process model verified with the long-term operation data.

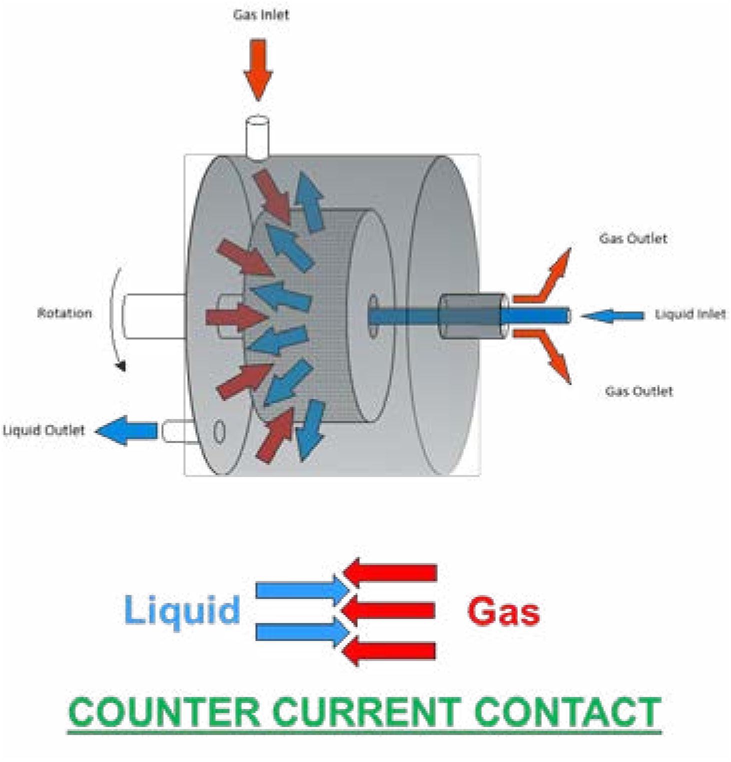

Figure 1: RPB gas-liquid contactor.

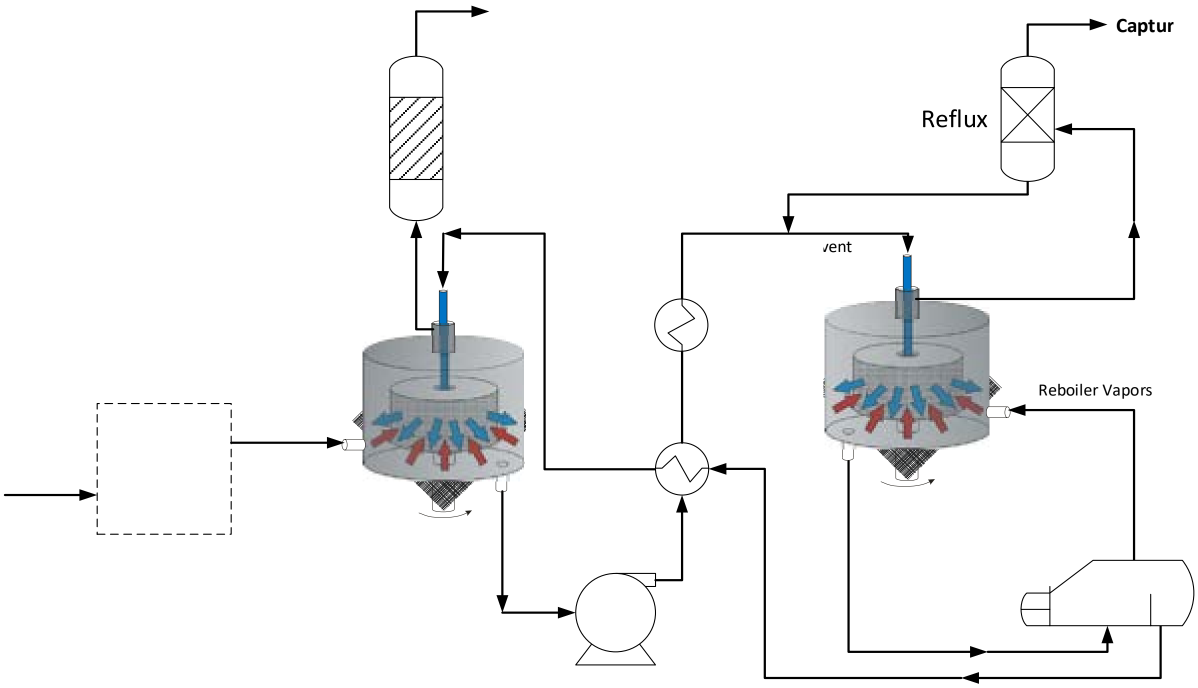

Figure 2: ROTA-CAP bench-scale test skid process flow diagram.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	57.29	57.29
Normal Boiling Point	°C	104-220	104-220
Normal Freezing Point	°C	N/A	N/A
Vapor Pressure @ 15°C	bar	18.2	18.2
Manufacturing Cost for Solvent	$/kg	—	—
Working Solution			
Concentration	kg/kg	0.425	0.425-0.55
Specific Gravity (15°C/15°C)	—	1.007	>1.007
Specific Heat Capacity @ STP	kJ/kg-K	3.344	>3.344
Viscosity @ STP	cP	2.839	>2.839
Absorption			
Pressure	bar	0.1	0.1
Temperature	°C	40	40
Equilibrium CO_2 Loading	mol/mol	3.3	>3.3
Heat of Absorption	kJ/mol CO_2	75.2	>75.2
Solution Viscosity	cP	4.4	>4.4
Desorption			
Pressure	bar	0.07	0.07
Temperature	°C	120	120
Equilibrium CO_2 Loading	mol/mol	0.7	>0.7
Heat of Desorption	kJ/mol CO_2	2.7-3.0	2.55-2.85

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The solvent utilizes a chemical reaction with acid gases to remove them from the feed gas stream. The reaction is reversed in the stripper unit operation through the application of heat to the solvent.

Solvent Contaminant Resistance – Besides physical contamination (e.g., feed gas solids), the main contaminant expected in the solvent is heat-stable salts (HSSs). HSSs are a byproduct of heat and solvent reaction with components in the feed gas (e.g., oxygen [O_2], nitrogen oxide [NO_X], sulfur oxide [SO_X]). In long-term testing by CCSL, the solvent has superior resistance to HSS generation when compared to other commercial solvents.

Solvent Foaming Tendency – Foaming has not been reported in any test campaign or commercial operation of the solvent to date.

Flue Gas Pretreatment Requirements – Pretreatment would include:

- Reduction of particulate matter, NO_X, and SO_X to current U.S. Environmental Protection Agency (EPA) limits.
- Cooling and water saturation of the feed gas to approximately 110°F.

Solvent Makeup Requirements – Solvent makeup is minimal as HSS generation and physical loses should be low. It is expected that less than 0.35 kg solvent per tonne of CO_2 should be added intermittently.

Waste Streams Generated – A water bleed is expected from the regenerator reflux to maintain the solvent concentration and remove any trapped ammonia salt species. During long-term testing, HSSs could be removed through reclaiming. The HSS sludge would need to be disposed. However, with only a 1,000-hour target for the long-term testing, reclaiming is not anticipated during this test campaign.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	68	30
Cost of Carbon Avoided	\$/tonne CO_2	—	—
Capital Expenditures	\$/ tonne CO_2	42	12
Operating Expenditures	\$/ tonne CO_2	26	18
Cost of Electricity	\$/MWhr	—	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – The current research and development (R&D) value is based on a pre-front-end engineering design study conducted by CCSL with an independent engineering, procurement, and construction firm. The study evaluated capital costs for a 100 tonne per day (TPD) RPB system. The operating expenses are based on using CCSL commercial solvent. The target R&D values are for a projected 500 TPD RPB system. Savings in RPB manufacturing, packing fabrication, plot plan reduction, and utilizing an intensified solvent are included.

All costs are for the carbon capture island only. The typical unit operations include a booster fan, direct contact cooler, absorber, regenerator, pumps, and heat exchange.

Carbon dioxide product handling and transportation, site preparation, and duct connections are excluded.

The cost of capture economics, reported as 2021 USD, are based on:

- 25-year project lifetime.
- 8% discount rate.
- 3% escalation over the life of the project.
- 350-days-per-year operation.
- $3.50/MMBtu heat source.
- $0.05/kWh electricity.
- $2/1,000 gallons cooling water make-up.
- $39/gallon solvent.

technology advantages

- The RPB technology provides intense micro-mixing and internal mass transfer, thereby facilitating significant size reductions in the absorber and regenerator relative to conventional columns, resulting in lower capital costs.
- ROTA-CAP allows the ability to use high-viscosity solvents and lower liquid/gas (L/G) ratios. This means ROTA-CAP can operate with higher solvent concentration and higher CO_2 loading of the rich solvent compared to conventional solvent processes.
- Process intensification in ROTA-CAP leads to a highly compact system with lower CAPEX than conventional columns due to significant contactor size reduction, lower circulation rate, and less mass flow through heat exchangers and pumps. Lower residence time in the regenerator section also reduces oxidative and thermal degradation of the solvent.
- A simulation process model for integrated RPB carbon capture systems has been developed, which can be used in future larger-scale deployments.
- RPB reactors are non-selective to the solvent used. ROTA-CAP can also take advantage of the advanced class of low-aqueous solvents that cannot be fully exploited in a conventional packed column.
- Advanced solvents typically have lower regeneration energy requirements than conventional solvents and reduce the cost of capture, which adds to the advantages of RPBs, further reducing ROTA-CAP carbon capture cost.

R&D challenges

- The integrated use of RPBs as both absorber and regenerator in a single system.
- The mechanical design parameters of rotating equipment.

- Solvent stability performance during operation.
- Integrating and achieving required solvent regeneration using an RPB regenerator.
- During testing, GTI will determine the solvent performance and modify it as needed to achieve a 90% CO_2 removal rate. The optimum CO_2 removal rate to achieve the lowest cost of removal will be calculated.
- Scale-up limitations exist with rotating equipment. Modular design may be useful to overcome size limitations of RPBs for larger systems. Capital cost and added complexity of the system will need to be managed.

status

GTI designed and costed the bench-scale ROTA-CAP test skid, a 50-kilowatt-electric (kWe) (1,000-kg/day CO_2 removal) equivalent-scale integrated carbon capture skid. The skid has a flue gas cooling and filtration section available to be used when necessary.

Test skid construction and testing with synthetic gas and natural gas-fired flue gas with elevated CO_2 concentration (10.4% vol.) was completed. After initial testing, the skid was transported to and operated for more than 1,600 hours at NCCC with coal- or natural gas-fired flue gas.

The skid operated continuously 24 hours a day, seven days a week for seven test campaigns ranging from two to 3½ weeks each campaign. During these campaigns, seal, bearing, liquid pump, and material compatibility issues were resolved.

Data to determine bearing life, maintenance, and solvent circulation performance, as well as solvent usage and degradation, were collected.

The skid was operated for more than 1,000 hours with flue gas containing 10% (vol.) CO_2. Capture rates of greater than 95% were achieved.

Parametric testing was done with the skid operating between 4% CO_2, as indicative of NGCC flue gas applications, and 22% CO_2, as indicative of industrial flue gas applications. Long-term testing was followed by a 100+ hour test with 20% CO_2 flue gas at 95% capturing efficiency.

ROTO-CAP Field-Testing Learnings

- RPBs are very responsive to operations—skid startup and shutdown takes a few hours; steady-state operation achieved within 45–60 minutes.
- High-viscosity liquid circulation is not a problem in the RPBs.
- Solvent viscosity determines liquid-level control and solvent circulation pump specifications.
- Insulation and heat management is important for good regenerator performance.
- Solvent inventory is about 20% of equivalent capacity conventional column skids (based on NCCC experience).
- ROTA-CAP can be used with water-lean solvents.

available reports/technical papers/presentations

Akpolat, O., "ROTA-CAP: An Intensified Carbon Capture System Using Rotating Packed Beds," GTI Energy, May 2024 Project Close Out Meeting, Pittsburgh, PA. *https://netl.doe.gov/projects/files/ROTA-CAP%20An%20Intensified%20Carbon%20Capture%20System%20Using%20Rotating%20Packed%20Beds.pdf*.

Akpolat, O., "ROTA-CAP: An Intensified Carbon Capture System Using Rotating Packed Beds," GTI Energy, August 2023 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC29_Okpolat.pdf*.

Akpolat, O., “ROTA-CAP: An Intensified Carbon Capture System Using Rotating Packed Beds,” Gas Technology Institute, August 2022 Carbon Management Project Review Meeting - Point Source Carbon Capture. *https://netl.doe.gov/sites/default/files/netl-file/22CM_PSC16_Akpolat.pdf*.

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Akpolat, O., “ROTA-CAP: An Intensified Carbon Capture System Using Rotating Packed Beds,” Budget Period 1 Review Meeting, Pittsburgh, PA, March 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10540&filename=ROTA-CAP+-+An+Intensified+Carbon+Capture+System+Using+Rotating+Packed+Beds.pdf*.

Akpolat, O., H. Meyer, D. Bahr, “ROTA-CAP: An Intensified Carbon Capture System Using Rotating Packed Beds,” 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting, Pittsburgh, PA. *https://netl.doe.gov/sites/default/files/netl-file/O-Akpolat-GTI-ROTA-CAP.pdf*.

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Akpolat, O., H. Meyer, W. Shimer, D. Bahr, J. Hall, “ROTA-CAP: An Intensified Carbon Capture System Using Rotating Packed Beds,” Project Kickoff Meeting, Pittsburgh, PA, Dec 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10538&filename=ROTA-CAP+-+An+Intensified+Carbon+Capture+System+Using+Rotating+Packed+Beds.pdf*.

Mixed-Salt-Based Transformational Solvent Technology for CO_2 Capture

primary project goal

SRI International and project partners developed a novel, water-lean, mixed-salt-based transformational solvent technology that will provide a step-change reduction in the carbon dioxide (CO_2) capture cost and energy penalties. The advanced mixed-salt process (A-MSP) has the potential to meet the U.S. Department of Energy's (DOE) Carbon Capture Program's goal for the development of transformational technologies for a coal-fired power plant.

technical goals

- Demonstrate that the A-MSP can:
  - Operate as a solvent-rich system with a very high cyclic CO_2-loading capacity (greater than 0.10 kilogram [kg] CO_2/kg of solvent).
  - Regenerate CO_2 at greater than 10 bar at temperatures less than 120°C.
  - Operate continuously in an integrated absorber-regenerator using simulated flue gas with 13–15% CO_2 and balance air.
  - Capture CO_2 with 95% CO_2 purity and a cost of electricity (COE) at least 30% lower than a supercritical pulverized-coal power plant with CO_2 capture, or approximately $30 per tonne of CO_2 captured, ready for demonstration by 2030.
- Perform thermodynamic modeling and vapor-liquid equilibrium (VLE) measurements of multi-component systems.
- Conduct kinetic measurements of CO_2 absorption of select compositions.
- Conduct thermal and oxidative solvent degradation studies.
- Perform bench-scale testing of integrated absorber-regenerator system.
- Develop a rate-based model and process flowsheet and perform a techno-economic analysis (TEA) to aid in identification of development pathways for technology advancement.

technical content

SRI International, in collaboration with SINTEF, Technical University of Denmark (DTU), OLI Systems Inc., and Trimeric Corporation, utilized the knowledge gained during a DOE-funded project (FE0012959) in the design of a mixed-salt process (MSP) that uses a solvent formulation comprised of ammonium (NH_4) and potassium (K) salt solutions to develop a transformational technology that achieves further improvements in performance. An analysis conducted by SRI indicates that inclusion of a tertiary amine to the mixed-salt formulation yields a high CO_2-loading capacity and high-pressure solvent regeneration at a low temperature, thus further reducing the energy penalty of CO_2 capture.

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

Advanced Mixed-Salt Solvent Process

participant:

SRI International

project number:

FE0031597

predecessor projects:

N/A

NETL project manager:

Krista Hill
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principal investigator:

Palitha Jayaweera
SRI International
palitha.jayaweera@sri.com

partners:

OLI Systems Inc.; SINTEF; Technical University of Denmark; Trimeric Corporation

start date:

06.01.2018

percent complete:

100%

Bench-scale testing of SRI's first-generation MSP under FE0012959 showed that the two-component system has significant advantages over single-component systems. In the MSP chemistry, ammonia (NH_3) plays a dual role—the role of catalyst and the role of the absorbent, due to its high mobility and reactivity with CO_2. Ammonia absorbs large amounts of CO_2 at low temperature and releases CO_2 at high temperature and pressure, making it a highly useful chemical in CO_2 absorption formulations. By blending NH_3 with other low-capacity and low-reactivity components to suppress the undesirable high vapor pressure of NH_3, SRI has identified a next-generation A-MSP formulation that can provide a step-change reduction in CO_2 capture costs. Based on preliminary examinations, adding an amine such as methyl diethanolamine (MDEA) into the MSP formulation significantly improves the capture performance, yielding a regeneration energy of 1.5–1.8 megajoules (MJ)/kg-CO_2 while operating with less than 50% water. The solvent and process parameters are provided in Table 1.

The A-MSP concept includes two isothermal absorbers, a multi-stage regenerator, and auxiliary equipment, as shown in Figure 1. Absorber 1 operates with high-NH_3/(Amine+K) solvent composition and absorber 2 operates with low-NH_3/(Amine+K) solvent composition, resulting in efficient absorption and minimum NH_3 slip. In the range of 60–80% of the CO_2 in the flue gas stream is absorbed in absorber 1, and the remaining CO_2 is absorbed in absorber 2. The dual-stage absorber system reduces NH_3 carryover, resulting in less than 10 parts per million (ppm) NH_3 in the clean flue gas stream exiting the water wash. Both absorbers operate with liquid recycle using heat exchangers to remove the heat of reaction. The bottom stage operates with the highest CO_2 loading (up to 0.7 mol/mol). The CO_2-rich solutions from the absorbers are then sent to the regenerator through crossflow heat exchangers, which recover the heat from returning lean solutions. The A-MSP multi-stage regenerator produces two CO_2-lean salt streams with high and low NH_3 content, drawn from the lower-middle and bottom stages of the regenerator. The regenerator is operated under high-pressure isobaric conditions (10–20 bar) and has a temperature gradient in the column (top ~30°C and bottom ~120°C). At high temperature, the NH_3 at the bottom of the regenerator is vaporized along with CO_2, making a lean, low-NH_3/(Amine+K) ratio solution to be used in absorber 2. Vaporized NH_3 gets re-absorbed as the vapor moves up the regenerator column, thereby creating a high-NH_3/(Amine+K) ratio solution in the mid-section of the regenerator for use in absorber 1. In the A-MSP design, operating the regenerator at relatively low temperature and high pressure eliminates the water stripping, thereby producing an almost-dry CO_2 stream ($H_2O_{vap}/CO_2 < 0.02$) at high pressure. Figure 2 shows equilibrium modeling data comparing MSP and A-MSP systems, illustrating the high-CO_2 regeneration pressure advantage (almost doubled for 0.55 mol/mol CO_2 loading) of A-MSP with the inclusion of MDEA to the solvent. Figure 3 shows results of static autoclave tests conducted for compositions 622 and 822 at four loading levels. For the 622 formulation, the CO_2 pressure was approximately 8 bar at 120°C with a 0.40 loading. The 822 formulation reached the ~10 atm of pressure at 120°C with a CO_2 loading as low as 0.40. This figure illustrates the feasibility of attaining high-CO_2 regeneration pressure at relatively low temperatures, particularly with inclusion of MDEA in the A-MSP solvent. The A-MSP solvent leads to a reduction of both regeneration and CO_2 compression energy costs, thereby lowering operating expenses. Moreover, it eliminates the need for the expensive first stage of CO_2 compression, resulting in capital cost reduction. In addition, the lower regeneration temperature and lower reboiler duty significantly reduce power plant energy loss due to low-pressure steam extraction, improving the net power output of the plant (Figure 4).

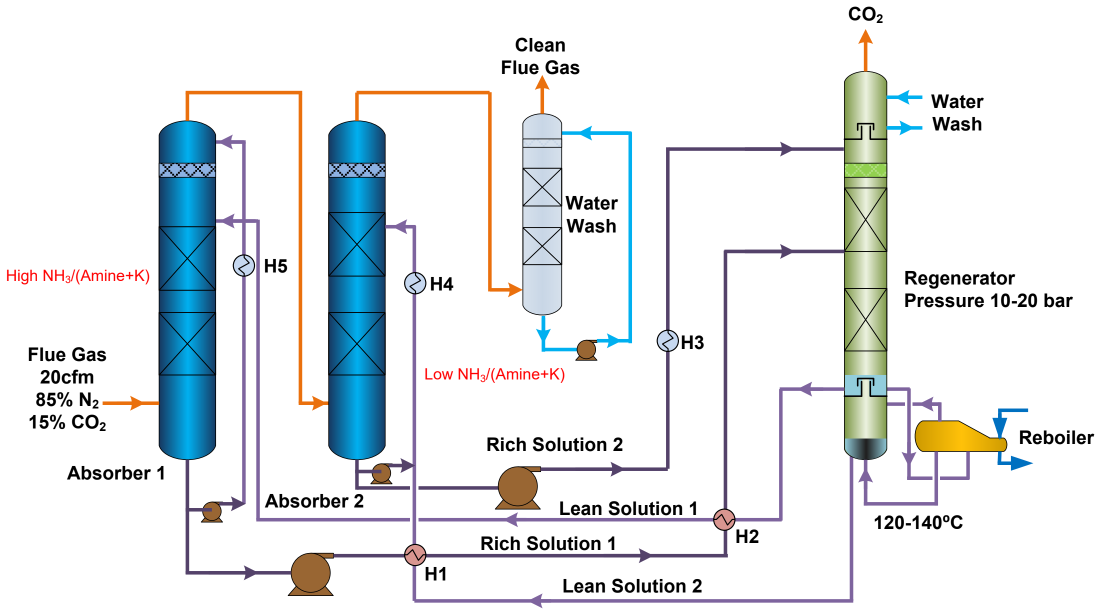

Figure 1: Conceptual process flow diagram for the A-MSP.

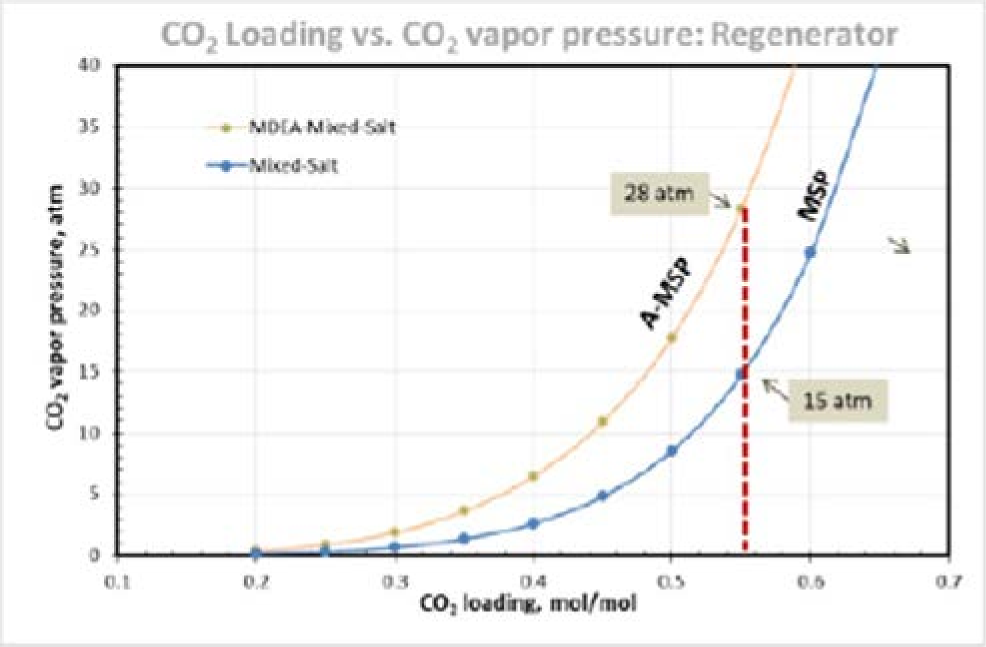

Figure 2: CO_2 loading versus CO_2 pressure at 100°C for (i) 10 molal mixed-salt and (ii) 10 molal MDEA-mixed-salt formulations.

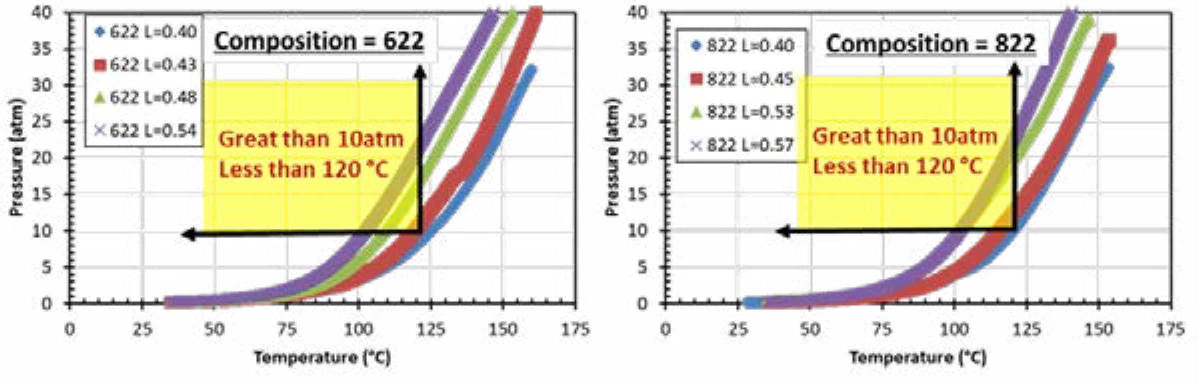

Figure 3: Measured CO_2 regeneration pressures for 622 and 822 formulations at various CO_2 loading as a function of temperature.

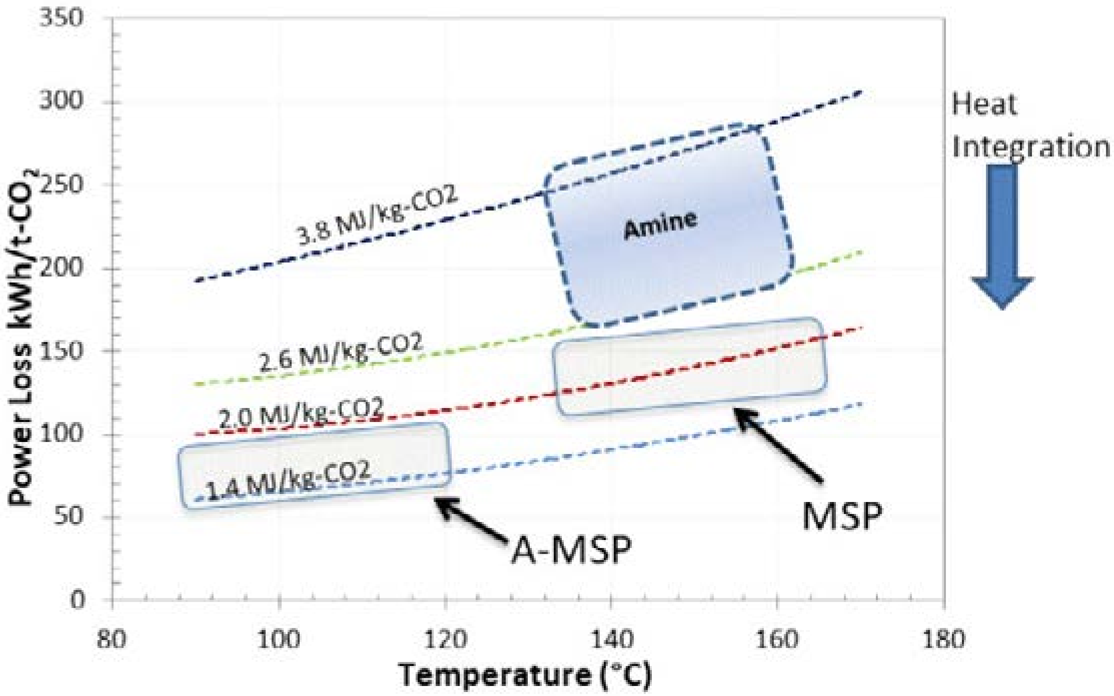

Figure 4: Power plant energy loss due to steam extraction.

Following lab-scale and small bench-scale testing, SRI's large bench-scale integrated CO_2 absorber-regenerator system (Figure 5), originally built for testing the MSP, was used without any major modifications for dynamic and steady-state testing of A-MSP. Additionally, the SRI bench-scale system was simulated using the OLI flowsheet program, and the data were utilized for model validation. The new thermodynamic data for organic-inorganic multi-species interactions obtained during this project was included in the flowsheet model database. Using the updated database and the latest version of OLI studio flowsheet program, a flowsheet model was generated, and heat and mass balances of streams at a 550-megawatt-electric (MWe) scale were obtained for the TEA. The carbon capture power plant economics data given in Table 2 were obtained from the TEA. The project was successfully completed on December 31, 2023. A patent application for A-MSP was filed in 2023 and the technology was licensed to Baker Hughes. Technology gaps have been identified and will be addressed in future studies at engineering-scale.

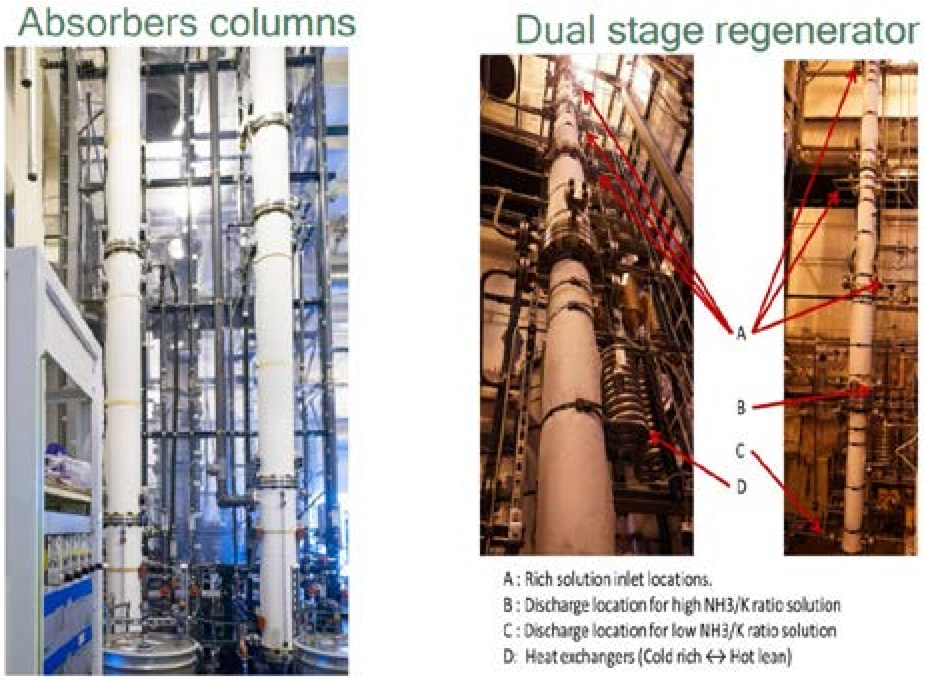

Figure 5: SRI's large bench-scale integrated absorber-regenerator system (gas flow rates up to 600 standard liters per minute).

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	18	18
Normal Boiling Point	°C	100	100
Normal Freezing Point	°C	0	0
Vapor Pressure @ 15°C	bar	0.017	0.017
Manufacturing Cost for Solvent	\$/kg	—	—
Working Solution			
Concentration	kg/kg	0.20-0.55	0.30-0.55
Specific Gravity (15°C/15°C)	—	1.17	1.17
Specific Heat Capacity @ STP	kJ/kg-K	2.9-3.7	2.9-3.0
Viscosity @ 20°C	cP	1.6-2.1	1.6-2.1
Surface Tension @ STP	dyn/cm	66.2	66.2
Absorption			
Pressure	bar	1	1
Temperature	°C	20-40	20-40
Equilibrium CO_2 Loading	gmol CO_2/kg	1.5-3.5	2.5-3.5
Heat of Absorption	kJ/kg CO_2	909-1,436	<1,500
Solution Viscosity	cP	1.6-2.1	1.6-2.1
Desorption			
Pressure	bar	8-10	10-15
Temperature	°C	120-140	120-140
Equilibrium CO_2 Loading	gmol CO_2/kg	0.2-0.6	0.2-0.6
Heat of Desorption	kJ/kg CO_2	1,700-2,000	<2,000
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	2475	

CO_2 Recovery, Purity, and Pressure	% / % / bar	90%	95%	12
Absorber Pressure Drop	bar		<0.1	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$		TBD	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – “Current” is market price of chemical, if applicable; “Target” is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The reaction involves chemical absorption of CO_2 through gas/liquid phase mass transfer followed by chemical reactions in the liquid phase.

These reactions are as follows:

1. $CO_2\ (g) \leftrightarrow CO_2\ (aq)$
2. $NH_3\ (aq) + CO_2\ (aq) + H_2O\ (liq) \leftrightarrow (NH_4)HCO_3\ (aq)$

3. $(NH_4)_2CO_3$ + $2CO_2$ (aq) + H_2O (liq) ↔ $2(NH_4)HCO_3$ (aq)
4. $2NH_3$ (aq) + CO_2 (aq) ↔ $(NH_4)NH_2CO_2$
5. $(NH_4)NH_2CO_2$ (aq) + CO_2 (aq) + $2H_2O$ (liq) ↔ $2(NH_4)HCO_3$ (aq)
6. K_2CO_3 (aq) + CO_2 (aq) + H_2O (liq) + catalyst ↔ $2KHCO_3$ (aq) + catalyst
7. R1R2R3N (aq) + CO_2 (aq) + H_2O (liq) + catalyst ↔ $(R1R2R3NH)HCO_3$ (aq) + catalyst

where R1=R2=CH_2CH_2OH and R3=CH_3

Solvent Contaminant Resistance – High.

Solvent Foaming Tendency – Low.

Flue Gas Pretreatment Requirements – The process is installed downstream of the FGD unit.

Solvent Makeup Requirements – To be determined.

Waste Streams Generated – To be determined.

Process Design Concept – Flowsheet/block flow diagram shown above in Figure 1.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	41.73	-
Cost of Carbon Avoided	\$/tonne CO_2	58.68	-
Capital Expenditures	\$/MWhr	49.4	-
Operating Expenditures*	\$/MWhr	51.4	-
Cost of Electricity	\$/MWhr	100.8	-

* Operating expenditures includes fuel cost of \$23.5 MWhr.

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – The numbers provided in the table are based on the reference plant provided by NETL for TEA analysis, found in the "Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity" report (*https://www.netl.doe.gov/energy-analysis/details?id=3745*), Revision 3.

Scale of Validation of Technology Used in TEA – Technology numbers were validated for use in the TEA analysis by modeling and laboratory testing.

Qualifying Information or Assumptions – Detailed qualifying information or assumptions regarding the economic numbers will be understood upon completion of the final TEA.

technology advantages

- Low NH_3 emissions.
- High CO_2 absorption rate and high CO_2 loading capacity.

- Reduced reboiler energy demand.
- Addition of tertiary amine to NH_4-based mixed-salt solvent reduces regeneration energy need and water use.
- Lower reboiler duty and regeneration temperature improve net power output, increasing net plant efficiency.
- Low-temperature, high-pressure regeneration of greater than 99% pure dry CO_2 reduces compression requirements.
- Oxidative degradation results show the A-MSP amine is more stable than MEA and other widely used amines.
- Very low corrosion rates for low-cost steels under absorber conditions.

R&D challenges

- Precipitation of solids in the absorber during cold weather conditions.
- Residual amine and/or NH_3 in exit gas stream.
- Solvent interaction with acid gases.
- Thermal management of absorber columns and regenerator.
- Long-term thermal degradation of A-MSP absorbent.

status

The project team successfully completed all tasks and the VLE model development, along with the integrated absorption/desorption testing in SRI's large bench-scale system, demonstrating the lower regeneration (less than 120°C) potential of the A-MSP solution. It was determined that a 9-molal (total) formulation comprised of potassium carbonate (K_2CO_3), NH_3, and MDEA exhibited the highest overall carbon capture efficiency. It was observed that the CO_2 capture efficiency decreases with an increase in loading and gas flow rate, due to gas contact time with the solvent being reduced on increasing flow rate. The capture efficiency was observed to range between 80% to 98% depending upon the experimental parameters.

available reports/technical papers/presentations

Jayaweera, P., "Mixed-Salt Based Transformational Solvent Technology for CO_2 Capture," Final Technical Report, March 2024. *Mixed-Salt Based Transformational Solvent Technology for CO2 Capture (Technical Report) | OSTI.GOV*.

Jayaweera, P., "Mixed-Salt Based Transformational Solvent Technology for CO_2 Capture," presented at the Project Closeout Meeting, January 2024. *https://netl.doe.gov/projects/files/Mixed%20Salt-Based%20Transformational%20Solvent%20Technology%20for%20CO2%20Capture.pdf*.

Jayaweera, P., "Mixed-Salt Based Transformational Solvent Technology for CO_2 Capture," presented at 2022 NETL Carbon Management Project Review Meeting - Point Source Carbon Capture, August 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_PSC18_Jayaweera_2.pdf.*

Jayaweera, P., "Mixed-Salt Based Transformational Solvent Technology for CO_2 Capture," presented at 2021 NETL Carbon Management Research Project Review Meeting, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Jayaweera_SRII.pdf*.

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Jayaweera, P., "Mixed-Salt Based Transformational Solvent Technology for CO_2 Capture," presented at the 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/P-Jayaweera-SRI-Mixed-Salt-Solvent.pdf*.

Jayaweera, P., "Mixed-Salt Based Transformational Solvent Technology for CO_2 Capture," Project Kick-Off Meeting, September 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10459&filename=Mixed-Salt+Based+Transformational+Solvent+Technology+for+CO2+Capture.pdf*.

Jayaweera, P., "Mixed-Salt Based Transformational Solvent Technology for CO_2 Capture," presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/P-Jayaweera-SRI-Mixed-Salt-Based-Transformational-Solvent.pdf*.

Fog- and Froth-Based Post-Combustion CO_2 Capture in Fossil Fuel Power Plants

primary project goal

The University of Kentucky (UK) developed a transformational compact carbon dioxide (CO_2) absorber with internal fog and froth formation for use in a solvent-based post-combustion CO_2 capture process in order to surmount the limitations of packed-bed CO_2 absorption columns and to lower the cost of CO_2 capture with a significantly smaller absorber.

technical goals

- Design and fabricate a bench-scale compact absorber with internal fog and froth sections.
- Develop and finalize the atomizing nozzle and froth-generating screens and operation conditions for fog and froth formation and destruction.
- Evaluate the fog and froth sections performance in a cold test unit.
- Integrate the compact absorber, including the fog and froth sections, into an existing bench-scale CO_2 capture unit with continuous solvent regeneration via stripping and fossil fuel-generated flue gas supply.
- Complete a bench-scale parametric testing campaign followed by a long-term campaign to assess performance and investigate the effects of solvent degradation on fog and froth formation.
- Investigate effects of controlling the temperature at the bottom of the compact absorber on the rich solvent loading and overall capture costs.
- Complete a techno-economic analysis (TEA) and environmental, health, and safety (EH&S) assessment.

technical content

UK developed an open-tower compact absorber with internal fog and froth for enhanced solvent-based CO_2 capture, as shown in Figure 1. In the process, the flue gas enters the bottom of the absorber and contacts the solvent in a counter-current flow through a section containing structured packing, capturing approximately 30% of the total CO_2 before passing through a riser to the top of the fog/froth capture section. In this section, the gas first contacts a lean amine solvent mist in a co-current flow, temperature-controlled environment, with approximately 7.5 times the liquid/gas contact area. Both the gas and liquid exiting from the fog section are forced through froth-generating and -propagating screens in the froth section. In this temperature-controlled environment, approximately six times the liquid/gas contact area is achieved. Additionally, the mass transfer is increased because a thin (target of ~10 µm) liquid film virtually eliminates the CO_2-amine diffusion resistance that typically impedes mass transfer

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
High Contact Compact Absorber

participant:
University of Kentucky

project number:
FE0031733

predecessor projects:
N/A

NETL project manager:
Carl Laird
carl.laird@netl.doe.gov

principal investigator:
Heather Nikolic
University of Kentucky
heather.nikolic@uky.edu

partners:
Industrial Climate Solutions Inc.; NexantECA; ALL4

start date:
05.01.2019

percent complete:
100%

in conventional capture technologies using packing. By greatly increasing the liquid/gas contact area and minimizing the diffusion resistance, the absorber column size can be reduced by up to 70% compared to a standard absorber design. The TEA compared to the "Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity" report Revision 4, September 24, 2019 B12B found that combining this fog/froth process with other UK CO_2 capture technologies could potentially achieve:.

- A CO_2 capture system bare erect cost (BEC) of $360,985/kWh, which is a 22.8% reduction compared to 2019 B12B.
- A levelized cost of electricity (LCOE), excluding transportation and storage, of $95.6/MWh, which is a 9% reduction compared to 2019 B12B.
- A total capital cost of $45/MWh, which is a 12% reduction from 2019 B12B.
- Specifically, the cost of the UK compact absorber was estimated at $14,987,000, which is 16% lower than the estimated cost of a traditionally packed absorber.
- A cost of CO_2 capture of $36.70/tonne, which is a 20% reduction compared to 2019 B12B.
- A net power output of 686 MWe, which is a 5.5% increase compared to 2019 B12B.

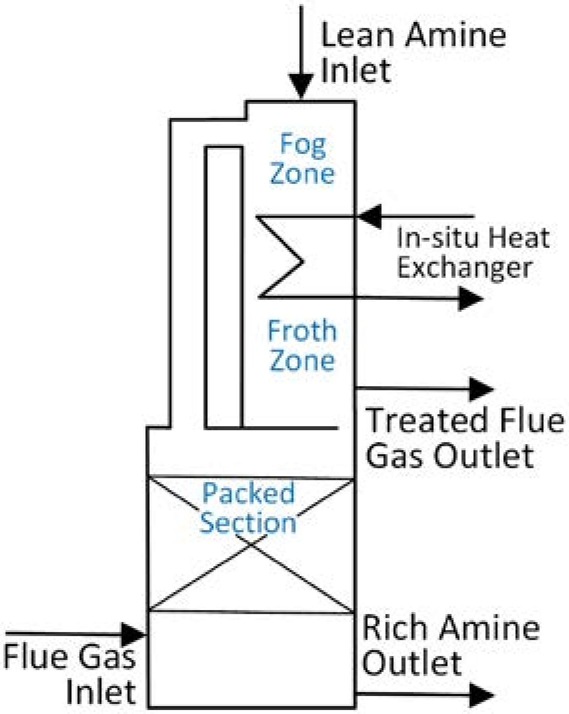

Figure 1: Schematic of UK compact absorber.

Figure 2: Completed bench-scale UK compact absorber.

The complete compact absorber, as shown in Figure 2, was designed, fabricated, operated, and analyzed, including the atomizing nozzle, froth-generating and froth-propagating screens, and in situ heat removal units. The frothing screens, as shown in Figure 3, are optimized for froth generation and propagation. They were designed and supplied by Industrial Climate Solutions Inc. Fog generation includes spray nozzle selection and optimization of the nozzle arrangement, as well as mist size distribution in the column, via liquid supply parameters and solvent properties. Individual testing of the fog section and froth section was followed by parametric and long-term testing of the compact absorber integrated in UK's bench-scale post-combustion capture facilities using simulated and actual flue gas. Data from testing supported completion of a TEA and EH&S assessment for the process.

Figure 3: Froth-generating and froth-propagating screens.

Consistent with the UK solvent state point data table, the solvent and process parameters are provided in Table 1.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value at Bench Scale	Next Target R&D Value at Pilot Scale
Molecular Weight	g/mol	<90, Amine	<90, Amine
Normal Boiling Point	°C	160	160
Normal Freezing Point	°C	2	2
Vapor Pressure @ 15°C	bar	0.0007	0.0007
Manufacturing Cost for Solvent	$/kg (pure chemical)	6 (estimated in 2023)	6 (estimated in 2023)
Working Solution			
Concentration	kg/kg	< 0.45	< 0.45
Specific Gravity (15°C/15°C)	-	~1.01	~1.01
Specific Heat Capacity @ 40°C	kJ/kg-K	3.5	3.5
Viscosity @ 40°C, rich condition	cP	4.3	4.3
Absorption			
Pressure	bar	1	1
Temperature	°C	35-55	35-55
Equilibrium CO_2 Loading	mol CO_2/kg	2.3	2.3
Heat of Absorption	kJ/mol CO_2	55-60	55-60
Solution Viscosity	cP	3-5	3-5
Desorption			
Pressure	bara	1.6-2.2	1.6-2.2
Temperature	°C	117-120	117-120
Equilibrium CO_2 Loading	mol CO_2/kg	1.1-1.4	1.1-1.4
Heat of Desorption	kJ/mol CO_2	55-60	55-60
Completed Bench Scale Module		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	28	
CO_2 Recovery, Purity, and Pressure	% / % / bara	90 >95% 1.65	
Absorber Pressure Drop	"WC	<20	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$	$170K	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution). The chemical agent of the UK solvent used in this project is a non-MEA, commercially available primary amine.

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

Pressure	Temperature	Composition						
psia	°F	vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Chemical/Physical Solvent Mechanism – The UK solvent is an aqueous solution of a hindered primary amine. A carbamate species is formed upon CO_2 absorption. In a CO_2 capture absorber, the absorption rate, **R**, as a function of temperature, T, and carbon loading, **C/N**, can be expressed as: $\mathbf{R(T, C/N) = k_G \cdot a \cdot (P_{CO2} - P^*_{CO2})}$ where $\mathbf{k_G}$ is mass transfer coefficient, **a** is effective wetted surface area, and $\mathbf{(P_{CO2} - P^*_{CO2})}$ is the driving force, the difference in the concentration of CO_2 in liquid from the gas. Significant increase in **R**, via $\mathbf{k_G}$ and **a**, and corresponding reduction of capital cost comes from the mass transfer enhancement of the aqueous system compared to any 2nd-generation technology because there is an order of magnitude greater effective wetted surface area in the top of the absorber.

Solvent Contaminant Resistance – UK analysis shows the solvent is more resistant to degradation, 40–50% improvement than 30 wt% MEA. Accumulation of metals within the solvent is expected to be equivalent to that within 30 wt% MEA.

Solvent Foaming Tendency – Unstable froth formation (not persistent foaming) is a key aspect to the compact absorber. Surfactant is added to reduce the solvent surface tension and therefore control the frothing behavior. Initial CO_2 capture experiments on solvent physical properties were performed in a packed column (2-inch internal diameter [ID] mini-scrubber). Adding surfactant to change the solvent surface tension led to a CO_2 capture efficiency increase of 15–20% throughout the carbon loading range. The key reason for this enhancement is the presence of fine froth (bubbles) that increase surface area with the addition of surfactant. It was also found that as carbon loading increases, the tendency to form bubbles decreases due to increased viscosity and surface tension. For an unstable froth, the dispersion rate is also important. A surfactant was chosen with the faster dispersion rate compared to others considered.

Flue Gas Pretreatment Requirements – When applied to coal-fired flue gas, the pretreatment requirement is sulfur dioxide (SO_2) removal to less than 5 parts per million (ppm) to minimize heat stable salt formation. This can be done with a standard counter-current pretreatment column with a circulating solution of either of soda ash (Na_2CO_3) or sodium hydroxide (NaOH). The solvent used is a hindered primary amine and is not known to form stable nitrosamine species, therefore no additional nitrogen oxide (NO_X) removal is required. No additional moisture removal required, as it is for ionic liquids.

Solvent Makeup Requirements – Two factors contributing to solvent makeup rate are degradation and emission. UK analysis shows the solvent has degradation rates less than 30 wt% MEA and when the UK developed solvent recovery technology is applied, the solvent emission will be about 0.5 ppm. The anticipated solvent makeup rate is less 0.6 kg/tonne CO_2 captured for routine transition state operation by following external load change for power generation. However, the anticipated solvent makeup rate could be less 0.3 kg/tonne CO_2 captured for industrial applications that are routinely operated at near-steady state.

Waste Streams Generated – The waste streams of the post-combustion CO_2 capture process using the compact absorber are the same as any other post-combustion CO_2 capture process. There will be a blowdown stream from the SO_2 pretreatment column and a reclaimer waste stream from the solvent loop.

Process Design Concept – The initial design concept is shown in Figure 4. A 3-inch column is used for the fogging and frothing sections where the flue gas and solvent flow in a co-current fashion. The bottom section contains typical structured packing with the flue gas and solvent moving in a counter-current fashion. Later, the diameter of the fogging section was increased to accommodate the full solvent cone produced by the nozzle.

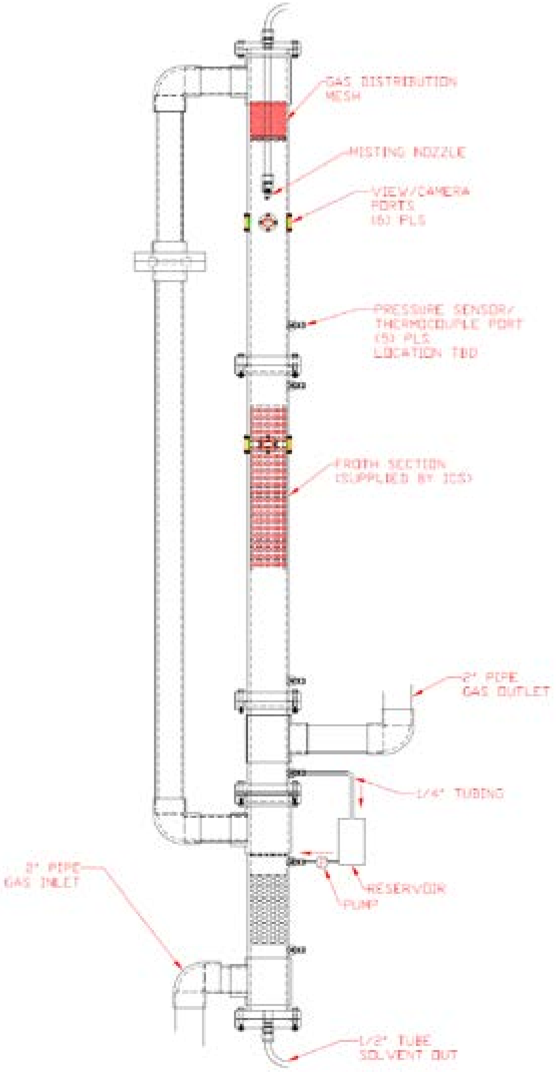

Figure 4: Compact absorber design concept.

Proposed Module Design – The absorber is modular with a natural divide between the bottom packed section and the top fog and froth section.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values, compared to 2019 B12B	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured (excluding TS&M)	2018\$/tonne CO_2	37.00	—
Cost of Carbon Avoided (excluding TS&M)	2018\$/tonne CO_2	47.7	—
Capital Expenditures (Total Plant Cost)	2018\$/MWhr	33.34	—
Operating Expenditures (Variable O&M)	2018\$/MWhr	13.00	—
Levelized Cost of Electricity (excluding TS&M)	2018\$/MWhr	96.00	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – The numbers provided in the table are based on the reference plant provided by the National Energy Technology Laboratory (NETL) for TEA, found in the "Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity" report Revision 4, September 24, 2019, $2018.

Scale of Validation of Technology Used in TEA – 0.1 megawatt-thermal (MWth) bench.

technology advantages

- 65–90% of absorption occurs in the fogging and frothing sections of the UK compact absorber.
- 6.8 times increase in liquid/gas contact area over 250Y structured packing.
- Up to four times increase in mass transfer over conventional columns due to increased liquid/gas contact and decreased CO_2-amine diffusion resistance with a thin solvent film ~10 µm liquid film that can impede the overall mass transfer of a capture technology.
- 64–75% reduction in absorber height from a typical packing height of 70–100 ft.
- ~40% reduced CO_2 capture auxiliary power requirement.
- Maintain carbon loading as close as achieved with conventional column containing structured packing.
- Rich loading maintained at lower L/G even when CO_2 partial pressure is reduced with a packing bottom temperature controlled of less than 95°F.
- A 20% reduction in overall cost of capture compared to current (2019) U.S. Department of Energy (DOE) estimates.

R&D challenges

- Demonstration at the bench scale due to wall effects in the small column.
- Pressure drop associated with froth generation and propagation.

status

The project concluded on December 31, 2023. The complete compact absorber was successfully designed, constructed, and integrated into the University of Kentucky's 0.1-MWth bench-scale CO_2 capture unit for evaluation with coal-fired flue gas.

Specific project achievements include:

- Solvent fog droplets of less than 50 µm and froth bubbles of less than 4 mm in size were demonstrated.
- 60+% CO_2 capture and 2.3 mol C/kg rich loading was demonstrated, on par with traditional absorber performance with greater than 2X absorption height.
- Statistical analysis of long-term campaign data show that at this scale residence time is limiting factor for CO_2 absorption.
- Measured degradation rates of 0.2–0.7 ppm organic degradation product and 1.8 ppm HSS per operational hour.
- Solvent emissions at absorber exhaust consistent with small pilot data, supporting less than 1 ppm after water wash.
- Absorber packing bottom temperature of less than 95°F achieved with chilled rich solvent spray applied, leading to maintenance of rich loading, at lower L/G even when CO_2 partial pressure is reduced.
- EH&S assessment completed, finding no impediment to scale up.
- Completion of conservative, realistic TEA compared to DOE's 2019 Vol. 1 report's Case B12B. TEA findings include:
    - Net power output of 686 MWe, which is a 5.5% increase.

- o An LCOE, excluding CO_2 transportation and storage, of $95.6/MWh, which is a 9% reduction.
- o A total capital cost contribution of $45/MWh, which is a 12% reduction.
- o The cost of the UK compact absorber was estimated at $14,987,000, which is 16% lower than the estimated cost of a traditionally packed absorber.
- o A net CO_2 capture cost of $36.70/tonne, which is a 20% reduction.

available reports/technical papers/presentations

Nikolic, H. & Liu, K., 2023, "Fog and Froth-based Post Combustion CO_2 Capture in Fossil Fuel Power Plants." *Final Technical Report.* Report No. DOE-UKY-31733-1. University of Kentucky: Lexington, KY. *https://www.osti.gov/biblio/2274747*.

Nikolic, H., 2023, "Fog+Froth-based Post-Combustion CO_2 Capture in Fossil-Fuel Power Plants," Presented at the 2023 FECM/NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC30_Nikolic.pdf*.

Nikolic, H., 2021, "Fog+Froth-based Post-Combustion CO_2 Capture in Fossil-Fuel Power Plants," Presented at the 2021 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Nikolic.pdf*.

Nikolic, H., 2021, "Fog+Froth-based Post-Combustion CO_2 Capture in Fossil-Fuel Power Plants," Presented at the CO_2 Capture BP1 Review Meeting, Pittsburgh, PA. *https://netl.doe.gov/projects/plp-download.aspx?id=10750&filename=Fog+and+Froth+Based+Post+Combustion+CO2+Capture+in+Fossil+Fuel+Power+Plants.pptx*.

Nikolic, H., 2019, "Fog+Froth-based Post-Combustion CO_2 Capture in Fossil-Fuel Power Plants," Presented at 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA. *https://netl.doe.gov/sites/default/files/netl-file/H-Nikolic-UKY-CAER-Fog-Froth-Capture.pdf*.

Nikolic, H., 2018, "Fog+Froth-based Post-Combustion CO_2 Capture in Fossil-Fuel Power Plants," Presented at the Project Kickoff Meeting, Pittsburgh, PA. *https://netl.doe.gov/projects/plp-download.aspx?id=10752&filename=Fog+and+Froth+Based+Post+Combustion+CO2+Capture+in+Fossil+Fuel+Power+Plants.pdf*.

Development and Bench-Scale Testing of a Novel Biphasic Solvent-Enabled Absorption Process for Post-Combustion Carbon Capture

primary project goal

The University of Illinois at Urbana-Champaign (UIUC) advanced the development of a novel biphasic carbon dioxide (CO_2) absorption process (BiCAP) and validated its technical advantages by testing an integrated system at a 40-kilowatt-electric (kWe) bench scale with actual coal-derived flue gas. This project moves the technology development forward via fully integrated bench-scale testing in a relevant flue gas environment.

technical goals

- Develop process simulations using an Aspen Plus model to determine the optimal process configuration and operating conditions.
- Investigate biphasic solvent losses, emission control, and reclamation of the degradation products.
- Design, fabricate, and test a 40-kWe integrated bench-scale biphasic solvent-based capture unit with simulated flue gas. A subsequent test used a flue gas slipstream from a coal-fired power plant.
- Assess the techno-economic performance of the technology integrated into a net 650-megawatt-electric (MWe) coal-fired power plant.
- Analyze technology gaps and potential environmental, health, and safety (EH&S) risks to advance the technology toward further scale-up and commercialization.

technical content

The BiCAP utilizes biphasic solvents, which are water-lean solvent blends, that can form and develop dual liquid phases, with the absorbed CO_2 highly enriched in one of the phases and lean in the other. The phase transition behavior of a biphasic solvent is illustrated in Figure 1. The process features multiple stages of liquid-liquid phase separation (LLPS) during CO_2 absorption to maximize the CO_2 absorption kinetics and minimize the increase in solvent viscosity.

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Biphasic Solvents for Post-Combustion CO_2 Absorption in Coal-Derived Flue Gas

participant:
University of Illinois at Urbana-Champaign

project number:
FE0031600

predecessor project:
FE0026434

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partners:
Trimeric Corporation

start date:
4.06.2018

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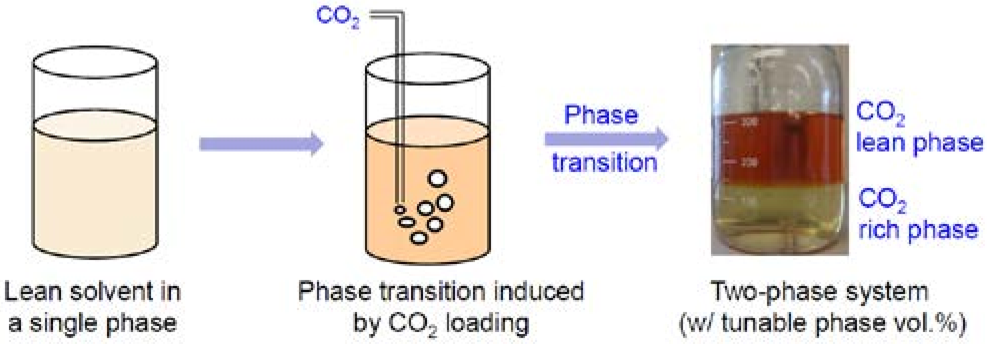

Figure 1: Phase transition behavior of a biphasic solvent.

A schematic diagram of the BiCAP is shown in Figure 2. The flue gas, after the cooling and sulfur dioxide (SO_2) polishing stages, enters the absorption column, which contains multiple stages of packed beds, and the CO_2 is absorbed into a biphasic solvent. At each stage, upon CO_2 loading, the biphasic solvent undergoes a phase transition and forms dual liquid phases. The heavy, CO_2-enriched phase is separated and pumped to a rich solvent tank. The CO_2-lean phase then flows via gravity to a heat exchanger to reduce the solvent temperature before entering the next stage of the packed bed. At the last stage, the solvent exiting the absorber is sent to an LLPS tank, in which the CO_2-enriched phase is pumped into the rich solvent tank. Both the warm and cold rich solvents are fed to a stripper to remove CO_2, while the CO_2-lean phase is mixed with the regenerated solvent from the CO_2 stripper before recycling to the absorber. The CO_2 product stream from the stripper is cooled and compressed.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	60-240	<230
Normal Boiling Point	°C	140-300	>140
Normal Freezing Point	°C	-30 to 110	<20
Vapor Pressure @ 20 °C	bar	1×10^{-5} to 4×10^{-3}	$<1.0 \times 10^{-3}$
Manufacturing Cost for Solvent	$/kg	3-10	<15
Working Solution			
Concentration	kg/kg	0.6-0.8	>0.5
Specific Gravity (15 °C/15 °C)	-	~1.0	0.9–1.4
Specific Heat Capacity @ STP	kJ/kg-K	2.5–3.5	<3.5
Viscosity @ STP	cP	2-15	<20
Absorption			
Pressure	bar	<0.05 (equilibrium P_{CO2} at absorber bottom)	<0.07
Temperature	°C	30-50	30–50
Equilibrium CO_2 Loading	mol/mol	0.375-0.625 in mixed phase (0.7-1.0 in CO_2-enriched phase)	>0.375
Heat of Absorption	kJ/mol CO_2	65-85	~75
Solution Viscosity	cP	5–10/30–50 (lean/enriched phases)	<50 (CO_2-enriched phase)
Desorption			
Pressure	bar	P_{CO2}=1-3 (3-7.5 in total)	P_{CO2}≥1.5 (≥4 in total)
Temperature	°C	120-150	<150
Equilibrium CO_2 Loading	mol/mol	0.05-0.35	<0.35
Heat of Desorption	kJ/mol CO_2	65-85	~75

Proposed Module Design		*(for equipment developers)*
Flue Gas Flowrate	kg/hr	not available
CO_2 Recovery, Purity, and Pressure	%/%/bar	>90% / >99% / >4
Absorber Pressure Drop	Bar	<0.07
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	not available

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

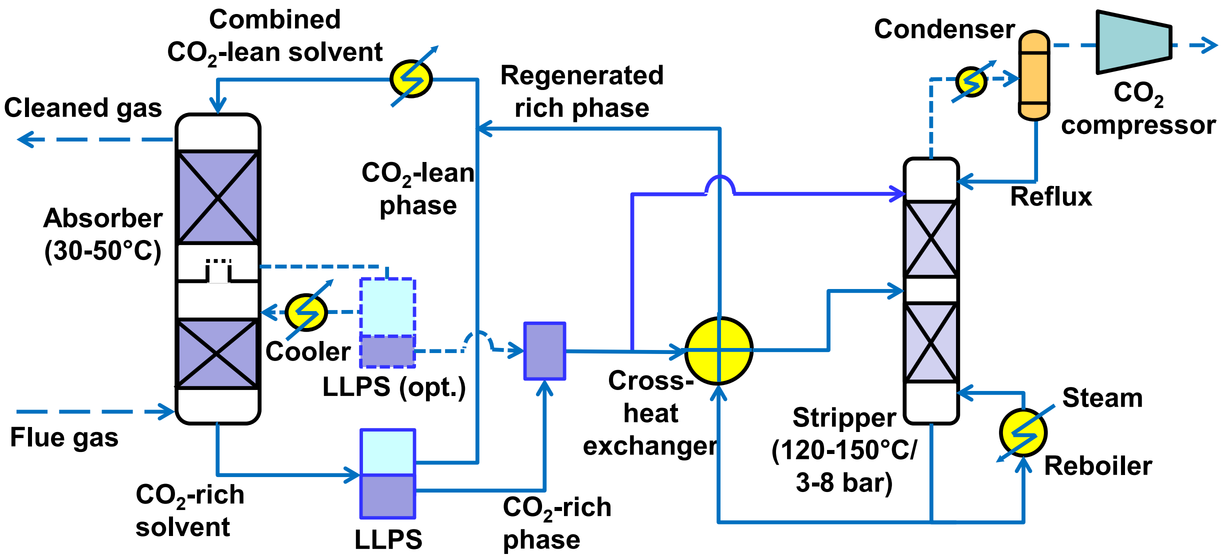

Figure 2: Schematic diagram of the BiCAP with multiple stages of LLPS. (Pumps are not shown in the figure.)

The novel water-lean biphasic solvents have previously demonstrated (FE0026434) the desired vapor-liquid equilibrium (VLE) behavior, rapid absorption kinetics, and high stability in lab-scale characterization experiments, and individual major process steps have been tested on the lab-scale equipment or assessed by modeling studies. Key features of the BiCAP include: (1) a unique process configuration of multi-stage CO_2 absorption and phase transition allows continual separation and removal of the CO_2-enriched liquid phase, maintaining rapid kinetics and low solvent viscosity throughout CO_2 absorption; (2) only the CO_2-enriched liquid phase is used for CO_2 desorption, thus lowering the mass flow of solvent required for regeneration; (3) the concentrated CO_2 loading in the solvent feed stream to the stripper allows the high pressure of CO_2 desorption to further improve the energy efficiency; and (4) a portion of cold feed stream enters the stripping column, bypassing the cross heat exchanger, further reducing the stripping heat requirement.

In a previous U.S. Department of Energy (DOE)-funded project (FE0026434), the BiCAP was tested at laboratory scale (10 kWe) and exhibited a 34% reduction in parasitic power requirements and twice the CO_2 working capacity for desorption when compared with a process using the amine-based solvent, monoethanolamine (MEA). After determining the optimal process configuration and operating conditions, the team has designed and fabricated the 40-kWe integrated bench-scale capture unit at UIUC's Abbott power plant. Parametric testing for two of the best-performing biphasic solvents identified from previous research (FE0026434) has been conducted with simulated flue gas over a period of seven months. One selected biphasic solvent underwent further evaluation with a slipstream of coal-derived flue gas at the power plant in two continuous test campaigns for a total of 31 days. In the first test campaign, targeting 90% CO_2 removal, the heat duty averaged 2,183 kJ/kg and CO_2 desorption pressure ranged between 60–67 pounds per square inch absolute (psia). The second test campaign, targeting 95% CO_2 removal, exhibited an average heat duty of 2,450 kJ/kg and CO_2 desorption pressure at approximately 60 psia. Throughout the two test campaigns, no noticeable trends of solvent degradation and emissions losses were observed. Based on the test results, a techno-economic analysis (TEA) was conducted to compare the BiCAP technology to DOE's baseline cases at a 650-MWe net output scale. The TEA results indicated that for the integration of BiCAP into a 650-MWe pulverized coal-fired power plant, the parasitic power loss was reduced by approximately 20%, and the cost of CO_2 capture was lowered to \$36.7/tonne on a December 2018 dollar basis, representing a reduction of approximately 21% compared to the DOE's baseline Case B12B. The system-wide results of this analysis are shown in Table 2.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS*

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	36.7	30.0
Cost of Carbon Avoided	\$/tonne CO_2	45.9	37.7

Capital Expenditures	$/MWhr	45.8	51.9
Operating Expenditures	$/MWhr	49.9	55.5
Cost of Electricity (Excluding Transport & Storage)	$/MWhr	95.7	107.4

*Estimated based on DOE/NETL baseline Cases B12A and B12B, Revision 4, September 2019, DOE/NETL-PUB-22638.

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The developed solvent belongs to a new class of biphasic solvents. The solvent is a blend of amines or the like and is a water-lean system containing less than 30 wt% water. The solvent absorbs CO_2 through chemical reactions between amines and CO_2. The solvent undergoes a phase transition to form dual liquid phases based on the difference of hydrophobicity between different species.

Solvent Contaminant Resistance – The developed biphasic solvent is highly resistant to oxygen and heat. Experiments revealed that the oxidative degradation of the biphasic solvent was eight times slower than the benchmark MEA under similar absorption conditions and its thermal stability at 150°C was comparable to the benchmark MEA at 120°C.

Solvent Foaming Tendency – No foaming issues were observed for the biphasic solvent, either in a gas bubbler tested continually for two weeks, in a laboratory absorption column operated intermittently for several months in a previous project (FE0026434), or in the bench-scale parametric and continuous testing at Abbott power plant in this project.

Flue Gas Pretreatment Requirements – The flue gas leaving the FGD needs be further polished to reduce the content of SO_2 below 10 parts per million volume (ppmv).

Solvent Makeup Requirements – Laboratory solvent stability experiments in a previous project (FE0026434) indicated that the makeup requirement of the biphasic solvent was lower than the benchmark MEA (i.e., less than 2 kg/ton CO_2 captured). In this project, no noticeable solvent degradation was observed during a total of 31 days of continuous testing with a slipstream of coal combustion flue gas at Abbott power plant.

Waste Streams Generated – Waste streams from the BiCAP are similar to those from amine-based processes, including flue gas condensate, water wash blowdown, cooling water blowdown, heat stable salts, spent solvent wastes, and spent solvent reclamation materials (e.g., activated carbon).

Process Design Concept – See Figure 2.

technology advantages

- BiCAP maintains rapid kinetics throughout the CO_2 absorption process and thus can reduce the footprint and cost of absorption equipment compared with either MEA or other biphasic solvent-based processes.
- BiCAP can maintain the solvent at a lower viscosity and thus retain rapid mass transfer in the absorber, potentially increasing the CO_2 working capacity of the solvent and reducing the footprint and capital cost of the absorber.
- The highly concentrated CO_2 loading in the solvent feed stream entering the stripping column results in high-pressure CO_2 desorption and thus lowers the energy use for CO_2 separation and compression.
- BiCAP desorption configuration with a cold rich solvent stream directly fed to the top of the stripper, in addition to the main rich solvent feed, results in reduced water vapor in the CO_2 stream and thus further reduces the stripping heat duty.
- The energy efficiency advantages of the BiCAP coupled with reduced equipment sizes when scaled-up for commercial systems leads to reductions in both capital and operating expenses compared to the conventional process.

R&D challenges

- Developing methods for controlling solvent losses caused by volatility of the selected biphasic solvents.
- Developing methods for controlling solvent losses caused by aerosols present in flue gas.
- Identifying the optimal design and operating conditions for the phase separation equipment.
- Developing methods for solvent reclamation with high efficiency and low environmental impact.

status

The project has concluded. Researchers identified a cold bypass stripping configuration to be the most energy efficient for the BiCAP process. The reclamation of simulated solvent degradation products was investigated in the laboratory, leading to the identification of several effective methods for biphasic solvent recovery. A 40-kWe bench-scale BiCAP unit was designed, fabricated, and installed at Abbott Power Plant. This bench-scale unit underwent successful testing, initially with simulated flue gas intermittently for 7 months, followed by continuous testing with a slipstream of coal-combustion flue gas from the power plant for a total of 31 days. The test results indicate that the BiCAP process can achieve 95% CO_2 removal and has superior energy performance. Finally, the project team modeled the process using highly detailed Aspen Plus models and conducted a TEA study to demonstrate its cost advantages compared to the DOE's baseline capture system.

available reports/technical papers/presentations

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Du, Y. et al., 2017"A Novel Biphasic Solvent for Post-Combustion CO_2 Capture," presented at the 4th Post-Combustion Capture Conference, Birmingham, AL.

Lu, Y., 2017, "Development of a Novel Biphasic CO_2 Absorption Process with Multiple Stages of Liquid-Liquid Phase Separation for Post-Combustion Carbon Capture," presented at the 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA. *https://netl.doe.gov/sites/default/files/event-proceedings/2017/co2%20capture/2-Tuesday/Y-Lu-ISGS-Biphasic-CO2-Absorption-Process.pdf*.

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Lu, Y., 2016, "Development of a Novel Biphasic CO_2 Absorption Process with Multiple Stages of Liquid-Liquid Phase Separation for Post-Combustion Carbon Capture," presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA. *https://www.netl.doe.gov/sites/default/files/event-proceedings/2016/c02%20cap%20review/4-Thursday/Y-Lu-ISGS-Biphasic-CO2-Absorption-Process.pdf*.

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Emissions Mitigation Technology for Advanced Water-Lean Solvent-Based CO_2 Capture Processes

primary project goal

Research Triangle Institute (RTI) developed a comprehensive solvent emission mitigation toolset for reducing the solvent and aerosol emissions from carbon dioxide (CO_2) capture systems using water-lean solvents (WLSs). RTI's toolset was designed specifically for WLS systems, implementing an advanced organic solvent wash system in conjunction with water wash, acid wash and other commercially available, state-of-the-art emissions-reduction technologies.

technical goals

- Identify the contribution of vapor loss, entrainment and aerosols to the overall emissions for WLS systems.
- Determine the significance of CO_2 capture system operating parameters to the amine emissions.
- Develop an empirically derived emissions model based on the solvent physical properties and on critical operating parameters from the absorber and wash section.
- Evaluate suitable process arrangements for emissions-reduction devices.
- Evaluate the effectiveness of emissions mitigation devices to reduce the amine emissions to less than 1 part per million (ppm).
- Determine the contribution of the emissions control technologies (ECTs) to the overall CO_2 capture cost.

technical content

RTI has developed an effective toolset to reduce amine emissions for WLSs by means of reducing the vapor loss, liquid entrainment and aerosol formation altogether. WLS systems are an emerging class of advanced systems that have advantages compared to aqueous amine (water-rich) systems for CO_2 capture. Because of the low energy requirement for solvent regeneration, low viscosity and low equipment corrosion, WLS systems can substantially reduce the cost of CO_2 capture and improve the economic viability of the CO_2 capture technology over aqueous systems.

By implementing an advanced solvent wash system together with commercially available, state-of-the-art emissions reduction devices, this integrated approach can lead to a substantial reduction of amine emissions through the suppression of

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

Water-Lean Solvent Emission Control

participant:

Research Triangle Institute

project number:

FE0031660

predecessor projects:

N/A

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partners:

Technology Centre Mongstad; Linde

start date:

10.01.2018

percent complete:

100%

three key emission mechanisms: vapor loss, liquid entrainment and aerosol formation. The effectiveness of the ECTs in controlling the amine emissions in WLS systems, specifically RTI's non-aqueous solvent (NAS) systems, was evaluated using coal-derived and natural gas-derived flue gases through testing performed in RTI's Bench-scale Gas Absorption System (BsGAS). RTI's NAS-5 was tested to evaluate the impact of various process parameters that affect the overall amine emissions and aerosols formation using BsGAS. The BsGAS has been used for the large bench-scale testing of various CO_2 capture solvents to better understand operating parameters, capture performance, and the solvent regeneration energy requirement or specific reboiler duty (SRD) at a wide range of conditions. The BsGAS system features an absorber, a crossover heat exchanger, multiple options for regeneration and two water wash sections. The BsGAS possesses highly flexible process arrangements for absorption and regeneration, including a conventional absorber with structured packing and interstage coolers, a conventional regenerator with structured packing and interstage heaters, a conventional thermosiphon reboiler, and one- or two-stage flash regeneration. For emissions evaluation of NAS, the conventional absorber with three interstage coolers was set up as an absorber and the regenerator with three interstage heaters was used for regenerating CO_2.

More than 2,000 of BsGAS operating hours were used to investigate process improvements, which led to a selection of vital changes that effectively control the amine emissions. These process improvements are lime-coated filters for absorber gas inlet, advanced demister at the top of the absorber, and a second water wash with amine recovery unit. The BsGAS was modified to include the flue gas generation system and the ECTs. The flue gas generation system consists of a residential coal burner and natural gas burner capable of generating both coal- and natural gas-derived flue gases with the composition of the gaseous species highly resembling that of power plant flue gases.

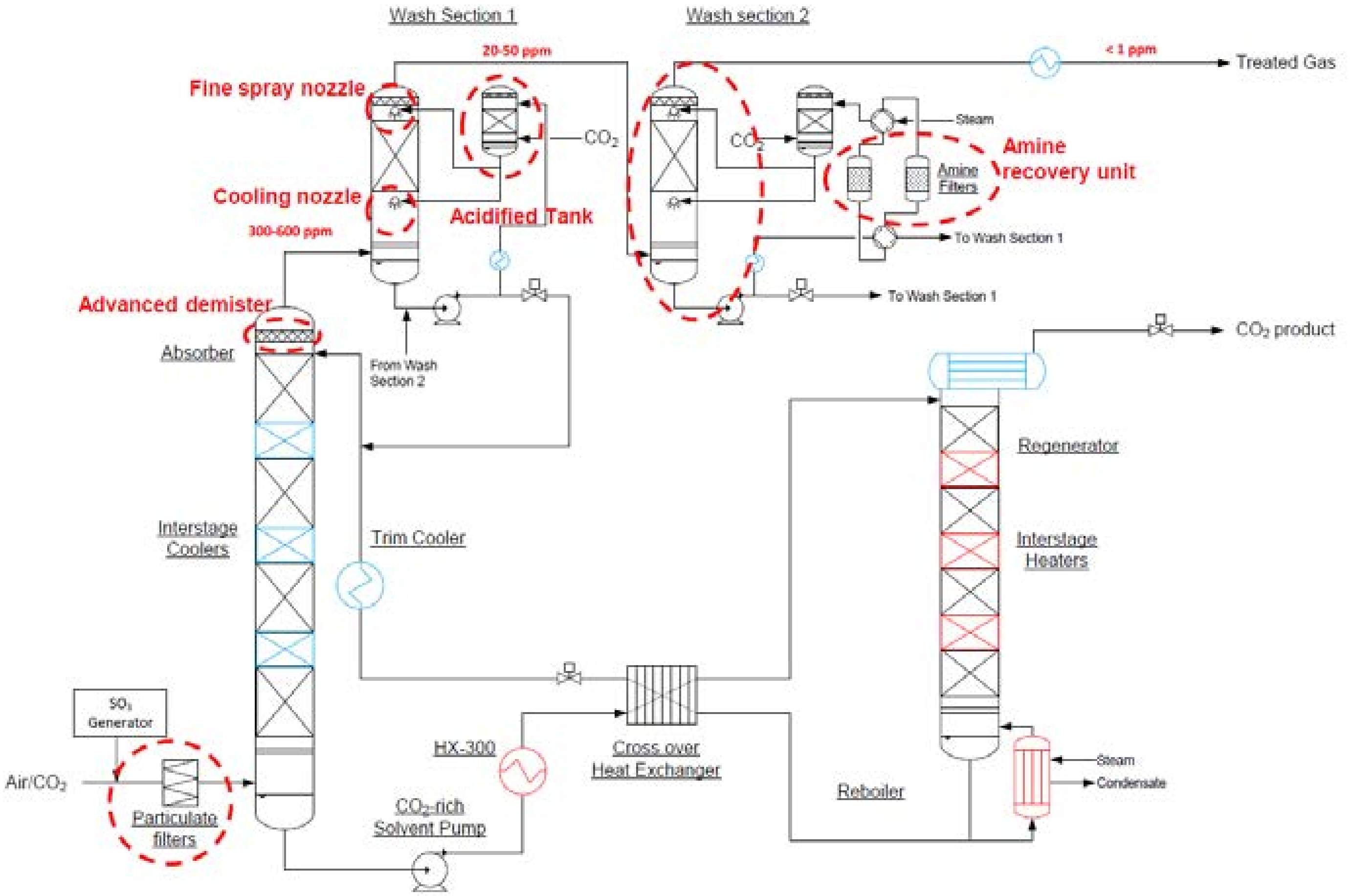

Figure 1: RTI's BsGAS with ECT and flue gas generation system.

The project goals were to determine RTI's NAS and selected WLS emissions characteristics from the absorber column; develop an empirical emissions model based on critical operating parameters; screen organic solvents and amine adsorbents; determine, implement and evaluate the effectiveness of the ECTs at BsGAS; modify the BsGAS to include the flue gas generation system, the lime-coated filters, advanced demisters and second water wash with amine; and demonstrate low amine emissions with ECTs using actual coal-derived flue gas with the NAS CO_2 capture technology.

Various emissions reduction strategies for advanced WLSs were studied, including minimizing aerosols through optimizing NAS running condition and the addition of ECTs; minimizing degradation through antioxidant, thermal and nitrogen oxide (NO_X) reduction studies; and minimizing vapor pressure through solvent formulation.

RTI's NAS-5 was tested to establish the baseline amine emissions from the CO_2 capture process under different CO_2 capture conditions and to derive a simple reduced order emissions model based on the data collected during the testing. The key parameters that were evaluated, and that could impact the emissions, were water wash temperature, liquid-to-gas ratio, CO_2 capture rate and the temperature in the absorber.

The lime-coated filter was found to significantly reduce the mass of aerosols in the 1–20 µm range; however, no significant change in measured amine emissions resulted from changes in aerosol size. As a result, the high-efficiency filter may not be needed to control the amine emissions from aerosols. Instead, the use of two water washes and the amine sorbent beds was shown to reduce the amine loss by aerosols. It was found that high CO_2 capture rates and lower CO_2 flue gas concentrations both reduce the CO_2 concentration in the treated gas and lead to higher amine emissions. Future work is needed to reduce the amine emissions for high CO_2 capture rates from natural gas combined cycle (NGCC) flue gas and other low CO_2 concentration flue gas sources. In addition, further screening of amine sorbents is required for higher temperature dew point operation with increased amine selectivity in higher temperature wash water.

An empirical model was developed to predict aerosol-based amine emissions from a CO_2 capture process using RTI's NAS-5. Principal Component Analysis (PCA) was used to identify data outliers and to reduce the dimensionality of the aerosol distribution data for use in a multivariate statistical model. The model used a combination of process control variables, process response variables, and aerosol characterization data to predict aerosol emissions from the process. The empirical model achieved a predictive capability of 15% average absolute deviation, and a predictability of 0.85.

A detailed techno-economic analysis (TEA) has been carried out for a supercritical pulverized coal (SCPC) plant using RTI-NAS technology for CO_2 capture and compared against the U.S. Department of Energy (DOE) reference cases for an SCPC plant with and without CO_2 capture. The cost of capturing 90% CO_2 was estimated to be \$38.2/tonne-CO_2, meeting the DOE target of \$40/tonne CO_2.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	95–115**	99
Normal Boiling Point	°C	185–243**	200
Normal Freezing Point	°C	(-6 to -24)**	-9.15
Vapor Pressure @ 15°C	bar	4.47e–4**	4.47e–4
Manufacturing Cost for Solvent	\$/kg	14	5
Working Solution			
Concentration	kg/kg	0.5–0.6*	0.55
Specific Gravity (15°C/15°C)	-	0.9–1.035*	1.035
Specific Heat Capacity @ STP	kJ/kg-K	2.78*	2.78
Viscosity @ STP	cP	4.38–4.7*	4.7
Absorption			
Pressure	bar	0.133*	0.133
Temperature	°C	35–45*	38
Equilibrium CO_2 Loading	mol/mol	2.04–2.22*	2.04
Heat of Absorption	kJ/mol CO_2	1,700–2,000*	1,931
Solution Viscosity	cP	4–30*	28

Desorption			
Pressure	bar	2–7.8*	2
Temperature	°C	90–110*	105
Equilibrium CO_2 Loading	mol/mol	0.45-1.13*	0.45
Heat of Desorption	kJ/mol CO_2	2,100*	2,045

* Experimentally measured data.

** Calculated data for different concentrations and conditions using standard mixing rules from pure components data.

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – “Current” is market price of chemical, if applicable; “Target” is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

		Composition						
Pressure	**Temperature**	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical

Solvent Contaminant Resistance – More resistant than MEA to sulfur oxide (SO_X) and nitrogen oxide (NO_X).

Solvent Foaming Tendency – Less foaming than aqueous amine solvent.

Flue Gas Pretreatment Requirements – Temperature adjustment and SO_X control.

Solvent Makeup Requirements – 0.2 to 0.5 kg/tonne CO_2.

Waste Streams Generated – None.

Process Design Concept – Absorber with interstage coolers coupling with regenerator with interstage heaters.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS*

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	38.2	—
Cost of Carbon Avoided	\$/tonne CO_2	72.1	—
Capital Expenditures	\$/MWhr	46.3	—
Operating Expenditures	\$/MWhr	45.1	—
Cost of Electricity	\$/MWhr	106.2	—

*Economics parameters were not set as an R&D Target.

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – The calculation basis are the Case 11 for the reference plant and Case 12 for the CO_2 capture plant, provided by NETL for TEA analysis found in "Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity Revision 2a, September 2013" and the costs updated using "Updated Costs June 2011 Basis for Selected Bituminous Cases," DOE/NETL-341/082312.

Scale of Validation of Technology Used in TEA – The TEA was performed using a process model validated with data from pilot and bench scale. The technology for CO_2 capture has been validated at the pilot plant scale. The technology for emissions control has been validated at bench-scale testing.

Qualifying Information or Assumptions – All numbers are provided using June 2011 cost basis. Capital expenditure costs were calculated using the total overnight cost (TOC).

technology advantages

- WLS systems have a low energy requirement for solvent regeneration and other added benefits, which reduce cost of CO_2 capture.
- Project will provide a model that predicts the amine emissions using the solvent properties, key process parameters, and the recommended emissions mitigation devices required for solvents specific to the developers.

R&D challenges

- Aerosol particle generation.
- Development of aerosols and particle counts technique for WLSs.
- Quantification and speciation of the emissions from WLSs.

- Emissions model development.
- Solvent screening for organic wash section.
- Process arrangement for amine extraction.
- Parametric and long-term testing.

status

This project was completed on March 31, 2022. More than 2,000 hours of testing was completed for the BsGAS operation in the investigation of aerosols and ECTs. It was determined that ECTs could be used to reduce amine emissions to near 1 ppm and an empirical model was successfully developed that achieved an aerosol-based emissions predictability of 0.85. Through TEA, it was found that the cost of capturing of capturing 90% CO_2 for an SCPC plant using RTI-NAS technology for CO_2 capture is \$38.2/tonne-CO_2, meeting the DOE target of \$40/tonne CO_2. ETCs investigated here only contribute \$2.4/tonne CO_2 captured to the total cost.

available reports/technical papers/presentations

Tanthana, J. et al, "Emissions Mitigation Technology for Advanced Water-Lean Solvent-Based CO_2 Capture Processes," Final Report, March 2022, *https://www.osti.gov/biblio/1875691*.

Tanthana, J., "Emissions Mitigation Technology for Advanced Water-Lean Solvent Based CO_2 Capture Processes," Presented at the 2021 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Tanthana.pdf*.

Tanthana, J., "Emissions Mitigation Technology for Advanced Water-Lean Solvent Based CO_2 Capture Processes," Presented at the 2020 Project Continuation Meeting, March 2020. *https://netl.doe.gov/projects/plp-download.aspx?id=10603&filename=Emissions+Mitigation+Technology+for+Advanced+Water-Lean+Solvent+Based+CO2+Capture+Processes.pdf*.

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Tanthana, J., "Emissions Mitigation Technology for Advanced Water-Lean Solvent Based CO_2 Capture Processes," Poster presentation by Jak Tanthana, RTI International, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, *https://netl.doe.gov/sites/default/files/netl-file/J-Tanthana-RTI-Solvent-Emissions-Mitigation.pdf*.

Tanthana, J., "Emissions Mitigation Technology for Advanced Water-Lean Solvent Based CO_2 Capture Processes," Project kick-off meeting presentation, Nov 2018. *https://www.netl.doe.gov/sites/default/files/2019-01/FE0031660-kickoff.pdf*.

A New Thermal Swing Adsorption Process for Post-Combustion Carbon Capture From Natural Gas Combined Cycle Plants

primary project goal

TDA Research Inc. is developing a transformational polymer sorbent-based microwave-assisted thermal swing adsorption (MTSA) process to efficiently capture carbon dioxide (CO_2) from natural gas combined cycle (NGCC) flue gas. The project goal is to fabricate and test sorbent structures (laminates) in a bench-scale reactor module under rapid cycling conditions with simulated NGCC flue gas.

technical goals

- Synthesize the required quantities of sorbent to produce tetraethylenepentamine (TEPA)-appended mixed matrix polymeric resin sheets/laminates to support the bench-scale experimentation.
- Develop an adsorption model and a computational fluid dynamics model to support the reactor design work for both the bench-scale test module and the final commercial system.
- Complete a detailed design of the bench-scale system, including the microwave wave guides for effective microwave energy distribution inside the module.
- Fabricate a bench-scale sorbent reactor module that can treat 2–3 standard cubic feet per minute (scfm) flue gas, and commission the system.
- Carry out accelerated life cycle tests to assess long-term performance of sorbent sheets under relevant process conditions.
- Carry out bench-scale testing of the rapid cycling TSA process integrated with microwave-assisted desorption.
- Demonstrate continuous (pseudo) steady-state operation of the thermal swing system for a minimum of 1,000 hours, as well as dynamic operation such as trip conditions, quick start-up and shutdown, varying flue gas flowrates and increased flue gas contaminants.
- Validate models with the experimental data collected to support the techno-economic and life cycle analyses and an environmental health and safety analysis of the technology.

technical content

TDA Research's sorbent-based CO_2 capture process uses a highly stable, high-capacity functionalized mixed matrix polymer (MMP) sorbent manufactured into a structure with well-defined flow channels to achieve a very low pressure drop throughout the sorbent bed. The sorbent is a composite that includes a highly

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Sorbents

project focus:
Microwave-Assisted Thermal Swing Adsorption

participant:
TDA Research, Inc.

project number:
FE0032151

predecessor projects:
N/A

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galpteki@tda.com

partners:
Membrane Technology and Research Inc.; Mitsubishi Chemicals; Schlumberger; GE Gas Power

start date:
09.23.2022

percent complete:
50%

reactive TEPA phase tethered to methyl ester groups in a polymethacrylate (PMA) resin dispersed in a porous polyether sulfone (PES) polymer. The TEPA/PMA is mixed into PES monomer and cast into a porous polymer film to make a laminate sorbent sheet. The sorbent on supported thin films can be assembled into modules with desired flow characteristics for capturing CO_2 from NGCC plants. TDA is working with Membrane Research and Technology Inc. (MTR) to fabricate the engineered sorbent sheets/laminates in 1-by-1-foot size and larger modules to be integrated with a microwave heater. The sorbent achieves a very high working capacity (6 wt.%) when cycled between 60°C adsorption and 90°C desorption under NGCC flue gas conditions. The sorbent is regenerated using a thermal swing of only 30°C, which allows for a short cycle duration and increases sorbent utilization. The sorbent is prepared in the form of sheets (laminates) instead of pellets, which significantly reduce the mass and heat transfer distances, resulting in complete thermal cycling of the sorbent in less than 30 minutes. The system also uses directed microwave energy to assist with the rapid heating of the bed, reducing the heat requirement.

Figure 1 shows a schematic of TDA's MTSA process integrated into a new or existing NGCC power plant. The flue gas (at 83°C) is first cooled to less than 40°C. During adsorption, more than 95% of the CO_2 and some amount of the water (H_2O) is removed from the flue gas. Regeneration heat is supplied by microwave energy to rapidly increase the surface temperature of the sorbent to 90°C and mild vacuum (10 pounds per square inch absolute [psia]) is applied to recover the CO_2 and H_2O from the bed; this CO_2/H_2O stream is then compressed and cooled and the water is condensed to recover CO_2 as a high-purity product. The flue gas actively cools the sorbent bed, bringing the bed surface temperatures to about 60°C in 15 minutes. The bed design and cycling sequence are optimized to keep the CO_2 slip to a minimum to meet the 95% capture target. The very high selectivity of the sorbent (greater than 2,000 CO_2/nitrogen [N_2]) ensures a very high purity CO_2 product (greater than or equal to 95% by volume).

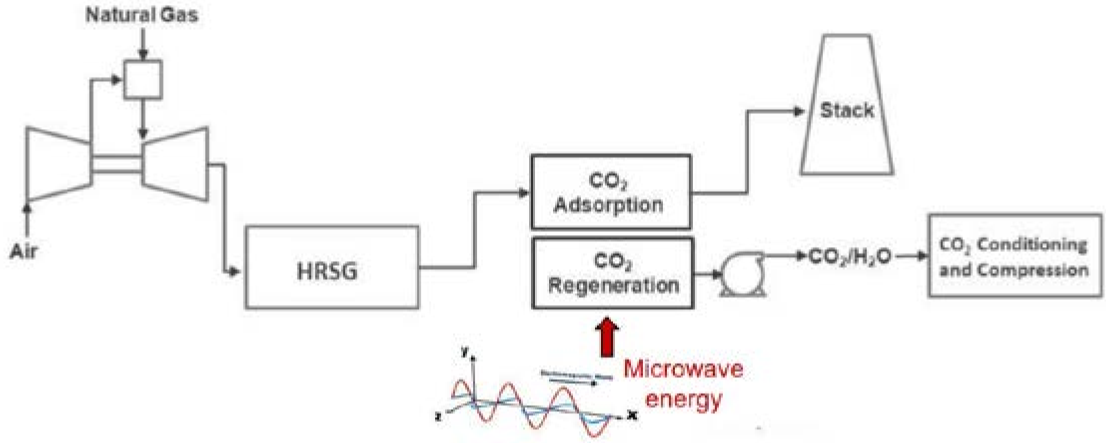

Figure 1: TDA's rapid cycling MTSA-based carbon capture system integrated to an NGCC power plant.

The bench-scale laminate sheets (Figure 2) are sized at 12-by-12 inches to fit within MTR's roll-to-roll coating machine. Two bench-scale modules of 12-by-12-by-12 inches are being incorporated into TDA's existing test apparatus to perform testing with simulated NGCC flue gas.

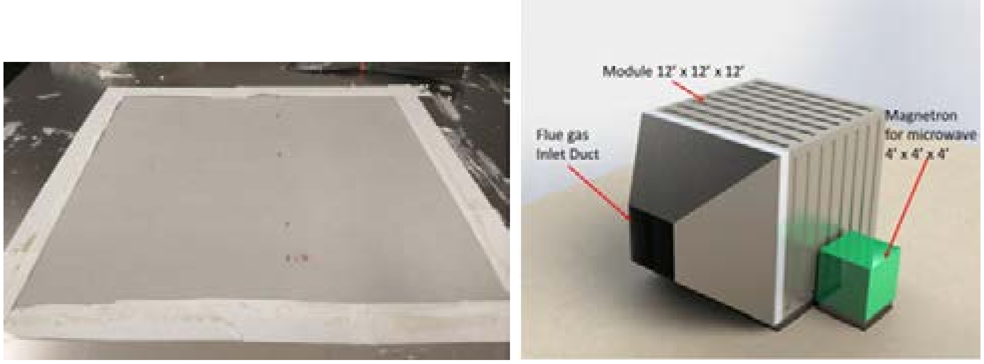

Figure 2. Bench-scale laminate sheets (left). Sorbent module with magnetron microwave generator on the side (right).

The primary focus of the project is to build the sorbent module that uses the optimal sorbent structures (sorbent sheets/laminates in planar geometry). Key design parameters, such as the active material (polymer sheet) thickness and the size of the flow channels, are also optimized while considering the impact on pressure drop, mass and heat transfer, and active material packing density.

TABLE 1: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	47	—
Cost of Carbon Avoided	\$/tonne CO_2	63	—
Capital Expenditures	\$/ MWhr	—	—
Operating Expenditures	\$/ MWhr	—	—
Cost of Electricity	\$/MWhr	—	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Process Design Concept – A full-scale module design is shown in Figure 3. TDA's MTSA process uses multiple trains (16 total) with a total of 32 beds/towers per train. Each bed/tower contains 24 structured sorbent modules made from thin sorbent laminates.

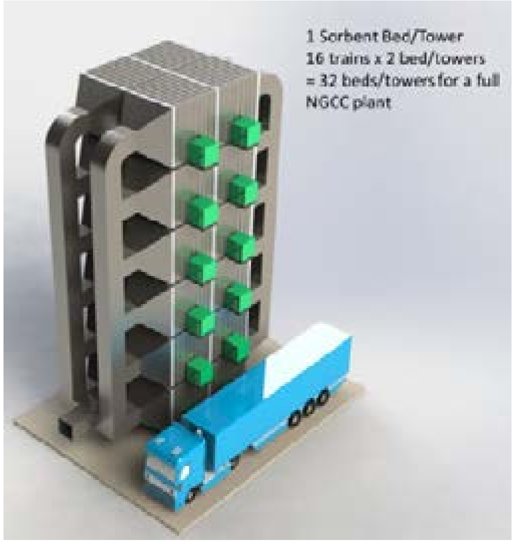

Figure 3: Single sorbent bed/tower with 24 individual sorbent modules (two each in series in flue gas flow direction and 12 such two-in-series modules in parallel). Bed height is 72 feet.

technology advantages

- The use of microwave heating allows for direct heating of the sorbent at the CO_2 adsorption site without first heating a reactor vessel or any inactive components, increases the speed of heating and reduces the energy input.
- The sorbent bed is repressurized and cooled using raw flue gas for energy savings.
- Sorbent material design in a structured form with well-defined gas flow channels minimizes the pressure drop in the sorbent bed and the associated parasitic power losses.
- High CO_2 uptake at a small thermal gradient.

R&D challenges

- Minimizing sorbent attrition.
- Performance of structured sorbent modules.
- Optimizing the size of the flow channels and thickness of the sorbent sheets to minimize pressure drop and achieve optimum heat transfer.

status

Sorbent has been synthesized and processed into 12-by-12-inch sorbent sheets/laminates by MTR. Accelerated life testing of the sheets/laminates is underway. A detailed design of the bench-scale sorbent module system integrated with heating and cooling for rapid cycling was completed. The reactive polymer sheets are being assembled into a minimum of two sorbent reactor modules and incorporated into an existing bench-scale flue gas system for testing with simulated NGCC flue gas.

available reports/technical papers/presentations

G. Alptekin, “A New Thermal Swing Adsorption Process for Post-Combustion Carbon Capture from Natural Gas Plants,” 2024 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_Posters_Alptekin.pdf*.

G. Alptekin, et.al., “A New Thermal Swing Adsorption Process for Post-Combustion Carbon Capture from Natural Gas Plants,” 2023 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC29_Alptekin.pdf*.

Transformational Molecular Layer Deposition, Tailor-Made, Size-Sieving Sorbents for Post-Combustion CO_2 Capture

primary project goal

Rensselaer Polytechnic Institute (RPI) and partners are developing a transformational molecular layer deposition (MLD), tailor-made, size-sieving sorbent/pressure swing adsorption (PSA) process (MLD-T-S/PSA) that can be installed in new (or retrofitted into existing) pulverized coal (PC) power plants for carbon dioxide (CO_2) capture. The project's technical activities include mathematical modeling, development of MLD tailor-made sorbents, MLD sorbent design, construction and testing of an MLD-T-S/PSA system.

technical goals

- Generate tailor-made, size-sieving sorbents by using MLD to coat sorbents.
- Identify promising sorbent materials through computational screening.
- Optimize MLD process to develop sorbents with high CO_2 adsorption capacity and stability in the presence of water vapor.
- Perform single-bed testing and simulation with the developed sorbents.
- Identify allowable contaminant levels for sorbents by further single-bed testing and simulation.
- Design PSA cycle schedule tailored to best MLD-modified sorbent.
- Design and construct MLD-modified sorbent/PSA skid system.
- Test skid system under simulated flue gas and actual flue gas conditions.
- Perform a TEA of the process integrated with a 550-megawatt-electric (MWe) power plant.

technical content

RPI, in collaboration with University of South Carolina (USC) and Gas Technology Institute (GTI), is developing a process that integrates transformational, tailor-made, MLD-modified sorbents with a novel PSA process concept to achieve U.S. Department of Energy (DOE) CO_2 capture performance and cost goals. The project team will conduct sorbent performance testing, PSA process optimization, and system design and construction. GTI will evaluate the influence of impurities on sorbent performance; construct a testing skid; and transport the testing skid to the National Carbon Capture Center (NCCC) in Wilsonville, Alabama, for field testing.

RPI has developed sorbents with CO_2/nitrogen (N_2) selectivity as high as 130—much higher than state-of-the-art commercial sorbents, such as 13X zeolite, with

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Sorbents

project focus:
Size-Sieving Sorbent Integrated with Pressure Swing Adsorption

participant:
Rensselaer Polytechnic Institute

project number:
FE0031730

predecessor projects:
N/A

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partners:
University of South Carolina; Gas Technology Institute; Southern Company Services Inc.

start date:
10.01.2019

percent complete:
70%

similar CO_2 capacity under similar adsorption conditions—enabling achievement of 95% CO_2 purity in a single-stage PSA for CO_2 capture from flue gas. The sorbents are coated with an inorganic material to achieve pore misalignment, which allows for fine-tuning the pore mouth size on the surface of sorbents (Figure 1). Using MLD, a vapor-phase deposition technique utilizing self-limiting surface reactions, the external surface of the base sorbent is uniformly coated by ultrathin (less than 20 nanometers [nm]) microporous coatings. A wide range of porous materials (zeolites, activated carbon, and metal-organic frameworks [MOFs]) in different forms (powder or pellets) can be used directly as the base material for MLD coating, and the pore mouth size can be precisely designed by controlling the coating layer composition and thickness, as well as the thermal treatment conditions. The MLD-modified sorbents provide precise pore mouth size control in the range of 0.01 nm, which is crucial for achieving highly selective separation of CO_2 from N_2, as illustrated in Figure 2. MLD treatment results in minimal loss to the CO_2 adsorption capacity of the base sorbent.

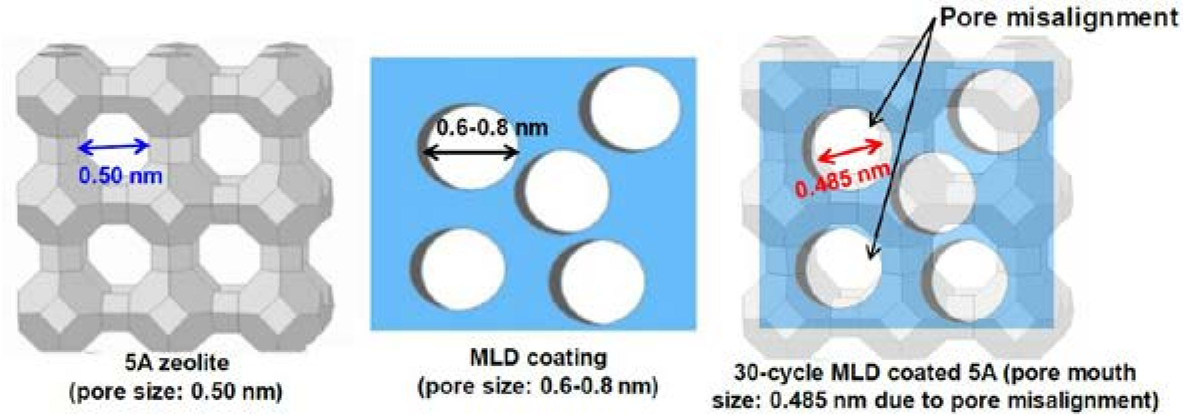

Figure 1: Schematic of pore misalignment for fine-tuning pore mouth size of sorbents.

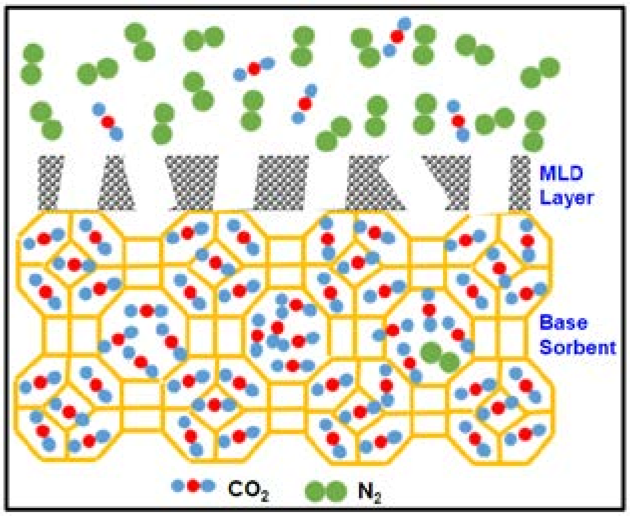

Figure 2: High CO_2/N_2 selectivity achieved by size-sieving for the MLD tailor-made sorbent.

Early studies on the pore misalignment concept show that 5A zeolite with and without MLD coatings have almost identical surface areas (343.5 ± 8.3 m^2/g) and micropore volume, suggesting that the coatings are only on the external surface and the internal cavity of the zeolite is maintained (Figure 3). Furthermore, the effective pore size of the treated 5A zeolite can be precisely controlled by the number of MLD cycles. Preliminary experiments on MLD-coated 13X zeolite show that almost no N_2 is adsorbed, suggesting a molecular sieving mechanism, and indicate a reduction in the heat of adsorption of CO_2. The sorbent and process parameters are provided in Table 1. In addition to 5A and 13X zeolites, other microporous sorbents have the potential to achieve high CO_2 adsorption capacity and CO_2/N_2 selectivity with MLD modification.

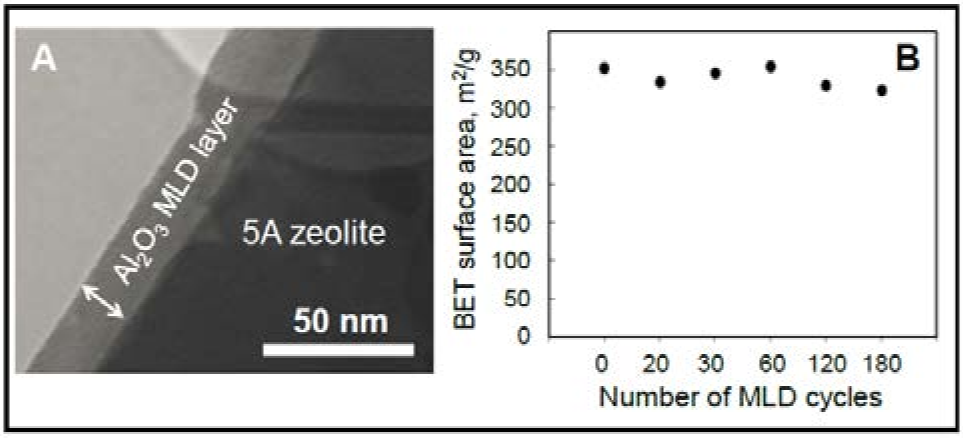

Figure 3: Characterization of MLD-modified 5A zeolite: (A) transmission electron microscopy (TEM) image of 5A zeolite with 60 cycles of aluminum oxide coating; (B) BET surface area of 5A zeolite with different cycles of MLD.

USC has developed a proprietary PSA cycle schedule concept for CO_2 capture from flue gas that involves the use of fewer number of beds than employed in their previously DOE-supported project DE-FE0007639, thereby reducing the CO_2 capture cost significantly. The number of required beds is reduced from 240 to 48 (i.e., six, eight-bed PSA systems operating in parallel) for the MLD-coated sorbent/PSA process integrated into a 550-MWe power plant. Figure 4 shows a diagram of the process, including identification of the numbered streams. The flow sheet incorporates desiccant wheels for water vapor removal upstream of the PSA process that are regenerated by a simple concentration swing with the light product from the PSA system and ambient air without the use of any heating. The dry light product (~2.4 mol% CO_2) produced by the PSA system is used to regenerate Dryer 2, and slightly compressed ambient air is used to regenerated Dryer 1. A reflux compressor produces a concentrated recycle stream containing approximately 83 mol% CO_2, facilitating the production of greater than 95 mol% CO_2 in the final CO_2 product. The system is uniquely designed with six adsorption beds being fed simultaneously, while two beds are being regenerated. This ensures low pressure drop during the feed step with a beaded adsorbent for large flow rate feed streams, allowing for the use of fewer number of adsorption beds in the PSA system since the adsorption bed height can be increased without a pressure drop penalty.

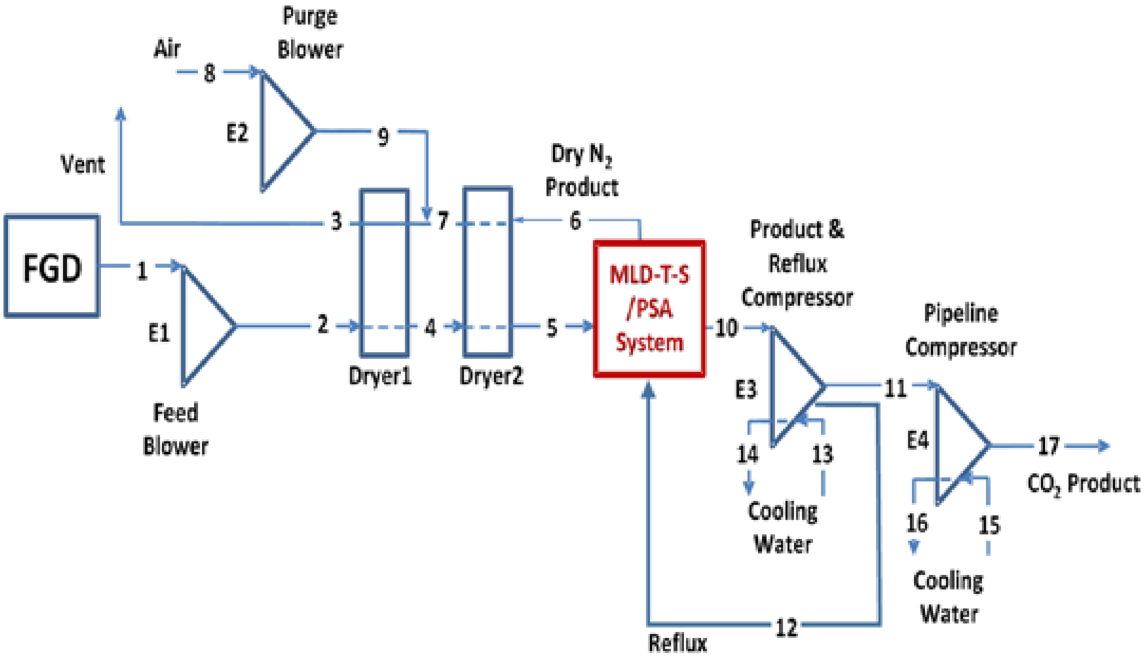

Figure 4: USC's PSA process flow diagram integrated with the MLD sorbent/PSA system.

USC's dynamic adsorption process simulator (DAPS) has been used to design a hypothetical MLD-treated sorbent/PSA system, showing a 6% reduction in separation energy when using MLD-coated 13X zeolite compared to commercial 13X. Preliminary TEA results compared to the DOE/National Energy Technology Laboratory (NETL) Base Case 9 (subcritical PC plant without CO_2 capture) and Base Case 10 (subcritical PC plant with amine scrubbing) are shown in Figure 5, indicating that the MLD-treated sorbent/PSA system can achieve 90% CO_2 capture rate with 95% CO_2 purity with a cost of $35/tonne CO_2. This cost uses the residual power of 422 MW remaining from a 550-MW power plant after accounting for the power consumed by the PSA unit and compression to pipeline (128 MW).

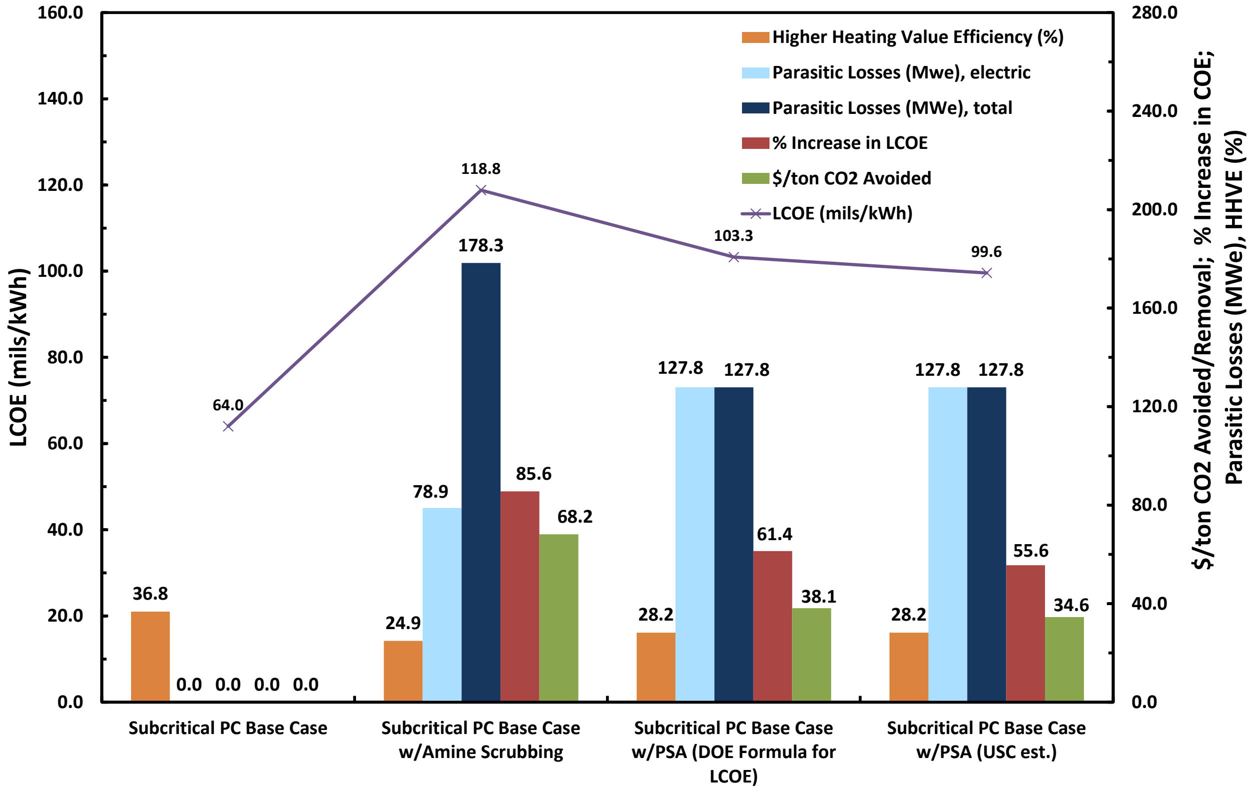

Figure 5: Comparison of the cost of CO_2 capture between DOE/NETL Base Case 9 (subcritical PC plant without CO_2 capture), Base Case 10 (subcritical PC plant with amine scrubbing), and the MLD-coated sorbent/PSA process.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,800	1,800
Bulk Density	kg/m^3	1,130	1,130
Average Particle Diameter	mm	0.003-0.005	0.003-0.005
Particle Void Fraction	m^3/m^3	0.374	>0.3
Packing Density	m^2/m^3	$3.96x10^8$–$5.82x10^8$	$3.96x10^8$–$6.33x10^8$
Solid Heat Capacity @ STP	kJ/kg-K	0.96	<1
Crush Strength	kg_f	3.6	3.6
Manufacturing Cost for Sorbent	$/kg	TBD	3.6
Adsorption			
Pressure	bar	0.15	0.15
Temperature	°C	30	20-60
Equilibrium Loading	g mol CO_2/kg	2.3	>1.5
Heat of Adsorption	kJ/mol CO_2	35	<35
Desorption			

Pressure	bar	0.05	>0.05
Temperature	°C	30	40-80
Equilibrium CO_2 Loading	g mol CO_2/kg	1.3	<0.3
Heat of Desorption	kJ/mol CO_2	35	<35
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	Fixed/cyclic	
Flue Gas Flowrate	kg/hr	2.32×10^6	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90 / 95 / 152.7	
Adsorber Pressure Drop	bar	0.07	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	60.5	

*Sorbent BET surface area is used for packing density.
+Pressure is in bar

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – “Current” is market price of material, if applicable; “Target” is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical PC power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD (flue gas desulfurization; wet basis) should be assumed as:

		Composition						
		vol%					ppmv	
Pressure	Temperature	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	135°F	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – See Figure 1 and Figure 2.

Sorbent Contaminant Resistance – TBD.

Sorbent Attrition and Thermal/Hydrothermal Stability – TBD.

Flue Gas Pretreatment Requirements – TBD.

Sorbent Make-Up Requirements – TBD.

Waste Streams Generated – TBD.

Process Design Concept – See Figure 4.

Proposed Module Design – TBD.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value*	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	19.5 (32.2)	32.2
Cost of Carbon Avoided	\$/tonne CO_2	21.0 (34.6)	34.6
Capital Expenditures	\$/MWhr	7.7 (10.8)	10.8
Operating Expenditures	\$/MWhr	13.8 (24.8)	24.8
Cost of Electricity	\$/MWhr	21.6 (35.6)	35.6

* The first number is for the PSA process and the number in parentheses is the total including compression to pipeline.

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis –

A rigorous TEA was carried out by the USC team.

Scale of Validation of Technology Used in TEA –

The technology numbers were based on rigorous simulation (modeling) of a full-scale PSA system. The simulation was carried out with the USC DAPS, which was validated at the bench scale with numerous experiments.

technology advantages

- High CO_2/N_2 selectivity (greater than 130), enabling a 95 vol% CO_2 purity to be achieved in a single stage for a typical coal flue gas containing 12–15 vol% CO_2.
- Uses low-cost commercial sorbents as base material.
- Metal and organic precursors required to form the coating materials are low cost.

- MLD is comparable to commercially available atomic layer deposition technology and suitable for roll-to-roll manufacturing.
- MLD tailor-made sorbent technology allows for reduced vacuum level and reduced light reflux flow during regeneration, thereby reducing the size and energy required by the product and reflux vacuum pump.
- Advanced sorbent fabrication procedure reduces manufacturing cost.
- Low pressure drop during feed step leads to use of fewer adsorption beds in PSA cycle, reducing capital costs.
- Compact, stand-alone, and modularized system design, reducing upfront installation costs and footprint.
- Serves as a platform for CO_2 capture from both coal-fired and natural gas-fired power plants.

R&D challenges

- Precise control of the MLD coating properties to form appropriate pore misalignment for molecular sieving.
- Degradation of MLD sorbent performance in the presence of flue gas contaminants.
- Lower CO_2 purity when integrating MLD sorbent with the new PSA cycle.

status

The project team is using MLD to apply microporous coatings of less than 30 nm thickness on base sorbent material. Computational screening of various sorbent materials is being used to identify the sorbents for this technology. DAPS is being used to design the PSA system based on commercial 13X zeolite to establish baseline performance. A unique six-bed PSA system was designed, constructed, and became operational at USC. It was modified and upgraded to operate with two feed or two light reflux beds. The targeted CO_2 purity and CO_2 recovery were achievable in the six-bed PSA system. Molecular Dynamics (MD) simulations were used to identify how the transport at the MLD/base sorbent interface can enhance the overall selectivity. The optimized sorbent showed almost no loss in CO_2 working capacity and approximately a doubling of CO_2/N_2 selectivity under relevant PSA conditions. Results indicate the CO_2 and N_2 adsorbent-adsorbate interactions with the MLD adsorbent were reduced, potentially favoring less vacuum for desorption of CO_2.

available reports/technical papers/presentations

Yu, M., et al., “Transformational Molecular Layer Deposition Tailor-Made Size-Sieving Sorbents for Post-Combustion CO_2 Capture,” presented at the 2024 FECM/NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2024. *24CM_Posters_Yu.pdf*.

Underhill, P., Ritter, J., Yu, M., “Transformational Molecular Layer Deposition Tailor-Made Size-Sieving Sorbents for Post-Combustion CO_2 Capture,” presented at the 2021 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Underhill.pdf*.

Yu, M., et al. “Transformational Molecular Layer Deposition Tailor-Made Size-Sieving Sorbents for Post-Combustion CO_2 Capture,” Kickoff Meeting Presentation, Pittsburgh, PA, November 2019. *http://netl.doe.gov/projects/plp-download.aspx?id=10733&filename=Transformational+Molecular+Layer+Deposition+Tailor-Made+Size-Sieving+Sorbents+for+Post-Combustion+CO2+Capture.pdf*.

Yu, M., et al. “Transformational Molecular Layer Deposition Tailor-Made Size-Sieving Sorbents for Post-Combustion CO_2 Capture,” presented at the 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/M-Yu-RPI-Tailor-Made-Sorbents.pdf*.

A New Sorbent Process for Transformational Carbon Capture Process

primary project goal

TDA Research Inc. (TDA), in collaboration with Membrane Technology and Research Inc. (MTR), is developing sorbents based on amine-functionalized resins to remove carbon dioxide (CO_2) selectively and with high capacity from flue gases generated from pulverized coal combustion power plants.

technical goals

- Optimize the sorbent formulations to achieve higher CO_2 capacity and uptake rates and evaluate use of co-polymers to increase the processability of the materials into structures easily integrated into modules.
- Screen polymers and structures in bench-scale testing and prepare test modules using the best identified polymers.
- Test the modules in the TDA test apparatus using the vacuum swing adsorption (VSA) cycle and optimize operating conditions and cycle sequence.
- Complete a minimum of 20,000 adsorption/desorption cycles in presence of flue gas contaminants.
- Design a CO_2 capture process around this new material.
- Assess the techno-economic viability of the process as a retrofit option for existing pulverized coal power plants.

technical content

TDA is developing a sorbent based on amine-functionalized resin structures for the capture of CO_2 from coal-fired power plants. In Phase I, TDA modified commercial polymeric resins with amines and tuned them for CO_2 uptake. In-house polymers were also prepared with amine functionalities and showed higher CO_2 loading than the commercial resins, along with high selectivity and kinetics. The presence of moisture enhanced the CO_2 loading. Furthermore, the TDA resins provide the flexibility to be used as coatings on engineered structures, which can reduce pressure drop and allow for the treatment of high volumes of flue gas. The sorbent regeneration occurs using a VSA cycle, and the mild vacuum conditions required results in lower regeneration energy. TDA is continuing efforts to optimize the sorbent to enhance its CO_2 capacity and further improve its resistance to flue gas impurities such as moisture, sulfur oxide (SO_X), and nitrogen oxide (NO_X).

In Phase II, TDA is optimizing the sorbent formulations for improved CO_2 capacity and processability to form engineered structures capable of integration into modules. Polymer scale-up is being executed in a 50-gallon reactor system, and then the polymers are shaped into various forms, including pellets, extruded

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post Combustion Power Generation PSC

key technology:
Sorbents

project focus:
Amine-Functionalized Resin Sorbent

participant:
TDA Research Inc.

project number:
SC0018682

predecessor projects:
N/A

NETL project manager:
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principal investigator:
Gökhan Alptekin
TDA Research Inc.
galptekin@tda.com

partners:
Membrane Technology and Research Inc.

start date:
07.02.2018

percent complete:
94%

honeycomb structures, and polymer films via spin coating. Polymer beads are processed into thin sheets, which are then made into spiral-wound and planar modules by project partner MTR. Examples are shown in Figure 1.

Evaluation of the sorbent as loose granules and as modules is performed in TDA's existing VSA prototype test system (shown in Figure 2), which can treat 5 standard cubic feet per minute (scfm) of flue gas and remove up to 2.5 kilogram (kg)/hour of CO_2. Testing includes optimization of the process and the VSA cycle sequence, as well as long-term tests in the presence of contaminants. Test results are used to inform the design of a CO_2 capture process around this new polymer-based adsorbent material.

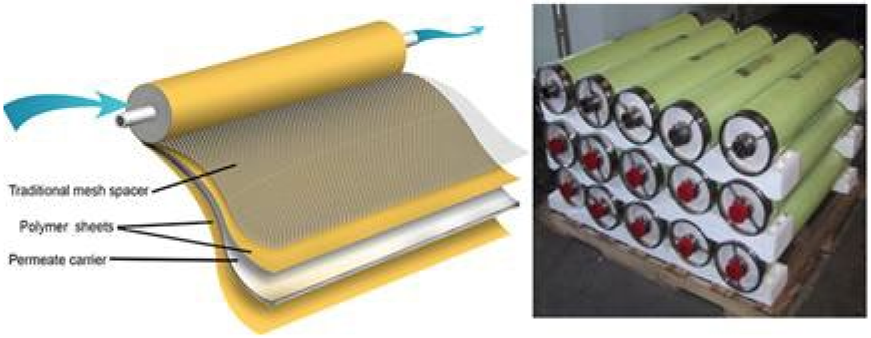

Figure 1: Example of preparation of spiral-wound modules (left) and of MTR's polymer membrane modules (right).

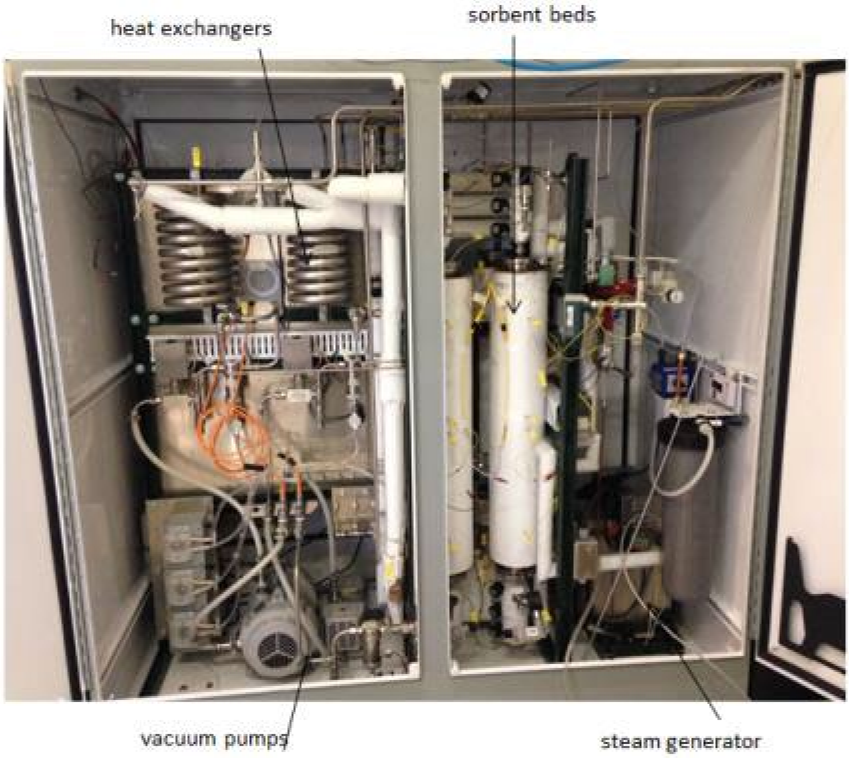

Figure 2: TDA's four-bed VSA system.

technology advantages

- Structured sorbents have potential for high CO_2 uptake with low pressure drop while treating high volumes of gas.
- Use of sorbents in a structured form instead of pellets favors use of a modular design.
- Reduced regeneration energy through a regeneration process using mild vacuum.

R&D challenges

- Preparation of the functionalized resin sorbent in engineered structures.
- Life cycle of sorbents in operational conditions with flue gas contaminants.
- Economic viability in large power plant applications due to the volume of sorbent required and cost of ancillary equipment (ductwork distribution system, vacuum pumps, etc.).

status

TDA has identified new polymers that can be formed into desirable structures (monoliths or planar contactors) with amine functionalities tuned for high CO_2 uptake and selectivity. Structured sorbents are being used to lower the pressure drop during CO_2 removal. Carbon dioxide capture cost was estimated to be $29.9/tonne, excluding transportation, storage, and monitoring (T&SM). TDA is currently demonstrating the efficacy of the new polymer sorbent for post-combustion carbon capture at bench-scale (2–5 kilowatt [kW]) size. TDA is finalizing the techno-economic analysis (TEA) on the viability of the new technology and final cost of captured CO_2.

available reports/technical papers/presentations

Alptekin, G., "A New Sorbent Process for Transformational Carbon Capture Process," Phase II Final Briefing/Phase IIB Kickoff Meeting, Pittsburgh, PA, September 2022. *https://netl.doe.gov/projects/files/A%20New%20Sorbent%20Process%20for%20Transformational%20Carbon%20Capture.pdf*.

Alptekin, G. and Jayaraman, A., "A New Sorbent Process for Transformational Carbon Capture Process," Presented at the Phase I Final Briefing/Phase II Kickoff Meeting, Pittsburgh, PA, August 2019. *http://www.netl.doe.gov/projects/plp-download.aspx?id=12085&filename=A+New+Sorbent+Process+for+Transformational+Carbon+Capture.pdf*.

Alptekin, G, et al., "A New Sorbent Process for Transformational Carbon Capture Process," Presented at the Phase I Project Kickoff Meeting, Pittsburgh, PA, August 2018. *http://www.netl.doe.gov/projects/plp-download.aspx?id=12087&filename=A+New+Sorbent+Process+for+Transformational+Carbon+Capture.pdf*.

Transformational Sorbent System for Post-Combustion Carbon Capture

primary project goal

TDA Research, partnered with University of Alberta, University of California Irvine, and the Wyoming Integrated Test Center (ITC), is developing a transformational metal organic framework (MOF) sorbent system for post-combustion carbon dioxide (CO_2) capture capable of capturing more than 90% of the CO_2 emissions from a coal-fired power plant and recovering CO_2 at 95% purity with a cost of electricity 30% lower than an amine-based system. TDA's system uses a novel, highly stable, high-capacity CO_2 sorbent in a vacuum/concentration swing adsorption (VCSA) process that uses a single-stage vacuum pump with low auxiliary load.

technical goals

- Optimize the sorbent formulation.
- Assess impact of flue gas contaminants (sulfur dioxide [SO_2], nitrogen oxide [NO_X], hydrogen chloride [HCl]).
- Scale-up sorbent production.
- Complete long-term sorbent cycling experiments at bench scale using simulated flue gas.
- Design and construct a prototype system with fixed-bed radial flow reactors.
- Design the VCSA cycle sequence.
- Perform field-testing in a prototype test unit using actual flue gas for a minimum of 4,000 hours.
- Prepare a high-fidelity techno-economic analysis (TEA) and environmental, health, and safety (EH&S) assessment.

technical content

TDA Research is developing a high-capacity sorbent for CO_2 capture in a system that uses a novel adsorption cycle scheme. TDA's MOF sorbent has very high CO_2 uptake, high CO_2 selectivity over nitrogen (N_2), and a relatively low energy requirement for regeneration. The process, shown in Figure 1, includes sorbent that operates at approximately 50°C during adsorption under mild vacuum (~0.2–0.3 atmosphere [atm]). The regeneration occurs in a two-step process, using vacuum to recover the CO_2 and a purge using the boiler intake air, which then feeds the CO_2-laden air back to the boiler. This approach generates a flue gas that is rich in CO_2, thereby benefiting the adsorption of the CO_2 on the sorbent while allowing use of a practical, single-stage vacuum pump with a low auxiliary load.

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Sorbents

project focus:
Metal Organic Framework-Based Sorbent System

participant:
TDA Research Inc.

project number:
FE0031734

predecessor projects:
N/A

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galptekin@tda.com

partners:
University of California Irvine;
University of Alberta;
Wyoming Integrated Test Center

start date:
06.01.2019

percent complete:
90%

The project team is designing a fixed-bed radial flow reactor-based test unit for field-testing at a project partner host site with actual coal-derived flue gas to show the performance of their CO_2 capture system. TDA's radial flow contactor increases the viability of using sorbents in fixed beds for post-combustion capture by reducing the pressure drop through the beds and allowing for rapid regeneration of the sorbent. The radial flow reactor configuration allows for use of multiple modular beds for ease of scale-up to large-scale processes.

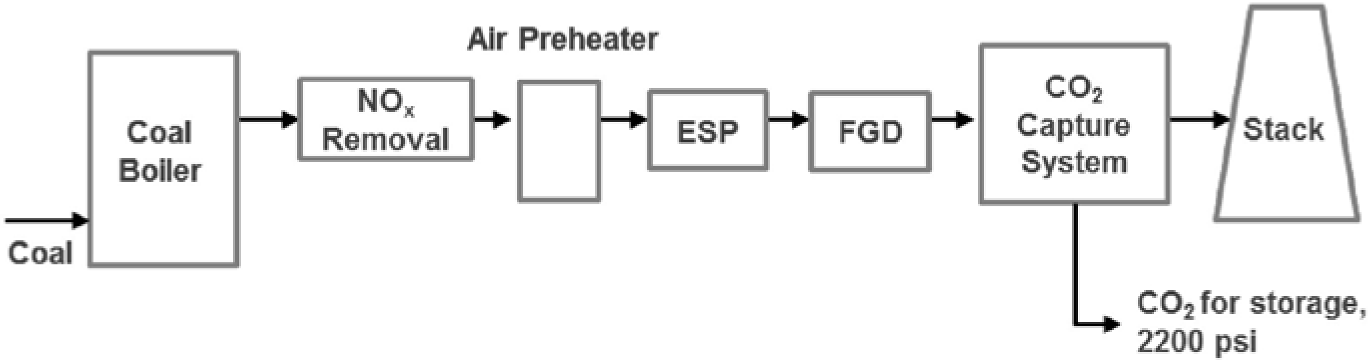

Figure 1: Schematic of TDA's CO_2 capture system.

TDA Research is optimizing sorbent performance through lab-scale experiments and using computational modeling to show the technical merit of both the sorbent and the capture process. The impacts of flue gas contaminants, including SO_2, NO_X, and HCl, on sorbent performance are being evaluated. The project team will also design and construct the prototype system, design the VCSA cycle, optimize the process design, and complete a detailed cost analysis to compare this process technology against amines. Evaluations using the prototype test unit will be completed first with simulated flue gas in the lab and then at the Wyoming ITC with actual coal-based flue gas, followed by optimization of the cycle design, finalization of the process design, and completion of an engineering analysis to fully assess the techno-economic viability of the process.

This technology provides a cost-effective solution for controlling CO_2 emissions from existing coal-fired power plants. The low heat of adsorption of CO_2 and the use of a VCSA process that eliminates any steam purge results in reduced energy input for sorbent regeneration. The radial outflow sorbent reactor beds can be constructed into modules that can be added together, allowing for easy scale-up.

technology advantages

- Very high CO_2 uptake (2–3 mmol/g) at 0.15–0.20 bar CO_2 partial pressure.
- High CO_2 selectivity over N_2.
- Relatively low energy input requirement for sorbent regeneration.

R&D challenges

- Minimizing the loss in adsorption capacity due to the sorbent pelletization process.
- Designing the sorbent to maintain stability and life in the presence of moisture.
- Maintaining the low vacuum and purge requirements for the process upon scale-up.
- MOFs are difficult to pelletize or granulate due to conventional powder compaction techniques damaging MOF structure.

status

TDA Research MOF synthesis improvements have produced space yield improvements of 10–15X and time yield improvements of 5–8X. The research team developed a pill-pressing method that resulted in pelletized sorbent to retain greater than 95% of their capacity when normalized based on active MOF weight. TDA employed multiple fixed-bed adsorption systems to carry out adsorption breakthrough and adsorption/desorption cycle tests. Scale-up testing was performed to 1.6 kg/batch with 22 L vessels. TDA Research demonstrated a high working capacity in excess of 5 wt%. CO_2 at approximately 15 vol%. CO_2 and approximately 2.5 wt% CO_2 at 4 vol% CO_2. TDA Research also demonstrated how temperature and humidity levels have limited impact on sorbent's working capacity. Higher temperatures resulted in lower working capacity. There was no significant impact in the presence of humidity up to 65%. Stable working capacity was also demonstrated in the presence of flue gas contaminants such as NO_X and sulfur oxide (SO_X). The TEA indicated the total cost of the CO_2 capture system, including flue gas treatment, is $207.8 Million ($378/kW), and the cost of CO_2 capture is approximately $37/tonne, which meets the U.S. Department of Energy's (DOE) current target of less than $40/tonne at less than $450 Million.

available reports/technical papers/presentations

Alptekin, G., et al., "Transformational Sorbent System for Post-Combustion Carbon Capture," 2023 NETL Carbon Capture Management Research Project Budget Period 2 Review Meeting, Pittsburgh, PA, May 2023. *https://netl.doe.gov/projects/files/Transformational%20Sorbent%20System%20for%20Post-Combustion%20Carbon%20Capture.pdf*.

Alptekin, G., et al., "Transformational Sorbent System for Post Combustion Capture," 2022 Carbon Management Project Review Meeting, Pittsburgh, PA, August 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_PSC18_Alptekin.pdf*.

Alptekin, G., et al. "Transformational Sorbent System for Post Combustion Carbon Capture," 2021 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Alptekin_TDA.pdf*.

Alptekin, G., et al. "Transformational Sorbent System for Post Combustion Carbon Capture," Budget Period 1 Review Meeting, Pittsburgh, PA, January 2021.

Alptekin, G., et al. "Transformational Sorbent System for Post Combustion Carbon Capture," 2019 Carbon Capture, Utilization, Storage, and Oil & Gas Technologies Integrated Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/G-Alptekin-TDA-Next-Gen-Sorbent.pdf*.

Alptekin, G., et al. "Transformational Sorbent System for Post Combustion Carbon Capture," Kickoff Presentation, Pittsburgh, PA, August 2019.

Bench-Scale Test of a PEI-Monolith CO_2 Capture Process for NGCC Point Sources

primary project goal

Cormetech Inc. is developing a novel, lower-cost sorbent-based technology for point-source capture (PSC) of carbon dioxide (CO_2) from natural gas combined cycle (NGCC) plant flue gas. The project aims to achieve a minimum of 95% carbon capture efficiency with a 95% purity CO_2 product stream for at least one-month continuous operation through bench-scale testing at the National Carbon Capture Center (NCCC).

technical goals

- Complete a basic engineering design for a bench-scale integrated process unit.
- Develop a process model to simulate process performance.
- Characterize the durability of poly(ethyleneimine) (PEI) monolith adsorber under NGCC conditions to improve certainty of adsorber lifetime estimation.
- Improve durability of the PEI monolith adsorber as feasible to further increase adsorber lifetime.
- Complete detailed engineering design for bench-scale unit.
- Construct the bench-scale adsorber unit and complete factory acceptance testing.
- Execute the Technology Collaboration Agreement with NCCC and conduct a hazards review.
- Manufacture relevant quantities of PEI monolith adsorbers for bench-scale testing.
- Conduct lab-scale parametric testing of process components and refine the process model with testing data to simulate and optimize process performance in preparation for the bench-scale testing.
- Complete the test campaign for the bench-scale unit at NCCC.
- Conduct a techno-economic analysis, life cycle analysis, and environmental health and safety analysis for comparative U.S. Department of Energy (DOE) reference case B31.B.

technical content

The process incorporates an oxide monolith combined with an amine structured contactor consisting of benchmark PEI sorbent. Recent lab studies have shown that the PEI contactors experience better-than-expected resistance to oxidative degradation when operated under PSC conditions (i.e., high PCO_2). In PSC applications, the process involves the flow of NGCC flue gas over a monolithic amine contactor to capture the CO_2 followed by steam-mediated thermal

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Sorbents

project focus:
PEI Sorbent-Based Process for CO_2 Capture from NGCC Flue Gas

participant:
Cormetech Inc.

project number:
FE0032138

predecessor projects:
N/A

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partners:
Southern Company Services Inc.; Middle River Power LLC; Nooter/Eriksen Inc.

start date:
02.01.2022

percent complete:
75%

desorption and CO_2 collection. The process occurs in a multi-bed cyclic process unit without the use of vacuum (Figure 1). Note that the system may also be operated in a two-bed sequence.

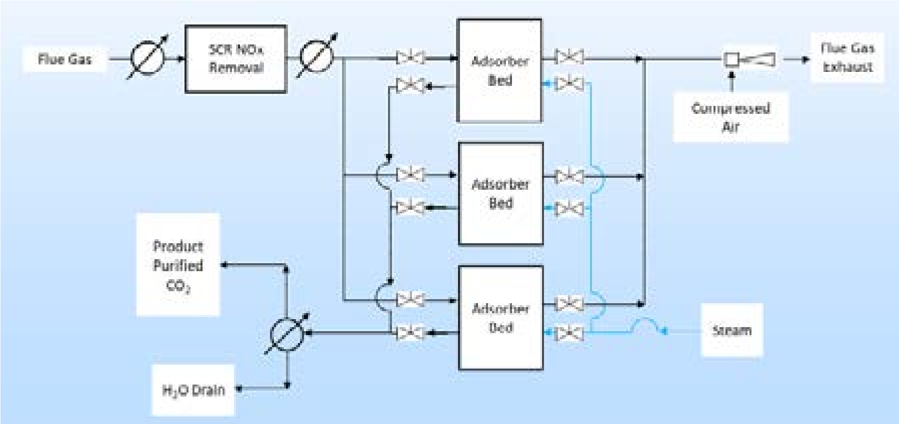

Figure 1: Block diagram of integrated process unit.

The PSC (NGCC flue gas after the heat recovery steam generator) and direct air capture (DAC; ambient air capture) applications differ significantly with respect to the design space velocity of the contactors. For DAC, the main goal is to maximize CO_2 capture productivity, and as such the adsorber is run in a more differential mode, with higher inlet gas velocity, with CO_2 slip. In contrast, the main goal for PSC is to maximize CO_2 capture efficiency; thus, the adsorber is run at a much lower inlet gas velocity (i.e., lower space velocity) to minimize CO_2 slip.

The long-term performance potential of the oxide monolith + PEI-structured contactor is being assessed through accelerated lab-scale life cycle tests under relevant process conditions — a key step to validating the novel PSC process for use in full-scale NGCC plants. Quantitative assessments of the PEI monolith sorbent material under NGCC PSC conditions (i.e., exposure to high-temperature oxidative conditions with high PCO_2, and exposure to nitrogen oxide [NO_X] and sulfur oxide [SO_X] flue gas contaminants) are key to assessing the potential long-term durability of the material. Based on the results of durability testing, substrate properties (monolith cell density, bulk density, wall thickness, meso- and macro-porosity) and PEI loading can then be modified to enhance durability performance. Parametric tests conducted at lab scale under NGCC flue gas conditions for the process components provides additional data to further characterize CO_2 adsorption/desorption rates, capacities, space velocity impacts, heat burden, water sorption, and cycle time, which are incorporated into the process model to optimize the performance of the process. Testing of a bench-scale unit with simulated NGCC flue gas is necessary to validate capacity fade under NGCC flue gas conditions with long-term cyclical operation. The test campaign at NCCC includes parametric testing to assess the impact of flow rate, cycle time and dynamic operation (i.e., trip conditions and quick startups/shutdowns), followed by continuous steady-state testing, and concluding with parametric testing to characterize any material deterioration after the continuous operation test and to assess the impact of flue gas contaminants. Through process experimentation and optimization on both the lab-scale and bench-scale units, the goal is to reduce the process cycle timing in order to facilitate a reduction in the total installed adsorber volume for a given installation. Performance and durability data collected during the project are used to refine the process model and optimize the process prior to bench-scale testing.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.7	140-194	3.5-5	7-11		11-15		<2	~2

technology advantages

- Consolidates three-unit processes (adsorption, stripping and reclamation) into one unit operation.
- Simple unit design with no vacuum.
- Monolith PEI adsorbers utilize existing amine-supported substrate technology.
- Adsorbers operate with lower pressure drop.
- Efficient CO_2 capture due to high contact area between flue gas and adsorbers.
- Monolith PEI adsorbers only require low-quality steam to regenerate (desorb CO_2), resulting in low energy requirement.
- Monolith substrates can be recycled and reused for cost savings.

R&D challenges

- Optimizing the unit module design.
- Efficiency of sorbent desorption step.
- Adsorber life.
- Steam/energy demand.

status

Durability validation testing was completed in the core test unit, with approximately 1,000 cycles performed at multiple relevant temperatures. The detailed engineering design package was completed, and the process operating cycle parameters have been established. A process hazards analysis was completed between CORMETECH and NCCC. Factory acceptance testing of the bench-scale integrated process unit was completed and the unit has been installed at NCCC.

available reports/technical papers/presentations

Bertole, C. "Bench-Scale Test of a Polyethyleneimine Monolith Carbon Capture Process for NGCC Point Sources." Presented at the FECM/NETL Carbon Management Project Review Meeting, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_Posters_Bertole.pdf*.

Bertole, C. "Bench-Scale Test of a Polyethyleneimine Monolith Carbon Capture Process for NGCC Point Sources." Presented at the Budget Period 2 Review Meeting, Pittsburgh, PA, December 2023. *https://netl.doe.gov/projects/files/Bench%20Scale%20Test%20of%20a%20Polyethyleneimine%20Monolith%20Carbon%20Capture%20Process%20for%20Natural%20Gas%20Combined%20Cycle%20Point%20Sources.pdf*.

Bertole, C. "Bench-Scale Test of a Polyethyleneimine Monolith Carbon Capture Process for NGCC Point Sources." Presented at the Budget Period 1 Review Meeting, Pittsburgh, PA, January 2023. *https://netl.doe.gov/projects/files/Bench%20Scale%20Test%20of%20a%20Polyethyleneimine%20Monolith%20Carbon%20Capture%20Process%20for%20NGCC%20Point%20Sources.pdf*.

Bertole, C. "Bench-Scale Test of a Polyethyleneimine Monolith Carbon Capture Process for NGCC Point Sources." Presented at the 2022 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_PSC18_Bertole.pdf*.

Transformational Sorbent-Based Process for a Substantial Reduction in the Cost of CO_2 Capture

primary project goal

InnoSepra LLC is developing a sorbent-based process using novel microporous materials to reduce the cost of carbon dioxide (CO_2) capture. The project includes identification of sorbent materials, process development, and lab-scale testing with simulated flue gas, culminating in bench-scale testing with actual flue gas at Technology Centre Mongstad (TCM).

technical goals

- Identify suitable materials through literature search and Monte Carlo simulations and produce/procure suitable materials for lab-scale testing.
- Complete lab-scale testing of multiple materials in simulated flue gas to determine CO_2 capture performance and down-select best materials.
- Simulate process to obtain heat and mass transfer parameters.
- Design and build the bench-scale test unit.
- Test the best identified materials on the bench-scale unit using actual flue gas at TCM.
- Perform engineering design and complete a techno-economic analysis (TEA) on the process for installation of the technology at a commercial 550-megawatt (MW) power plant to estimate CO_2 capture cost.

technical content

InnoSepra is developing a sorbent-based CO_2 capture process, utilizing physical sorbents based on microporous materials. These sorbents have low heats of adsorption (26–44 kJ/mole CO_2), high net CO_2 capacity (greater than 9 wt%), and high surface area-to-volume ratio (greater than 10 x 10^6 m^2/m^3). The combination of the process and sorbent materials provides capture performance similar to or better than amines, although needing much lower regeneration energy. The process schematic of the CO_2 capture process is shown in Figure 1. After the removal of moisture and sulfur oxides (SO_X) in a pretreatment system, the CO_2 is captured in an adsorber at 25–40ºC. A high-purity CO_2 is produced during sorbent regeneration at 90–100ºC. Some of the heat of adsorption is removed during the adsorption process; the remaining heat is removed during the cooling steps. Regeneration heat is supplied via low-pressure steam, as well as by utilizing other process waste heat in the system.

The first-generation of the InnoSepra process using the physical sorbents was developed and tested at the bench-scale in a previous U.S. Department of Energy

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Post-Combustion Power Generation PSC

key technology:

Sorbents

project focus:

Low Regeneration Energy Sorbent Process for CO_2 Capture from Coal-Based Flue Gas

participant:

InnoSepra LLC

project number:

FE0031722

predecessor projects:

FE0007948
SC0010208

NETL project manager:

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principal investigator:

Ravi Jain
InnoSepra LLC
ravi.jain@innosepra.com

partners:

Main Line Engineering; Plant Process Equipment; Arizona State University

start date:

05.01.2019

percent complete:

75%

(DOE)-funded project (DE-FE0007948). Testing occurred at NRG Energy's Indian River Plant using actual flue gas, taken off the process after the dry flue gas desulfurization (FGD) unit, containing about 50 parts per million (ppm) sulfur dioxide (SO_2) and 10–12% CO_2, with 80–100 standard cubic feet per minute (scfm) flow rate. The adsorption test skid used at the testing at NRG is shown in Figure 2. Eight weeks of testing was completed showing 8–10.5 wt% net CO_2 capacity, greater than 94% CO_2 recovery, and greater than 98% purity.

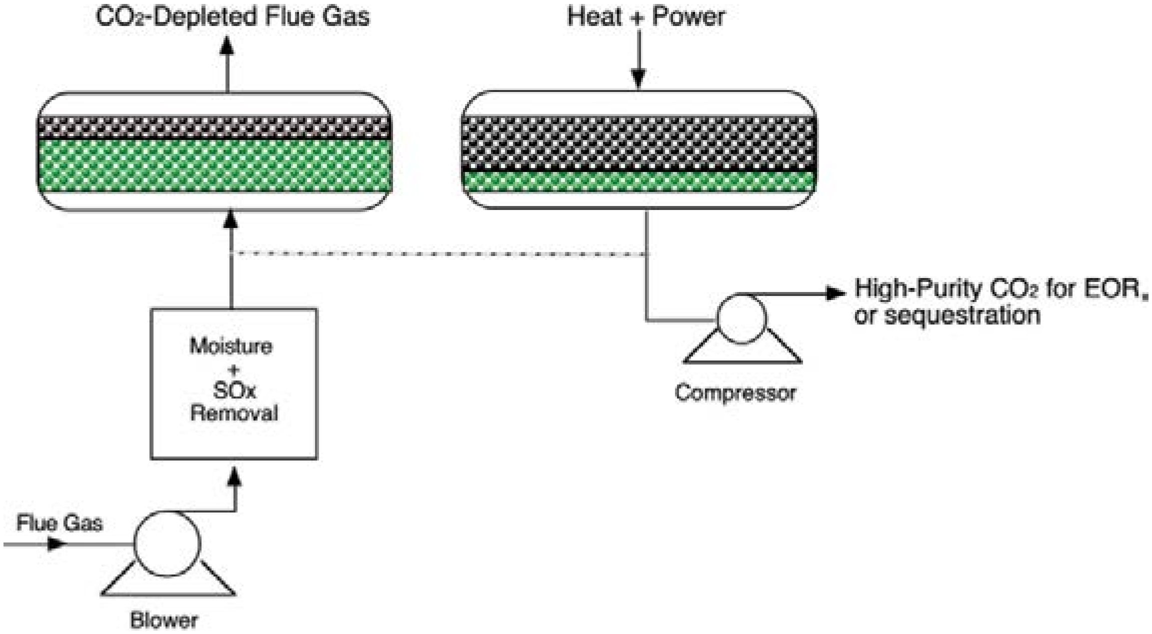

Figure 1: InnoSepra capture process schematic.

Figure 2: InnoSepra test skid used for testing at NRG Energy.

Projections based on detailed engineering evaluations show that at commercial scale, the first-generation process can reduce the power consumption for CO_2 capture by more than 40%, including CO_2 compression. There is about a 70% lower power loss due to steam extraction for the InnoSepra process compared to the amine process and approximately 48% reduction in capture cost compared to monoethanolamine (MEA).

In this project, InnoSepra is developing the second-generation process, which is simpler, with capital savings, compared to the first-generation process. In testing of the second-generation process at lab scale, an absolute energy requirement (excluding compression) of 1.6 gigajoule (GJ)/metric tonnes (MT) of CO_2 was obtained, which is 50% lower than the absolute energy requirement for an MEA-based capture process, and lower than the 2.1 GJ/MT obtained for the first-generation process of InnoSepra's technology in field testing. The lower energy requirement results from a breakthrough sorbent regeneration method. The lower absolute amount of regeneration energy coupled with lower regeneration temperature leads to a 78% lower power loss due to steam extraction compared to MEA. The key feature of the second-generation process is a significant reduction in the heating requirement (from 1.3–0.7 GJ/MT) through a combination of the sorbent selection and regeneration method. The project team is demonstrating the effectiveness of the InnoSepra sorbent-based post-combustion capture technology to achieve at least 90% CO_2 removal with greater than 98% purity. Suitable materials with at least 6 wt% CO_2 capture capacity were identified and down-selected for subsequent testing in a newly constructed lab unit. Testing at lab scale, along with recently developed process simulations, helps support verification of the material properties and optimization of the process. This system shows potential to reduce the parasitic power required for regeneration by more than 65%, and the capital required by about 45%, leading to about 50% reduction in the CO_2 capture cost. A newly designed bench-scale testing unit has been designed and is being built. The unit will be shipped and tested at TCM at a scale greater than 100 scfm.

The sorbent and process parameters are provided in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value		Target R&D Value
True Density @ STP	kg/m^3	1,990		1,990
Bulk Density	kg/m^3	690		690
Average Particle Diameter	mm	1.5-3.0		0.5-1.5
Particle Void Fraction	m^3/m^3	0.45		0.45
Packing Density	m^2/m^3	1.79e8		1.79e8
Solid Heat Capacity @ STP	kJ/kg-K	0.96		0.96
Crush Strength	kg_f	2.9		2.9
Manufacturing Cost for Sorbent	$/kg	4.0		3.0-4.0
Adsorption				
Pressure	bar	1.15		1.1
Temperature	°C	25-32		25-32
Equilibrium Loading	g mol CO_2/kg	3.25		3.5-4.0
Heat of Adsorption	kJ/mol CO_2	38		38
Desorption				
Pressure	bar	0.3-1.0		0.3-1.0
Temperature	°C	100		90-110
Equilibrium CO_2 Loading	g mol CO_2/kg	1.0-1.5		1.0-1.5
Heat of Desorption	kJ/mol CO_2	38		38
Proposed Module Design			*(for equipment developers)*	
Flow Arrangement/Operation	—		fixed/cyclic	
Flue Gas Flowrate	kg/hr		2,320,000	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90	99	1.0
Adsorber Pressure Drop	bar	0.14		0.10
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$		336	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – “Current” is market price of material, if applicable; “Target” is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – The adsorption is physical sorption based on weak van der Waals forces. This leads to low heats of adsorption.

Sorbent Contaminant Resistance – Under normal operation, the sorbent is not irreversibly damaged by any contaminant in the flue gas. If substantial quantities of SO_2 are present in the feed to the CO_2 adsorption section, the sorbent may require higher than normal regeneration temperature to restore performance.

Sorbent Attrition and Thermal/Hydrothermal Stability – The process design protects the adsorbent from moisture and potential hydrothermal degradation. If moisture should break through onto the adsorbent, the adsorbent can be regenerated completely. The adsorbent is thermally stable at temperatures of more than 300ºC.

Flue Gas Pretreatment Requirements – No special flue gas pretreatment is required. A conventional FGD and a direct contact cooler (DCC) are sufficient for normal process operation.

Sorbent Makeup Requirements – Based on prior experience with similar sorbents in similar operating environments, the adsorbent life would be between five and 10 years. An adsorbent life of five years has been assumed to estimate the makeup requirements.

Waste Streams Generated – Except for the sorbents loaded with flue gas components, SO_X and mercury (Hg), no other waste streams are generated in the process. These can be disposed of as per current power plant practices for materials loaded with SO_X and Hg.

Process Design Concept – The commercial process configuration is shown in Figure 3. The adsorption equipment is modular in nature and five adsorption skids are needed for a 550-MW power plant. The rest of the process equipment, such as the feed blower, DCC, and the CO_2 compressor, is very similar to the amine process.

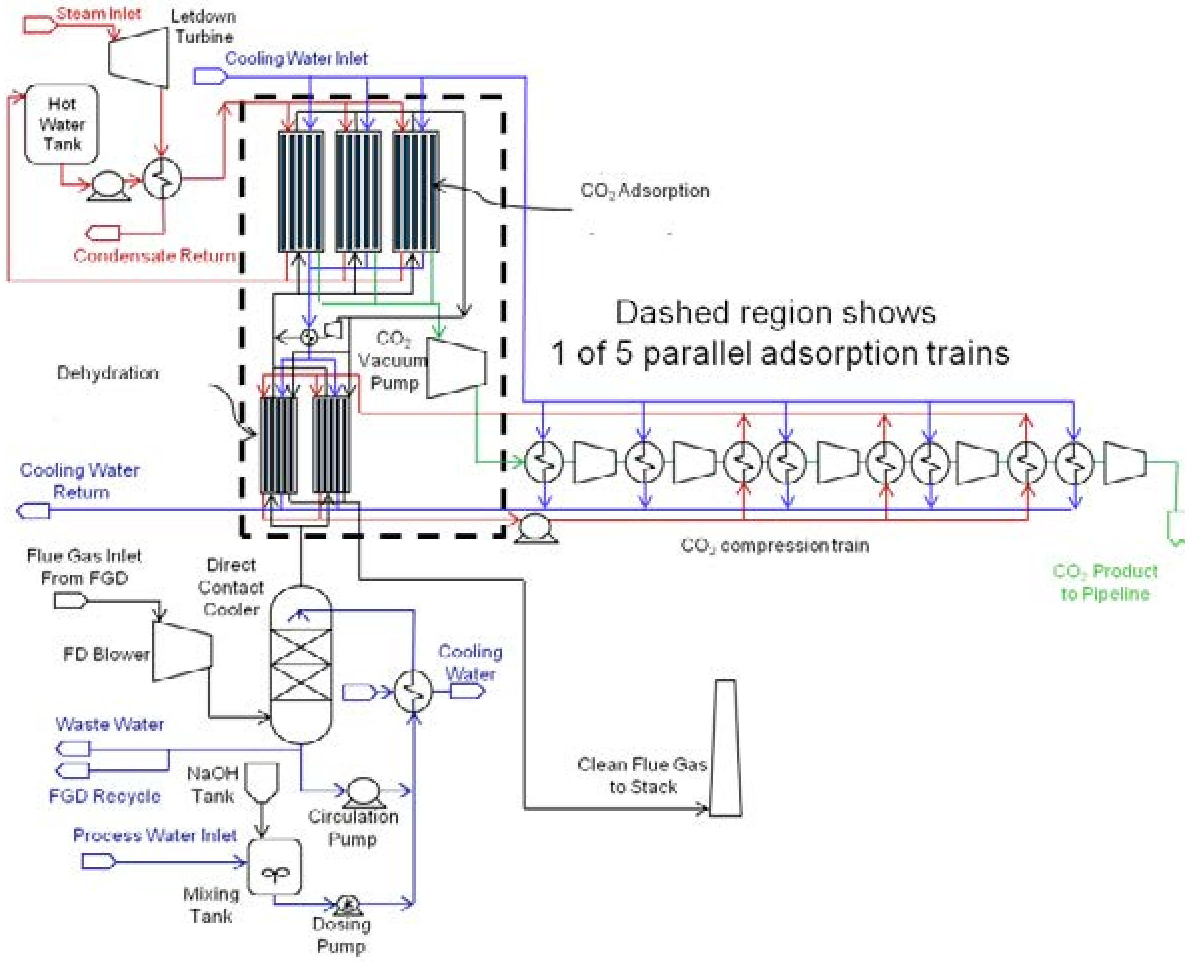

Figure 3: Commercial process configuration.

Proposed Module Design – The CO_2 capture modules will be designed to capture CO_2 from a 550-MW pulverized coal power plant. Multiple modules will be used to minimize field fabrication and maximize offsite fabrication. The separation skid will consist of a feed preparation section (flue gas compression and cooling), the CO_2 adsorption section (removal of impurities, CO_2 adsorption, and desorption), and the CO_2 compression section.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	35	30
Cost of Carbon Avoided	\$/tonne CO_2	39.5	31.5
Capital Expenditures	\$/ MWhr	53	45
Operating Expenditures	\$/ MWhr	14	12
Cost of Electricity	\$/MWhr	94	88

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

technology advantages

- The physical sorbents have a low heat of adsorption (approximately 0.8 GJ/MT).
- Combination of lower absolute amount of heat needed and lower steam extraction temperature leads to a 78% lower power loss compared to MEA.
- The process can produce high-purity CO_2 (greater than 98%) and recovery (greater than 90%).
- The estimated absolute energy required for the process, excluding compression, is 1.6 GJ/MT of CO_2, less than half of the absolute energy requirement for an MEA-based process.
- Regeneration energy can be utilized at approximately 110ºC, compared to greater than 170ºC for amines.
- The process has a projected capture cost below \$30/MT CO_2, excluding transportation, storage, and monitoring (TS&M) costs.

R&D challenges

- Heat management during both adsorption and regeneration.
- Maintaining heat transfer rate upon scale-up.
- Assuring effective moisture and contaminant removal from the flue gas prior to adsorption to prevent decrease in sorbent performance over time.

status

Suitable materials were identified, down-selected, and tested in a constructed lab-scale unit. Process models were developed, and a detailed engineering design was completed for a bench-scale unit to be tested at TCM. The bench-scale unit was fabricated at InnoSepra, followed by its shipment to TCM for testing on supercritical pulverized coal flue gas. A report on 200 hours of field-testing is being completed, with the results informing process simulations to provide updated energy requirements and equipment sizing for the final TEA to be delivered at the end of the project.

available reports/technical papers/presentations

Jain, R. "Transformational Sorbent-Based Processes for a Substantial Reduction in the Cost of CO_2 Capture," Presented at the Project Closeout Meeting, Pittsburgh, PA, August 2024. *https://netl.doe.gov/projects/files/Transformational%20Sorbent-Based%20Process%20for%20a%20Substantial%20Reduction%20in%20the%20Cost%20of%20CO2%20Capture.pdf*.

Jain, R. "Transformational Sorbent-Based Processes for a Substantial Reduction in the Cost of CO_2 Capture," Presented at the 2023 FECM/NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC30_Jain.pdf*.

Jain, R. "Transformational Sorbent-Based Processes for a Substantial Reduction in the Cost of CO_2 Capture," Presented at the 2022 Carbon Management Project Review Meeting, Pittsburgh, PA, August 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_PSC18_Jain.pdf*.

Jain, R. "Transformational Sorbent-Based Processes for a Substantial Reduction in the Cost of CO_2 Capture," Presented at the 2021 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10722&filename=Transformational+Sorbent-Based+Process+for+a+Substantial+Reduction+in+the+Cost+of+CO2+Capture.pdf*.

Jain, R. "Transformational Sorbent-Based Processes for a Substantial Reduction in the Cost of CO_2 Capture," Presented at the Budget Period 1 Meeting, Pittsburgh, PA, April 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10721&filename=Transformational+Sorbent-Based+Process+for+a+Substantial+Reduction+in+the+Cost+of+CO2+Capture.pdf*.

Jain, R. "Transformational Sorbent-Based Processes for a Substantial Reduction in the Cost of CO_2 Capture," Presented at the Project Kickoff Meeting, Pittsburgh, PA, September 2019. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10719&filename=Transformational+Sorbent-Based+Process+for+a+Substantial+Reduction+in+the+Cost+of+CO2+Capture.pdf*.

Jain, R. "Transformational Sorbent-Based Processes for a Substantial Reduction in the Cost of CO_2 Capture," Presented at the 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2019. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10718&filename=Transformational+Sorbent-Based+Process+for+a+Substantial+Reduction+in+the+Cost+of+CO2+Capture.pdf*.

Transformational Cryogenic Process for Carbon Dioxide Capture

primary project goal

InnoSepra LLC identified, through lab-scale testing, physical sorbents and membranes that have significantly better performance at near-cryogenic conditions compared to their performance at ambient conditions. The aim of the project was to demonstrate the technical and economic feasibility of the novel cryogenic process through lab-scale testing, process modeling and simulation, and a techno-economic analysis (TEA).

technical goals

- Demonstrate the effectiveness of the sub-ambient temperature CO_2 capture technology, to achieve at least 90% CO_2 removal with a purity greater than 95% and a cost of electricity at least 30% lower than a supercritical pulverized coal (SCPC) plant with capture or about $30/MT by 2030.
- Scale up the technology to bench scale using the data from the lab-scale testing.
- Develop commercial relationships to enable rapid technology commercialization after the conclusion of the project.

technical content

InnoSepra identified sorbents that have low heats of adsorption, high net carbon dioxide (CO_2) capacities (15–25 wt%), and high CO_2-nitrogen (N_2) separation factors (35–125), and identified membranes that have high CO_2 permeabilities (greater than 3,000 barrer) and CO_2-N_2 separation factors (greater than 50) at near-cryogenic conditions. During this project, InnoSepra obtained additional data for cryogenic CO_2 capture at the laboratory and bench scale, determined the optimum operating conditions for cryogenic capture, and optimized the process to enable a reduction in the parasitic power. Through process simulation and TEA, InnoSepra also demonstrated that cryogenic CO_2 capture can lead to both a lower capital and a lower parasitic power, leading to a lower cost process for CO_2 capture compared to other CO_2 capture processes. The overall goal was to demonstrate the technical and economic viability of CO_2 capture under cryogenic conditions. The process is expected to have lower parasitic power as well as lower capital cost compared to solvent-based capture processes, resulting in greater than 40% lower capture cost.

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Post-Combustion Power Generation PSC

key technology:

Sorbents

project focus:

Sorbent and Membrane-Cryogenic Carbon Capture

participant:

InnoSepra, LLC

project number:

SC0021774

predecessor projects:

N/A

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partners:

N/A

start date:

06.28.2021

percent complete:

100%

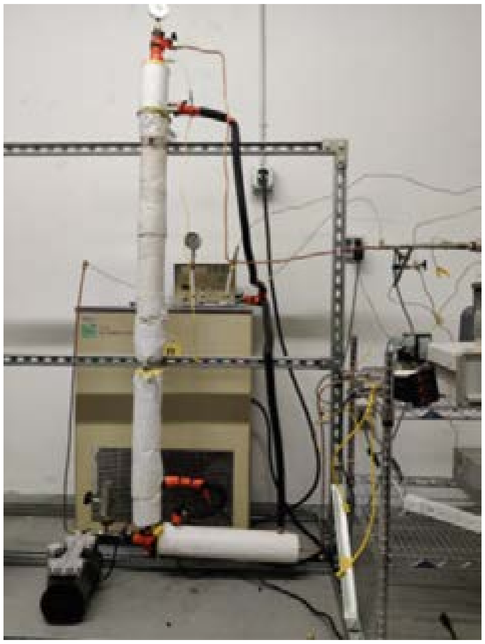

Figure 1: Lab-scale cryogenic testing unit.

technology advantages

- The feed purification step removes more than 98% water with little or no heat input. A low moisture level in the feed entering the CO_2 enrichment section allows the operation of this section at near-cryogenic conditions without any operational issues.
- The membranes used in the CO_2 enrichment section have very high CO_2 permeabilities (greater than 3,000 barrer) and high CO_2-N_2 separation factors (greater than 50).
- The sorbents used in the CO_2 upgrading section have high absolute CO_2 capacities (greater than 50 wt%) and high net CO_2 capacities (greater than 25 wt%).

R&D challenges

- Scaling up the technology to a bench scale.

status

The project was completed on August 21, 2024. InnoSepra successfully demonstrated the feasibility of using novel cryogenic processes for post-combustion CO_2 capture. The process has the potential to significantly reduce capital cost and parasitic power, leading to a significant decrease in levelized cost of electricity (LCOE), reduction in lost power output due to capture, and a CO_2 capture cost of less than $40/tonne. InnoSepra is currently working on scale-up of the technology to demonstrate the feasibility of the novel cryogenic CO_2 capture process at a relevant scale.

available reports/technical papers/presentations

N/A.

High-Efficiency Post-Combustion Carbon Capture System

primary project goal

Precision Combustion Inc. (PCI) developed a compact, modular system utilizing high-capacity modified metal organic framework (MOF) nanosorbents in a low pressure drop system design to capture carbon dioxide (CO_2) from power plant flue gas.

technical goals

- Optimize the sorbent to higher capacities with good selectivity toward CO_2, as well as resistance to humidity and contaminants (sulfur oxide [SO_X], nitrogen oxide [NO_X]).
- Optimize mesh geometry and coating process to achieve higher loadings without affecting sorbent structure at increased production capacity.
- Simulate a scaled-up plant design with steady and dynamic process and computational fluid dynamic (CFD) modeling of the system.
- Assemble small-scale module and test with actual coal-derived flue gas to show the efficacy of the system and further refine the operating conditions.
- Perform full-scale techno-economic modelling of CO_2 capture with sensitivity analysis.

technical content

PCI's innovation is a compact, modular post-combustion carbon capture system (PCCCS) utilizing high internal volume regenerable nanosorbents for carbon capture supported on a tailorable mesh substrate (Figure 1). The system enables low pressure drop, high volumetric utilization and high mass transfer rates, and is suitable for the rapid heat transfer and low-temperature regeneration operating modes needed for cost-effective carbon capture. Capital and operating costs are reduced based on lowered energy demand from enhanced CO_2 capture efficiency and projected large-scale material costs of under $10/kg.

Figure 1: Microlith mesh coated with sorbent—cell opening 600 µm.

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Post Combustion Power Generation PSC

key technology:

Sorbents

project focus:

Metal Organic Framework Nanosorbent on Microlith Substrate

participant:

Precision Combustion Inc.

project number:

SC0017221

predecessor projects:

N/A

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partners:

Boston University; National Carbon Capture Center

start date:

02.21.2017

percent complete:

100%

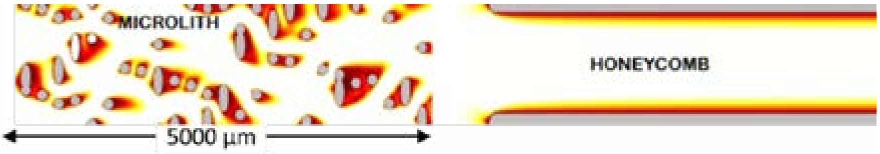

Figure 2: CFD analysis of fluid flow behavior in 2D cross-sections through a stack of 21 Microlith mesh elements (left), a single channel in a honeycomb monolith (right). Microlith mesh disrupts boundary layer formation and intensifies the adsorption process.

The modular cartridge form factor enables low-cost retrofit to existing systems. For the high space velocity sorbent structure, PCI has developed and patented a short contact time mesh-based substrate, trademarked Microlith®, coated with the densified nanostructured sorbent (Figure 1). The combination enables higher surface area per unit volume and decreased bed volume with equivalent effectiveness to other types of monolithic or loose packing, without pressure drop penalty. Additionally, up to 20 times higher mass and heat transfer coefficients are obtainable as compared to other sorbent systems such as monoliths and pellets. This is due primarily to boundary layer minimization and break-up, boosting CO_2 removal rates with greater sorbent bed utilization and less bypass inherent to packed beds or monoliths (Figure 2). This sorbent manufacturing technology allows for adherent and durable MOF coatings (as well as alternative future high surface area sorbents) on the Microlith substrate. Advantages of this approach include:

- Energy savings driven by: (a) the use of solid physisorption rather than liquid chemisorption, which lowers energy of desorption and requires less sensible heating due to lower heat capacity and heat of adsorption of CO_2 on the sorbent (under 30 kJ/kg); (b) reduced regeneration temperature -80°C; (c) the ability to use lower-quality, much less-expensive waste heat for regeneration rather than the higher-cost steam extracted from the power cycle as needed for amines; (d) lower pressure drop during sorption and desorption; and (e) faster regeneration times versus powder bed or pellets for reduced heat losses.
- Compared to the liquid amine system, MOF regeneration uses considerably less energy.
- Capital and other operating cost savings are driven by the Microlith structure and the coatings technology, including: (a) higher sorbent bed utilization; (b) high mass transfer rates and reduced channeling; (c) greater capture efficiency; (d) five to seven times lower pressure drop compared to a pellet bed; and (e) reduced gross energy requirements leading to reduced coal processing, handling, and other auxiliaries. The underlying architecture of the system and cartridge modularity enables future technology upgradability to permit facile use of future solid sorbent technology as it becomes available. Furthermore, the sorbents utilized have a low sorbent degradation rate and excellent regenerability (Figure 3).

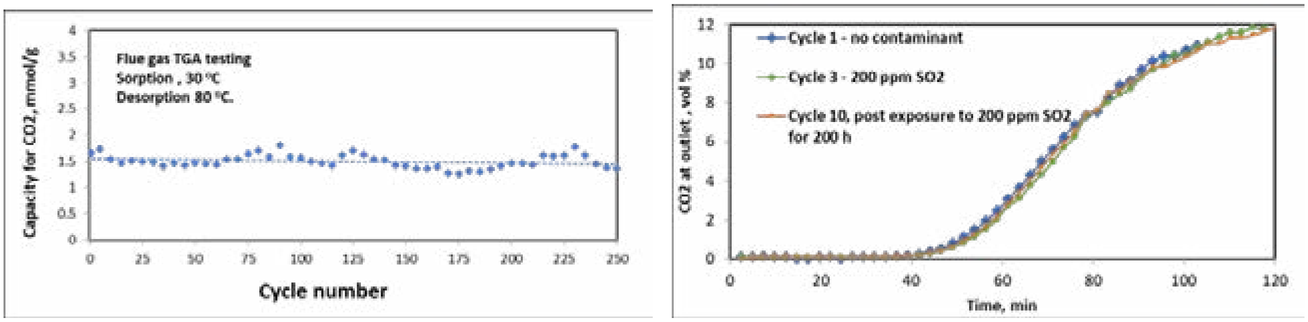

Figure 3: Cyclical performance of PCI sorbent over 250 cycles of sorption and thermal regeneration with simulated coal-fired flue gas showing stable sorbent performance (left). Carbon dioxide breakthrough curves on sorbent bed exposed to SO_2 contaminated simulated flue gas (right). No apparent deactivation is measured.

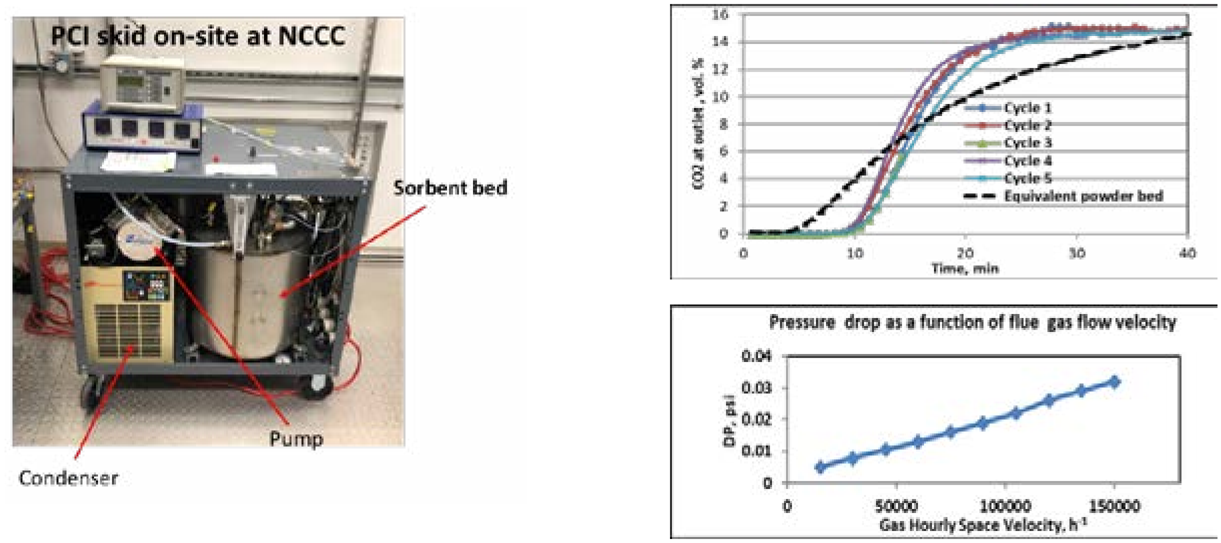

Figure 4: Onsite testing of PCI-coated mesh sorbent bed at the National Carbon Capture Center with simulated flue gas (left). Top cyclical performance of coated mesh versus an equivalent powder bed showing improved bed utilization (simulated coal flue gas, adsorption at 30°C, thermal regeneration at 80°C, average capacity 1.5 mmol/g) (right). Pressure drop through coated sorbent bed as a function of space velocity (bottom). System was sized for a 20–30-min cycle time for brevity.

These materials can function under conditions of humidity typical of flue gas. An example is shown in figure 5 where the material is exposed to dry flue gas mixture for the first six cycles to establish a baseline, followed by 30 cycles with fully saturated mixture at 30°C. The capacity drops by 10–15% due to competitive water adsorption, but then remains stable. Regeneration was done under the same conditions for each cycle (80°C for 20 minutes). The mesh coated material is very flexible and can be designed to fit available space.

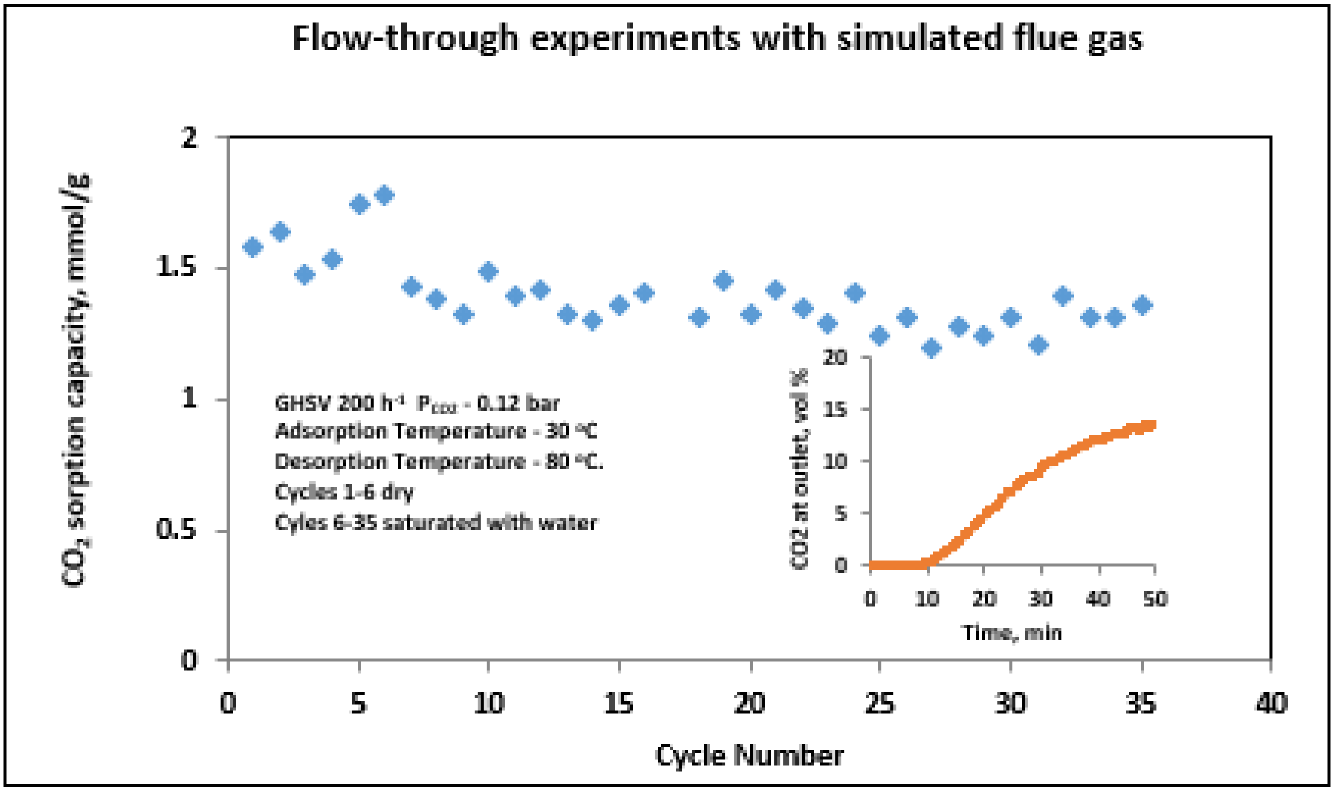

Figure 5: Effect of water on CO_2 sorption. A 10–15% reduction in material capacity is noted. Inset shows a typical humid cycle. The amount of heat delivered in the sorbent bed for CO_2 recovery remains constant.

technology advantages

- The MOF materials have a lower regeneration energy and a lower degradation rate due to their physical adsorption capture mechanism as opposed to chemical reaction.
    - Greatly reduces boundary layer formation, with reduced pressure drop for similarly performing PCCCSs (pellets or monoliths-based), resulting in process intensification with corresponding reduction in PCCCS volume.
    - Increased mass and heat transfer coefficients and enhanced diffusion of gas in the sorbent.
    - Immobilizing the sorbent increases its lifetime by reducing attrition.
    - Modular design flexibility (e.g., planar, radial); easily scalable.
- PCI's Microlith mesh substrate supporting the MOF material has higher surface area per unit volume and much higher mass and heat transfer coefficients, as well as low pressure drop compared to other monolith substrates or pellets, resulting in increased CO_2 capture rate and reduced regeneration energy.

R&D challenges

- Maintaining higher CO_2 loadings without affecting sorbent structure at increased production capacity.
- Identifying optimal sorbent to maximize capacity and selectivity.
- Achieving acceptable sorbent cost at large-scale production.
- Optimizing the material for long-term (thousands of cycles) operation in flue gas environment.

status

PCI developed and demonstrated a means for deploying an MOF-based sorbent at large scale by coating it on Microlith support and matured the operational map of the PCCCS unit in thermal swing adsorption (at 30°C) and desorption (at 70–80°C) to bring down energy expense. The sorbent was stable over multiple thermal cycles and showed stability to contaminants and humidity, as well as high selectivity for CO_2 over other components of the flue gas. The system was demonstrated to have energy-saving performance due to enhanced sorption properties, heat and mass transfer, low pressure drop, and no need for steam input. A techno-economic analysis (TEA) shows potential for achieving the U.S. Department of Energy (DOE) goal of $35/tonne of CO_2 captured. Several test campaigns with live flue gas were completed at the National Carbon Capture Center to validate system performance.

available reports/technical papers/presentations

Loebick, C., et al., "High-Efficiency Post Combustion Carbon Capture System," Presented at the Phase II/Phase IIA Project Review Meeting, Pittsburgh, PA, June 2020. *http://www.netl.doe.gov/projects/plp-download.aspx?id=12072&filename=High-Efficiency+Post+Combustion+Carbon+Capture+System.pdf*.

Loebick, C., et al., "High-Efficiency Post Combustion Carbon Capture System," Presented at the Phase II Project Review Meeting, Pittsburgh, PA, November 2018. *http://www.netl.doe.gov/projects/plp-download.aspx?id=12073&filename=High-Efficiency+Post+Combustion+Carbon+Capture+System+(Nov+2018).pdf*.

Loebick, C. and Weisman, J., "High-Efficiency Post Combustion Carbon Capture System," Presented at the Phase I Project Review Meeting, Pittsburgh, PA, December 2017. *http://www.netl.doe.gov/projects/plp-download.aspx?id=12074&filename=High-Efficiency+Post+Combustion+Carbon+Capture+System+(Dec+2017).pdf*.

Advanced Structured Adsorbent Architectures for Transformational Carbon Dioxide Capture Performance

primary project goal

Electricore, teamed with Svante and Susteon, optimized Svante's transformational VeloxoTherm™ Technology via the development and field testing of an advanced structured adsorbent bed (SAB) to enhance its performance and lifetime. The project team selected, synthesized at large scale, and characterized tailored solid adsorbents; optimized the SAB laminate and rotary adsorption machine (RAM) contactor structure and geometry; developed a final process cycle using process simulations and state-of-the-art modelling; and completed dynamic bench-scale testing with natural gas-fired boiler flue gas and cement plant flue gas.

technical goals

- Synthesis at large scale (greater than 500 kg) of tailored solid adsorbents, including a metal organize framework (MOF).
- Optimize the design and fabrication of the segmented bed with, possibly, different geometries to optimized sorbent utilization and keep low pressure drop and laminar flow.
- Optimize the rapid cycle temperature swing adsorption (RC-TSA) process to increase the carbon dioxide (CO_2) capture efficiency of two different sorbents in the same cycle.
- Develop a segmented bed configuration for both low (less than 12%) and high (greater than or equal to 12%) CO_2 concentration.
- Build and test segmented beds using multi-bed field demonstration units with flue gas from a natural gas-fired boiler (low CO_2 concentration) and from a cement plant (high concentration).
- Assess the techno-economic performance of the technology integrated into a 550-megawatt-electric (MWe) coal-fired power plant.

technical content

The project team developed an advanced SAB geometry and rotary contactor architecture including a segmented-layers bed for post-combustion CO_2 capture in order to develop Svante's Mark II VeloxoTherm technology. Two configurations of segmented beds were explored: low concentration (less than 12% CO_2) and high concentration (greater than 12% CO_2). The low-concentration configuration was tested in-house in a multi-bed process demonstration unit (PDU) to demonstrate key performance indicators (KPIs), such as recovery, product purity, regeneration energy, lifetime, and the integrated system's productivity. The second configuration of segmented beds, for higher CO_2 concentration, was

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Sorbents

project focus:
Structured Sorbent Beds for CO_2 Capture

participant:
Electricore Inc.

project number:
FE0031732

predecessor projects:
N/A

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partners:
Svante Inc.; Susteon Inc.

start date:
05.01.2019

percent complete:
100%

tested at a 1-tonne-per-day (TPD) unit at an industrial site (cement plant) to provide bench-scale validation of performance in an industrial setting.

The segmented bed configuration combines two or more sorbents in the direction of the sorption. As a result of the counter-flow of the steam and flue gas streams, and the fast process cycle (less than 60 seconds), temperature and relative humidity (RH) conditions are different throughout the length of the bed with some areas suffering more from oxidation and some areas with higher RH, which could decrease the CO_2 capacity of a MOF sorbent. The segmented bed concept permits the use of the optimal sorbent for the given local condition (Figure 1). The advantage of the segmented bed is the ease of retrofitting to existing plants design and to extend the lifetime and performance.

The process and segmented bed design needs to be optimized to efficiently use the same process for both the adsorption, desorption, and regeneration, keeping equivalent CO_2 capacity for each sorbent section, minimizing the flow resistance and loss of laminar at the interface and ease of manufacturing. Overall, this process has potential for increased sorbent CO_2 capacity, increased lifetime, and reduced steam demands.

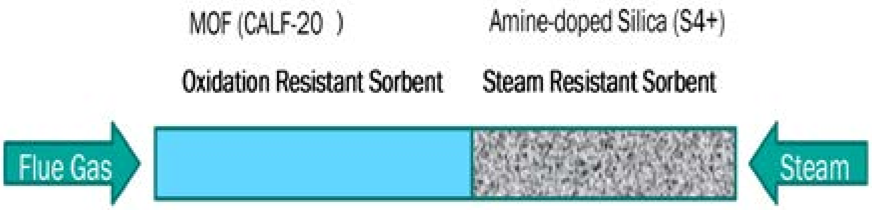

Figure 1: Typical example of the segmented bed concept design.

Optimization of the segmented bed geometry and process was tested in a single-bed sorbent test using simulated coal-fired flue gas in the Svante Variable Test Station (VTS) shown in Figure 2, at a scale of approximately 1–10 kg of CO_2/day captured. Afterwards, the Mark II advanced structure was tested using the VeloxoTherm process with a multi-bed testing station. The low-concentration series was tested in the Svante RAM in the PDU that was coupled with a natural gas-fired boiler for testing at a maximum of 10 kg of CO_2/day captured. The high-concentration series was tested in the 1-TPD field unit running flue gas from a Lafarge cement plant in Richmond, Canada.

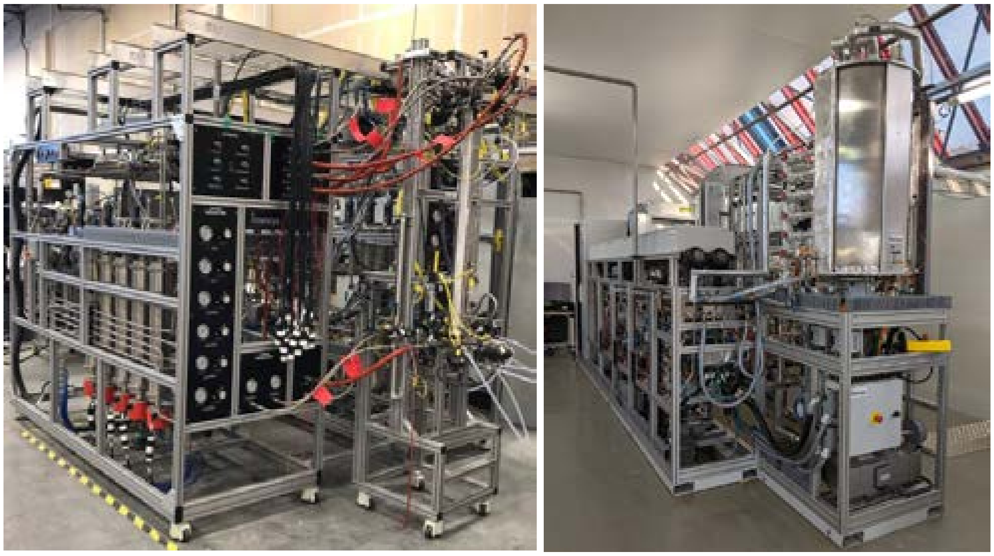

Figure 2: The variable test station at Svante (VTS, left) and the Process Demonstration Unit (PDU, right).

Figure 3: CO_2MENT field Unit (1 TPD) at a Lafarge cement plant in Richmond BC showing the pre-treatment system and capture plant (left) and the RAM showing the beds (right).

The sorbent and process parameters are provided in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	350-380	350-380
Bulk Density	kg/m^3	N/A	N/A
Average Particle Diameter	mm	0.31-0,35	0.31-0.25
Particle Void Fraction	m^3/m^3	N/A	N/A
Packing Density	m^2/m^3	2,300-2,500	2,300-2,500
Solid Heat Capacity @ STP	kJ/kg-K	1.4-1.6	1.4-1.6
Crush Strength	kg_f	N/A	N/A
Manufacturing Cost for Sorbent	$/kg	30-35	20-25
Adsorption			
Pressure	bar	1-1.1	1-1.1
Temperature	°C	50	50
Equilibrium Loading (20% CO2)	g mol CO_2/kg	1.7-1.8	1.9-2.0
Heat of Adsorption	kJ/mol CO_2	35-38	35-38
Desorption			
Pressure	bar	0,8-1.0	0.8-1.0
Temperature	°C	110-120	110-140
Equilibrium CO_2 Loading (20% CO2)	g mol CO_2/kg	0.3-0.4	0.4-0.5
Heat of Desorption	kJ/mol CO_2	35-38	35-38
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	Rapid cycle rotary valves moving beds	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90-95	95 150

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process dependent.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the laminated sorbent composite sheet area/filter bed volume.

Equilibrium Loading – The basis for CO_2 loading is mass of dry sorbent measured with 20% CO_2 in nitrogen (N_2) mixture without moisture.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Physisorption.

Sorbent Contaminant Resistance – High oxidation resistance below 50 parts per million (ppm) sulfur oxide (SO_X) and nitrogen oxide (NO_X).

Sorbent Attrition and Thermal/Hydrothermal Stability – Very stable under direct steam regeneration.

Flue Gas Pretreatment Requirements – Conventional direct contact cooler (DCC). Chemical scrubber to decrease contaminants and particulates (SO_X less than 10 ppm; nitrogen dioxide [NO_2] less than 10 ppm; dust less than 20 mg/Nm^3).

Sorbent Make-Up Requirements – Five-year lifetime without bed replacement.

Waste Streams Generated – No chemicals in depleted N_2 and typical cooling water blow-down.

TABLE 2: CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	50	30
Cost of Carbon Avoided	\$/tonne CO_2	Site-specific	Site-specific
Capital Expenditures	\$/TPD	70,000-80,000	60,000-70,000
Operating Expenditures	\$/tonnes CO_2	26-28	20-23
Cost of Electricity	\$/tonnes CO_2	12-18	12-18

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided is site specific depending on the source of electricity and steam.

Capital Expenditures – Projected capital expenditures in dollars per tonne per day of capacity.

Operating Expenditures – Projected operating expenditures in dollars per unit of tonne of CO_2 produced, including filter bed replacement and compression cost.

Cost of Electricity – Projected cost of electricity per unit of tonne of CO_2 produced for a range of price of electricity of 3.5–6 cents per kilowatt-hour (kWh).

Scale of Validation of Technology Used in TEA – The technology numbers were validated for use in the techno-economic analysis (TEA) from pilot-scale data.

technology advantages

- Svante's technology has the potential to enable a 50% reduction in capital costs of the capture unit compared to first-generation approaches.
- Novel technology replaces large chemical solvent towers (conventional approach) with a single piece of compact equipment, significantly reducing capital expenses (CAPEX).
- Usage of ultra-stable solid sorbent prevent toxic emission.
- Advanced sorbent material exhibits sharper temperature and pressure swing absorption and desorption, which allows for lower energy loads and faster kinetic rates.
- The proprietary material also exhibits unique resistance to SO_X and NO_X, oxygen impurities, and moisture swings.
- Svante unique laminate technology unlocks to use of different sorbents for performance or lifetime optimization (segmented bed concept).

R&D challenges

Tuning the two sorbents—materials, coatings, and manufacturing—to work in synergy within the same process conditions.

status

The project team successfully built a dual-channel parallel film heat exchanger with adsorbent and an extremely low mass flow separator (bi-layered concept). They demonstrated the effectiveness of the approach to enable internal heat exchange within the structured sorbent stack. The project team also demonstrated fast indirect regeneration of sorbent across the barrier layer and found a significant reduction (~35%) in the steam ratio by avoiding excess steam addition. However, the increase in complexity of the manufacturing of the bi-layered beds combined with the required modification of the actual RAM is a drawback. The use of the segmented bed concept optimizing the lifetime or regeneration energy of a bed by the optimization of the sorbent choice for the local condition in a Svante bed is a highly promising Mark II design. The target KPIs at the VTS level were clearly identified for both low- and high-CO_2 concentration segmented bed concept. The Electricore team completed long-term testing (2,000 hours) using the VeloxoTherm RAM field demonstration unit. Svante was able to scale-up MOF manufacturing to the tonnes scale at target costs with the help of the BASF chemical company.

available reports/technical papers/presentations

Fagundo K, Electricor, Hovington P, Svante Inc, "Advanced Structure Adsorbent Architechtures for Transformative Carbon Dioxide Catpure Performance," 2023 FECM / NETL Carbon Management Research Project Review, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC30_Fagundo.pdf*.

Jelen, D, "Advanced Structured Adsorbent Architectures for Transformative CO_2 Capture Performance," Final Technical Report, June 2023. *osti.gov/servlets/purl/1987758/*.

Jelen, D, "Advanced Structured Adsorbent Architectures for Transformative CO_2 Capture Performance," 2023 FECM / NETL Carbon Management Research Project Closeout Meeting, March 2023.

Hovington, P., Electricore Inc, “Advanced Structured Adsorbent Architectures for Transformative CO_2 Capture Performance,” 2022 NETL Carbon Management Project Review Meeting, August 2022.

Jelen, D and Hovington, P. “Advanced Structured Adsorbent Architectures for Transformative CO_2 Capture Performance,” 2021 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Jelen.pdf*.

Jelen, D and Cizeron, J. “Advanced Structured Adsorbent Architectures for Transformative CO_2 Capture Performance,” 2020 NETL Project Review Meeting - Carbon Capture, Pittsburgh, PA, October 2020. *https://netl.doe.gov/sites/default/files/netl-file/20VPRCC_Jelen.pdf*.

Jelen, D. “Advanced Structured Adsorbent Architectures for Transformative CO_2 Capture Performance,” Budget Period 1 Review Meeting, Pittsburgh, PA, June 2020.

Jelen, D. “Advanced Structured Adsorbent Architectures for Transformative CO_2 Capture Performance,” 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/D-Jelen-Electricore-Adsorbent-Architectures.pdf*.

Jelen, D. “Advanced Structured Adsorbent Architectures for Transformative CO_2 Capture Performance,” Kickoff Presentation, Pittsburgh, PA, August 2019.

CO_2-Philic Block Copolymers with Intrinsic Microporosity for Post-Combustion CO_2 Capture

primary project goal

Helios-NRG and its partners, the University of Buffalo and TechOpp Consulting, are developing carbon dioxide (CO_2)-philic block copolymers with intrinsic microporosity (BCPIMs) for post-combustion CO_2 capture. Efforts are focused on optimizing and scaling-up of the fabrication of thin-film composite (TFC) membranes for CO_2/nitrogen (N_2) separation.

technical goals

- Develop BCPIMs exhibiting CO_2 permeability of 2,000 Barrer or above and CO_2/N_2 selectivity of 40 or greater.
- Demonstrate stability of the BCPIMs in the presence of water vapor, SO_X, and NO_X.
- Develop TFC membranes based on BCPIMs; achieve CO_2 permeance greater than 4,500 gas permeation units (GPU) and CO_2/N_2 selectivity greater than 40.
- Develop process cycles incorporating BCPIM membranes with potential to achieve less than $30/ton CO2.
- Test membranes for long-term resistance to contaminants using real flue gas, followed by bench-scale module fabrication and performance measurements over a range of operating conditions.

technical content

This project is developing scalable membranes based on BCPIMs to achieve superior CO_2/N_2 separation properties. The materials are being designed, synthesized, and characterized for carbon capture. The BCPIMs are micro-phase separated. The continuous phase is based on state-of-the-art amorphous polyethylene oxide (PEO) with superior CO_2/N_2 separation property. The discontinuous phase of polymer intrinsic microporosity (PolyIMs) has extremely high gas permeability, dramatically increasing gas permeability without reducing CO_2/N_2 selectivity. More importantly, the configuration of polymers only minimizes the formation of voids between polymers and MOFs in traditional MMMs and allows facile integration into the current membrane manufacturing trains.

To demonstrate the feasibility, to the project team is preparing two series of copolymers—block copolymers polymerizable metal-organic frameworks (BCPolyMOFs) derived from polyMOFs and interpenetrating networks (IPNs) containing polymers of intrinsic microporosity (PIMs). The team's preliminary results found that the optimized materials achieved CO_2 permeability of at least 2,000 Barrer and CO_2/N_2 selectivity of at least 40; the materials also showed good

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Composite Membranes Comprised of Block Copolymers for CO_2 Capture

participant:
Helios-NRG LLC

project number:
SC0020730

predecessor projects:
N/A

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partners:
Membrane Technology and Research Inc.; University at Buffalo

start date:
06.29.2020

percent complete:
68%

stability in the presence of water vapor, sulfur oxide (SO_X), and nitrogen oxide (NO_X). Initial techno-economic analysis (TEA) work confirmed the potential of the advanced membranes to achieve the project objective of $30/tonne CO_2 or lower.

Approach I: Design of PolyMOFs and BCPolyMOFs. First, the MOFs with amine groups on the organic ligand react with methacrylamide groups to graft methacrylate groups. Second, the polyMOFs with methacrylate groups can be copolymerized with propylene glycol methyl ether acetate (PEGMEA) and/or polyethylene glycol diacrylate (PEGDA) via photo- and thermal-polymerization or atom transfer radical polymerization (ATRP). PEGDA also serves as a cross-linker for the curing process. The resulting copolymers have a general chemical structure shown in Figure 1a. The cross-linking scheme is under mild conditions (e.g., room temperature); thus, the MOFs structure is not damaged during synthesis. The MOFs with large pore sizes and high porosity are preferred to provide high gas permeability, and yet they have amine groups to functionalize with the acrylate groups for polymerization.

Approach II: IPNs Containing PIMs. IPNs can be easily prepared by dissolving the PIMs (such as PIM-1 with chemical structure shown in Figure 1b) and the macromonomers of PEGMEA before the polymerization. PIMs can be prepared using widely reported methods in the literature. These polymers can provide a quick indication of the effect of the PIM phase on the CO_2/N_2 separation properties.

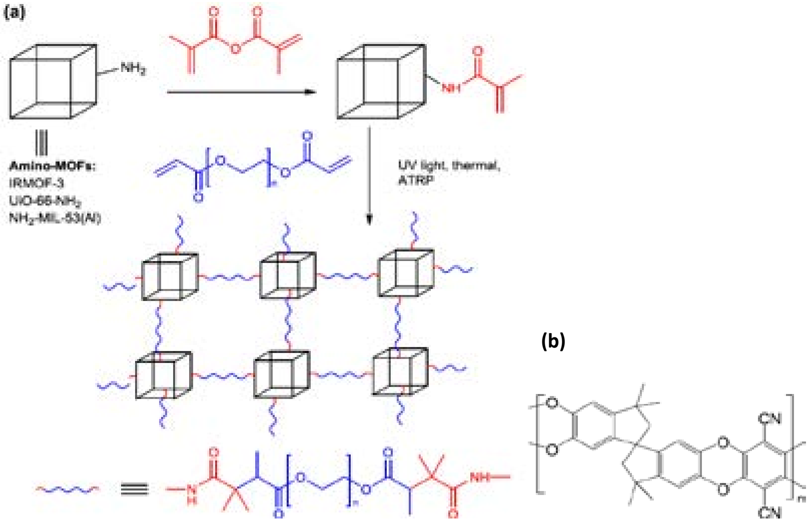

Figure 1: (a) Representative scheme to prepare polyMOFs and BCPolyMOFs, adapted from a reference. (b) PIM-1 chemical structure to be prepared into IPNs.

The project team identified UiO-66-NH_2 as a good candidate for polyMOFs because of its large pore size and high porosity to provide high gas permeability and excellent stability in the humid and acidic environment. It also has amine groups to functionalize with the acrylate groups for polymerization. The project team successfully prepared UiO-66-NH_2 nanoparticles as small as 50 nm (Figure 2a). Figure 2b shows that the reacted UiO-66-NH_2 exhibits the X-ray diffraction (XRD) patterns similar to the pristine ones, indicating that the crystal structure (including pore size and porosity) is not changed by the functionalization.

To prepare BCPolyMOFs, the project team first optimized the polymer matrix to improve the CO_2 permeability. Eighteen-Crown-six with the same ether oxygen content as PEO was added into prepolymer solutions of the PEGDA and PEGMEA (20/80) before the photopolymerization. Increasing the crown ether content significantly increased the CO_2 permeability without a significant effect on the CO_2/N_2 selectivity. For example, adding 50 wt% of crown ether in Cross-linked poly(ethylene oxide) (XLPEO) increases CO_2 permeability from 580 to 1,100 Barrer while retaining CO_2/N_2 selectivity of 43. Such an increase can be ascribed to the decrease in the glass transition temperature (Tg), indicating the increased flexibility of polymer chains and thus gas diffusivity.

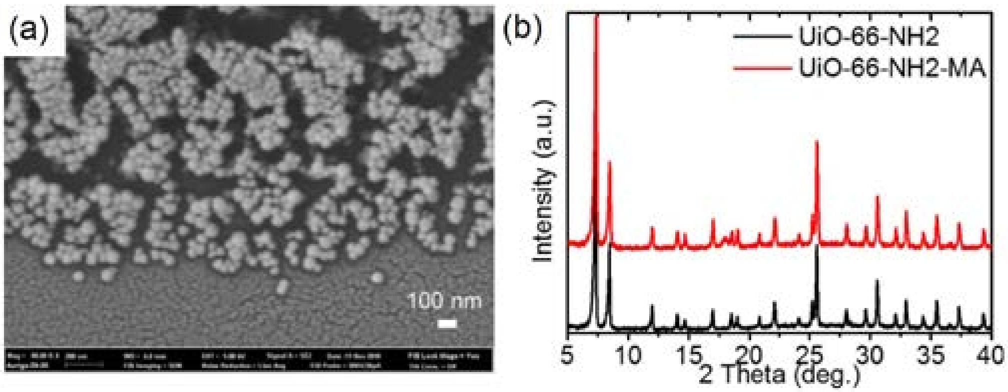

Figure 2: (a) SEM image of UiO-66-NH_2 nanoparticles; (b) XRD patterns of nanoparticles before and after the functionalization.

Second, the prepared UiO-66-NH_2 nanoparticles were also incorporated into the prepolymer solutions containing PEGDA, PEGMEA, and crown ether before the photopolymerization. Adding 1.0 wt% of MOF dramatically increased CO_2 permeability from 580 Barrer in XLPEO to 770 Barrer and from 1,100 Barrer in the blend containing 50% XLPEO and 50% crown ether (XLPEO-CE50) to 2,200 Barrer, as shown in Figure 3a. The increase in CO_2 permeability by adding the MOFs does not decrease CO_2/N_2 selectivity (Figure 3b). The BCPolyMOFs containing 1% MOFs in the XLPEO-CE50 (XLPEO-CE50-MOF1) showed the best CO_2/N_2 separation performance and were further evaluated with a gas mixture (20% CO_2/80% N_2) at different temperatures. Mixed-gas separation properties are more or less consistent with the pure-gas properties. Increasing the temperature increases CO_2 permeability and decreases CO_2/N_2 selectivity. Although there is a tradeoff between permeability and selectivity in operating these membranes, the BCPolyMOFs show CO_2 permeability of 2,200 Barrer and CO_2/N_2 selectivity of 50 at 35°C, which meets the targets for the project.

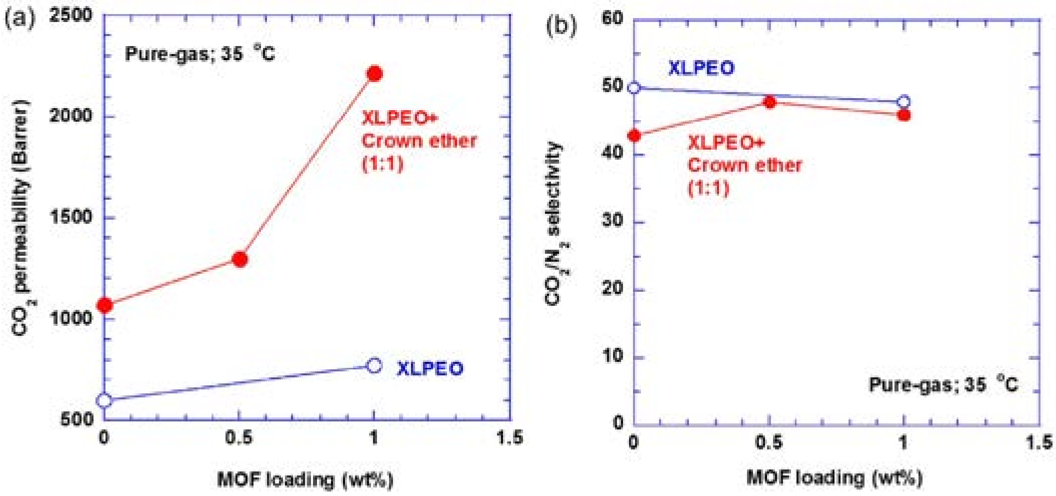

Figure 3: Effect of the MOF loading on (a) CO_2 permeability; (b) CO_2/N_2 selectivity at 35°C and 30 psig.

To demonstrate the promise of these new materials for practical applications, the project team prepared TFC membranes, as shown in Figure 4. The selective layer based on the BCPIMs provides the CO_2/N_2 separation properties. The gutter layer provides a smooth surface for the selective layer to deposit and provides extremely high gas permeance to channel the permeating gas to the open pores of the substrate. The porous support also provides mechanical properties needed for handling.

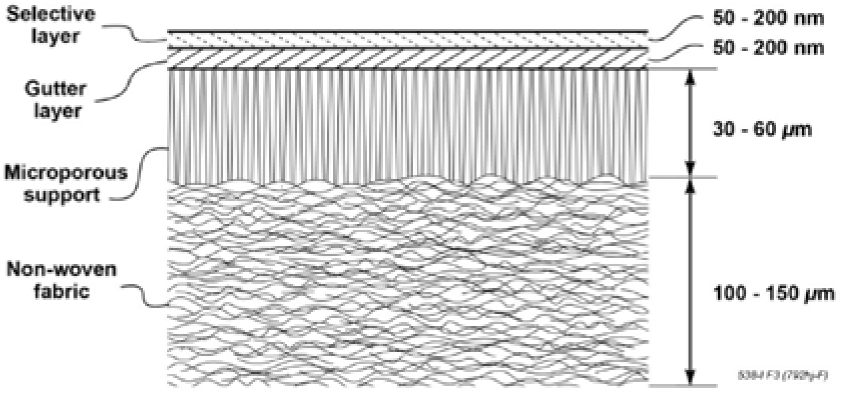

Figure 4: Schematic of TFC membranes comprising a selective layer, gutter layer, and porous support.

The project team identified polysulfone (PSF) ultrafiltration (UF) membranes as the porous support and polydimethylsiloxane (PDMS) with a CO_2 permeability of 3,000 Barrer and N_2 permeability of 300 Barrer as the gutter layer. PEGMEA was polymerized using ATRP, which was then coated onto the gutter layer using a dip-coater. The PEO layer increases the CO_2/N_2 selectivity compared with the PDMS layer. The performance of CO_2 permeance ranging from 630–2,500 GPU and CO_2/N_2 selectivity ranging from 43–30 is comparable with the leading membranes, demonstrating their potential. To improve the hydrophilicity of the gutter layer, the project team used polydopamine (PDA) to modify the PDMS gutter layer surface. After the PDA modification, the PDA/PDMS gutter layer shows water contact angle 60° and CO_2 permeance of 6,500 GPU. With the same coating solution, the membrane based on PDA/PDMS shows higher CO_2 permeance and higher CO_2/N_2 selectivity than that based on PDMS.

technology advantages

- Advanced materials with CO_2 permeability of 2,000 Barrer and CO_2/N_2 selectivity of 40.
- Material stability in the presence of acid gases.

R&D challenges

- Scale-up of TFC membrane fabrication.

status

Helios-NRG has developed a TFC membrane with CO_2 permeance of 4,500 GPU and CO_2/N_2 selectivity of 40 at 35–60°C. Current efforts include scaling-up TFC membrane fabrication, tuning fabrication parameters to optimize membrane performance, validating resistance to flue gas contaminates (H_2O, SO_X, NO_X) in long-term testing, and fabricating small modules and validating performance in process tests in preparation for testing at the National Carbon Capture Center (NCCC). Degradation testing on exposure to flue gas is also currently being conducted on the TFC membranes.

available reports/technical papers/presentations

Ravi Prasad and Haiqing Lin, "CO_2-Philic Block Copolymers with Intrinsic Microporosity (BCPIMs) for Post-Combustion CO_2 Capture," 2024 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_Posters_Prasad.pdf*.

Ravi Prasad and Haiqing Lin, “CO_2-Philic Block Copolymers with Intrinsic Microporosity (BCPIMs) for Post Combustion CO_2 Capture,” 2023 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, September 2023.

Ravi Prasad and Haiqing Lin, “CO_2-Philic Block Copolymers with Intrinsic Microporosity (BCPIMs) for Post Combustion CO_2 Capture,” Phase II Project kickoff meeting presentation, Pittsburgh, PA, November 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=12345&filename=CO2-Philic+Block+Copolymers+with+Intrinsic+Microporosity+(BCPIMs)+for+Post+Combustion+CO2+Capture.pdf*.

Bench-Scale Development of a Transformational Graphene Oxide-Based Membrane Process for Post-Combustion CO_2 Capture

primary project goal

Gas Technology Institute (GTI) is developing a transformational graphene oxide (GO)-based membrane process that can be installed in a new or retrofitted into an existing pulverized coal or natural gas power plant for carbon dioxide (CO_2) capture ready for demonstration by 2030. The expected product from this project will be a compact, GO-based membrane prototype system capable of achieving at least 70% CO_2 removal with a single-stage process and 90% CO_2 removal with a two-stage process. The system will be tested over an extended duration on actual flue gas at GTI and the National Carbon Capture Center (NCCC).

technical goals

- Scale-up the GO-based membranes to 50 to 100 cm^2 area and demonstrate that the scaled membranes show CO_2/nitrogen (N_2) selectivity ≥200 and CO_2 permeance ≥1,000 gas permeation units (GPU) for the high-selectivity membranes (designated as GO-1 membranes), and CO_2/N_2 selectivity ≥20 and CO_2 permeance ≥2,500 GPU for the high-flux membranes (designated as GO-2 membranes).
- Perform 100 hours of stability testing to demonstrate the CO_2 permeance and CO_2/N_2 selectivity decrease by less than 10% in the presence of flue gas contaminants (oxygen [O_2], sulfur oxide [SO_X], nitrogen oxide [NO_X]).
- Scale-up the GO-based membranes to 500 to 1,000 cm^2 area and demonstrate that the scaled membranes show CO_2/N_2 selectivity ≥200 and CO_2 permeance ≥1,000 GPU for the GO-1, and CO_2/N_2 selectivity ≥20 and CO_2 permeance ≥2,500 GPU for the GO-2.
- Achieve 95% CO_2 purity by integrating the GO-1 and GO-2 membranes in a skid (designated as GO^2) for both natural gas and coal-derived flue gases.
- Perform a techno-economic analysis (TEA) to validate that the cost of electricity (COE) is 30% less than the U.S. Department of Energy (DOE) baseline CO_2 capture approach.

technical content

GTI is developing GO-based membranes for CO_2 capture from flue gases. The high-selectivity membranes (GO-1) show CO_2 permeances as high as 1,020 GPU with a CO_2/N_2 selectivity of 680, which is much higher than state-of-the-art membranes. In addition, GTI is also developing high-flux membranes (GO-2) with CO_2

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Post-Combustion Power Generation PSC

key technology:

Membranes

project focus:

Graphene Oxide Membranes for CO_2 Capture from Coal-Derived Flue Gases

participant:

Gas Technology Institute

project number:

FE0031598

predecessor project:

FE0026383

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partners:

Rensselaer Polytechnic Institute; The State University of New York at Buffalo; Trimeric Corporation; National Carbon Capture Center

start date:

06.01.2018

percent complete:

90%

permeance as high as 2,500 GPU using GO quantum dots (GOQD) as a membrane building block. The transformational GO-based membrane process integrates the GO-1 and GO-2 membranes (GO^2), offering a new opportunity to explore further reductions in the cost of CO_2 capture.

Graphene-based materials, such as graphene and GO (Figure 1), have been considered as next-generation membrane materials. They are only sub-nanometer thick and thus may form ultrathin separation membranes to minimize transport resistance and maximize flux. The feasibility of using a vacuum filtration process to fabricate ultrathin GO membranes (thickness of ~1.8 nm) has been demonstrated. It was observed that the molecular-sized pores of structural defects on GO flakes could serve as a transport pathway for selective gas separations.

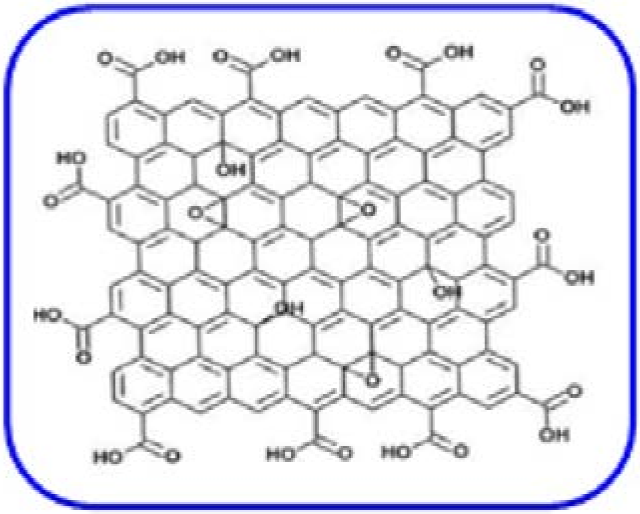

Figure 1: Chemical structural model of GO.

Because of the different morphologies of GO and GOQDs, ultrathin membranes (less than 20 nm) composed of these two different building blocks are expected to have different nanostructures. Figure 2 shows different membrane nanostructures of GO-1 and GO-2 membranes and the proposed transport pathways.

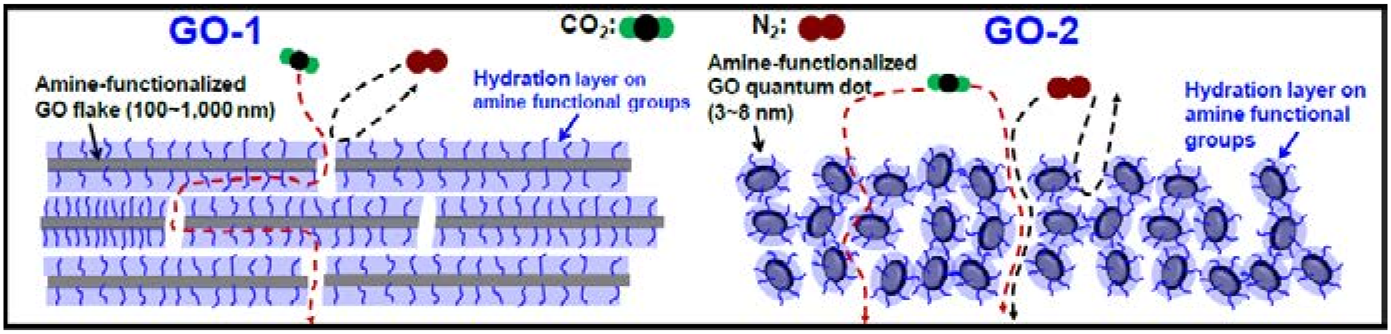

Figure 2: Membrane nanostructures of GO-1 and GO-2 membranes and proposed CO_2 separation mechanisms.

Large GO flakes (greater than 100 nm) with high aspect ratio of lateral size to the flake thickness typically led to regular and uniform lamellar structure (GO-1, left in Figure 2) with a negligible quantity of defects after hydration of surface functional amine groups with water in the flue gas. As a result, CO_2 molecules can quickly transport through the membrane by a facilitated transport mechanism via reaction with amine (CO_2 + R-NH_2 ⟷ R-NH_3+ + HCO_3-) and block the permeation of N_2 molecules. Therefore, GO-1 membranes have moderate CO_2 permeance but high CO_2/N_2 selectivity. In contrast, in GO-2 membranes, the small GOQDs may form a randomly packed nanostructure (right in Figure 2) containing defects that cannot be effectively sealed by the hydration layer. These defects greatly increase the CO_2 permeance, but also decrease the selectivity. Therefore, GO-2 membranes are expected to have high CO_2 permeance but lower CO_2/N_2 selectivity compared to the GO-1 membranes.

In addition to the hollow fiber GO-based membranes, the project team demonstrated for the first time an easy, fast, and scalable printing method with advanced computational controls to deposit ultrathin, high-quality GO-based membranes on a polymeric support for gas separation. A commercial ink cartridge was used to hold an appropriate GO dispersion for printing (Figure 3a). Using only GO "ink," ultrathin GO membranes for highly effective water nanofiltration have been printed. To promote membrane separation performance for a CO_2/N_2 mixture, an extra cartridge was added that holds various amine solutions, such as ethylene diamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), and pentaethylenehexamine (PEHA), to increase both CO_2 permeance and CO_2/N_2 selectivity (Figure 3b). Uniform GO coatings with well-controlled thickness and a membrane area as large as 225 cm^2 have been printed (Figure 3c). Figure 3d shows a typical cross-sectional scanning electron microscopy (SEM) of the printed membrane. Figure 3e indicates the thicknesses of the printed membranes are between 6 and 60 nm and can be well-controlled by the GO concentration.

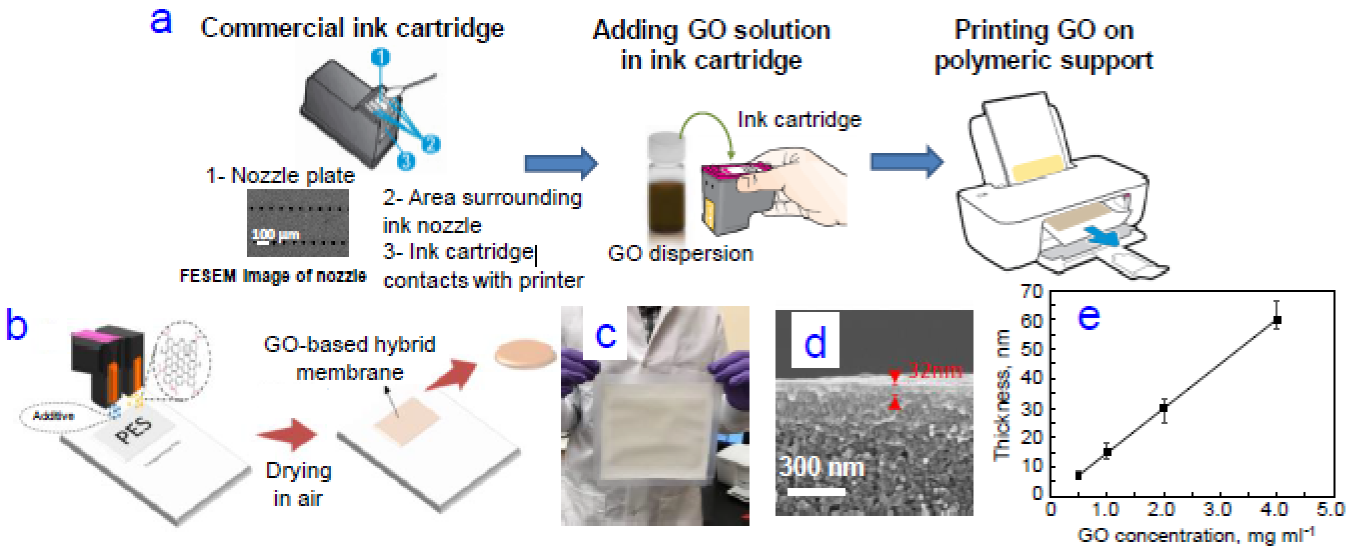

Figure 3: (a) Schematics of GO membrane fabrication by inkjet printing; (b) GO-based membrane preparation by printing from two cartridges containing GO ink and additives; (c) a picture of a printed GO membrane (15 cm × 15 cm); (d) cross-sectional SEM of the membrane; (e) dependence of membrane thickness on GO ink concentration.

The project team prepared GO-based flat-sheet membranes on a polyether sulfone (PES) substrate by printing. The resulting membrane was sealed in a plate-and-frame module for characterization and CO_2/N_2 separation testing. The process parameters for the membranes developed are given in Table 1.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Graphene Oxide	
Materials of Fabrication for Support Layer	—	Polyether sulfone	
Nominal Thickness of Selective Layer	µm	0.002-0.05 for GO-1 0.005-0.1 for GO-2	0.002-0.02 for GO-1 0.005-0.05 for GO-2
Membrane Geometry	—	Hollow fiber and flat sheet	Hollow fiber and flat sheet
Max Trans-Membrane Pressure	bar	<5	1
Hours Tested without Significant Degradation	—	100 (simulated flue gas)	>200 (actual flue gas)
Manufacturing Cost for Membrane Material	$/m^2	TBD	TBD

Membrane Performance			
Temperature	°C	50-80	50-80
CO_2 Pressure Normalized Flux	GPU	1,020 for GO-1 2,500 for GO-2	1,000 for GO-1 2,500 for GO-2
CO_2/H_2O Selectivity	—	1/10 for GO-1 N/A for GO-2	<1/10 for GO-1 <1/10 for GO-2
CO_2/N_2 Selectivity	—	680 for GO-1 >30 for GO-2	>200 for GO-1 >20 for GO-2
CO_2/SO_2 Selectivity	—	N/A for GO-1 N/A for GO-2	<1/10 for GO-1 <1/10 for GO-2
Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	Crossflow	
Packing Density	m^2/m^3	1,000	
Shell-Side Fluid	—	CO_2-rich permeate	
Flue Gas Flowrate	kg/hr	TBD	
CO_2 Recovery, Purity, and Pressure	%/%/bar	70-90%, >95%, TBD	
Pressure Drops Shell/Tube Side	psi/m	Feed and permeate: <1.5	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

The project team coated GO-based membranes on 50- to 100-cm^2 PES porous hollow-fiber modules by a vacuum filtration process. The sub-recipient systematically synthesized and optimized single-layered GO flakes via different GO synthesis methods. A variety of equipment was used to characterize the membrane morphology, thickness, composition, and structural defects density. The CO_2/N_2 separation properties were measured using an existing laboratory-scale testing system and simulated flue gas.

For coal-fired flue gas, the proposed GO^2 technology is designed to capture 90% CO_2 with greater than 95% CO_2 purity. The system will be installed downstream of flue gas desulfurization (FGD), as shown in Figure 4. It is a compact, stand-alone, membrane-based process, enabling easy integration into the power plant. For the TEA, the data for the current research and development (R&D) values is shown in Table 2.

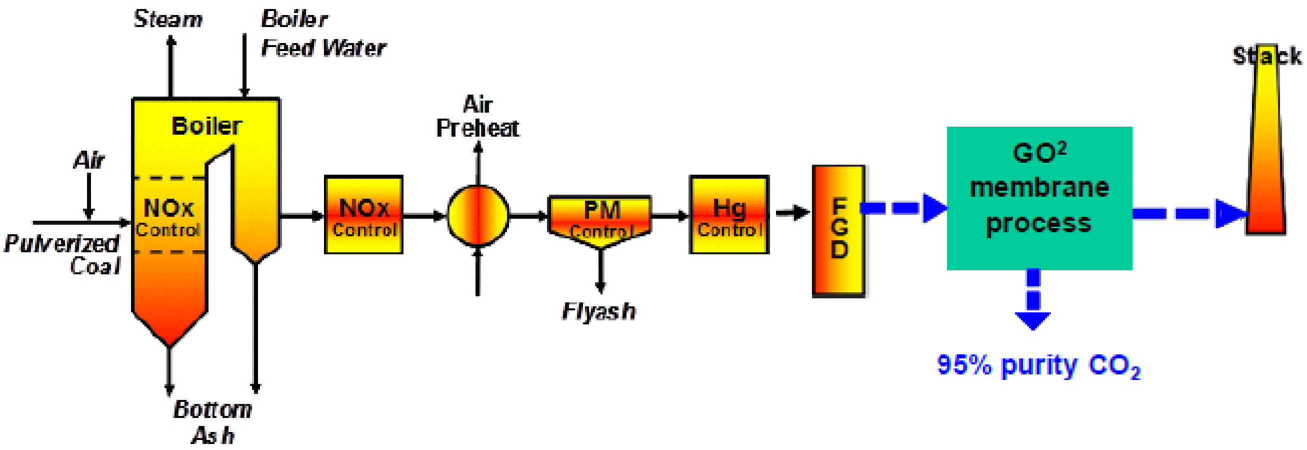

Figure 4: Process flow diagram for the proposed GO² process for CO_2 capture.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value*	Target R&D Value
Cost of Carbon Captured	$/tonne CO_2	NA	30
Cost of Carbon Avoided	$/tonne CO_2	NA	NA
Capital Expenditures	$/MWhr	NA	NA
Operating Expenditures	$/MWhr	NA	NA
Cost of Electricity	$/MWhr	NA	93.24

*** Current values are not available (NA). Techno-economic analysis will be performed at the end of the project under Task 10.**

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Other Parameter Descriptions:

Membrane Permeation Mechanism – A vacuum pump is used on the permeate side to provide a vacuum of 2.9 pounds per square inch absolute (psia; 0.2 bar). Because the GO-based membranes are highly water-permeable, the water vapor in the flue gas permeates through the membrane and lowers the partial pressure of CO_2 in the permeate side. Thus, the applied vacuum provides enough driving force for CO_2 permeation. The CO_2-depleted residue leaving the GO-1 unit is sent to a second membrane unit, GO-2, which also uses a vacuum on the permeate side to create the driving force for separation.

Contaminant Resistance – GO is typically prepared under strong acid and oxidation conditions in an aqueous solution, so it is expected to be very stable under these harsh conditions. Additionally, GO is hydrothermally stable at 150°C and has good chemical stability and mechanical strength. Therefore, GO is expected to be stable under flue gas conditions and with flue gas contaminants, such as nitrogen dioxide (NO_2), SO_X, etc.

Flue Gas Pretreatment Requirements – The proposed GO² system will be installed downstream of FGD.

Membrane Replacement Requirements – To be determined.

Waste Streams Generated – No waste streams are generated. The GO-based membranes are selective for water (H_2O) over CO_2, and the proposed GO^2 technology can recover the water vapor from the permeate streams. The recovered, mineral-free, high-purity water can be reused by the power plant.

technology advantages

- The technology achieves high CO_2 capture rates (≥70%) with 95% CO_2 purity.
- The water-permeable feature of the GO membrane overcomes the process pressure limitation issue, enhancing mass transfer.
- GO membranes have high thermal/chemical stability and mechanical strength.
- Graphene-based materials such as GO have been considered next-generation membrane materials. They are only sub-nanometer thick and thus may form ultrathin separation membranes to minimize transport resistance and maximize flux.
- GTI's printing method for GO membrane formation has several advantages, including:
    - Low-cost, fast, and scalable deposition of ultrathin GO-based membranes.
    - Capability of controlling coating properties by controlling printing parameters.
    - High utilization efficiency of GO material without waste.
    - Flexibility of forming GO-hybrid coatings by introducing desired additives.

R&D challenges

- When scaling-up GO-based membranes, the CO_2 permeance and/or CO_2/N_2 selectivity may not scale with size.
- There is risk that membrane sealing issues will be encountered in the development process.
- The commercial PES substrate quality is not currently sufficiently high for scale-up of GO-based membranes.

status

Both GO-1 and GO-2 membranes were successfully scaled to 1,000 cm^2 surface area. Good stability for both membranes was achieved under simulated flue gas conditions. The bench-scale system has been fully constructed and is undergoing testing at NCCC.

available reports/technical papers/presentations

Li, S., 2024, "Bench-Scale Development of a Transformational Graphene Oxide-Based Membrane Process for Post-Combustion CO_2 Capture." Presented at the 2024 FECM/NETL Carbon Management Project Review Meeting. Pittsburgh, PA. August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_PSCC_8_SLi.pdf*.

Li, S., 2024, "Bench-Scale Development of a Transformational Graphene Oxide-Based Membrane Process for Post-Combustion CO_2 Capture." Presented at the Final Project Review Meeting. Pittsburgh, PA. June 2024. *https://netl.doe.gov/projects/files/Bench-scale%20Development%20of%20a%20Transformational%20Graphene%20Oxide-based%20Membrane%20Process%20for%20Post-combustion%20CO2%20Capture.pdf*.

Li, S., 2023, "Bench-Scale Development of a Transformational Graphene Oxide-Based Membrane Process for Post-Combustion CO_2 Capture." Presented at the 2023 FECM/NETL Carbon Management Project Review Meeting. Pittsburgh, PA.

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Li, Shiguang, et al., 2018, "Bench-Scale Development of a Transformational Graphene Oxide-Based Membrane Process for Post-Combustion CO_2 Capture," presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA. *https://netl.doe.gov/sites/default/files/netl-file/S-Li1-GTI-Graphene-Oxide-based-Membrane.pdf*.

Li, S.; Xu, W.; Meyer, H.; Yu, M.; Zhang, S.; Zhou, F.; Ding, Y.; Sexton, A.; Sachde, D.; Biggott, B., 2020, "Energy Efficient GO-PEEK Hybrid Membrane Process for Post-Combustion Carbon Dioxide Capture." Final Scientific/Technical Report. Report No. GTI 21881. DOE Award No. DE-FE0026383.

Li, S., et al., 2018, "Energy Efficient GO-PEEK Hybrid Membrane Process for Post-Combustion Carbon Dioxide Capture," presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA. *https://netl.doe.gov/sites/default/files/netl-file/S-Li-GTI-Energy-Efficient-GO-PEEK-Hybrid-Membrane-Process.pdf*.

Li, S., et al., 2017, "Energy Efficient GO-PEEK Hybrid Membrane Process for Post-Combustion Carbon Dioxide Capture," presented at the 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA. *https://netl.doe.gov/sites/default/files/event-proceedings/2017/co2%20capture/2-Tuesday/S-Li-GTI-Hybrid-Membrane-Process.pdf*.

Li, S., et al., 2016, "Energy Efficient GO-PEEK Hybrid Membrane Process for Post-Combustion CO_2 Capture." Presented at the 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA. *https://netl.doe.gov/sites/default/files/event-proceedings/2016/c02%20cap%20review/4-Thursday/S-Li-GTI-Go-Peek-Hybrid-Membrane-Process.pdf*.

Rational Development of Novel Metal-Organic Polyhedra-Based Membranes for CO_2 Capture

primary project goal

The State University of New York (SUNY) at Buffalo, along with its partners, is developing solubility-selective mixed matrix membranes (MMMs) comprising highly polar rubbery polymers and soluble metal-organic polyhedra (MOPs) that, in terms of separation efficiency, outperform currently leading membranes by 50–100%. Implementing the new polymers and MOPs into Membrane Technology and Research Inc.'s (MTR) membrane processes may enable carbon dioxide (CO_2) capture at less than $30/tonne CO_2 from coal power plants.

technical goals

- Develop solubility-selective MMMs comprising polar rubbery polymers and MOPs.
- Develop thin-film composite (TFC) membranes achieving high CO_2 permeance (3,000 gas permeation units [GPU]), high CO_2/nitrogen (N_2) selectivity (75), and high CO_2/oxygen (O_2) selectivity (30) at 60°C.
- Demonstrate separation performance and stability with raw flue gas at the National Carbon Capture Center (NCCC).
- Perform techno-economic analysis (TEA) on the membrane processes.

technical content

The project team is developing transformative solubility-selective MMMs containing MOPs and rubbery polar polymers. These transformative MMMs are built upon three key unique approaches. First, rubbery polymers with CO_2-philicity (and N_2-phobicity) will be designed, in contrast with most of the literature approach in pursuing glassy polymers with strong size-sieving ability. Second, MOPs with strong CO_2 affinity will be designed and added to increase the CO_2/gas solubility selectivity. In contrast to the commonly pursued insoluble metal-organic frameworks (MOFs), these MOPs are discrete nano-cages and soluble in organic solutions, making it easier to prepare TFC membranes with selective layers as thin as 100 nm. Third, the structure of polymers and MOPs can be independently designed with enormous possibilities, which can be accelerated using computational simulation.

A consortium of six organizations with complementary capabilities was assembled to achieve these goals, including University at Buffalo (UB; SUNY–Buffalo), Rensselaer Polytechnic Institute (RPI), California Institute of Technology (Caltech), MTR, NCCC, and Trimeric Corporation (Trimeric). The UB team is conducting fundamental and industrial membrane development and MOP synthesis and

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Mixed Matrix Membranes for CO_2 Capture from Coal-Derived Flue Gas

participant:
State University of New York–Buffalo

project number:
FE0031736

predecessor projects:
N/A

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haiqingl@buffalo.edu

partners:
Rensselaer Polytechnic Institute; California Institute of Technology; Membrane Technology and Research Inc.; National Carbon Capture Center; Trimeric Corporation

start date:
07.01.2019

percent complete:
75%

application to develop the novel materials, performing laboratory parametric tests, and scaling-up the production. RPI is preparing functionalized polymers and scaling-up the production. Caltech is simulating gas permeation to guide the design of the MMMs. MTR is preparing TFC membranes and bench-scale modules and performing field tests at NCCC. Trimeric is updating the membrane process design and economic analysis based on MTR's patented processes. The endpoint of this project is a field test of bench-scale membrane modules, and a TEA of the newly developed membranes elucidating their potential to meet U.S. Department of Energy's (DOE) goals for CO_2 capture. A graph of the selectivities of the two chosen macromonomers is shown in Figure 1, while a simplified visual perspective of the membrane process is shown in Figure 2. The parameters governing membrane operation are shown in Table 1.

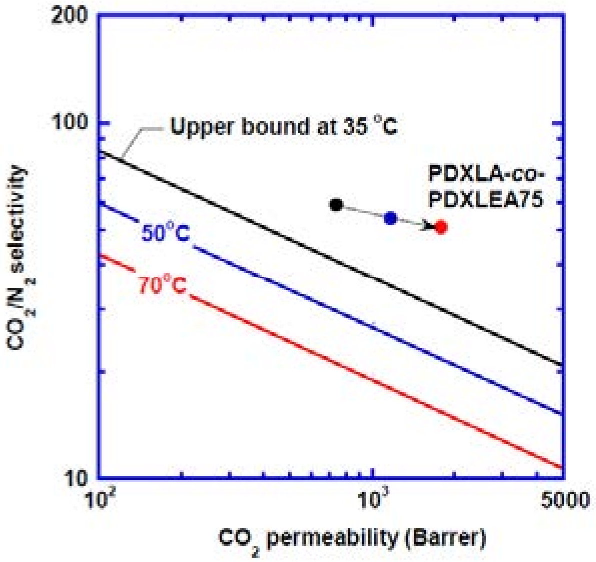

Figure 1: The "rubbery polymers": two macromonomers, poly(1,3-dioxolane) acrylate (PDXLA) and poly(1,3-dioxolane) ethyl ether acrylate (PDXLEA) are highly polar polymers that exhibit CO_2/N_2 separation properties above the upper bound in the Robeson's plot.

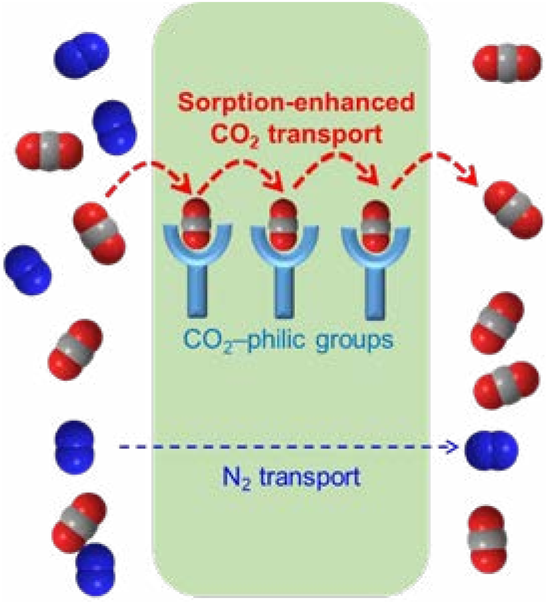

Figure 2: The highly branched amorphous polymers containing poly(1,3-dioxolane) (PDXL) in the branches interact favorably with CO_2, but not N_2, allowing for the design of solubility-selective membrane materials with superior performance for gas separations.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Mixed matrix materials of rubbery polymers and MOP	
Materials of Fabrication for Support Layer	—	Glassy polymers such as PAN, PSf	
Nominal Thickness of Selective Layer	nm	200–1,000	100–300
Membrane Geometry	—	flat sheet	flat sheet
Max Trans-Membrane Pressure	bar	10	10
Hours Tested without Significant Degradation	—	120	500
Membrane Performance			
Temperature	°C	60°C	60°C
CO_2 Pressure Normalized Flux	GPU	1,500–2,000	3,000
CO_2/H_2O Selectivity	—	0.3	0.3
CO_2/N_2 Selectivity	—	50	75
CO_2/SO_2 Selectivity	—	0.5	0.5
Type of Measurement	—	Mixed gas	Mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	Spiral-wound modules	
Packing Density	m^2/m^3	300–600	
Shell-Side Fluid	—	feed	
Flue Gas Flowrate	ft^3/min	–	
CO_2 Recovery, Purity, and Pressure	%/%/bar	–	
Pressure Drops Feed/Permeate Side	psi/m	–	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{m^2}$	–	

Definitions:

MOP – Metal-Organic Polyhedron (singular)/Polyhedra (plural); 2–5-nm-sized molecule with metal bonding sites for CO_2.

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} $cm^3/(cm^2 \cdot s \cdot cm$ mercury [Hg]) at 1 atmosphere (atm) and 0°C. For non-linear materials, the dimensional units reported shall be based on flux measured in $cm^3/(cm^2 \cdot s)$ (at 1 atm and 0°C) with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} $kgmol/(m^2 \cdot s \cdot kPa)$ (SI units).

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities shall be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either co-current, counter-current, cross-flow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate or retentate stream.

technology advantages

- This membrane process builds upon innovative membrane process design using CO_2-selective membranes developed by MTR.
- Could outperform current leading membranes by at least 50%.

R&D challenges

- Transport phenomena in new membrane materials.
- Fabrication and use of the novel membrane systems in effective process designs.

status

The project team has successfully enabled the production of the required polymers and MOPs in 10–20g batches. TFC membranes were successfully assembled, achieving a CO_2 permeance of 3,000 GPU, CO_2/N_2 selectivity of 50, and CO_2/O_2 selectivity of 20. A bench-scale system was successfully installed at NCCC, where field testing is to be performed.

available reports/technical papers/presentations

Lin, H., "Rational Development of Novel Metal Organic Polyhedra-based Membranes for CO_2 Capture (FE0031736)," presented by Haiqing Lin, University of Buffalo, The State University of New York, 2024 NETL Carbon Management Project Review Meeting, Pittsburgh, PA, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_PSCC_8_Lin.pdf*.

Lin, H., "Rational Development of Novel Metal Organic Polyhedra-based Membranes for CO_2 Capture (FE0031736)," presented by Haiqing Lin, University of Buffalo, The State University of New York, 2023 NETL Carbon Management Project Review Meeting, Pittsburgh, PA, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC30_Lin.pdf*.

Lin, H. 2022, "Rational Development of Novel Metal Organic Polyhedra-based Membranes for CO_2 Capture (FE0031736)," presented by Haiqing Lin, University of Buffalo, The State University of New York, 2022 NETL Carbon Management Project Review Meeting, Pittsburgh, PA, August 2022.

Lin, H.; Cook, T.; Bae, C.; Wang, Z.; Merkel, T.; Morton, F.; Sexton, A., 2020, "Rational Development of Novel Metal Organic Polyhedra-based Membranes for CO_2 Capture (FE0031736)," presented by Haiqing Lin, University of Buffalo, The State University of New York, NETL Project Kickoff Meeting, Morgantown, WV, January 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10761&filename=Aoi+%5b1c%5d+Rational+Development+of+Novel+Metal-Organic+Polyhedra-Based+Membranes+for+CO2+Capture.pdf*.

Lin, H.; Cook, T.; Bae, C.; Wang, Z.; Merkel, T.; Morton, F.; Sexton, A., 2019, "Rational Development of Novel Metal Organic Polyhedra-based Membranes for CO_2 Capture (FE0031736)," presented by Haiqing Lin, University of Buffalo, The State University of New York, 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/H-Lin-UB-SUNY-Metalorganic-Membrane.pdf*.

Development of Self-Assembly Isoporous Supports Enabling Transformational Membrane Performance for Cost-Effective Carbon Capture

primary project goal

Membrane Technology and Research, Inc. (MTR) is developing composite membranes with superior carbon capture performance using a novel transformational approach. Two membrane targets have been identified: (1) carbon dioxide (CO_2) permeance of 4,000 gas permeation units (GPU) with mixed-gas CO_2/nitrogen (N_2) selectivity of 25, and (2) CO_2 permeance of 3,000 GPU with mixed-gas selectivity of 50. The first type will be used in the CO_2 removal step and the second type will be used in the CO_2 sweep step, both of which are parts of MTR's post-combustion CO_2 capture process.

technical goals

- Develop methods to produce isoporous supports, first manufacturing single-layer supports (14 inches wide) using the laboratory's continuous casting system and then manufacturing dual-layer supports (40 inches wide) using MTR's commercial-scale casting equipment.
- Synthesize and characterize polymers containing high ether-oxygen content for CO_2/N_2 separation, and down-select polymers with most promising CO_2/N_2 separation properties for scale-up and production of composite membranes.
- Prepare composite membranes by coating selective layers onto isoporous support, first using a laboratory-scale coating machine (12 inches wide) and then using MTR's commercial-scale coater (40 inches wide).
- Perform a techno-economic analysis (TEA) and sensitivity analysis of the process.

technical content

MTR is developing composite membranes with superior CO_2 capture performance using a novel transformational approach. Composite membranes consist of a selective polymer layer coated on a support that, ideally, does not hinder transport in the selective layer. MTR has conclusively demonstrated that this objective is not met for current supports when coated with very thin selective layers, leading to a reduction in permeance by a factor of two or larger. The proposed three-year project consists of two parallel technology developments that address the support issue, as well as the development of more selective materials.

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Polymeric Membranes with Isoporous Supports

participant:
Membrane Technology and Research, Inc.

project number:
FE0031596

predecessor projects:
N/A

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partners:
State University of New York at Buffalo; University of Texas at Austin

start date:
06.01.2018

percent complete:
100%

The first development is replacing the conventional porous supports used to fabricate composite membranes with novel isoporous supports. The remarkable pore structure of isoporous supports is created through self-assembly of block copolymers and is the ideal surface to support the nonporous layers that perform the separation in composite membranes. Work at MTR has shown that the surface pore structure of conventional supports restricts diffusion in the adjacent selective layers, and this geometrical effect significantly reduces the permeance of layers thinner than 1 micron. The high surface porosity and uniformity in pore size and pore location of the isoporous supports (Figure 1) eliminates this restriction and allows fabrication of Polaris™ composite membranes with significantly increased CO_2 permeances as high as 4,000 GPU. Building on extensive work on isoporous membranes reported in the open literature, the isoporous support preparation methods were adapted to MTR's commercial membrane casting equipment.

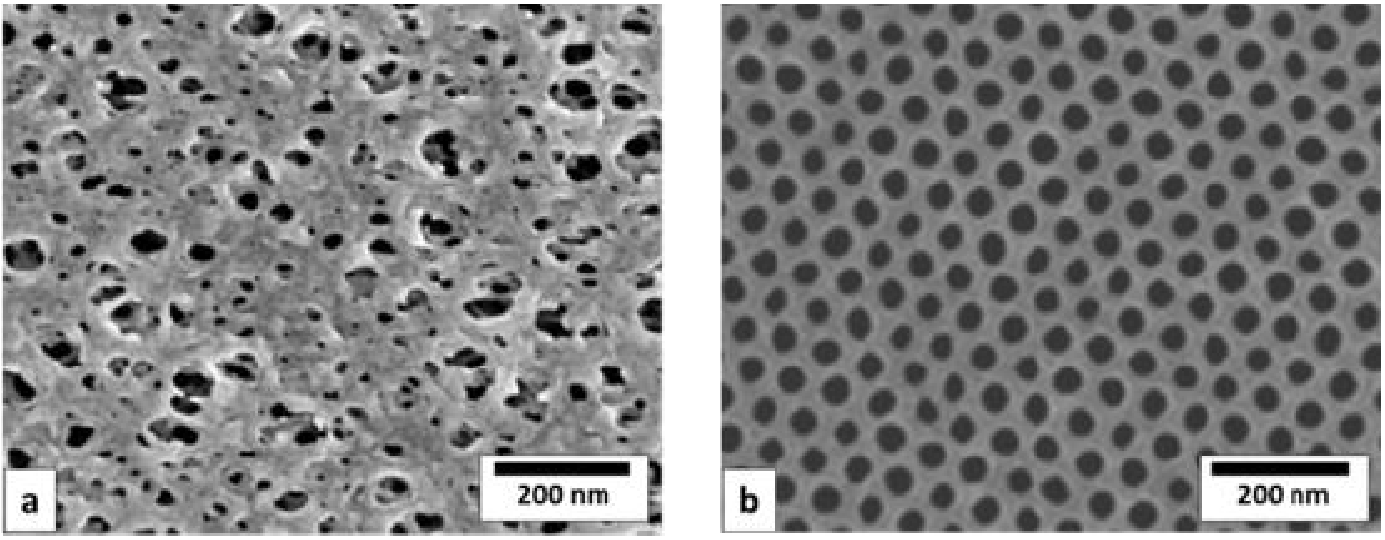

Figure 1: Surface pore structure of (a) a conventional porous support, and (b) an isoporous support.

The probability of successfully producing isoporous supports at commercial scale is high. The method to be used is very similar to existing methods for the manufacture of conventional supports. Moreover, the isoporous support, while of great importance, does not perform the actual separation, which means the occasional pore defects or misalignments are able to be tolerated. This is unlike the ultrafiltration and nanofiltration applications that are the traditional focus of isoporous membrane development.

The project team has prepared many support membranes using the Polystyrene-b-Poly-4-vinylpyridine (BCP1) polymer and has used scanning electron microscopes (SEMs) to evaluate the structures obtained. It became apparent that it is not easy to create the very perfect isoporous surfaces that are reported in the literature for these block copolymers. Figure 2(a) shows one of the few instances where MTR was able to produce a perfect isoporous surface. Figure 2(b) shows the top surface of a support prepared from a proprietary "less-than-perfect" block copolymer. Figure 3 shows that the restriction on CO_2 permeance by the pore structure of the support is substantially less for this support compared to the conventional support.

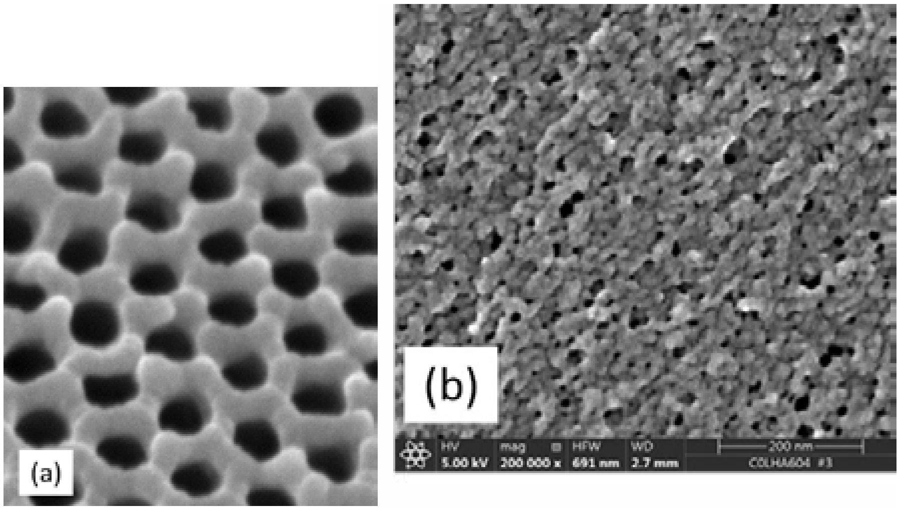

Figure 2: (a) Top surface of an isoporous support membrane prepared at MTR using the commercially available BCP1 block copolymer. (b) Top surface of a support prepared from an alternative "less-than-perfect" block copolymer that does not produce a perfect isoporous surface, but produces a finely porous, high-porosity surface that is advantageous.

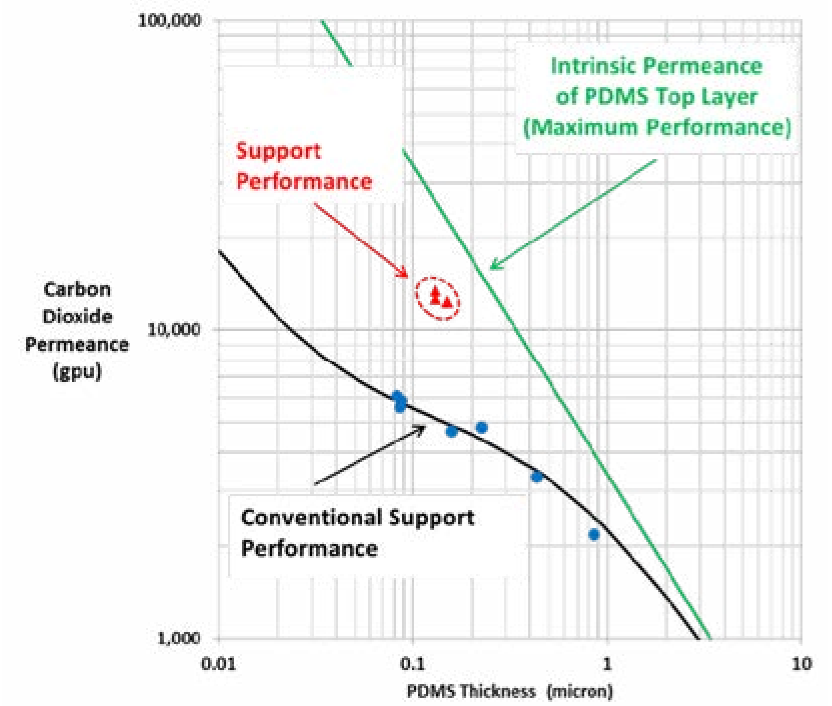

Figure 3: Plot of CO_2 permeance of PDMS layers of different thicknesses coated on a support prepared by MTR in this project.

The second development within this project is building on materials research carried out at the University of New York at Buffalo (NYUB), where materials have been identified that, in the form of films, have shown the potential to double the mixed-gas selectivity of the Polaris membrane, albeit at the expense of permeability. Variations of these materials based on poly(1,3 dioxolane) have been synthesized at NYUB, and MTR has produced and tested composite membranes using both conventional porous supports and the novel isoporous supports. These new materials are highly branched polymers rather than linear polymers, which, it was discovered, complicates the formation of layers with thicknesses substantially below 1 micron. This means that while successful in preparing membranes with high mixed gas selectivity of 45, the permeate of these membranes were not higher than 500 GPU.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	proprietary polymer	
Materials of Fabrication for Support Layer	—	proprietary polymer	
Nominal Thickness of Selective Layer	µm	<1	<1
Membrane Geometry	—	planar	planar
Max Trans-Membrane Pressure	Bar	70	70
Hours Tested without Significant Degradation	—	10,000+ hrs (coal)	10,000+ hrs (coal)
Manufacturing Cost for Membrane Material	\$/m^2	50	10
Membrane Performance			
Temperature	°C	30	30
CO_2 Pressure Normalized Flux	GPU or equivalent	Type 1: 2,500 Type 2: 500	Type 1: 4,000 Type 2: 3,000
CO_2/H_2O Selectivity	—	0.3	0.3
CO_2/N_2 Selectivity	—	Type 1: 25-30 Type 2: 45	Type 1: 25 Type 2: 50
CO_2/SO_2 Selectivity	—	0.5	0.5
Type of Measurement	—	pure gas	mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	crossflow and countercurrent	
Packing Density	m^2/m^3	1,000	
Shell-Side Fluid	—	N/A	
Flue Gas Flowrate	kg/hr	500	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%, >96%, 140 bar	
Pressure Drops Shell/Tube Side	bar	feed: <0.05/sweep: 0.05	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Permeation of individual components through the Polaris membrane is driven by partial pressure differences across the membrane generated by a permeate vacuum.

Contaminant Resistance – The membranes are known to be unaffected by water (H_2O), oxygen (O_2), and sulfur dioxide (SO_2). The effect of trace contaminants, such as Hg, arsenic, etc., is unknown.

Flue Gas Pretreatment Requirements – Currently, pretreatment requirements are unknown.

Membrane Replacement Requirements – Membrane lifetime is estimated at three years.

Waste Streams Generated – The membrane process will recover greater than 95% of the H_2O in flue gas as liquid.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	54	43
Cost of Carbon Avoided	\$/tonne CO_2	97	80
Capital Expenditures	\$/MWhr	23.9	18.4
Operating Expenditures	\$/MWhr	25.9	22.2
Cost of Electricity	\$/MWhr	50	50

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

technology advantages

- The novel isoporous supports increases the CO_2 permeance.
- The novel membrane selective layer material nearly doubles the CO_2/N_2 selectivity compared to membranes that use Polaris selective material.
- The two-stage capture process allows for high CO_2 capture rates and a high-purity product.
- The selective recycle of CO_2 to the boiler using the air sweep stream increases the CO_2 concentration in flue gas, reducing capital and operating expenditures.

R&D challenges

- Producing dual layer isoporous supports.
- Scale-up of polymer synthesis of improved selective layer materials.
- Tailoring the MTR coating techniques to the new NYUB materials.
- Producing defect-free top layers.

status

The project is near completion, with MTR working on the TEA and Final Report.

available reports/technical papers/presentations

Wijmans, H.,et al., "Development of Self-Assembly Supports Enabling Transformational Membrane Performance for Cost-Effective Carbon Capture," Final Project Report, July 2024. *https://doi.org/10.2172/2386964*.

Wijmans, H., et al., 2024, "Self-Assembly Isoporous Supports Enabling Transformational Membrane Performance for Carbon Capture." Presented at the 2024 DOE/NETL Carbon Management Project Review Meeting. Pittsburgh, PA. August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_PSCC_8_Wijmans.pdf*.

Wijmans, H. et al., 2023, "Self-Assembly Isoporous Supports Enabling Transformational Membrane Performance for Carbon Capture." Presented at the 2023 FECM/NETL Carbon Management Project Review Meeting. Pittsburgh, PA. August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC30_Wijmans.pdf*.

Wijmans, H. et al., 2023, "Self-Assembly Isoporous Supports Enabling Transformational Membrane Performance for Carbon Capture." Project Close Out Meeting. Pittsburgh, PA. May 2023.

Wijmans, H., et al., 2018, "Development of Self-Assembly Isoporous Supports Enabling Transformational Membrane Performance for Cost Effective Carbon Capture." Kickoff meeting presentation, Pittsburgh, PA.

Wijmans, H., et al., 2018, "Development of Self-Assembly Isoporous Supports Enabling Transformational Membrane Performance for Cost Effective Carbon Capture." Presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA. *https://netl.doe.gov/sites/default/files/netl-file/H-Wijmans-MTR-Self-Assembly-Isoporous-Supports.pdf*

Wijmans, H., et al., 2021, "Development of Self-Assembly Isoporous Supports Enabling Transformational Membrane Performance for Cost Effective Carbon Capture." Presented at the 2021 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Wijmans.pdf*

Novel Transformational Membranes and Process for CO_2 Capture from Flue Gas

primary project goals

The Ohio State University (OSU), along with its partners Gas Technology Institute, the National Carbon Capture Center (NCCC), and American Electric Power, developed a design and fabrication process for a novel transformational membrane and modules that capture carbon dioxide (CO_2) from flue gas, followed by bench-scale testing.

technical goals

- Optimize and characterize the transformational membrane (including morphology, transport properties, and stability).
- Synthesize an improved polymer support with a CO_2 permeance greater than 23,000 gas permeation units (GPU) for the membrane.
- Develop a polymeric composite membrane with CO_2 permeance greater than 3,300 GPU and CO_2/nitrogen (N_2) selectivity more than 140 at 77°C.
- Design and construct an integrated bench-scale testing system to be tested at OSU and NCCC.
- Complete a techno-economic analysis (TEA) of the project.

technical content

OSU and its partners developed a cost-effective design and fabrication process for a novel transformational membrane and its membrane modules that capture CO_2 from flue gas. Based on density functional theory (DFT) calculations indicating a new carrier with high reactivity with CO_2, OSU synthesized novel transformational polymer membranes with the new carrier, showing a very high CO_2 permeance of about 3,300 GPU (1 GPU = 10^{-6} cm^3 (STP [Standard Temperature and Pressure])/(cm^2/s/cm mercury [Hg]) and a very high CO_2/N_2 selectivity of greater than 140. Optimization of the novel transformational membrane, scale-up of the membrane to a prototype size of about 21 inches wide in continuous roll-to-roll fabrication, and construction and testing of a bench skid for the integrated membrane process were performed.

For the design of this membrane, OSU used a cost-effective polyethersulfone (PES) support and coating a thin top layer of the membrane (Figure 1). This membrane design offers a low cost for the membrane element in commercial spiral-wound configuration (less than \$2.00/ft^2 or \$21/m^2). Operating parameters and various properties of the membrane are detailed in Table 1. The prototype membrane was used to fabricate at least six pilot-size membrane modules (each about 20-inch length and 35-m^2 membrane area) for testing with simulated flue gas at OSU and subsequently with actual flue gas at NCCC (Wilsonville, Alabama), using the skid to

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Polymeric Composite Membranes

participant:
The Ohio State University

project number:
FE0031731

predecessor project:
FE0026919

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principal investigator:
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The Ohio State University
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partners:
Gas Technology Institute; National Carbon Capture Center; American Electric Power

start date:
07.01.2019

percent complete:
100%

capture the CO_2 (at 60–90%) with at least 95% CO_2 purity (Figure 2). The prototype membrane modules were in commercial spiral-wound configuration with a minimal pressure drop (less than 0.103 bar/meter or 1.5 psi/meter).

After the skid testing, OSU determined the identity and concentration of any possible contaminates on the membrane via laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS), Fourier transform infrared spectroscopy (FTIR), X-ray photoemission spectrometry (XPS), and nuclear magnetic resonance spectroscopy (NMR). Economic data is shown in Table 2.

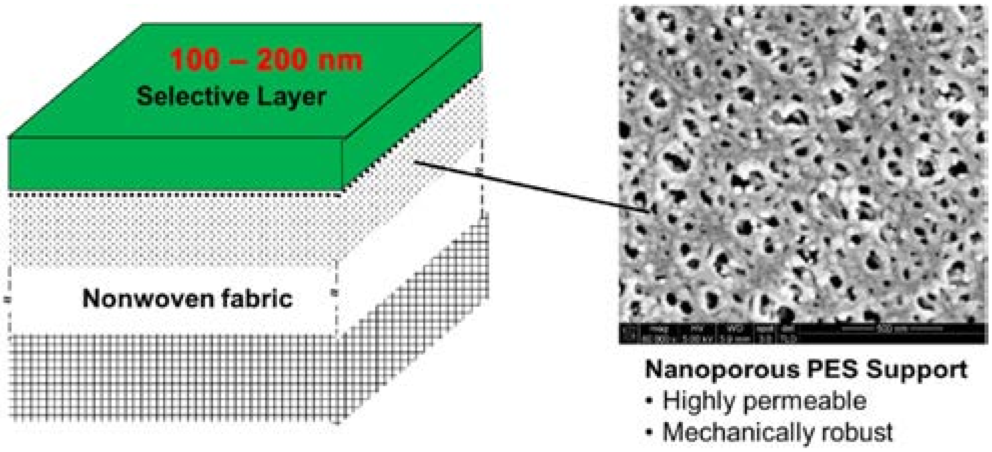

Figure 1: Schematic of thin-film composite membrane consisting of an amine-containing cover layer on a nanoporous PES support.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	amine-containing polymer	
Materials of Fabrication for Support Layer	—	polyethersulfone on non-woven fabric	
Nominal Thickness of Selective Layer	nm	170	150–200
Membrane Geometry	—	flat sheet	flat sheet
Max Trans-Membrane Pressure	bar	4	4
Hours Tested without Significant Degradation	—	2,500 hours	500 hours
Manufacturing Cost for Membrane Material	$/m^2	20	20
Membrane Performance			
Temperature	°C	57–77°C	57–77°C
CO_2 Pressure Normalized Flux	GPU	4,200 GPU	>3,300 GPU
CO_2/H_2O Selectivity	—	1	1
CO_2/N_2 Selectivity	—	160	>140
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	spiral-wound	
Packing Density	m^2/m^3	about 2,000	
Permeate-Side Fluid	—	vacuum or retentate recycle	
Flue Gas Flowrate	ft^3/min	130	
CO_2 Recovery, Purity, and Pressure	%/%/bar	>60%–90%, >95%, 1 bar	
Pressure Drops Feed/Permeate Side	psi/m	1.2/1.5	
Estimated Module Cost of Manufacturing and Installation (fully installed in membrane skid)	$\frac{\$}{m^2}$	40.3	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-10} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in desulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Permeate-Side Fluid – Either vacuum or a sweep gas.

Estimated Cost – Basis is m^2 membrane area.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Membrane Permeation Mechanism – Facilitated transport for amine-containing selective layer.

Contaminant Resistance – Resist up to 3 parts per million volume (ppmv) sulfur dioxide (SO_2).

Flue Gas Pretreatment Requirements – Removal of particulates and SO_2 polishing to 3 ppmv.

Membrane Replacement Requirements – Estimated approximately four years.

Waste Streams Generated – Nitrogen with water (H_2O), about 1% CO_2, and minor impurities.

Process Design Concept – See Figure 2.

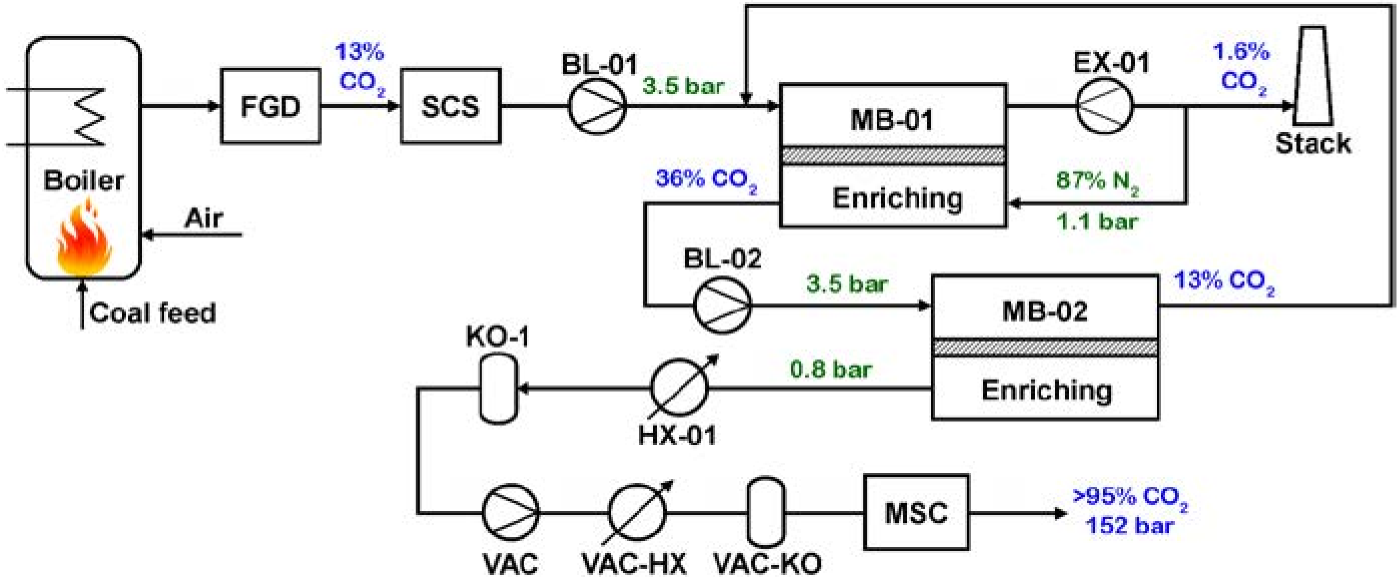

Figure 2: Process concept for two-stage membrane system. Initialisms: FGD = flue gas desulfurization; SCS = SO_2 caustic scrubber; BL = blower; MB = membrane; EX = turbo expander; HX = heat exchanger; KO = knockout; VAC = vacuum pump; MSC = multi-stage compressor.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	38.9	40.0
Cost of Carbon Avoided	\$/tonne CO_2	53.8	55.2
Capital Expenditures	\$/MWhr	47.5	50.0
Operating Expenditures	\$/MWhr	15.2	16.0
Levelized Cost of Electricity	\$/MWhr	99.3	101.0

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

technology advantages

- This membrane consists of a thin selective polymer layer on a polymer support so that it can be made efficiently in continuous roll-to-roll manufacturing.
- The membrane offers high CO_2/N_2 selectivity at greater than 57°C, which does not require flue gas cooling or cryogenic distillation.
- The simplicity of this membrane design offers a low cost for the membrane element in commercial spiral-wound configurations. If successful, the process can achieve less than \$30/tonne CO_2 for 70% recovery.

R&D challenges

- Membrane stability in the presence of high-level contaminants, such as SO_2 and nitrogen oxide (NO_X).
- Design and fabrication of prototype spiral-wound membrane module with 8-inch diameter.
- Requires two membrane stages.

status

The project concluded on March 31, 2023. The polymeric composite membranes were subjected to skid tests at NCCC. The tests demonstrated 90–99% CO_2 capture rates for 8.6% and 4.3% CO_2 concentrations in actual natural gas-derived flue gas—all with greater than 95% CO_2 purity. The TEA results show an overall cost of capture of $38.92/tonne of CO_2 (in 2018 dollars).

available reports/technical papers/presentations

Ho, W.; Han, Y.; Lin, L-C., 2023, “Novel Transformational Membranes and Process for CO_2 Capture from Flue Gas.” Final Technical Report. DE-FE0031731. Ohio State University: Columbus, OH. *https://www.osti.gov/servlets/purl/1985659*.

Ho, W.; Han, Y.; Lin, L-C., “Novel Transformational Membranes and Process for CO_2 Capture from Flue Gas.” National Energy Technology Laboratory. Carbon Management and Natural Gas & Oil Research Project Review Meeting. Pittsburgh, PA. August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Ho_0.pdf*.

R. Pang, K. K. Chen, Y. Han, and W. S. W. Ho, “Highly Permeable Polyethersulfone Substrates with Bicontinuous Structure for Composite Membranes in CO_2/N_2 Separation”, Journal of Membrane Science, 612, 118443 (2020).

Ho, W., Han, Y., “Novel Transformational Membranes and Process for CO_2 Capture from Flue Gas,” poster presented at the 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2019.

Ho, W., Han, Y., “Novel Transformational Membranes and Process for CO_2 Capture from Flue Gas,” presented at the 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/Y-Han-OSU-Transformational-Membrane.pdf*.

Solid-Phase Supports for Flue Gas CO_2 Separation with Molten Electrolytes

primary project goal

Luna Labs developed a systems-level approach to demonstrating a dual-phase membrane solid support technology for carbon dioxide (CO_2) separation with molten electrolytes. Luna evaluated yttria-stabilized zirconia (YSZ) and its derivatives, both as standalone solid-phase supports and in the presence of various molten electrolyte formulations. Through modification of the YSZ supports, development of structure-property relationships, and prototype modeling of scaled-up technology form factors, Luna's solid-phase supports and fully assembled membranes have the potential to provide the performance and scalability to separate CO_2 from flue gas in heat recovery steam generators (HRSGs).

technical goals

- Establish performance and design requirements for the dual-phase membrane technology, including the system, safety, and operating parameters for HRSG integration. Expand multitube module test capabilities.
- Design and fabricate a scalable CO_2 separation module prototype.
- Perform relevant testing on single and multitube membrane assemblies. Evaluate performance under relevant conditions in long-term (~months) tests to establish membrane durability and stability.
- Conduct a systems-level analysis and evaluate techno-economic viability.
- Evaluate membrane module performance results and create a module design for pilot-scale testing.

technical content

Luna Labs, in partnership with Nooter/Eriksen, led the scale-up and demonstration of a new type of dual-phase membrane technology. The dual-phase membrane consists of a thin wall of nanoporous ceramic solid support phase that retains a non-volatile molten phase within the pores through capillary action. The molten liquid phase selectively sorbs CO_2 in unrivaled combinations of permeability and selectivity. Advancements include engineering the molten phase chemistry for an active transport mechanism that powers CO_2 separation using larger water vapor (H_2O) concentrations across the membrane using low-pressure steam, lowering operational temperatures from greater than or equal to 450°C to 250–450 °C, introducing catalysts for the molten phase and ceramic surfaces, and adopting a bi-layer structure on the solid support phase to increase permeation rates. This Small Business Innovation Research (SBIR) program specifically focused on developing YSZ nanoporous solid-phase materials to achieve the `mechanical

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Post-Combustion Power Generation PSC

key technology:

Membranes

project focus:

Membrane Support Materials & Module Design

participant:

Luna Labs USA, LLC

project number:

SC0017124

predecessor projects:

N/A

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partners:

Lawrence Livermore National Laboratory; Nooter/Eriksen; University of Illinois Chicago; Trimeric Corporation

start date:

02.21.2017

percent complete:

100%

performance and form factors required for integration and operation inside an HRSG or boiler for operation at 250–450°C.

Currently, there is an unmet need for commercialized membrane systems that can efficiently separate CO_2 from power plant flue gas exhausts at thermally favorable conditions with reduced costs. The proposed solution was to develop an active transport membrane that uses the difference in water vapor concentration between low-pressure steam and the flue gas to drive CO_2 separation through the membrane. This approach has the potential to lower the total power plant parasitic power costs for carbon capture and compression by 30–40% in comparison with state-of-the-art solvent capture according to full-plant performance modeling in Thermoflex. These high-temperature membranes have greater potential for large-scale, energy-efficient separation by being directly integrated within power plant HRSGs, as shown in Figure 1. Luna's dual-phase membrane technology shows potential for meeting the power generation industry's needs by separating CO_2 from power plant flue gas under operational conditions (250–450°C) and with drastically reduced costs.

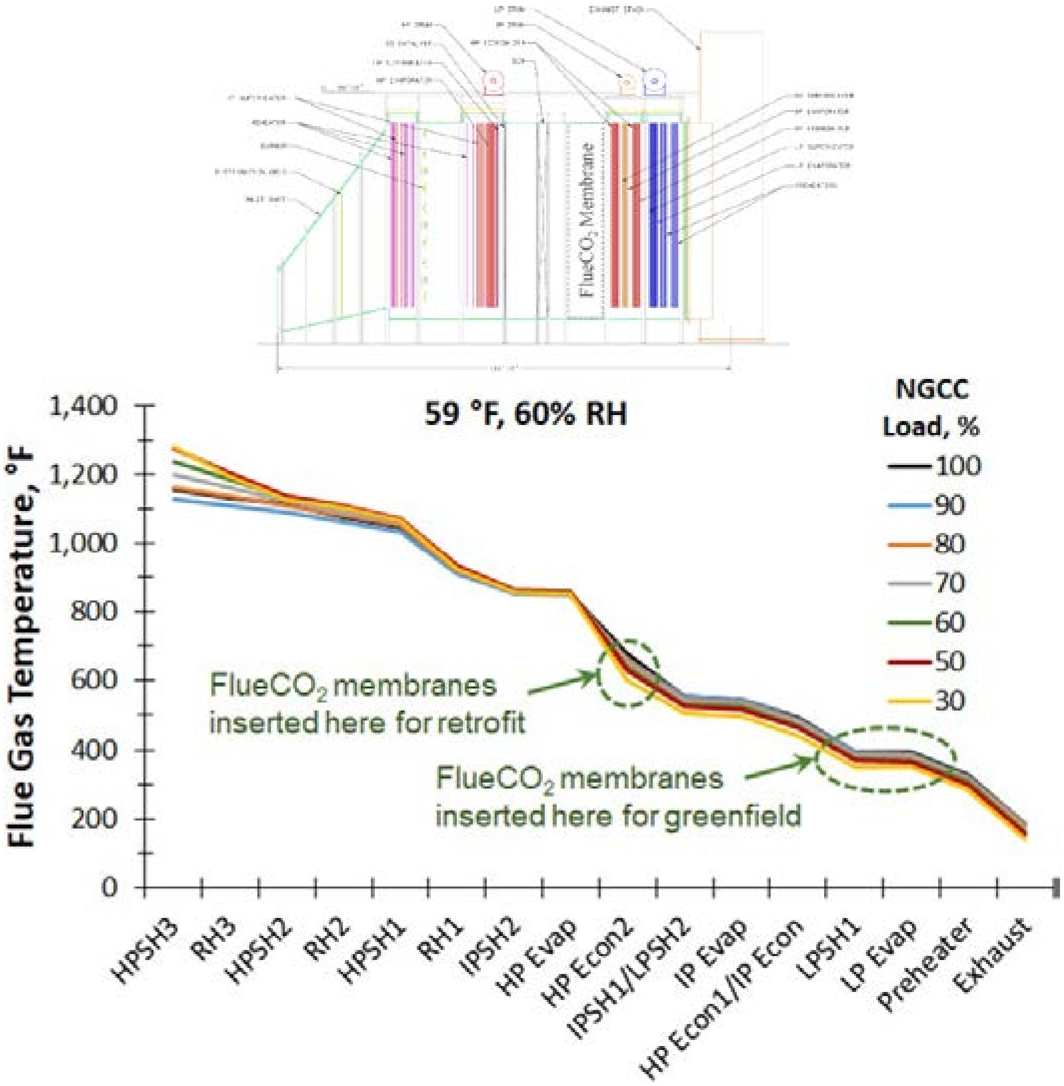

Figure 1: Luna's dual-phase membrane technology introduces a unique ability to implement carbon capture technologies into power plant HRSGs (250–450°C).

In the dual-phase membrane technology, a porous, solid material supports a non-volatile liquid electrolyte. Carbon dioxide actively absorbs into the molten electrolyte at the flue gas side, diffuses through the membrane as the carbonate ion (CO_3^{2-}) from high to low concentration, and desorbs from the membrane into a steam sweep gas (Figure 2). The steam sweep serves to both chemically desorb CO_2 and minimizes the concentration of permeated CO_2.

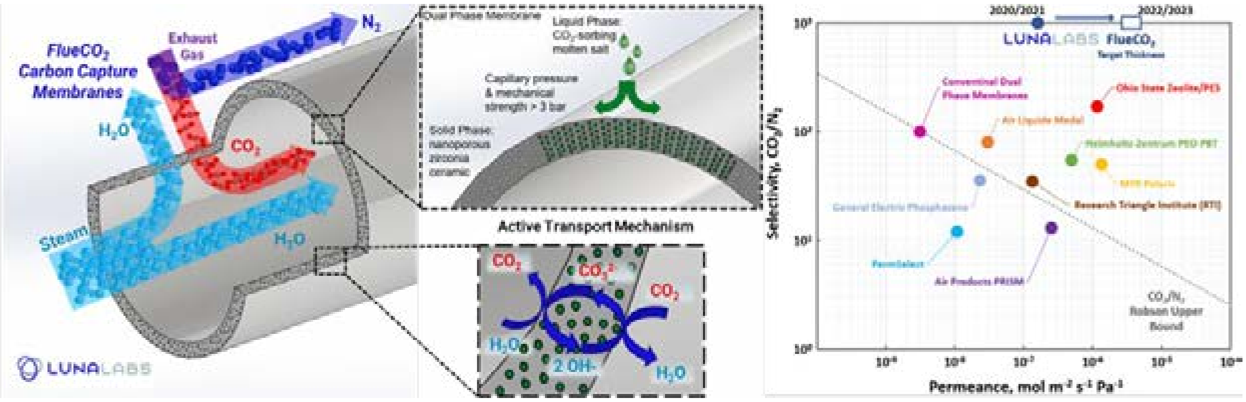

Figure 2: Luna Labs' dual-phase membrane technology for highly efficient and scalable CCS.

The unique operational conditions and performance capabilities of Luna's membrane enables a new opportunity to achieve more energy-efficient and less-expensive carbon capture. This membrane is not limited by the same physics governing Robeson's upper bound as conventional, polymer-based membranes and enables unrivaled combinations of permeability and selectivity (Figure 2, right). Before this project, such a novel system had never been scaled-up to demonstrate the technical feasibility at the membrane module scale. The operating parameters of the membrane system are shown in Table 1.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Molten hydroxide-carbonate dual phase	
Materials of Fabrication for Support Layer	—	Metal oxide	
Nominal Thickness of Selective Layer	µm	60	<40
Membrane Geometry	—	tubes	cartridge
Max Trans-Membrane Pressure	bar	1.3	1.3
Hours Tested without Significant Degradation	—	1000	5,000
Manufacturing Cost for Membrane Material	\$/m^2	750	300
Membrane Performance			
Temperature	°C	250 - 450	250 - 450
CO_2 Pressure Normalized Flux	GPU or equivalent	5000	9000
CO_2/H_2O Selectivity	—	undetermined	1
CO_2/N_2 Selectivity	—	1000	>10,000
CO_2/SO_2 Selectivity	—	undetermined	0.5
Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	crossflow and countercurrent	
Packing Density	m^2/m^3	75	
Shell-Side Fluid	—	Low-pressure steam	
Flue Gas Flowrate	kg/hr	2,200	
CO_2 Recovery, Purity, and Pressure	%/%/bar	98%, >99%, 140 bar	
Pressure Drops Shell/Tube Side	bar	feed: <0.01/sweep: <0.03	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Permeation through the membrane occurs by the high concentration of H_2O in the steam sweep, selective gas sorption reactions (bicarbonate and carbonate mechanisms).

Contaminant Resistance – Significant quantities of ash in coal power plants represents a contaminant hazard for the membranes. NGCC power plants have therefore been identified as the target application.

Flue Gas Pretreatment Requirements – The temperature must be less than 450°C.

Membrane Replacement Requirements – The membrane lifetime is currently unknown.

Waste Streams Generated – The membrane process will generate a zirconia-based composite that may be recyclable.

In Phase I of this project, the Luna team targeted solid-phase support materials with high strength, increased CO_2 separation capabilities, and stability in the presence of the new molten electrolyte formulations. It was critical that these materials were evaluated in context of the HRSG operational conditions to demonstrate their mechanical, thermal, and chemical stability, as well as their scale-up to larger membrane systems. Luna developed the capability to manufacture membranes using nanoporous YSZ tubes procured from CoorsTek Ceramics. The nanoporous (~100 nm) ceramic materials from CoorsTek are 4 mol% YSZ tubes with 1/4-inch outside diameter (OD) and 3/16-inch inside diameter (ID). These tubes are initially extruded to 120 centimeters (cm) and then cut into smaller segments for this stage of testing by Luna. The mechanical properties of this high-strength ceramic material were characterized and determined to be scalable for the operational conditions expected for the membrane. The solid-phase materials, fabrication methods, and design features were successfully developed in Phase I to manufacture and test multitube membrane modules in Phase II. Media and Process Technology began supplying the ceramic materials in Phase II of the project. The methods for manufacturing complete membrane systems from the ceramic materials has been scaled-up to simultaneously manufacture multiple tube membranes using process automation. Quality control procedures have been developed for key stages of the manufacturing process.

Luna has reviewed the options for designing the CO_2 separation membrane module. Tube-based form factor designs remain the most reliable option for further developing and scaling-up the membrane technology primarily based upon the maturity of possible ceramic material manufacturing methods, as well as the supporting technical capabilities required to develop a complete, functional membrane module. The current tube module design is based upon a Swagelok flange and custom interface to multiple short tube samples (Figure 3). This design minimizes module development costs by using commercially available off-the-shelf (COTS) parts whenever possible, while also supporting flexibility and adaptability. The goal was to develop and demonstrate the construction and operation of a small module of six 40-cm long single tubes. Once the basic design and construction approach is established, it was expected to be relatively easy to scale-up by using larger numbers of longer tubes. Larger Swagelok flange sizes enabled scale-up to 19 single-channel tubes or eight of the multichannel tubes. CoorsTek tube lengths can be extended to 120 cm. The initial multitube module has been manufactured and demonstrated to enable scaled-up testing and evaluation. A more advanced cartridge membrane design has been developed through multi-physics modeling that includes computational fluid dynamics. Proprietary cartridge membrane features have been developed to simplify manufacturing, increase surface area packing density, and minimize pressure drop while enhancing exhaust gas mixing. Intentional exhaust gas mixing was required because the laminar flow patterns developing at 2.0–2.5 m/s exhaust gas flow rates result in depleted CO_2 concentrations at the membrane surface.

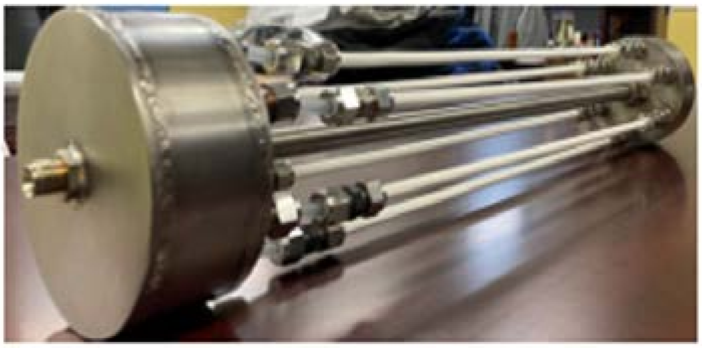

Figure 3: The non-proprietary multitube membrane module with six tubes has been revised to reduce the manufacturing time and costs, while also enabling easier and more flexible modifications for evolution and scale-up.

Luna has continued to achieve both faster CO_2 permeation rates and lower operational temperatures in the Phase IIA project (Figure 4). The transition to lower operational temperatures is important to enable installation of the membrane system into the HRSG near the low-pressure steam evaporator, where the flue gas has reached temperatures 150–200°C. Capturing the CO_2 at lower temperatures lowers separation energy costs. The present low-temperature electrolyte was selected for high CO_2 permeation rates, as well as a relatively wide operational temperature range of 250–450°C. The low-temperature limit of the membrane is generally governed by the freezing of the molten electrolyte phase.

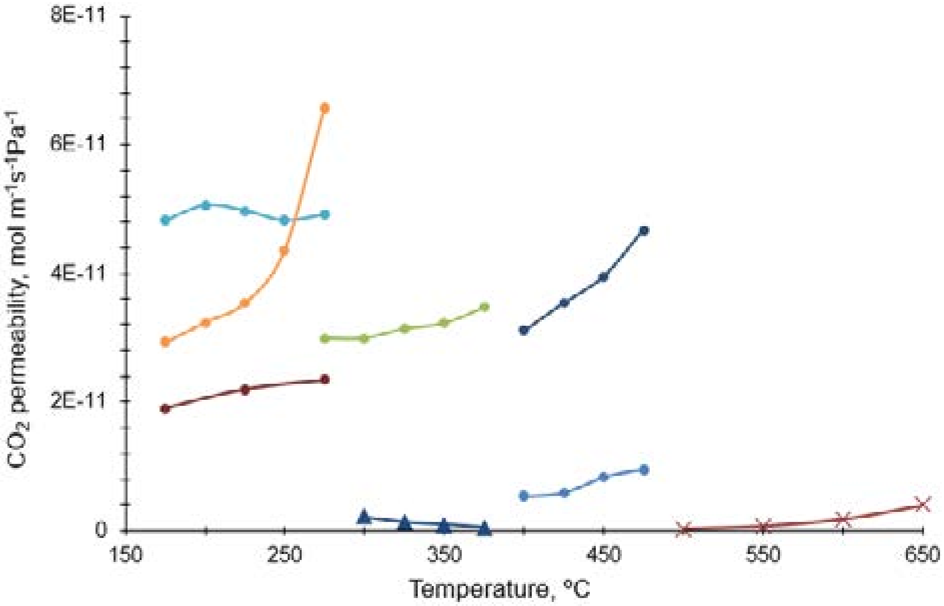

Figure 4: Progress in both improving the CO_2 permeability and decreasing the membrane operational temperatures for more efficient integration into new and retrofitted HRSGs of NGCC power plants.

Nooter/Eriksen has modeled the integration of the CO_2 capture membranes into a natural gas combined cycle (NGCC) power plant (Figure 5). The FlueCO$_2$ NGCC was derived directly from the National Energy Technology Laboratory (NETL) B31A base case and features a proprietary approach to recovering electrical power. The energy penalty of carbon capture by the FlueCO$_2$ NGCC are 7% in comparison against the simulated B31A case. The full plant model performances of

FlueCO$_2$ and B31A plants were simulated in Thermoflex as a function of gas turbine load, environmental conditions, and carbon capture rate. Half of the penalty (3.5%) is from the CO$_2$ compressors and the other half of the energy penalty (3.5%) is due to altered flow of low-pressure steam. The main risk to not achieving this performance target upon scaling-up is in losing the stoichiometric coupling of CO$_2$ to H$_2$O by the active transport mechanism (Figure 2). A dynamic cost modeling tool developed to evaluate the membrane unit size as a function of cost predicts a 98% CO$_2$ capture rate for optimized economics. Nooter/Eriksen has asserted that no features of the FlueCO$_2$ NGCC plant design will apparently affect the dynamic responsiveness of power output as the plant ramps up/down in load or cycling on/off. Retaining the dynamic flexibility of NGCC power plants is critical for retaining economic competitiveness when the supply and demand of power to the electrical grid cycle on a daily basis.

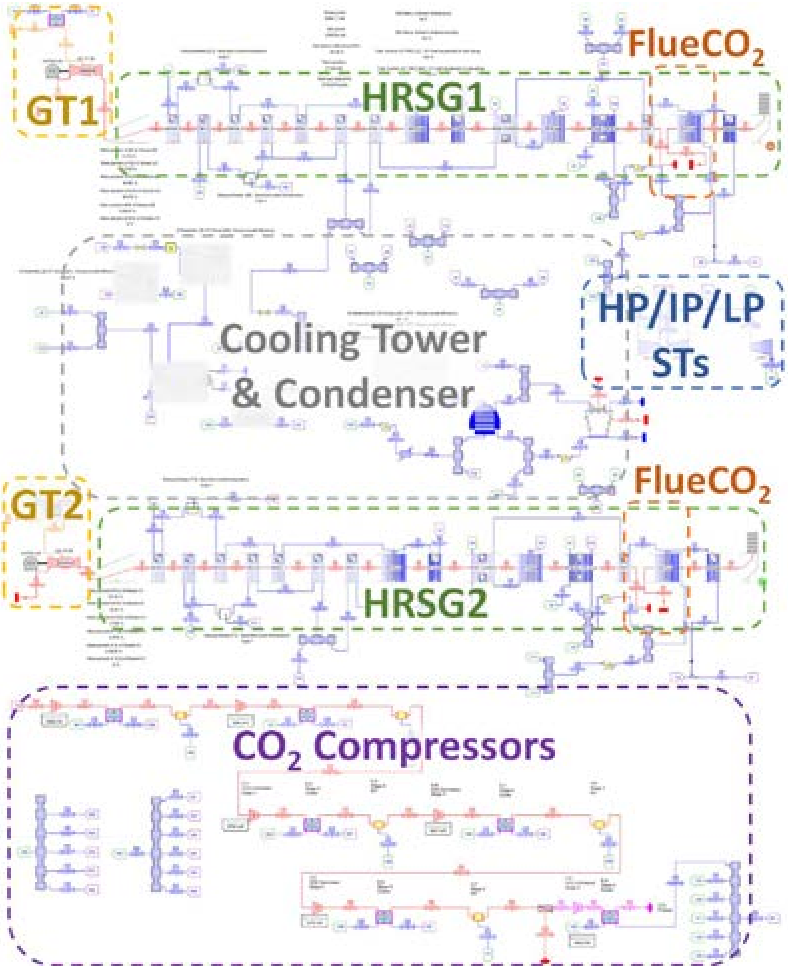

Figure 5: Thermoflex model of FlueCO$_2$ NGCC.

The costing methodology NETL prescribed for the B31A NGCC (base; no carbon capture) and B31B NGCC (control, solvent caron capture) cases were strictly adhered to for economic performance evaluations. Every line of the FlueCO$_2$, B31A, and B31B costing tables were converted into an interactive Microsoft spreadsheet tool that is available upon request for review. The formatting, color coding, and other features of the NETL costing tables have been replicated to facilitate ease of navigation of the spreadsheet costing tool. The spreadsheet costing tool enables direct comparisons between the three NGCC plants for relevant inputs (fuel price, electricity price, capacity factor, 45Q credits, carbon tax, CO$_2$ capture rate) and outputs (breakeven prices, levelized cost of electricity, 30-year net present value, capital and operating expenses). The FlueCO$_2$ NGCC outperforms the B31B NGCC in plausible scenarios due to higher energy efficiency and lower capital costs (Figure 7). The FlueCO$_2$ capital costs of capture are dominated by the membranes and CO$_2$ compressors. The main risk is failing to achieve the target membrane costs within a five-year lifetime (all other additional equipment is commercially available with established costs). The high capital costs of the B31B plant are compounded by taxes, insurance, and interest. A techno-economic analysis (TEA) was performed as a part of this study. The economic data obtained from the systems-level analysis is shown in Table 2.

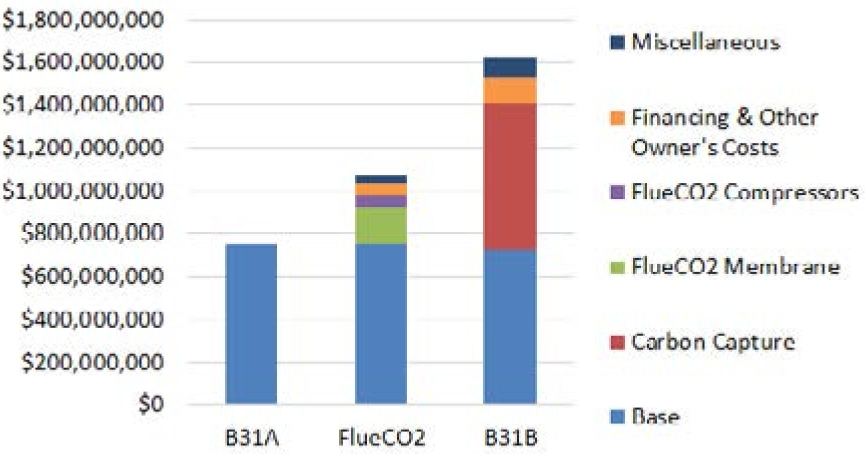

Figure 6: Total as-spent cost (TASC) contributions to the 30-year net present value (NPV) analyses, where B31A = 760 MWe.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Reference (B31B)	Reference (B31A)	Current R&D Value	Target R&D Value
Total As-Spent Cost	$/MW	2,635	1,040	1,713	<1,800
Heat Rate	BTU/kWhr	7,159	6,363	6,775	<7,100
Cost of Carbon Captured	$/tonne CO_2	69.16	N/A	29.69	35
Cost of Carbon Avoided	$/tonne CO_2	90.48	N/A	42.59	45
Breakeven CO_2 Price	$/tonne CO_2	79.60	N/A	38.18	40
Capital Expenditures	$/MWhr	25.03	9.88	15.9	<18
Operating Expenditures	$/MWhr	14.22	5.31	10.3	<10
Cost of Electricity	$/MWhr	39.25	15.19	25.93	28
Levelized Cost of Electricity	$/MWhr	70.89	43.31	56.9	<60

The approach to retrofitting existing NGCCs is presently under consideration. If the target membrane performance metrics are achieved, there is enough space already available in the HRSG to incorporate the membrane system. The membranes could therefore be incorporated to retrofit existing HRSGs for carbon capture. Retrofits of HRSGs of existing NGCC power plants are expected to comprise the largest and most valuable market to target for commercialization.

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

technology advantages

- High performance separation with active transport mechanism.
- Highly efficient NGCC/HRSG integration approach.
- Low capital and operational costs.
- Modular design allows for easy integration with new and existing power plants.

R&D challenges

- Long-term stability of ceramic materials.
- Retaining membrane cost projections throughout the scale-up process.
- Avoiding steam leakage by active transport mechanism.

status

The project was completed on November 11, 2022. The results show that capital costs are generally lower than the equivalent U.S. Department of Energy (DOE) Case (Vol. 1, Case B31B), while operating costs were similar.

available reports/technical papers/presentations

Kelly, J.C., 2022, "Solid Phase Supports for Flue Gas CO_2 Separation with Molten Electrolytes." *Final Report.* DE-SC0017124.

Ceron, M., Lai, L., Amiri, A., Monte, M., Katta, S., Kelly, J., Worsley, M., Merrill, M., Kim, S., Campbell, P. "Surpassing the conventional limitations of CO_2 separation membranes with hydroxide/ceramic dual-phase membranes," Journal of Membrane Science, 2018, Vol. 567, pages 191-198. *https://www.sciencedirect.com/science/article/pii/S0376738818318209*.

Merrill, M. "Passive CO_2 Separation Membranes for Hot Flue Gases," presented at the 2018 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/sites/default/files/2018-12/M-Merrill-Luna-Passive-Separation-Membranes_Aug%202018.pdf*.

Merrill, M. "Solid Phase Supports for Flue Gas CO_2 Separation with Molten Electrolytes," Phase I Final Review Meeting, Pittsburgh, PA, November 2017. *https://www.netl.doe.gov/sites/default/files/2018-12/DE-SC0017142%20Solid%20Membrane%20Materials%20Final%20Review%20NETL%2020171129.pdf*.

Merrill, M. "Passive CO_2 Separation Membranes for Hot Flue Gases," presented at the 2017 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/sites/default/files/2018-12/M-Merrill-Luna-Passive-CO2Separation_Aug%202017.pdf*.

A Process with Decoupled Absorber Kinetics and Solvent Regeneration Through Membrane Dewatering and In-Column Heat Transfer

primary project goal

The University of Kentucky Research Foundation teamed with Media and Process Technology Inc. and Lawrence Livermore National Laboratory (LLNL) (through support project FWP-FEW0242) to develop an intensified, innovative carbon dioxide (CO_2) capture process.

technical goals

- Design and fabricate an advanced structured packing and a dewatering membrane module.
- Use 3D-printed two-channel structured packing material to control absorber temperature profile and increase the CO_2 absorption rate, thereby allowing decreases in absorber size by up to 50%.
- Implementation of a zeolite membrane dewatering unit capable of at least 15% dewatering of carbon-rich solvent to decouple solvent concentrations that are optimum for CO_2 absorption and desorption.
- Utilization of a two-phase flow heat exchanger prior to the stripper, providing a secondary point of vapor generation for CO_2 stripping resulting in significant energy savings.
- Retrofit and test the intensified process on the University of Kentucky's small and large (0.1-megawatt-thermal [MWth]) bench-scale post-combustion CO_2 capture facilities with simulated and coal-derived flue gas.
- Perform a techno-economic analysis (TEA); an environmental, health, and safety (EH&S) risk assessment; and a technology gap analysis.
- Demonstrate the process at 0.1-MWth bench-scale on coal-derived flue gas.
- Collect data to perform the detailed TEA of CO_2 capture process integration to a full-scale, coal-fired power plant.
- Advance this technology to meet U.S. Department of Energy (DOE) capture goals of 95% CO_2 purity at a cost of approximately $30 per tonne of CO_2 captured.

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Post-Combustion Power Generation PSC

key technology:

Membranes

project focus:

Integrated Advanced Solvent Process for Coal Flue Gas

participant:

University of Kentucky

project number:

FE0031604

NETL project manager:

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partners:

Media and Process Technology Inc.; Lawrence Livermore National Laboratory (LLNL); Smith Management Group; Trimeric Corporation

start date:

05.01.2018

percent complete:

100%

technical content

The University of Kentucky's starting point for development of this technology was consideration of the drivers for capital and operating costs of aqueous post-combustion capture process systems. While still utilizing the general process arrangement of CO_2 absorption-desorption by contacting the flue gas with solvent (which might even be a commonly used aqueous solvent such as an amine) in the absorber and water vapor stripping the rich solvent in the regenerator, the University of Kentucky has postulated that significant efficiency and cost savings could be obtained by deploying several reactor improvements in this process and innovations in certain units. The basic process arrangement and units involved are depicted in Figure 1.

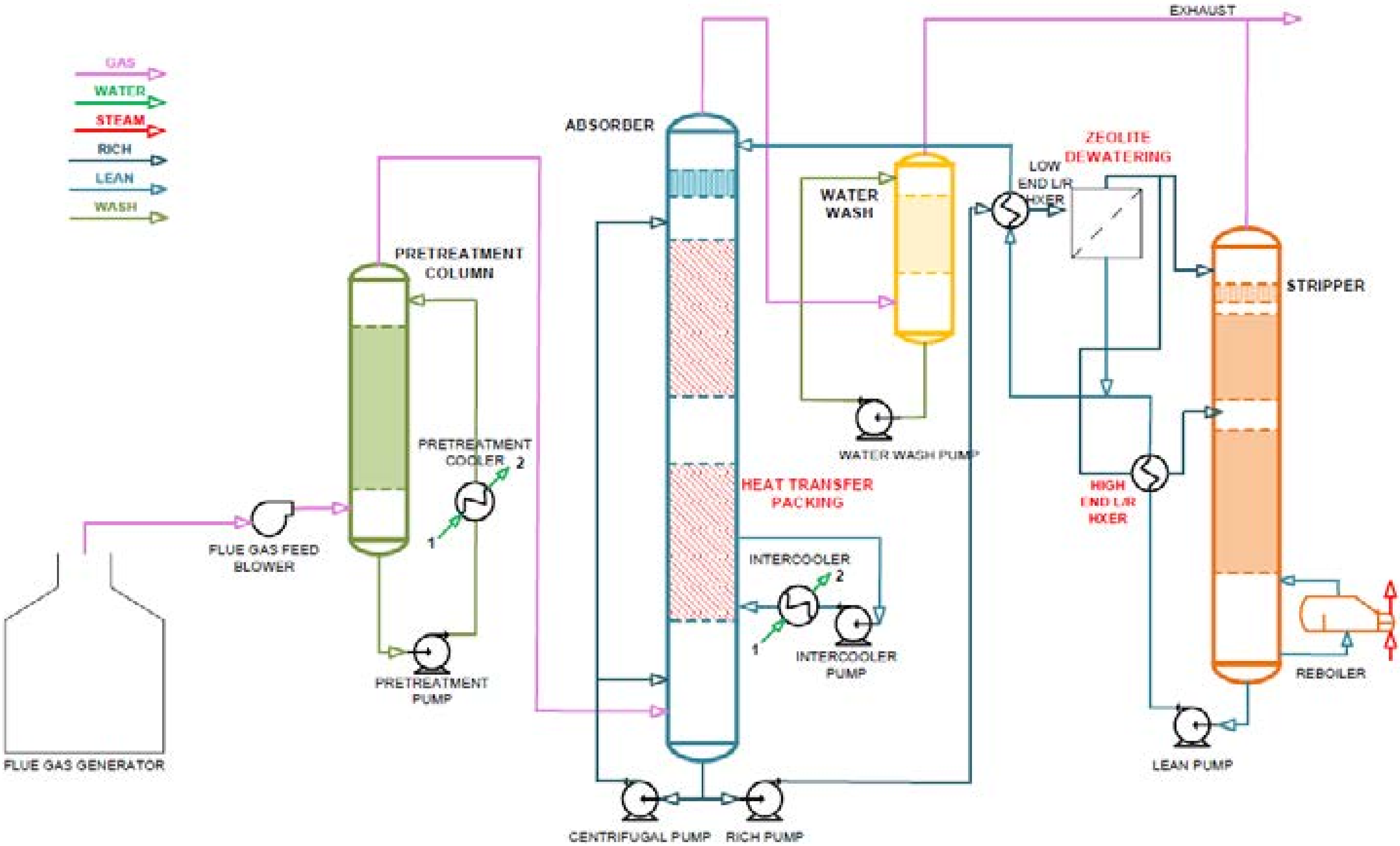


Figure 1: University of Kentucky CO_2 capture process.

Improvement of Temperature Profile in the Absorber—3D-Printed Packing

The absorber for contacting flue gas with solvent to remove the CO_2 from the flue gas was a packed column type containing either random or structured packing to increase mixing/contacting of the gas and liquid solvent. The diameter of the absorption column was determined by the flooding point at the liquid/gas (L/G) ratio; the diameter must be large enough to prevent flooding. The highest flooding potential for a fast-reacting solvent occurred at a characteristic temperature bulge, which typically occurs in the top packing section, 15–30% of packing height from the top. A measured temperature profile for the University of Kentucky's 0.7-megawatt-electric (MWe) small pilot-scale absorber is shown in Figure 2 for contacting flue gas with amine solvent. With L/G of approximately 3.2, a temperature rise of approximately 50°F is observed about 10 feet below the lean amine feed.

Because the driving force for CO_2 absorption is inhibited by high temperature, temperature excursions like this decrease performance, which means that larger internal column diameter and increased column height (translating directly into increased column cost) would be necessary to accomplish a given required amount of CO_2 capture. However, if internal temperatures in the column can be aggressively managed, column size can be substantially reduced.

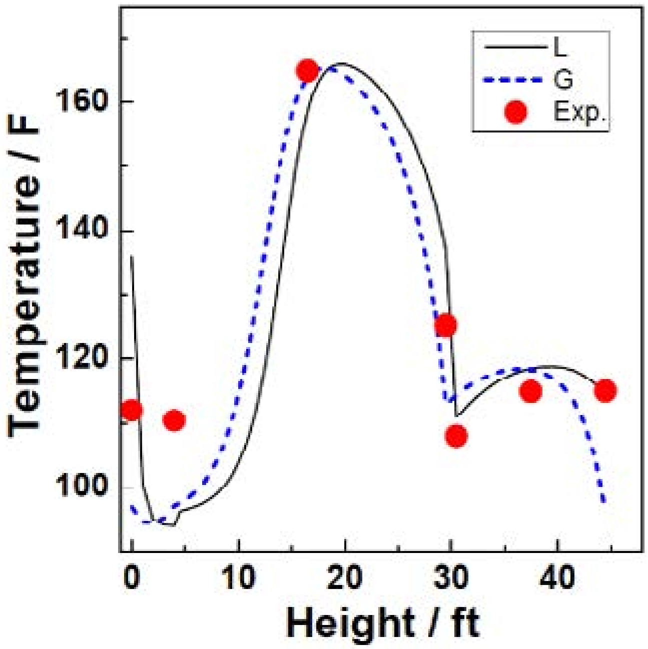


Figure 2: Absorber temperature profile (solid lines indicate model predictions for liquid and gas, experimental data in dots).

The University of Kentucky team's approach for temperature management in the absorber was to deploy innovative, 3D-printed structured packing that incorporates heat transfer channels in the packing. This provided in-process cooling at appropriate locations without the need for separate, multiple external inter-stage cooling sections (reducing column height). Use of 3D printing/additive manufacturing provided the capability to fabricate the packing with the complex dimensional patterns required at reasonable cost.

Polymeric materials, such as acrylonitrile butadiene styrene (ABS), polystyrene, and high-density polyethylene, were investigated for use. They are stable in the presence of loaded amine solvent at operating temperatures and are readily amenable to 3D printing via methods such as fused deposition modeling and stereolithography. Figure 3 shows the design (left) and a fabricated unit printed in thermoset resin via stereolithography (middle). Instances of leakage, structural integrity issues, and fouling have occurred with certain polymeric materials made by certain methods; recently, use of direct metal laser sintering to fabricate packing from 316 stainless steel (Figure 3, right) has delivered promising results.

Figure 3: 3D-printed packing.

Evaluation of packing performance for improving the temperature profile in the absorber column has been ongoing using the bench-scale unit at the University of Kentucky. Figure 4 shows results of putting the heat transfer packing material into the column. The solid line is the baseline without the heat transfer packing, and the dotted and dashed lines are with the heat transfer packing in place. Thermocouples were located at regular intervals from position 1 at the top of the column (lean solvent inlet) to position 7 at the bottom (flue gas inlet). Note that the typical temperature increase at positions 2 and 3 in the baseline has been greatly improved when the heat transfer packing is deployed.

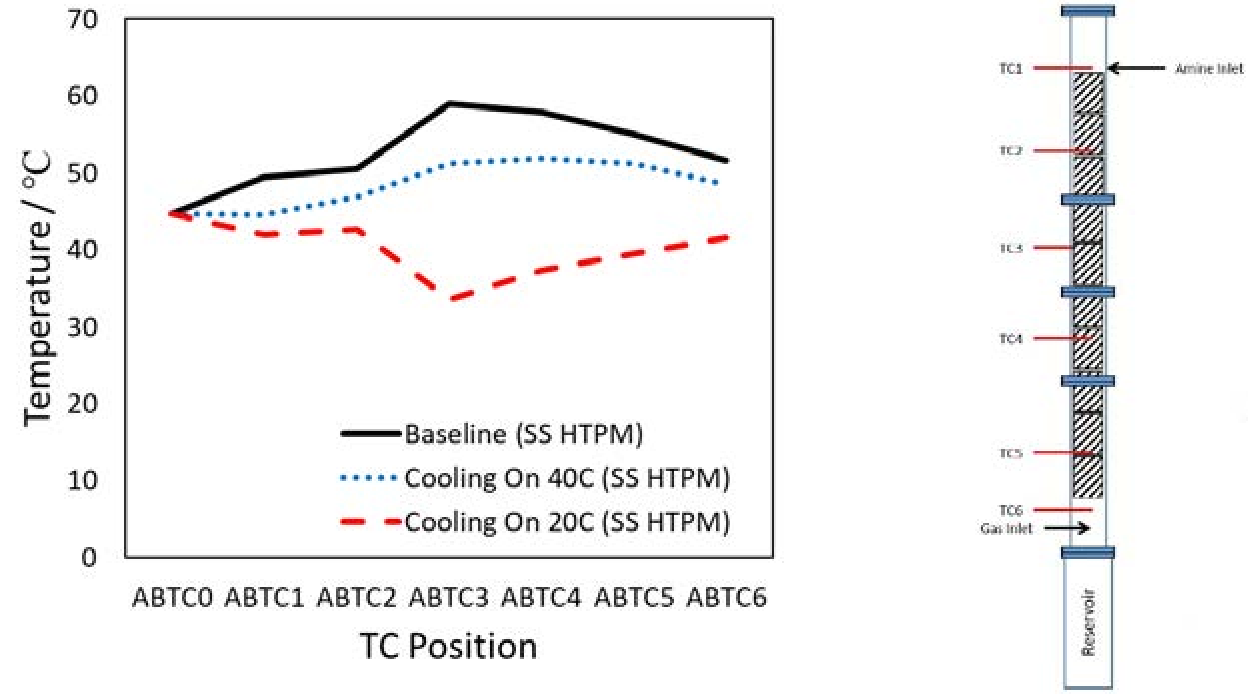


Figure 4: Heat transfer packing effect on absorber column temperature profile.

Dewatering Rich Solvent—Membrane-Based Dewatering Unit

Another element of this innovative process approach was tackling the conflicting requirements for solvent concentrations between the absorber and stripper. In terms of transport phenomena, it is well accepted that the stripper is equilibrium-controlled while the absorber is mass transfer/diffusion-controlled. For the equilibrium-controlled stripper, the carbon loading via CO_2 partial pressure will determine the size of the stripper as well as the energy associated with stripping gases, which typically accounts for approximately 40% of the overall energy required for solvent regeneration. Higher solvent concentrations typically produce higher carbon loadings per kilogram solution at a given temperature compared to a diluted solvent, so more concentrated solvents are preferable for stripper applications. However, higher solvent concentrations always correspond to higher viscosities. For a diffusion-controlled absorber using any advanced fast solvent, the mass transfer coefficient was dominated by the resistance from the chemical reaction of CO_2 and amine in the reaction film as well as diffusion of unreacted amine and carbamate between the reaction interface and bulk solvent. Unfortunately, the diffusivity between the reaction interface and the bulk solvent was governed by a mildly exponential relationship in which higher solvent viscosity increases the diffusion resistance, thereby reducing mass transfer.

To better attain desired solvent concentrations between the absorber and stripper, a dewatering unit using zeolite membranes was developed and evaluated. The unit receives rich solvent from the absorber and passes it through membranes, resulting in concentrated solvent retentate and a permeate stream of mostly water. The target was to accomplish at least 15% dewatering of the solvent coming from the absorber in this membrane-based dewatering unit. The permeate water was returned to the absorber after heat recovery, leaving a carbon- and solvent-concentrated solution to enter the stripper for regeneration. This has the dual desired result of lowering energy consumption in the stripper, while simultaneously maintaining more dilute solvent in the absorber so as not to negatively impact CO_2 absorption rates there. The dewatering step is indicated in Figure 1 as Zeolite Dewatering; note that the recovered water is mixed with the lean solvent from the stripper and the combined stream goes to the top of the absorber.

Design and fabrication of the zeolite membrane dewatering modules is an important aspect of technology development. The membranes themselves consist of a thin zeolite layer on a sublayer of dense alumina, all of which is supported on tubes of highly porous conventional alumina. The very dense alumina layer is needed to confine the molecular seed particles to the surface of the alumina, from which the zeolite layer is grown. Figure 5 shows a scanning electron microscopy (SEM) cross-section of a membrane displaying the juxtaposition of these layers, with a fully formed 3.5-µm layer of zeolite on the outside. The membrane tubes are to be deployed in bundles in modules, per the design depicted in Figure 6 for the intended bench-scale testing. Membrane packing density can reach approximately 322 m^2/m^3 in these modules.

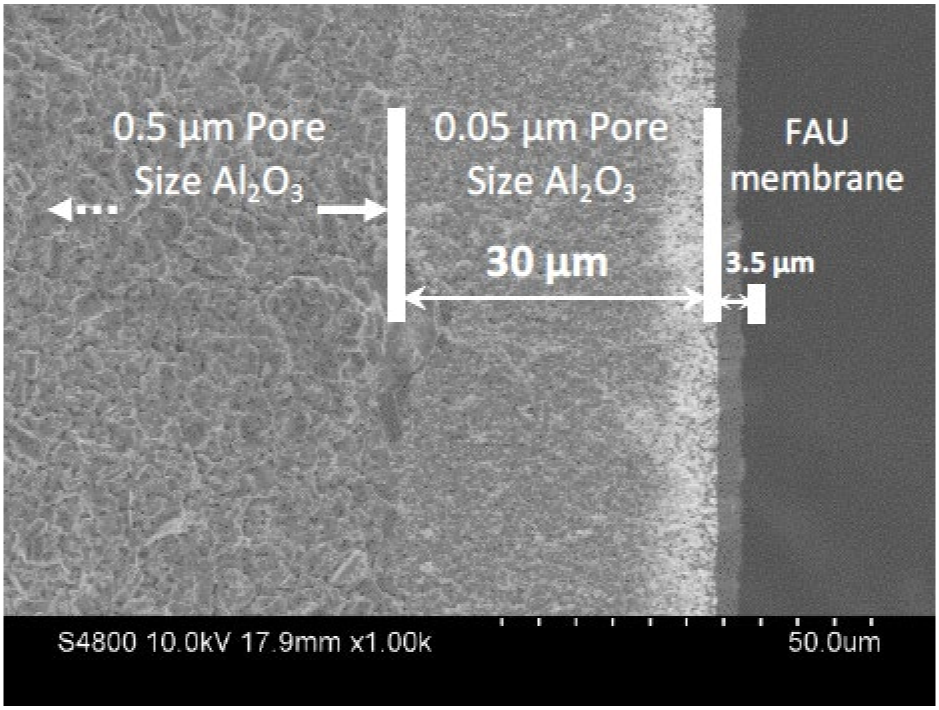
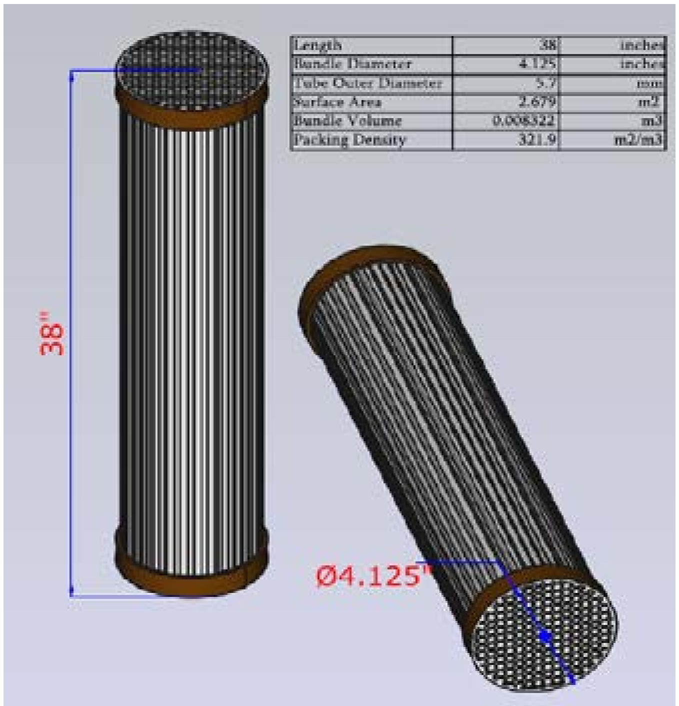


Figure 5: Dewatering membrane structure.



Length	38	inches
Bundle Diameter	4.125	inches
Tube Outer Diameter	5.7	mm
Surface Area	2.679	m2
Bundle Volume	0.008322	m3
Packing Density	321.9	m2/m3

Figure 6: Dewatering membrane module design.

Advanced Stripping and Secondary Vapor Generation Point

The third improvement in this process approach targets reduction of steam consumption by considerations of phase transitions occurring in the stripper and optimization of heat recovery and points of solvent feed to the stripper. In a conventional stripping process, the stripper reboiler uses extracted steam to evaporate water in the solvent, both as a carrier gas to strip CO_2 out of the solvent and as an energy carrier to heat the stripper to a desired temperature profile as required by the solvent and stripper operating pressure. During this process, significant energy is lost. Secondarily, high rich solvent temperature from the rich/lean heat exchanger entering the stripper prevents the gaseous phase from condensing at the top of the stripper, reducing heat recovery within the system as more water vapor is lost with the gaseous exhaust. Consequentially, the typical temperature profile (left) and CO_2 and water fluxes (right) as a function of height in the stripper have been observed on the University of Kentucky's 0.7-MWe post-combustion capture facility and modeled as plotted in Figure 7. This clearly indicates that most of the CO_2 was liberated from the solvent in the bottom 14 feet or so of the 30-foot-long stripper (corresponding with the nearly flat plateau seen in the right-side panel).

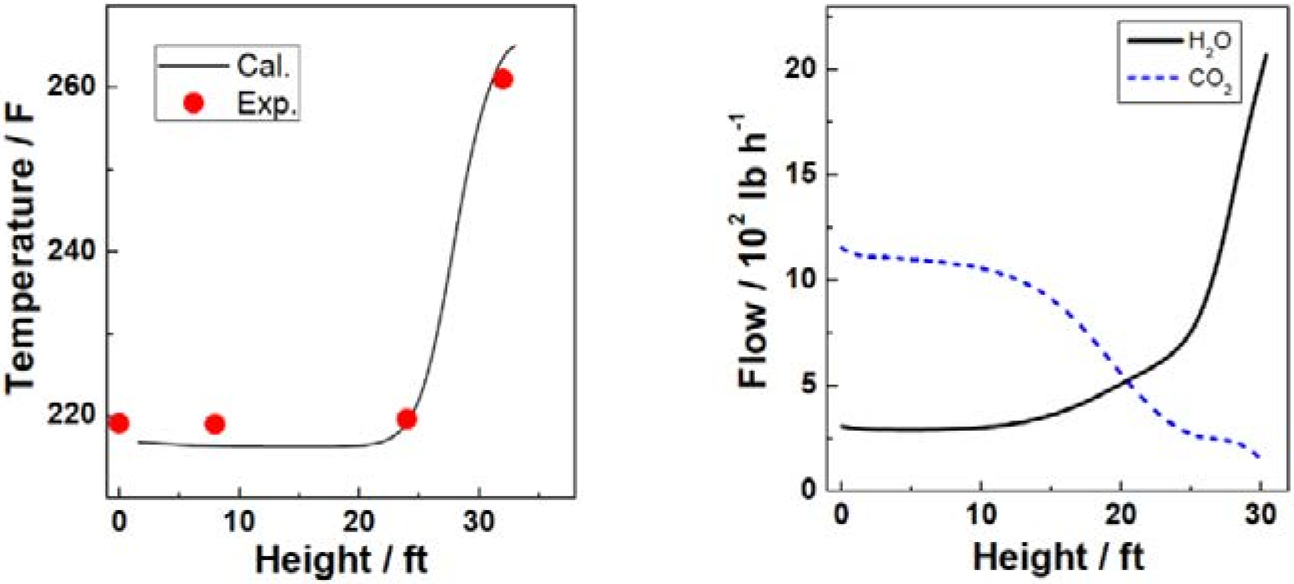


Figure 7: Temperatures and mass fluxes in solvent stripper.

To overcome these inefficient characteristics of the conventional stripper regenerator, the University of Kentucky evaluated a reactor configuration using a secondary entry point for rich solvent feed. The multi-point rich solvent feed was accomplished by dividing the traditional lean/rich (L/R) heat exchanger into two sections—a low-end L/R exchanger and a high-end L/R exchanger (which essentially creates a second source for vapor generation). The basic arrangement of these is diagrammed in Figure 1. The feed to the stripper from the dewatering unit was split into two streams: (1) after the low-end exchanger, about half of the total rich flow with a temperature (solvent and carbon-loading dependent) is fed to the top of stripper packing as a heat sink to condense water vapor and subsequently reduce the water (H_2O)/CO_2 ratio; and (2) the remaining rich flow is heated through the high-end exchanger so that two-phase flow is achieved with 4–6% vapor (solvent and carbon-loading dependent) entering the middle of the stripper packing. This vapor will act as a secondary source of carrier gas for CO_2 stripping. University of Kentucky modeling indicates the H_2O/CO_2 ratio in the stripper exhaust was significantly reduced from 0.8–1.0 as experienced conventionally, to 0.3–0.4, allowing an approximately 26% reduction in steam consumption.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Zeolite Y	
Materials of Fabrication for Support Layer	—	(if applicable)	
Nominal Thickness of Selective Layer	µm	3.5	5
Membrane Geometry	—	cylindrical	
Max Trans-Membrane Pressure	bar	5	7
Hours Tested without Significant Degradation	—	50	>1000
Manufacturing Cost for Membrane Material	$/m^2	>500	250
Membrane Performance			
Temperature	°C	130	115
CO_2 Pressure Normalized Flux	kg/m^2-h	10	15
Permeate Rejection Rate	—	95%	80%
CO_2/N_2 Selectivity	—	Not applicable	
CO_2/SO_2 Selectivity	—		
Type of Measurement	—	Flux and Carbon Loading in the Liquid	
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	Counter-current Flow	
Packing Density	m^2/m^3	400	
Shell-Side Fluid	—	Feed (rich solvent)	
Liquid Flowrate	kg/hr	150	
CO_2 Recovery, Purity, and Pressure	%/%/bar	Not Applicable	
Pressure Drops Shell/Tube Side	bar	<0.5	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	Not Available	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	135°F	13.17	17.25	66.44	2.34	0.80	42	74

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	34.97	30
Cost of Carbon Avoided	\$/tonne CO_2	57.5	—
Capital Expenditures	\$/MWhr	43.1	40
Operating Expenditures	\$/MWhr	28.3	—
Levelized Cost of Electricity	\$/MWhr	94.8	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – The design basis for the TEA was done following guidelines established for DOE/National Energy Technology Laboratory (NETL) Baseline Report, Rev 4, from which Case B12B was compared with the University of Kentucky carbon capture and storage (CCS) technology on a 650-MWe net plant scale.

Scale of Validation of Technology Used in TEA – University of Kentucky CCS technology was modeled in Aspen Plus on a 650-MWe plant with material and heat balance data used as inputs for the TEA.

Qualifying Information or Assumptions – Operating expenditure reported is the sum of the fixed and variable operating costs. The reported levelized cost of electricity excludes (transportation, storage, and monitoring).

technology advantages

- Reduction in absorber column size, reducing both capital and operating costs.
- Reduction in stripper column size and steam demand for solvent regeneration, reducing both capital and operating costs.
- Applicability to a variety of solvents in absorption-based capture process implementation.

R&D challenges

- Innovative absorber packing fabrication cost, structural/performance integrity, fouling.
- Dewatering membrane unit zeolite membrane fabrication, module integrity.

- Increased controls and control schemes, mainly because of more complicated process flows and heat exchange around the dewatering unit.
- Potential liquid channel flow from in situ heat transfer packing—effective liquid distribution is needed with in situ heat transfer packing to enhance capture in absorber.

status

The project was completed on Februrary 28, 2022. Absorber testing with deployment of 3D-printed packing material resulted in 10°C temperature reductions, confirming the design concept of structured packing enabling column size reductions. The zeolite membrane-based dewatering has been validated on amine solvent at 10 kg/m^2/hr, and modules with required membrane packing density have been developed. Secondary vapor generation from split rich stream to stripper effectively lowered water vaporization and reduced solvent regeneration energy by at least 15%. Dewatering with zeolite membrane is not cost-effective due to low flux and chemical instability in large quantity fabrication. The University of Kentucky process improvements provide capital expenditure (CAPEX) reduction, which contribute to a lower cost of CO_2 capture, as well as lowering the parasitic energy demand, resulting in 23% reduction in CO_2 capture cost compared to the reference case B12B. Control of absorber temperature profile with 3D heat transfer packing demonstrates potential for enhanced absorption and column size reduction by increasing liquid turbulence, enhancing gas-solid contact, and reducing diffusion limitation to enhance capture efficiency. Maximizing heat recovery with split streams in stripper reduces water evaporation in solvent regeneration. An energy savings of approximately 15% is achieved by cooling the stripper exhaust temperature by approximately 12°C.

available reports/technical papers/presentations

Kunlei Liu, "*A Process with Decoupled Absorber Kinetics and Solvent Regeneration through Membrane Dewatering and In-Column Heat Transfer*," University of Kentucky, Final Technical Report, April 2022. *https://www.osti.gov/servlets/purl/1864587*.

Kunlei Liu, "*A Process with Decoupled Absorber Kinetics and Solvent Regeneration through Membrane Dewatering and In-Column Heat Transfer*," University of Kentucky, Final Project Briefing, Pittsburgh, PA, February 2022. *http://www.netl.doe.gov/projects/plp-download.aspx?id=12846&filename=A+Process+with+Decoupled+Absorber+Kinetics+and+Solvent+Regeneration+through+Membrane+Dewatering+and+In-Column+Heat+Transfer.pdf*.

Kunlei Liu, "*A Process with Decoupled Absorber Kinetics and Solvent Regeneration through Membrane Dewatering and In-Column Heat Transfer*," University of Kentucky, NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Liu.pdf*.

Kunlei Liu, "*A Process with Decoupled Absorber Kinetics and Solvent Regeneration through Membrane Dewatering and In-Column Heat Transfer*," University of Kentucky, NETL Project Review Meeting - Carbon Capture, Pittsburgh, PA, October 2020. *https://netl.doe.gov/sites/default/files/netl-file/20VPRCC_Liu.pdf*.

James Landon, "*A Process with Decoupled Absorber Kinetics and Solvent Regeneration through Membrane Dewatering and In-Column Heat Transfer*," University of Kentucky, NETL CCUS Integrated Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/J-Landon-UoK-Membrane-Dewatering.pdf*.

James Landon, "*A Process with Decoupled Absorber Kinetics and Solvent Regeneration through Membrane Dewatering and In-Column Heat Transfer*," University of Kentucky, NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/J-Landon-UK-Decoupling-Absorber-Kinetics-and-Solvent-Regeneration.pdf*.

James Landon, "*A Process with Decoupled Absorber Kinetics and Solvent Regeneration through Membrane Dewatering and In-Column Heat Transfer*," Project kickoff meeting presentation, May 18, 2018.

http://www.netl.doe.gov/projects/plp-download.aspx?id=10495&filename=A+Process+with+Decoupled+Absorber+Kinetics+and+Solvent+Regeneration+through+Membrane+Dewatering+and+In-Column+Heat+Transfer.pdf.

Advancing Post-Combustion CO_2 Capture Through Increased Mass Transfer and Lower Degradation

primary project goal

This University of Kentucky Center for Applied Energy Research's (UK CAER) project developed three technologies: a 3-D printed dynamic polarity packing material, solvent additives that enhance mass transfer and reduce energy consumption, and an electrochemical treatment cell to reduce nitrosamine content. Combined, these technologies enable post-combustion carbon dioxide (CO_2) capture to meet the U.S. Department of Energy (DOE) performance and cost targets of 90% CO_2 capture and 95% purity at a cost of less than $30/tonne CO_2 captured.

technical goals

- Develop a library of structure/property relationships that can be used as a guideline for choosing effective additives for a given solvent or blend.
- Design and fabricate a 3-D printed dynamic polarity packing material based on a range of solvent property parameters for a given liquid-gas ratio.
- Evaluate selected solvents in UK CAER's bench-scale CO_2 capture unit with conventional structured packing to serve as a baseline.
- Replace the conventional packing in the bench-scale unit with 3D-printed dynamic packing and test the selected solvents under the same operating conditions to determine mass transfer enhancement.
- Test selected solvent additives in the bench-scale unit to evaluate mass transfer enhancement and reduced energy demand.
- Evaluate the electrochemical cell using wash water collected at UK CAER's 0.7-MWe small pilot CO_2 capture system to measure the ability to maintain nitrosamine levels below 0.5 parts per million (ppm).
- Conduct parametric testing of the combined dynamic packing solvent/additive system and identify optimum operating conditions to achieve an increase in mass transfer.
- Perform a long-term testing campaign under optimized operating conditions to evaluate the stability of dynamic packing and electrochemical cell and examine aerosol formation, corrosion, and solvent degradation.
- Perform a high-level techno-economic analysis (TEA) based on the collected bench-scale test data.

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Post-Combustion Power Generation PSC

key technology:

Novel Concepts

project focus:

Solvent Enabling Techniques for Coal-Based Flue Gas

participant:

University of Kentucky

project number:

FE0031661

predecessor projects:

N/A

NETL project manager:

Krista Hill
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partners:

Lawrence Livermore National Laboratory

start date:

10.01.2018

percent complete:

100%

technical content

This UK CAER and Lawrence Livermore National Laboratory (LLNL) project involves the development and fabrication of customized 3D-printed dynamic packing using advanced manufacturing techniques to increase CO_2 mass transfer in the absorber column. UK CAER is designing, fabricating, and testing an electrochemical cell with stationary carbon electrodes to adsorb and decompose nitrosamines from water wash solutions collected from UK CAER's 0.7 MWe-scale carbon capture system installed at Kentucky Utilities' E.W. Brown Generating Station. After both systems have been constructed, they will be tested on UK CAER's bench-scale (0.1 megawatt-thermal [MWth]) CO_2 capture unit. The specific activities in this project include: (1) quantifying the CO_2 mass transfer improvement from the customized 3D-printed dynamic polarity packing in the absorber by utilizing UK CAER's existing less-than-0.1-MWth, 3-inch ID CO_2 capture column; (2) quantifying the energy consumption savings associated with the mass transfer enhancement from the dynamic polarity packing; (3) conducting detailed studies to understand how the solvents' physical properties can be utilized to form controllable gas bubbles to boost the mass transfer area and impact wettability, degradation, and aerosol formation; (4) quantifying the benefits of UK CAER's electrochemical cell in regards to decomposing nitrosamines; and (5) collecting the necessary information/data to conduct a high-level TEA of the proposed technologies.

A systematic approach was taken to develop understanding of the structure/function relationships for additives in a rational series of amine solvents in terms of bubble formation, the stability of gas-liquid interface film, and solvent polarity. First, physical properties such as surface tension, viscosity, elasticity, and contact angle were measured in aqueous amine solvents with different pKa, polarity, and functional groups (i.e., –OH, -N, -R). Commercially available amines, including primary, secondary, and tertiary amines, as well as amines with different functional groups, were prepared and examined at various concentrations (e.g., 3–5 M) and at lean (~0.2 carbon/nitrogen ratio) and rich CO_2 loading (~0.4 carbon/nitrogen ratio). Water-soluble chemical additives were then selected with different functionality and chemical structures (surfactants, inorganic metal corrosion inhibitors, organic oxidation inhibitors, and metal-ligand CO_2 hydrolysis catalyst) and added to the amine solvents. The physical properties of the amine solvents with the additives were then measured at lean and rich CO_2 loading to assess how the additives changed the solvent physical properties. The main physical property modification came from addition of a surfactant, which resulted in a decrease in the surface tension of the solvent and a reduction in the contact angle relative to a hydrophobic surface, such as a polymeric material. The decrease in contact angle implied better wetting (coating) on the packing by the solvent, leading to better gas-liquid contact. This result has implications when considering the use of plastic 3D-printed packing material as a substitute for steel structure packing in the absorber column.

One important factor when exploring the use of polymer packing is the stability of the polymer when exposed to the caustic CO_2-loaded amine solution at elevated temperatures. The stability of the polymeric packing material after exposure to CO_2-loaded amine solvent at absorber temperature (60°C) was examined through an estimated 5,000 hours. Changes to mass, thickness, and contact angle versus water and the amine solvent were monitored every 1,000 hours. The results are shown in Figure 1. The three polymer materials examined showed minimal changes in mass, thickness, and contact angles versus both water and the CO_2-loaded amine solvent. Based on the amine stability studies, acrylonitrile butadiene styrene (ABS), nylon, and high-density (impact) polystyrene (HDPS) were shown to be stable upon exposure to CO_2-loaded amine solvent at anticipated absorber temperatures.

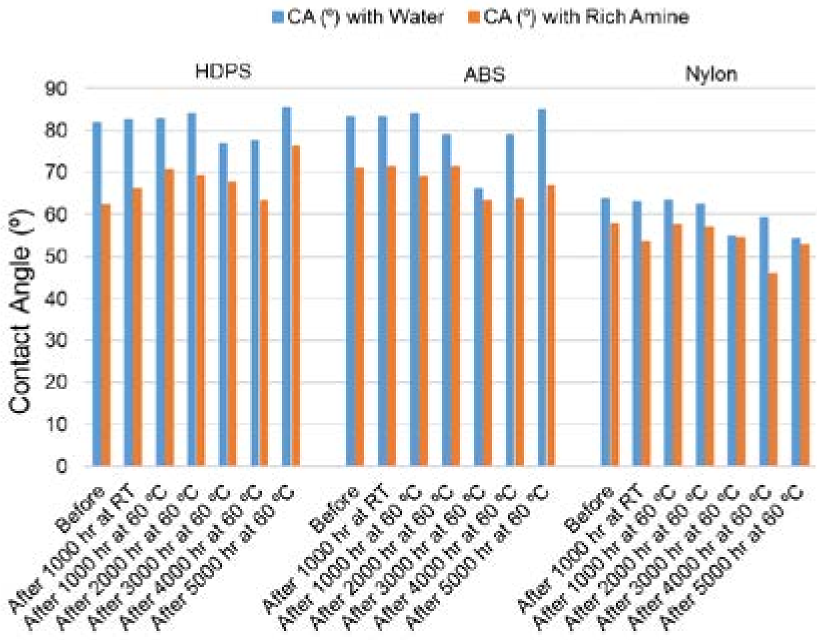

Figure 1: Contact angle (°) changes of polymeric materials after long-term exposure to CO_2-loaded amine solvent.

To compare the wettability of the polymer packing, polished coupons of the HDPS, ABS, nylon, and stainless steel (SS) were collected, and contact angles were measured with water and an amine solution (Figure 2). The contact angle (wettability) versus water of HDPS and ABS are similar, while nylon and SS are lower and closer to each other. All the packing materials showed a lower contact angle with the amine solvent compared to water. The contact angle of nylon was the closest to SS, with both ABS and HDPS having two to three times larger contact angles.

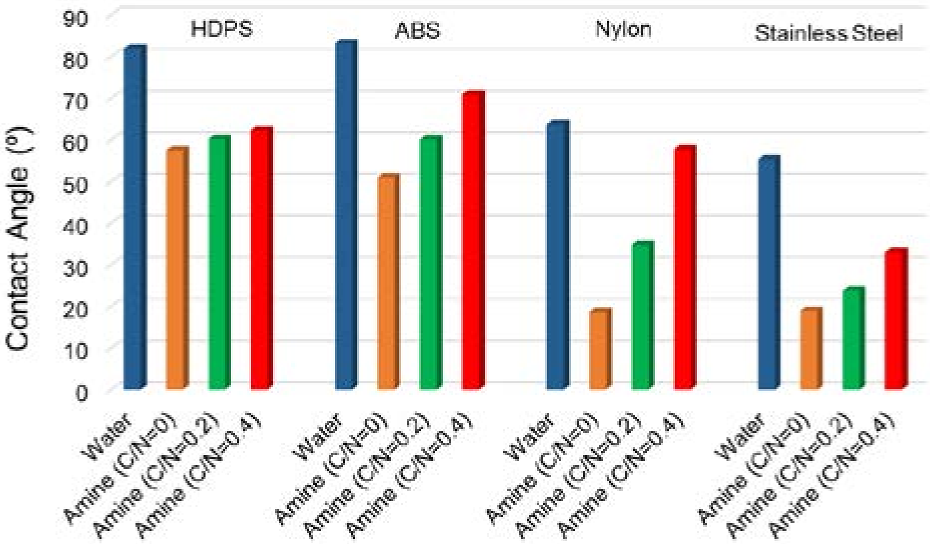

Figure 2: Contact angle of water and aqueous amines (at different CO_2 loadings) on different packing material surfaces.

Four different packings, including SS, ABS, nylon, and three dynamic packings (DPs), were prepared for testing in a small bench CO_2 capture unit (Figure 3). All of the 3D-printing packings are in 250Y shape to compare with regular steel packing. The DPs have an ABS external shell with nylon as the core material and co-printed with additional section of HDPS as the more hydrophobic material. DP-1 has a nylon base with a small amount of HDPS embedded in the packing interior with a staggered pattern; DP-2 has stacked alternating interior pattern with 50% HDPS and 50% nylon material; DP-3 also has a nylon base with a small amount of HDPS embedded in arrow patterns.

Figure 3: 250Y-type packing comparison with different dynamic design patterns (left to right) SS, DP-1, DP-2, DP-3.

The best performing polymer packing from a detailed parametric testing campaign was tested for long-term performance and stability. The long-term packing verification test included 500 hours of stable CO_2 capture under optimal conditions. The polymer packing shows a consistent improvement in mass transfer, leading to an average relative 15.9% improvement in CO_2 absorption and 19.7% decrease in energy consumption compared to the baseline Mellpak 250Y SS packing (Figure 4).

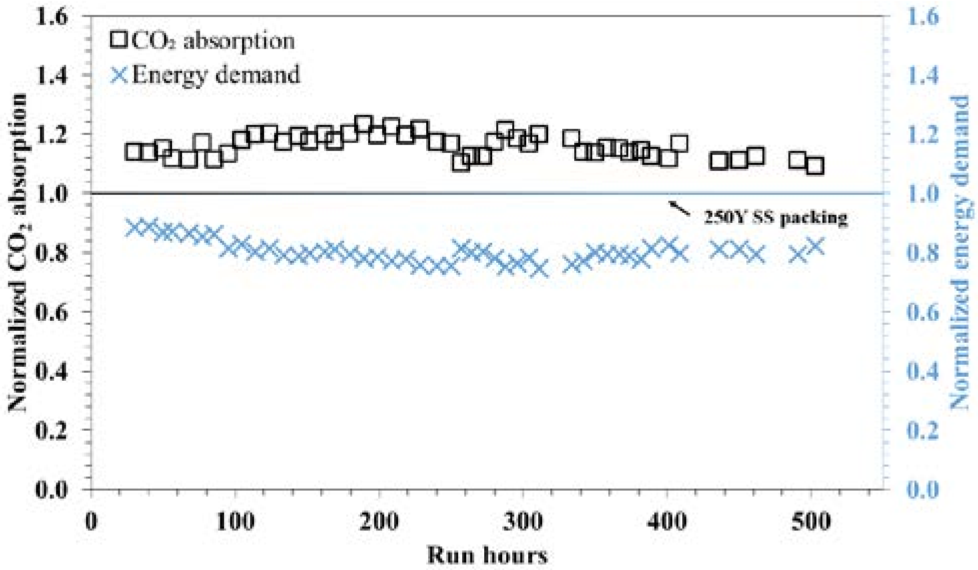

Figure 4: CO_2 absorption efficiency and energy demand during the 500-hour long-term testing.

To address the potential environmental concerns associated with nitrosamine formation in CO_2 capture systems, an electrochemical treatment cell is being developed to destruct nitrosamines from the absorber water wash. The electrochemical cell is being evaluated using wash water solutions collected at UK CAER's 0.7-MWe small pilot CO_2 capture system. The liquid under investigation represents the actual composition of wash water from an operating pilot CO_2 capture system that treats coal flue gas. A preliminary design of a flow-through electrochemical cell with carbon xerogel (CX) electrodes was generated (Figure 5, top) and fabrication has been completed. Recent testing demonstrated the ability to continuously reduce at least 85% of the nitrosamines present in the water wash with an efficiency above 15%, well above the original target values.

Using the knowledge learned during flow-through electrochemical cell (e-cell) experiments with the CX electrodes, where variable solution flow rates, currents, and nitrosamine concentrations were evaluated, nitrosamine removal and efficiency was optimized. A simulated water wash solution was spiked with concentrated nitrosamines to create nitrosamine concentrations of approximately 50 ppm N-Nitrosopyrrolidine (NPY), N-Nitrosodiethylamine (NDEA), and N-Nitrosomorpholine (NMOR), for a total of around 150 ppm. The spiked solution flowed through the e-cell for 12 hours with a 25-mA charge. The removal behavior of NPY, NDEA, and NMOR during the 12-hour electrolysis period are shown in Figure 5 (bottom). The concentrations of all three nitrosamines reached the limit of detection (LOD) within 12 hours and were removed with a 99% removal efficiency. The total charge efficiency during the 12-hour electrolysis period was calculated with an average efficiency of 33% during this time.

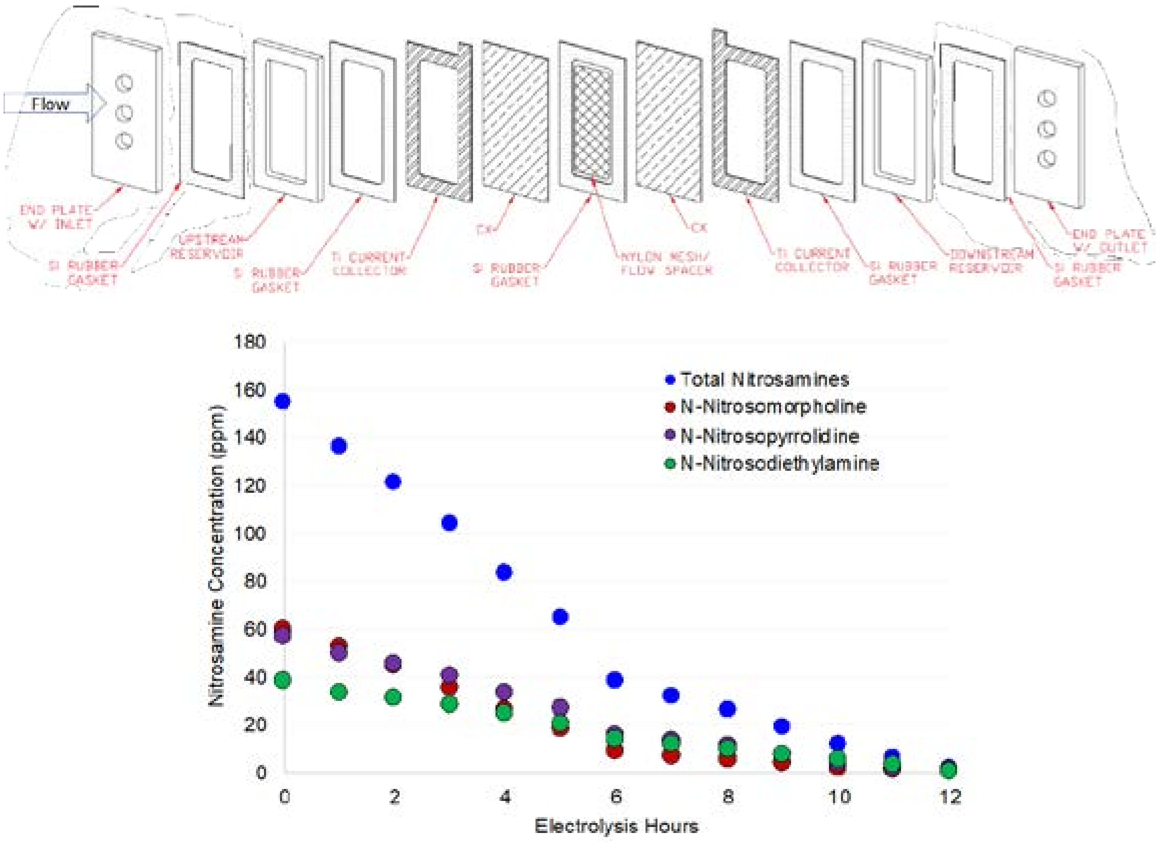

Figure 5: Flow-through e-cell schematic with CX electrodes (top) and nitrosamine destruction to below detection limit within 12 hours of electrolysis (bottom).

The TEA completed as part of this study compared various CO_2 capture solvent configurations. The most promising results are shown in Table 1.

TABLE 1: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	\$34.49	\$30
Cost of Carbon Avoided	\$/tonne CO_2	\$51.88	\$45
Capital Expenditures	\$/MWhr	\$42.80	\$40
Operating Expenditures	\$/MWhr	\$51.50	\$45
Cost of Electricity	\$/MWhr	\$94.30	\$80

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

technology advantages

- Increased CO_2 mass transfer and lower solvent regeneration energy.
- Enhanced CO_2 absorption rate reduces absorber size, lowering capital and operating costs.
- Use of solvent additives increases solvent wetting on packing.
- Electrochemical treatment process addresses environmental concerns at high selectivity with very low operational cost.
- Technology can extend over a broad spectrum of CO_2 capture systems, including many solvent-based systems.

R&D challenges

- Compatibility of packing material with actual flue gas and solvent impurity.
- Foaming with additives in long-term operation.
- Controlling the amine emissions rate.

status

The project concluded on September 30, 2022. Researchers succeeded in testing the polymer-packed absorber bed for 500 hours, with stable CO_2 capture operation under optimal conditions. The polymer packing setup shows a consistent improvement in mass transfer leading to an average CO_2 absorption rate of 60.1% and an energy demand of 233.8 kJ/mol CO_2. Overall, this translated to a relative 17.4% improvement in CO_2 absorption and 18.6% decrease in energy consumption compared the baseline 250Y stainless steel packing. With UK CAER's packed absorber, compared to the Shell CANSOLV® system in the DOE Vol 1. B12B case, the cost of electricity and cost of capture for a supercritical Rankine cycle plant both decrease, by 10.4% and 24.4%, respectively. The overall cost of capture was found to be approximately \$34.49/tonne of CO_2.

available reports/technical papers/presentations

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High-Efficiency, Integrated Reactors for Sorbents, Solvents, and Membranes Using Additive Manufacturing

primary project goal

Lawrence Livermore National Laboratory (LLNL), as part of the Discovery of Carbon Capture Substances and Systems (DOCCSS) Initiative, has designed and fabricated high-efficiency reactors supporting advanced sorbents, solvents, or membranes for transformational carbon capture. An integrated design process coupling computational design optimization with additive manufacturing (AM) was used to create novel reactor geometries customized for new carbon dioxide (CO_2) capture materials.

technical goals

- Assess new reactor geometries and identify design principles.
- Assess AM for each reactor type.
- Identify the most promising reactor class (sorbent, solvent, or membrane) for the next phase of development.
- Design and test the first-generation bench-scale reactor.
- Evaluate a small-scale integrated prototype of the first-generation reactor design with simulated flue gas.
- Design and test a second-generation bench-scale reactor.
- Design an integrated prototype of the second-generation reactor concept.

technical content

LLNL designed high-efficiency reactors to support advanced sorbents, solvents, or membranes for CO_2 capture. An integrated design process utilizing computational design optimization combined with AM was utilized to create new reactor geometries designed for advanced carbon capture materials resulting in efficient, low-cost carbon capture. The reactors can offer a range of improvements for CO_2 capture, including absorbers and fixed beds with integrated heat exchange, enabled by the unique structure of the triply periodic minimal surfaces (TPMS). They can also enable membrane-based separators with minimal pressure drop and strippers capable of extreme high pressure. The conceptual basis of these novel reactors are hierarchical networks and TPMS, shown in Figure 1. These new geometries were fabricated using AM techniques at LLNL. An example of a TPMS structure fabricated using metal AM at LLNL is shown in Figure 2. The TPMS geometries can be made into structured packings for columns. These TPMS-printed packings provide surface area for solvent and flue gas to interact, and can allow for integrated heat exchange. LLNL has demonstrated printed packings in

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post Combustion Power Generation PSC

key technology:
Novel Concepts

project focus:
Additively Manufactured High-Efficiency Reactors for Sorbents, Solvents, and Membranes

participant:
Lawrence Livermore National Laboratory

project number:
FWP-FEW0225

predecessor projects:
N/A

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partners:
N/A

start date:
08.01.2017

percent complete:
100%

multiple different plastics, including acrylonitrile butadiene styrene (ABS), high-density polyethylene, polycarbonate, nylon, and acrylic-based photopolymers. An ABS-based packing showing the same geometry as a conventional stainless steel packing is shown in Figure 3.

LLNL evaluated novel geometries and identified the design concepts and principles for these new reactor types. The AM techniques were assessed. The most promising reactor class, either sorbent, solvent, or membrane, was identified to move forward with in the development process. A first-generation reactor was designed, fabricated with the AM techniques, and tested on simulated flue gas at bench scale. Based on the test results, the team designed a more advanced second-generation reactor.

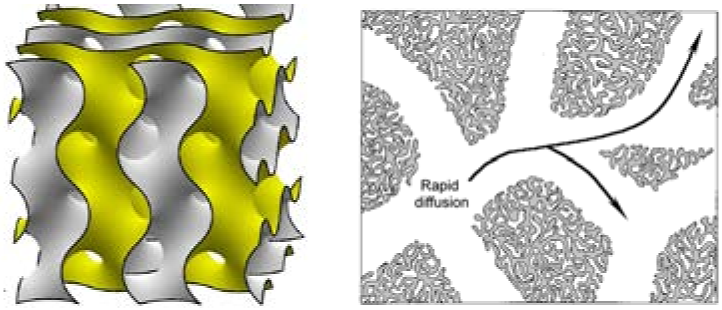


Figure 1: Design features focused on at LLNL: triply periodic minimal surface (left), hierarchical flow channels (right).

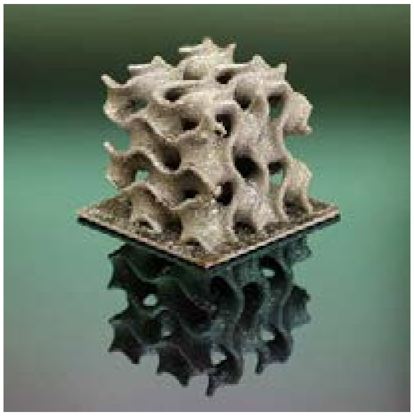


Figure 2: TPMS structure printed using metal AM at LLNL.

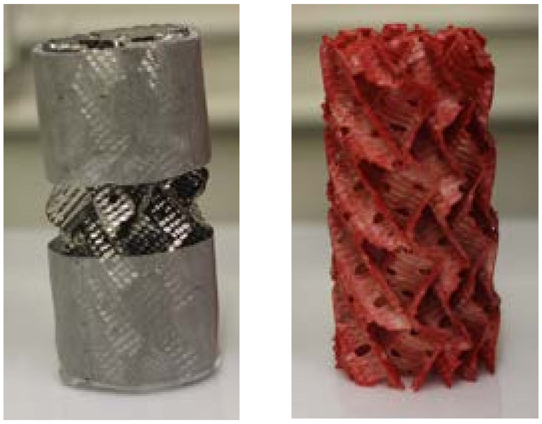


Figure 3: Conventional stainless steel packing (left) and ABS-printed packing (right).

The first-generation reactors were based on a membrane system where flue gas flowed through one side of a TPMS geometry and a solvent flowed through the other, separated by a gas-permeable membrane. Since TPMS reactors were known to have high heat transfer performance, similar advantages were expected in mass transfer reactors. This method of reactor required the development of a CO_2 permeable membrane that could be printed into the TPMS geometry, which was successful and is shown in Figure 4. In this manner, a TPMS mass transport reactor would behave similarly to a heat transfer reactor.

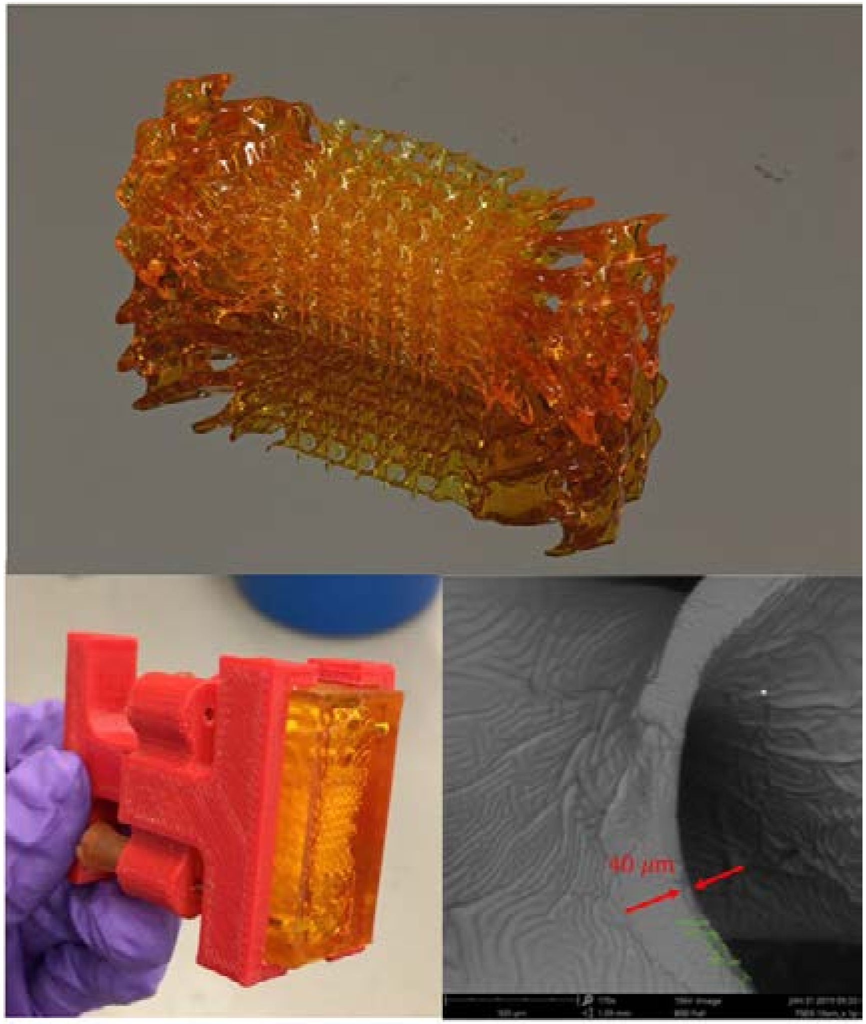


Figure 4: Hierarchically structured TPMS membrane reactor (top). TPMS membrane reactor in holder with fluidic connections (left). Scanning electron microscopy (SEM) image of TPMS membrane reactor (right).

Significant development was necessary to enable the AM of silicone with micron-scale shape fidelity. A hierarchically structured Schwarz-D membrane reactor was successfully fabricated that could survive fluid and gas flowing through the interpenetrating domains without leaks. The hierarchical structure aided in manifolding fluidic ports to the reactor for counter-current flow. The performance was promising for the geometries used, but the calculated volumetric mass transfer coefficients were lower than typical values for conventional monoethanolamine (MEA) solvent towers. Since the performance matched well with theoretical analysis of the membrane reactors, it was identified that the limiting factor of the reactor performance was due to the thickness silicone walls of the prototypes, where wall thicknesses less than 50 µm were necessary to achieve good mass transfer coefficients in a large-scale reactor design.

The second generation of reactor designs centered on using the TPMS geometries for structured packings in absorption towers. The current state of the art in absorption columns for CO_2 capture typically uses commercially available structured packings (e.g., Mellapak 250Y). The most common of these structures uses corrugated sheets of metal that are stacked in an alternating manner within an absorption tower. Liquid solvents and rich flue gas are flowed counter-currently in these towers, using the packings as a means of providing surface area for the two streams to react with each other. AM-based TPMS geometries have the advantage of improving the flow distributions, integrating multi-functional material features, and enhancing fluid mixing. A qualitative improvement of liquid distribution is shown in Figure 5.

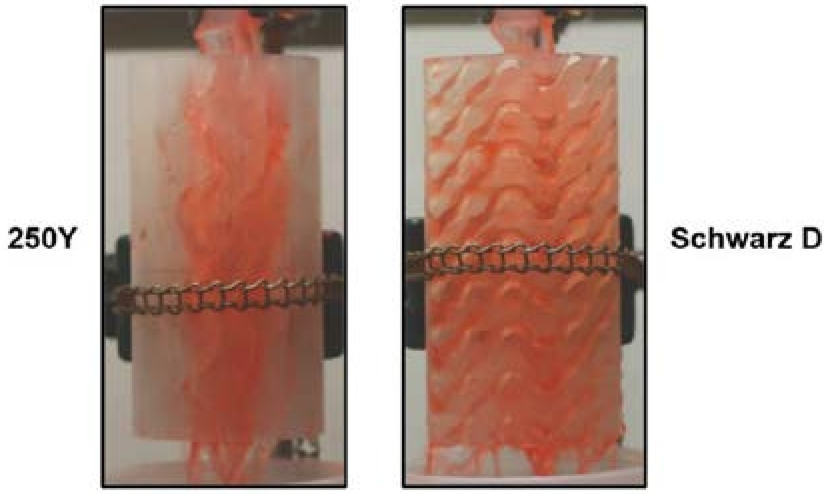


Figure 5: Fluid flow through conventional packing geometry (left) and TPMS packing geometry (right).

Alongside experimental measurements, computational mass transfer simulations were also explored. The model was incorporated into the open source computational fluid dynamics (CFD) package “OpenFOAM.” The model couples the Volume of Fluid (VOF) method, which simulates the multi-phase gas and liquid flows, with an interfacial reactive mass transfer modeling procedure to incorporate reactive mass transport mechanism into the simulations. Using the simulations, a range of TPMS structures were explored for their potential use as structured packings. These results shown in Figure 6 indicate that the Schwarz-D geometry is predicted to have the best mass transport, followed by the $J_S I_{xxx} I_{zx} I P_2 I Z$ structure. Quantitative metrices of fluid distribution and interfacial area based on experimental and computational modeling are shown in Figure 7.

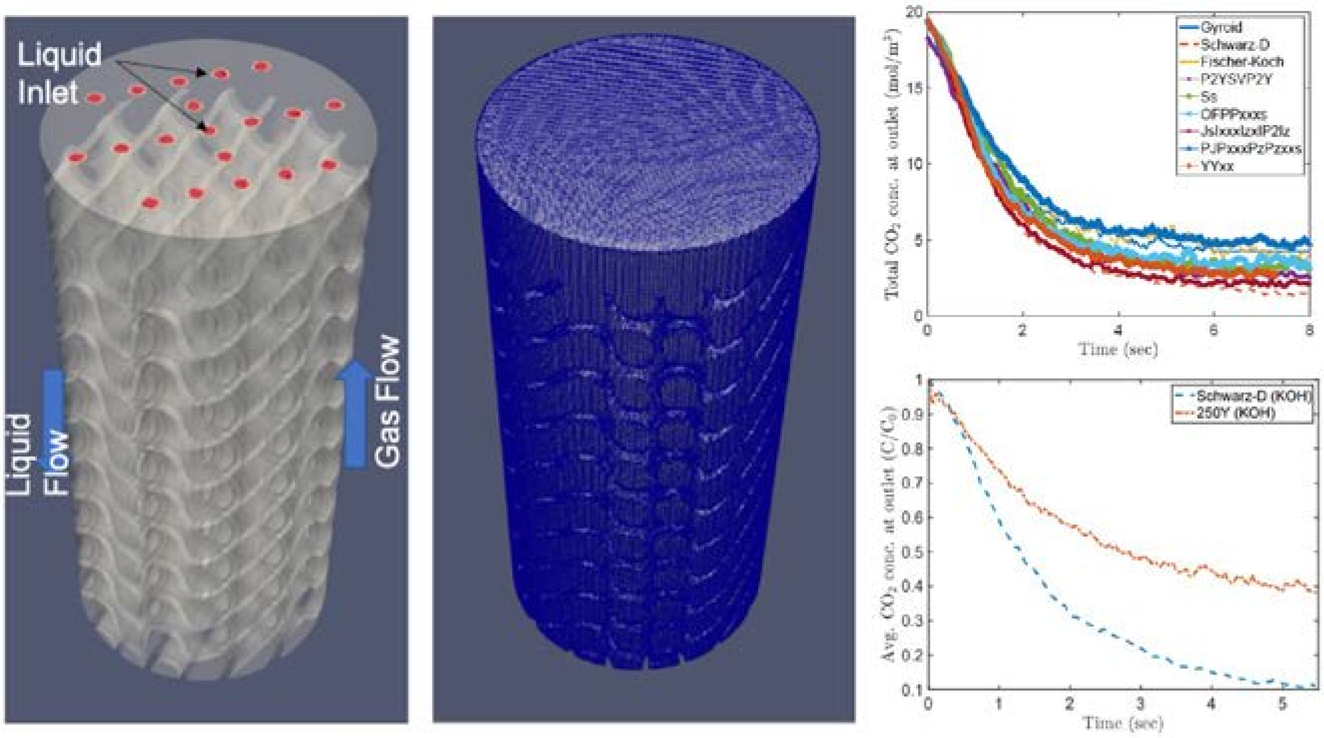


Figure 6: Computational modeling of TPMS-structured packings. Across a range of different TPMS geometries, the Schwarz-D structure resulted in the best capture performance.

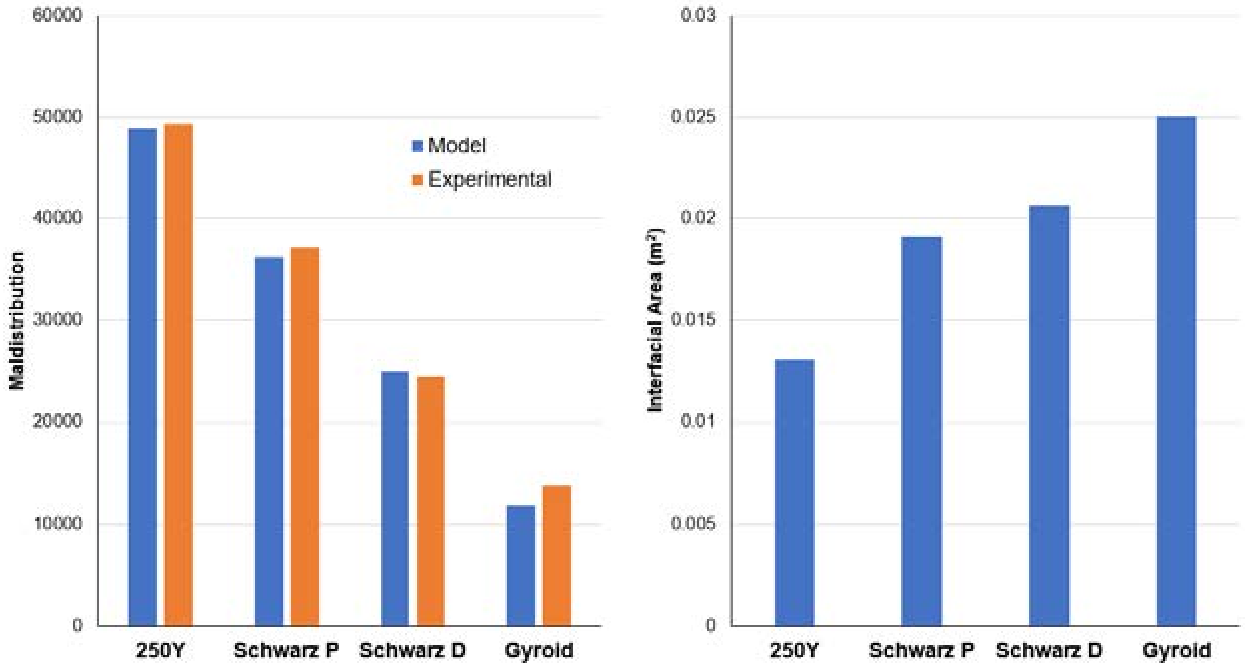


Figure 7: Liquid maldistribution and interfacial area of different geometries. TPMS structures all exhibit better liquid flow properties compared to conventional 250Y geometries.

To visually demonstrate the improved performance of the printed TPMS-structured packings compared to printed 250Y packing sections, a CO_2 capture experiment incorporating a pH-sensitive dye was performed. The partially transparent nature of the printed column allowed for facile visualization of the liquid flow and thus the time to color change, clearly indicating the difference in packing performance. The experiment utilized aqueous potassium carbonate (K_2CO_3) as a solvent with a pH-indicating dye. Figure 8 highlights the color change visualization and shows the pH change profiles of the two experiments, indicative of the effective solvent loading over time and thus the CO_2 removal rate. The more rapid pH change with Schwarz-D packings was attributed to improved mass transfer and effective interfacial area with identical nominal specific surface areas.

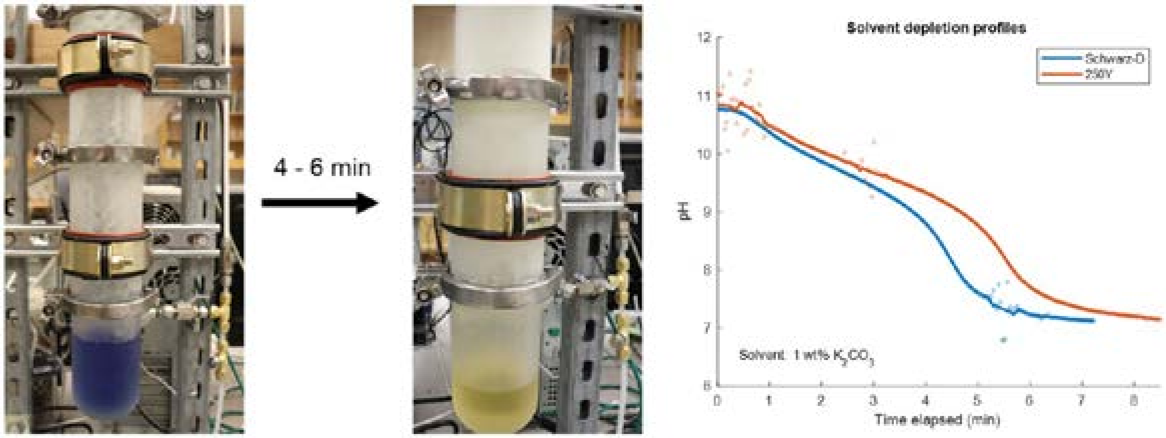
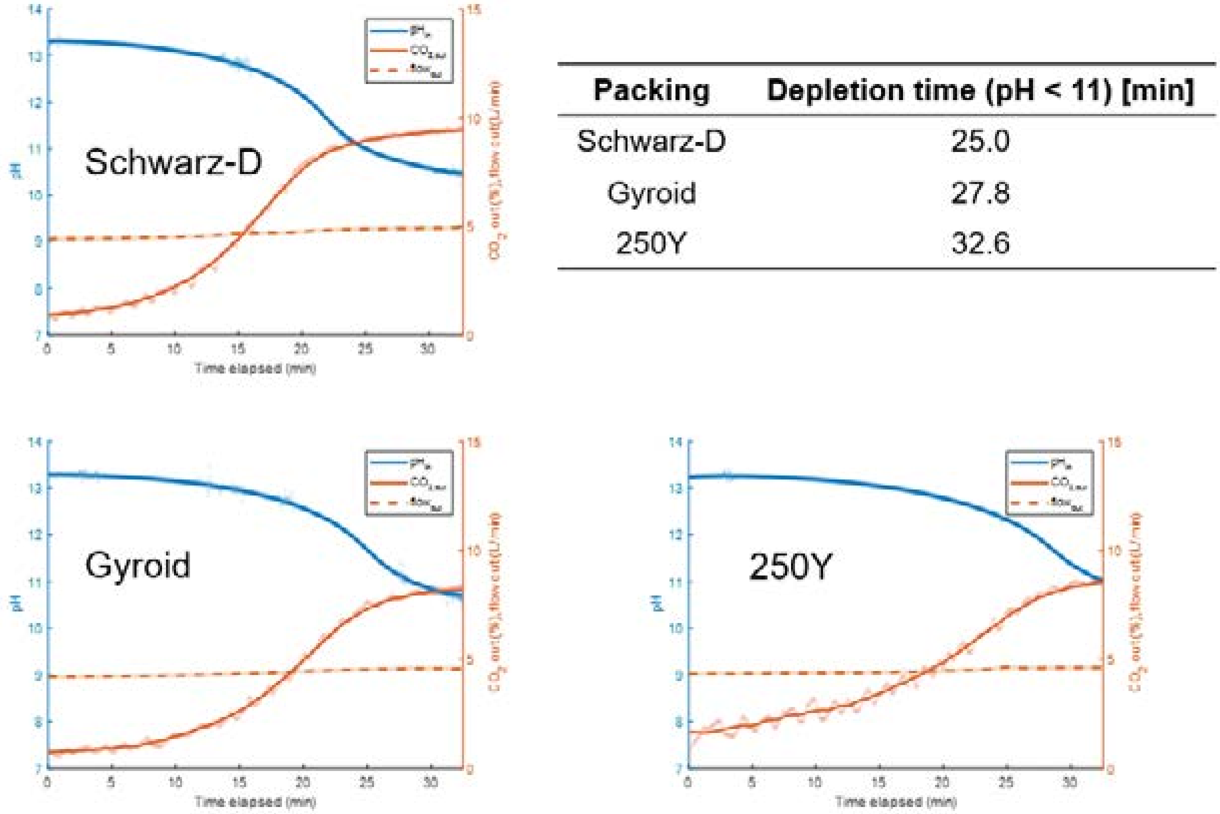


Figure 8: Colorimetric change of an aqueous K_2CO_3 solvent using thymol blue as an indicator dye. pH evolution profiles for two absorber experiments using a TPMS Schwarz-D geometry and a conventional 250Y geometry.

The Schwarz-D, Gyroid, and 250Y structures were quantitatively compared to each other using this method of measuring the depletion time of a solvent (Figure 9). Experiments were conducted using a reservoir of sodium hydroxide (NaOH) and 10% CO_2 in a counter-current flowing column. The solvent depletion time was then measured to determine the effects of the use of TPMS packings. Similar to the visual experiments with K_2CO_3, the hydroxide solutions also depleted faster in the TPMS geometries when compared to the 250Y structure. Furthermore, the Schwarz-D structure achieved a faster depletion than the gyroid structure.



Packing	Depletion time (pH < 11) [min]
Schwarz-D	25.0
Gyroid	27.8
250Y	32.6

Figure 9: Relative comparisons of Schwarz-D, Gyroid, and 250Y structures. The Schwarz-D structure was found to be the best performing of the geometries.

The heat transfer performance of a set of TPMS and periodic nodal surface (PNS) structures were also evaluated by numerically computing the friction factors and Nusselt numbers in the laminar flow regime. In this evaluation, these structures were found to have higher friction factors when compared to straight channels, but also had higher Nusselt numbers. Furthermore, the Nusselt number enhancement improved with increasing Reynolds number. Among the TPMS geometries studied, the Schwarz-D had the best heat transfer performance while the Schwarz-P was the worst performing structure, as shown in Figure 10. No correlation between being a TPMS versus PNS and the associated heat transfer performance was found.

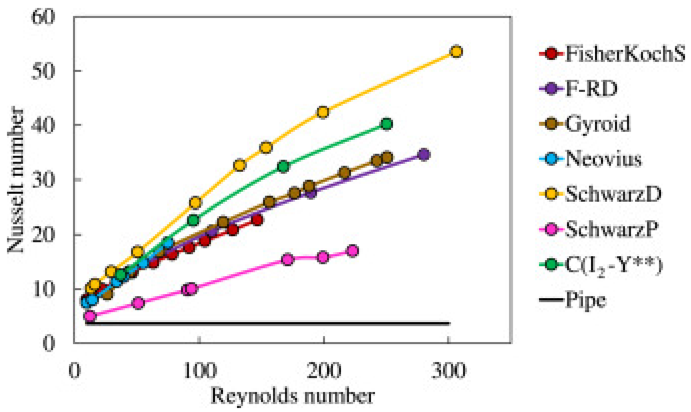


Figure 10: Nusselt numbers for the TPMS and PNS structures.

A rate-based model of an absorption column was also developed and used to analyze several intercooling strategies utilizing these "heat exchange packings." A number of optimal temperature profiles were calculated, which minimized the column height required to achieve a fixed degree of separation for a given set of gas and liquid inlet flow rates (Figure 11). While these optimal profiles may not be realized in an actual system, their calculation provides a base case that is useful when comparing different intercooling approaches and determining whether more advanced intercooling may be worthwhile. The optimal temperature at any point along the column represents a trade-off between lowering the temperature to increase the absorption driving force and increasing the temperature to increase absorption kinetics.

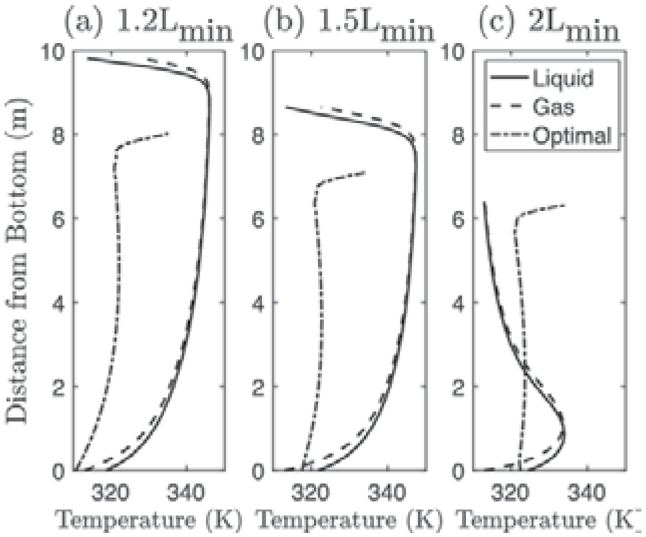


Figure 11: Optimal and adiabatic temperature profiles under conditions for (a) 1.2 L_{min}, (b) 1.5 L_{min}, and (c) 2 L_{min}.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD (wet basis) should be assumed as:

		Composition						
		vol%					ppmv	
Pressure	**Temperature**	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.7 psia	135°F	13.17	17.25	66.44	2.34	0.80	42	74

technology advantages

- Novel reactor geometries enable absorbers and fixed beds with integrated heat exchange, membrane separators with minimal pressure drop, and high efficiency heat exchangers.
- TPMS packings are predicted to have better liquid distributions and liquid-gas interfacial area and enhance fluid mixing.
- Lower cost of plastic printed packings compared to stainless steel at bench-scales.

R&D challenges

- Optimizing geometry of TPMS for best performance at the process level.
- Identifying new material or fabrication strategy for TPMS membrane reactors.
- Part-scale fabrication using AM.

status

The project was completed on February 28, 2022. LLNL has concluded that for single-phase flow in membrane reactors, smaller feature sizes are better, to the limits of fabrication. Printed plastic packings using multiple materials were demonstrated. Hydrophobic surfaces in the stripper are promising for polarity-swing solvents. Kg-scale testing and kg-scale production was solved for larger-scale demonstrations. TPMS membrane reactors showed promise, but the fabrication process was limited by scalability. TPMS geometries exhibit high thermal transport properties within a wide range of geometries (the Schwarz-D structure demonstrated the best performance). LLNL developed an optimization framework for structured packings with integrated heat exchange. TPMS-structured packings exhibited improved liquid distributions and improved performance. Altogether, a 20–50% reduction in absorber capital cost may be possible with these TPMS packings; however, manufacturing costs at scale are uncertain.

available reports/technical papers/presentations

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Stolaroff, J., "High-Efficiency, Integrated Reactors for Sorbents, Solvents, and Membranes Using Additive Manufacturing," Presented at 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/Stolaroff%20-%20NETL%20Program%20Review%202019.pdf*.

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Y Fu, J Bao, C Wang, RK Singh, Z Xu, G Panagakos. CFD study of countercurrent flow in triply periodic minimal surfaces with CO_2BOL solvent. $CCSI^2$ Technical Report (2019) [with LLNL design files]

Second-Generation Non-Aqueous Solvents (GEN2NAS) for CO_2 Capture from Natural Gas Combined Cycle Plants

primary project goal

RTI International is developing a novel two- or three-component second-generation non-aqueous solvent formulation (GEN2NAS) and optimizing the process for greater than 97% efficient carbon dioxide (CO_2) capture that lowers the cost of CO_2 capture at natural gas combined cycle (NGCC) plants.

technical goals

- Screen solvent formulations and select primary GEN2NAS candidates.
- Test the primary GEN2NAS solvent formulation candidates in a rotatory packed bed (RPB) absorber.
- Demonstrate that the GEN2NAS RPB process can remove at least 97% CO_2 from simulated NGCC flue gas.
- Measure the overall mass transfer kinetics.
- Show via techno-economic analysis (TEA) a cost reduction of at least 40% in the cost of CO_2 capture compared with U.S. Department of Energy (DOE) Case B31B rev. 4 Sep. 2019.

technical content

RTI International is evaluating second-generation water-lean solvent formulations and processes optimized for CO_2 capture from NGCC plants using a synthetic flue gas blend and an RPB absorber. (First-generation non-aqueous solvent [NAS] experimentation was performed by RTI in Projects FE0031590, FE0026466 and FE0013865.) RTI resources are being used for experimental determination of all thermodynamic and physical properties needed for future advanced process modeling, including experimental measurement of vapor/liquid equilibrium (VLE), reaction rates, heat of absorption, specific heat capacity, thermal conductivity, density, viscosity, thermal degradation, and oxidative degradation. Optimization entails maximizing the concentration of the amine to reach the lowest specific reboiler duty (SRD) and highest working capacity while balancing viscosity. Amine emissions and engineering system operational challenges such as water-balancing, material compatibility, and foaming of the promising solvent candidates are being evaluated by lab-scale gas absorption system testing where the solvent will be tested under realistic operating conditions.

RTI screened more than 400 formulation candidates based on chemical structure, viscosity, density, cost, availability and vapor pressure. The screening of amines was broadened to incorporate solid amines and salts of amines that benefit from

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
GEN2NAS Water-Lean Solvent

participant:
RTI International

project number:
FE0032218

predecessor projects:
N/A

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jtanthana@rti.org

partners:
N/A

start date:
04.01.2023

percent complete:
70%

essentially non-existent vapor pressure. This work built upon previous RTI solvent testing in projects FE0031590, FE0026466 and FE0013865. In the current work, one amine candidate, A2, showed significantly lower vapor pressure than the first-generation NAS and monoethanolamine (MEA). A two-component formulation containing A2 as an amine component and D9 as a diluent was chosen as a prime candidate due to its low vapor pressure, low viscosity and high working capacity. Three-component formulations containing A2 and another amine with diluent were also chosen to be further screened alongside A2+D9. The three-component formulation was devised as another solvent screening and optimization strategy, as it could improve the CO_2 absorption kinetics as well as CO_2 loading.

Figure 1: GEN2NAS solvent.

RTI determined that the 40% cost reduction from the DOE Case B31B is possible. Factors that drove this reduction include:

- Solvent formulation: Utilizing low-cost and commercially available components.
- Simplified gas polishing section: Low vapor pressure of GEN2NAS requires only simple wash section while emissions are kept at a minimum.
- Replacing absorber with RPB: Lower capital expenditure (CAPEX) of the capture process through process intensification.
- Replacing stripper with flash tanks: Lower CAPEX with simpler regeneration process.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	171	150-200
Normal Boiling Point	°C	288	>250
Normal Freezing Point	°C	N/A	<0
Vapor Pressure @ 15°C	bar	3×10^{-7}	N/A
Manufacturing Cost for Solvent	$/kg	15-20	<10
Working Solution			
Concentration	kg/kg	0.85	0.55-0.8
Specific Gravity (15°C/15°C)	-	0.95	0.9-1.1
Specific Heat Capacity @ STP	kJ/kg-K	1.90	1.9-2.3
Viscosity @ STP	cP	19.6	10-40
Absorption			
Pressure	bar	1	1
Temperature	°C	30	30-40
Equilibrium CO_2 Loading	mol/mol	0.2	0.1-0.5
Heat of Absorption	kJ/mol CO_2	90	85-100
Solution Viscosity	cP	39.3	10-40
Desorption			
Pressure	bar	2	2

Temperature	°C	110	90-110
Equilibrium CO_2 Loading	mol/mol	0.01	<0.05
Heat of Desorption	kJ/mol CO_2	60	50-70

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					Ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
1 bar	40°C	3-4	7-8	79	10	0	0	15

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – GEN2NAS is a water-lean solvent class that uses amine as an active CO_2 removal component in its formulation. The reaction between the GEN2NAS amine and CO_2 produces carbamate as well as bicarbonate salts.

Solvent Contaminant Resistance – GEN2NAS amine reacts with acidic contaminants in the flue gas like those reported in literature. Heat stable salts (HSS) are produced from the presence of sulfur oxide (SO_X) and nitrogen oxide (NO_X) in the flue gas. A commercially available solvent recovery unit can be used to remove the HSS from the solvent.

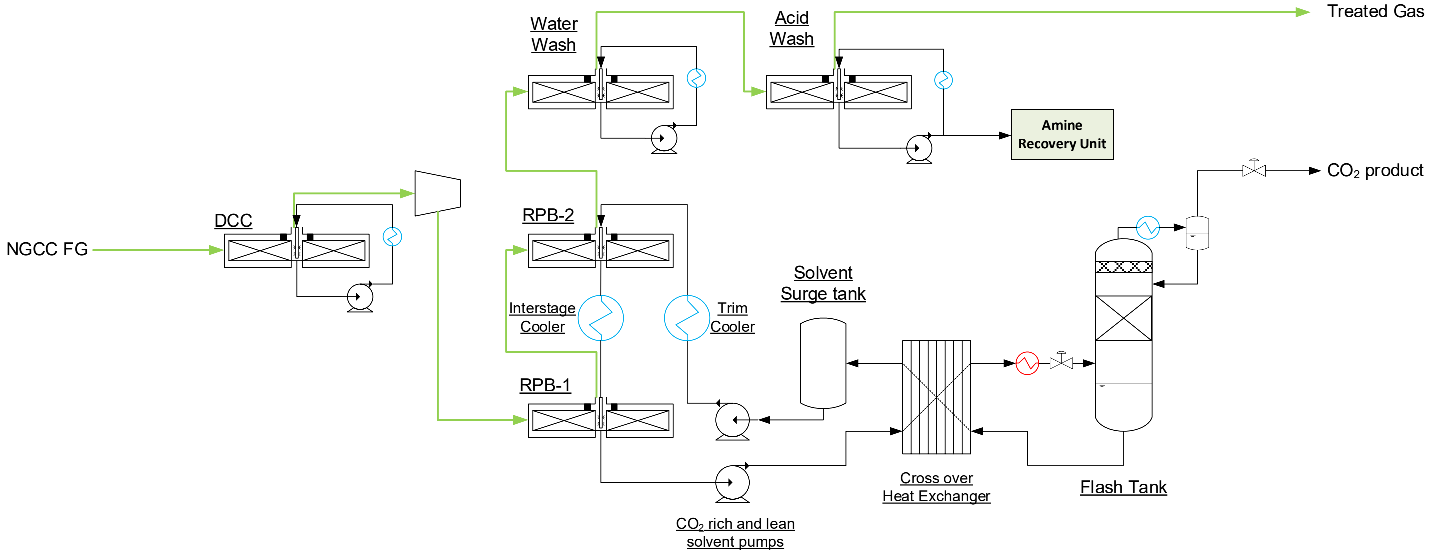
Solvent Foaming Tendency – Foaming tendency of GEN2NAS is expected to be like the first-generation NAS, which demonstrates no foaming under the target operating condition at engineering-scale at Technology Centre Mongstad (TCM).

Flue Gas Pretreatment Requirements – A direct contact cooler (DCC) is used to lower the flue gas temperature and balance water for the GEN2NAS CO_2 capture plant. No additional pretreatment is required.

Solvent Makeup Requirements – The solvent makeup for GEN2NAS has shown to be minimal. In this project, GEN2NAS was subjected to more than 1,000 hours of testing under simulated natural gas flue gas at RTI's bench-scale gas absorption system. No solvent makeup was used to maintain the system volume or capture performance.

Waste Streams Generated – Wastewater from DCC is generated to maintain the water balance of the system. The GEN2NAS capture process could produce an additional wastewater from the acid wash section if the amine recovery unit is not used. The two streams can be combined into a single wastewater stream, which can be treated as a nonhazardous wastewater.

Process Design Concept – GEN2NAS process flow diagram with RPBs is shown below.



Proposed Module Design – GEN2NAS CO_2 capture is envisioned to be highly modular with a small footprint and flexibly operates using RPBs as DCC, absorber, water wash and acid wash.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	52.3	<48
Cost of Carbon Avoided	\$/tonne CO_2	71.6	62
Capital Expenditures	\$/MWhr	20.4	N/A
Operating Expenditures	\$/MWhr	10.6	N/A
Cost of Electricity	\$/MWhr	66.9	N/A

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – The current research and development (R&D) values shown in Table 2 are based the most recent TEA conducted on first generation NAS using National Energy Technology Laboratory (NETL) methodology laid out in the "Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity" report Rev.4 Oct 2022. All cost values are based on 2018$. Cost of CO_2 captured and avoided exclude transportation and storage.

Scale of Validation of Technology Used in TEA – The current R&D value is based on the results obtained at TCM's 200 tonne per day amine plant using NAS capturing 97% of the CO_2. The target R&D values are based on the GEN2NAS with RPB process configuration. The TEA of GEN2NAS was derived based on RTI's bench-scale system at 0.1 TPD.

Qualifying Information or Assumptions – First-of-a-kind cost is translated to n^{th}-of-a-kind (NOAK) for RPB based on the learning rate of the NGCC industry. The reported costs are full-scale NGCC plant CO_2 capture using two process trains. The GEN2NAS solvent cost was estimated to be the same as NAS for NOAK. GEN2NAS makeup rate, which contributes to the operating expenditures (OPEX), is based on emissions and degradation products formations determined at bench-scale, while the nitrosamine formation rate is based on lab-scale experiment. Acid wash and amine recovery from the acid wash are included in the costs reported for GEN2NAS as a conservative estimate.

technology advantages

- Higher efficiency (greater than 97%) CO_2 capture with less energy consumption.
- High turn-down ratio to accommodate the transient operation of NGCC application.
- Commodity-scale production ready.
- Lowers the cost of CO_2 capture at NGCC plants by 40% compared with the DOE baseline Case B31B rev. 4 Sep 2019.
- Decreases both CAPEX and OPEX and drives the cost of CO_2 capture to approximately $50/ton CO_2.

R&D challenges

- Solvent scale-up.
- Formulation optimization.
- Process configuration.

status

The project team conducted parametric testing of the GEN2NAS in a 0.1-TPD bench-scale system for more than 1,000 hours of operation. The RPB and conventional absorber was tested during the parametric testing campaign. The operating conditions that allow greater than 97% capture have been identified from these tests. The amine loss through emissions and speciation of the degradation products have been determined. The solvent physical and chemical properties have been measured at the relevant conditions through various instruments. The data collected is being used to update the current GEN2NAS process model. The TEA is being finalized.

available reports/technical papers/presentations

Bhattacharya, M. *"Generation 2 Non-Aqueous Solvents (GEN2NAS) for CO_2 Capture from Natural Gas Combined Cycle Plants,"* presented at the 2024 FECM/NETL Carbon Management Research Project Review Meeting, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_Posters_MBhattacharya.pdf*.

Tanthana, J., *"GEN2NAS Solvents for CO_2 Capture from NGCC Plants,"* presented at the 2023 FECM / NETL Carbon Management Research Project Review Meeting, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC30_Tanthana.pdf*.

Tanthana, J., *"Generation Non-Aqueous Solvents (GEN2NAS) for CO_2 Capture from Natural Gas Combined Cycle Plants,"* Project Kick-off Meeting, Apr 2023. *https://netl.doe.gov/projects/files/Generation%20Non-Aqueous%20Solvents%20(GEN2NAS)%20for%20CO2%20Capture%20from%20Natural%20Gas%20Combined%20Cycle%20Plants.pdf*.

Lail, M., *"Engineering-Scale Testing of Transformational Non-Aqueous Solvent-Based Carbon Dioxide Capture Process at Technology Centre Mongstad,"* pp. 136-143 in US Department of Energy, *Compendium of Carbon Capture Technology: Carbon Capture Program R&D,* Sept. 19, 2022.

High-Performance Solvent for Natural Gas Combined Cycle (NGCC) Flue Gas CO_2 Capture

primary project goal

Susteon Inc., with its industrial partner TotalEnergies, is developing a novel high-performance solvent, Sustenol™, to capture greater than 97% of the carbon dioxide (CO_2) from the flue gas of a natural gas combined cycle (NGCC) power plant. This solvent can provide high CO_2 capture working capacity, fast kinetics and reduced energy requirements for solvent regeneration, with a high oxidative, thermal and hydrothermal stability for reduced solvent loss and emissions.

technical goals

- Develop and test a novel solvent formulation with higher working capacity and higher reaction rate for NGCC flue gas (approximately 4% CO_2) capture.
- Improve solvent formulation for greater than 97% CO_2 capture.
- Advance solvent formulation to have a lower reboiler duty.
- Mature pathway to 40% reduction CO_2 capture cost.

technical content

Susteon has formulated a highly efficient drop-in solvent composition for NGCC flue gas, which has been trademarked as Sustenol (Figure 1). Susteon has identified promoters to enhance solvent CO_2 absorption/desorption rates and solvent working capacity. Susteon has tested the solvent in a contractor-built bench-scale unit (absorber and desorber, 0.2 kg/day) and in a 1-tonne-per-day (TPD) pilot test unit. Production of the solvent at a 4,000 kg scale has been achieved with completion of comprehensive solvent characterization.

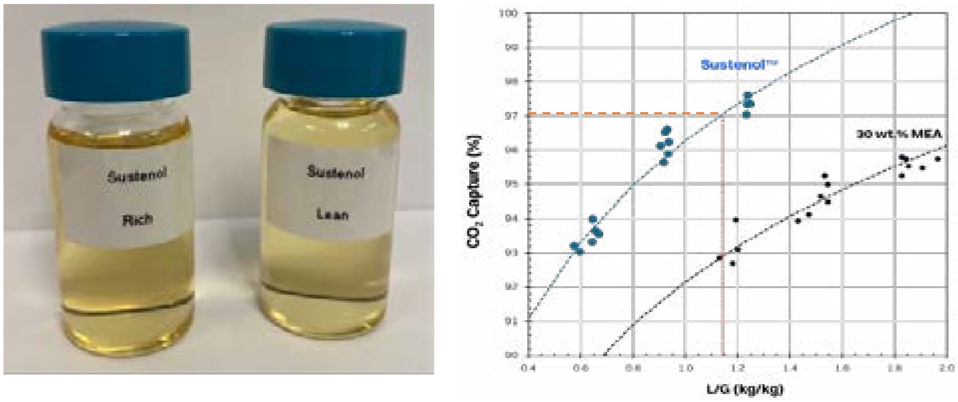


Figure 1: (left) Sustenol™ solvent samples; (right) superior CO_2 capture performance of Sustenol over 30wt.% MEA in 1 TPD pilot unit.

Specific reboiler duty (SRD) of Sustenol was found to be around 2.2 GJ/tonne CO_2, which is lower than both monoethanolamine (MEA) and Shell's Cansolv® (Figure 2).

program area:

Point Source Carbon Capture

ending scale:

Laboratory Scale

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

High-Performance Solvent for NGCC Flue Gas CO_2 Capture

participant:

Susteon Inc.

project number:

FE0032216

predecessor projects:

N/A

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partners:

TotalEnergies

start date:

01/01/2023

percent complete:

90%

Bench-scale testing showed a lower surface tension (wettability), heat capacity and heat of vaporization than the reported values for Cansolv. Using this initial bench-scale data, Susteon has also developed and validated a process model for a 650-MW NGCC power plant (6,000 TPD of captured CO_2).

The preliminary techno-economic analysis (TEA) showed a CO_2 capture cost of $45/tonne CO_2 for Sustenol at a commercial scale. This analysis suggests that a CO_2 capture process utilizing Sustenol has the potential to reduce the total plant cost of a 650-MW power plant by 16% and the CO_2 capture costs by 40% from a B31B case (NETL Report, 2019). Additionally, a technology pathway was developed to meet the U.S. Department of Energy (DOE) target of greater than 30% cost reduction compared to Cansolv (NETL Report, 2022).

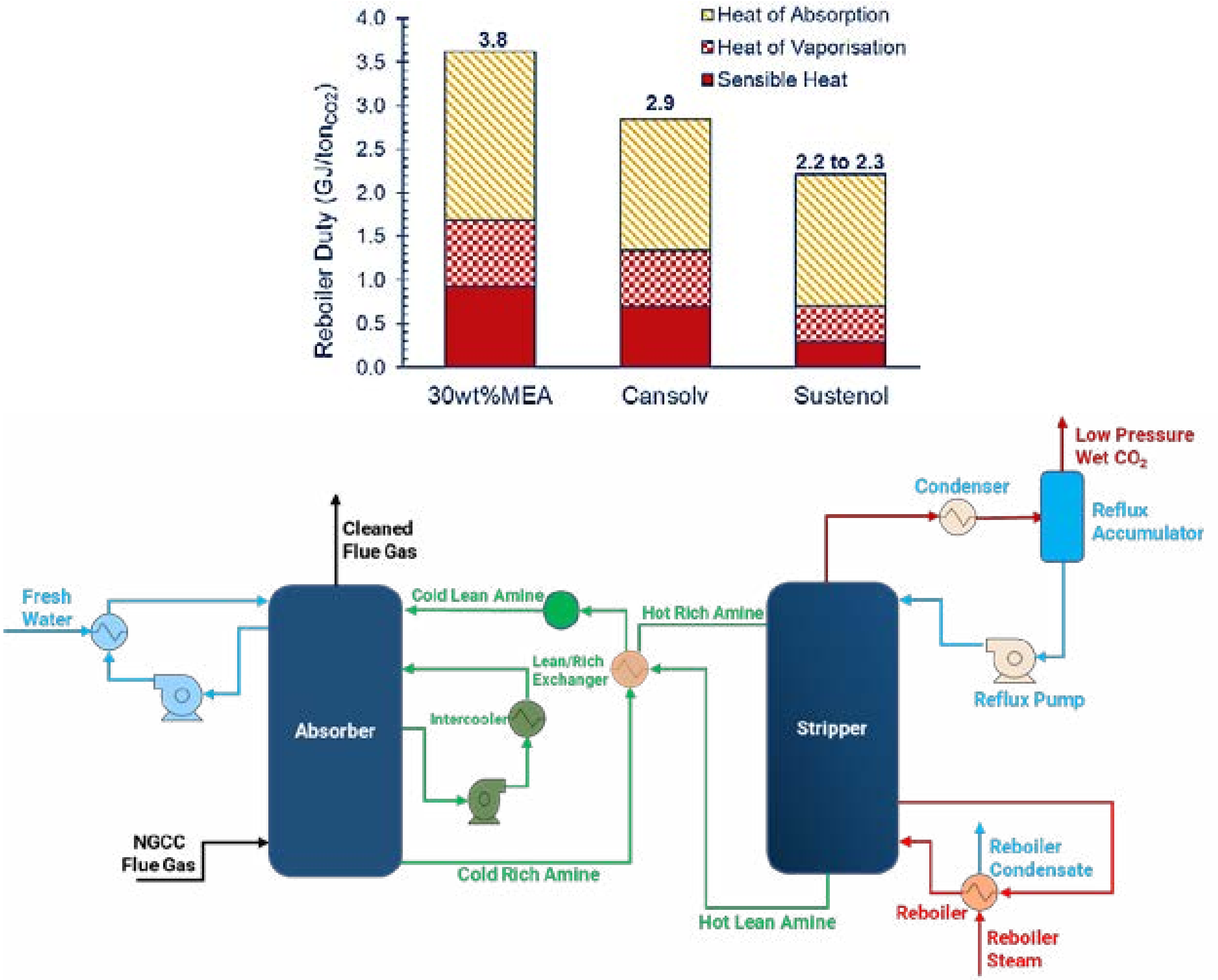

Figure 2: (top) Preliminary reboiler duty analysis reveals Sustenol™ improvement over MEA and Cansolv®; (bottom) typical simple plant configuration for Sustenol™ technology.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	110.6	110 - 130
Normal Boiling Point	°C	211	200 - 250
Normal Freezing Point	°C	-0.32	-10 to 10
Vapor Pressure @ 15°C	bar	6.67e-6	< 0.05
Manufacturing Cost for Solvent	$/kg	proprietary	proprietary
Working Solution			
Concentration	kg/kg	51	45 - 65

Specific Gravity (15°C/15°C)	-	1.08	0.95 - 1.2
Specific Heat Capacity @ STP	kJ/kg-K	3.01	2.5 - 3.5
Viscosity @ STP	cP	9	6 - 15
Absorption			
Pressure	bar	1.00	1.00
Temperature	°C	40	40
Equilibrium CO_2 Loading	mol/mol	0.45	0.4 - 0.6
Heat of Absorption	kJ/mol CO_2	70	65 - 75
Solution Viscosity	cP	9	10 - 15
Desorption			
Pressure	bar	1.6	1.2 - 5
Temperature	°C	120	115 - 150
Equilibrium CO_2 Loading	mol/mol	0.1	0.05 - 0.15
Heat of Desorption	kJ/mol CO_2	70	65 - 75
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	3,927,398	
CO_2 Recovery, Purity, and Pressure	% / % / bar	97% / 99.98% (dry) / 3.4 bar(a)	97% / 99.98% (dry) / 3.4 bar(a)
Absorber Pressure Drop	bar	0.1	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	proprietary	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical NGCC power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 4.3%. Therefore, the partial pressure of CO_2 is roughly 0.04 atm or 0.04 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

		Composition						
		vol%					ppmv	
Pressure	Temperature	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.7 psia	135°F	4.3	17.25	66.44	14	0.80	0	15

Chemical/Physical Solvent Mechanism – CO_2 in the flue gas chemically binds to the Sustenol aqueous mixed-amine solvent via an exothermic absorption step and the solvent is regenerated by the endothermic desorption via heat provided by steam in the reboiler of the regenerator column, generating pure CO_2.

Solvent Contaminant Resistance – The Sustenol solvent is highly resistant against major contaminants in the flue gas, such as oxygen (O_2), nitrogen oxide (NO_X), sulfur oxide (SO_X) and particulate matter.

Solvent Foaming Tendency – During the pilot plant operation, there was no foaming tendency observed.

Flue Gas Pretreatment Requirements – The pretreatment includes reducing SO_X in the flue gas to 2 to 5 parts per million (ppm) in order to limit solvent degradation and will be implemented in a direct contact cooler in conjunction with flue gas cooling.

Solvent Makeup Requirements – The Sustenol solvent makeup rate is determined by the sum of the amine losses in the treated gas leaving the absorber column and the rate of solvent degradation during operation over time. Low makeup rates were observed during long-term testing well below an operationally manageable threshold. Low solvent makeup is expected at a scale when processing flue gas from power plants with a baghouse filter for particular removal or with upstream flue gas pretreatment for aerosol mitigation.

Waste Streams Generated – The main waste liquid stream is from the direct contact cooler where SO_X and NO_X are removed; this stream is typically handled in the power plant wastewater treatment facility.

Process Design Concept – See Figure 2.

Proposed Module Design – Free standing absorber and stripper columns will be tied into a modularized process skid. There will be associated containers for electrical equipment, analytical equipment and process control.

TABLE 2: NGCC POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	54.7	40 - 60
Cost of Carbon Avoided	\$/tonne CO_2	74.1	60 - 80
Capital Expenditures	\$/MWh	20.3	15 - 25
Operating Expenditures	\$/MWh	11.8	10 - 15
Cost of Electricity	\$/MWh	31.9	30 - 35

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – The numbers provided in the table are based on the reference plant provided by NETL for TEA analysis, found in the "Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity" report, October 14, 2022 (*https://netl.doe.gov/energy-analysis/details?id=e818549c-a565-4cbc-94db-442a1c2a70a9*).

Scale of Validation of Technology Used in TEA – Experimental results from the 1 TPD CO_2 pilot test unit.

Qualifying Information or Assumptions – N/A.

technology advantages

- Fast kinetics of CO_2 absorption and desorption.
- High thermal and oxidative stability.
- Lower reboiler duty.
- Lower environmental impact.
- Reduced CO_2 capture cost by up to 40%.
- Drop-in solvent for the existing solvent-based CO_2 capture plants.

R&D challenges

- Optimizing solvent working capacity and rate of absorption/desorption.
- Ensuring good oxidative, thermal and hydrothermal stability.
- Minimizing the risk of precipitation, corrosion, fugitive emissions, evaporative losses and foaming.
- Ensuring water-lean tolerance.
- Scaling up the module.
- Bulk production and quality control.

status

Susteon has synthesized Sustenol and measured its physical and chemical properties. It has begun testing the solvent with a bench-scale module that it designed and optimized. It has updated its preliminary TEA. This solvent will be demonstrated at 0.5-MW scale with real flue gas from an NGCC power plant in 2025.

available reports/technical papers/presentations

Rabindran, A., Susteon Inc., et al, *"High Performance Solvent for Natural Gas Combined Cycle (NGCC) Flue Gas CO_2 Capture,"* Closeout Meeting Presentation, October 2024. *https://netl.doe.gov/projects/files/High%20Performance%20Solvent%20for%20Natural%20Gas%20Combined%20Cycle%20(NGCC)%20Flue%20Gas%20CO2%20Capture.pdf*.

Zhou, J., Susteon Inc., et al, *"Engineering Scale Testing of a High-Performance Solvent for NGCC Flue Gas CO_2 Capture,"* 2024 FECM/NETL Carbon Management Research Project Review Meeting. August 2024. *https://netl.doe.gov/events/24CM*.

Rabindran, A., Susteon Inc., et al, *"High Performance Solvent for Natural Gas Combined Cycle (NGCC) Flue Gas CO_2 Capture,"* Net-zero Flexible Power: High Capture Rate Project Review Meeting, Location: Delta Philadelphia Airport, June 6-7, 2024. *https://netl.doe.gov/sites/default/files/netl-file/24HCR_Rabindran.pdf*

Rabindran, A., Susteon Inc., et al, *"High Performance Solvent for Natural Gas Combined Cycle (NGCC) Flue Gas CO_2 Capture,"* 2023 FECM / NETL Carbon Management Research Project Review Meeting, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC30_Rabindran.pdf*.

Rabindran, A., Susteon Inc., et al, *"High Performance Solvent for Natural Gas Combined Cycle (NGCC) Flue Gas CO_2 Capture,"* Project Kickoff Meeting, January 2023. *https://netl.doe.gov/projects/files/High%20Performance%20Solvent%20for%20Natural%20Gas%20Combined%20Cycle%20(NGCC)%20Flue%20Gas%20CO2%20Capture.pdf*.

Reducing the Degradation of Carbon Capture Solvents

primary project goal

Pacific Northwest National Laboratory (PNNL) conducted research to mitigate common mechanisms of solvent degradation and byproduct formation in carbon dioxide (CO_2) capture processes. Research and development (R&D) efforts focused on studying the effects of steel interfaces on oxidation and nitrosation for both aqueous and water-lean solvents and studying the molecular underpinnings of solvent degradation (e.g., hydrolysis, nitration, oxidation) and design new formulations that are resistant to these chemical degradations.

technical goals

- Develop fundamental understanding of degradation mechanisms for multiple solvent components on steel interfaces such that oxidative degradations from oxygen (O_2) and nitrogen oxide (NO_X) can be mitigated.
- Study the effects of steel interfaces on oxidation and nitrosation for up to six solvents from aqueous and water-lean classes (three from each).
- Develop experimental and computational studies of solvent degradation for neat solvents and then solvents in the presence of 304 carbon and 316 stainless steels uncoated or treated with urethane or imidazole coatings.
- Down select solvents/conditions for confirmation testing in PNNL's small-scale continuous testing platform.
- Evaluate two CO_2BOLs, including N-(2-ethoxyethyl)-3-morpholinopropan-1-amine (2-EEMPA), as an additive in commercial aqueous solvents with the aim of fast-tracking commercialization for aqueous solvents.
- Perform an initial techno-economic analysis (TEA) based on the material property measurements.
- Develop molecular model and batch testing to ascertain degradation/byproduct behavior for the most viable aqueous blends identified in the earlier tasks.

technical content

Commercial and pre-commercial solvents for CO_2 capture from flue gas sources have advanced considerably over the years. R&D has focused on lowering overall regeneration energy via solvent chemistry advances and related process development. Additionally, work on quantifying and reducing solvent degradation was undertaken in the previous DOE-funded Field Work Proposal (FWP)-72396. Solvent degradation not only impacts solvent costs, but can ultimately hinder fielding if hazardous products are formed (e.g., carcinogenic nitrosamines). The purpose of this research was to leverage prior PNNL investigations on the fundamental understanding of degradation mechanisms of multiple solvent components. PNNL's molecular modeling experts provide mechanistic insights to

program area:

Point Source Carbon Capture

ending scale:

Laboratory Scale

application:

Post Combustion Power Generation PSC

key technology:

Solvents

project focus:

Methods for Mitigating Mechanisms of Solvent Degradation

participant:

Pacific Northwest National Laboratory (PNNL)

project number:

FWP-77217

predecessor projects:

FWP-72396

NETL project manager:

Carl Laird
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principal investigator:

Phillip Koech
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phillip.koech@pnnl.gov

partners:

N/A

start date:

01.01.2021

percent complete:

100%

observed degradation pathways and potential chemistry for additives or process modifications for ultimate mitigation. Other degradation measurements for solvents, such as data from SINTEF's solvent degradation test rig, are also used for validation. Further, there is interest in understanding the impacts of intentional dilution of PNNL's water-lean CO_2BOLs in aqueous solvent blends as a means of commercially fast-tracking those solvents. This fast-track approach requires an understanding of solvent performance impacts, as well as any unique degradation/byproduct impacts.

PNNL's previous work in FWP-72396 showed a previously undiscovered solvent degradation that occurs on the interfaces of stainless steels. In this study, PNNL had discovered direct chelation of specific chemical motifs of carbon capture solvents directly coordinating to stainless steel interfaces and chemically activating them for degradations such as hydrolysis and oxidation (Figure 1). It is believed that the chromium oxide (CrO) coating that makes stainless steel corrosion resistant acts as the catalyst for oxidative degradation reactions with O_2 and NO_X. Chromium oxides are known oxidative catalysts for alcohols and amines, and unsurprisingly, previous studies indicated that the structural motifs that showed the highest deactivation in the presence of steels were those that contained alcohols and imines, with the former present in all alkanolamines and the latter in the CO_2BOL alkanol guanidine solvent class. The finding that steel interfaces directly coordinate and activate specific chemical moieties means that all carbon capture solvents are susceptible to these degradations. Learning how to stop these catalytic activations for decomposition reactions provides a new means to increase solvent lifetime for all solvent-based processes. Thus, this research effort aimed to shut down this newly discovered mechanism of catalytic decomposition by steel interfaces for both aqueous and water-lean solvents by simply passivating the interface with durable organic coatings. Further, if the CrO coating on stainless is the culprit, passivation of a less expensive carbon steel (304) with a chemically durable organic coating could result in significant cost-savings for infrastructure and avoid the use of costly 316 stainless steel.

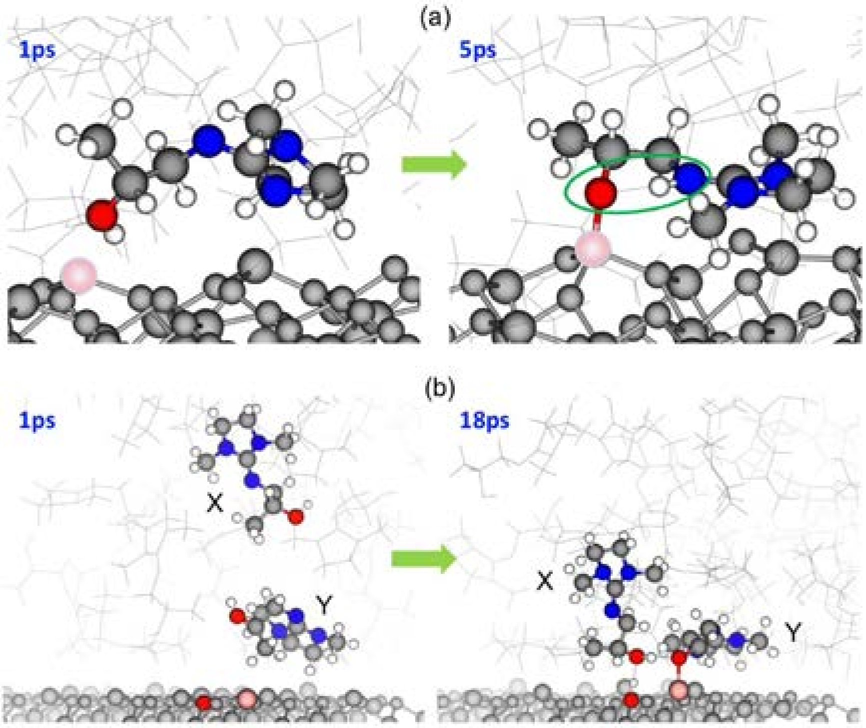

Figure 1: Representative interfacial activation of a water-lean solvent by stainless steel. 1-IPADM-2-BOL/hematite(steel) interface: (a) structure of a molecule right at the solid surface at 1 picosecond (ps) and 5 ps of an Ab initio molecular dynamics (AIMD) simulation, the surface atom in pink indicates the iron atom that assists the proton transfer from the OH group to an N atom of the same molecule; (b) structure of two molecules X and Y at 1 ps and 18 ps of the same AIMD simulation, surface atoms O (red) and Fe (pink) directly assisted the proton transfer from X to the surface and from Y to X. Most of surface atoms and surround molecules are in grey for clarification.

The project team showed that they could increase solvent lifetime by as much as 50% by simply removing contact with a steel interface. The retardation of chemical degradation of solvents was achieved by removing the steel interfaces that were acting as catalysts for the degradation reactions. Thus, removal or passivation of the interface had the effect of increasing the degradation activation energies (thermal, oxidation, hydrolysis) for three solvents by approximately 2,000–

3,000 calorie (cal)/mol. PNNL aimed to show that comparable retardation could be achieved for other modes of amine degradation in solvent-based post-combustion CO_2 capture processes.

Reactions of carbon capture solvents with NO_X remains a challenge for solvent developers as nitrosation results in the formation of potentially carcinogenic nitrosamines. Often, nitrosation cannot be avoided, and multiple solvent formulations have had to be used with caution (e.g., piperazine, 2-AMP) or outright abandoned (e.g., a subcomponent in an experimental Fluor solvent) due to unacceptable levels of nitrosamine formation. Nitrosation occurs via an oxidation reaction, which PNNL hypothesizes to be catalyzed by stainless steel interfaces, not just dissolved metals that accumulate in the solvents from corrosion. Nitrosamines are specifically problematic for secondary amine chemical moieties, which are often utilized due to their more favorable energetics as compared to primary amines such as monoethanolamine (MEA). Thus, if nitrosation could be mitigated by coating steel interfaces, previously established energetically favorable and cost-effective solvents could be revitalized and rapidly expedited for commercialization.

Mechanistic studies are being performed systematically with dissolved metal catalysts to determine which, if any, catalyze the nitrosation reaction. With this data, PNNL designed new aqueous amine formulations that have different functional groups that would disfavor nitrosation. PNNL also performed experimental and computational studies of solvent degradation for neat solvents and solvents in the presence of 304 carbon and 316 stainless steels that are both uncoated and treated with urethane or imidazole coatings. The goal was to confirm that coated 304 steels do not catalyze oxidative degradations and are resistant to corrosion.

There is interest in using PNNL's water-lean CO_2BOLs solvents to initially enable more conservative concentrations in aqueous blends, despite the outstanding performance with minimal water. The logic in this interest is that one commercialization barrier is the risk to technology providers of using a new solvent in water-lean form in existing/initial commercial equipment. Fluor used this approach when developing their latest Econamine FG+ solvent, which increased the solvent concentration from approximately 30% up to 50%. PNNL is assessing two CO_2BOLs as active additives to commercial aqueous solvents with water loading ranging from 50–80%. The project team is utilizing molecular modeling and batch testing to ascertain degradation/byproduct behavior. The most viable aqueous blends are then being subjected to steady-state continuous testing using simulated coal-derived flue gas. By using a CO_2BOL solvent as an active ingredient in an aqueous system, higher initial concentrations would be achievable, along with the prospect to drive those loadings up to greater than 90% over time, reducing the overall commercialization risk.

There are four primary goals of this project:

- Mitigate the mechanism of catalytic oxidative decomposition by steel interfaces for both aqueous and water-lean solvents that have been assessed in various platforms, including the SINTEF degradation test rig, by simply passivating the interface with novel monolayer coatings.
- Enable utilization of cheaper carbon steel (304) by modifying the surface with chemically novel monolayer organic coatings, resulting in significant cost-savings for infrastructure by avoiding the use of costly 316 stainless steel.
- Evaluate water-lean CO_2BOLs as active ingredients in next-generation aqueous solvent systems, utilizing higher initial concentrations with the goal to increase loadings up to greater than 90% over time, thus reducing the overall commercialization risk of water-lean solvents.
- Perform steady-state continuous flow testing using PNNL's laboratory-continuous flow system (LCFS) for the best-performing aqueous and water lean solvents to demonstrate, for at least for 72 hours, achieving 90% capture from simulated coal-derived flue gas (15% CO_2, 84% N_2 with sulfur oxide [SO_X], NO_X, O_2) and validate TEA projections.

technology advantages

- Potential to shut down oxidative decomposition by steel interfaces through passivation of the liquid-solid interface.
- Enable utilization of less-expensive carbon steel (304).

R&D challenges

- Demonstrate a minimum of 72 hours of continuous flow testing achieving greater than 95% capture from simulated coal-derived flue gas.

status

The project was completed on March 31, 2023. PNNL identified candidate steel coatings and batch tested multi-solvents and additives, along with coated and uncoated steels. Additionally, molecular modeling was conducted to theoretically study the solvent properties; these were correlated to the experimental test data collected from the small-scale continuous testing apparatus.

available reports/technical papers/presentations

Koech, P., "Reducing the Degradation of Carbon Capture Solvents," Project kickoff meeting presentation, Pittsburgh, PA, February 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11576&filename=Reducing+Degradation+of+Carbon+Capture+Solvents.pptx*.

Koech, P., "Reducing the Degradation of Carbon Capture Solvents," NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Koech.pdf*.

Parametric Testing of CO_2-Binding Organic Liquids (CO_2BOLs)

primary project goal

Pacific Northwest National Laboratory (PNNL) performed testing and optimization of three advanced carbon dioxide (CO_2)-binding organic liquid (CO_2BOL) water-lean formulations for post-combustion CO_2 capture. PNNL leveraged its carbon capture laboratory infrastructure and testing methodologies to collect comprehensive physical and thermodynamic property test data for each solvent. Aspen Plus® models were utilized to project the energetics (e.g., reboiler duty, parasitic load) and preliminary capture costs based on the physical property translations of the collected data.

technical goals

- Accelerate scale-up focus for three third-generation, low-viscosity CO_2BOL solvent formulations (two from aminopyridine [AP] class and one from diamine [DA] class).
- Perform testing and evaluation at laboratory scale to inform a techno-economic assessment (TEA) of the solvents' performance toward the U.S. Department of Energy's (DOE) $40/tonne CO_2 target.
- Engage new industry partners for subsequent scale-up and testing at the National Carbon Capture Center (NCCC) or an equivalent facility.

technical content

Under prior DOE-funded studies, PNNL developed a number of single-component, water-lean CO_2BOLs as post-combustion CO_2 capture solvents. One DA formulation in particular, N-(2-ethoxyethyl)-3-morpholinopropan-1-amine (2-EEMPA), was evaluated extensively, achieving 40 hours of steady-state CO_2 capture rates of at least 90% on simulated flue gas. While 2-EEMPA shows promise as a single-component water-lean solvent and is being scaled up with industrial partners, it is unclear if EEMPA has the highest chemical durability, lowest reboiler duty, or lowest total costs of capture that water-lean solvents can achieve. This offers an opportunity to identify and develop other unique CO_2BOLs solvents with their own intellectual property portfolios that could be licensed independently and, therefore, draw in other industrial partners.

In DOE-funded project FWP-72396, PNNL completed a study of AP and DA solvent classes to identify solvents with the lowest volatility and viscosity, respectively. The result of that work led to the design, synthesis and testing of two viable derivatives from each of the DA and AP solvent classes. The four solvents were synthesized and tested for vapor-liquid equilibrium (VLE), viscosity and mass transfer measurements in PNNL's custom pressure-volume-temperature (PVT) cell, and were found to have comparable CO_2 bonding strength to that of the leading 2-EEMPA solvent, making

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
CO_2-Binding Organic Liquid Solvents

participant:
Pacific Northwest National Laboratory

project number:
FWP-76270

predecessor project:
FWP-72396

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partners:
Carbon Capture Simulation for Industry Impact

start date:
05.01.2020

percent complete:
100%

them suitable for post-combustion CO_2 capture. Three final candidate CO_2BOL solvents were shown to exhibit CO_2-rich viscosities as low as 2.9 centipoise (cP) and to have the potential to meet or exceed PNNL's EEMPA solvent in performance: N^1-(2-ethoxyethyl)-N^2,N^2-diisopropylethane-1,2-diamine (EEDIDA), (2-morpholino-N-(pyridin-2-ylmethyl)ethan-1-amine (MPMEA), and (3-methoxy-N-(pyridin-2-ylmethyl)propan-1-amine (MPMPA). This project was designed to measure the critical data needed to project performance of these CO_2BOL water-lean formulations for post-combustion CO_2 capture, ultimately enabling slip stream testing and subsequent industry adoption.

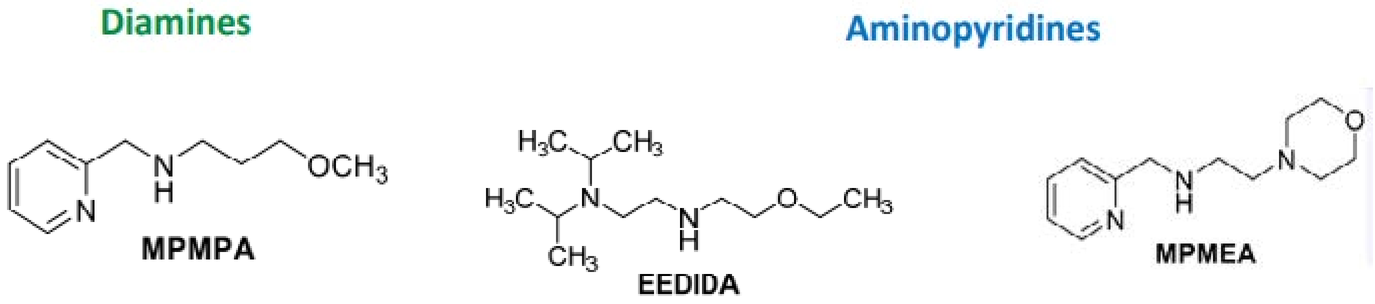

Figure 1: Final CO_2BOL derivatives for evaluation.

The aim of this project was to verify that MPMPA, MPMEA and EEDIDA are energetically efficient and cost-effective post-combustion CO_2 capture solvents. The chemical durability of the solvents was expected to be at least comparable to that of monoethanolamine (MEA) with similar, if not reduced, solvent makeup rate. The project goal was to show that all solvents exhibit steady-state capture of 90% CO_2 on simulated flue gas for a period of at least 40 hours with and without 5 wt% water at acceptable liquid/gas (L/G) ratios (~4). The reboiler duty was projected to be 2 GJ/tonne CO_2 or less in at least one process configuration (e.g., inter-heated column or lean vapor compressor), with each solvent having at least one configuration with total costs of capture at or below \$50/tonne CO_2. EEDIDA was expected to behave comparably to 2-EEMPA, albeit with lower energies associated with pumping and heat exchange performance due to its lower viscosity. The aromatic AP solvents were expected to be lower in enthalpy as they are more hydrophobic, which could lower the steady-state water loadings and lessen any upstream flue gas refrigeration needs to manage water, though this may be offset by the chilling required to prevent solvent loss from the top of the absorber due to higher vapor pressures than 2-EEMPA. Nevertheless, the preliminary total costs of capture for the AP solvents are still expected to net out at favorable overall energy and cost performance.

Each of the solvents were scaled up for comprehensive property testing on PNNL's custom PVT, wetted-wall contactor (WWC), and laboratory continuous flow system (LCFS) test apparatuses. A myriad of tests were used to measure physical and thermodynamic properties, which were then used to construct thermodynamic models in Aspen Plus. Key measurements included VLE, viscosity, density, thermal conductivity, vapor pressure, flashpoint, contact angles, and liquid-film mass transfer coefficients; preliminary chemical durability studies of flue gas impurities (i.e., sulfur oxide [SO_X], nitrogen oxide [NO_X] and oxygen [O_2]); and foaming and aerosol formation studies. The project team synthesized more than five liters of EEDIDA and three-liter quantity of MPMPA and MPMEA solvents, at 99% or better purity, for solvent property testing. VLE and absorption rate data were collected on solvent-CO_2-H_2O systems using the customized PVT cell and a WWC apparatus. The property data sets were fed to model regression using Aspen properties software to generate an Aspen property package, which enabled rigorous process simulations of various capture plant configurations using Aspen Plus.

Results show that EEDIDA and MPMPA are stronger absorbents than EEMPA, as the CO_2 heat of solutions in these solvents are higher than those in EEMPA. Compared with known data on EEMPA, MPMEA is slightly weaker with slower kinetics and somewhat higher viscosity. The solvents EEDIDA and EEMPA have very similar VLE and kinetics at the same temperature and CO_2 loading.

TEAs were conducted for EEDIDA, MPMPA, and MPMEA solvents with both the simple stripper (SS) and the two-stage-flash (TSF) configurations. The process models were developed in Aspen Plus using the validated property packages for each of the solvent-CO_2-H_2O systems, while Case B12B in the National Energy Technology Laboratory's (NETL) baseline reports were used as the reference for flue gas condition, plant scale, and economic assumptions. The water-lean feature of CO_2BOLs can significantly reduce the reboiler duty, especially contribution from the heat of vaporization, without introducing any advanced configuration for solvent regeneration. Overall, CO_2BOLs can provide a \$4–9/tonne CO_2 fuel cost saving associated with reboiler. The capital cost of a CO_2BOLs-based carbon capture unit is about 12–26% lower than that of Cansolv, and 32–43% lower than that of MEA. Among all CO_2BOLs, EEDIDA has the lowest capital cost, mainly because it has the lowest rich solvent viscosity and highest heat of absorption.

TABLE 1: SOLVENT PROCESS PARAMETERS

	Units	Current R&D Value			Target R&D Value
Pure Solvent		EEDIDA	MPMPA	MPMEA	
Molecular Weight	mol^{-1}	206	180	221	—
Normal Boiling Point	°C	158	157	177	—
Normal Freezing Point	°C	<0	<0	<0	—
Vapor Pressure @ 15°C	bar	2×10^{-4}	3×10^{-5}	1×10^{-4}	—
Manufacturing Cost for Solvent	\$/kg	10	10	10	5
Working Solution					
Concentration	kg/kg	0.96	0.97	0.94	—
Specific Gravity (15°C/15°C)	-	0.86	0.93	1.09	—
Specific Heat Capacity @ STP	kJ/kg-K	2.02	2.36	2.09	—
Viscosity @ 15°C	cP	4.72	12.03	—	—
Absorption					
Pressure	bar	1.01	1.01	1.01	—
Temperature	°C	35	35	35	—
Equilibrium CO_2 Loading	mol/mol	0.35	0.27	0.30	—
Heat of Absorption	kJ/mol CO_2	76	64	60	—
Solution Viscosity	cP	18.4	29.2	207.6	—
Desorption					
Pressure	bar	2.3	1.8	1.8	—
Temperature	°C	87	101	100	—
Equilibrium CO_2 Loading	mol/mol	0.11	0.07	0.07	—
Heat of Desorption	kJ/mol CO_2	76	64	60	—
Proposed Module Design		*(for equipment developers)*			
Flue Gas Flowrate	kg/hr			3.35E6	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90		95	—
Absorber Pressure Drop	bar			<0.1	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$			pending	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of inorganic salt and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical.

Solvent Foaming Tendency – Depending on the tendency to foam, anti-foaming agents may need to be added to the solvents during testing.

Flue Gas Pretreatment Requirements – It is assumed that a pre-scrubber will be used to reduce sulfur dioxide (SO_2) and NO_X to about 5 parts per million (ppm) and 50 ppm, respectively. Fuel gas chilling is required to maintain water balance in the system.

Process Design Concept – Two-stage flash configuration is considered for solvent regeneration for less capital investment and less energy consumption for CO_2 compression.

TABLE 2A: POWER PLANT CARBON CAPTURE ECONOMICS (2-EEDIDA)

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	39.2	—
Cost of Carbon Avoided	\$/tonne CO_2	58.7	—
Capital Expenditures	\$/MWhr	45.1	—
Operating Expenditures	\$/MWhr	59.6	—

Cost of Electricity	\$/MWhr	104.7	—

TABLE 2B: POWER PLANT CARBON CAPTURE ECONOMICS (2-MPMPA)

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	40.6	—
Cost of Carbon Avoided	\$/tonne CO_2	60.6	—
Capital Expenditures	\$/MWhr	46.0	—
Operating Expenditures	\$/MWhr	60.0	—
Cost of Electricity	\$/MWhr	106.0	—

TABLE 2C: POWER PLANT CARBON CAPTURE ECONOMICS (2-MPMEA)

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	42.2	—
Cost of Carbon Avoided	\$/tonne CO_2		—
Capital Expenditures	\$/MWhr		—
Operating Expenditures	\$/MWhr		—
Cost of Electricity	\$/MWhr		—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced, including fuel cost and variable and fixed operating costs.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced, including fuel cost, variable and fixed operating costs, and transportation, sequestration, and monitoring cost.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – Case B12B, a 650-megawatt (MW) supercritical pulverized coal plant, in NETL's Rev. 4 Report, "Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity," was used as the baseline for TEA. The flue gas composition, carbon capture rate, and economic assumptions were set the same as the Rev 4 report. The coal flow rate was adjusted to achieve a net power output of 650 MW.

Scale of Validation of Technology Used in TEA – Current TEA was conducted based on the process model developed in Aspen Plus. These CO_2BOLs have been tested in an LCFS recirculating roughly 3–4 L solvent and processing simulate flue gas. The absorber size in the LCFS is about 2.5E-8 of the absorber size required in a 650-MW power plant.

Qualifying Information or Assumptions – The manufacturing cost of solvent is set to \$10/kg.

technology advantages

- Low solvent volatility.
- Lower CO_2-rich viscosity than early versions of CO_2BOL solvents.
- Significantly lower regeneration energy compared to aqueous amines.

- The project leverages active collaborations with industry, national labs, and academia through the Carbon Capture Simulation for Industry Impact (CCSI^2) Program.

R&D challenges

- The hydrophobic MPMPA and MPMEA solvents may promote foaming during continuous flow testing on PNNL's LCFS testing cart, which could lead to decreased capture efficiency, disrupt pumping flow rates, and potentially aerosolize solvent outside of the absorber column.
- The higher viscosity may adversely impact the performance of the AP solvents during testing and prohibit collection of data in an operable L/G regime.
- Chemical impurities (NO_X and SO_X) in flue gas during continuous-flow testing may adversely impact solvent performance by forming heat-stable salts or nitrosamines.
- Achieving DOE's $40/tonne cost target.

status

The project team successfully operated PNNL's LCFS with each of the three new solvents and demonstrated 40-hour steady-state operations under realistic flue gas conditions. For EEDIDA and MPMPA, more than 90% CO_2 capture rates were achieved. For MPMEA, a CO_2 capture rate more than 83% was achieved. No visible degradation, foaming, or solid precipitation were observed during the LCFS testing.

The results of the TEA showed a carbon capture cost for EEDIDA of about $47.7/tonne with SS, which is 18% lower than Cansolv (NETL's baseline) and 4% lower than EEMPA. The carbon capture cost of EEDIDA with TSF can be reduced to $46.6/tonne, of which the cost can be further reduced by optimizing the regeneration pressure of EEDIDA. The projected carbon capture costs of MPMPA are $41.6/tonne CO_2 with the SS configuration, and $40.6/tonne CO_2 with the TSF configuration, which are close to DOE's $40/tonne CO_2 target.

available reports/technical papers/presentations

Heldebrant, D, et al. "Parametric Testing of CO_2-binding Organic Liquids (CO_2BOLs) to Enable Industry Adoption," Final Review and Project Closeout Meeting, December 2022.

Heldebrant, D, et al. "CO_2-binding Organic Liquids (CO_2BOLs) Enabling Energy- and Cost-Effective Carbon Capture from Point-Sources: At or Below $40/tonne at High Carbon Capture Rates," December 2022. *https://www.osti.gov/pages/servlets/purl/1922381*.

Heldebrant, D. "Parametric Testing of CO_2BOLs to Enable Industry Adoption (FWP-76270)." NETL Carbon Management and Oil and Gas Research Project Review Meeting - Point Source Capture - Lab, Bench, and Pilot-Scale Research, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Heldebrant.pdf*.

Heldebrant, D. "Molecular Refinement of Transformational Solvents for CO_2 Separations," Presented at the 2020 CO_2 Integrated Project Review Meeting – Carbon Capture, October 2020. *https://netl.doe.gov/sites/default/files/netl-file/20VPRCC_Heldebrant.pdf*.

Freeman, C. "Molecular Refinement of Transformational Solvents for CO_2 Separations," Presented at the 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/C-Freeman-PNNL-Molecular-Refinement.pdf*.

"Low-Viscosity, Water-Lean CO_2BOLs with Polarity-Swing Assisted Regeneration," Presented at the 2018 NETL CO_2 Capture Technology Meeting, August 13, 2018. *https://www.netl.doe.gov/sites/default/files/event-proceedings/2018/co2%20capture/monday/D-Heldebrant-PNNL-Polarity-Swing-Regeneration.pdf*.

Universal Solvent Viscosity Reduction via Hydrogen Bonding Disruptors

primary project goal

Liquid Ion Solutions LLC, along with Carnegie Mellon University (CMU) and Carbon Capture Scientific LLC, performed laboratory-scale development and evaluation of novel additives that lower the viscosity of water-lean amine solvents (amine>water) for post-combustion carbon dioxide (CO_2) capture. The project focused on developing a solvent additive that minimizes the formation of long-range hydrogen bonding (HB) networks, in turn decreasing the solvent viscosity and improving the process economics.

technical goals

- Perform computer simulations to understand the molecular interactions in water-lean CO_2 capture solvents.
- Synthesize and characterize HB disruptor molecules with the specific goal of significantly reducing the viscosity of water-lean carbon capture solvents in the presence of CO_2.
- Conduct proof-of-concept performance testing to demonstrate the effectiveness of HB disruptors in lowering viscosity.
- Optimize HB disruptor chemical structure based on insights gained from computational modeling and experimental proof-of-concept studies.
- Demonstrate the effectiveness of the optimized HB disruptors in the presence of synthetic flue gas.
- Achieve 95% capture efficiency with a viscosity below 10 cP for the rich solvents.

technical content

Liquid Ion Solutions, in partnership with CMU and Carbon Capture Scientific, has developed additives that significantly reduce the viscosity of water-lean amine CO_2 capture solvents by breaking the long-range electrostatic and hydrogen bonding into clusters upon the absorption of CO_2, as illustrated in Figure 1. The project work included development of computer simulation to understand the molecular interaction in water-lean CO_2 capture solvents; design, synthesis, and performance testing of HB disruptors as additives to reduce solvent viscosity; optimization of the HB disruptor; and performance testing of the optimized additive in the presence of synthetic flue gas.

The project team developed an ab initio molecular model and performed computer simulation to develop the relationship between HB and viscosity. The team then performed quantitative analysis of the additive on the viscosity of the solvent. The team completed a computational comparative study on a range of

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Novel Additives for Water-Lean Amines

participant:
Liquid Ion Solutions LLC

project number:
FE0031629

predecessor projects:
N/A

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partners:
Carbon Capture Scientific;
Carnegie Mellon University

start date:
10.01.2018

percent complete:
100%

organic functional groups, such as ethers, esters, cyclic carbonates, alkanes, and ammonium salts for their effect on viscosity, gaining key insights into molecular interactions and the impact of various functional groups and molecular shapes on viscosity.

Assisted with molecular simulation insights, the project team conducted additive synthesis and testing, including a proof-of-concept study, additive screening, optimization, and synthetic flue gas testing.

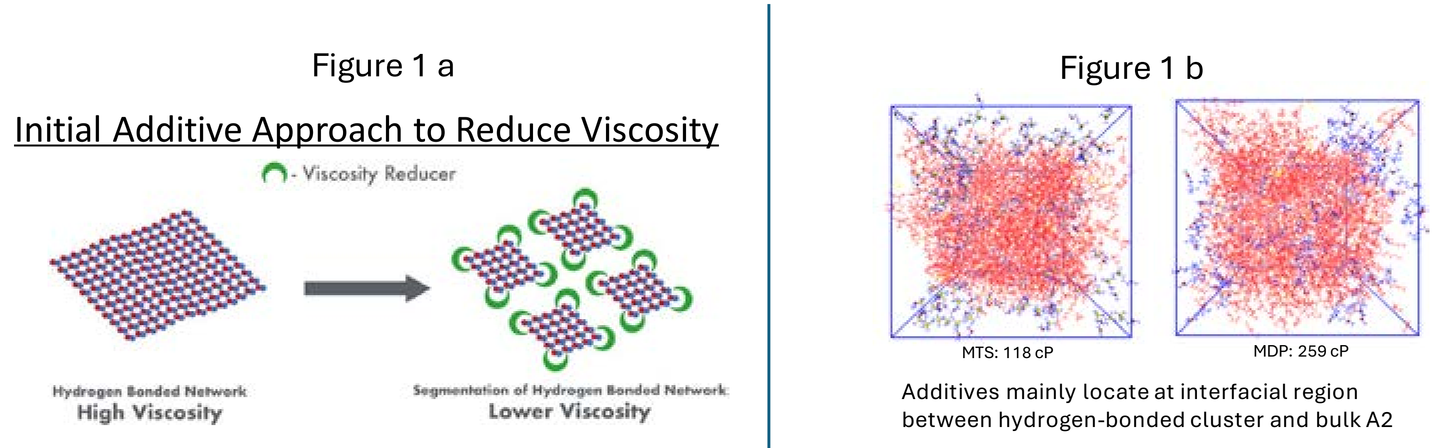
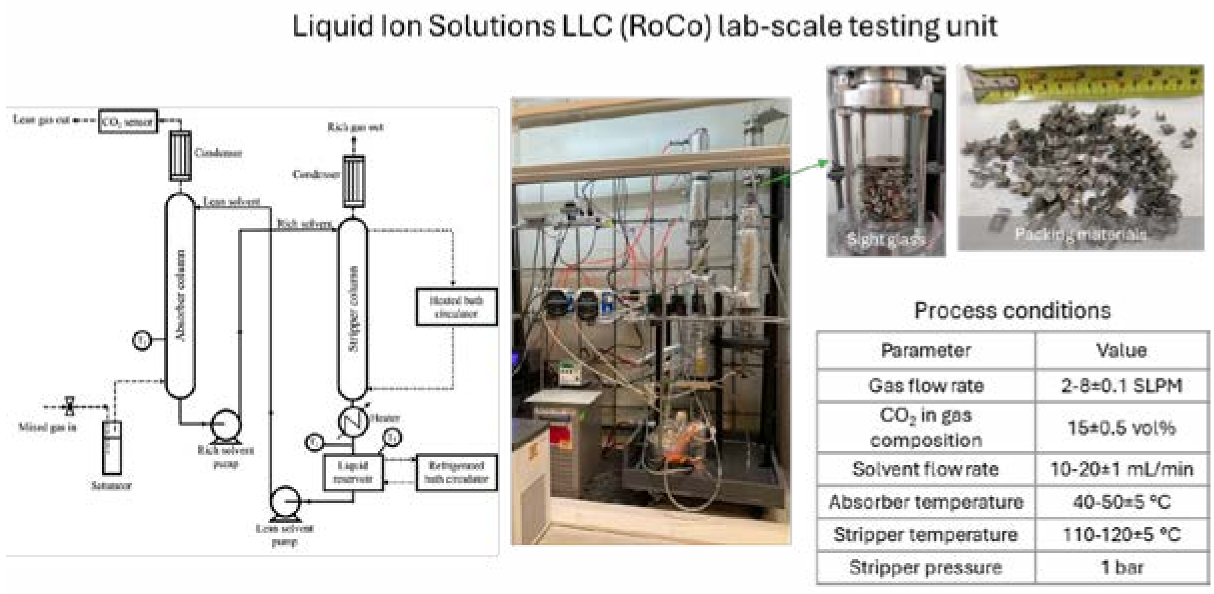


Figure 1a: Illustration of fully HB network (left) and the breakage of the HB network by addition of HB acceptors (right) as the initial approach on reducing the viscosity of water-lean solvents. Figure 1b: Computational insight and proof that additive approach results in segregation resulting in reduced viscosity.

The experimental proof-of-concept study proved that the HB acceptors result in significant decrease of viscosities. Detailed additive screening (exploring various functionalities and molecular structures) has been performed using computational insights (Figure 1b). Few promising additives showed excellent reduction in viscosity (30–41%) at 5% additive loading, and more than 50% viscosity reduction at 10% additive loading for the model solvents. The team also performed complex screening studies on additive loadings and mixing effect among additives using the design of experiments. Based on multiple screening experiments, the best-performing additive-solvent candidate was selected for continuous synthetic flue gas testing.



Process conditions

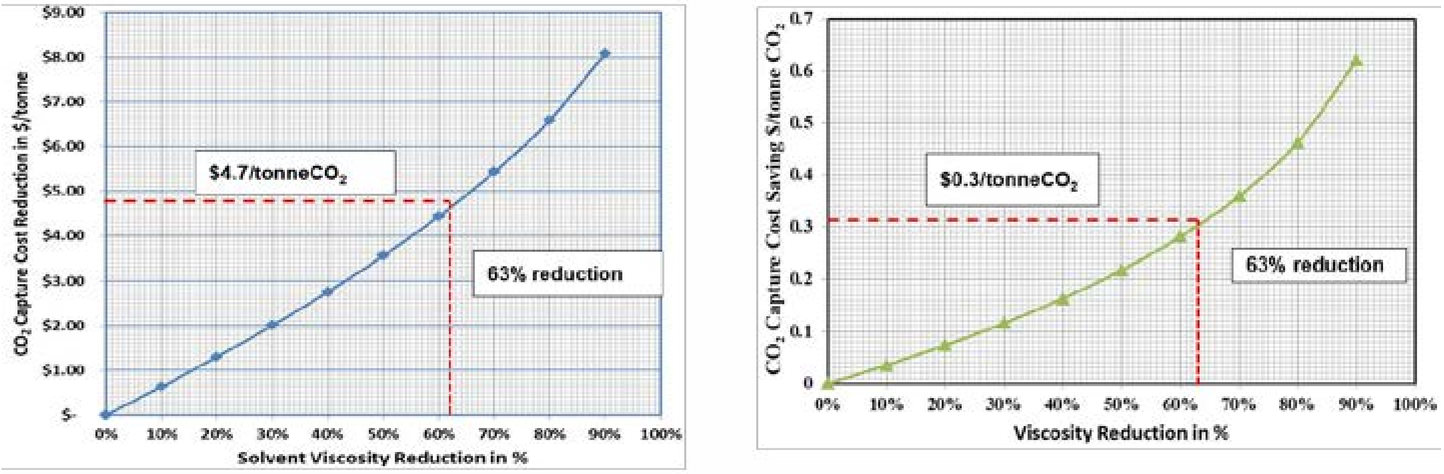
Parameter	Value
Gas flow rate	2-8±0.1 SLPM
CO_2 in gas composition	15±0.5 vol%
Solvent flow rate	10-20±1 mL/min
Absorber temperature	40-50±5 °C
Stripper temperature	110-120±5 °C
Stripper pressure	1 bar

Figure 2: Image of the test system and processing conditions used in this program.

A 100-hour continuous absorption/desorption study was conducted under simulated flue gas using a laboratory-scale continuous capture and separation system (Figure 2). No degradation (for both solvent and additive) was observed based on the gas chromatography (GC) results of the solvent samples collected from the continuous study. The solvent/additive solution resulted in 63% reduction in viscosity with greater than 95% capture efficiency.

Initial engineering analysis on the data obtained showed that significant capital cost reduction is achieved. A $5 per metric ton of CO_2 capture cost saving is achieved by reducing the viscosity as illustrated in Figure 3. Initial health and safety assessment of the additives was performed showing that the additives have low physical, chemical, and health hazards associated with them due to their chemical inertness and higher molecular weight.

Impact of solvent viscosity reduction on CO_2 capture cost



The total benefit: $4.7+0.3=$5.0/tonneCO_2 captured

The net benefit: $4.32~$4.86/tonne CO_2 captured, surpassing the success criterion of $2/tonne$CO_2$

Figure 3: Impact of solvent viscosity reduction on the capital cost saving.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	140-260	<140
Normal Boiling Point	°C	226.8	226.8
Normal Freezing Point	°C	4.4	4.4
Vapor Pressure @ 15°C	Bar	<0.01	<0.01
Manufacturing Cost for Solvent	$/kg	$20 at scale	$20 at scale
Working Solution			
Concentration	kg/kg	95/100	50/100
Specific Gravity (15°C/15°C)	—	1.02-1.07	1.05
Specific Heat Capacity @ STP	J/g/°C @25	2.0-3.0	2.0-3.0
Viscosity @ STP	cP (20 °C)	2-6	12.5
Absorption			
Pressure	Bar	1.01	1.01
Temperature	°C	40	40
Equilibrium CO_2 Loading	mol/mol	0.48	0.48
Heat of Absorption	kJ/mol CO_2	70-80	0-80
Solution Viscosity @40°C	cP	2-6	20
Desorption			

Pressure	Bar	1	1
Temperature	°C	120	120
Equilibrium CO_2 Loading	mol/mol	0.140	0.33
Heat of Desorption	kJ/mol CO_2	70-80	70-80.0
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	2,716,229	
CO_2 Recovery, Purity, and Pressure	% / % / bar	99/99.9/1	
Absorber Pressure Drop	Bar	0.05	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	200	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hour of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical (additive).

Solvent Foaming Tendency – None.

Waste Streams Generated – CO_2.

Process Design Concept – Standard absorption/desorption column.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	54.3	56
Cost of Carbon Avoided	\$/tonne CO_2	83.3	86
Capital Expenditures	\$/MWhr	69.0	70.2
Operating Expenditures	\$/MWhr	70.3	70.6
Cost of Electricity	\$/MWhr	139.3	140.8

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – The cost data in Table 2 are calculated based on the Baseline Report (2016, rev.3) Case B12B. It is assumed that the absorption/stripping columns and heat exchange equipment take 60% and 25% of the capital cost of the capture section, excluding compression and drying. It is also assumed that the viscosity of the baseline solvent (CANSOLV solvent) can be reduced 50% after adding the optimal additive developed in this project. Fifty percent is used because several additive-amine solvent systems reached viscosity lower than 50% of a PZ/MDEA (15/35 wt%) mixed aqueous solvent. It is further assumed that the unit prices of the CANSOLV solvent and the additive are $5/kg and $15/kg, respectively.

Scale of Validation of Technology Used in Techno-Economic Assessment (TEA) – The validity of the additive approach has been proven at the laboratory scale showing reduction in cost of capture.

Qualifying Information or Assumptions – Several new solvent/additive candidates were developed in this project, which could provide better economic performance than the current baseline solvent. Further detailed information is provided in the final report.

technology advantages

The development of an HB disruptor additive capable of significantly reducing the viscosity of any water-lean chemical solvent will allow for increased heat exchanger and mass transfer efficiency, thus lowering the capital and operating costs for CO_2 capture.

- Additives reduced the viscosity of amine solvents by up to 60% upon CO_2 loading.
- Amine additive solvent achieved up to 95% capture efficiency under simulated flue gas containing 15 vol% CO_2.

- Preliminary engineering analysis showed that a 50% reduction in viscosity will potentially save capital cost by about 16% and achieve \$3.8/tonne CO_2 in capture cost savings without considering additive cost.
- Cost-benefit analysis demonstrated that the net benefit generated from adding a viscosity-reducing agent into the CO_2 capture solvent was significant, and that the cost of an additive itself compared to the benefit was insignificant.

R&D challenges

- Determining effective additive molecules that can disrupt the overall HB network and reduce the viscosity of a water-lean solvent upon CO_2 uptake.
- Optimization of additive package maximizing viscosity-reduction effect without compromising CO_2 uptake capability for water-lean solvents.
- Identifying process conditions for the performance testing of solvent candidates using the laboratory-scale continuous capture and separation system.
- Detailed studies are needed to further this technology and understand the impact of various contaminants on the solvent performance.

status

The laboratory-scale additive development was completed on March 31, 2022. The team is evaluating its options on how to further this technology as the energy landscape is changing rapidly. The project team completed the testing and benchmarking of the optimized solvent-additive systems in the synthetic flue gas. The team has completed performance testing on a formulated model solvent using a lab-scale continuous capture system. A 100-hour continuous absorption and desorption run was completed, showing constant performance and little degradation using a GC-FID technique. A refined cost-benefit analysis based on the data collected from the 100-hour test was completed, showing significant reduction in cost when compared to the Baseline Case B12B. The updated cost-benefit analysis has been included in the final report.

available reports/technical papers/presentations

Zhou, X., Nulwala, H., Li, Y., Kim, H., Chen, S., “Universal Solvent Viscosity Reduction Via Hydrogen Bonding Disruptors,” Final Technical Report, June 2022. *https://www.osti.gov/biblio/1873907*.

Zhou, X., Brown, D., Nulwala, H., Liu, J., Li, Y., Kim, H., Chen, S., “Universal Solvent Viscosity Reduction Via Hydrogen Bonding Disruptors,” Presented at the 2021 NETL Carbon Management and Oil Gas Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Zhou.pdf*.

Zhou, X., Brown, D., Nulwala, H., Liu, J., Li, Y., Kim, H., Chen, S., “Universal Solvent Viscosity Reduction Via Hydrogen Bonding Disruptors,” Presented at the 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/X-Zhou-LIS-Solvent-Viscosity.pdf*.

Zhou, Xu; Nulwala, Hunaid B.; Kim, Hyung; Chen, Shiaoguo, "Universal solvent viscosity reduction via hydrogen bonding disruptors," From Abstracts of Papers, 257th ACS National Meeting & Exposition, Orlando, FL, United States, March-April 2019.

Nulwala, H., “Universal Solvent Viscosity Reduction Via Hydrogen Bonding Disruptors,” Poster at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/H-Nulwala-LIon-Solutions-Solvent-Viscosity-Reduction.pdf*.

Process Intensification for Carbon Capture

primary project goal

Altex Technologies Corporation, in partnership with Pennsylvania State University (PSU), developed an integrated temperature and pressure swing (ITAPS) carbon capture system that utilizes advanced molecular basket sorbents (MBSs) on microchannel heat exchangers, which can be quickly cycled between carbon dioxide (CO_2) sorption from coal-derived syngas and desorption into low-pressure steam exhausted from steam turbines in an integrated gasification combined cycle (IGCC) power system. This would replace the typical three-stage Selexol system (for acid gas removal and pre-combustion carbon capture in the context of IGCC) with smaller and more energy-efficient desorption and sorption units.

technical goals

- Design a prototype-scale system for Compact Rapid Cycling CO_2 Capture (CRC3) to improve the MBSs for higher heat- and mass-transfer rates.
- Improve sorbent capacity and sorption/desorption rates.
- Demonstrate heat integration of sorption and desorption processes.
- Conduct prototype-scale testing of a post-combustion, capture-geared prototype unit on actual flue gas at 10–50 standard liters per minute (slpm), equivalent to 0.2–1.0 kilowatt-electric (kWe), and perform techno-economic analysis (TEA) of the system.

technical content

The project is currently in Phase IIB, with the goal of developing the CRC3 system that would extend the concept of using the MBSs on microchannel heat exchangers to post-combustion applications. Work is continuing to reduce the size (and therefore costs) of the Altex CO_2 capture system by tight integration of the heats of sorption and desorption. The Altex team previously developed the ITAPS process with a view to produce a low-cost CO_2 capture technology that leverages process intensification principles (i.e., process capital and energy costs of the capture systems are shared with other unit operations of the power plant). In ITAPS, Altex-developed microchannel heat exchangers were wash-coated with PSU's advanced MBSs. By wash-coating the MBS on the microchannel heat exchanger, high heat- and mass-transfer rates were obtained. These high rates allow for quick cycling between CO_2 sorption and desorption. This should allow smaller sorption units with a lower capital cost than a typical three-stage Selexol system. Operating costs are also lower than a three-stage Selexol system because the system can operate at lower pressures and does not require circulation of a liquid amine sorbent. In terms of process integration, Figure 1 depicts the ITAPS units' process with boiler feed water flows and steam turbine flows (for sorption and desorption modes, respectively), which would be encountered in integrating an ITAPS system within the context of an IGCC cycle or a traditional power plant.

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Post Combustion Power Generation PSC

key technology:
Sorbents

project focus:
Molecular Basket Sorbents on Microchannel Heat Exchangers

participant:
Altex Technologies Corporation

project number:
SC0013823

predecessor projects:
N/A

NETL project manager:
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principal investigator:
Kenneth Lux
Altex Technologies Corporation
ken@altextech.com

partners:
Pennsylvania State University; NCCC

start date:
06.08.2015

percent complete:
98% (combined Phases I, II and IIB)

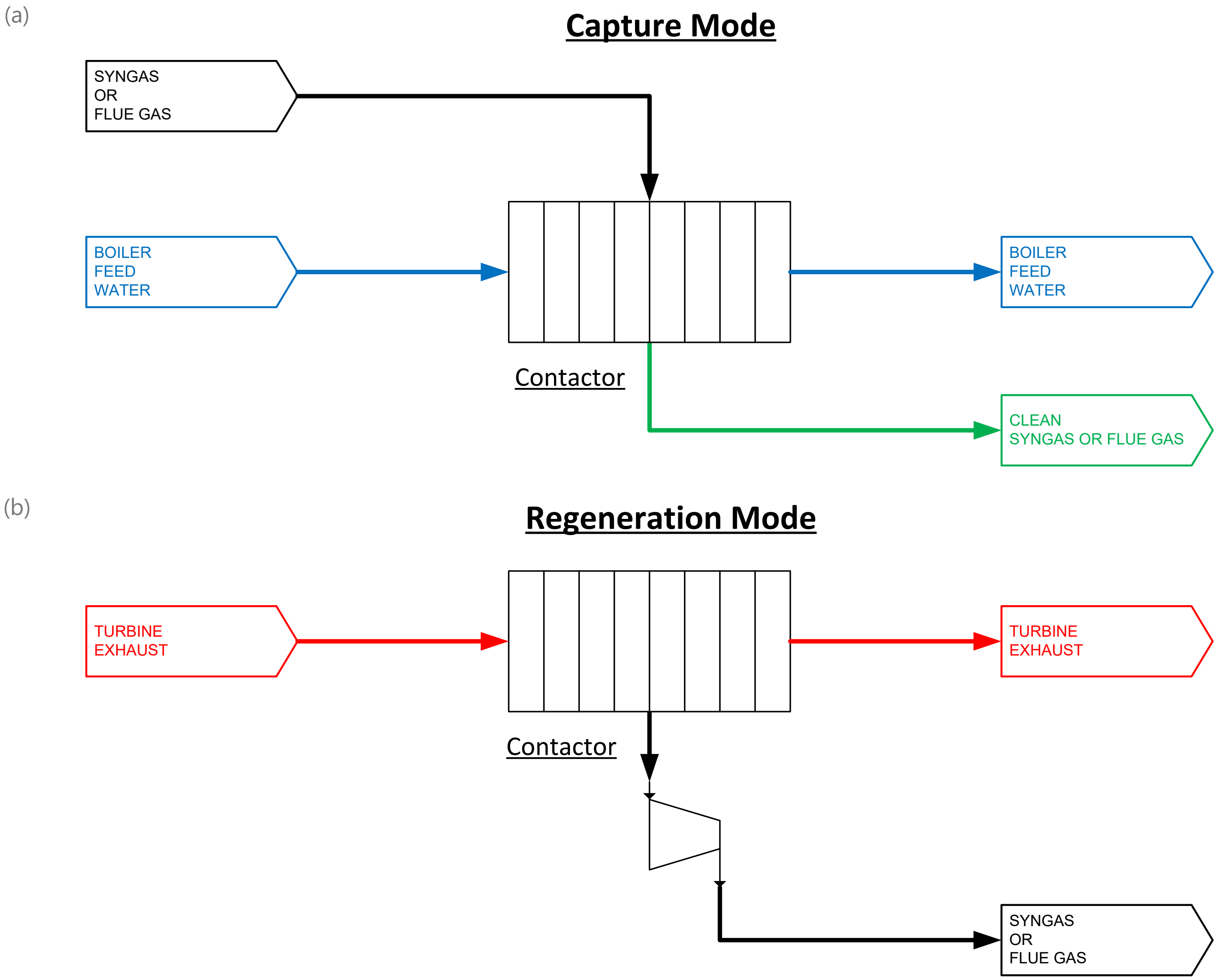

Figure 1: Simplified process flow diagram for the Altex integrated temperature and pressure swing carbon capture process. (a) Capture Mode—Cooling provided by boiler feed water; (b) Regeneration Mode—Heating provided by turbine exhaust.

PSU has been responsible for development of the sorbents they term as MBSs. The idea is to load CO_2-philic polymers such as polyethyleneimine (PEI) onto high-surface-area nano-porous inorganic materials such as MCM-41 and SBA-15, thereby increasing the accessible sorption sites per weight/volume of sorbent and improving the mass-transfer rate in sorption/desorption processes by increasing the gas-PEI interface. These sorbents can selectively adsorb large quantities of CO_2 compared to typical sorbents such as zeolites or activated carbons. The sorbents also pack CO_2 in a condensed form in the mesoporous molecular sieve basket and hence show a high CO_2 capacity and selectivity. The basic idea for preparation of MBS is illustrated in Figure 2.

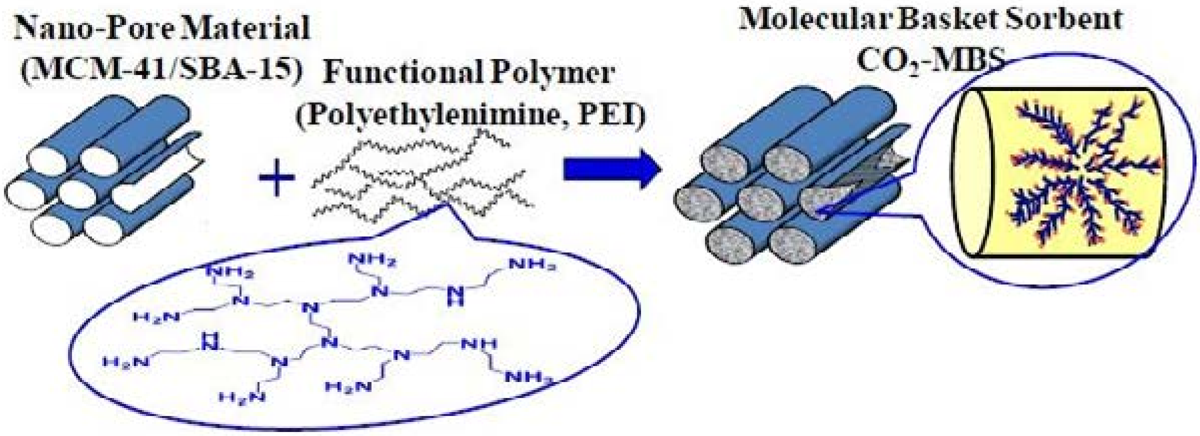

Figure 2: Principle for preparation of MBS.

The sorbents are applied by wash-coating the surfaces of microchannel heat exchangers. Altex is leveraging their expertise in design of these heat exchangers, which have been deployed in a wide range of sizes (fractions of kW to multiple megawatt [MW] capacities); materials (aluminum, copper, stainless steel, high-temperature alloys, corrosion-resistant alloys); and flow configurations (counter-flow, cross-flow). These have been designed for use in several fields, including oil and gas platform processes, separators, liquefied natural gas (LNG) processing, chillers, heat pumps, fuels reforming, waste heat power systems, and electronics cooling applications. In particular, Altex is currently producing thousands of an energy management product for the military that uses ISO9001:2015 certified processes. This product has been qualified by field tests, including shock, vibration and corrosion testing. For ITAPS, Altex developed the bench-scale prototype depicted in Figure 3. Note that finned inserts within the unit provide ample surface area onto which MBS can be wash-coated. In the pre-combustion capture case, the process stream of syngas containing CO_2 passes through the absorber. Extensive surface area facilitates efficient heat transfer needed to accomplish the sorption and desorption steps for capture of CO_2.

Figure 3: Illustration of ITAPS microchannel heat exchanger units/reactors. Highly efficient, low-cost heat exchanger.

In earlier project phases, PSU advanced the MBS material to improve the CO_2 capacity, and Altex demonstrated and established the feasibility of wash-coating this sorbent onto the microchannel heat exchanger. Advancements were made in reducing the cost of the material comprising the solid matrix, improving the mechanism of loading of the polymer into the solid matrix of the sorbent, and improving the process for wash-coating the reactor.

The bench-scale system prototype was tested for multiple cycles of CO_2 sorption/desorption, validating the feasibility of cycling and heat recovery. Data from these tests were used to determine the required wash-coat thickness needed to meet the target cost of electricity (COE) and ensure that this thickness can maintain a high effectiveness. From findings of the testing, analysis showed that the ITAPS process could significantly reduce cost of capture and COE.

Currently, the project is extending application of this technology into the area of post-combustion CO_2 capture. Figure 4 depicts the process concept for the CRC3 system, which deploys the Altex technology to capture of CO_2 from post-combustion flue gas.

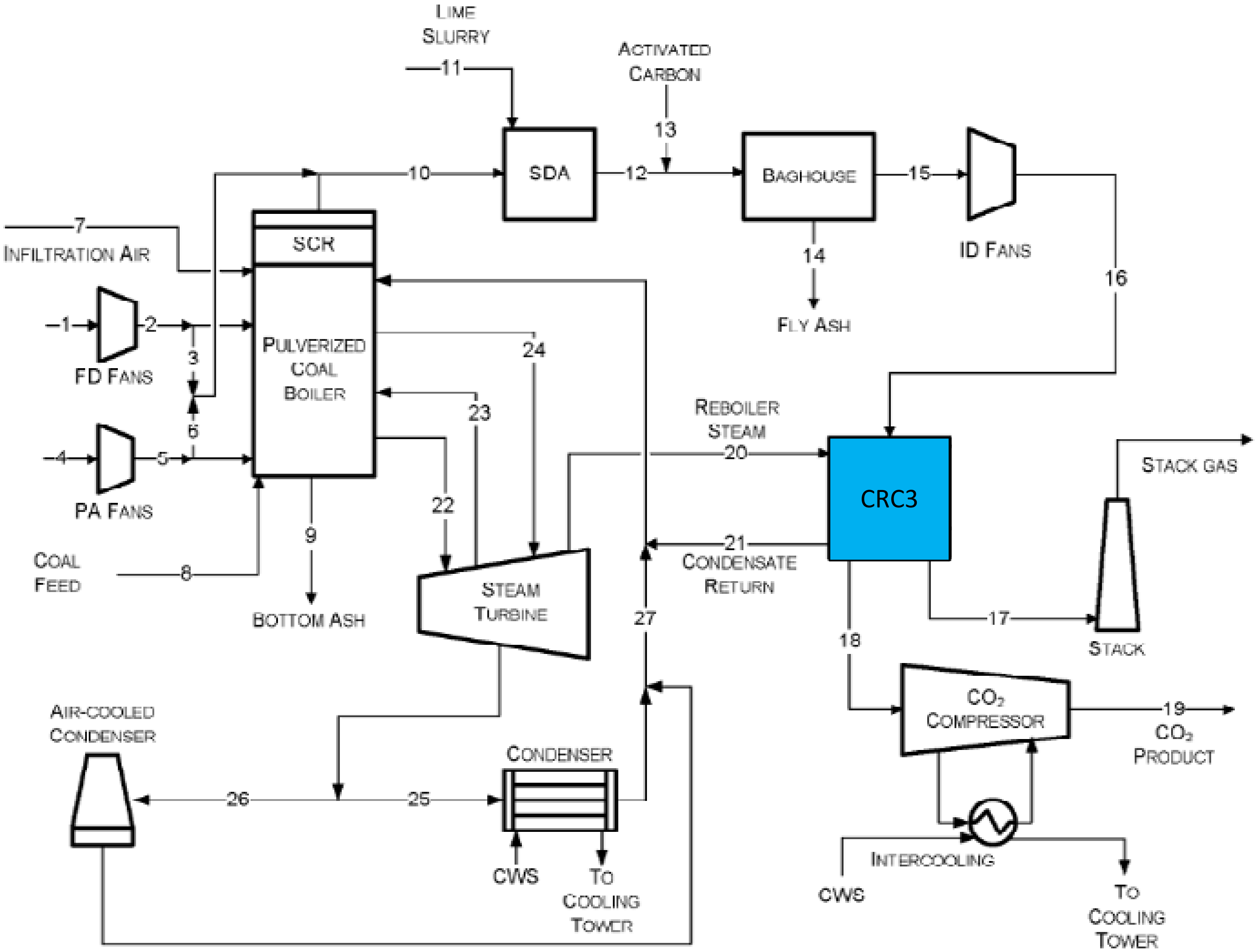

Figure 4: Process concept for the CRC3 system.

Within this post-combustion capture context, current work is targeting better process approaches to integrate heat of sorption with the heat of desorption and to further improve sorbent performance, all of which are intended to reduce capture costs and enable the commercial potential of this technology.

technology advantages

- The CRC3 approach of applying sorbent to the high surface area, wash-coated mini-channel reactor walls enables indirect heating and cooling of the sorbent.
- The sorbent on the mini-channel reactor walls remains fixed in place and is not subject to particle attrition resulting from particle-particle contact, as would occur in a fluidized bed.
- The dispersion of sorbent over the high surface area of the walls of the mini-channel reactor enables high mass-transfer rate of CO_2 to the sorbent.
- The pressure drop through the mini-channel reactor can be reduced relative to a packed-bed absorber, much in the same way that monolith-supported catalysts reduce the pressure drop in selective catalytic reactors (SCRs) and, more commonly, in automobile catalytic converters. This will enable ITAPS to handle high gas-flow rates.
- The CO_2 MBSs developed by PSU exhibit high capacity and operate at low-desorption temperatures and with lower heat of sorption, requiring less parasitic energy draw and thereby boosting plant net efficiency.
- The MBSs are engineered with specific chemical surface functionality, which allows for high CO_2 sorption capacities in high-humidity conditions.
- Sorbent performance and the CRC3 approach enable lower round-trip energy costs for a complete sorption-desorption cycle.
- Enabling the production of CRC3 reactors at low cost and integrating a carbon capture system with existing unit operations should result in lower capital and operating costs for CO_2 capture from coal-fired power plants.

R&D challenges

- Operation at lower CO_2 partial pressures in flue gas as compared to syngas used in Phase I and Phase II.
- Tightly integrating the recovery of heat generated during sorption with the delivery of heat required for desorption.
- Operating with real flue gas.

status

Altex Technologies Corporation developed a bench-scale ITAPS unit constructed utilizing Altex's highly effective, low-cost microchannel heat exchangers coated with molecular-basket sorbents previously developed and optimized by PSU's EMS Energy Institute. A prototype process simulating a portion of the power plant was designed, including fabrication of a prototype reactor. Testing of the monolith element exhibited three-times better capacity than a packed-bed configuration for the capture and release of CO_2 absorption and desorption cycles. For post-combustion applications, the CRC3 system is being developed and tested at the prototype scale.

available reports/technical papers/presentations

N/A.

Plastic Additive, Sorbent-Coated, Thermally Integrated Contactor for CO_2 Capture ($PLASTIC4CO_2$)

primary project goal

GE Vernova (GEV) is developing a design for a plastic additive, sorbent-coated, thermally integrated contactor for carbon dioxide (CO_2) capture ($PLASTIC4CO_2$) for post-combustion CO_2 capture from natural gas combined cycle (NGCC) power plant flue gas. The key objective is to demonstrate an integrated system of plastic additive contactor and sorbents to capture 95% of CO_2 from NGCC flue gas and demonstrate the potential for a 15% or greater reduction in the levelized cost of electricity (LCOE) compared to liquid amine technologies.

technical goals

- Combine current sorbents with a binder coating to produce a sorbent-integrated, additive two-channel contactor.
- Synthesize, characterize and scale up components and evaluate for chemical and mechanical stability for accelerated testing.
- Perform a techno-economic analysis (TEA) to evaluate capital and operating costs and determine the lower LCOE with the new design.

technical content

GEV Advanced Research, in partnership with TDA Research Inc., the University of California Berkeley, and the University of South Alabama, proposes to develop a design for the $PLASTIC4CO_2$ system in an NGCC flue gas. The team's key objective will be to demonstrate an integrated system of plastic additive contactor and current metal/covalent organic frameworks (MOF/COF) sorbents to capture 95% of CO_2 from flue gas, and to demonstrate the potential for a 15% or greater reduction in LCOE.

The program will synthesize candidate sorbents that selectively remove CO_2 from natural gas turbine flue emissions. These sorbents are integrated with an additively manufactured two-channel plastic contactor using a coating process for the sorbent channel. The sorbent-integrated contactor is used to demonstrate removal of CO_2 from a simulated flue gas. The captured CO_2 will be desorbed with heat in the second channel to demonstrate that it can be desorbed at a lower energy than current liquid amine capture systems. A TEA will confirm energy and cost savings versus the baseline liquid amine process.

In 2019, power production accounted for more than 13 giga tonne (Gt) CO_2 per year and was about 40% of global energy-related CO_2 emissions. By 2040, even with renewables growth, these emissions are still expected to be nearly 10 Gt CO_2

program area:

Point Source Carbon Capture

ending scale:

Laboratory scale

application:

Post-Combustion Power Generation PSC

key technology:

Sorbents

project focus:

Structured Sorbent with Thermally Integrated Contactor

participant:

GE Vernova

project number:

FE0032132

predecessor projects:

N/A

NETL project manager:

Nicole Shamitko-Klingensmith
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principal investigator:

Albert Stella
GE Vernova
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partners:

GEV Gas Power; TDA Research Inc.; University of California – Berkeley; University of South Alabama

start date:

02.25.2022

percent complete:

79%

per year if left unabated by any carbon capture technology. Carbon capture, utilization and storage (CCUS) technology can be retrofit to existing fossil fuel power plants to provide significant reduction in CO_2 emissions and can provide flexibility in generating reliable power for the energy grid as demand outpaces renewable energy growth.

The PLASTIC4CO_2 system can be made from lower-density plastic materials and can reduce the energy requirements for carbon capture by 30% and capital costs by 50%. Implementation of this economical carbon capture system can remove 95% of CO_2 emissions from NGCC plant flue gas while maintaining the reliability of the U.S. power grid. The technology will reduce the LCOE by 15% compared to liquid amine technologies.

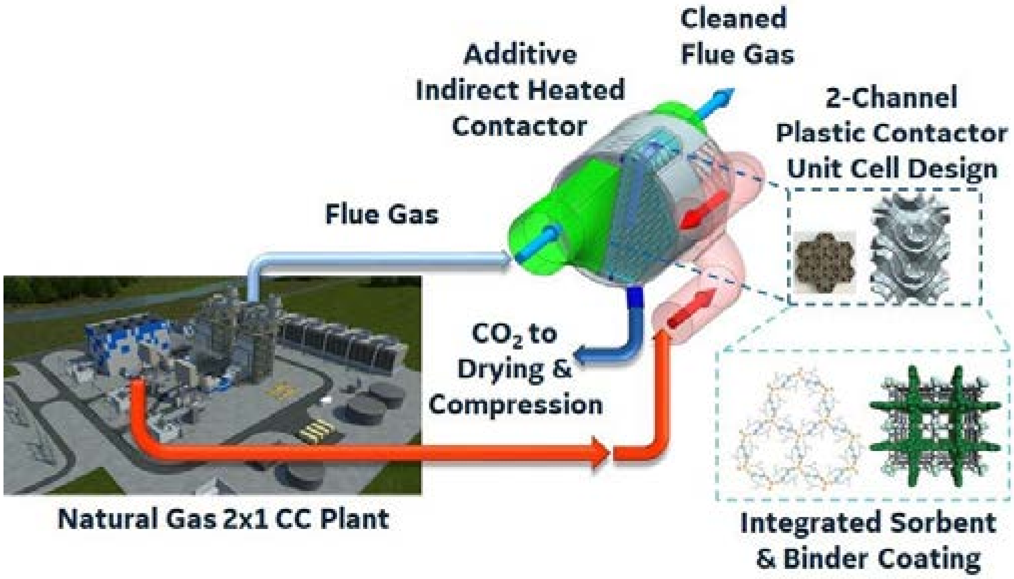


Figure 1: Schematic of the two-channel, sorbent-integrated plastic contactor for CO_2 capture from NGCC flue gas.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3		>1000
Bulk Density	kg/m^3	153	250
Average Particle Diameter	mm	<0.3	<0.3
Particle Void Fraction	m^3/m^3	0.37	0.4
Packing Density	m^2/m^3	1.1x10^8	2.0x10^8
Solid Heat Capacity @ STP	kJ/kg-K	1.2	<1.0
Crush Strength	kg$_f$	N.D.	1.5-3.0
Manufacturing Cost for Sorbent	$/kg	>250	<50
Adsorption			
Pressure	bar	1.0	1.0
Temperature	°C	25-40	>50
Equilibrium Loading	g mol CO_2/kg	3.55	>3.0
Heat of Adsorption	kJ/mol CO_2	50(dry)-80(wet)	<60
Desorption			
Pressure	bar	0.1	0.1
Temperature	°C	90-120	100
Equilibrium CO_2 Loading	g mol CO_2/kg	0.01-0.2	<0.5
Heat of Desorption	kJ/mol CO_2	64(dry)-81(wet)	<50

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

		Composition						
		vol%					ppmv	
Pressure	**Temperature**	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.7 psia	135°F	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Chemisorption with amine functionalized MOF.

Sorbent Contaminant Resistance – Amine susceptible to nitrogen oxide (NO_X) and sulfur oxide (SO_X) degradation.

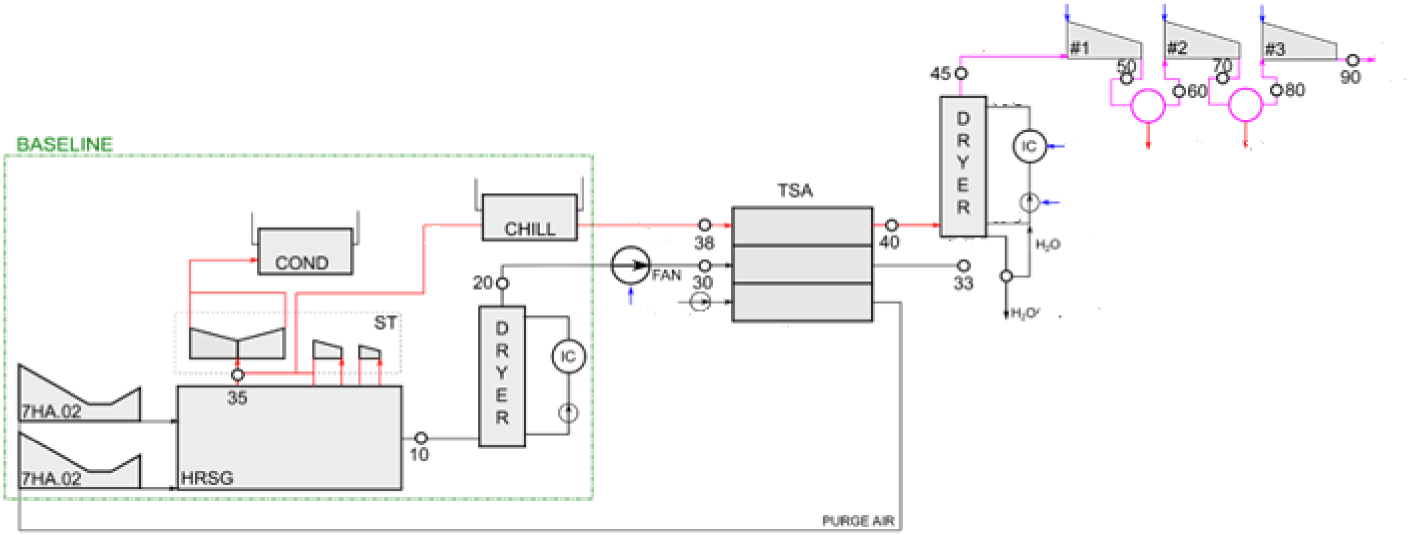
Sorbent Attrition and Thermal/Hydrothermal Stability – Less than 0.04% capacity fade/cycle.

Flue Gas Pretreatment Requirements – SO_X scrubbing and selective catalytic reduction (SCR) already in place on NGCC for NO_X reduction.

Sorbent Make-Up Requirements –25% per year assumed in TEA.

Waste Streams Generated – Process condensate water and compressor condensate water.

Process Design Concept –



Proposed Module Design – Additively printed contactor or plate-and-tube heat exchanger stacked modules with sorbent coating.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	75	53
Cost of Carbon Avoided	\$/tonne CO_2	100	75
Capital Expenditures	\$/tonne CO_2	52	35
Operating Expenditures	\$/tonne CO_2	23	18

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Calculations Basis – These cost calculations are based on using a one-dimensional material balance model for the adsorption of CO_2 and water from flue gas streams from 7FA and 7HA NGCC plants, using the stream data provided in the “Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity” report (*https://www.netl.doe.gov/energy-analysis/details?id=3745*) dated October 14, 2022. Energetics were determined using an energy balance model that includes the sensible heats for the contactor, sorbent, water and CO_2, as well as the latent heats of adsorption for the water and CO_2. The electrical loads and fan power were based on the models developed in the above reference. The lowest capital cost contactor used was an aluminum plate and copper tube heat exchanger coated with a GEV MOF-based sorbent.

Scale of Validation of Technology Used in TEA – This TRL 3 program tested small coated additive plastic and plate-and-tube contactors at 1 standard liter per minute (SLPM) and 20 SLPM gas flows to validate the sorbent capacity and mass-transfer coefficients (kinetics).

Qualifying Information or Assumptions –

- 30-minute cycle time (15 min adsorb, 15 min heat, desorb and cool)
- 7,500 hr./yr. capacity factor (per reference plant)
- 0.75mm thick film coating
- \$25/kg sorbent cost, \$20/kg additive material cost, and \$100/m^2 additive printing cost.
- 30% thermal heat integration for the plant.

technology advantages

- A key benefit of the two-channel geometry is its ability to physically partition the desorbed CO_2 from the regeneration fluid (e.g., steam) in independent channels.
- Indirect steam minimizes hydrolytic sorbent degradation and allows for low-pressure CO_2 desorption.
- Thermal advantages: the indirect steam-driven desorption avoids the energy required for bulk steam condensation in direct steam contactors.

R&D challenges

- Lack of a high-surface-area, low-pressure-drop contactor.
- Scaling and lowering of cost of additive printing needed to mature this technology.

status

The project team has completed design of the two-channel trifurcating architecture. They have Identified candidate plastics and associated printing modalities. The team also printed test parts for both materials and coatings studies, and measured sorbent capacity and kinetics. The TEA has been analyzed for one of the GEV candidate sorbents for both an additive contactor and a plate-and-tube contactor.

available reports/technical papers/presentations

Stella, Albert, "Plastic Additive, Sorbent-Coated, Thermally Integrated Contactor for CO_2 Capture (PLASTIC4CO_2)," presented at the 2024 FECM / NETL Carbon Management Research Project Review Meeting, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_Posters_Stella.pdf*.

Stella, Albert, "Plastic Additive, Sorbent-Coated, Thermally Integrated Contactor for CO_2 Capture (PLASTIC4CO_2)," presented at Budget Period 1 Review Meeting for Continuation to Budget Period 2, June 2023. *https://netl.doe.gov/projects/files/Plastic%20Additive,%20Sorbent-Coated,%20Thermally%20Integrated%20Contactor%20for%20CO2%20Capture%20(PLASTIC4CO2).pdf*.

Stella, Albert, "Plastic Additive, Sorbent-Coated, Thermally Integrated Contactor for CO_2 Capture (PLASTIC4CO_2)," presented at 2022 NETL Carbon Management Project Review Meeting - Point Source Carbon Capture, August 2022. *https://netl.doe.gov/projects/files/Plastic%20Additive,%20Sorbent-Coated,%20Thermally%20Integrated%20Contactor%20for%20CO2%20Capture%20(PLASTIC4%20CO2).pdf*.

Stella, Albert, "Plastic Additive, Sorbent-Coated, Thermally Integrated Contactor for CO_2 Capture (PLASTIC4CO_2)," presented at 2022 NETL Kickoff Meeting, May 2022. *https://netl.doe.gov/projects/files/Plastic%20Additive,%20Sorbent-Coated,%20Thermally%20Integrated%20Contactor%20for%20CO2%20Capture%20(PLASTIC4CO2).pdf*.

Intensified, Flexible, and Modular Carbon Capture Demonstration with Additively Manufactured Multi-Functional Device

primary project goal

Oak Ridge National Laboratory (ORNL) is developing and validating 3D-printed intensified devices (i.e., mass exchange packing with internal cooling channels) to effectively achieve mass and heat exchange functionalities in carbon dioxide (CO_2) absorption columns at the desired scale, using process intensification as an approach to reduce CO_2 capture cost in scaled-up processes.

technical goals

- Design, construction, and demonstration of a 0.3-m in diameter, 4.3-m tall column to validate enhanced CO_2 capture with the 3D-printed intensified devices.
- Demonstrate that this column can be modularized with the intensified devices for low aqueous advanced-solvent based capture.
- Demonstrate that the column can be easily configured to effectively capture CO_2 from different inlet gas CO_2 compositions (i.e., coal-fired power plants and natural gas-fired power plants) and during process transients (i.e., capacity ramping up and down anticipating the intermittent nature of renewable generations).

technical content

Process intensification is considered by the U.S. Department of Energy's (DOE) Office of Fossil Energy and Carbon Management (FECM) Carbon Capture Program as one approach to reducing CO_2 capture cost in scaled-up processes. Process intensification with new equipment manufacturing methods has shown great potential in process footprint and construction cost reductions. Conventional solvent-based carbon capture equipment designs usually involve multiple unit operations and utilize sequentially coupled stages for mass transfer and heat transfer. In the work funded by the DOE/FECM Capture Program for FY 2018–2019 under Field Work Proposal (FWP)-FEAA130, the ORNL advanced manufacturing and chemical engineering research team has demonstrated that a 3D-printed intensified device (i.e., a mass exchange packing with built-in heat exchange channels at the device scale) can effectively achieve the mass and heat exchange functionalities at the desired scale. Testing of the 3D-printed intensified device was performed with a 0.2-m in diameter, 2.1-m tall, packed absorption column (Column A, Figure 1), and enhanced CO_2 capture was demonstrated for various gas and liquid flow rates for monoethanolamine (MEA).

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Post-Combustion Power Generation PSC

key technology:
Enabling Technologies

project focus:
3D-Printed Intensified Devices

participant:
Oak Ridge National Laboratory (ORNL)

project number:
FWP-FEAA384

predecessor projects:
FWP-FEAA130
FWP-FEAA375

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partners:
N/A

start date:
01.01.2021

percent complete:
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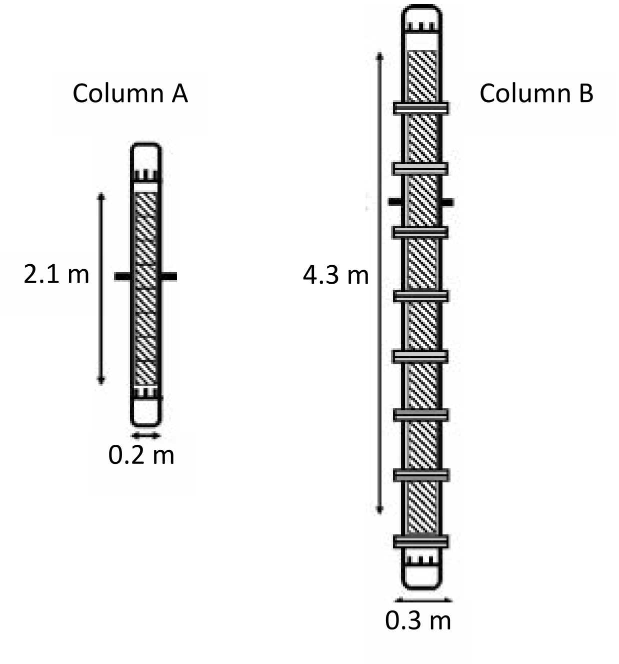

Figure 1: 0.2-m diameter, 2.1-m tall packed absorption column (Column A) and 0.3-m diameter, 4.3-m tall packed modular absorption column (Column B).

At-scale capture efficiency with different solvents and incoming flue gas compositions relies heavily on simultaneously approaching the thermodynamic and kinetic limits of the solvents at different locations of the absorber. Thus, a flexible and modular CO_2 capture demonstration column needs to be constructed with process intensification to further demonstrate and quantify the efficiency enhancements with one or more process-intensified devices with a scaled-up equipment design under more realistic operating conditions and under process transients.

Column B (Figure 1) is a scaled-up version of Column A. Special care was taken during column construction to minimize heat loss through the wall and to allow for easy transfer of the intensified device from one point along the column to another. The column was constructed with modular packing units that allow movement of the intensified device to different axial positions along the absorption column height. The column was also constructed with a liquid distributor, installed at the top of the column, based on the solvent's maximum flowrate. Special attention to safety is also key, and therefore, a heavy-duty ventilation system was installed to dilute CO_2 in case there is a leak. In addition, the research team developed the means to draw fluid samples along the column for chemical analysis. The objective is not only to be able to prove capture enhancement, but also to obtain experimental data needed for model development and validation.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	61	—
Normal Boiling Point	°C	170	—
Normal Freezing Point	°C	10.5	—
Vapor Pressure @ 20°C	bar	5.0e-04	—
Manufacturing Cost for Solvent	$/kg	—	—
Working Solution			
Concentration	kg/kg	0.30	—
Specific Gravity (15°C/15°C)	-	1.013	—
Specific Heat Capacity @ STP	kJ/kg-K	3.7	—

Viscosity @ STP	cP	2.5	—
Absorption			
Pressure	bar	atm.	—
Temperature	°C	40	—
Equilibrium CO_2 Loading	mol/mol	—	—
Heat of Absorption	MJ/kg CO_2	-1.8	—
Solution Viscosity	cP	2.0	—
Desorption			
Pressure	bar	1.8	—
Temperature	°C	120	—
Equilibrium CO_2 Loading	mol/mol	—	—
Heat of Desorption	MJ/kg CO_2	3.4	—
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	500	
CO_2 Recovery, Purity, and Pressure	% / % / bar	— — —	
Absorber Pressure Drop	bar	—	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD (flue gas desulfurization; wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	135°F	13.17	17.25	66.44	2.34	0.80	42	74

technology advantages

- Integrated regeneration of solvent reduces solvent inventory.
- Modular column design provides flexibility in testing packing configurations with commercial packing and the intensified device.

R&D challenges

- Temperature control using the intensified device may not be necessary for aqueous MEA in a small column, especially for natural gas flue gas.
- Controlling process transients may push the column operation into flooding conditions.
- Dimensional changes may be required to reduce pressure drop of the intensified device.

status

ORNL has finalized the design and construction phase of the larger column and based on design comparisons with Column A, the scale-up factor from Column A to Column B was approximately 10-fold in terms of flue gas-throughput of the absorption column. ORNL helped RTI develop a pilot-scale system to demonstrate enhanced CO_2 capture from a cement plant using intensified packing devices (DOE's Advanced Materials and Manufacturing Technologies Office [AMMTO]-funded project).

available reports/technical papers/presentations

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Tsouris C., "Intensified, Flexible, and Modular Carbon Capture Demonstration with Additively Manufactured Multi-Functional Device," 2022 Carbon Management Project Review Meeting, Pittsburgh, PA, August 2022.

Thompson, J. and Tsouris, C., "Intensified, Flexible, and Modular Carbon Capture Demonstration with Additively Manufactured Multi-Functional Device," Project Status Update, Pittsburgh, PA, May 2022.

Tarancon, A., et al. "2022 Roadmap on 3D Printing for Energy," JPhys Energy, 4, 011501 (2022). *https://doi.org/10.1088/2515-7655/ac483d*.

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Jang, G.G.; Thompson, J.A.; Sun, X.; Tsouris, C. "Process Intensification of CO_2 Capture by Low-Aqueous Solvent," *Chemical Engineering Journal*, **426**, 131240, (2021). doi.org/10.1016/j.cej.2021.131240

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A High-Efficiency, Modular Pre-combustion Capture System for 21st Century Power Plant Polygeneration Process

primary project goal

TDA Research, Inc. is developing a novel, modular pre-combustion carbon capture technology platform that integrates the water-gas-shift (WGS) reaction with a physical adsorbent to eliminate carbon dioxide (CO_2) emissions, coupled with a sulfur removal process, for a coal-based polygeneration system (i.e., co-production of power and chemicals) with increased efficiency and lower cost, and testing at small pilot-scale.

technical goals

- Achieve WGS/CO_2 sorbent bed CO_2 capacity of 4 wt.% to enable an overall carbon monoxide (CO) conversion greater than 98%.
- Develop and build a test unit for integrated WGS and CO_2 adsorption with a capacity of 10 standard cubic feet per minute (SCFM) of raw syngas from coal gasification.
- Capture CO_2 at 90+% purity via an integrated purification subsystem to 95+%.
- Enable desulfurization via a sulfur sorbent with stable working capacity in excess of 3 wt.% hydrogen sulfide (H_2S) and not more than 10% reduction in capacity over 200 cycles, assuming syngas with inlet sulfur in the 500–1,000 parts per million (ppm) range.
- Develop a techno-economic analysis (TEA) showing that the polygeneration system can capture CO_2 at $35/tonne or lower while meeting the above CO_2 purity and capture targets.

technical content

Syngas produced by gasification contains mostly hydrogen (H_2), CO, and CO_2. In order to affect a high degree of carbon capture, it is necessary to add steam to the syngas for reaction with CO via WGS to convert the CO to more H_2 and CO_2. Carbon dioxide is extracted from the shifted syngas, leaving mostly H_2, useful for multiple applications, including decarbonized power generation, chemicals synthesis (e.g., ammonia), and transportation fuels synthesis. Conventionally, a multistage WGS process with interstage cooling is required to attain substantial syngas conversion because WGS is an equilibrium-limited, exothermic reaction. The conventional multistage WGS process scheme is depicted in Figure 1. Although such WGS units can completely shift the CO to CO_2, they incur significant capital equipment and process cost, including a significant excess steam demand to suppress carbon formation on the WGS catalyst and help drive the WGS reaction to completion.

program area:
Point Source Carbon Capture

ending scale:
Small Pilot

application:
Pre-Combustion Power Generation PSC

key technology:
Sorbents

project focus:
Integrated PSA-WGS with Coal Syngas

participant:
TDA Research, Inc.

project number:
FE0031926

predecessor projects:
N/A

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partners:
Gas Technology Institute; Susteon; Clariant; University of California Irvine

start date:
10.01.2020

percent complete:
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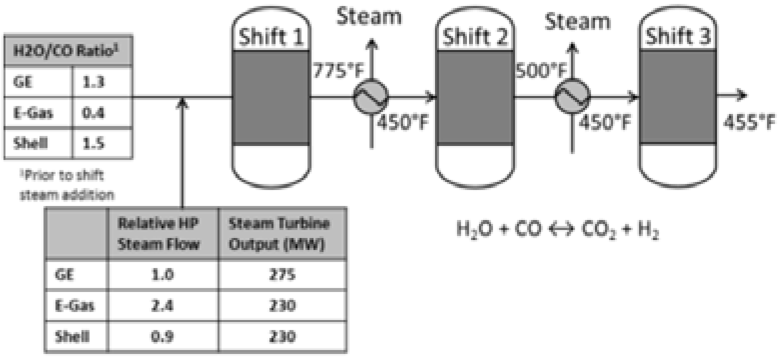


H2O/CO Ratio[1]	
GE	1.3
E-Gas	0.4
Shell	1.5

[1]Prior to shift steam addition

	Relative HP Steam Flow	Steam Turbine Output (MW)
GE	1.0	275
E-Gas	2.4	230
Shell	0.9	230

Figure 1: Three-stage, conventional WGS unit.

TDA's process approach seeks to achieve high CO conversion at low steam-to-CO ratios by combining, in the same bed, the WGS catalyst with a CO_2 sorbent capable of withstanding the temperatures experienced in a low-temperature WGS reactor as it selectively removes CO_2 from the syngas above the dew point of the gas. The proprietary sorbent consists of a mesoporous carbon grafted with surface functional groups that remove CO_2 via strong physical adsorption, with those surface interactions strong enough to allow operation at elevated temperatures. Because CO_2 is not bonded via a covalent bond, energy input for regeneration is low (heat of CO_2 adsorption is 4.9 kcal/ mol for the TDA sorbent). Although net energy loss in sorbent regeneration is similar to Selexol, much higher integrated gasification combined cycle (IGCC) efficiency can be achieved due to high-temperature CO_2 capture that is facilitated. The sorbent also has favorable material properties, with pore size tunable to 10 to 100 A into the mesopore range where diffusion limitations are eliminated.

The combination of the WGS and CO_2 removal improves the overall power cycle efficiency by reducing the amount of water needed for the WGS. TDA's overall process is depicted in Figure 2. Note that a high-temperature WGS reactor is followed by a single integrated low-temperature shift and CO_2 removal unit with the combined WGS catalyst and sorbent. Essentially, the conventional three-stage WGS with downstream CO_2 capture (four steps) is replaced with a two-stage WGS, with the second stage adding integrated CO_2 capture. This represents a significant degree of process intensification by reducing WGS stages and combining CO_2 capture in one of those stages.

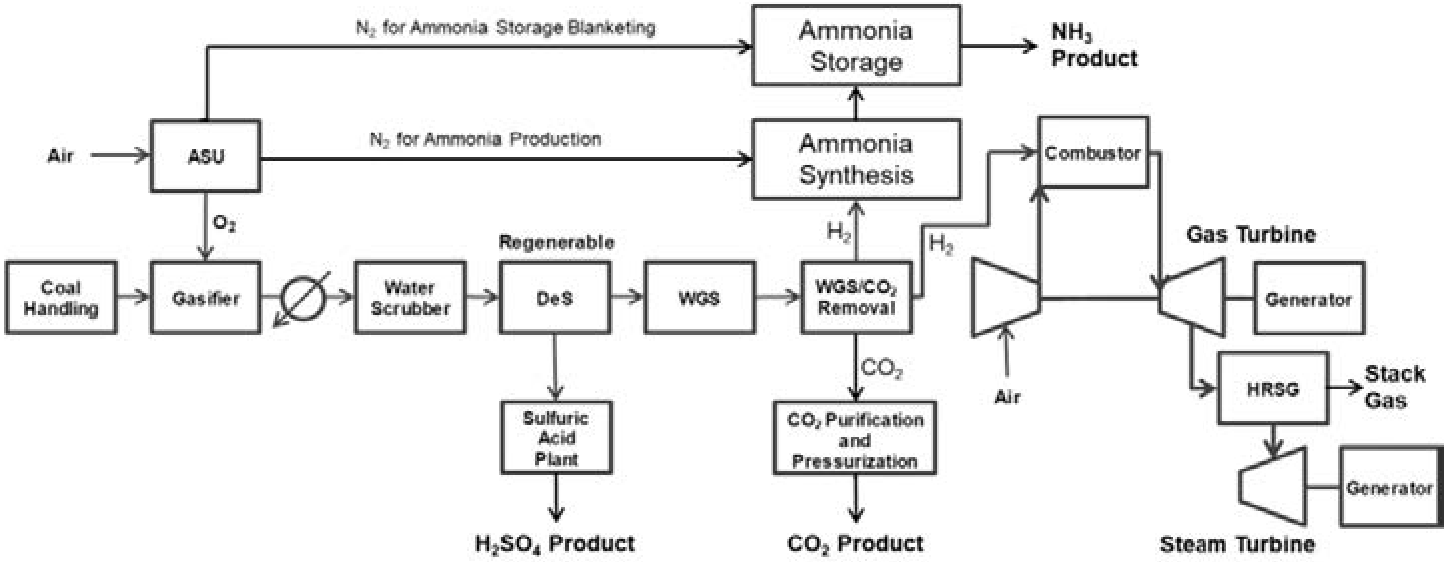


Figure 2: TDA polygeneration process concept.

The process is also integrated with a simplified fixed-bed temperature swing adsorption-based warm gas desulfurization system upstream of the WGS (using a desulfurization sorbent previously developed with the assistance of U.S.

Department of Energy [DOE] funding) and contaminant removal technologies (for hydrogen cyanide [HCN] and trace metals such as silver [As], mercury [Hg], and selenium [Se]). This will ensure robust protection of the catalysts used in downstream chemical synthesis processes while maintaining the water content of the gas to achieve high efficiency in polygeneration schemes. In the present process concept, ammonia synthesis from hydrogen produced is assumed as a polygeneration pair to decarbonized power generation using the hydrogen, here consisting of a typical combined cycle with gas turbine topping and steam turbine bottoming cycle. The process also includes a catalytic CO_2 purification process essential to attain CO_2 product purity requirements (residual CO and oxygen [O_2] in the CO_2 product must be reduced to very low levels for utilization in enhanced oil recovery [EOR] application).

Figure 3 depicts the combined WGS and CO_2 adsorber reactor column that has been demonstrated at bench scale. The basic engineering deployed in the column is diagrammed.

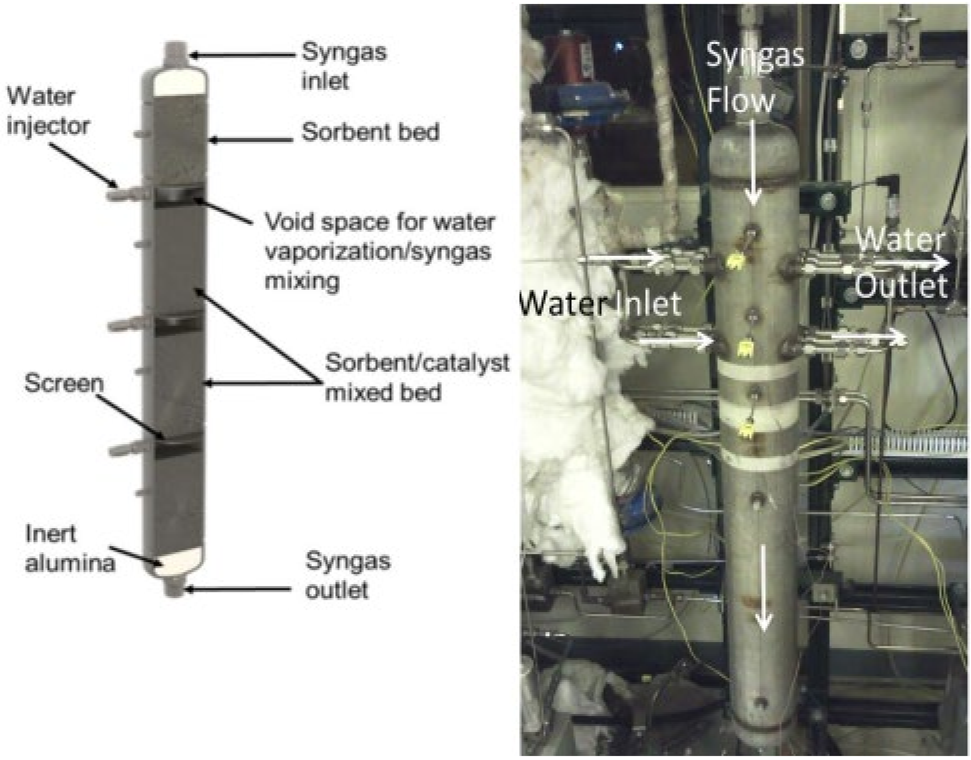


Figure 3: Bench-scale WGS and CO_2 adsorption column.

Combining WGS catalyst and CO_2 sorbent in the same column creates challenges in the form of proper heat management and temperature control. Uniform temperature without hot or cold spots is required for both optimal WGS conversion of the CO in the syngas and CO_2 removal from the syngas. TDA found that advanced heat management based on direct water injection greatly improves temperature control, and that optimal temperature rise occurs when the WGS catalyst is distributed into two layers with water injections before each layer. This is depicted in Figure 4; the top image of Figure 4 shows large, unfavorable temperature variations in a reactor column not employing water injection, while the bottom image of the figure shows excellent temperature uniformity and control attained with staged water injection and two-layer WGS catalyst distribution.

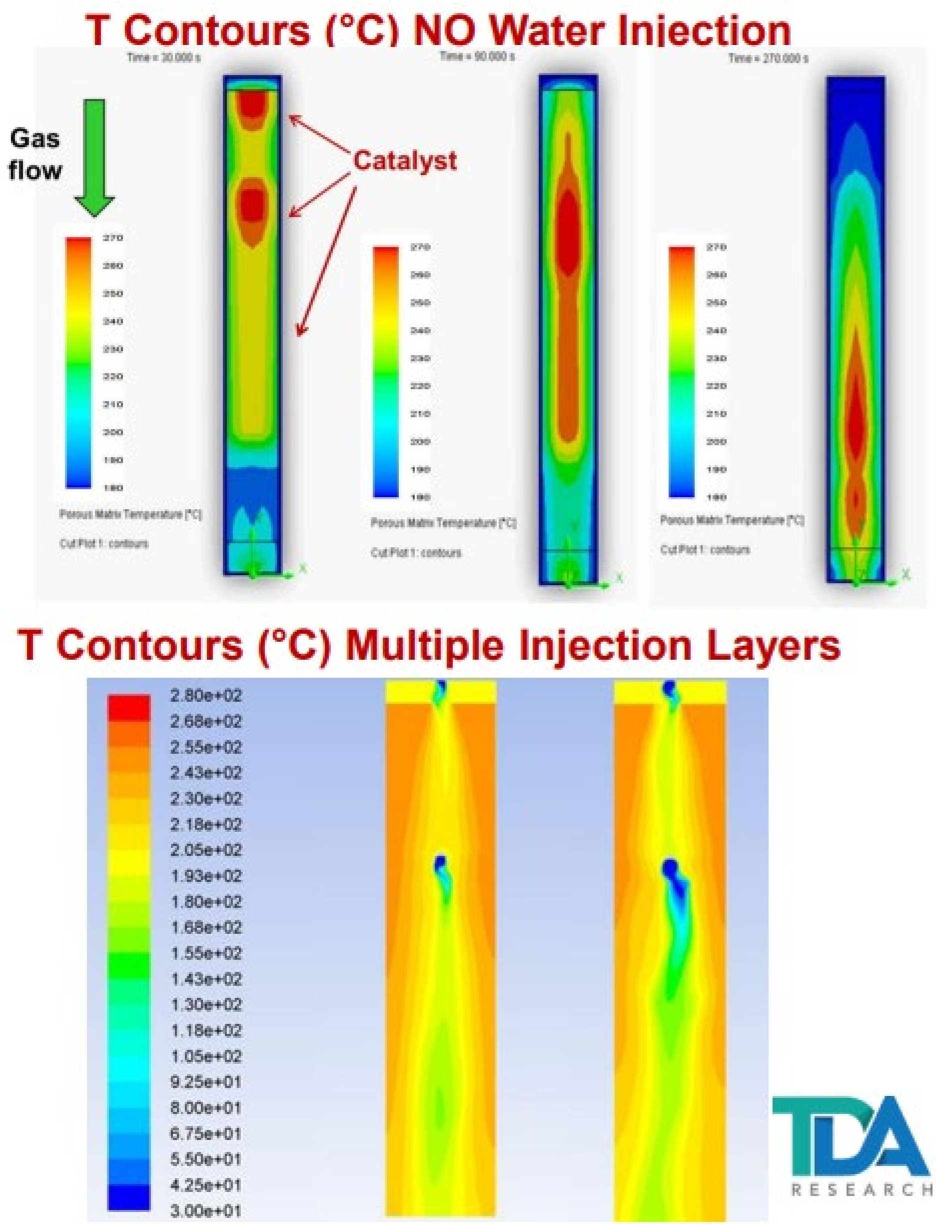


Figure 4: Heat-integrated WGS and CO_2 capture.

The integrated WGS and CO_2 capture system uses multiple columns that switch operating modes between adsorption and regeneration of the CO_2 sorbent. Pressure is high for adsorption (up to 500 pounds per square inch gauge [psig]) and low for regeneration (50–65 psig), constituting the CO_2 removal as a pressure swing adsorption (PSA) cycle. The alternating modes are obviously required for operation of the CO_2 sorbent, not the WGS catalyst, which raises the question of whether the pressure cycling has any adverse effect on the WGS catalyst. TDA completed 32,000 cycles of the combined WGS catalyst and sorbent and determined that catalytic activity of the WGS catalyst was unaffected. Temperature is relatively isothermal (200–215°C), which is ideal for sorbent performance. In quantifying sorbent performance, TDA determined heat of adsorption at 5–7 kcal/mol and measured CO_2 capacities as a function of pressure, as shown in Figure 5. TDA's target for capacity was 4 wt.% CO_2 at 500 psi; this was well exceeded with 6.2 wt.% achieved at that pressure.

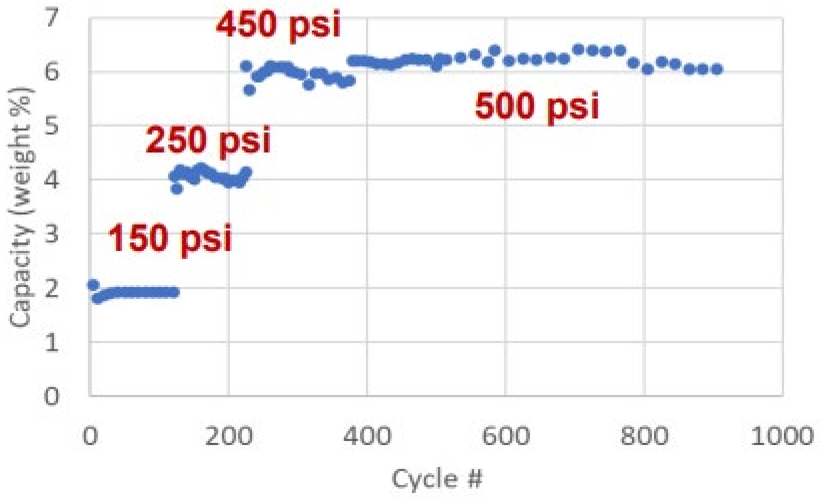


Figure 5: TDA capture sorbent CO_2 capacity.

The offgas from regeneration of the combined WGS and CO_2 sorbent columns is high in CO_2 but does contain H_2, methane (CH_4), and CO as minor constituents, which must be removed or converted to achieve pipeline quality, consistent with typical use of the product CO_2 in EOR. Accordingly, a CO_2 purification subsystem is necessary. The subsystem process is depicted in Figure 6. It uses oxygen (sourced from the main air-separation unit [ASU] associated with the gasifier) in a catalytic oxidizer, and excess oxygen downstream of the catalytic oxidation step is dealt with by leveraging trace oxygen removal sorbents previously developed for removing residual oxygen from oxy-combustion processes (refer to National Energy Technology Laboratory [NETL] project FE0029090).

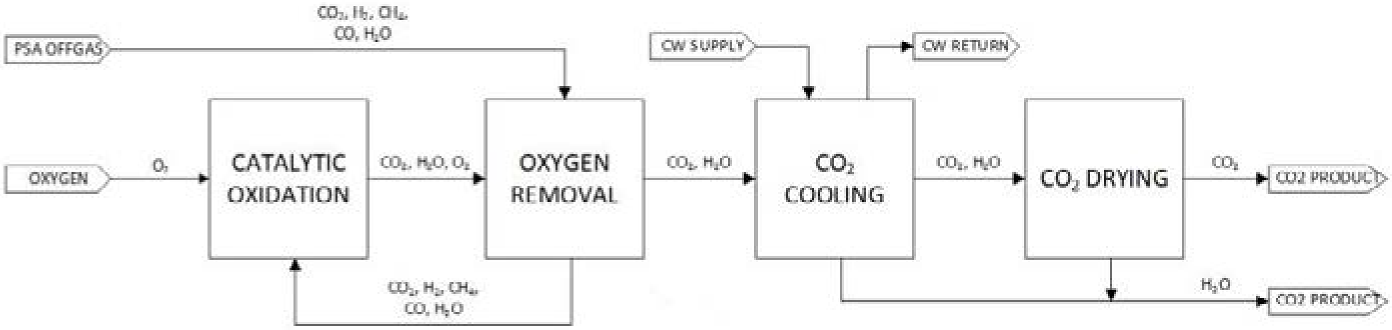


Figure 6: CO_2 purification subsystem.

TDA has been developing a test unit designed to treat 10 SCFM of actual syngas flow. This will deploy eight sorbent beds and two accumulator tanks. The test unit will contain three sub-assemblies/skids: (1) integrated WGS and CO_2 separation skid with the new column/reactor design, (2) a regenerable warm gas desulfurization gas processing skid, and (3) a CO_2 purification skid. It is planned that testing will occur at partner GTI's pilot gasifier test site, using real syngas generated by either the fluidized bed U-GAS® gasifier or the R-GAS™ gasifier pilots that GTI has onsite.

Figure 7: Eight-column integrated WGS and CO_2 capture unit.

The TDA sulfur removal subsystem is illustrated in Figure 8. It consists of a two-bed system of regenerable sulfur sorbent, one adsorbing while the other is regenerating. Hydrogen sulfide is removed during adsorption by reacting with metal oxides to form metal sulfides. Regeneration occurs by reacting O_2 with metal sulfides to form sulfur dioxide (SO_2). Electric heaters on inlet gas to achieve required adsorption and regeneration operating temperatures deliver a constant stream of desulfurized syngas to the integrated CO_2/WGS system.

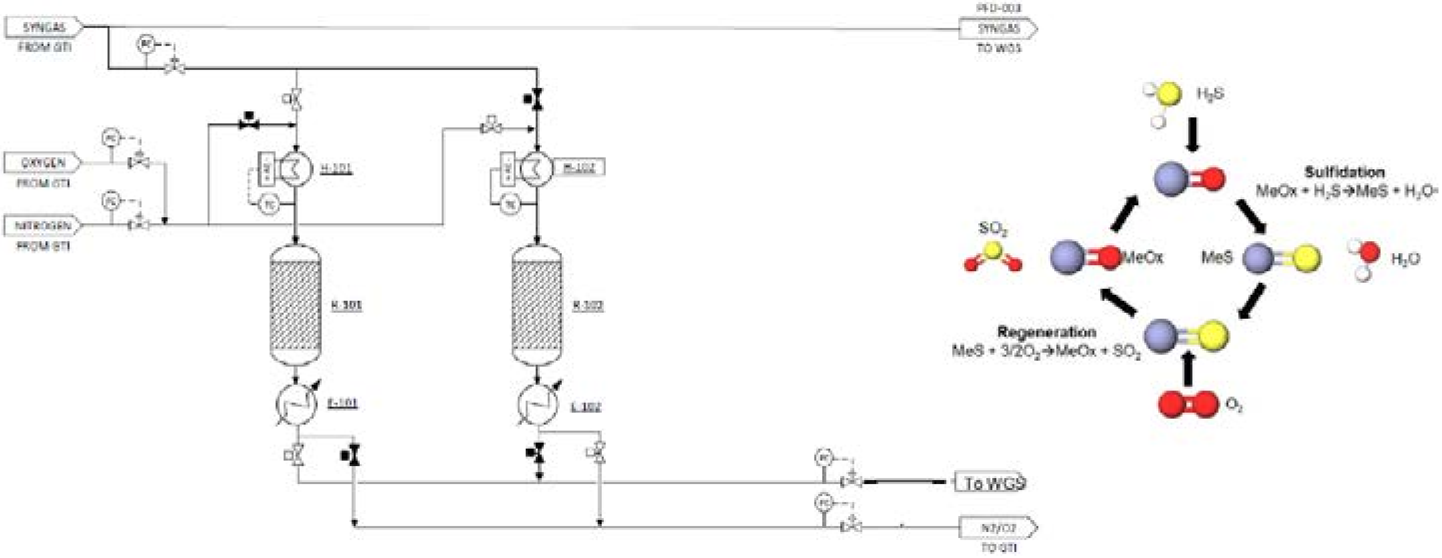
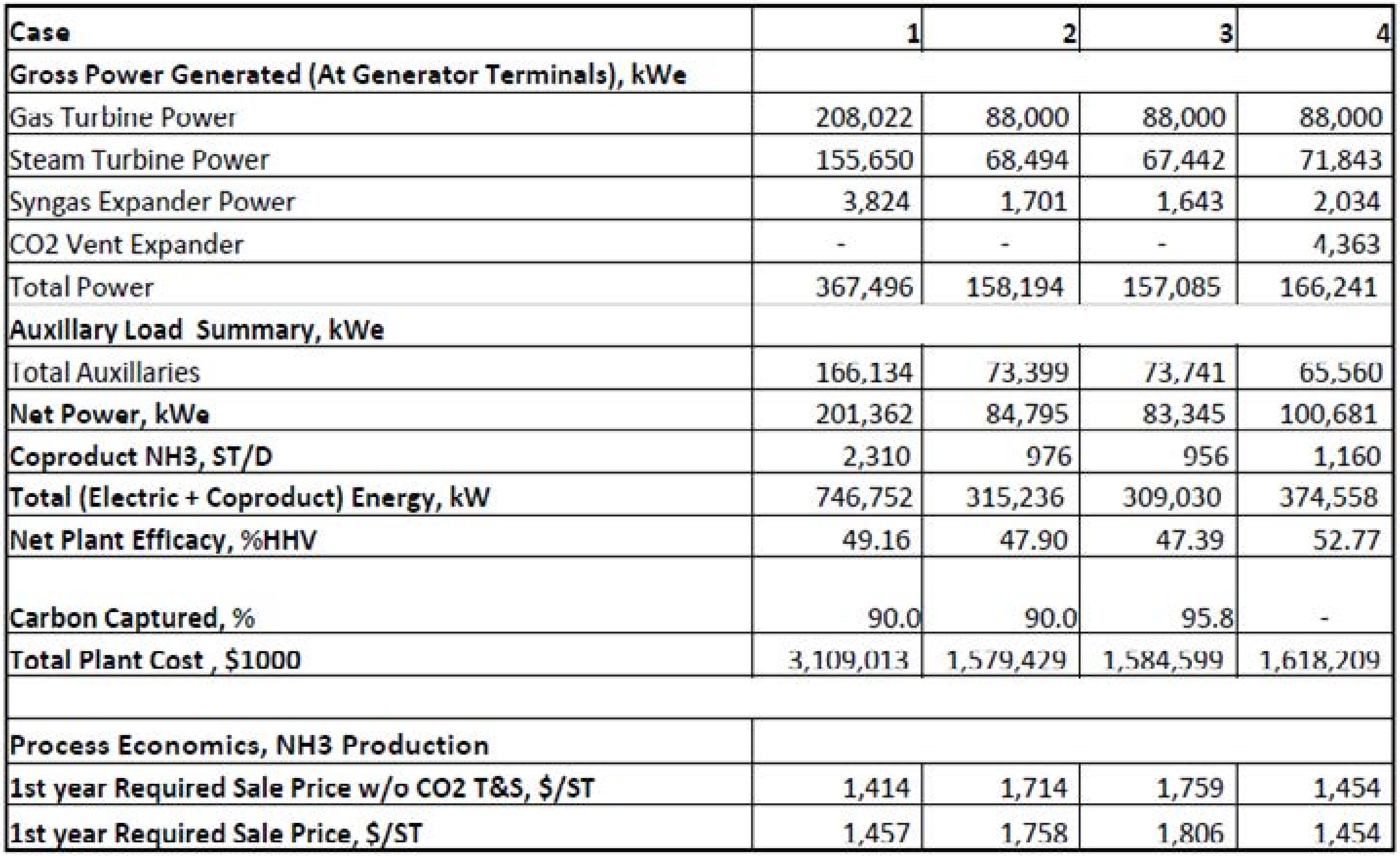


Figure 8: Design of regenerable sulfur sorbent system.

The sulfur sorbent was cycled through more than 500 adsorption/regeneration cycles in laboratory testing, with an absorption cycle ending when sulfur reached 3 wt.% in the sorbent. At this cycle end point, H_2S concentration was consistently/successfully reduced to a few ppm level in the bed outlet syngas.

A preliminary TEA was performed, considering sensitivities of a process plant (incorporating the TDA combined WGS/capture technology) for polygeneration of electricity and ammonia. Four cases were developed (see Figure 9), with Cases 1 and 2 showing the effect of economies of scale, while Cases 2, 3, and 4 showed the effect of degree of carbon capture. The plant design for Case 1 is based on using two trains of a GE Power type gasifier, and one train of GE 7F class type of gas turbine. Cases 2, 3, and 4 are based on using a single train of the GE Power gasifier and one train of GE 6F class type of gas turbine. All cases utilize Illinois No. 6 bituminous coal, and the excess syngas after providing the fuel to the gas turbine is available for ammonia (NH_3) coproduction after shifting and H_2 separation.



Case	1	2	3	4
Gross Power Generated (At Generator Terminals), kWe				
Gas Turbine Power	208,022	88,000	88,000	88,000
Steam Turbine Power	155,650	68,494	67,442	71,843
Syngas Expander Power	3,824	1,701	1,643	2,034
CO2 Vent Expander	-	-	-	4,363
Total Power	367,496	158,194	157,085	166,241
Auxillary Load Summary, kWe				
Total Auxillaries	166,134	73,399	73,741	65,560
Net Power, kWe	201,362	84,795	83,345	100,681
Coproduct NH3, ST/D	2,310	976	956	1,160
Total (Electric + Coproduct) Energy, kW	746,752	315,236	309,030	374,558
Net Plant Efficacy, %HHV	49.16	47.90	47.39	52.77
Carbon Captured, %	90.0	90.0	95.8	-
Total Plant Cost , $1000	3,109,013	1,579,429	1,584,599	1,618,209
Process Economics, NH3 Production				
1st year Required Sale Price w/o CO2 T&S, $/ST	1,414	1,714	1,759	1,454
1st year Required Sale Price, $/ST	1,457	1,758	1,806	1,454

Figure 9: System analysis with polygeneration options, case study sensitivities.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,314	1,314
Bulk Density	kg/m^3	620	620
Average Particle Diameter	mm	0.42–1.68	0.42–1.68
Particle Void Fraction	m^3/m^3	0.368	0.368
Packing Density	m^2/m^3	4.59E+08	4.59E+08
Solid Heat Capacity @ STP	kJ/kg-K	0.93	0.93
Crush Strength	kg_f	3	3
Manufacturing Cost for Sorbent	$/kg	3.88	3.88
Adsorption			
Pressure	bar	33.8	33.8
Temperature	°C	198	198
Equilibrium Loading	g mol CO_2/kg	1.04	1.04
	g mol CO_2/m^3	645	645
Heat of Desorption	kJ/mol CO_2	-28.5	-28.5
Desorption			
Pressure	bar	10	10

Temperature	°C	195.5		195.5
Equilibrium CO_2 Loading	g mol CO_2/kg	0.005		0.005
	g mol CO_2/m^3	3.22		3.22
Heat of Desorption	kJ/mol CO_2	28.5		28.5
Proposed Module Design			*(for equipment developers)*	
Flow Arrangement/Operation	—		radial-flow fixed bed/cyclic	
Syngas Flowrate	kg/hr		668,083	
CO_2 Recovery, Purity, and Pressure[+]	%/%/bar	90.0%	96.0%	10
Adsorber Pressure Drop	bar		1.41	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$		212.8	

[+] CO_2 is recovered at 10 bar from TDA's CO_2 capture system, which is further purified and compressed to 152.7 bar with a final CO_2 purity of 99.96%.

Definitions:

STP – Standard temperature and pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Surface functionalized mesoporous carbon removing CO_2 via weak interactions similar to physical adsorption at temperatures above the dew point of the syngas.

Sorbent Contaminant Resistance – The sorbent is highly resistant to contaminants such as H_2S, carbonyl sulfide (COS), ammonia (NH_3) and trace metals such as mercury (Hg), arsenic (As), etc. If needed, additional functionalities can be incorporated into the sorbent to remove these contaminants simultaneously with CO_2. Results of 707-hour-long testing with coal-derived syngas with the 0.1-MWe pilot unit at the NCCC in Wilsonville, Alabama, showed excellent resistance to contaminants that could be present in syngas.

Sorbent Attrition and Thermal/Hydrothermal Stability – The sorbent has good thermal/hydrothermal stability; it is stable in nitrogen up to 900°C and in steam stable up to 400°C. The attrition index for the sorbent is estimated to be 0.1% loss per 1,000 hours of operation.

Syngas Pretreatment Requirements – Syngas sulfur content needs to be reduced to less than 100 parts per million (ppm) before WGS and CO_2 removal.

Sorbent Make-Up Requirements – The expected life of the sorbent is five years. The annualized sorbent make-up requirement is expected to be 261.5 tonnes on the 550-MWe process plant basis.

Waste Streams Generated – Condensate from cooling the raw CO_2 stream.

Process Design Concept – See Figure 2.

Proposed Module Integration – TDA's combined WGS and CO_2 removal module is located downstream of the syngas desulfurization unit as shown in Figure 2; syngas composition and conditions entering module are as follows:

Pressure	Temperature	Composition						
		vol%						ppmv
psia	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
722.2	388.4	28.30	8.16	0.10	0.54	44.76	17.46	<10

TABLE 2: INDUSTRIAL PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	28.1	35.0
Cost of Carbon Avoided	\$/tonne CO_2	69.9	70.0
Capital Expenditures	\$/tonne CO_2	13.7	15.0
Operating Expenditures	\$/tonne CO_2	14.4	20.0

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Calculations Basis – The TEA numbers provided in the Table for both current and target values are all based on Rev. 2a DOE Baseline Study. Capital expenditures are \$ per tonne CO_2 captured, based on the recommended capacity charge factor of 0.124 in Rev. 2a DOE Baseline Study.

Scale of Validation of Technology Used in TEA – The numbers were from modeling data that was validated from pilot-scale testing.

technology advantages

- Warm gas removal of CO_2, sulfur, and contaminants improves process efficiency.
- Reducing the use of excess steam improves power cycle efficiency by lowering parasitic energy requirements for the process.
- Process intensification should reduce the number of hardware components and their cost.

R&D challenges

- Integrated WGS and CO_2 adsorption results in higher temperatures as heat from the exothermic WGS reaction accumulates in the beds—this makes CO_2 capture more difficult.

- Achieving more uniform cooling of the WGS and CO_2 adsorption bed without having hot or cold spots.
- Need for modular warm gas sulfur removal technologies.

status

TDA finished detailed design of the integrated WGS and CO_2 removal skid, CO_2 purification skid, and regenerable sulfur skid, and performed various tests of the CO_2 purification catalyst and regenerable sulfur sorbent. They are currently fabricating and modifying prior skids/subassemblies (built under other prior DOE-funded work) with intention to begin field-testing a fully integrated unit in the summer of 2024. The preliminary TEA shows favorable polygeneration plant efficiencies for combined electricity and ammonia production.

available reports/technical papers/presentations

"A High Efficiency, Modular Pre-combustion Capture System for 21st Century Power Plant Poly-generation Process," Gokhan Alptekin, TDA Research, Inc., prepared for 2023 Carbon Management Project Review Meeting, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_PSCC_7_Alptekin.pdf*.

"A High Efficiency, Modular Pre-combustion Capture System for 21st Century Power Plant Poly-generation Process," Gokhan Alptekin, TDA Research, Inc., prepared for 2023 Carbon Management Project Review Meeting, September 2023.

"A High Efficiency, Modular Pre-combustion Capture System for 21st Century Power Plant Poly-generation Process," presented by Gokhan Alptekin, TDA Research, Inc., 2022 Carbon Management Project Review Meeting - Point Source Carbon Capture, August 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_PSC16_Alptekin_2.pdf*.

"A High Efficiency, Modular Pre-Combustion Capture System for CoalFIRST Poly-generation Process," presented by Gokhan Alptekin and Ambalavanan Jayaraman, TDA Research Inc., 2021 NETL Carbon Management Research Project Review Meeting, August 13, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Alptekin_cap.pdf*.

"A High Efficiency, Modular Pre-combustion Capture System for CoalFIRST Poly-generation Process," Project Kickoff Presentation, November 3, 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11001&filename=A+High+Efficiency%2c+Modular+Pre-combustion+Capture+System+for+CoalFIRST+Poly-generation+Process.pdf*.

Pilot Testing of a Highly Effective Pre-Combustion Sorbent-Based Carbon Capture System

primary project goal

TDA Research Inc. continued development of a new sorbent-based pre-combustion carbon capture technology for integrated gasification combined cycle (IGCC) power plants. The process uses an advanced physical adsorbent that selectively removes carbon dioxide (CO_2) from coal-derived synthesis gas (syngas) above the dew point of the gas. The project aimed to prove the viability of the new technology by using data collected from the pilot plant tests to complete high-fidelity engineering and cost analyses to calculate the impact of the carbon capture system on the cost of electricity generation at a coal fired IGCC power plant and the potential of the technology to meet the U.S. Department of Energy (DOE) goals of 90% CO_2 capture and 95% purity at a cost of less than $40/tonne CO_2 captured.

technical goals

- Enable pre-combustion CO_2 capture from syngas at 200–250°C and pressures up to 60 bar, with greater than 90% recovery and CO_2 purity of at least 95%, using a functionalized carbon sorbent in a pressure swing adsorption (PSA)-based cycle.
- Improve adsorber reactor design, including the optimized reactor internals and bed geometry through computational fluid dynamics (CFD) analysis and PSA cycle optimization with adsorption modeling.
- Complete pilot-scale field tests on coal-derived syngas slipstreams at 0.1 megawatt-electric (MWe) equivalent, at design conditions and for extended durations (e.g., greater than 3,000 hours), to demonstrate capability to meet all performance objectives (e.g., CO_2 removal efficiency, hydrogen [H_2] recovery, sorbent life, and performance).
- Validate long-term performance and lifetime of the sorbent through 60,000 cycles with no more than 2% decrease in adsorption capacity over fresh sorbent (enabling projected lifetime of five years for the sorbent).
- Enable improved IGCC plant efficiency (3 to 4 percentage points) over IGCC plants using conventional CO_2 removal technology, thereby improving cost of electricity in coal-based power production.

technical content

TDA Research Inc. designed, constructed, and operated a slipstream 0.1-MWe pilot-scale process for pre-combustion CO_2 capture to assess their novel adsorbent for the selective removal of CO_2 from syngas. The adsorbent consists of

program area:
Point Source Carbon Capture

ending scale:
Small Pilot

application:
Pre-Combustion Power Generation PSC

key technology:
Sorbents

project focus:
High-Capacity Regenerable Sorbent for Coal IGCC Plants

participant:
TDA Research Inc.

project number:
FE0013105

predecessor projects:
FE0000469

NETL project manager:
Andrew O'Palko
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principal investigator:
Gökhan Alptekin
TDA Research Inc.
galptekin@tda.com

partners:
Gas Technology Institute; University of California at Irvine (UCI); University of Alberta; Sinopec

start date:
10.01.2013

percent complete:
100%

a mesoporous carbon grafted with surface functional groups that remove CO_2 via an acid-base interaction. The novel process is based on TDA's high-temperature PSA technology, using the new adsorbent to selectively remove CO_2 from syngas in an IGCC power plant. The integration of the CO_2 separation unit into the IGCC plant is shown in Figure 1.

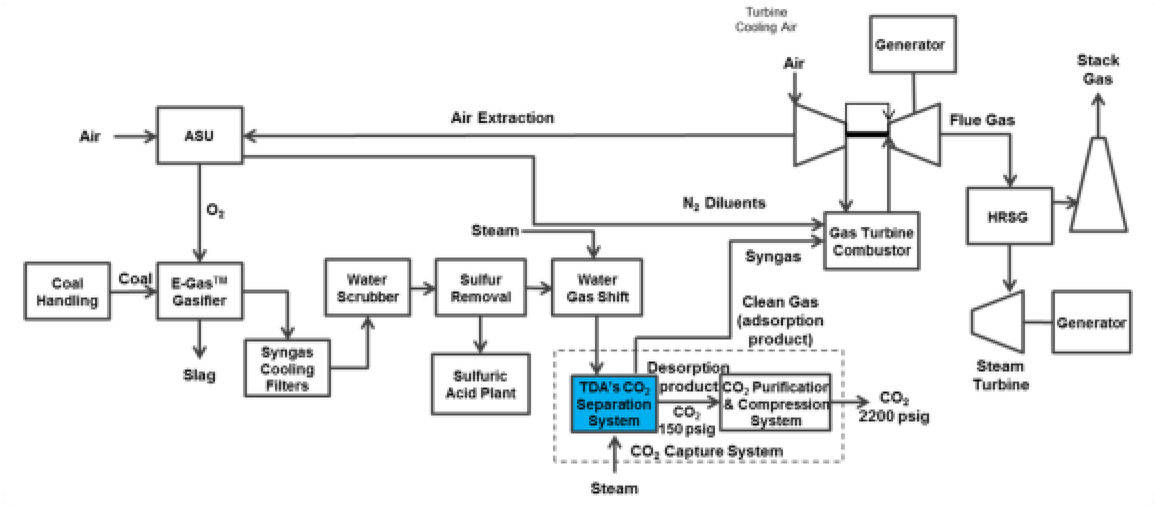


Figure 1: TDA's CO_2 capture system integration in an IGCC power plant.

The CO_2 capture system uses multiple sorbent beds that switch operating modes between adsorption and regeneration. In adsorption mode, which is operated isothermally (temperature of about 160–240°C) and at syngas pressure of about 500 pounds per square inch absolute (psia), the sorbent removes CO_2 via strong physical adsorption. The CO_2 surface interaction is strong enough to allow operation at these elevated temperatures. A detailed breakdown of the carbon capture and storage (CCS) system's operating parameters is given in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,314	1,314
Bulk Density	kg/m^3	620	620
Average Particle Diameter	mm	0.42–1.68	0.42–1.68
Particle Void Fraction	m^3/m^3	0.368	0.368
Packing Density	m^2/m^3	4.59E+08	4.59E+08
Solid Heat Capacity @ STP	kJ/kg-K	0.93	0.93
Crush Strength	kg_f	3	3
Manufacturing Cost for Sorbent	$/kg	3.88	3.88
Adsorption			
Pressure	bar	33.8	33.8
Temperature	°C	198	198
Equilibrium Loading	g mol CO_2/kg	1.04	1.04
	g mol CO_2/m^3	645	645
Heat of Desorption	kJ/mol CO_2	-28.5	-28.5
Desorption			
Pressure	bar	10	10
Temperature	°C	195.5	195.5
Equilibrium CO_2 Loading	g mol CO_2/kg	0.005	0.005
	g mol CO_2/m^3	3.22	3.22
Heat of Desorption	kJ/mol CO_2	28.5	28.5

Proposed Module Design		(for equipment developers)		
Flow Arrangement/Operation	—		radial-flow fixed bed/cyclic	
Syngas Flowrate	kg/hr		668,083	
CO_2 Recovery, Purity, and Pressure$^+$	%/%/bar	90.0%	96.0%	10
Adsorber Pressure Drop	bar		1.41	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$		212.8	

$^+$ CO_2 is recovered at 10 bar from TDA's CO_2 capture system, which is further purified and compressed to 152.7 bar with a final CO_2 purity of 99.96%.

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

In regeneration mode, also operated isothermally (temperature of about 160–240°C), CO_2 is recovered via combined pressure and concentration swing by contacting the sorbent with a steam purge stream. The operating pressure ranges from 150–158 psia and partial pressure of CO_2 ranges from 0–75 psi. Because the CO_2 is recovered at approximately 75–150 psia, the energy requirement for CO_2 compression for storage is reduced. Also, the isothermal operation eliminates heat/cool transitions, and rapid cycling reduces cycle times and increases sorbent utilization. Because the CO_2 is not bonded via a covalent bond, the energy input to the regeneration is low—only 4.9 kcal/mole of CO_2 removed (comparable to Selexol™). This energy requirement is much lower than that of the chemical absorbents (e.g., sodium carbonate [Na_2CO_3] requires 29.9 kcal/mol) and amine solvents (≈14 kcal/mol). The energy output loss of the IGCC plant is expected to be like that of Selexol's; however, a higher overall IGCC efficiency can be achieved due to higher temperature CO_2 capture.

The pilot plant design includes a gas conditioning unit and a high-temperature PSA-based CO_2 separation unit, as shown in Figure 2. The gas conditioning unit allows for adjustment of the concentration and purity of the syngas. The CO_2 separation unit consists of eight high-temperature sorbent beds. The design of the CO_2 capture skid for the 0.1-MW pilot unit is shown in Figure 3.

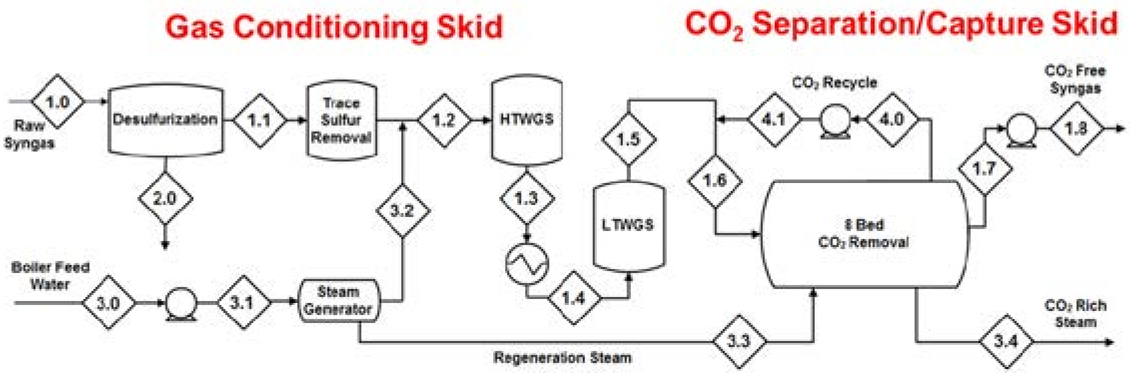


Figure 2: Flow diagram for TDA's pilot test unit.

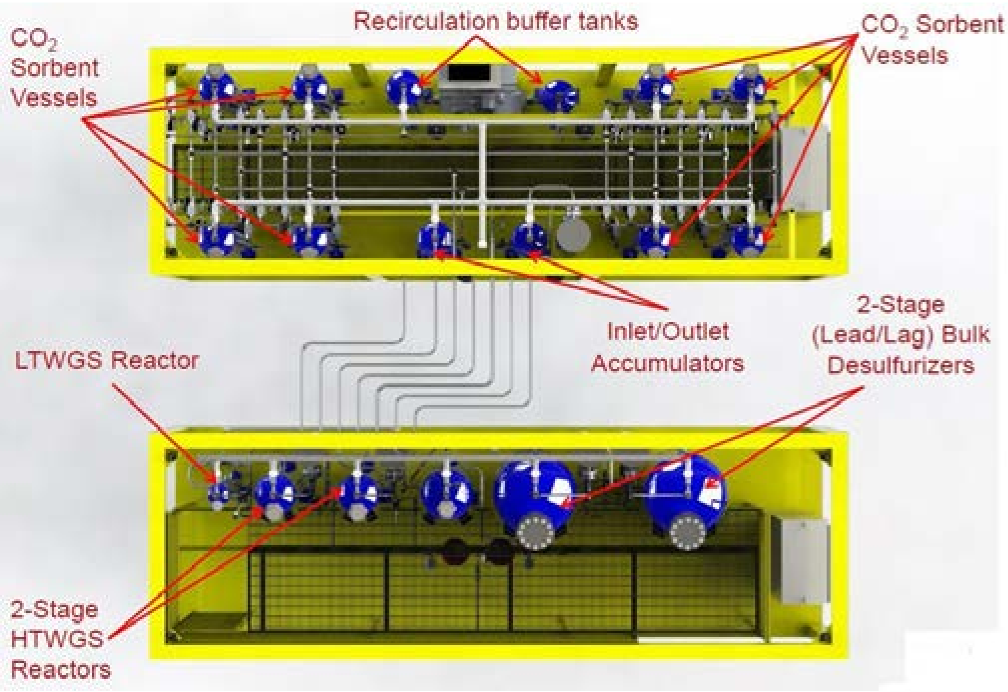
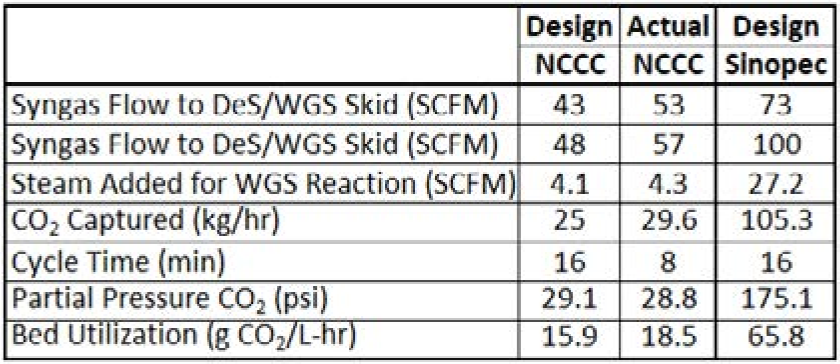


Figure 3: Overhead view of carbon capture skid.

In 2017, TDA's 0.1-MWe pilot-scale eight-bed PSA unit was installed at the National Carbon Capture Center (NCCC; Figure 4) and tested in real coal-derived syngas. The pilot unit ran for 707 hours of continuous operation at up to 97.3% carbon capture at 53 standard cubic feet per minute (SCFM) of syngas flow, exceeding design specifications. The summary results are given in Table 2. This table also shows the upcoming design performance parameters for the Sinopec oxygen-based gasifier testing at considerably increased throughput.

Figure 4: TDA's 0.1-MWe pilot unit installed in the test pad at the NCCC (Wilsonville, Alabama).

TABLE 2: SUMMARY PERFORMANCE RESULTS OF PILOT-SCALE TESTING



	Design NCCC	Actual NCCC	Design Sinopec
Syngas Flow to DeS/WGS Skid (SCFM)	43	53	73
Syngas Flow to DeS/WGS Skid (SCFM)	48	57	100
Steam Added for WGS Reaction (SCFM)	4.1	4.3	27.2
CO_2 Captured (kg/hr)	25	29.6	105.3
Cycle Time (min)	16	8	16
Partial Pressure CO_2 (psi)	29.1	28.8	175.1
Bed Utilization (g CO_2/L-hr)	15.9	18.5	65.8

In 2018 and 2019, TDA shipped, installed, and performed shakedown testing on field units at Sinopec (see Figure 5), which allow oxygen-based gasifier testing at considerably increased throughput.

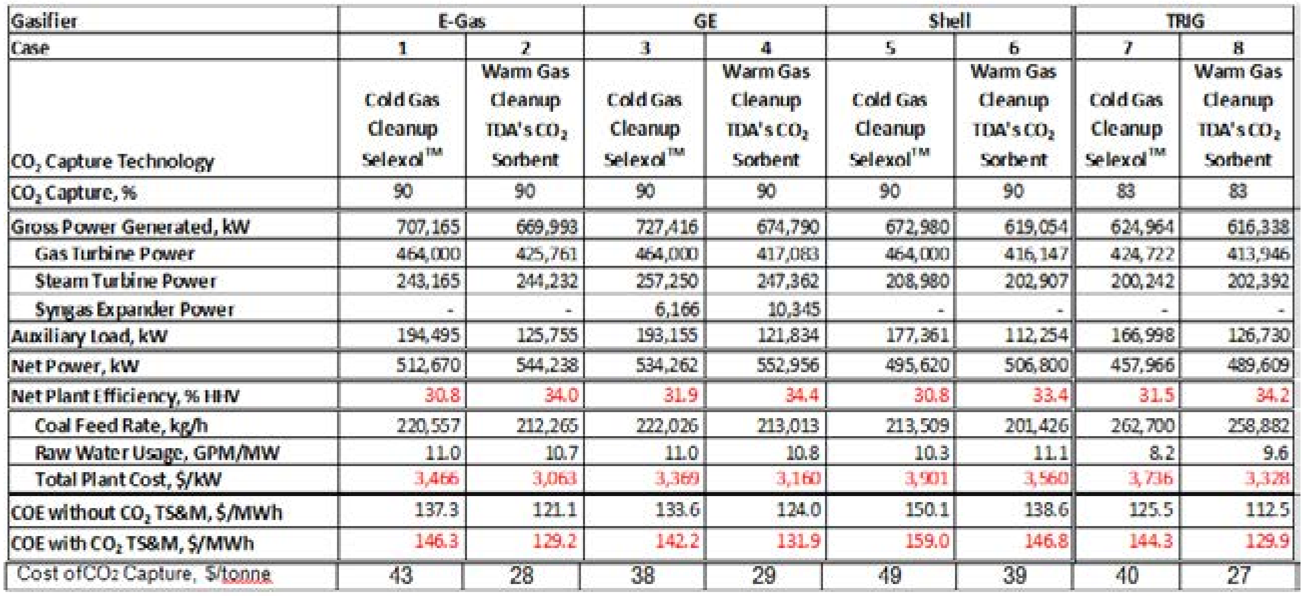
Very early testing results at 88 SCFM syngas flow have resulted in approximately 85% CO_2 removal efficiency at a rate of approximately 110 kg/hr CO_2.

TDA has also performed preliminary techno-economic analyses (TEAs) of cases assuming application of TDA's sorbent-based CO_2 capture system in IGCC plant cycles, based upon performance data available to date from recent testing. The comparisons involve a baseline of conventional cold-gas cleanup and Selexol acid gas removal, compared to TDA's assumption of warm-gas cleanup combined with the sorbent units for CO_2 capture. Results are summarized in Table 3. Overall, the findings are as follows:

- TDA system achieves higher efficiencies (34.5% and 34.1%) than IGCC with Selexol (32.0% and 31.0%) for E-Gas™ and GE gasifier-based plants.
- Cost of CO_2 capture is calculated as $31 and $30/tonne for GE and E-Gas gasifier-based plants, respectively (16–30% reduction against Selexol).
- Cost of CO_2 capture is calculated as $40 and $28/tonne for Shell and TRIG gasifier-based plants, respectively (15–28% reduction against Selexol).

Figure 5: Field test units at Sinopec, China.

TABLE 3: PRELIMINARY TECHNO-ECONOMIC COMPARISONS



Gasifier	E-Gas		GE		Shell		TRIG	
Case	1	2	3	4	5	6	7	8
CO_2 Capture Technology	Cold Gas Cleanup Selexol™	Warm Gas Cleanup TDA's CO_2 Sorbent	Cold Gas Cleanup Selexol™	Warm Gas Cleanup TDA's CO_2 Sorbent	Cold Gas Cleanup Selexol™	Warm Gas Cleanup TDA's CO_2 Sorbent	Cold Gas Cleanup Selexol™	Warm Gas Cleanup TDA's CO_2 Sorbent
CO_2 Capture, %	90	90	90	90	90	90	83	83
Gross Power Generated, kW	707,165	669,993	727,416	674,790	672,980	619,054	624,964	616,338
Gas Turbine Power	464,000	425,761	464,000	417,083	464,000	416,147	424,722	413,946
Steam Turbine Power	243,165	244,232	257,250	247,362	208,980	202,907	200,242	202,392
Syngas Expander Power	-	-	6,166	10,345	-	-	-	-
Auxiliary Load, kW	194,495	125,755	193,155	121,834	177,361	112,254	166,998	126,730
Net Power, kW	512,670	544,238	534,262	552,956	495,620	506,800	457,966	489,609
Net Plant Efficiency, % HHV	30.8	34.0	31.9	34.4	30.8	33.4	31.5	34.2
Coal Feed Rate, kg/h	220,557	212,265	222,026	213,013	213,509	201,426	262,700	258,882
Raw Water Usage, GPM/MW	11.0	10.7	11.0	10.8	10.3	11.1	8.2	9.6
Total Plant Cost, $/kW	3,466	3,063	3,369	3,160	3,901	3,560	3,736	3,328
COE without CO_2 TS&M, $/MWh	137.3	121.1	133.6	124.0	150.1	138.6	125.5	112.5
COE with CO_2 TS&M, $/MWh	146.3	129.2	142.2	131.9	159.0	146.8	144.3	129.9
Cost of CO_2 Capture, $/tonne	43	28	38	29	49	39	40	27

Definitions:

COE – Cost of electricity.

TS&M – Transport, storage, & monitoring.

HHV – Higher heating value.

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Surface functionalized mesoporous carbon removing CO_2 via weak interactions similar to physical adsorption at temperatures above the dew point of the syngas.

Sorbent Contaminant Resistance – The sorbent is highly resistant to contaminants such as hydrogen sulfide (H_2S), carbonyl sulfide (COS), ammonia (NH_3) and trace metals such as mercury (Hg), arsenic (As), etc. If needed, additional functionalities can be incorporated into the sorbent to remove these contaminants simultaneously with CO_2. Results of the 707-hour-long testing with coal-derived syngas with the 0.1-MWe pilot unit at the NCCC in Wilsonville, Alabama, showed excellent resistance to contaminants that could be present in syngas.

Sorbent Attrition and Thermal/Hydrothermal Stability – The sorbent has good thermal/hydrothermal stability; it is stable in nitrogen up to 900°C and in steam stable up to 400°C. The attrition index for the sorbent is estimated to be 0.1% loss per 1,000 hours of operation.

Syngas Pretreatment Requirements – Syngas needs to be shifted to convert carbon monoxide (CO) present into CO_2 and H_2 via water-gas shift (WGS) reaction and sulfur content needs to be reduced to less than 100 parts per million (ppm) before CO_2 removal.

Sorbent Makeup Requirements – The expected life of the sorbent is five years. The annualized sorbent makeup requirement is expected to be 261.5 tonnes on the 550-MWe process plant basis.

Waste Streams Generated – Condensate from cooling the raw CO_2 stream.

Process Design Concept – See Figure 1.

Proposed Module Integration – TDA's CO_2 separation, purification, and compression systems are located downstream of the warm-gas sulfur removal and the WGS processes as shown in Figure 1.

Feed Gas Assumptions –The pressure, temperature, and composition entering the module are as follows:

Pressure	Temperature	Composition						
psia	°F	vol%						ppmv
		CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
497.5	388.4	30.28	0.73	2.04	0.45	39.11	26.59	<10

technology advantages

- Warm-gas CO_2 capture above dew point of syngas leads to more steam in the hydrogen-rich gas entering the turbine.
  - Improved efficiency.
  - Higher mass throughput to gas turbine.
  - Lower-gas turbine temperature, which lowers the need for high-pressure nitrogen (N_2) dilution and lowers nitrogen oxide (NO_X) formation.
- High steam content feed more suited for next-generation hydrogen turbines under development.
- High working capacity and cycle life of sorbent.
- Carbon dioxide recovered at pressure reduces compression costs for storage.
- A weak CO_2 surface interaction allows fast regenerations at lower temperature with minimal or no heat input.
- Short adsorption/regeneration cycles reduce bed size and weight, corresponding to reduced adsorber vessel size and costs.

R&D challenges

- Assuring consistency in sorbent material and minimizing batch-to-batch variation for large-scale manufacture.
- Reducing the use of purge gas during regeneration.
- Confirming resistance to syngas contaminants.

status

The project was completed on September 30, 2022. The results show that TDA's capture system improves the efficiency of IGCC with CCS by at least three percentage points compared to Selexol. In addition, the cost of CO_2 capture was found to be below $30/tonne for three out of four cases. A cost of capture of $40/tonne was observed for the Shell gasifier. These systems are between 20% and 35% cheaper than traditional systems that use Selexol.

available reports/technical papers/presentations

Alptekin, G. "Pilot Testing of a Highly Efficient Pre-Combustion Sorbent-Based Carbon Capture System." Topic Report: Field Test Results at Sinopec, December 26, 2022. *https://www.osti.gov/servlets/purl/1906977*.

"Pilot Testing of a Highly Efficient Pre-Combustion Sorbent-Based Carbon Capture System." TDA Research. 2022 Carbon Management Project Review Meeting. August 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_PSC16_Alptekin_3.pdf*

"Pilot Testing of a Highly Efficient Pre-Combustion Sorbent-Based Carbon Capture System." TDA Research. 2021 Carbon Management and Oil and Gas Research Project Review Meeting. August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Alptekin_sor.pdf*.

"Pilot Testing of a Highly Efficient Pre-combustion Sorbent-based Carbon Capture System," presented by Gökhan Alptekin of TDA Research, Inc. at the 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies

Integrated Review Meeting – Capture and Utilization Sessions, Pittsburgh, Pennsylvania, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/G-Alptekin-TDA-Precombustion-Sorbent.pdf*

"PSA Based CO_2 Capture Above the Dew Point of Synthesis Gas for IGCC Power Plants," presented at the 2017 AIChE Annual Meeting, Minneapolis, MN, November 2017. *https://www.aiche.org/conferences/aiche-annual-meeting/2017/proceeding/paper/628c-psa-based-co2-capture-above-dew-point-synthesis-gas-igcc-power-plants*

"Highly Efficient Warm Gas Carbon Capture System for IGCC Power Plants," presented at the 2016 AIChE Annual Meeting, Minneapolis, MN, November 2016. *https://aiche.confex.com/aiche/2016/webprogram/Paper470738.html*

"Pilot Testing of a Highly Efficient Pre-combustion Sorbent-based Carbon Capture System," presented by Gökhan Alptekin, TDA Research, Inc., 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://netl.doe.gov/sites/default/files/event-proceedings/2017/co2 capture/2-Tuesday/G-Alptekin-TDA-Evaluation-of-Carbon-Capture-Process.pdf*

"Pilot Testing of a Highly Efficient Pre-Combustion Sorbent-Based Carbon Capture System," presented by Gökhan Alptekin, TDA Research Inc., 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/sites/default/files/event-proceedings/2016/c02 cap review/1-Monday/G-Alptekin-TDA-Sorbent-Based-Carbon-Capture.pdf*

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"Pilot Testing of a Highly Efficient Pre-Combustion Sorbent-Based Carbon Capture System," Project Kick-Off Meeting, January 2013. *https://www.netl.doe.gov/sites/default/files/2017-12/FE0013105-Kickoff-Pilot-Testing-PreCombustion-CO2Capture-2014-01-16.pdf*

Alptekin, G., Jayaraman, A., Dietz, S., Bonnema, M., Rao, A., "Low Cost, High Capacity Regenerable Sorbent for Precombustion CO_2 Capture," Final Report, September 2012. *https://www.osti.gov/servlets/purl/1082143*

Alptekin, G., "A Low Cost, High Capacity Regenerable Sorbent for CO_2 Capture," presented at the International Colloquium on Environmentally Preferred Advanced Power Generation (ICEPAG), Costa Mesa, CA, February 2012.

Alptekin, G., Jayaraman, A., Dietz, S., and Schaefer, M., "High Capacity Regenerable Sorbent for Pre-Combustion CO_2 Capture," presented at the 28th Annual International Pittsburgh Coal Conference (IPCC), Pittsburgh, PA, September 2011.

Critical Component/ Technology Gap in 21st Century Power Plant Gasification-Based Polygeneration: Advanced Ceramic Membranes/Modules for Ultra-Efficient H_2 Production/CO_2 Capture for Coal-Based Polygeneration Plants

primary project goal

Media and Process Technology Inc. (MPT), in collaboration with the University of Southern California, is advancing inorganic membrane technology for pre-combustion carbon dioxide (CO_2) capture from syngas in a gasification-based polygeneration plant. The primary project goal is two-fold: (1) to transition the current single-ended "candle filter" configuration of the ceramic membrane support to a dual-end (open both ends), full ceramic multiple-tube bundle configuration that will enable permeate sweep/purge capability; and (2) to develop the housing design for the dual-end bundles with emphasis on minimization of stresses associated with the membrane to housing seals and incorporation of multiple bundles into a pre-commercial-scale unit.

technical goals

- Demonstrate durability/robustness of the full ceramic multiple-tube membrane bundle and multi-bundle module at operating conditions of up to 400°C and at up to 800 pounds per square inch gauge (psig). Testing syngas flowrate is to be 10 standard cubic feet per minute (SCFM).
- Achieve the greater than 30% cost of electricity (COE) cost savings target for CO_2 capture relative to baseline capture costs.
- Develop, fabricate, and demonstrate a membrane module incorporating multiple membrane bundles in a series-parallel configuration with permeate purge capability.
- Conduct long term performance stability testing of multiple membrane bundles in the dual-end configuration.

program area:

Point Source Carbon Capture

ending scale:

Small Pilot

application:

Pre-Combustion Power Generation PSC

key technology:

Membranes

project focus:

Ceramic Membranes with Coal Syngas

participant:

Media and Process Technology Inc.

project number:

FE0031930

predecessor projects:

N/A

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partners:

University of Southern California

start date:

10.01.2020

percent complete:

80%

technical content

Gasification-based polygeneration takes advantage of the primary gasification product, hydrogen (H_2), not only as fuel for power generation, but also a feedstock for chemicals production (specifically ammonia [NH_3] in this case) in conjunction with co-produced nitrogen (N_2). Polygeneration confers the ability to rapidly adjust the plant output to market need, and enhances suitability of gasification-based processes in smaller-scale, distributed co-production facilities. Carbon capture from syngas is essential to yield H_2 for NH_3 synthesis or for decarbonized power generation in these cycles.

Conventionally, carbon capture is based on amine solvent-based capture (e.g., Selexol) requiring cooling of the syngas to low temperatures. However, plant efficiency can be greatly improved by H_2-CO_2 separations from warm syngas using alternative technology. MPT has developed an inorganic/ceramic membrane-based Dual-Stage Membrane Process (DSMP, DE-FE0013064), which eliminates the need for a high-cost conventional two-stage, Selexol-based CO_2 capture process. The membranes themselves consist of carbon molecular sieve, palladium, zeolites, or zeolitic imidazolate framework (ZIF) applied via thin active layer deposition on ceramic substrate. Membrane-based unit operation is recognized for its simplicity, modular configuration, and quick turn-up/turn-down, making it well suited for small-scale distributed production facilities. Figure 1 depicts the overall polygeneration cycle, in this case showing where the inorganic membrane-based warm/hot gas processing unit fits into the cycle for polygeneration of power and NH_3.

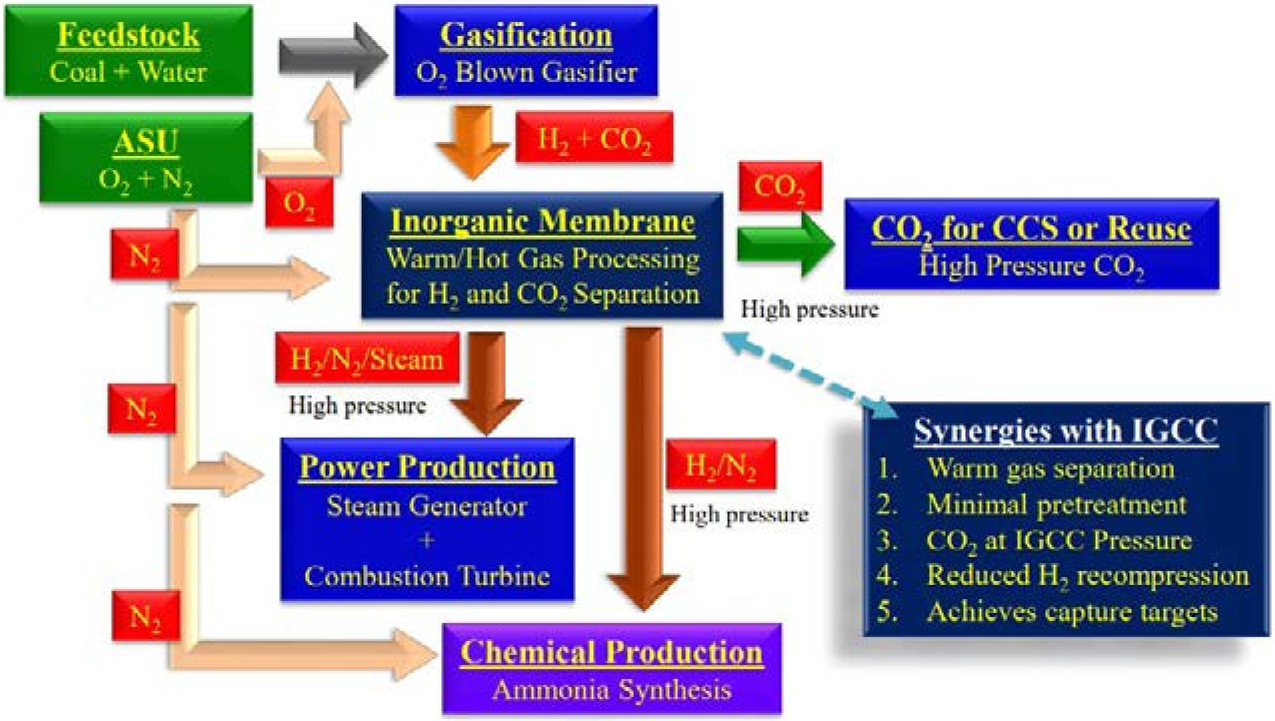


Figure 1: Inorganic membrane technology role in polygeneration cycle.

For the DSMP (and any membrane process in pre-combustion capture) to operate commercially, permeate sweep/purge with high-pressure N_2 (from the air separation unit [ASU]) and/or steam (from steam cycle of the power generating unit) is required. Unfortunately, this “permeate purge” capability is not currently available in large-format inorganic membranes rated for use at temperatures above approximately 200°C. MPT has prepared multiple-tube membrane bundles for high-temperature gas separation service (up to approximately 450°C; greater than 1,200 psig) that have been performance-demonstrated at the National Carbon Capture Center (NCCC). However, these bundles were fabricated in a “candle filter” configuration and are not permeate purgeable. Thus, the critical technology gap for the proposed process to be implemented commercially in polygeneration operation mode is the development of a purgeable inorganic membrane module. Such a module includes multiple dual-end open bundles in a series/parallel configuration, introducing additional technical challenges to be overcome such as inter-bundle sealing and shell-side feed flow distribution. Figure 2 depicts the concept for the permeate purgeable multiple bundle housing, bundles, and seals in question.

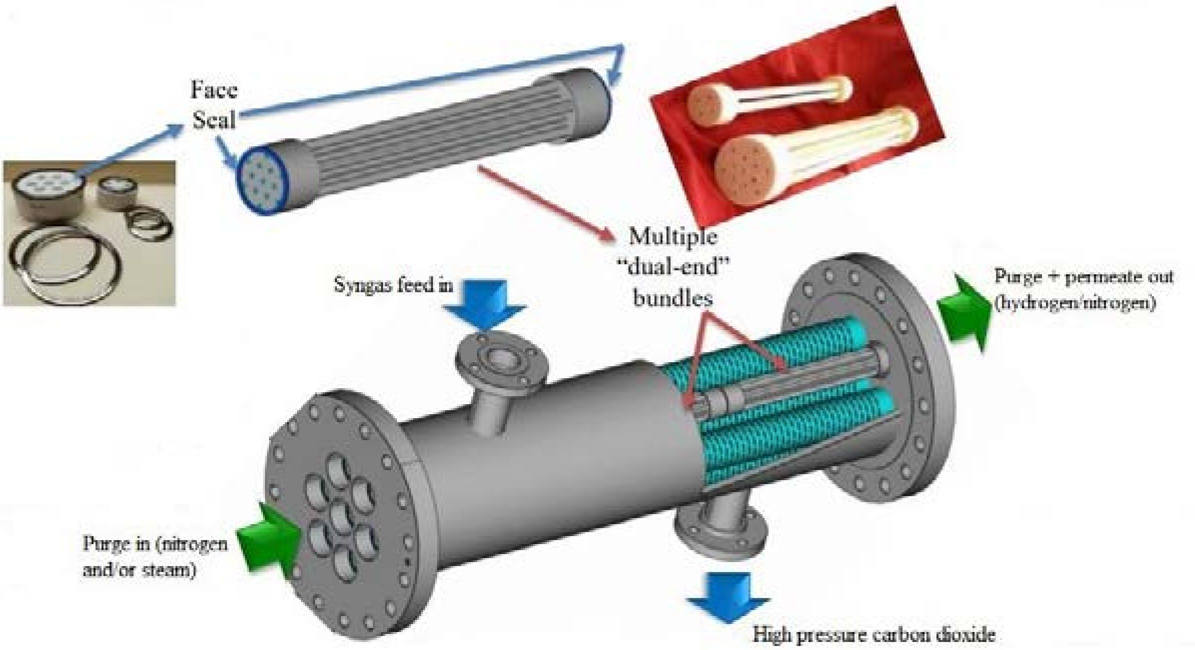


Figure 2: Permeate purgeable multiple bundle housing and seals.

MPT developed and fabricated permeate-purgeable multiple-tube bundles, with attention to the bundle housing with appropriate seals. Bundles sized up to 4-inch diameter and up to 38-inch length are ultimately targeted; 1.5-, 2-, and 3-inch diameter, 38-inch dual-end bundles have been successfully fabricated. Figure 3 shows actual membrane bundles and the multiple bundle seal housings being assembled.

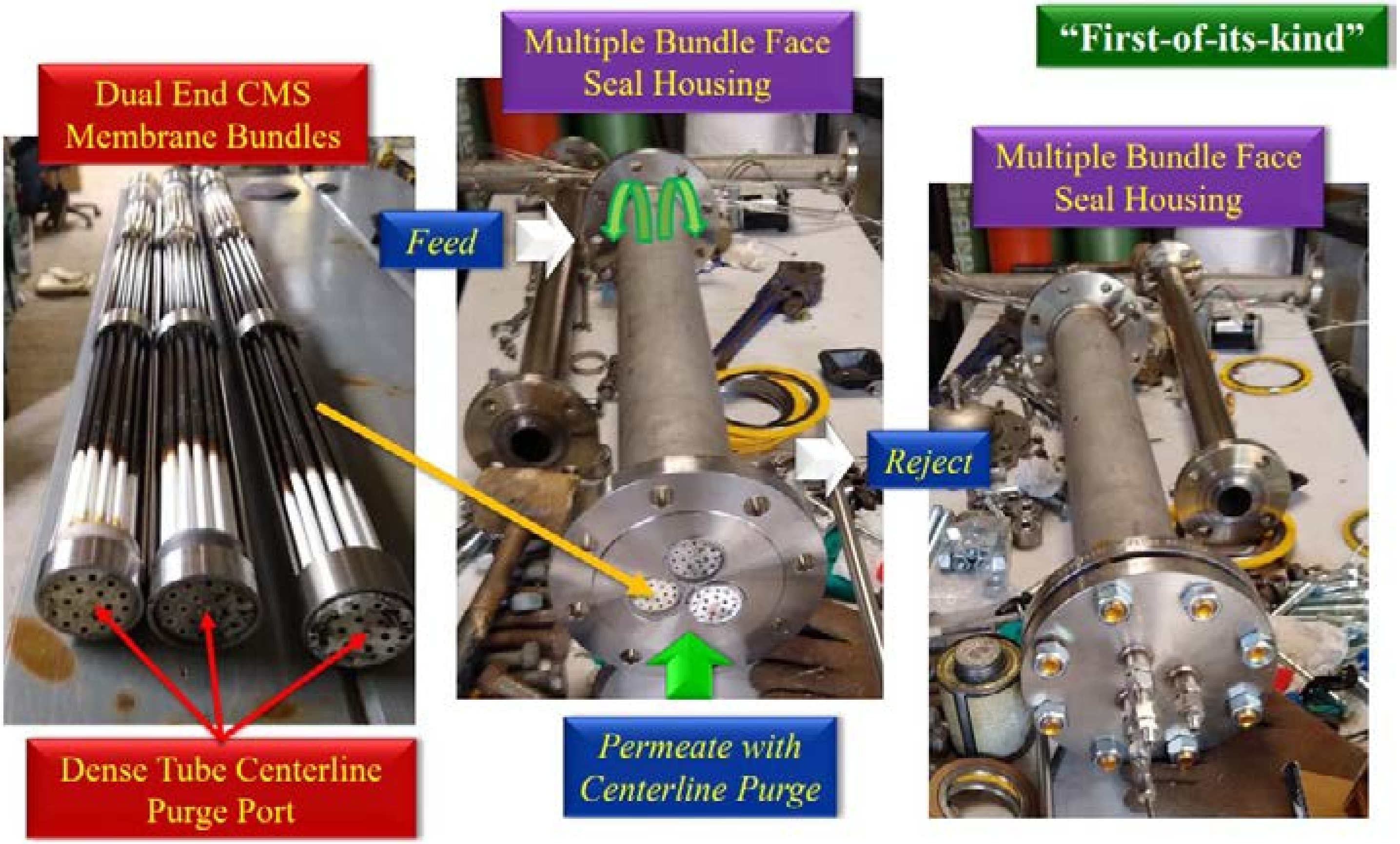


Figure 3: Multiple membrane bundle housing.

A range of challenge tests to demonstrate bundle/housing stability have been performed, essential to establish long-term mechanical/performance stability at target operating conditions. In earlier work, 43 dual-end purgeable dense and porous tube bundles at up to 3-inch diameter were tested. No mechanical failures occurred in more than 2,000 challenge tests up to 450°C. Both Carbon Molecular Sieve (CMS) and palladium alloy (Pd-Ag and Pd-Cu) have been performance-tested, including multiple-tube membrane bundles at the NCCC. Membrane process parameters for these membranes (CMS Membrane #1 and Pd alloy Membrane #2) are summarized in Table 1A and 1B, respectively.

In more recent work, the palladium alloy and CMS dual-end bundles were tested for long-term performance stability under permeate purge; Figure 4 illustrates the results of the stability testing of the CMS bundle in a face seal housing, showing excellent stability over run time approaching 1,500 hours.

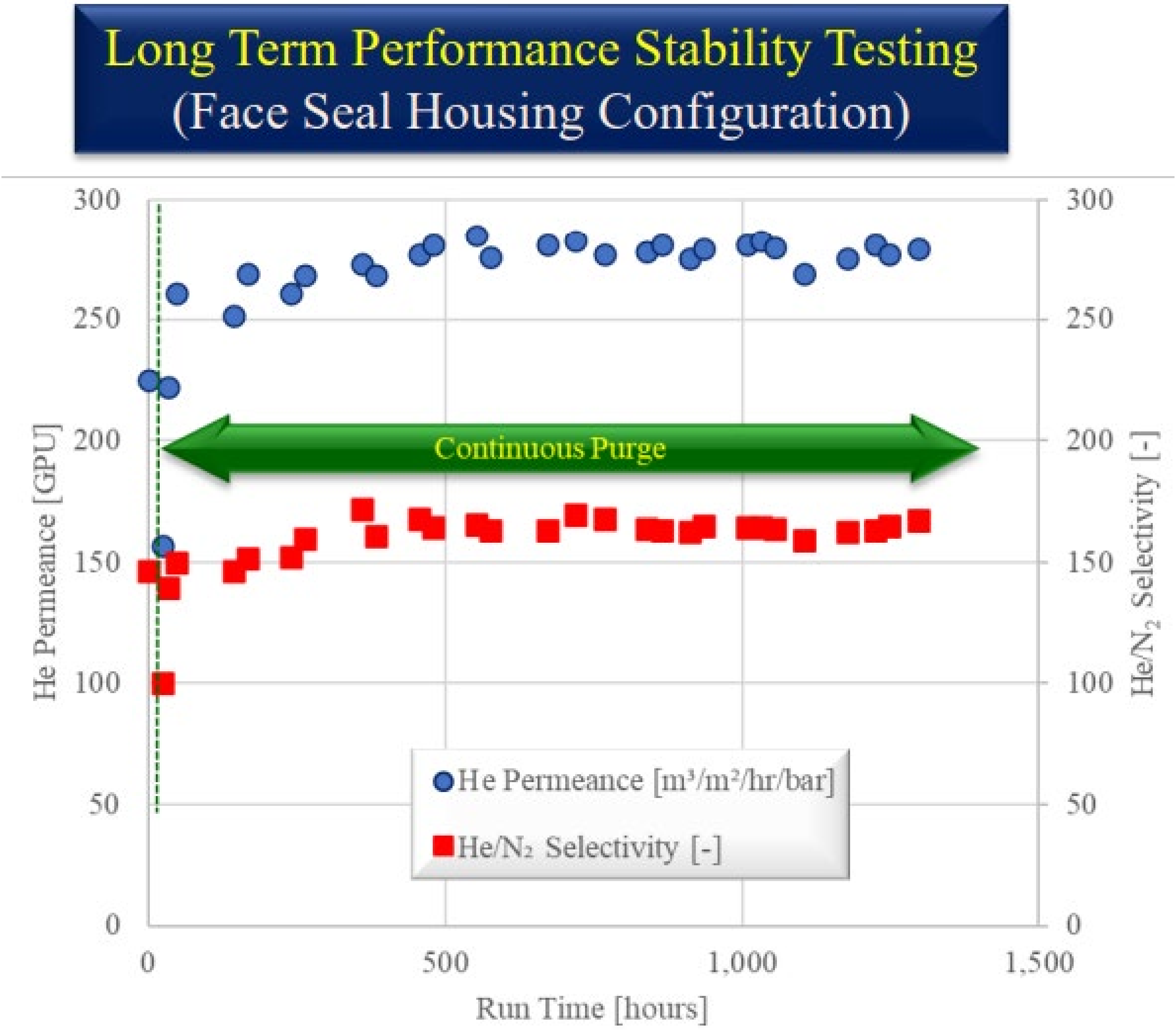
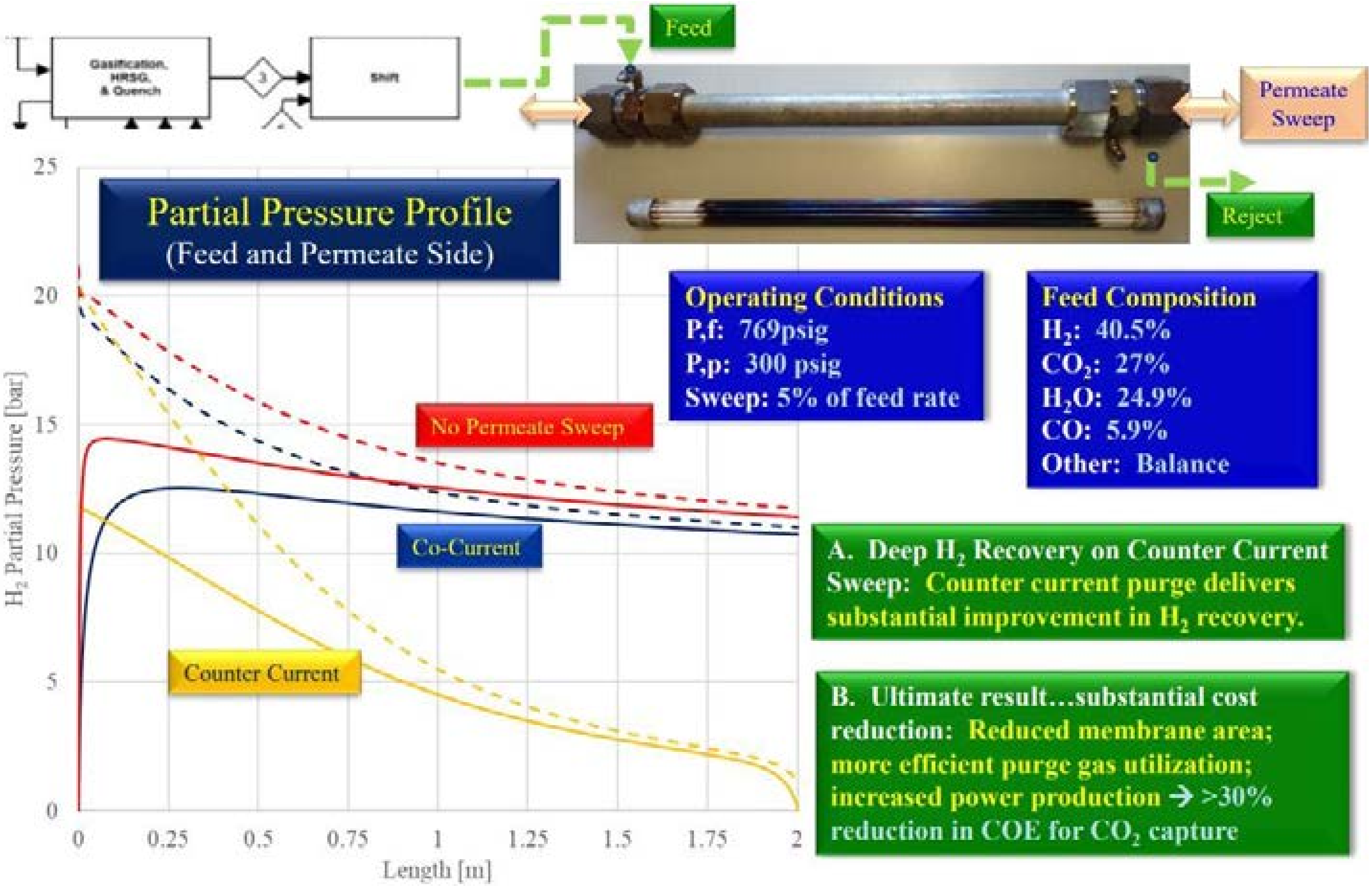


Figure 4: CMS bundle challenge testing.

Computational fluid dynamics (CFD) modeling, assisted by experimental measurements/validation, has been performed for membrane performance prediction and large-scale housing design optimization, and is being utilized in polygeneration process performance modeling to support TEA development. One of the notable modeling efforts has been for prediction of the mixed gas performance of the 18-tube membrane bundles with permeate sweep. Figure 5 illustrates this, showing the concentration of hydrogen (partial pressure) in permeate gases without sweep, and with co-current and counter-current nitrogen sweep. As expected, counter-current sweep maximizes hydrogen recovery.



Operating Conditions
P,f: 769psig
P,p: 300 psig
Sweep: 5% of feed rate

Feed Composition
H_2: 40.5%
CO_2: 27%
H_2O: 24.9%
CO: 5.9%
Other: Balance

A. Deep H_2 Recovery on Counter Current Sweep: Counter current purge delivers substantial improvement in H_2 recovery.

B. Ultimate result…substantial cost reduction: Reduced membrane area; more efficient purge gas utilization; increased power production → >30% reduction in COE for CO_2 capture

Figure 5: Sweep modeling of membrane bundle.

TABLE 1A: MEMBRANE PROCESS PARAMETERS

Materials Properties (Membrane #1)	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Carbon Molecular Sieve (CMS)	
Materials of Fabrication for Support Layer	—	Alumina	
Nominal Thickness of Selective Layer	µm	2 to 3	2 to 3
Membrane Geometry	—	Tubular	Tubular
Maximum Trans-Membrane Pressure	bar	>80	>80
Hours Tested without Significant Degradation	hour	>1,500 in coal gasifier syngas (NCCC)	>20,000
Manufacturing Cost for Membrane Material	$\$/m^2$	2,400	<1,200
Membrane Performance (Membrane #1)			
Temperature	°C	250 to 300	250 to 300
H_2 Pressure Normalized Flux	GPU	350 to 750	350 to 750
H_2/H_2O Selectivity	—	2 to 4	2 to 4
H_2/CO_2 Selectivity	—	>50	>80
H_2/H_2S Selectivity	—	>100	>100
Sulfur Tolerance	ppm	>5,000	>5,000
Type of Measurement	—	Mixed gas and gasifier offgas (NCCC)	Same

TABLE 1B: MEMBRANE PROCESS PARAMETERS

Materials Properties (Membrane #2)	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Palladium Alloy	
Materials of Fabrication for Support Layer	—	Alumina	
Nominal Thickness of Selective Layer	µm	2 to 5	1 to 3
Membrane Geometry	—	Tubular	Tubular
Maximum Trans-Membrane Pressure	bar	>80	>80
Hours Tested without Significant Degradation	—	>35,000 hours in lab testing >150 in pre-treated coal gasifier syngas (NCCC)	>2,000 hours in laboratory simulated syngas
Manufacturing Cost for Membrane Material	$\$/m^2$	9,500	<4,500
Membrane Performance (Membrane #2)			
Temperature	°C	350 to 450	350 to 450
H_2 Pressure Normalized Flux	GPU (at 20psig)	2,000 to >5,500	2,000 to >5,500
H_2/H_2O Selectivity	—	>3,000	>5,000
H_2/CO_2 Selectivity	—	>3,000	>5,000
H_2/H_2S Selectivity	—	NA (high)	NA (high)
Sulfur Tolerance	ppm	<50	<50
Type of Measurement	—	Mixed gas and pretreated gasifier offgas (NCCC)	Same

Proposed Module Design				
Flow Arrangement	—	Co-, counter-, or cross flow		
Packing Density	m^2/m^3	>450		
Shell-Side Fluid	—	Feed/retentate		
Syngas Gas Flowrate	kg/hr	—		
CO_2 Recovery, Purity, and Pressure	%/%/bar	>90	~95	>50
H_2 Recovery, Purity, and Pressure	%/%/bar	>98.8	>97	5 to 15
Pressure Drops Shell/Tube Side	bar	Unknown		
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	Housing cost is estimated at ca. \$350 to \$700/m^2.		

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in desulfurized syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either co-current, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – CMS Membrane: Molecular Sieving; Pd Alloy Membrane: Solution-Diffusion.

Contaminant Resistance – CMS Membrane: Resistant to all coal/biomass gasifier off-gas contaminants; Pd Alloy Membrane: Sulfur species are a significant problem. Unknown for other gas phase contaminants.

Syngas Pretreatment Requirements – CMS Membrane: None except upstream particulate removal at >50µm.

Pd Alloy Membrane: Desulfurization required.

Membrane Replacement Requirements – Unknown; assume 10 years.

Waste Streams Generated – None.

Process Design Concept – See Figure 1.

Proposed Module Design – See Figure 2. Composition of gas entering the membrane subsystem is assumed to be:

Pressure	Temperature	Composition						
		vol%						ppmv
psig	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
800	550	27	6	<1	<1	41	25	500

TABLE 2: INDUSTRIAL PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	$/tonne CO_2	33.2	21.5
Capital Expenditures	$/tonne CO_2	644	644
Operating Expenditures	$/tonne CO_2	26.3	26.3

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Calculations Basis – This work has been developed using Case B5B of DOE/NETL Report 2015/1727 – "Cost and Performance Baseline for Fossil Energy Plants," Volume 1b Rev 2b, July 31, 2015, GEE IGCC with CO_2 Capture as the base case.

Scale of Validation of Technology Used in TEA – Testing was conducted at the NCCC with pilot scale multiple tube membrane bundles at gasifier syngas feed rates up to 5 scfm.

technology advantages

- Inorganic membranes have been demonstrated to be highly effective for and ideally suited to pre-combustion capture.

- Warm gas removal of CO_2, sulfur, and contaminants minimizes gas recompression demand and improves process efficiency.
- Potential for greater than 40% reduction in COE versus baseline amine solvent-based capture.
- DSMP modified polygeneration cycle is well suited to co-production of NH_3.

R&D challenges

- Permeate purge capability with nitrogen or steam is assumed in various technoeconomic analyses, but not yet available in practice.
- Multiple bundle housing design concerns and restrictions: minimizing stress between the ceramic membrane bundles and steel housing, and maintaining bundle interconnects that maintain axial compression.
- Multiple bundle feed flow maldistribution (shell-side) resulting in poor mixed gas performance.

status

Dual-end purgeable dense and porous tube bundles at up to 3-inch diameter have been successfully fabricated and tested, with seal leak rates below target at 400°C and pressures to 800 psig. The Pd and CMS dual-end bundles were gas tested with co-/counter-current permeate sweep. CFD modeling for membrane performance prediction was successful; modeling efforts continue to support polygeneration process development and TEA work is underway.

available reports/technical papers/presentations

"Critical Component/Technology Gap in 21st Century Power Plant Gasification Based Poly-Generation: Advanced Ceramic Membranes/Modules for Ultra Efficient H_2 Production/CO_2 Capture for Coal-Based Poly-generation Plants," Final Project Briefing, September, 2024. *https://netl.doe.gov/projects/files/Critical%20ComponentTechnology%20Gap%20in%2021st%20Century%20Power%20Plant%20Gasification%20Based%20Poly-generation%20%20%20Advanced%20Ceramic%20MembranesModules%20for%20Ultra%20Efficient%20%20H2%20ProductionCO2%20Capture%20for%20Coal-Based%20Poly-generation%20Plants.pdf*.

"Critical Component/Technology Gap in 21st Century Power Plant Gasification Based Poly-Generation: Advanced Ceramic Membranes/Modules for Ultra Efficient H_2 Production/CO_2 Capture for Coal-Based Poly-generation Plants," Carbon Management Project Review Meeting, September 1, 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC1_Ciora.pdf*.

"Critical Component/Technology Gap in 21st Century Power Plant Gasification Based Poly-Generation: Advanced Ceramic Membranes/Modules for Ultra Efficient H_2 Production/CO_2 Capture for Coal-Based Poly-generation Plants," Carbon Management Project Review Meeting, August 16, 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_PSC16_Ciora.pdf*.

"Critical Component/Technology Gap in 21st Century Power Plant Gasification Based Poly-Generation: Advanced Ceramic Membranes/Modules for Ultra Efficient H_2 Production/CO_2 Capture for Coal-Based Poly-generation Plants," Project Budget Period 1 Review Meeting, March 11, 2022. *https://www.netl.doe.gov/projects/plp-download.aspx?id=13015&filename=Critical+Component%2fTechnology+Gap+in+21st+Century+Power+Plant+Gasification+Based+Poly-generation%3a+++Advanced+Ceramic+Membranes%2fModules+for+Ultra+Efficient++H2+Production%2fCO2+Capture+for+Coal-Based+Poly-generation+Plants.pdf*.

"Critical Component/Technology Gap in 21st Century Power Plant Gasification Based Poly-Generation: Advanced Ceramic Membranes/Modules for Ultra Efficient H_2 Production/CO_2 Capture for Coal-Based Poly-generation Plants,"

Presented by Richard Ciora, Media and Process Technology, Inc., 2021 NETL Carbon Management Research Project Review Meeting, August 13, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Ciora.pdf*.

"Critical Component/Technology Gap in Coal FIRST Gasification Based Poly-generation: Advanced Ceramic Membranes/ Modules for Ultra Efficient H_2 Production/CO_2 Capture for Coal-Based Poly-generation Plants," Project Kickoff Meeting, November 5, 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11008&filename=Critical+Component%2fTechnology+Gap+in+Coal+FIRST++Gasification+Based+Poly-generation%3a+++Advanced+Ceramic+Membranes%2fModules+for+Ultra+Efficient++H2+Production%2fCO2+Capture+for+Coal-Based+Poly-generation+Plants.pdf*.

Development and Testing of a High-Temperature PBI Hollow-Fiber Membrane Technology for Pre-Combustion CO_2 Capture

primary project goal

SRI International developed a technically and economically viable carbon dioxide (CO_2) capture system based on a high-temperature polybenzimidazole (PBI) polymer hollow-fiber membrane separation technology. The system is intended for deployment at elevated temperatures to separate hydrogen (H_2) and CO_2 in shifted syngas, enabling pre-combustion carbon capture in integrated gasification combined cycle (IGCC) power plants. The project extended previous work on PBI hollow-fiber membranes to further evaluate second-generation (Gen-2) fibers having improved selectivity through the development and field testing of Gen-2 PBI-based membrane modules on actual coal-derived syngas from an oxygen-blown gasifier.

technical goals

- Produce at least 100 kilometers of Gen-2 fibers that provide an H_2/CO_2 selectivity of about 40 and H_2 permeance of 80–120 gas permeation units (GPU) at greater than 150°C at a 150 pounds per square inch (psi) pressure differential.
- Modify the existing 50-killowatt-thermal (kWth) bench-scale test skid (fabricated and used in FE0012965) with Gen-2 hollow-fiber modules of 4- to 6-inch diameter, and complete bench-skid acceptance testing for 50 hours achieving H_2/CO_2 selectivity greater than 35.
- Perform bench-scale testing at temperatures ≈225°C and up to a pressure of 30 bar under various operating conditions, including long-term steady-state conditions using actual coal-derived syngas (throughput equivalent to 50 kWth) from the entrained flow oxygen-fed gasifier at the University of Kentucky's Center for Applied Energy Research (CAER).
- Prepare techno-economic analysis (TEA) based on Gen-2 bench-scale testing results to re-evaluate technology performance to achieve DOE's pre-combustion capture targets.

technical content

SRI's PBI membrane-based technology was developed for high-temperature pre-combustion separation of H_2 from shifted syngas, leaving a high-concentration, high-pressure CO_2-rich stream in the retentate and yielding a high H_2-content permeate stream. SRI's membranes consist of asymmetric hollow-fiber PBI

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Pre-Combustion Power Generation PSC

key technology:
Membranes

project focus:
PBI Polymer Membrane for CO_2 Capture from Coal Syngas

participant:
SRI International

project number:
FE0031633

predecessor projects:
FC26-07NT43090; FE0012965

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partners:
Enerfex Inc.; PBI Performance Products; University of Kentucky Research Foundation

start date:
10.01.2018

percent complete:
100%

(molecular structure of the polymer shown in Figure 1), which is chemically and thermally stable at temperatures up to 300°C and pressures up to 55 atmospheres (atm; 800 pounds per square inch gauge [psig]). PBI membranes are also sulfur tolerant. These characteristics permit the use of the PBI membrane for CO_2 capture downstream of a sour water-gas shift (WGS) reactor without requiring further gas cooling before the PBI membrane, significantly increasing plant efficiency. In addition, the CO_2 is recovered at high pressure, decreasing CO_2 compression requirements.

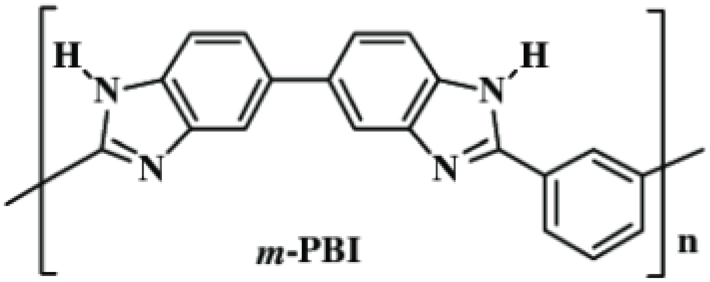


Figure 1: m-polybenzimidazole molecular structure.

Single-bore PBI-based hollow fibers have been shown to be highly durable, with near-constant levels of permeability and selectivity over the course of 330 days while in the presence of H_2, carbon monoxide (CO), methane (CH_4), nitrogen (N_2), CO_2, and hydrogen sulfide (H_2S) at 250°C. Therefore, PBI fiber modules can be successfully used in pre-combustion CO_2 capture applications.

PBI-based hollow fibers, as seen in various magnified views in Figure 2, offer a considerable advantage over coated stainless-steel tubes. They require as much as 24 times less membrane surface area and 305 times less membrane volume when using a 0.1–0.5 micrometer separation layer (the dense layer). Ease of large-scale manufacturability, high packing density, and reduced cost are notable advantages of hollow-fiber membrane systems.

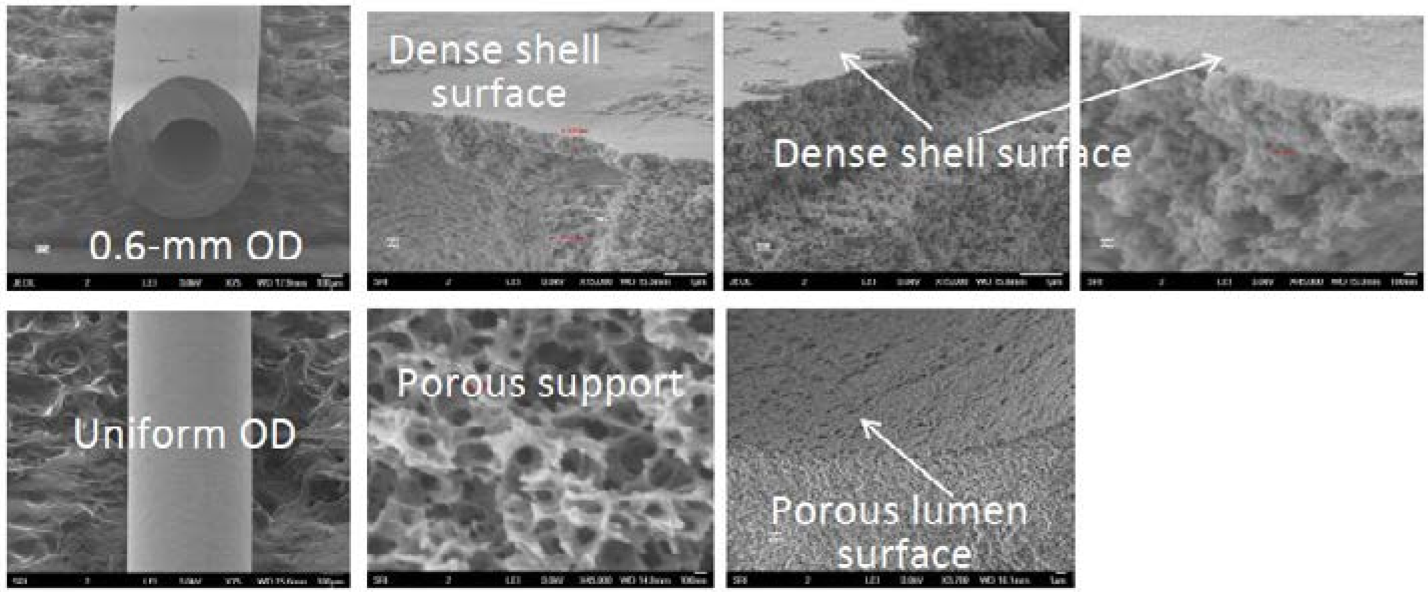


Figure 2: PBI hollow-fiber membranes and details of physical structure.

Fiber Fabrication and Modules

Hollow-fiber membrane fabrication is accomplished in a spinning line as depicted in Figure 3. An important part of technology maturation involves improvements in fiber spinning technology, enabling an improved and robust spinning process that can be transferred to industry. Improvements in the spinning line have enabled use of multiple coagulation solvents, increased productivity (one-gallon reservoir size), process monitoring and data collection, precise flow controls and draw ratios, optimization of fiber diameter, and optimization of the fiber dense-layer thickness.

SRI has been improving its developed protocols to enable spinning dense layer hollow-fiber membranes that are less than 0.3-µm in thickness, with outer diameters (ODs) of 450–650 µm. Figure 2 includes photographs of a hollow-fiber membrane well within this range, with around 0.1-µm dense layer fibers having approximately 600-µm OD. Optimization of OD and dense layer has been supported through testing of more than 100 fiber bundles (1-inch). Fabrication of the Gen-1 hollow-fiber membrane with a very thin, dense layer (less than 0.3 µm) in kilometer lengths has been accomplished with very good reproducibility. In previous work, more than 100 kilometers of Gen-1 fibers have been spun for both Generon and SRI modules (4-inch diameter size fiber modules). In the latest work, more than 10 kilometers of the improved performance Gen-2 fibers have been produced so far for deployment in the new modules to be used in upcoming testing at the University of Kentucky's CAER. Performance parameters for the Gen-2 membranes are shown in Table 1.

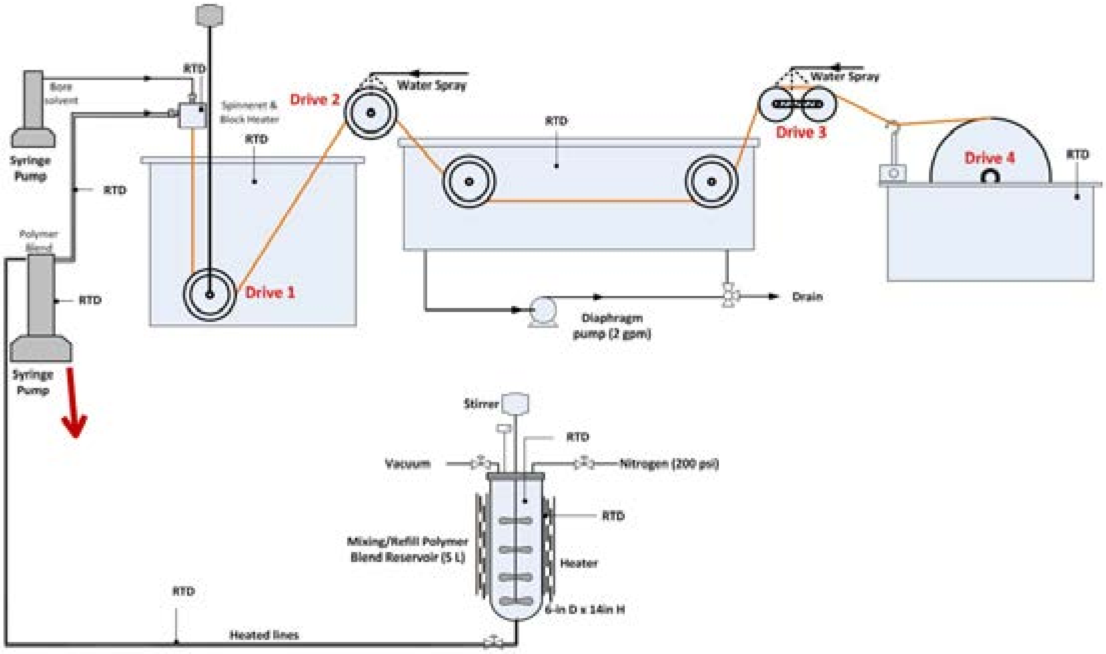


Figure 3: SRI hollow-fiber membrane spinning line.

Large bundles of hollow fibers are potted in tube sheet modules (currently in 4- or 6-inch diameters), which can then be assembled into larger-scale gas separation units/skid for process implementation. Figure 4 shows the cross-section of an actual 4-inch fiber module as fabricated at SRI (on the left); these are the type of modules that had been incorporated in the bench-scale skid, which was deployed in past testing at the National Carbon Capture Center (NCCC) on a syngas slip stream. SRI fiber modules are designed for easy fabrication, easy handling, and easy drop-in replacement. A new tube sheet module design is being deployed (images on right side of Figure 4). These will enable faster module swapping and reduced gas bypass characteristics.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer		PBI	PBI
Materials of Fabrication for Support Layer		PBI	PBI
Nominal Thickness of Selective Layer	µm	0.3–2	<0.5
Membrane Geometry		hollow fiber	hollow fiber
Max Trans-Membrane Pressure	bar	≈14	>20
Hours Tested without Significant Degradation	hr.	1,000	1,000

Manufacturing Cost for Membrane Material	$\$/m^2$	30–80	TBD
Membrane Performance			
Temperature	°C	200–250	225
H_2 Pressure Normalized Flux	GPU or equivalent	80–120	80–120
H_2/H_2O Selectivity	—	<1	<1
H_2/CO_2 Selectivity (Dense layer thickness)	—	40 (>1 µm) and 27 (<0.3 µm)	40 (<0.3 µm)
H_2/H_2S Selectivity (Dense layer thickness)	—	>200 (>1 µm)	>200 (<0.3 µm)
Sulfur Tolerance	ppm	300	300
Type of Measurement		pure and mixed	mixed gases
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement		countercurrent	
Packing Density	m^2/m^3	>3,000	
Shell-Side Fluid		retentate or permeate	
Syngas Flowrate	kg/hr	22	
CO_2 Recovery, Purity, and Pressure	%/%/bar	TBD	
H_2 Recovery, Purity, and Pressure	%/%/bar	>98%, >49%, 30 bar	
Pressure Drops Shell/Tube Side*	bar	<0.007/0.03	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{\mathrm{kg/hr}}$	TBD	

*A commercial 4-inch module design with 200 µm bore diameter and 28–48 bar feed pressure was assumed.

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Figure 4: Potted module cross-section (left-most); new tube sheet module design (right).

Testing Results

Results of testing PBI modules at NCCC on air-blown gasifier syngas have established performance characteristics of both the Gen-1 and Gen-2 PBI modules. Specifically, membrane element TS-1 (consisting of SRI Gen-1 fibers having GPU ~150, H_2/CO_2 selectivity ~25 at 150°C) was tested for about 500 hours. Membrane element TS-2 (consisting of SRI Gen-2 fibers having GPU ~100, H_2/CO_2 selectivity ~40 at 200°C, and at 200 psi) was tested for 48 hours. Figure 5 plots selectivity results of various testing runs for both Gen-1 and Gen-2 testing campaigns. Selectivity of Gen-2 shows definite improvement with potential for superior performance at target operating temperatures of approximately 200°C. Taken with gas permeance measurements (Figure 6), the Gen-2 modules evidence significant performance advantages over Gen-1.

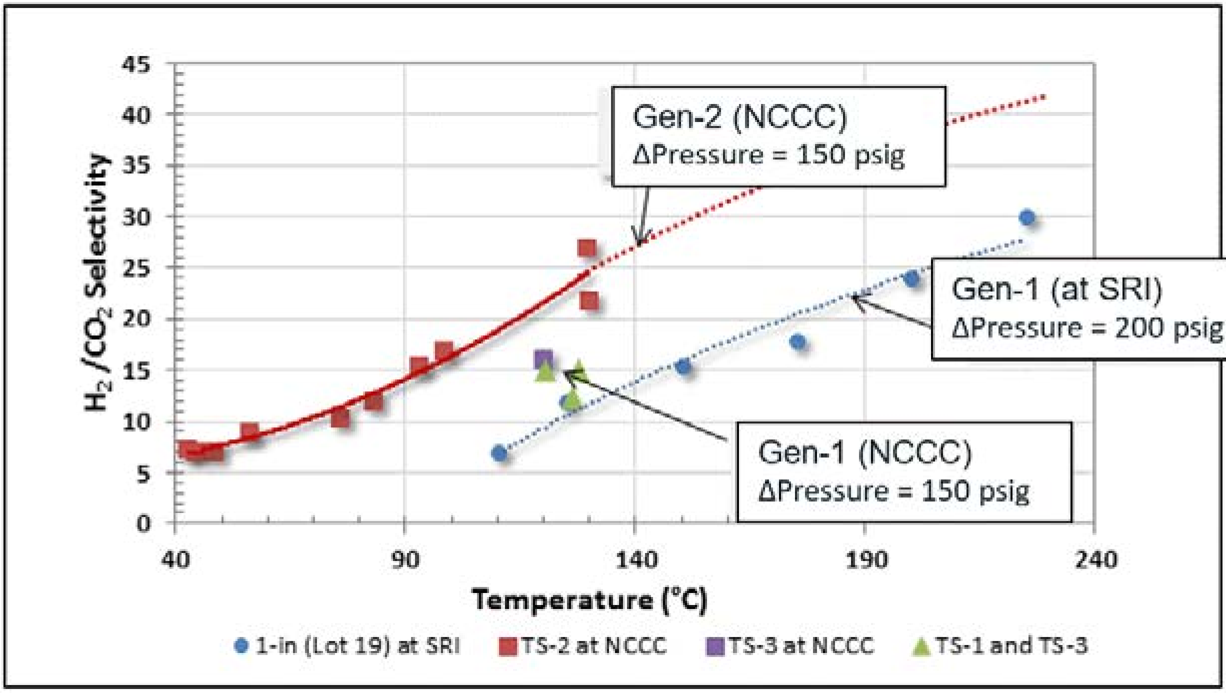


Figure 5: Comparison of measured H_2/CO_2 selectivity for Gen-1 and Gen-2 PBI modules.

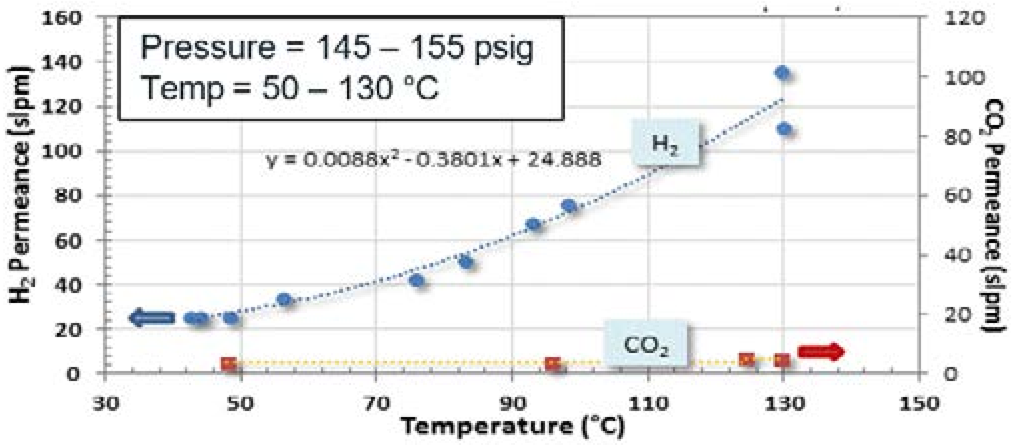


Figure 6: Measured H_2 and CO_2 permeances for the Gen-2 module at varying temperatures under a pressure differential of 145–155 psi.

Preliminary Techno-Economic Analysis Findings

SRI has previously made estimations of cost of electricity (COE) reductions that should be possible by application of the PBI membrane technology in process implementation in the context of an IGCC power plant cycle. From testing of Gen-1 and Gen-2 membranes, performance parameters have been quantified. Given expected Gen-1 and Gen-2 gas selectivities and different gas permeance assumptions, it is possible that the PBI membrane technology can meet National Energy Technology Laboratory (NETL) targets, assuming the membrane system has capital cost reductions that are expected to emerge in industrial-scale economies and savings associated with high levels of system optimization, which are anticipated as higher Technology Readiness Levels (TRLs) are attained. Current research and development (R&D) techno-economic data is shown in Table 2.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	\$32	\$32
Cost of Carbon Avoided	\$/tonne CO_2	—	—
Capital Expenditures	\$/MWhr	\$75	\$75
Operating Expenditures	\$/MWhr	\$60	\$60
Cost of Electricity	\$/MWhr	\$135*	\$135

* >99% hydrogen recovery with 90% CO_2 capture.

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Molecular sieving and activated diffusion.

Contaminant Resistance – PBI is resistant to acidic contaminants.

Syngas Pretreatment Requirements – Tar removed.

Membrane Replacement Requirements – Required frequency of membrane replacement to be determined.

Waste Streams Generated – Gaseous waste stream generated includes CO_2 and H_2S separated from the syngas. This stream will be further treated to remove H_2S.

Process Design Concept – Flowsheet/block flow diagram is shown in Figure 7. Note that the PBI hollow-fiber membrane is both a water and H_2 transporting membrane, so most water vapor/steam in the shifted syngas will segregate into the permeate stream along with the H_2.

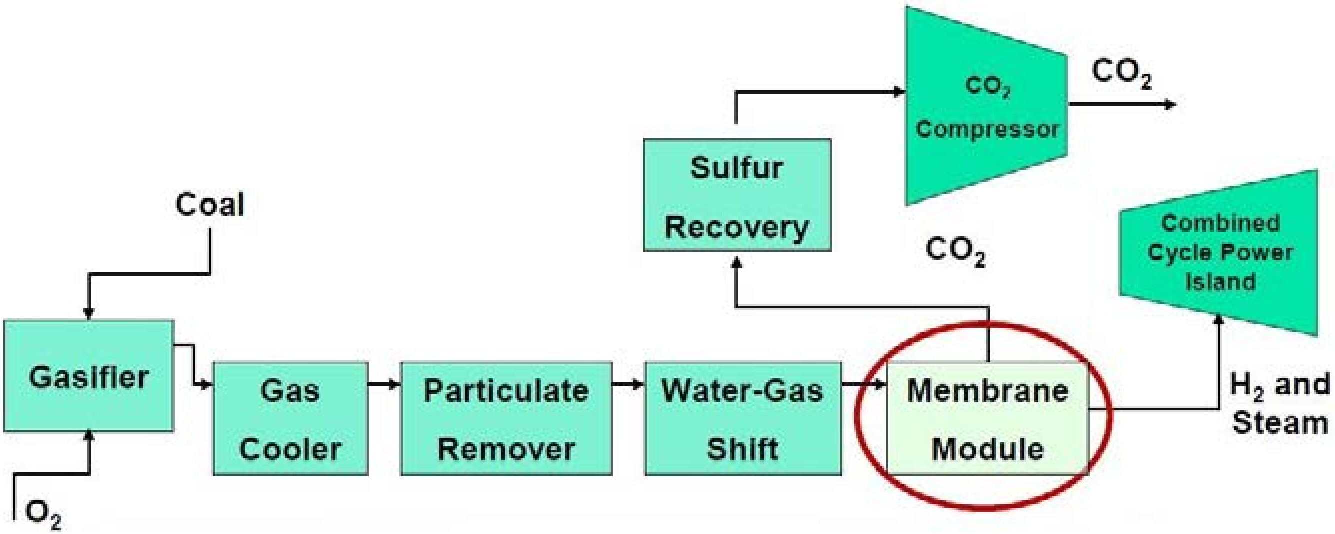
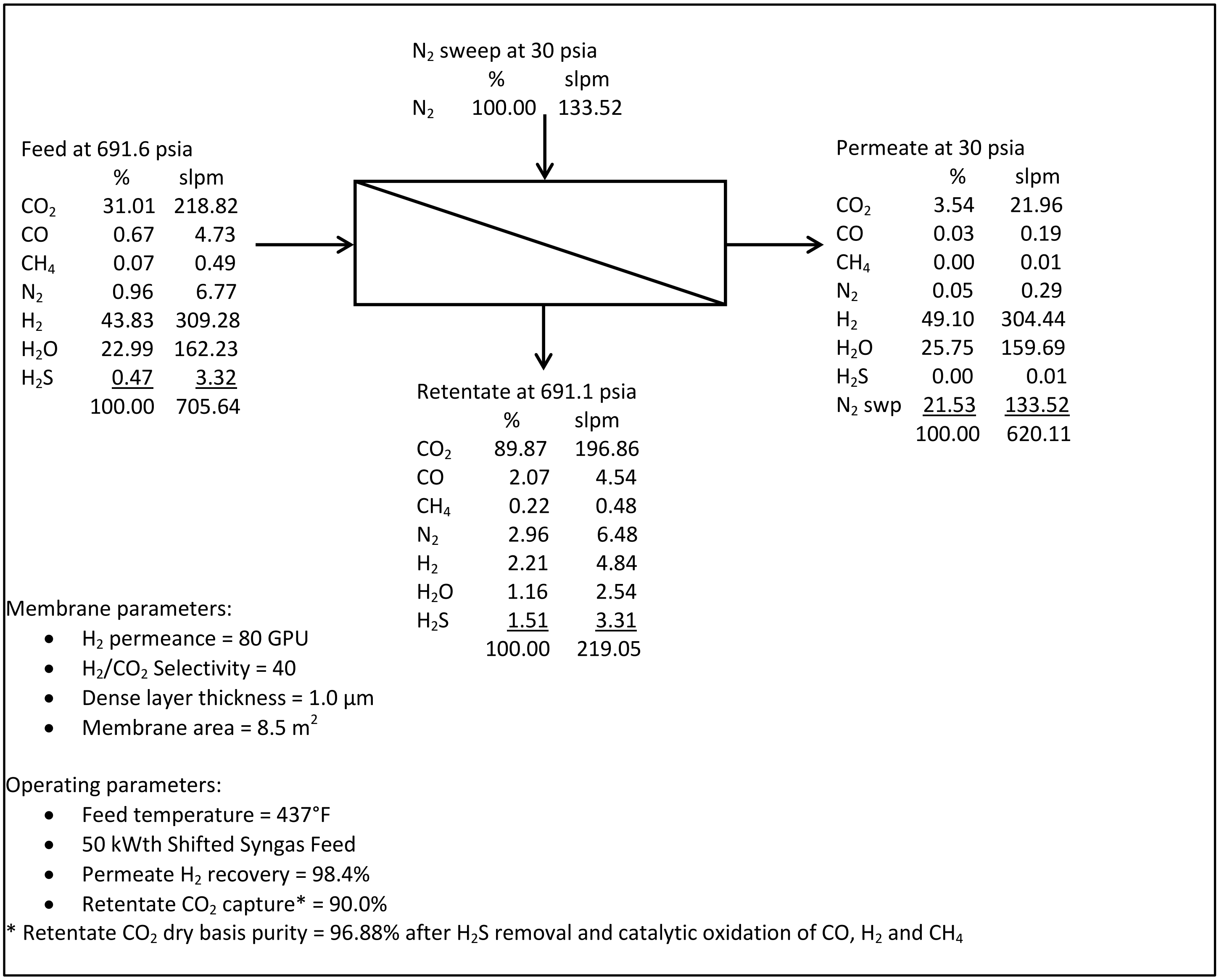


Figure 7: Flowsheet/block flow diagram showing PBI membrane module integration in the IGCC plant process.

Proposed Module Integration – Module design is tubular with 4-inch diameter and 36-inch length. Figure 8 shows the simulated module performance: the pressure, temperature, and composition of the gas entering the module, assuming H_2/CO_2 selectivity of 40. Note that the module feed gas is from an oxygen-blown gasifier with a shifted syngas feed to the membrane. In an oxygen-blown gasifier (assumed in TEA), the permeate recovers 98.4% of the feed H_2 and the retentate captures 90% of the feed CO_2. The retentate stream is further processed in a Claus plant to remove H_2S and a catalytic oxidizer to convert CO and CH_4 to CO_2 and H_2 to water (H_2O). The final retentate dry basis CO_2 purity is 96.88%.

The composition of the gas entering the module is shown below:

Pressure	Temperature	Composition						
		vol%						
psia	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
691.1	437	31.01	0.67	0.07	0.96	43.83	22.99	0.47



N_2 sweep at 30 psia

	%	slpm
N_2	100.00	133.52

Feed at 691.6 psia

	%	slpm
CO_2	31.01	218.82
CO	0.67	4.73
CH_4	0.07	0.49
N_2	0.96	6.77
H_2	43.83	309.28
H_2O	22.99	162.23
H_2S	0.47	3.32
	100.00	705.64

Permeate at 30 psia

	%	slpm
CO_2	3.54	21.96
CO	0.03	0.19
CH_4	0.00	0.01
N_2	0.05	0.29
H_2	49.10	304.44
H_2O	25.75	159.69
H_2S	0.00	0.01
N_2 swp	21.53	133.52
	100.00	620.11

Retentate at 691.1 psia

	%	slpm
CO_2	89.87	196.86
CO	2.07	4.54
CH_4	0.22	0.48
N_2	2.96	6.48
H_2	2.21	4.84
H_2O	1.16	2.54
H_2S	1.51	3.31
	100.00	219.05

Membrane parameters:

- H_2 permeance = 80 GPU
- H_2/CO_2 Selectivity = 40
- Dense layer thickness = 1.0 µm
- Membrane area = 8.5 m^2

Operating parameters:

- Feed temperature = 437°F
- 50 kWth Shifted Syngas Feed
- Permeate H_2 recovery = 98.4%
- Retentate CO_2 capture* = 90.0%

* Retentate CO_2 dry basis purity = 96.88% after H_2S removal and catalytic oxidation of CO, H_2 and CH_4

Figure 8: Simulation of a PBI module performance with an oxygen-blown gasifier and a 50-kWth shifted syngas feed.

technology advantages

- PBI combines both useful throughput (permeability) and degree of separation (selectivity).
- PBI is thermally stable up to 300°C and is sulfur tolerant.
- PBI asymmetric hollow fibers can be fabricated at increasingly small diameters, allowing increased fiber packing densities in modules realistically consistent with 7,000 m^2 of membrane surface area per m^3 of module volume.
- Membrane gas separation systems have reduced costs for syngas cooling and CO_2 compression.
- Membrane gas separation systems do not produce amine emissions.
- Membrane gas separation systems may have decreased capital costs (assuming membrane costs are managed).
- Membrane gas separation systems have relatively low maintenance demands.
- Membrane gas separation systems are scalable and modular.

R&D challenges

- Maintaining fiber and module fabrication quality/performance (avoiding membrane pinholes, macrovoids, module seal integrity) in scale-up/transfer of technology to larger-scale manufacturing.
- Designing and synthesizing materials structure and configurations.
- Integration and optimization of membrane-based CO_2 separation systems in coal gasification-based plants.

status

The project concluded on March 31st, 2023. The membranes were successfully tested for more than 500 continuous hours with no loss of performance. The results showed that, for a 30% H_2 concentration in the incoming syngas, greater than 90% H_2 and CO_2 recoveries could be achieved at a temperature of approximately 150°C. The H_2/CO_2 was found to be as high as 27 at 145°C. The TEA results showed that the cost of capture could be as low as $30/tonne of CO_2 (with a capture rate of 87.8%).

available reports/technical papers/presentations

Jayaweera, I., Jayaweera, P., Perea, E., Yavari, M., “Development and Testing of a High-Temperature PBI Hollow-Fiber Membrane Technology for Pre-Combustion CO_2 Capture.” Final Technical Report, June 2023. *https://www.osti.gov/servlets/purl/1986300/*

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Perea, E., “Development and Testing of a High-temperature PBI Hollow-fiber Membrane Technology for Pre-combustion CO_2 Capture,” presented at the 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting - Capture and Utilization Sessions, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/E-Peria-SRI-High-Temperature-PBI.pdf*.

Jayaweera, I., “Development and Testing of a High-temperature PBI Hollow-Fiber Membrane Technology for Pre-Combustion CO_2 Capture,” Final Project Review (FE0012965) and Project Kickoff (FE0031633), January 2019. *https://netl.doe.gov/projects/plp-download.aspx?id=10555&filename=Development+and+Testing+of+a+High-Temperature+PBI+Hollow-Fiber+Membrane+Technology+for+Pre-Combustion+CO2+Capture.pdf*.

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Jayaweera, I., "Development of Pre-Combustion CO_2 Capture Process Using High-Temperature PBI Hollow-Fiber Membranes," presented at the 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File Library/Events/2015/co2captureproceedings/I-Jayaweera-SRI-High-Temperature-PBI-HF-Membranes-for-Pre-c.pdf*.

Krishnan, G., "Development of a Pre-Combustion Carbon Dioxide Capture Process Using High Temperature Polybenzimidazole Hollow-Fiber Membrane," presented at the 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2014. *http://www.netl.doe.gov/File Library/Events/2014/2014 NETL CO2 Capture/G-Krishnan-SRI-PBI-Hollow-Fiber-Membranes.pdf*.

"Development of a Pre-Combustion Carbon Dioxide Capture Process Using High Temperature Polybenzimidazole Hollow-Fiber Membrane Fact Sheet," July 2014. *https://www.netl.doe.gov/sites/default/files/2017-12/FE0012965.pdf*.

"Development of a Pre-Combustion CO_2 Capture Process Using High-Temperature PBI Hollow-Fiber Membranes," Project Kickoff Meeting Presentation, Pittsburgh, PA, June 9, 2014. *https://www.netl.doe.gov/sites/default/files/2017-12/DE-FE0012965-Kickoff-Meeting-June-2014.pdf*.

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Krishnan, G.; Jayaweera, I.; Sanjurjo, A.; O'Brien, K.; Callahan, R.; Berchtold, K.; Roberts, D.; and Johnson, W.," Fabrication and Scale-up of Polybenzimidazole (PBI) Membrane Based System for Precombustion-Based Capture of Carbon Dioxide," DOE Contract Number: FC26-07NT43090, 2012-March 31. *http://www.osti.gov/scitech/biblio/1050227*.

Bench-Scale Development of a Transformative Membrane Process for Pre-Combustion CO_2 Capture

primary project goal

Membrane Technology and Research Inc. (MTR) and partners Susteon and the Energy and Environmental Research Center (EERC) matured a technology based on a novel, hydrogen (H_2)-selective, multi-layer composite polymer membrane called Proteus™ for use in the separation of H_2 from post-shifted syngas. Project work focused on the goal of scaling-up a second-generation Proteus membrane, including the fabrication of high-temperature prototype modules using second-generation (Gen-2) membranes and validating module performance in laboratory tests, followed by designing, constructing, and installing a prototype test system at EERC for parametric and lifetime testing of the modules with actual coal-derived syngas.

technical goals

- Optimize the Gen-2 Proteus membrane and develop modules capable of operation up to 200°C.
- Demonstrate membrane module performance while processing coal-derived syngas during a field test at EERC by demonstrating an H_2/carbon dioxide (CO_2) selectivity = 30 and recovering 2.5 lb/h H_2 at 75% purity at a syngas flow rate of 20 lb/h.
- Advance the Gen-2 Proteus membrane pre-combustion membrane capture technology from Technology Readiness Level (TRL) 4 to TRL 5.
- Optimize processes for integrating membrane modules into the integrated gasification combined cycle (IGCC) process with carbon capture (including evaluating sulfur treatment options), showing the potential via a techno-economic analysis (TEA) to attain a cost of electricity (COE) 30% less than baseline capture approaches (Selexol).

technical content

MTR has been developing composite membranes for application in pre-combustion carbon capture where essential membrane characteristics include high H_2/CO_2 selectivity and high H_2 permeance rates. The MTR composite membrane for high temperature H_2 separation is called Proteus. Figure 1 illustrates the membrane structure and some characteristic composite membrane layers. Note that the key to competitive industrial performance is a very thin selective layer, which is required to allow high gas fluxes (or permeances) for given membrane surface areas.

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Pre-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Composite Polymeric Membranes for CO_2 Capture from Coal Syngas

participant:
Membrane Technology and Research Inc.

project number:
FE0031632

predecessor projects:
FE0001124

NETL project manager:
Carl Laird
Carl.Laird@netl.doe.gov

principal investigator:
Jay Kniep
Membrane Technology and Research Inc.
jay.kniep@mtrinc.com

partners:
Susteon Inc.; Energy and Environmental Research Center

start date:
10.01.2018

percent complete:
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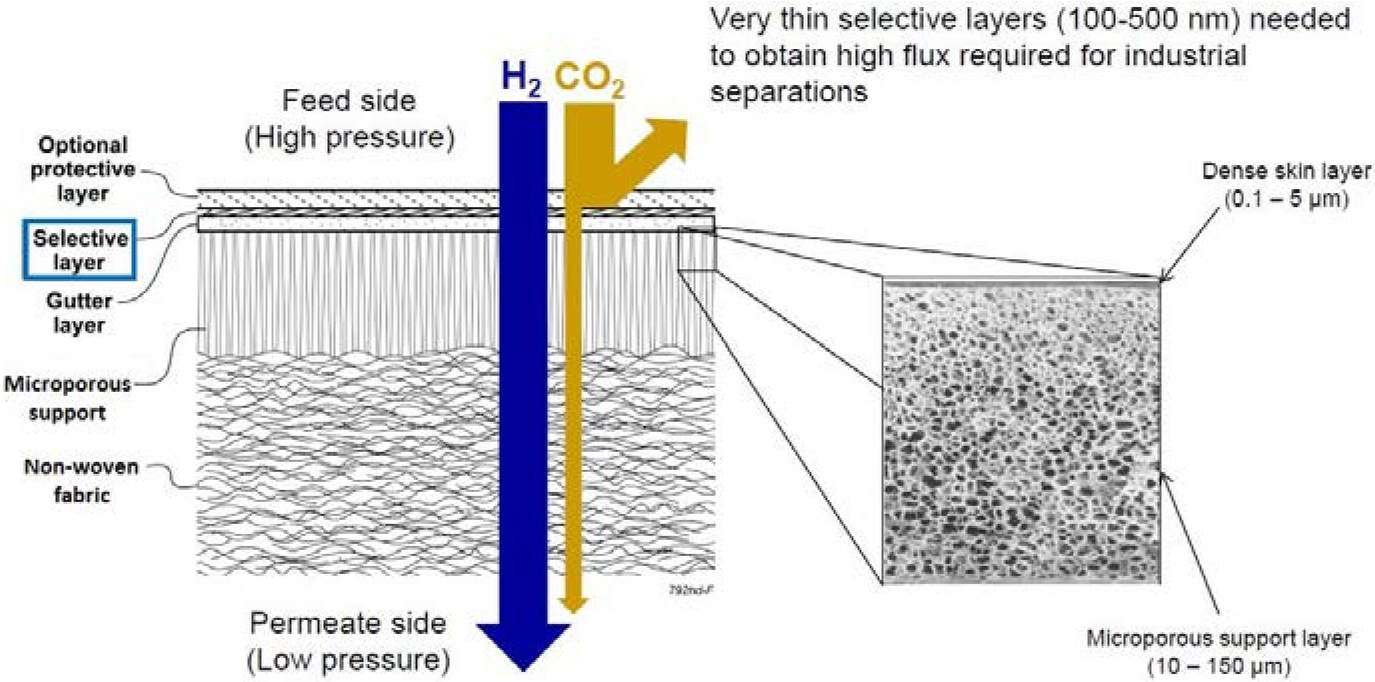


Figure 1: Proteus membrane multi-layer composite structure.

The H_2-selective Proteus membranes were first developed by MTR in work funded by the U.S. Department of Energy (DOE; DE-FE0001124). The first-generation membrane (Gen-1 Proteus) had an upper temperature limit of 150°C. Semi-commercial modules made from this membrane demonstrated stable operation for extended periods in the presence of sulfur and other contaminants in slipstream tests of actual coal-derived syngas from an air-blown gasifier at the National Carbon Capture Center (NCCC). By the end of testing in 2017, Gen-1 Proteus was evaluated in more than 15 different gasification campaigns accumulating 5,500 hours of run time for membrane stamps or lab-scale modules and 3,625 hours for semi-commercial modules at NCCC.

The subsequently developed Gen-2 Proteus has a higher temperature limit compared to the Gen-1 membrane (200°C versus 150°C), which allows for better heat integration into pre-combustion processes. The Gen-2 membrane also has improved H_2/CO_2 selectivity compared to the Gen-1 membrane, with an average value of 32 measured in membrane stamp testing at NCCC (compared to 15 to 20 for Gen 1 in the same tests). A new membrane treatment technique was developed that improves the membrane H_2/CO_2 selectivity; the optimized membrane has achieved a selectivity of 37, which exceeds the project success criteria of 30. This improved selectivity reduces energy use and the required purification equipment size, thereby lowering operating and capital expenses.

To highlight the improved permeation performance of the Gen-2 Proteus membrane, Figure 2 compares the selectivity and permeance of this membrane with other polymers on a Robeson tradeoff plot.

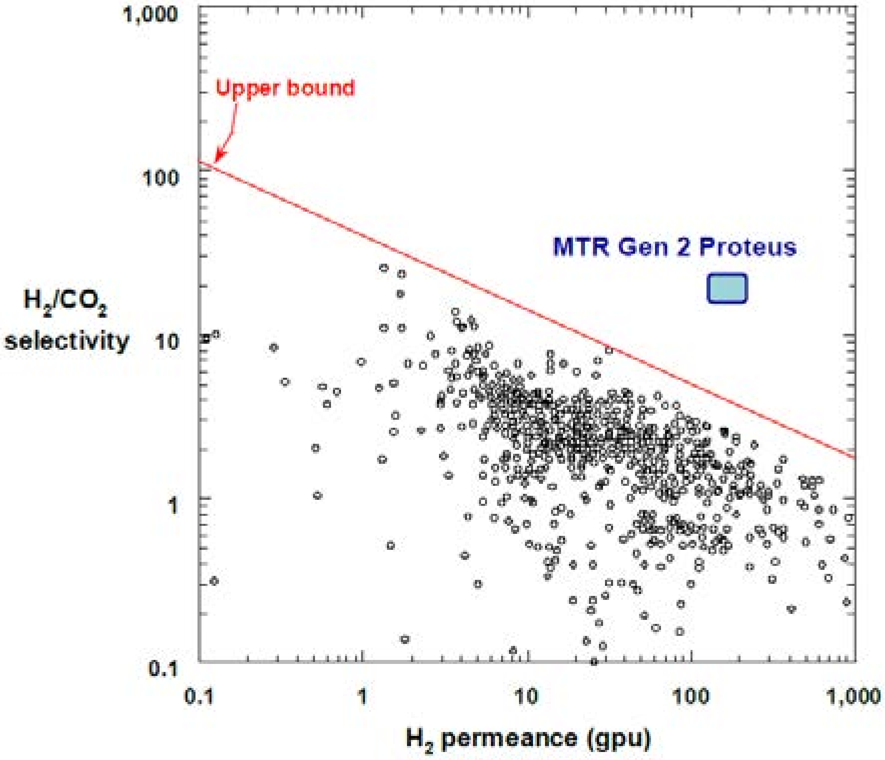


Figure 2: Robeson plot with Gen-2 Proteus membrane performance.

MTR has thoroughly tested the Gen-2 Proteus membrane to determine if all performance targets have been met. The membrane was both temperature- and pressure-cycled to verify robustness; gas permeance values were found to be very stable over multiple heating and cooling cycles, as shown in Figure 3. In addition, the membrane was pressure-cycled in nitrogen between 100 and 1,000 pounds per square inch gauge (psig); nitrogen permeance increased to 5 gas permeation units (GPU) at high pressure and consistently returned to 2 GPU at low pressure. The optimized Gen-2 Proteus membrane retained its high selectivity after operational cycling, showing the robustness of the membrane.

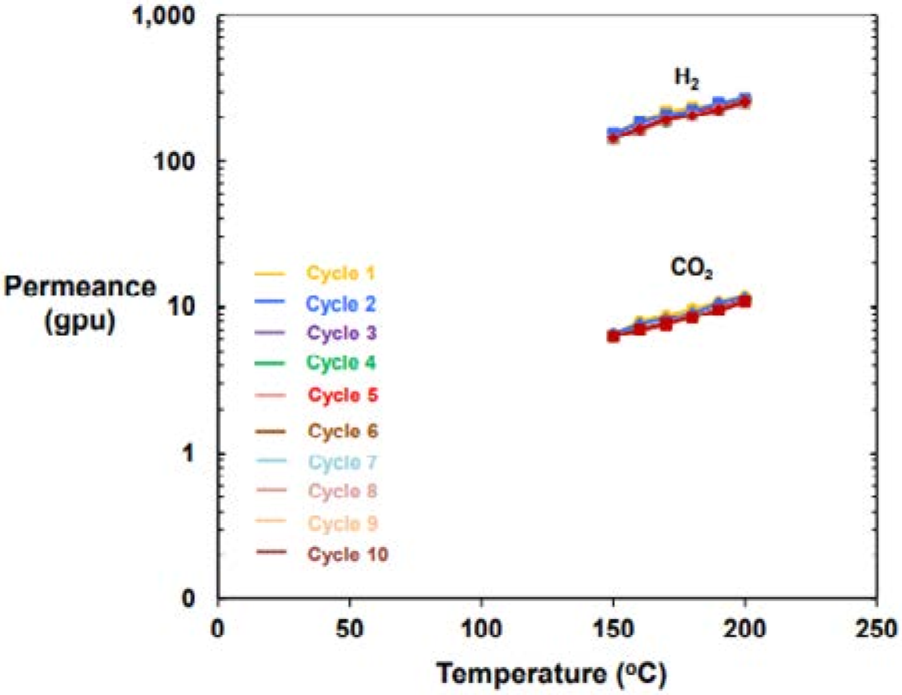


Figure 3: Gen-2 Proteus membrane temperature cycling results.

Process Scenarios

A simplified process flow diagram for carbon capture with membranes in an IGCC power cycle is depicted in Figure 4. Coal is converted by oxygen-based pressurized gasification resulting in a raw syngas. This syngas is shifted via the water-gas shift (WGS) reaction to produce syngas consisting mostly of H_2 and CO_2. This shifted syngas is introduced at the high-pressure feed side of the membrane capture unit. The high-partial pressure driving force, combined with a nitrogen (N_2) sweep on the lower-pressure permeate side of the membrane, causes selective H_2 permeation into the N_2 sweep, which serves as fuel gas in a combustion turbine. The high-pressure membrane retentate is enriched in CO_2 that can then be further purified, compressed, and sent to storage.

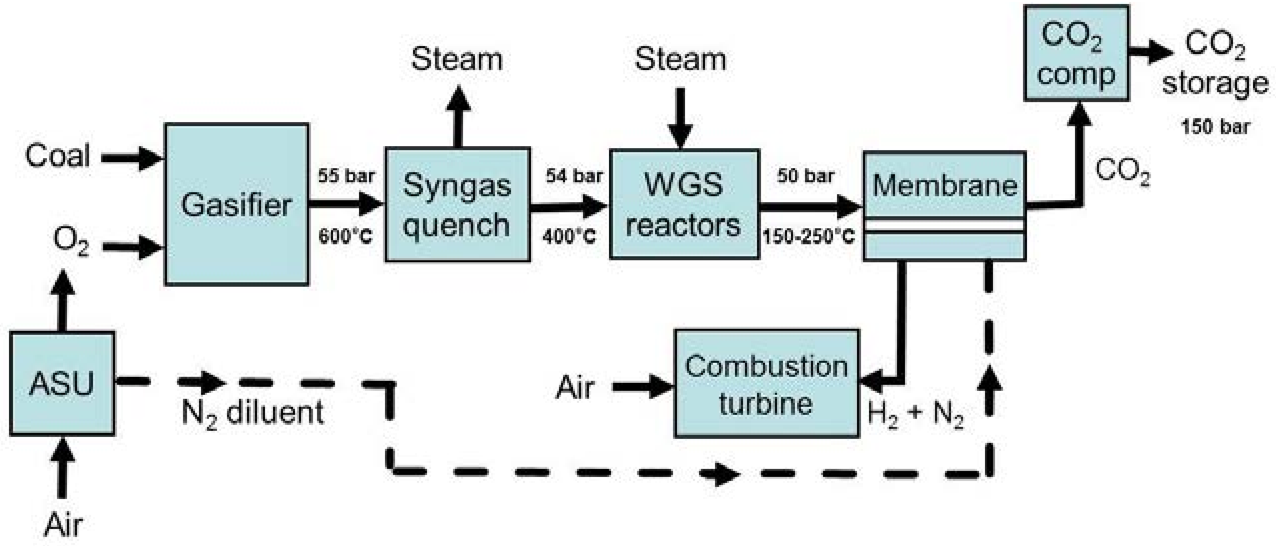


Figure 4: Overall process design for the pre-combustion capture membrane system.

Figure 5 shows additional process details for the MTR pre-combustion CO_2 capture process. After using the Proteus membrane to recover H_2, a series of steps are used to purify CO_2. These steps include (1) sulfur removal, (2) gas drying, (3) refrigeration to produce liquid CO_2, (4) additional CO_2 recovery with the MTR Polaris™ membrane, and (5) pumping liquid CO_2 to storage pressure. The CO_2 purity can be readily increased to greater than 99% in this process. In comparison to a baseline case (GE Gasifier with two-stage Selexol [i.e., Case 2 of DOE Bituminous Baselines Study]), prior studies showed that the MTR membrane process provides a 27-megawatt-electric (MWe) net power improvement and a 7.4% lower cost of energy (COE) using Gen-1 Proteus membrane properties. Both the warm (H_2 membrane) and cold (CO_2 membrane) portions of the MTR process have been validated in independent skid field tests at NCCC.

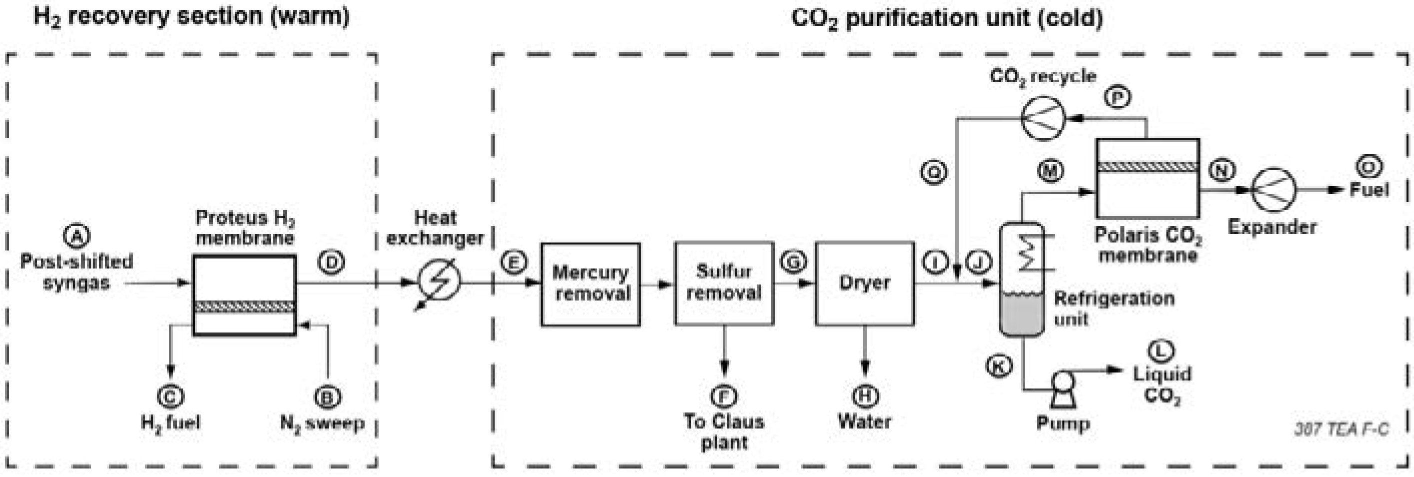


Figure 5: MTR dual-membrane process for H_2 recovery and CO_2 capture in IGCC power generation.

For industrial applications, Proteus membranes can be packed into spiral-wound membrane modules, a commonly used module design for commercial membrane installations. Spiral-wound modules are robust, resistant to fouling, and economical; they are used in 95% of the reverse osmosis (RO) desalination industry and more than 70% of the membrane market for CO_2 removal from natural gas. Figure 6 shows the general design features of a spiral-wound membrane module. The module consists of a permeate collection tube with a spiral formation of permeate spacers and feed spacers, allowing separated H_2 to be swept by N_2 on the permeate side and CO_2 retained on the feed side to flow through the device. In bench-scale work, modules have a membrane area of 1 to 4 m^2, and accommodate gas flow of about 50 lb/h. Commercial modules have a membrane area of 20 to 50 m^2, and accommodate gas flow of about 500 lb/h.

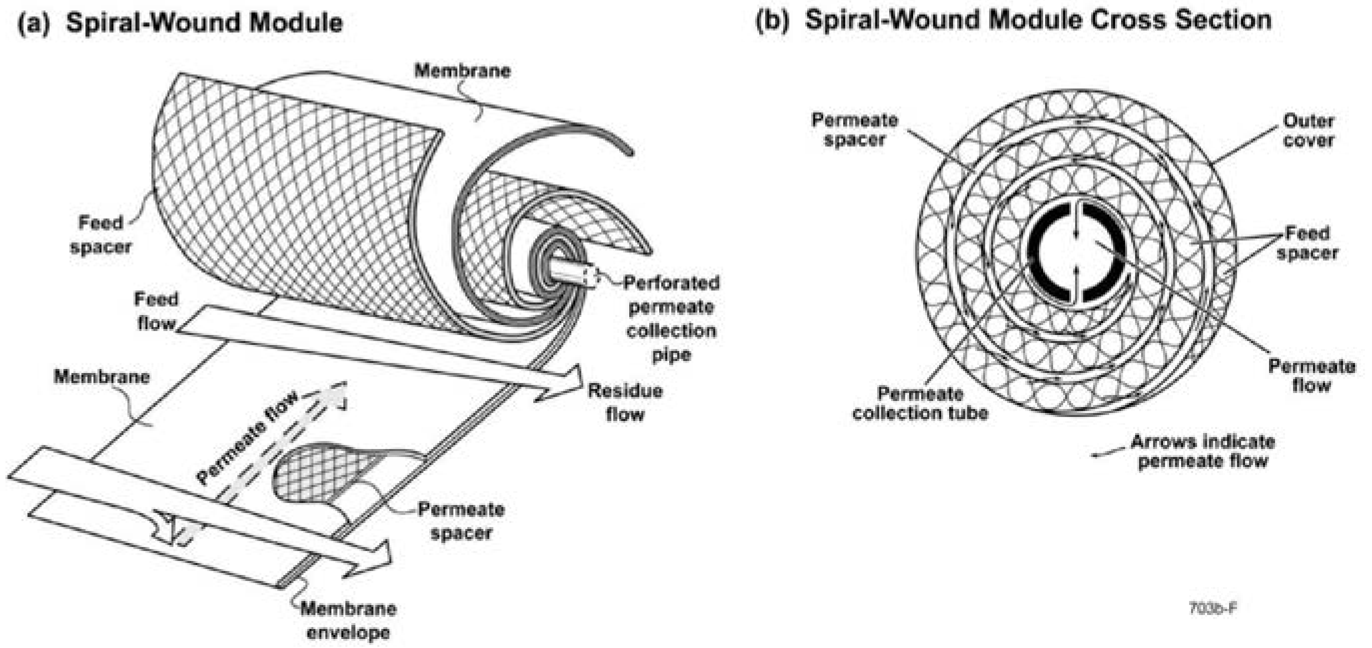


Figure 6: Schematic diagram of a spiral-wound membrane module.

Bench-Scale Field Testing

MTR constructed a bench-scale testing unit incorporating semi-commercial-scale spiral-wound modules. The bench-scale unit was deployed in field-testing at EERC in 2021. EERC's oxygen-blown fluidized bed gasifier supplied syngas for the testing; syngas conditions were as follows:

- 300 to 500 psig gas pressure.
- 30 to 35% H_2; 40 to 50% CO_2.
- Up to 3,000 parts per million (ppm) hydrogen sulfide (H_2S).

A full parametric test matrix of temperature and feed syngas pressures was completed in the testing. For assessment of operational robustness, modules were temperature-cycled up to a simulated process upset condition of 215°C at a syngas pressure of 300 psig. Initial and final 170°C H_2 permeance values were in excellent agreement with the MTR laboratory mixed gas value of 255 GPU, as shown in Figure 7. Overall, testing findings were encouraging, with post-field test examination of the modules finding no membrane pin-hole leaks, good membrane/spacer compatibility and spacers condition, glue lines intact, and no evidence found of module degradation due to high-temperature syngas exposure.

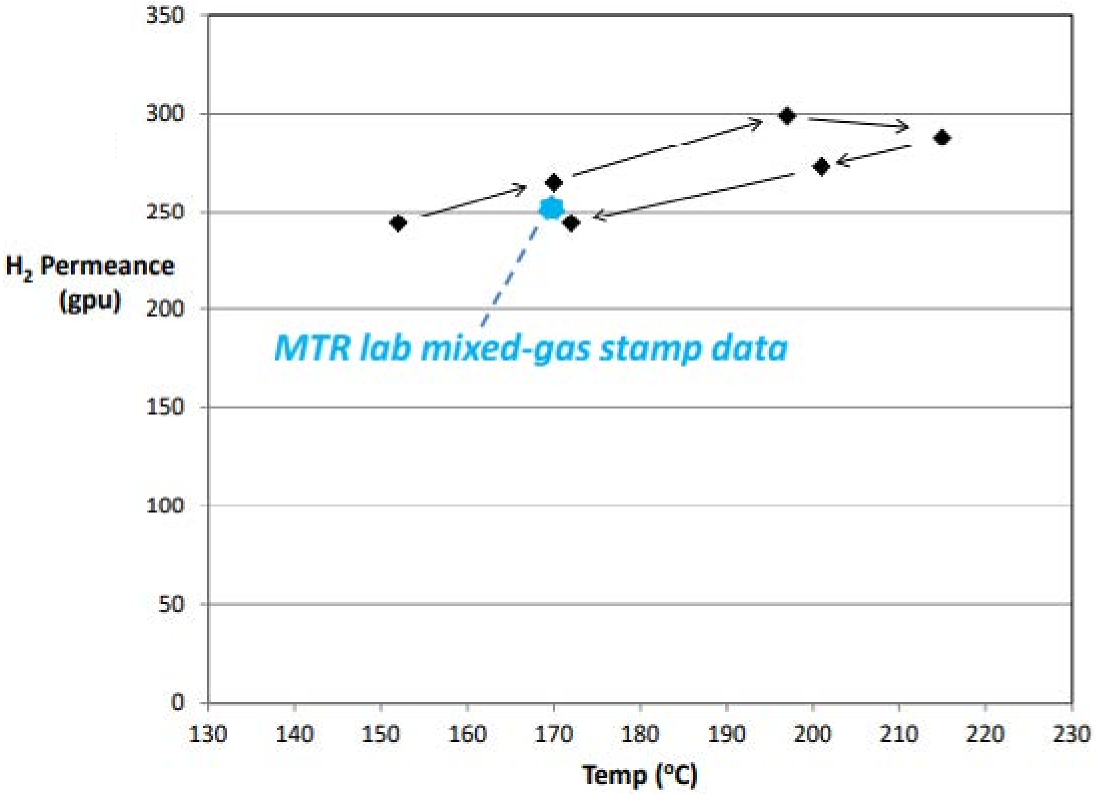
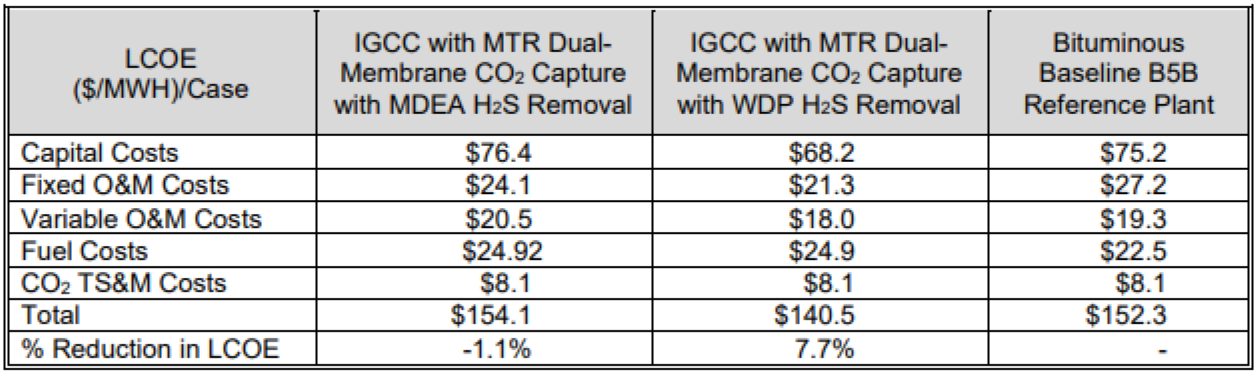


Figure 7: Influence of temperature on H_2 permeance during EERC field test of the Gen-2 Proteus module.

Techno-Economic Analysis

The TEA for this project adopted the plant context from the baseline IGCC power plant with two-stage Selexol for CO_2 and H_2S removal (reference plant B5B found in the National Energy Technology Laboratory's (NETL) Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity Rev. 4), substituting MTR's dual-membrane pre-combustion CO_2 capture process for the baseline's two-stage Selexol. The TEA included process optimization studies, including varying the Gen-2 Proteus operating temperature, resulting in sensitivity analysis of a total of 12 process cases. Gen-2 Proteus membrane performance numbers used in the TEA had been validated during a bench-scale field test (TRL 5) at EERC with an oxygen-blown fluidized bed gasifier as the coal-derived syngas source.

Although the NETL baseline case utilizes a methyl diethanolamine (MDEA) desulfurization unit operation, MTR and Susteon discovered, in the course of the TEA, that an alternative desulfurization technology is preferred for pairing with the MTR dual-membrane process design. After reviewing all traditional and novel solutions for desulfurization of the DOE IGCC baseline case and evaluation of each technology with respect to feed flow rate capability, inlet sulfur concentration range, and the ability to separate H_2S from CO_2, it was found that the warm desulfurization process (WDP) provides best cost performance. This is tabulated in Figure 8, showing cost components and overall percent reduction in levelized cost of electricity (LCOE) for the NETL reference baseline case B5B, best case MTR dual-membrane CO_2 capture paired with MDEA H_2S removal, and best case MTR dual-membrane CO_2 capture paired with WDP H_2S removal. Note that the pairing with WDP provides a significant reduction of 7.7% in LCOE compared to the baseline. This can be attributed primarily to WDP allowing lower Proteus membrane temperature operation at which H_2 separation is still quite efficient, while allowing more heat to be available to produce low-pressure and intermediate pressure steam in the overall plant power cycle.



LCOE ($/MWH)/Case	IGCC with MTR Dual-Membrane CO_2 Capture with MDEA H_2S Removal	IGCC with MTR Dual-Membrane CO_2 Capture with WDP H_2S Removal	Bituminous Baseline B5B Reference Plant
Capital Costs	$76.4	$68.2	$75.2
Fixed O&M Costs	$24.1	$21.3	$27.2
Variable O&M Costs	$20.5	$18.0	$19.3
Fuel Costs	$24.92	$24.9	$22.5
CO_2 TS&M Costs	$8.1	$8.1	$8.1
Total	$154.1	$140.5	$152.3
% Reduction in LCOE	-1.1%	7.7%	-

Figure 8: LCOE breakdown for the best cases for MTR's dual-membrane process design with MDEA and WDP compared with bituminous baseline case B5B reference plant.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Proprietary polymers	
Materials of Fabrication for Support Layer	—	Proprietary polymers	
Nominal Thickness of Selective Layer	µm	< 1 micron	< 1 micron
Membrane Geometry	—	Flat sheet	Flat sheet
Maximum Trans-Membrane Pressure	bar	75	75
Hours Tested without Significant Degradation	—	1 month	3 months
Manufacturing Cost for Membrane Material	$/m²	500	250
Membrane Performance			
Temperature	°C	200	200
H_2 Pressure Normalized Flux	GPU or equivalent	275	200
H_2/H_2O Selectivity	—	0.4	0.4
H_2/CO_2 Selectivity	—	37	30
H_2/H_2S Selectivity	—	>50	50
Sulfur Tolerance	ppm	Inert to Sulfur	Inert to Sulfur
Type of Measurement	—	mixed-gas	mixed-gas
Proposed Module Design			
Flow Arrangement	—	Spiral-wound modules	
Packing Density	m^2/m^3	1,000	
Shell-Side Fluid	—	Syngas	
Syngas Gas Flowrate	kg/hr	717,000	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90 99.5 152.7	
H_2 Recovery, Purity, and Pressure	%/%/bar	99.4 44 % in N_2 as fuel 30	
Pressure Drops Shell/Tube Side	bar	feed: 1 /sweep: 1	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	15	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in desulfurized syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Permeation through the Proteus membrane occurs by the passive solution-diffusion mechanism.

Contaminant Resistance – The MTR membranes and membrane module components are compatible with the species found in coal-derived syngas. This is one of the major findings from syngas field tests conducted at NCCC between 2009 and 2017 for both the Polaris™ (5,200 cumulative hours online) and Proteus (9,125 cumulative hours online) membranes.

Syngas Pretreatment Requirements – The MTR pre-combustion CO_2 capture membrane process design does not require syngas pretreatment.

Membrane Replacement Requirements – The target membrane module lifetime is three years, which is at the conservative end of the typical industrial gas separation module lifetime of three to five years.

Waste Streams Generated – No additional waste streams are generated when adding the MTR pre-combustion CO_2 capture system to an IGCC process. Similar to the stand-alone IGCC process, water removed from the MTR process can be recycled to process demand and the removed sulfur species can be sent to a Claus plant for processing. The high-purity CO_2 product can be used for enhanced oil recovery or other industrial applications.

Proposed Module Design – Spiral-wound modules; see Figure 6.

The pressure, temperature, and composition of the gas entering the membrane module are as follows:

Pressure	Temperature	Composition						
psia	°F	vol%						ppmv
		CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
740	392	40.73	1.19	0.01	0.77	55.79	0.18	6230

Power Plant Applications

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	88	—
Cost of Carbon Avoided	\$/tonne CO_2	103	—
Capital Expenditures	\$/MWhr	68.2	—
Operating Expenditures	\$/MWhr	39.3	—
Cost of Electricity	\$/MWhr	140.5	106.61

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – The TEA for this project adopted the plant context from the baseline IGCC power plant with two-stage Selexol for CO_2 and H_2S removal (reference plant B5B found in NETL's Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity Rev. 4).

Scale of Validation of Technology Used in TEA – The TEA for this project used the technology performance numbers validated at bench-scale gasification testing (TRL 5) at EERC.

technology advantages

- The Proteus membrane allows separation of H_2 from syngas at elevated temperatures. This ability to operate warm/hot reduces the need for heat exchange (e.g., membrane modules operate at a higher temperature than conventional acid gas removal processes like Selexol, reducing the need for syngas cooling and water condensation).
- A membrane system does not contain moving parts or involve chemical reactions, making it simple to operate and maintain.
- The membrane material has a high tolerance to acid gases and is inert to all primary syngas species.
- The membrane capture system has a compact footprint and low energy cost.
- The membrane capture system permeates water in syngas (increase mass to turbine and reduces CO_2 dehydration costs).
- Membrane modules downstream from pressurized WGS maintain CO_2 effluent at pressure; therefore, less compression of CO_2 product is required compared to conventional acid gas removal processes.
- The proposed N_2 sweep on the H_2 permeate side increases the partial pressure driving force for separation and decreases the required membrane area.

R&D challenges

- Countercurrent sweep module design could result in several potential inefficiencies, including sweep-side pressure drop, concentration polarization, poor utilization of the membrane area, and non-countercurrent flow patterns.
- Feed and permeate side pressure drops could lead to excessive energy losses if modules are not designed properly.
- Membrane module cost reductions will be needed if the technology is to become economically viable.
- Scale-up and integration issues are possible given the large number of modules needed to service a 550-MWe plant.

status

This project was completed on March 30, 2022. A second-generation Proteus membrane has been made with performance that exceeds H_2/CO_2 selectivity targets. The membrane was incorporated in near-commercial-scale robust membrane modules, which were deployed in a bench-scale field-test skid for evaluation of capture performance on oxygen-blown, gasifier-produced, high-temperature syngas at EERC. The membrane and module were found to perform robustly and maintain durability after exposure to the sulfur-containing syngas at elevated temperatures. Field test data analysis has been completed and the results were incorporated into the final TEA, which revealed that a best-case process scenario utilizing the MTR dual-membrane CO_2 capture process could deliver 7.7% reduction in LCOE over an established NETL baseline IGCC case.

available reports/technical papers/presentations

"Bench-Scale Development of a Transformative Membrane Process for Pre-Combustion CO_2 Capture," Final Project Report, July 27, 2022. *https://www.osti.gov/servlets/purl/1878227*.

"Bench-Scale Development of a Transformative Membrane Process for Pre-Combustion CO_2 Capture," presented by Jay Kniep, Membrane Technology and Research Inc., DOE NETL Virtual Review Meeting, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Kniep.pdf*.

"Bench-Scale Development of a Transformative Membrane Process for Pre-Combustion CO_2 Capture," presented by Jay Kniep, Membrane Technology and Research Inc., 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/J-Kniep-MTR-Precombustion-Membrane.pdf*.

"Bench-Scale Development of a Transformative Membrane Process for Pre-Combustion CO_2 Capture," presented by Jay Kniep, Membrane Technology and Research Inc., 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/J-Kniep-MTR-Transformative-Membrane-Process.pdf*.

"Bench-Scale Development of a Transformative Membrane Process for Pre-Combustion CO_2 Capture," Project kickoff meeting presentation, December 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10543&filename=Bench-Scale+Development+of+a+Transformative+Membrane+Process+for+Pre-Combustion+CO2+Capture+.pdf.*

"Novel Polymer Membrane Process for Pre-combustion CO_2 Capture from Coal-fired Syngas," Final Report for DE-FE0001124, Membrane Technology and Research Inc., December 2011. *https://www.osti.gov/servlets/purl/1080044.*

Bench-Scale Testing of a High-Efficiency, Ultra-Compact Process for Pre-Combustion CO_2 Capture

primary project goal

University of Southern California completed scale-up and field-testing of their membrane- and adsorption-enhanced water-gas shift (WGS) process that employs a carbon molecular sieve (CMS) membrane reactor (MR), followed by an adsorption reactor (AR), for pre-combustion carbon dioxide (CO_2) capture. The project began at Technology Readiness Level (TRL) 4, as the system prototype was already validated in the laboratory on simulated syngas (under the predecessor project FE0026423). The project ended at TRL 5, via scaling-up of the prototype system and its testing on actual syngas at the University of Kentucky (UKy).

technical goals

- Demonstrate CO_2 capture from actual coal gasification syngas at a bench-scale syngas flow rate of 50.7 to 253 kg/day, at a temperature of 250°C, at a pressure of 25 atmosphere [atm], and for 500 hours of testing.
- Increase stability of membranes and adsorbents in the process system in terms of degradation by syngas constituents, with an interim target of less than 30% decline in performance over 500 hours of testing at typical syngas conditions.
- Achieve hydrogen (H_2) permeance greater than 1 m^3/m^2.hr.bar for the H_2-selective membrane, with a target range for H_2/carbon monoxide (CO) selectivity exceeding 80.
- Achieve sorbent working capacity greater than 2.5 weight % CO_2 and sorbent attrition rate less than 0.2.
- Demonstrate progress (TRL 4 to TRL 5) toward enabling an MR-AR system in a 550-megawatt-electric (MWe) integrated gasification combined cycle (IGCC) plant, capable of CO_2 capture with greater than 95% purity, while reducing the cost of electricity (COE) by 30% over IGCC plants employing conventional methods of CO_2 capture.

technical content

The working hypothesis of this project is that the conventional WGS unit found in an IGCC plant (for shifting the syngas toward primarily H_2 and CO_2) and the downstream conventional amine absorption unit for capturing the CO_2 from the shifted syngas could be replaced in whole by a unique membrane- and adsorption-enhanced WGS reactor system (previously developed for H_2 production via methane steam reforming) that allows for in situ preferential H_2 permeation and simultaneous CO_2 adsorption. The reactor system is depicted, in the context of a

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Pre-Combustion Power Generation PSC

key technology:
Hybrid

project focus:
Combined Membrane Reactor and Adsorption Reactor System

participant:
University of Southern California

project number:
FE0031737

predecessor projects:
FE0026423

NETL project manager:
Katharina Daniels
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principal investigator:
Theodore Tsotsis
University of Southern California
tsotsis@usc.edu

partners:
Media and Process Technology Inc.; University of California Los Angeles; University of Kentucky Research Foundation

start date:
06.01.2019

percent complete:
100%

typical IGCC power plant cycle, within the blue border-surrounded process block in Figure 1.

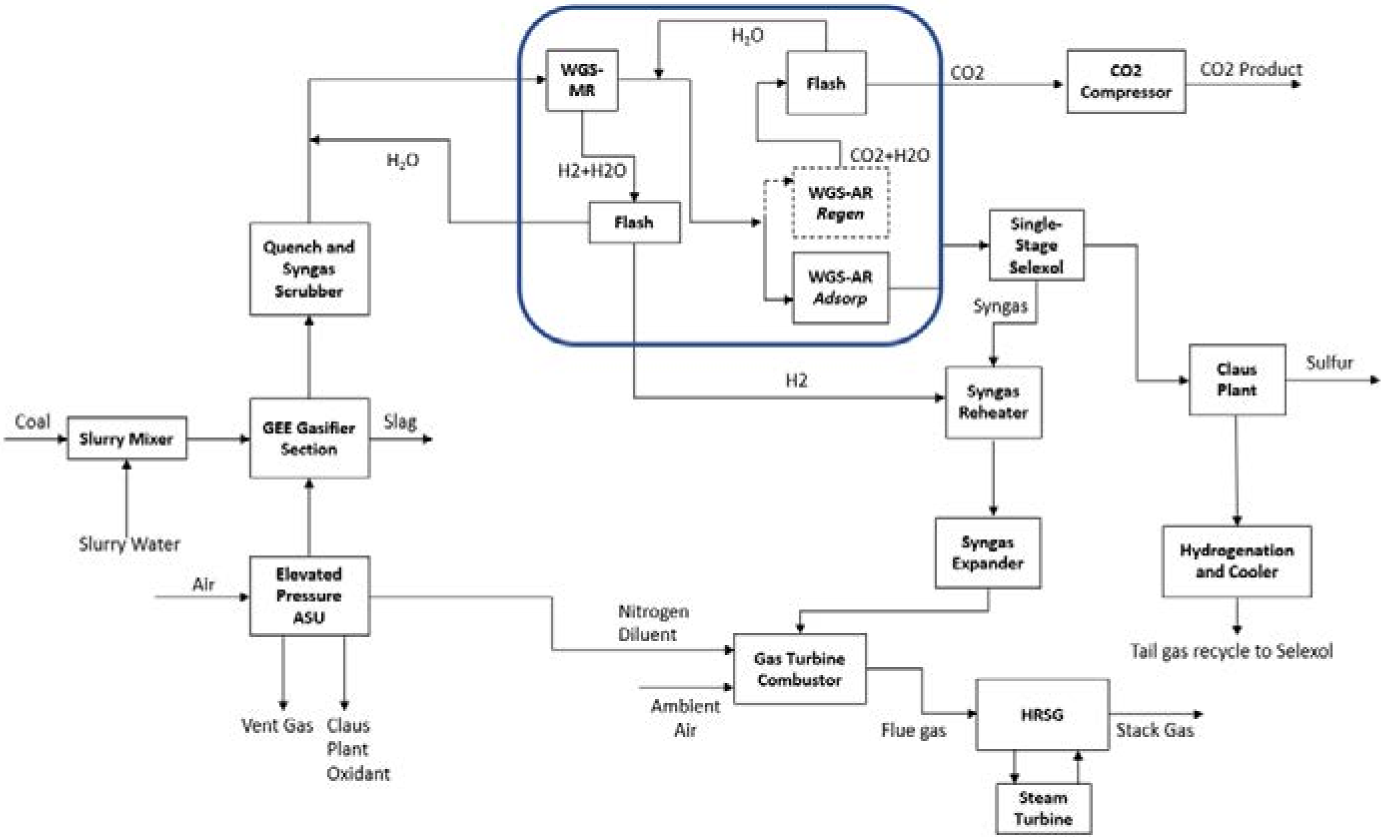

Figure 1: MR and AR system in the context of an IGCC plant process.

The system combines an MR and AR in tandem to continuously produce a pure H_2 product (while attaining greater than 99% CO conversion) until the adsorbent (in the AR unit) is saturated. The AR unit must then be taken off-stream and regenerated via steam-enhanced temperature swing adsorption (TSA). This unique reactor configuration can, therefore, be viewed as a hybrid MR-AR system with TSA cycling. Compared to conventional WGS followed by CO_2 capture using a conventional amine process, the MR-AR system is more efficient and compact. Furthermore, the use of a TSA rather than a pressure-swing CO_2 recovery step (as commonly practiced in AR systems) allows the recovery of CO_2 at higher pressures aiding system efficiency.

The combined MR-AR process is shown in more detail in Figure 2. Here, the syngas first passes into the MR vessel, consisting of WGS catalyst packed around an array of membrane tubes. The tubes are CMS-based membranes on ceramic support, which are highly selective to H_2. The MR permeate consists of high-purity H_2. As the H_2 is withdrawn from the MR vessel, the WGS reaction equilibrium is pushed toward further H_2 production. Retentate/rejected gases are passed to an array of ARs operating in a periodic manner, whereby at any given time some ARs are fed retentate gases and operate in reaction/adsorption mode, while the remaining ARs are fed steam and operate in a TSA regeneration mode. The ARs contain additional WGS catalyst, in addition to CO_2 sorbent. In this technology, hydrotalcite (HTC) is utilized as the CO_2 sorbent. This co-location of the WGS reaction and CO_2 separation functions in the AR allows traditional WGS reaction equilibrium limitations to be overcome, thus enabling enhanced shifting of the syngas to occur until most of the carbon, as CO, is converted into CO_2 and adsorbed. This results in a relatively pure H_2 gas exiting the AR at high pressure when the ARs operate in reaction/adsorption mode, while a high-pressure steam/CO_2 mixture exits the ARs when they operate in regeneration mode. In summary, the process configuration combining the MR and AR in tandem provides significant process flexibility, efficient high-pressure and high-purity H_2 production, and CO_2 recovery.

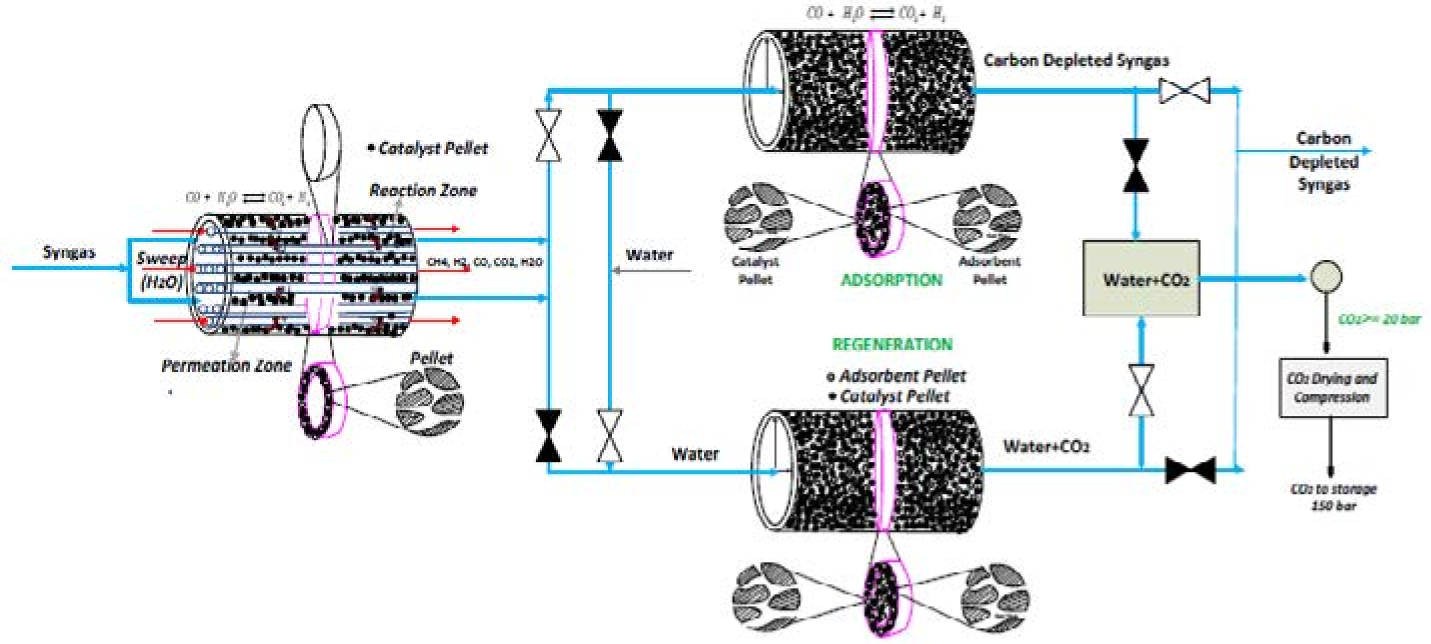

Figure 2: MR-AR process.

The HTC sorbent mentioned previously is an anionic clay magnesium (Mg)/aluminum (Al)-layered double hydroxide, as depicted in Figure 3. It has a relatively high CO_2 capacity over a wide range of temperatures and pressures; can be easily prepared by precipitation of Mg/Al from solution in sodium hydroxide (NaOH); and is unaffected by hydrogen sulfide (H_2S) and simulated tars at anticipated operating temperature, thereby conferring process stability.

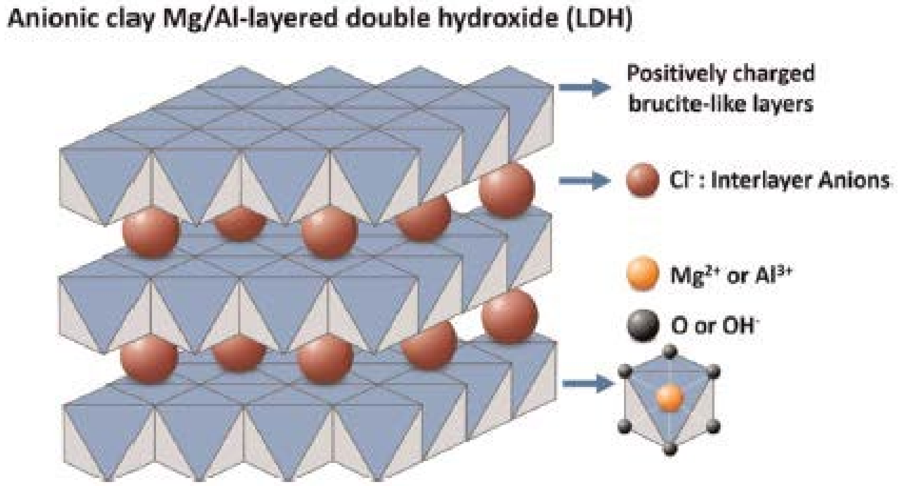

Figure 3: Hydrotalcite (HTC) adsorbent.

The main accomplishments and findings of the USC team's predecessor project included the following:

- CMS membranes were prepared and tested over the full range of expected operating temperatures (up to 300°C) and pressures (10 to 25 bar). Performance targets for H_2 permeance (350 to 550 gas permeation units [GPU]) and H_2/CO selectivity of greater than 80 were met.
- HTC sorbent was prepared, and adsorption/desorption kinetics and working capacity measured at expected operating conditions of 300 to 450°C and pressure up to 25 bar. A performance target for working capacity of greater than 3 weight % CO_2 was met.

- Kinetics of a commercially available sour-shift WGS catalyst were measured at expected operating conditions. This information is essential in modeling and in preparing a techno-economic analysis (TEA) of the MR-AR process.
- An MR-AR system operating run of greater than 500 hours was carried out on simulated syngas at a flow rate of less than 0.9 kg/day in a lab-scale integrated experimental apparatus. This effectively advanced the MR-AR technology to TRL 4. Also, the membranes, sorbents, and catalysts were shown to be robust at expected operating conditions.
- Preliminary TEA study results comparing an MR-AR integrated system to a baseline Selexol system (both in the IGCC context) show substantial reductions in required compression work and WGS catalyst requirements. The overall COE target of 30% lower cost than the baseline COE would be closely approached or met given known performance parameters and assumptions.

It should be noted that there are several major points of departure of the case of MR-AR within an IGCC power plant context from the baseline IGCC case. These become important in process performance and cost analysis:

1. The WGS reaction occurs in the MRs and ARs alongside H_2 removal (in the MRs) and CO_2 removal (in the ARs).
2. The amount of steam used in the MR-AR technology serves not only as a reactant but also as a sweep agent to separate the WGS reaction products.
3. A single-stage Selexol unit is needed for H_2S removal, as opposed to a dual-stage Selexol unit for H_2S and CO_2 removal in the baseline case.
4. Steam is used as diluent in the combustion turbine, as opposed to nitrogen (N_2) in the baseline case.

All four of the above items are beneficial from cost, efficiency, and environmental impact viewpoints. The simultaneously reactive-separative nature of the MR-AR units intensifies the kinetic and equilibrium behavior of the WGS reaction, thus resulting in lower catalyst use. It also delivers separate, high-pressure H_2 and CO_2 streams, thus improving process efficiency, economics, and environmental impact through reduced H_2/CO_2 compression costs and reduced Selexol solvent losses/emissions from the single-stage Selexol unit used in MR-AR for H_2S removal compared to the dual-stage Selexol unit used in the baseline process. Although, in the MR-AR process, water is used as a WGS reactant, sweeping agent, and H_2 combustion diluent, net water consumption in the MR-AR is only marginally higher than that of the baseline case. This is the result of heat/power/water integration strategies, which additionally result in the availability of N_2 or possible sales that significantly improve process economics, and can also potentially reduce environmental impact, by reducing the possibility of nitrous oxide (NO_X) emissions in H_2 turbine combustion. The use of N_2 as raw material for ammonia (NH_3) production and the current commercialization of NH_3 as an H_2 transport medium greatly enhance the marketability of the MR-AR technology.

Bench-scale testing was sited at UKy's Center for Applied Energy Research (CAER) to enable testing on actual coal-derived syngas from CAER's entrained-flow coal gasifier. The bench-scale unit utilizes 30-inch membrane tubes in 2-inch outer diameter modules for the MR, the process parameters for which are shown in Table 1, while those of the sorbent are shown in Table 2. Test campaigns totaling 500 hours were carried out, enabling determination of performance at this larger scale, and affording an opportunity to evaluate membrane, catalyst, and sorbent stability over time. The performance data allowed improved TEA of the MR-AR system.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	carbon molecular sieve (CMS)	
Materials of Fabrication for Support Layer	—	alumina	
Nominal Thickness of Selective Layer	µm	2–3	2–3
Membrane Geometry	—	tubular	tubular
Maximum Trans-Membrane Pressure	bar	>82 bar	>82 bar
Hours Tested without Significant Degradation	—	>16,000 hours in lab, >1,000 hours at NCCC	—
Manufacturing Cost for Membrane Material	$/m²	<1,500	<750
Membrane Performance			

<table>
<tr><td>Temperature</td><td>°C</td><td colspan="3">250–300</td><td colspan="3">250–300</td></tr>
<tr><td>H_2 Pressure Normalized Flux</td><td>GPU or equivalent</td><td colspan="3">500</td><td colspan="3">900</td></tr>
<tr><td>H_2/H_2O Selectivity</td><td>—</td><td colspan="3">2–4</td><td colspan="3">>3</td></tr>
<tr><td>H_2/CO Selectivity</td><td>—</td><td colspan="3">.200</td><td colspan="3">>200</td></tr>
<tr><td>H_2/H_2S Selectivity</td><td>—</td><td colspan="3">>100</td><td colspan="3">>100</td></tr>
<tr><td>Sulfur Tolerance</td><td>ppm</td><td colspan="3">>10,000</td><td colspan="3">>10,000</td></tr>
<tr><td>Type of Measurement</td><td>—</td><td colspan="3">mixed gas</td><td colspan="3">mixed gas</td></tr>
<tr><td colspan="8">Proposed Module Design</td></tr>
<tr><td>Flow Arrangement</td><td>—</td><td colspan="6">co/counter-current or cross-flow</td></tr>
<tr><td>Packing Density</td><td>m^2/m^3</td><td colspan="6">>450</td></tr>
<tr><td>Shell-Side Fluid</td><td>—</td><td colspan="6">Permeate</td></tr>
<tr><td>Syngas Gas Flowrate</td><td>kg/hr</td><td colspan="6">—</td></tr>
<tr><td>CO_2 Recovery, Purity, and Pressure</td><td>%/%/bar</td><td colspan="2">90</td><td colspan="2">95</td><td colspan="2">>60</td></tr>
<tr><td>H_2 Recovery, Purity, and Pressure</td><td>%/%/bar</td><td colspan="2">>80</td><td colspan="2">>90</td><td colspan="2">Up to 20</td></tr>
<tr><td>Pressure Drops Shell/Tube Side</td><td>bar</td><td colspan="6">—</td></tr>
<tr><td>Estimated Module Cost of Manufacturing and Installation</td><td>$\frac{\$}{kg/hr}$</td><td colspan="6">1,500</td></tr>
</table>

TABLE 2: SORBENT PROCESS PARAMETERS

<table>
<tr><th>Sorbent</th><th>Units</th><th colspan="3">Current R&D Value</th><th colspan="3">Target R&D Value</th></tr>
<tr><td>True Density @ STP</td><td>kg/m^3</td><td colspan="3">2,849–3,066</td><td colspan="3">2,849–3066</td></tr>
<tr><td>Bulk Density</td><td>kg/m^3</td><td colspan="3">1,322–1,423</td><td colspan="3">1,322–1,423</td></tr>
<tr><td>Average Particle Diameter</td><td>mm</td><td colspan="3">0.6–0.8</td><td colspan="3">2–3</td></tr>
<tr><td>Particle Void Fraction</td><td>m^3/m^3</td><td colspan="3">0.536</td><td colspan="3">0.536</td></tr>
<tr><td>Packing Density</td><td>m^3/m^3</td><td colspan="3">0.406</td><td colspan="3">0.406</td></tr>
<tr><td>Solid Heat Capacity @ STP</td><td>kJ/kg-K</td><td colspan="3">0.5–0.65</td><td colspan="3">0.5–0.65</td></tr>
<tr><td>Crush Strength</td><td>kg_f</td><td colspan="3">N/A</td><td colspan="3">10-15</td></tr>
<tr><td>Manufacturing Cost for Sorbent</td><td>$/kg</td><td colspan="3">—</td><td colspan="3">—</td></tr>
<tr><td colspan="8">Adsorption</td></tr>
<tr><td>Pressure</td><td>bar</td><td colspan="3">25</td><td colspan="3">>25</td></tr>
<tr><td>Temperature</td><td>°C</td><td colspan="3">250–300</td><td colspan="3">250–300</td></tr>
<tr><td>Equilibrium Loading</td><td>g mol CO_2/kg</td><td colspan="3">~3</td><td colspan="3">~3</td></tr>
<tr><td>Heat of Adsorption</td><td>kJ/mol CO_2</td><td colspan="3">~10 kJ/mol</td><td colspan="3">~10 kJ/mol</td></tr>
<tr><td colspan="8">Desorption</td></tr>
<tr><td>Pressure</td><td>bar</td><td colspan="3">25</td><td colspan="3">>25</td></tr>
<tr><td>Temperature</td><td>°C</td><td colspan="3">400–450</td><td colspan="3"><400</td></tr>
<tr><td>Equilibrium CO_2 Loading</td><td>g mol CO_2/kg</td><td colspan="3">0.1-0.2</td><td colspan="3"><0.1</td></tr>
<tr><td>Heat of Desorption</td><td>kJ/mol CO_2</td><td colspan="3">—</td><td colspan="3">—</td></tr>
<tr><td colspan="2">Proposed Module Design</td><td colspan="6"><i>(for equipment developers)</i></td></tr>
<tr><td>Flow Arrangement/Operation</td><td>—</td><td colspan="6">See Figure 2</td></tr>
<tr><td>Flue Gas Flowrate</td><td>kg/hr</td><td colspan="6">—</td></tr>
<tr><td>CO_2 Recovery, Purity, and Pressure</td><td>% / % / bar</td><td colspan="2">>90</td><td colspan="2">95</td><td colspan="2">25</td></tr>
<tr><td>Adsorber Pressure Drop</td><td>bar</td><td colspan="6">—</td></tr>
<tr><td>Estimated Adsorber/Stripper Cost of Manufacturing and Installation</td><td>$\frac{\$}{kg/hr}$</td><td colspan="6">—</td></tr>
</table>

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

STP – Standard temperature and pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Sorbent Packing Density – Ratio of the active sorbent volume to the bulk sorbent volume.

Sorbent Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – See Figures 1 and 2.

Estimated Cost (Sorbent + Membrane) – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met (see Table 3).

Other Parameter Descriptions:

Membrane Permeation Mechanism – Molecular sieving.

Contaminant Resistance – Resists all chemical contaminants in gasifier off-gas including H_2S, NH_3, heavy metals, organic vapors, tars, etc., based on bench-scale testing conducted at the National Carbon Capture Center (NCCC).

Syngas Pretreatment Requirements – Particulate removal should be practiced.

Membrane Replacement Requirements – Not known presently but assumed to be five to 10 years. More than 16,000 hours of laboratory thermal stability testing has been demonstrated with no failure. More than 1,000 hours of live syngas testing at NCCC has been conducted with no failure.

Waste Streams Generated – None.

Process Design Concept – See Figure 1.

Proposed Module Integration – See below.

Entering Module	Pressure psia.	Temperature °F	Composition vol%						ppmv
			CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
MR	800	440-540	0.1089	0.2823	0.0010	0.0055	0.2689	0.3190	5700
AR	800**	440-540*	0.2480	0.1466	0.0009	0.0055	0.2590	0.3253	5700

* Species compositions shown for inlet temperature of 440°F; ** To match the exit gasifier conditions.

TABLE 3: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	-4.62, 39.87 – 80.60 (Ar Sold, Yes - No N_2 sold) 98.06 (B5B Baseline)	N/A
Capital Expenditures	\$/MWhr	65.5, 65.1 – 65.1 (Ar Sold, Yes - No N_2 sold) 75.2 (B5B Baseline)	N/A
Operating Expenditures	\$/MWhr	47.0, – 45.2 – 45.2 (Ar Sold, Yes - No N_2 sold) 46.5 (B5B Baseline)	N/A
Levelized Cost of Electricity (LCOE) Excluding T&S	\$/MWhr	61.8, 96.2 – 131.7 (Ar Sold, Yes - No N_2 sold) 144.2 (B5B Baseline)	100.9

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

technology advantages

- Improved WGS efficiency: hybrid concept process allows the simultaneous removal from the reacting phase and recovery of both H_2 and CO_2, resulting in significant reaction rate enhancement over the conventional WGS system.
- Significantly reduced catalyst weight usage requirements: reaction rate enhancement (over conventional WGS) permits operation at lower weight of catalyst/inlet molar flow rate of CO (W/F_{CO}), thus resulting in significant catalyst savings.
- No syngas pretreatment required given use of sour-shift catalyst and use of CMS membranes, which have demonstrated stability to all gaseous contaminants present in coal-derived syngas.
- Efficient H_2 production and superior CO_2 recovery and purity: the synergy of the MR and AR units satisfies the CO_2 recovery/purity, carbon utilization (CO conversion), and H_2 recovery/purity goals.

R&D challenges

- Heat management in reactors.
- Process integration with IGCC.
- Particulate matter needs to be controlled to reduce its potential impact on the reactor units.
- Scale-up and integration issues, given the large number of reactor modules needed to service a 550-MWe plant.
- Opportunities for additional saleable products.

status

The project concluded on May 31, 2023. The MR-AR process was successfully field-tested using real syngas generated at the UKy gasifier facility. In addition, USC completed a TEA showcasing the performance and economics of the completed system. The results showed that an IGCC plant utilizing the MR-AR capture process is about 2 percentage points more efficient than the equivalent U.S. Department of Energy (DOE) reference case (Vol. 1, Case B5B). In addition, a levelized cost of electricity (LCOE) as low as $0.062/kW-hr could be achieved, which would result in a negative cost of carbon capture for the plant, depending on conditions. Finally, the project team completed a technology gap analysis and an environmental, health, and safety (EH&S) risk assessment.

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High-Temperature Ceramic-Carbonate Dual-Phase Membrane Reactor for Pre-Combustion Carbon Dioxide Capture

primary project goal

Arizona State University (ASU), in collaboration with the University of South Carolina (USC), developed technology for a high-temperature, high-pressure, ceramic-carbonate dual-phase (CCDP) membrane reactor for performing the water-gas shift (WGS) reaction. The project goal was to design and fabricate CCDP membranes with improved CO_2 permeance and mechanical strength for testing in a laboratory-scale reactor with simulated coal-derived syngas, with results informing a mathematical model used to support process design and a techno-economic analysis (TEA) for a scenario of incorporation of a CCDP membrane reactor in a full-scale integrated gasification combined cycle (IGCC) plant.

technical goals

- Synthesize chemically and thermally stable CCDP membranes with CO_2 permeance greater than 2,000 gas permeation units (GPU) (6.5×10^{-7} mol/m^2·s·Pa), CO_2/H_2 selectivity greater than 500, and resistant to poisoning from hydrogen sulfide (H_2S) to the extent that CO_2 flux drops less than 5% after 24 hours of exposure to typical levels of H_2S.
- Fabricate tubular CCDP membrane modules suitable for lab-scale WGS reactor operation (i.e., functional and durable at temperatures in excess of 700°C) and at pressures in excess of 20 atmosphere (atm), and experimentally verify performance at simulated syngas flow rate of 0.25 kg per day equivalent to 0.007 kilowatt-thermal (kWth).
- Determine CCDP membrane WGS reactor process conditions/protocols enabling 99% carbon monoxide (CO) conversion for the WGS reaction, 90% CO_2 recovery, 99% purity of the CO_2 permeate stream, and 90% purity of the H_2 retentate stream.

technical content

The working hypothesis of this project was that the conventional WGS unit found in a coal gasification-based power plant (for shifting the syngas toward primarily H_2 and CO_2) and downstream conventional amine absorption unit for capturing the CO_2 from the shifted syngas could be replaced, in whole, by a novel WGS shift reactor that integrates CO_2-selective CCDP membranes and WGS catalyst. Within the CCDP membrane WGS reactor, CO_2 would be withdrawn directly from the reaction chamber, efficiently increasing the driving force for the WGS reaction to completion. As such, the multiple stages of the conventional WGS unit are

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Pre-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Ceramic-Carbonate Dual-Phase Membrane Reactor for CO_2 Capture from Coal Syngas

participant:
Arizona State University

project number:
FE0031634

predecessor projects:
N/A

NETL project manager:
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principal investigator:
Jerry Lin
Arizona State University
jerry.lin@asu.edu

partners:
University of South Carolina

start date:
10.01.2018

percent complete:
100%

replaced by a single, elegantly performing reactor. This process concept, with the unified CCPD membrane reactor (depicted in callout) replacing the multistage conventional WGS process and amine absorption unit (both within red dotted line), is depicted in Figure 1.

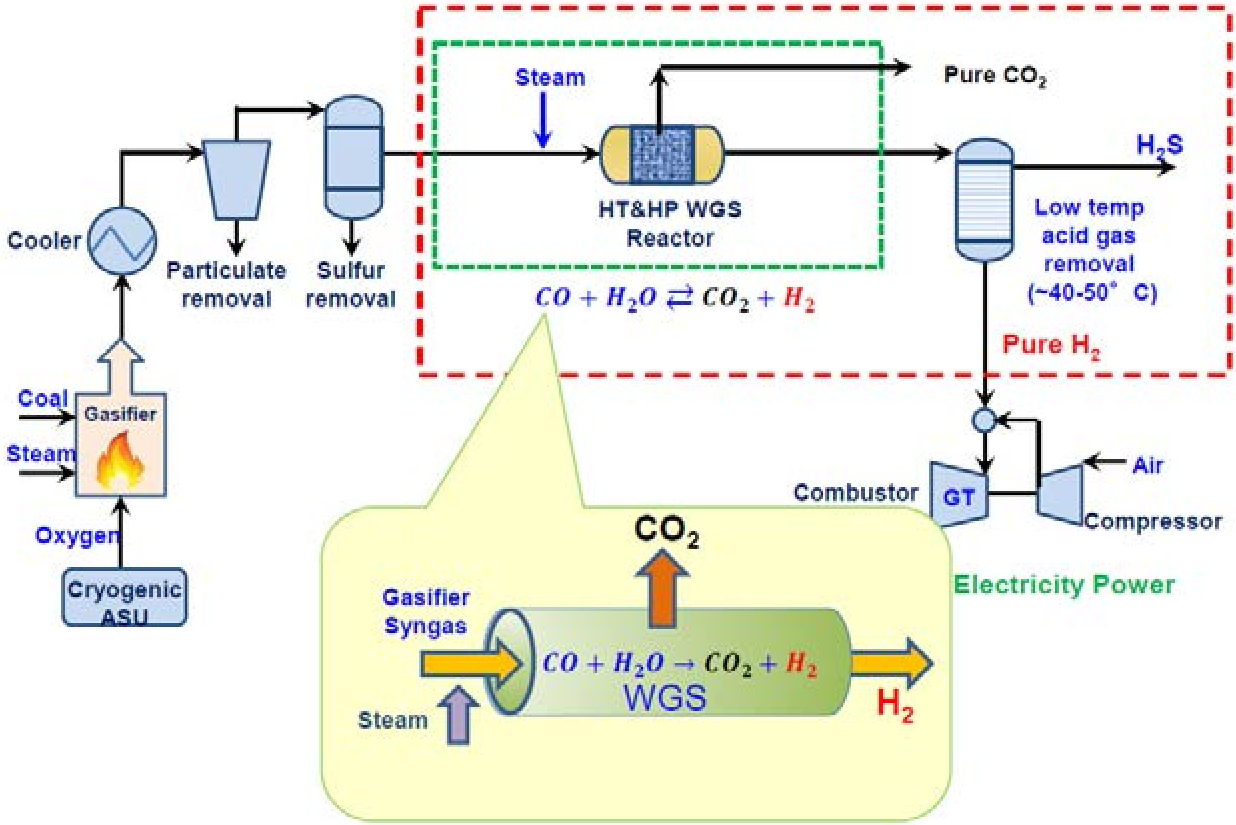


Figure 1: CCDP membrane reactor for WGS reaction and CO_2 capture in context of coal gasification plant cycle.

CCDP membranes are composed of a porous ceramic phase as the structural support matrix, infiltrated with a molten carbonate phase, as illustrated in Figure 2. At working temperatures of 600–900°C, the CCDP membrane possesses extremely high CO_2 selectivity and high CO_2 permeance.

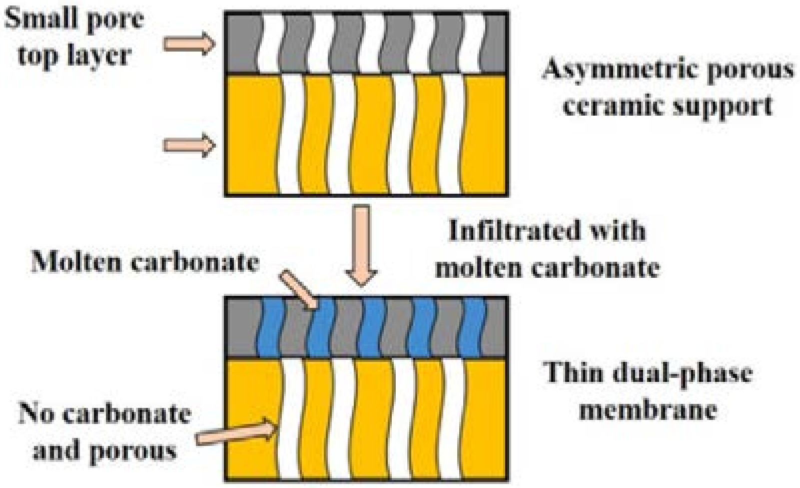


Figure 2: Physical structure of CCDP membrane.

Scanning electron microscopy (SEM) images of actual CCDP membranes are shown in Figure 3. Note that the bright areas in the SEM images are the ceramic phase, while dark zones consist of carbonate mixture. These illustrate the formation of a dense, highly gas-tight dual-phase membrane, which has been verified by pre- and post-infiltration gas permeation measurements.

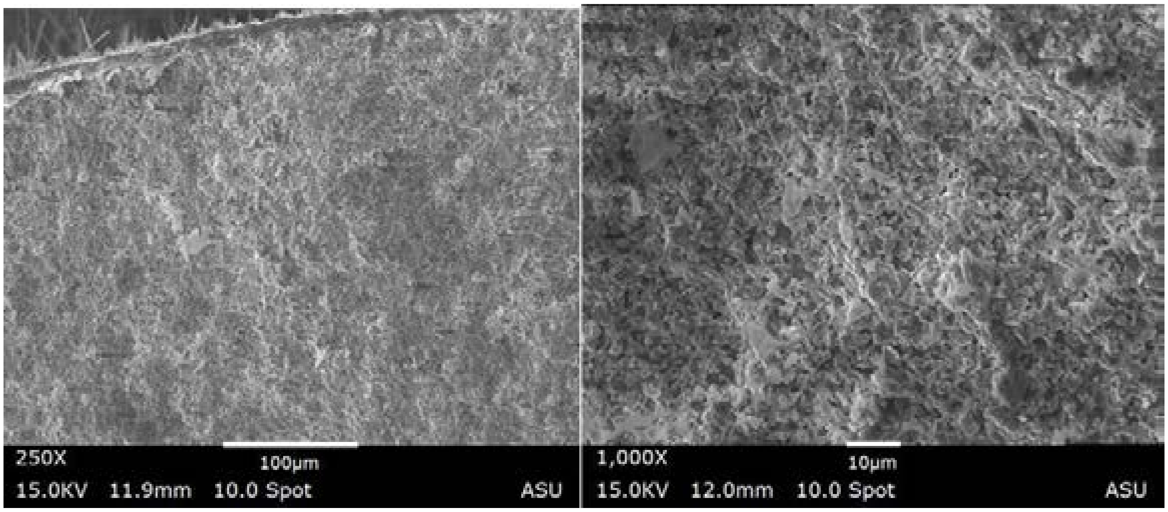


Figure 3: SEM images of CCDP membrane cross-section at 250x (left) and 1,000x (right).

The high selectivity and permeance for CO_2 in the CCDP membrane are a result of the electrochemical transport mechanism illustrated in Figure 4. At elevated process operating temperatures, CO_2 tends to form carbonate ions (CO_3^{2-}) by combining with oxygen ions (O^{2-}), the latter readily transporting through the ionically conducting ceramic phase in the membrane. At the same time, carbonate ions readily transport through the molten carbonate phase in the opposite direction. Syngas on the feed side is at high pressure, resulting in high partial CO_2 pressure on that side. The permeate side is at ambient pressure (and possibly swept), resulting in low partial CO_2 pressure. The CO_2 partial pressure differential provides the driving force for the ionic transport behavior in the membrane. High CO_2 permeance values are expected for the CCDP membrane if the functional layer is made of suitably thin (10–100 µm) ceramic with high oxygen ionic conductivity.

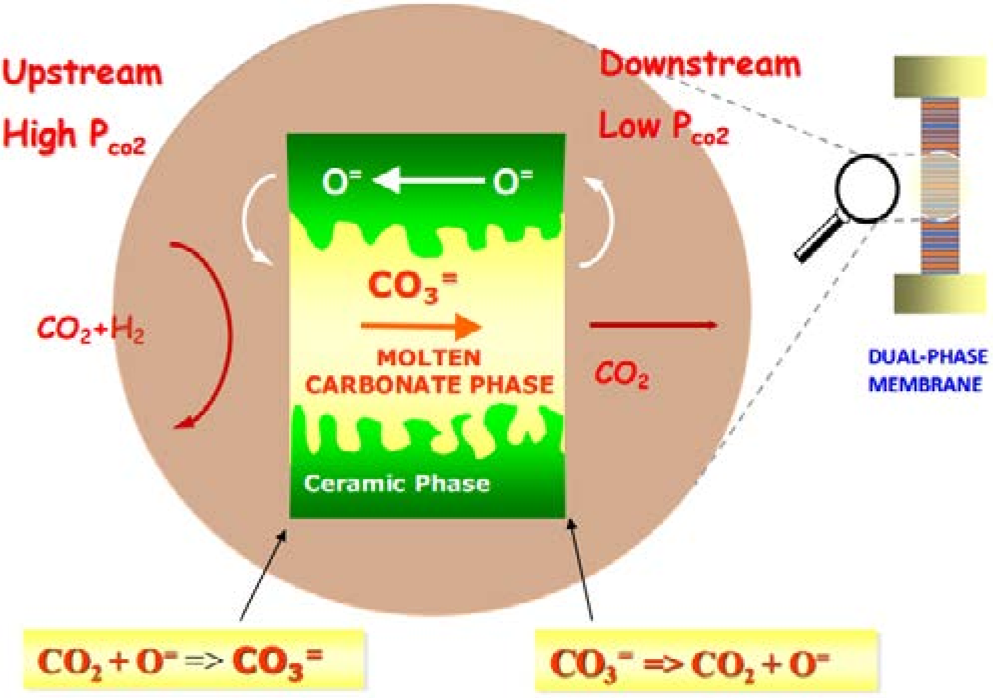


Figure 4: CO_2 separation mechanism in CCDP membrane.

The novel choice of ceramic-carbonate membrane in a WGS reactor overcomes various problems observed with possible alternatives. Theoretically, H_2 could be removed from the WGS reactor through H_2-selective membranes, which would also constitute removal of product of the WGS reaction to drive conversion forward to completion. Inorganic membranes with good H_2 perm-selectivity at high temperatures do exist and include amorphous microporous carbon; amorphous silica; microporous crystalline zeolite; and dense, perovskite-type, proton-conducting ceramics. However, all of those choices are hampered by one or more serious issues, including insufficient H_2 permeance (particularly at the elevated temperatures involved in the WGS reactor), poor H_2 stability, poor hydrothermal stability, and membrane fabrication difficulty and high cost, which translate into high costs for a membrane WGS reactor solution. Finally, organic membranes of any type are simply incapable of application at the high operating temperatures involved. Considering these shortcomings, a CO_2-selective ceramic-carbonate membrane offers a favorable choice for this application.

An important aspect of technology development for the CCDP membrane concerns optimizing the choices of ceramic and carbonate materials deployed in the membrane, characterization of membrane morphologies and properties, and membrane fabrication. For the ceramic phase of the membrane, desired characteristics include high ionic conductivity, long-term chemical stability in presence of characteristic syngas species and contaminants (particularly H_2S), compatibility with molten carbonate, and controllability of pore size and porosity.

ASU had previously investigated several ceramics for application in the CCDP membrane. The ceramics are in the family of perovskite- or fluorite-structured metal oxides with oxygen vacancy defects:

$La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF)

Yttria-stabilized zirconia (YSZ)

$La_{0.85}Ce_{0.1}Ga_{0.3}Fe_{0.65}Al_{0.05}O_{3-\delta}$ (LCGFA)

$Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (Samarium Doped Ceria [SDC]). Note: Figure 3 SEM images are of an SDC-based membrane.

$Bi_{1.5}Y_{0.3}Sm_{0.2}O_3$ (BYS)

ASU had evaluated SDC as a choice for the ceramic phase of the membrane, and had also investigated a Sc_2O_3-doped ZrO_2 (ScSZ). ScSZ avoids the tendency to form compounds with sulfur that is characteristic of cerium (Ce)-containing ceramics. Fabrication methods for the latter have been optimized to deliver the desired microstructure. The ethylenediaminetetraacetic acid (EDTA)-citric acid method is effective; this involves dissolving Sc_2O_3 in nitric acid and mixing with $ZrO(NO_3)_2$, to which EDTA and citric acid are added to the stirred solution in sequence. The solution is pH adjusted and then heated until a clear, viscous gel is formed after water evaporation. The gel is dried and calcined, resulting in almost pure-phase ScSZ with good microstructure.

Tubular membranes for incorporation in modules are formed by establishing thin layers on suitable supports. The ScSZ-based CCDPs are established on BYS support tubes by dip coating them in ScSZ slurry, sintering, and infiltrating the molten carbonate (MC). Essential steps are diagrammed in Figure 5.

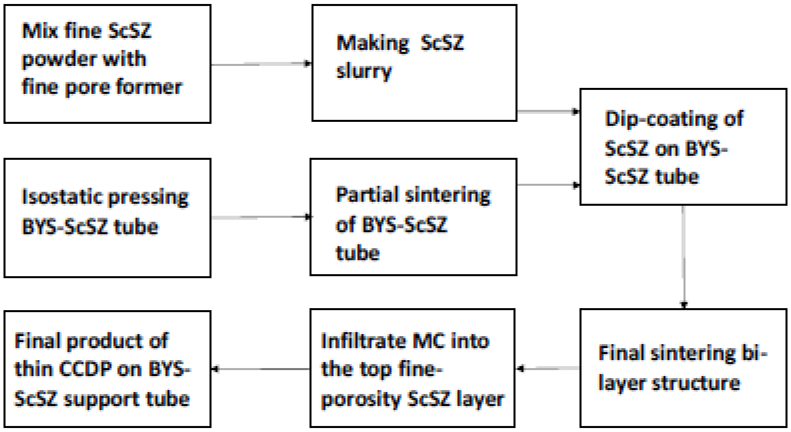


Figure 5: Tubular CCDP membrane fabrication.

For the molten carbonate phase, mixtures of common alkali metal carbonates (i.e., $Li_2CO_3/Na_2CO_3/K_2CO_3$) have been found to be suitable. Varying ratios of the alkali metal carbonates have been evaluated (e.g., a Li/Na/K ratio of 43.5/31.5/25 offers both relatively low melting point [less than 400°C] and good carbonate ion conductivity [1.24 S/cm]). In current work, a binary eutectic mixture of 52% Li_2CO_3 and 48% Na_2CO_3 (MC) is being used with both the SDC and ScSZ ceramics.

Figure 6 depicts the ScSZ-MC membrane tubes along stages of fabrication.

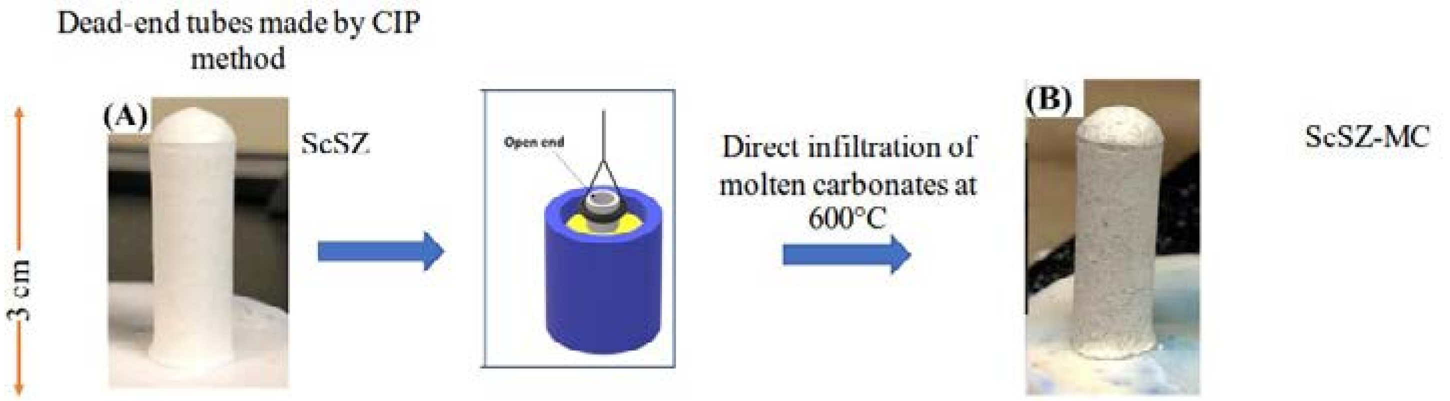


Figure 6: Sc-doped ZrO_2(ScSZ)—(52/48 Li/Na)$_2CO_3$(MC).

An apparatus for characterizing CCDP membrane performance at high temperature and feed pressures was developed and operated in laboratory-scale work, as depicted in Figure 7. Synthetic syngas can be mixed up and flowed to the tubular reactor module enclosed in a high-temperature furnace, while resulting gas compositions of permeate and retentate can be measured in a gas chromatograph. The fabrication of the tubular membrane reactor module itself was a challenge, with a notable point of development concerning seals able to withstand the high-targeted operating pressures and temperatures.

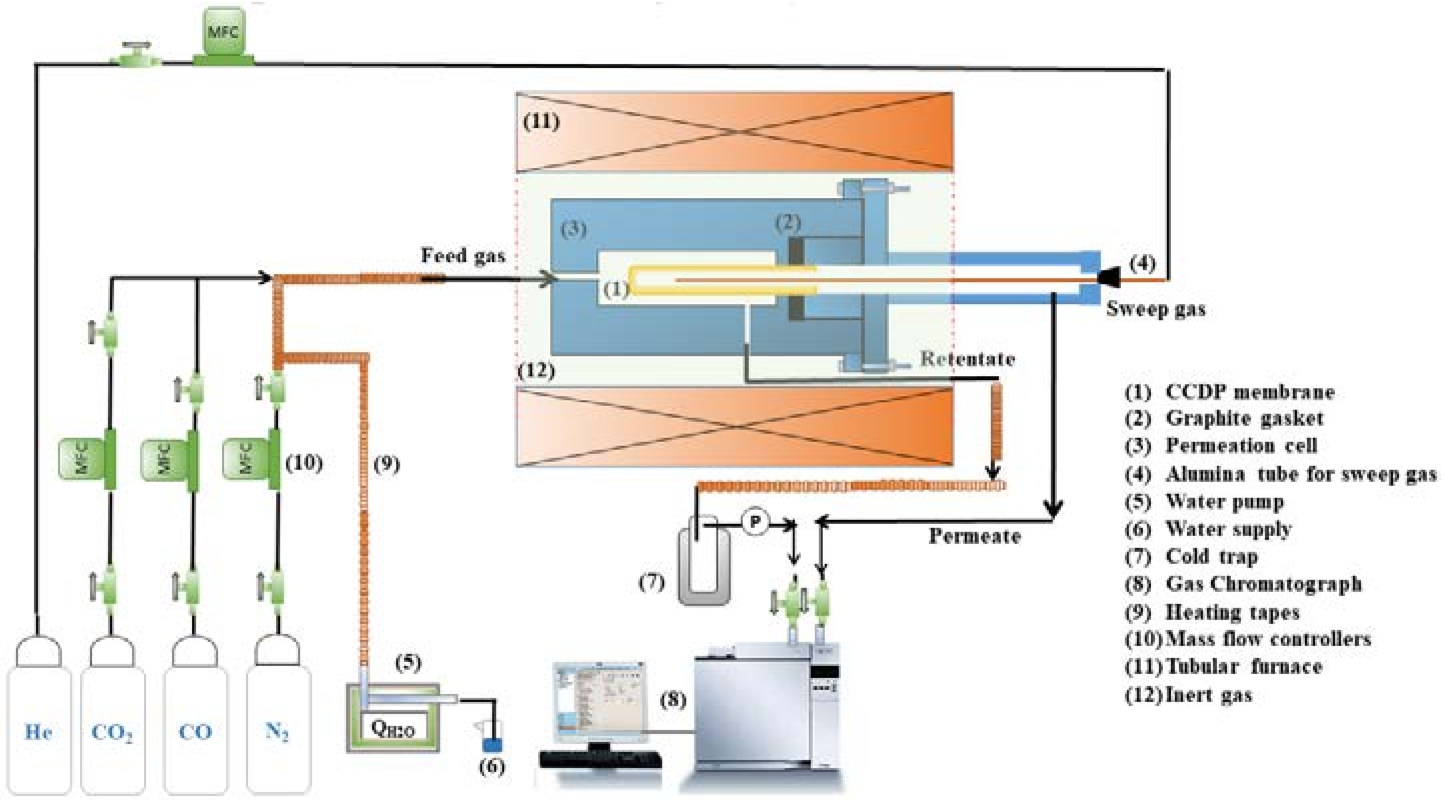


Figure 7: Laboratory-scale apparatus for CCDP membrane CO_2 permeation studies.

With this test bed, various experiments and evaluations are possible, which provide invaluable data for optimizing membrane and module materials and fabrication methods. For example, the reactor module with SDC ceramic infiltrated with Li_2CO_3/Na_2CO_3/K_2CO_3 carbonate mixture (SDC-MC) was evaluated under the following test conditions:

Temperature: 700–950°C.

Feed pressure: 1–20 atm.

Sweep-side pressure: vacuum to 1 atm.

Simulated syngas: 49.5% CO, 36% CO_2, 10% H_2, 4.5% N_2.

Feed-side flow rate: syngas 10–30 mL/min and N_2 10 mL/min.

Steam-to-CO molar ratio: 1.0–3.0.

Sweep-side flow rate: He 60 mL·min^{-1}.

Some results are depicted in Figure 8, which shows CO_2 partial pressure in the permeate side (P''_{CO_2}) and corresponding CO_2 permeation flux (J_{CO_2}) with different feed CO_2 partial pressure (P'_{CO_2}) at different temperatures for the SDC-MC membrane. As shown, the CO_2 permeation flux increases with feed CO_2 pressure and temperature. It should be noted that the feed gas is equal molar of CO_2:N_2. Thus, the highest CO_2 partial pressure data corresponds to the feed pressure of 15 atm. Also, the test bed allows long-term testing to evaluate changes to morphology of CCDP that may occur. For example, Figure 9 shows the high-pressure side of the SDC membrane (left), the SDC-MC infiltrated membrane (center), and the SDC-MC after high-temperature and high-pressure operation.

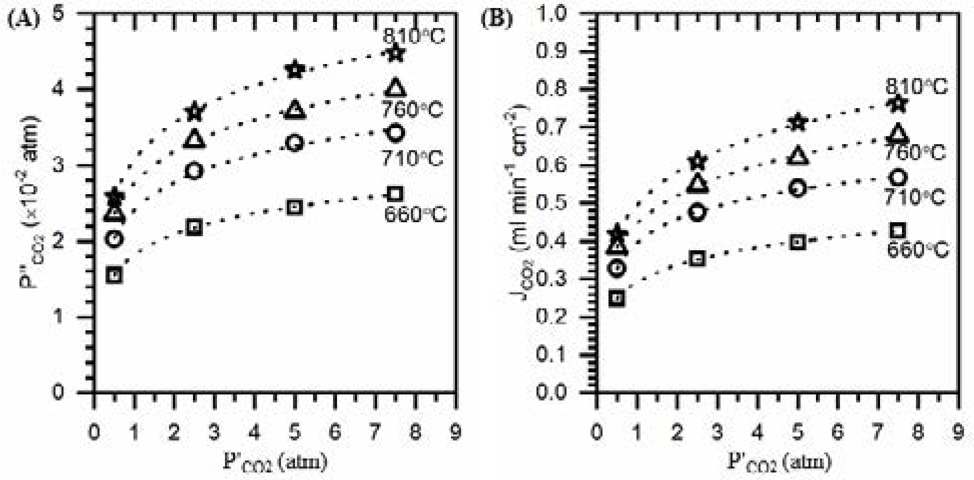


Figure 8: CO_2 partial pressure in the permeate membrane side and (B) CO_2 permeation flux as a function of feed CO_2 partial pressure at different temperatures.

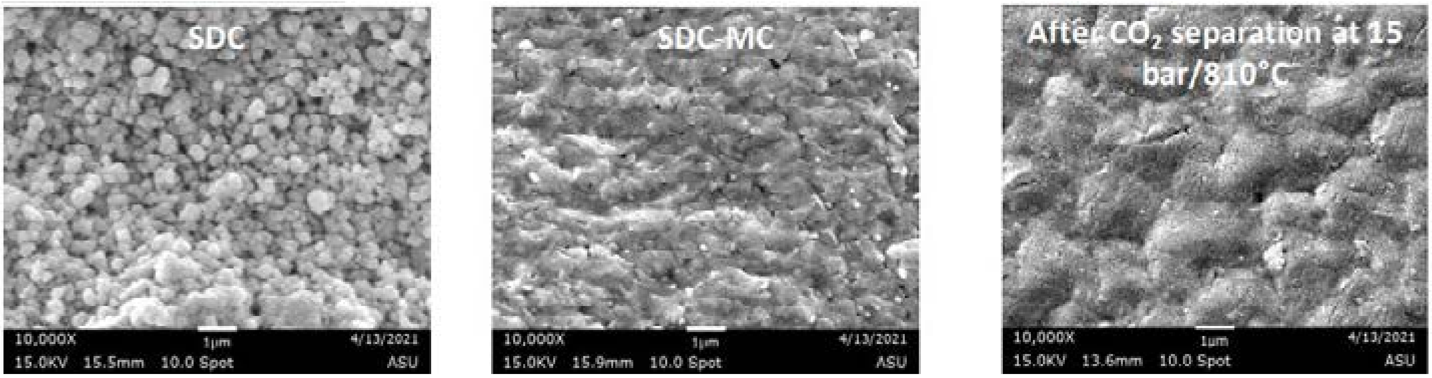


Figure 9: SEM images of high-pressure side of SDC membrane (left); SDC-MC (center); SDC-MC after high-pressure CO_2 permeation (right).

The CCDP membrane reactor has been evaluated for effectiveness in WGS conversion of simulated syngas. The CCDP membrane tubes are surrounded by a Co-Mo-Mg$(AlO_2)_2$-based shift catalyst, as shown in Figure 10. Testing has involved both SDC-MC membranes with catalyst on contaminant-free syngas, and with ScSZ-MC tubular membranes with syngas containing H_2S.

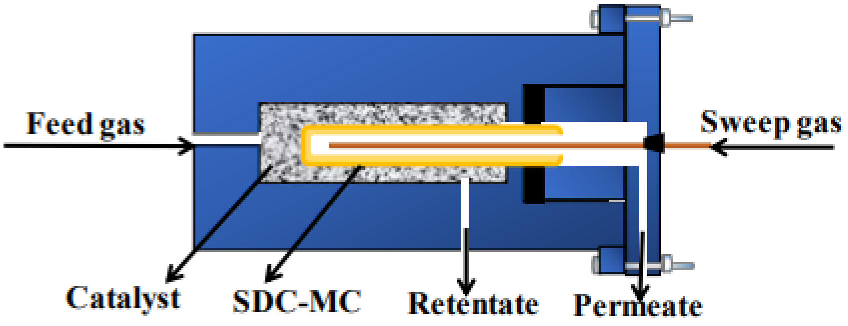


Figure 10: WGS reaction in membrane reactor with Co-Mo-Mg$(AlO_2)_2$-based shift catalyst.

WGS reaction testing with contaminant-free synthetic syngas successfully showed 95% CO conversion in the SDC-MC membrane reactor. The new ScSZ-based, H_2S-resistant CCDP membranes were fabricated in tubular configuration, with CO_2 permeance measured at 2,000 GPU and stability assessed under 30 atm transmembrane pressure drop. WGS reaction with catalyst was also performed in an improved SDC-MC membrane reactor under different operating conditions and a feed gas mixture of CO/N_2/H_2O (16.7/16.6/66.7 mol%) with H_2S (200 ppm) and free-H_2S; the sweep gas in the permeate side was helium at 200 ml/min. The results are observed in Figure 11 as a function of time. Carbon monoxide conversion reaches 100% between 800–850°C, at 10 bar, space velocity (SV) of 890 h^{-1}, and free-H_2S. However, the carbon balance is less than 70%. The carbon balance reaches 100% at 850°C, 8 bar, and SV of 890 h^{-1}, but the CO conversion decreases to 90%. The CO conversion increases to 95% at SV of 500 h^{-1}, the carbon balance remains at 100%, CO_2 recovery increases to 70%, and the H_2 purity is 60%. Carbon monoxide conversion overcomes the equilibrium due to the CO_2 removal, and the CO_2 recovery is high because of the high CO_2 partial pressure gradient across the membrane and the high temperature.

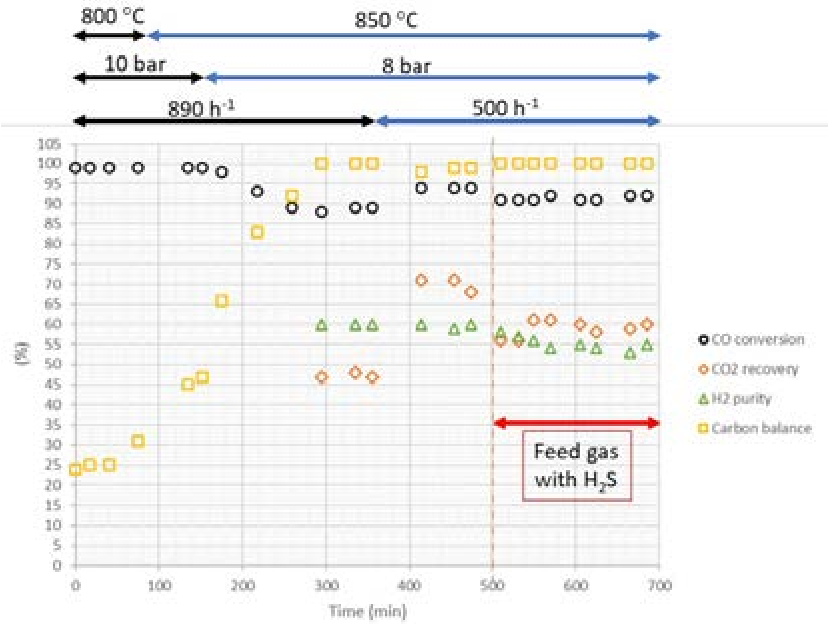


Figure 11: Results of WGS reaction with catalyst in MR made of SDC-MC membrane as a function of time at different operating conditions and feed gas with H_2S.

A TEA was performed to compare performance and costs for a conventional power plant using traditional multi-stage WGS reactors with CO_2 capture by MEA process (NETL IGCC baseline case B5B) to the same size of power plant using the CCDP membrane reactor in tube-shell process configuration for WGS, eliminating the need for a separate MEA unit operation. Figure 12 illustrates this process comparison as involved in the TEA.

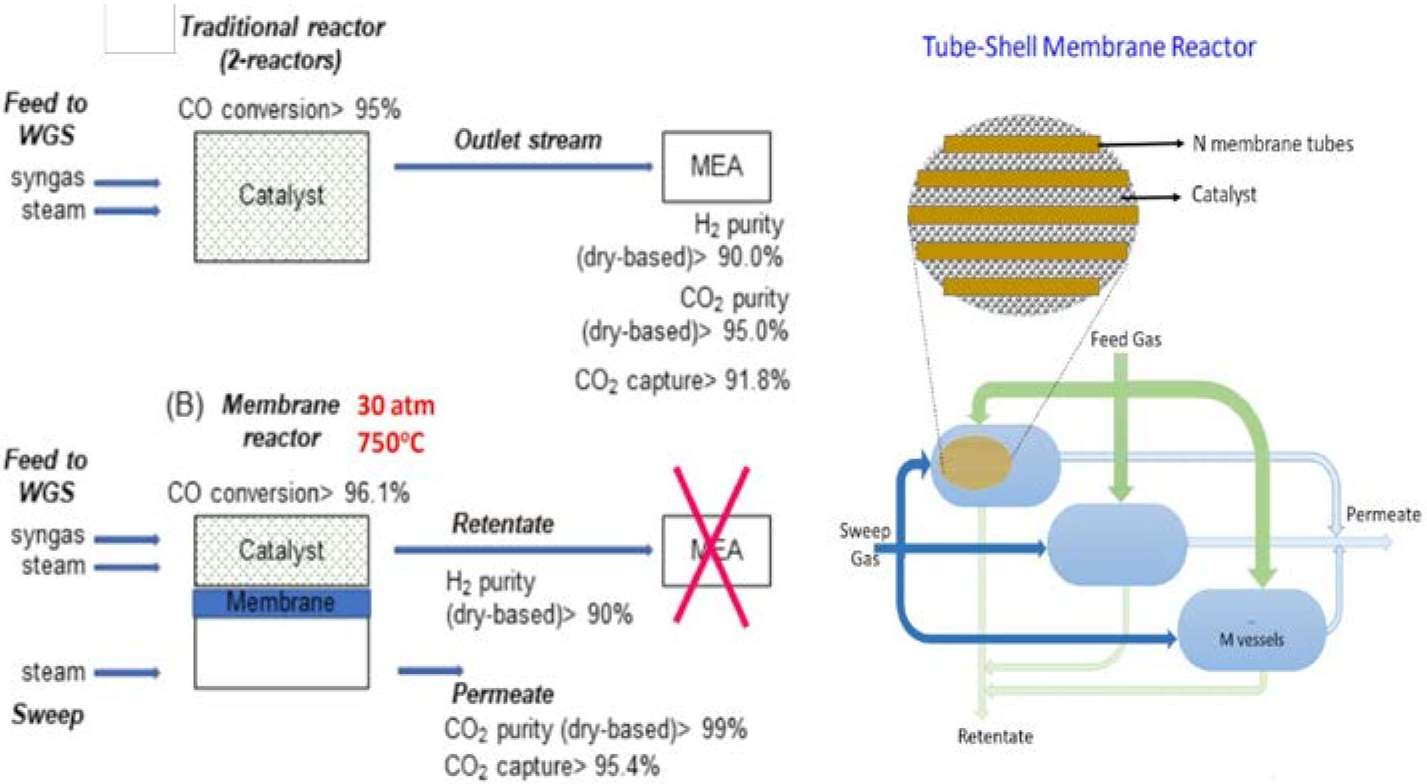
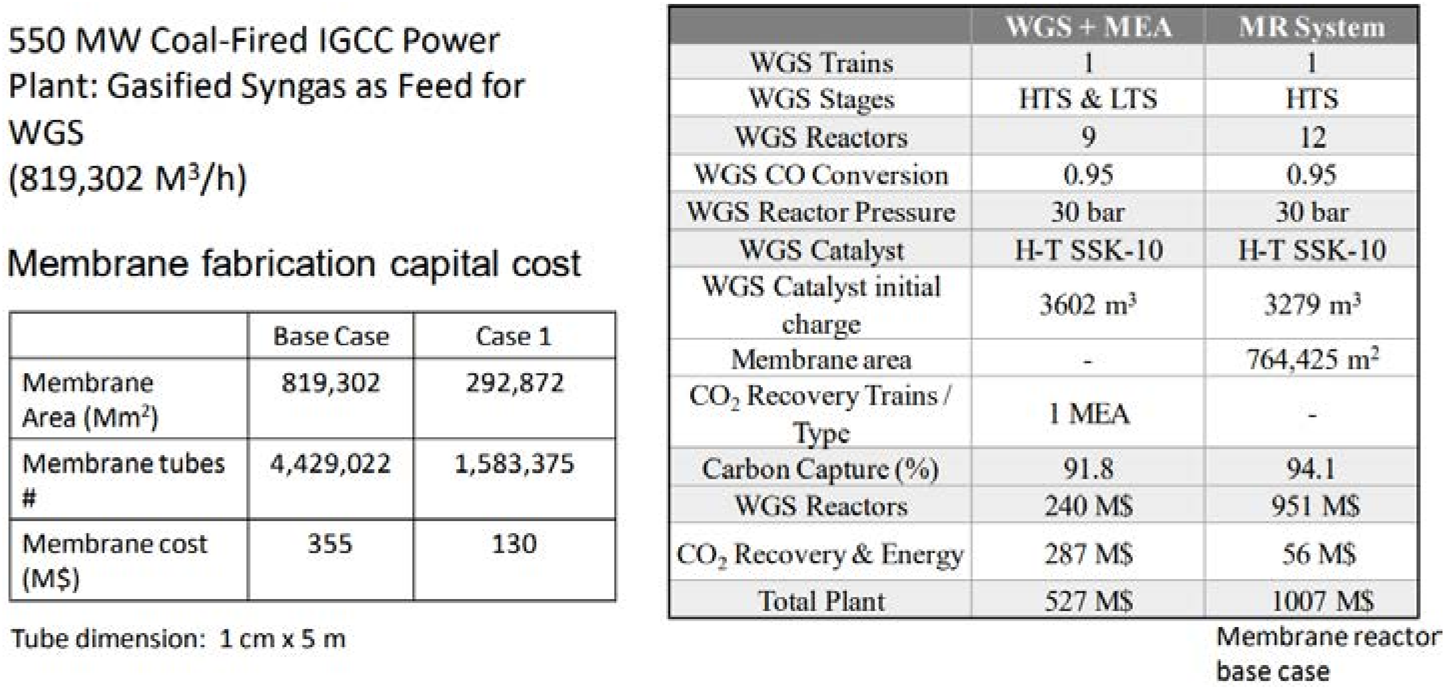


Figure 12: Comparison of baseline process configuration with membrane reactor substitution.

The baseline case and case scenario with the membrane reactor system substitution were compared and contrasted in the TEA. The membrane reactor system substitution lowers capture energy penalty associated with operational costs, but incurs higher capital costs, as can be seen in Figure 13. Unfortunately, the TEA prepared in the context of this project did not offer calculation of levelized cost of electricity (LCOE) to enable direct comparison to a baseline IGCC case electricity cost. A summary of the MR system's capture economics is shown in Table 2.



550 MW Coal-Fired IGCC Power Plant: Gasified Syngas as Feed for WGS
(819,302 M³/h)

Membrane fabrication capital cost

	Base Case	Case 1
Membrane Area (Mm²)	819,302	292,872
Membrane tubes #	4,429,022	1,583,375
Membrane cost (M$)	355	130

Tube dimension: 1 cm x 5 m

	WGS + MEA	MR System
WGS Trains	1	1
WGS Stages	HTS & LTS	HTS
WGS Reactors	9	12
WGS CO Conversion	0.95	0.95
WGS Reactor Pressure	30 bar	30 bar
WGS Catalyst	H-T SSK-10	H-T SSK-10
WGS Catalyst initial charge	3602 m³	3279 m³
Membrane area	-	764,425 m²
CO_2 Recovery Trains / Type	1 MEA	-
Carbon Capture (%)	91.8	94.1
WGS Reactors	240 M$	951 M$
CO_2 Recovery & Energy	287 M$	56 M$
Total Plant	527 M$	1007 M$

Membrane reactor base case

Figure 13: System design configuration, performance, and cost comparison.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value	
Materials of Fabrication for Selective Layer	—	$Ce_{0.8}Sm_{0.2}O_{2-\delta}$(SDC)-(42.5/32.5/25 Li/Na/K)$_2CO_3$ (MC)	Sc-doped ZrO_2 (ScSZ) (42.5/32.5/25 Li/Na/K)$_2CO_3$ (MC)	
Materials of Fabrication for Support Layer	—	BYS	BYS	
Nominal Thickness of Selective Layer	µm	1,500	50-200	
Membrane Geometry	—	tubes	tubes	
Maximum Trans-Membrane Pressure	bar	1	30	
Hours Tested without Significant Degradation	hour	120	>200	
Manufacturing Cost for Membrane Material	\$/m²	1,000	500	
Membrane Performance				
Temperature	°C	700-900	700-900	
CO_2 Pressure Normalized Flux	GPU	300-600	>2,000	
CO_2/H_2O Selectivity	—	>500	>500	
CO_2/H_2 Selectivity	—	>500	>500	
CO_2/H_2S Selectivity	—	>500	>500	
Sulfur Tolerance	ppm	<5 ppm	>400 ppm	
Type of Measurement	—	mixed-gas	mixed-gas	
Proposed Module Design				
Flow Arrangement	—	Counter-current		
Packing Density	m²/m³	50-200		
Shell-Side Fluid	—	Retentate, H_2-rich flow		
Syngas Gas Flowrate	kg/hr	0.005-0.01		
CO_2 Recovery, Purity, and Pressure	%/%/bar	90	99	~1
H_2 Recovery, Purity, and Pressure	%/%/bar	99	90*	~ 10

Pressure Drops Shell/Tube Side	bar	10-30
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	~1,000

* Gasifier, coal feedstock, and upstream unit operation (e.g., syngas pretreatment) specifications dependent.

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivity should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either co-current, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – At temperatures above 600°C, the separation of H_2 and CO_2 through CCDP membranes is governed by ionic transport of carbonate ion in MC phase in meso/macropores and oxygen ion in the ceramic phase support.

Contaminant Resistance – The developed CCDP membranes have resistance to syngas contaminants such as H_2S.

Syngas Pretreatment Requirements – Particulate removal is required.

Membrane Replacement Requirements – The multiple-tube membrane bundle is intended to operate in the membrane reactor continuously over 1,000 hours without replacement.

Waste Streams Generated – There are no waste streams generated in the flowsheet. All potential waste streams are recycled and used in the process somewhere.

Proposed Module Integration – The composition of the gas mixture is assumed:

Pressure	Temperature	Composition						
		vol%						ppmv
psia	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
435	1500	11.6	26.7	0.08	2.8	25.7	33.6	>400

Process Design Concept –

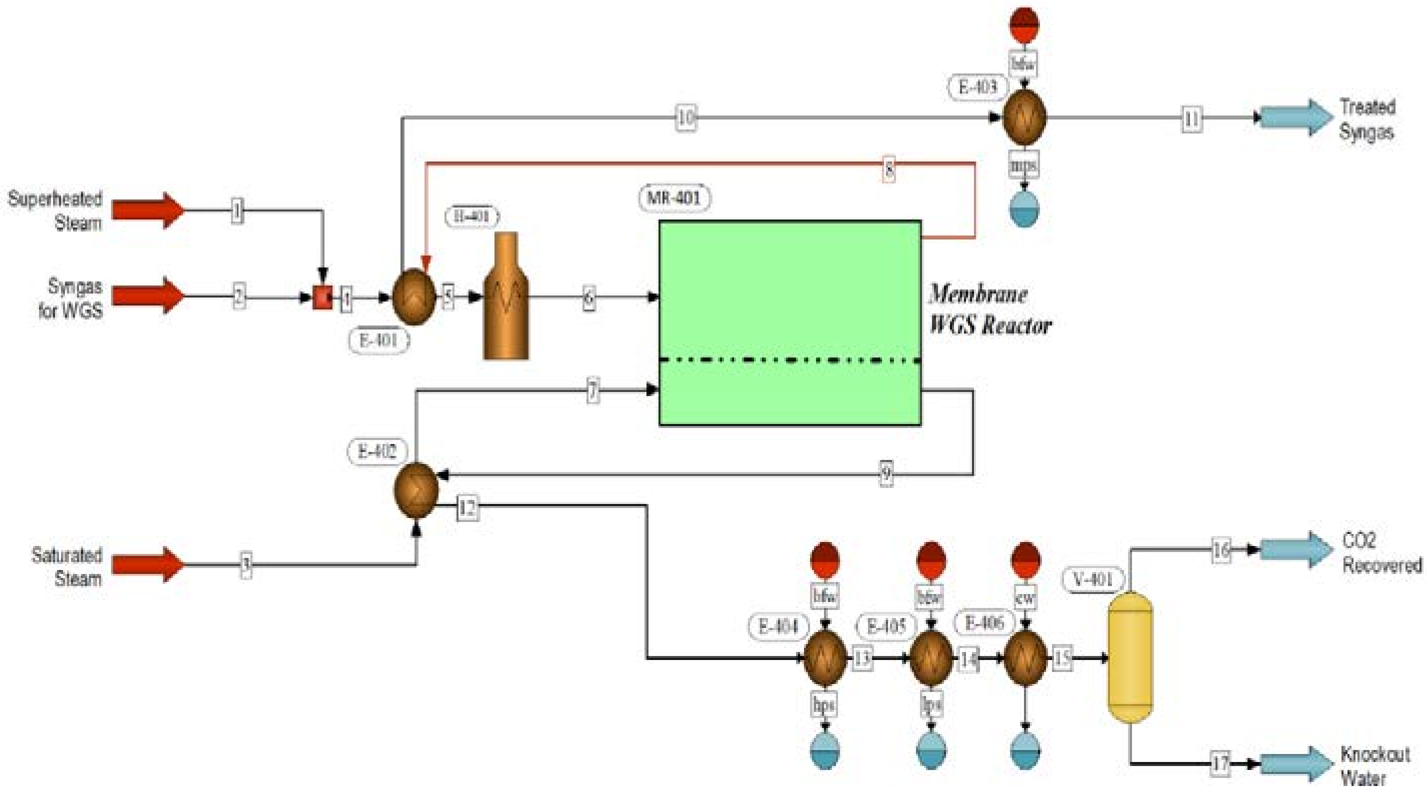


TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	65.9	40
Cost of Carbon Avoided	\$/tonne CO_2	80.2	48
Capital Expenditures	\$/MWhr	21.2	12.7
Operating Expenditures	\$/MWhr	15.8	9.5
Cost of Electricity	\$/MWhr	34	20

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

technology advantages

- The membrane reactor process could replace a conventional two-stage WGS reactor system requiring intercooling and a separate CO_2 capture unit, with a single WGS membrane reactor unit with potential for energy efficiency increase and equipment cost savings.

- WGS reactors containing CO_2-selective membranes to recover CO_2 have potential to achieve higher H_2 delivery to the turbine in an IGCC cycle than if H_2 were being selectively recovered from the syngas stream.
- Carbon dioxide removal through a membrane process in a WGS reactor retains the H_2 at high pressure, maximizing the efficiency of the combustion turbine in an IGCC cycle.
- Tubular membranes can be fabricated into robust and stable multiple-tube modules at a high packing density.

R&D challenges

- ScSZ has poor carbonate wettability making it difficult to infiltrate carbonate and achieve stability.
- Gas leakage through membrane from unsealed pores (imperfect carbonate infiltration).
- High-temperature stability of membrane bundle components and seals.
- Deterioration of strength of membrane tubes in use.
- CCDP thermal stability and poison resistance maintained at high pressures (greater than 20 atm) and temperatures (700–900°C).
- Removal of particulate matter from the hot syngas to reduce its potential impact on the membrane lifetime.
- Cost reductions for the membrane module materials if the technology is to become economically viable.

status

The project has been completed as of August 31, 2022. Findings were that the CCDP membrane reactor can significantly enhance the WGS reaction via its inherent in situ CO_2 capture capability, to the extent that it can meet WGS reaction/CO_2 capture targets without a subsequent CO_2 separation unit given at least 30 bar syngas supply pressure. Performance of the reactor as a function of membrane permeance, catalyst activity, and operation conditions (feed pressure, space velocity, and membrane surface to catalyst volume ratio) were well characterized in the experimental and modeling studies. In cost assessments, it was found that the membrane reactor process has much lower operation costs but higher capital costs compared to the conventional sequential WGS and CO_2 separation by MEA solvent absorption.

available reports/technical papers/presentations

"High Temperature Ceramic-Carbonate Dual-Phase Membrane Reactor for Pre-Combustion Carbon Dioxide Capture," Final Technical Report, November 2022. *https://www.osti.gov/servlets/purl/1899858/*.

"High Temperature Ceramic-Carbonate Dual-Phase Membrane Reactor for Pre-Combustion Carbon Dioxide Capture," presented by Jerry Lin, Arizona State University, 2022 NETL Carbon Management Research Project Review Meeting, August 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_PSC19_Lin.pdf*.

"High Temperature Ceramic-Carbonate Dual-Phase Membrane Reactor for Pre-Combustion Carbon Dioxide Capture," presented by Jerry Lin, Arizona State University, 2021 NETL Carbon Management Research Project Review Meeting, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Lin_ASU.pdf*.

"High-Temperature Ceramic-Carbonate Dual-Phase Membrane Reactor for Pre-Combustion Carbon Dioxide Capture," presented by Oscar Ovalle-Encinia, Arizona State University, 2019 NETL CO_2 Capture, Utilization, Storage, and Oil & Gas Technologies Integrated Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/O-Ovalle-Encinia-ASU-Ceramic-Carbonate.pdf*.

"High Temperature Ceramic-Carbonate Dual-Phase Membrane Reactor for Pre-Combustion Carbon Dioxide Capture," Kick-off meeting presentation, November 2018. *https://netl.doe.gov/projects/plp-download.aspx?id=10558&filename=High+Temperature+Ceramic-Carbonate+Dual-Phase+Membrane+Reactor+for+Pre-Combustion+Carbon+Dioxide+Capture+.pptx*.

"High Temperature Ceramic-Carbonate Dual-Phase Membrane Reactor for Pre-combustion Carbon Dioxide Capture," presented by Lie Meng, Arizona State University, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/L-Meng-ASU-High-Temperature-Ceramic-Carbonate-Dual-Phase-Membrane.pdf*.

J.YS Lin, O. Ovalle-Encinia, "Dual-phase ionic-conducting membranes: Pressure dependence of gas permeation flux," J. Membr. Sci. Letters, 3(1), 200041 (2023).

O. Ovalle-Encinia, J.Y.S. Lin, "Synthesis and characteristics of porous ceramic tubes: a comparison of centrifugal casting and cold isostatic pressing methods," J. Mater. Sci., 58, pages10261–10273 (2023).

O. Ovalle-Encinia and J. Y.S. Lin, "Water-gas shift reaction in ceramic-carbonate dual-phase membrane reactor at high temperatures and pressures," Chem. Eng. J., 448 (2022) 137653.

Ovalle-Encinia and J. Y.S. Lin, "High-pressure CO_2 permeation properties and stability of ceramic-carbonate dual-phase membranes," *J. Membr. Sci.*, 646, 120249 (2022).

M Anderson & YS Lin, Proc. ICIM 2006, pp. 678-681 (2006); J. Membr. Sci. 357, 122 (2010).

Integrated Multichannel Water-Gas Shift Catalytic Membrane Reactor for Pre-Combustion Carbon Capture

primary project goal

The Bettergy Corporation team developed an integrated catalytic membrane reactor (CMR) system that combines, in a one-stage process, a high-temperature water-gas shift (WGS) reaction with a hydrogen (H_2) separation membrane to produce H_2 while simultaneously delivering carbon dioxide (CO_2) at high pressure, minimizing the cost of CO_2 compression. The novel process depends on a robust modularized membrane supported on catalytic substrates, which is based on Bettergy's patented nanopore engineering membrane platform technology. Project goals were to optimize the process, develop and test a multichannel prototype system, and generate a commercialization plan.

technical goals

- Optimize the formulation for the catalytic membrane substrate.
- Develop and optimize the fabrication processes for making both tubular and multichannel membrane substrates.
- Optimize membrane synthesis procedures on the substrates.
- Optimize CMR performance to attain carbon monoxide (CO) conversion exceeding the thermodynamic limit at high temperature (up to 500°C) and pressure of 450 pounds per square inch (psi).
- Investigate the effect of impurities (e.g., hydrogen sulfide [H_2S]) on membrane performance, and achieve stability of at least 500 hours without appreciable degradation.
- Demonstrate prototype performance at syngas (simulated) flow rate of 5 kg/day.
- Enable improvement of energy efficiency of a WGS-CMR system integrated in a 550-megawatt-electric (MWe) integrated gasification combined cycle (IGCC) plant with CO_2 capture by 25 to 30%, relative to a multistage WGS reaction with amine-based carbon capture and pressure swing adsorption (PSA) H_2 purification.

technical content

The working hypothesis of this project was that the conventional WGS unit found in a coal gasification or steam reforming plant (for shifting the syngas toward primarily H_2 and CO_2) and downstream conventional amine absorption unit (for capturing the CO_2 from the shifted syngas) could be replaced in whole by a one-stage WGS-CMR process unit. In this one-stage process, the WGS reaction occurs in the CMR, which incorporates H_2 separation membranes that permit pure H_2 to

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Pre-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Water-Gas Shift Catalytic Membrane Reactor

participant:
Bettergy Corporation

project number:
SC0018853

predecessor projects:
N/A

NETL project manager:
David Lang
david.lang@netl.doe.gov

principal investigator:
Zhong Tang
Bettergy Corporation
ztang@bettergy.com

partners:
University of Cincinnati;
Dawnbreaker Inc.

start date:
07.02.2018

percent complete:
100%

be drawn off, efficiently increasing the driving force for the equilibrium WGS reaction to go to completion. Carbon dioxide exiting the WGS-CMR remains at relatively high pressure, reducing subsequent CO_2 compression costs. As a result, the multiple stages of the conventional WGS unit would be replaced by a single-stage reactor (or banks of reactors in parallel as syngas throughput requires). The process concept is depicted in Figure 1 (for a natural gas reforming scenario).

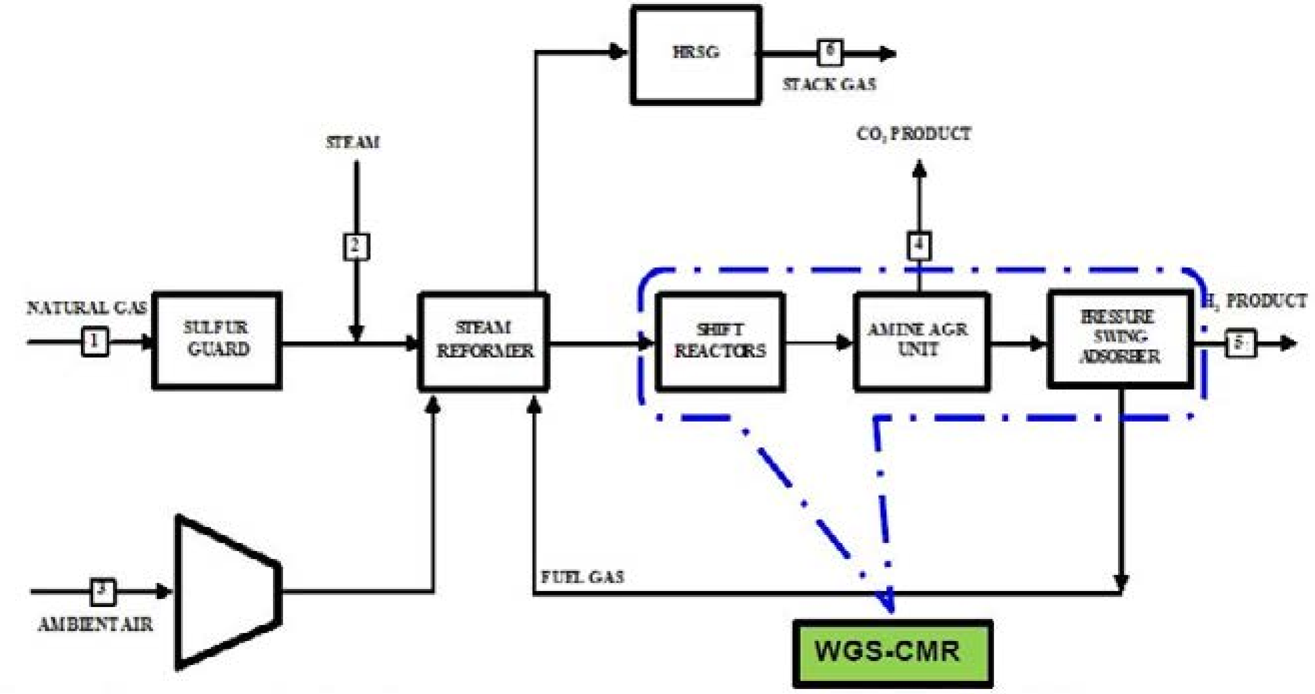


Figure 1: WGS-CMR (in green shadow) replacing two-stage shift, amine CO_2 capture, and PSA systems (in blue envelope) in natural gas steam reforming H_2 production process.

The basic structure of the WGS-CMR consists of tubular channels having a configuration of the sort illustrated in Figure 2. Each reactor gas channel consists of a porous tubular support on which two different active layers are applied. The internal tube layer is made of WGS catalyst, while the outer layer is an H_2-selective zeolite. Pressurized syngas flows through the bores of the tubes, where it contacts the WGS catalyst layer inducing increased H_2 production. The H_2 permeates through the support and can exit through the outside selective layer. Other syngas species do not readily permeate through the outside zeolite layer and remain at pressure inside the tubes. Given suitable WGS kinetics and gas flow rates, high levels of syngas conversion can be obtained, and a large fraction of H_2 can be recovered on the permeate side of the reactor. Retentate from the reactor can be made to contain most of the carbon in the incoming syngas in the form of CO_2. An alternate WGS-CMR configuration is similar but dispenses with the WGS layer and has only an H_2-selective layer on a porous substrate of WGS catalyst. In this case, the WGS catalyst may be in monolith form with many channels, with the H_2-selective zeolite layer on the outside surface of the monolith.

The dimensions of the gas channels may be made very small, and as such the WGS-CMR is a type of microchannel membrane reactor. Microchannel reactors offer multiple benefits, including better control over temperature profiles, minimal catalyst loading for given levels of gas throughput, moderate pressure drop, and favorable trade-off between capital cost and performance.

This novel WGS-CMR does pose developmental challenges, including optimizing the formulation of the high-temperature WGS catalyst (as either a layer on an inert porous support, or itself as the catalytically active porous substrate), preparing the H_2-selective composite zeolite thin layer membrane on the support/substrate, and development and optimization of WGS-CMR assemblies.

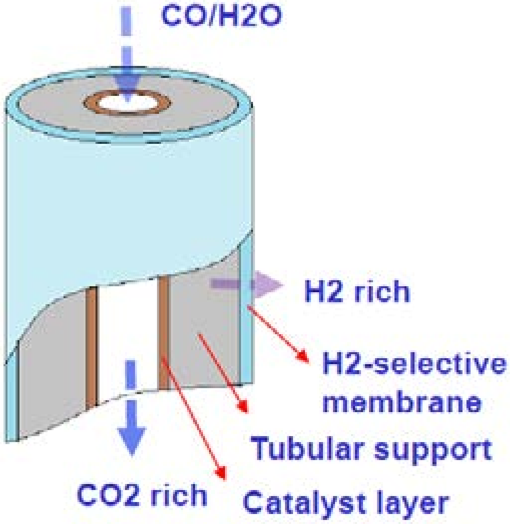


Figure 2: WGS-CMR tubular configuration.

One closely investigated configuration is a catalytic tubular substrate (CTS), which consists of WGS catalyst incorporated into the tubular support itself. A mixture of alumina and WGS catalyst powder (FeCr), plus binders/additives, has been extruded in single-channel tubes and sintered/heat treated (see Figure 3). This process has been optimized, resulting in CTSs with 1-inch diameter reliably prepared and reaching a length of 30 cm free of cracks. These include a surface modification technique for zeolite seed layer coating and membrane in situ growth.

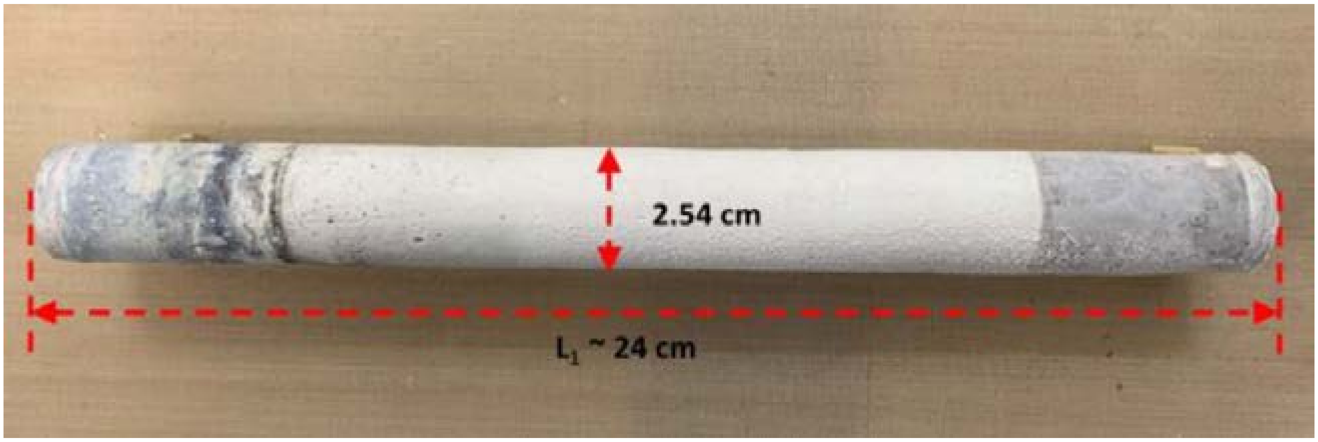


Figure 3: Post-heat-treated catalytic tube substrate.

To achieve high permeance of hydrogen, the hydrogen-selective layer on the substrate must be as thin as possible. The Bettergy team has been developing what is termed a zeolite nanosheet laminated membrane (ZNLM); they have succeeded in synthesizing a silicalite ZNLM on catalyst-alumina composite disc supports (Si-ZNLM-Cat) with minimized defects as indicated by favorable H_2/CO_2 separation selectivity of less than 0.5; also, the Si-ZNLM-Cat demonstrated enhanced CO conversion when operated as a membrane reactor for the WGS reaction at 500°C and 10 bar reaction pressure. The results indicate that ZNLM-Cat can be fabricated with reasonably well-preserved catalytic activity and membrane integrity for high-temperature WGS in a membrane reactor configuration. Figure 4 shows scanning electron microscopy (SEM) image of the Si-ZNLM on the catalytic disc support. Although the membrane surface appears to be covered by discrete zeolite particles, the Si-ZNLM is dense and continuous underneath, with uniform thickness of the membrane about 2.5 µm.

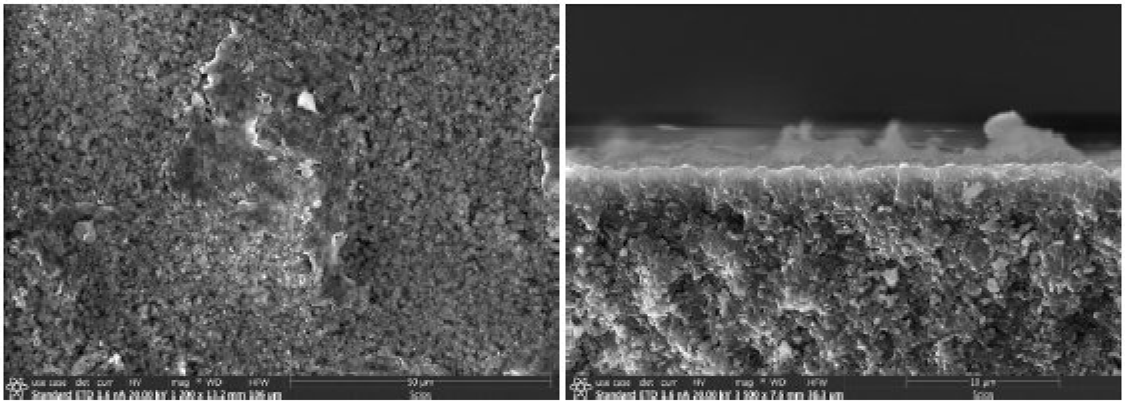


Figure 4: SEM images of the Si-ZNLM membrane: (left) surface and (right) cross-section.

The Bettergy team performed experimental testing of the WGS-CMR technology with disk-shaped CMR, single-tube CMR, and multichannel CMR operated in a tubular furnace. Simulated syngas was reacted and resulting gases measured in a gas chromatograph. Success was attained with the disk and single-tube configurations, which demonstrated WSG conversion well above the equilibrium conversion and significantly better than traditional WGS reactor performance. A WGS-CMR unit with optimized single-tube CMR configuration can achieve H_2 product purity greater than 95%, as well as retentate CO_2 greater than 80%. The single-tube CMR was tested to 186 hours, showing no significant CO conversion drop at any time over the testing interval.

A specially designed die for making multichannel catalytic substrates was fabricated and utilized to synthesize them for evaluation of a multichannel CMR (concept depicted in Figure 5). Testing of this showed that performance was worse than that of the single-tube CMR. This is probably due to bad membrane quality, which might stem from rough surface morphology, high curvature of individual channels causing potential defects, and sealing challenges given the larger outer diameter. Resolving these issues was not possible given project scope and budget limitations.

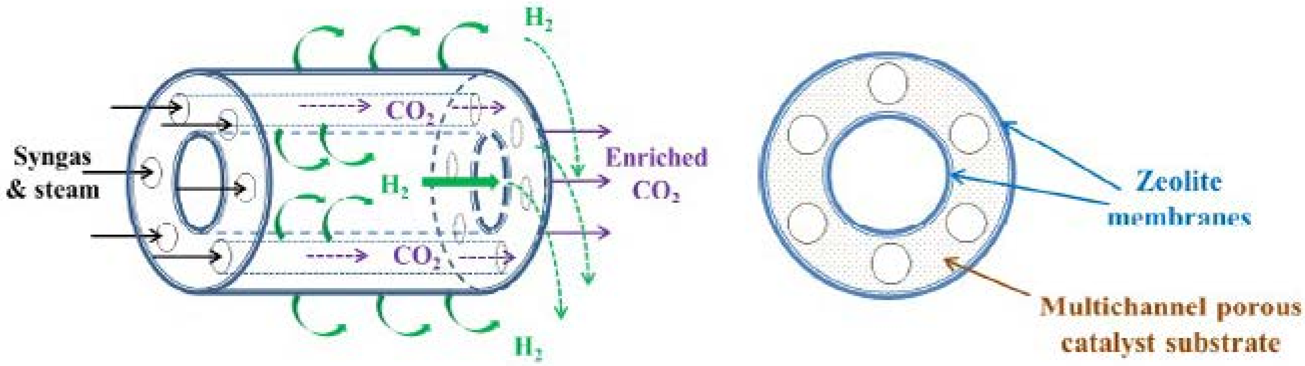


Figure 5: Schematic diagram showing multichannel CMR.

However, based on the favorable results of the single-tube CMR, a techno-economic analysis (TEA) was performed. This compared a coal gasification-based IGCC plant based on the GE quench gasifier with pre-combustion capture of CO_2 in a dual-stage Selexol unit (NETL Bituminous Baseline Case B5B), against essentially the same plant but with the dual-stage Selexol unit replaced by a WGS-CMR system sized to accomplish the same required extent of CO_2 capture while producing approximately the same plant net power output (nominally 550 MWe).

Results of the TEA showed that for the IGCC plant substituting the novel WGS-CMR unit, fixed operations and maintenance (O&M) cost would be $295.0M, compared to the Baseline B5B's O&M cost of $298.5M. Therefore, by using WGS-CMR, the total O&M cost would be comparable (98.8%) to the baseline technology. Total plant cost for the plant with the WGS-CMR substitution is reduced by 14.4%. The percentage increase in cost of electricity (COE) with WGS-CMR technology is 32.5%, compared with the 40.6% in Case B5B. Therefore, the WGS-CMR technology is showing a better than state-of-the-art system cost performance, even without the performance advantages of the multichannel configuration that might be possible when known technical issues with it are overcome.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	composite	composite
Materials of Fabrication for Support Layer	—	WGS catalyst	WGS catalyst
Nominal Thickness of Selective Layer	µm	10-20	10-20
Membrane Geometry	—	tubular	multichannel
Max Trans-Membrane Pressure	bar	10-30	30
Hours Tested without Significant Degradation	—	1,000	1,000
Manufacturing Cost for Membrane Material	$/m^2	500	355-657
Membrane Performance			
Temperature	°C	350-550	400-500
H_2 Pressure Normalized Flux	GPU or equivalent	150	50-250
H_2/H_2O Selectivity	—	N/A	N/A
H_2/CO_2 Selectivity (Dense layer thickness)	—	>50	>75
H_2/H_2S Selectivity (Dense layer thickness)	—	N/A	N/A
Sulfur Tolerance	ppm	200	500
Type of Measurement	—	mixed	mixed
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	counter flow	
Packing Density	m^2/m^3	n/a	
Shell-Side Fluid	—	retentate	
Syngas Flowrate	kg/hr	0.21	
CO_2 Recovery, Purity, and Pressure	%/%/bar	80%, 80%, 20 bar	
H_2 Recovery, Purity, and Pressure	%/%/bar	80%, >95%, 30 bar	
Pressure Drops Shell/Tube Side*	bar	1/1.5	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	0.12	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, monolith, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464 × 10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Molecular sieving and activated diffusion.

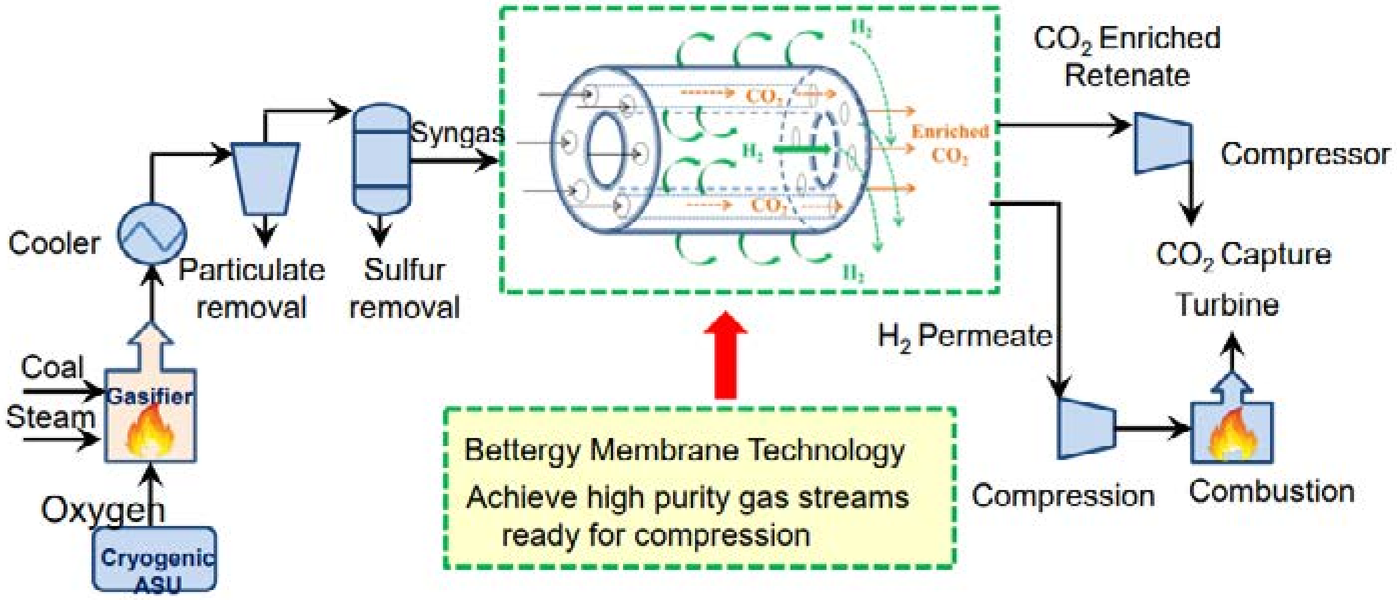
Contaminant Resistance – TBD.

Syngas Pretreatment Requirements – Tar removed.

Membrane Replacement Requirements – TBD.

Waste Streams Generated – Hydrogen sulfide would remain in the retentate and must be separated. This may result in a waste stream containing H_2S.

Process Design Concept –



Proposed Module Integration – See Figure 1.

The composition of the gas entering the module:

Pressure	Temperature	Composition (Dry)						
		vol%						
psia	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
435.1	842	15.95	49.75	0.12	1.15	32.55	0.46	0.02

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	108.88	90.00
Cost of Carbon Avoided	\$/tonne CO_2	151.96	104.65
Capital Expenditures	\$/MWhr	99.03	95.22

Operating Expenditures	$/MWhr	72.08	70.18
Cost of Electricity	$/MWhr	171.11	142.36

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – A system for an IGCC plant with net power generation of 550,000 kWe, the reference case B5B – GEP IGCC with capture in "Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity" report, Rev. 4 (*https://www.netl.doe.gov/energy-analysis/details?id=3745*).

Scale of Validation of Technology Used in TEA – Laboratory testing.

Qualifying Information or Assumptions – Assuming most costs are equivalent to Case B5B, except where the process is different—in those cases, WGS-CMR was used. The membrane cost is specific to each case.

technology advantages

- The novel pre-combustion CO_2 capture technology can be used in current gasification plants or future IGCC plants for industrial H_2 production while simultaneously capturing CO_2.
- Bettergy's CMR system offers substantial simplification of the CO_2 capture process, reduction in the cost of CO_2 capture, and increased energy efficiency, providing economic and environmental benefits for the general public.
- Microchannel reactors facilitate favorable operating temperature profiles in the reactor.
- Microchannel reactors minimize catalyst loading and limit pressure drop.
- Microchannel reactors provide optimized balance between capital cost and performance.

R&D challenges

- Optimizing the formulation of the high-temperature WGS catalyst (as either a layer on an inert porous support, or itself as the catalytically active porous substrate).
- Preparation of the H_2-selective composite zeolite thin layer membrane on the support/substrate.
- Development and optimization of WGS-CMR assemblies.
- "Trade-off" of membrane separation factor and catalyst activity, as governed by catalytic reaction intrinsic kinetics, gas diffusion mechanisms in the catalyst/membrane, and membrane properties.
- Fabrication of high-quality multichannel catalytic substrates due to lack of satisfactory commercially available extruding machines; resultant poor performance of the multichannel CMRs.

status

The project was completed on August 17, 2022. A novel WGS-CMR system was successfully demonstrated to achieve high WGS conversion, produce high concentration H_2 through membrane separation, and enrich CO_2 in the retentate stream. The WGS-CMR system substantially improved the system performance for high-temperature WGS reaction and

H_2/CO_2 separation. The system eliminates the catalyst loading process and accomplishes a combination of WGS reaction, H_2 separation, and CO_2 enrichment in a one-stage WGS-CMR process. In techno-economic evaluation, it was found that the percentage increase in COE with WGS-CMR technology is 32.5%, compared to 40.6% in a baseline case.

available reports/technical papers/presentations

Final Technical Report, "Integrated Multichannel WGS Catalytic Membrane Reactor for Pre-combustion Carbon Capture," September 16, 2022. *https://www.osti.gov/biblio/1508831*.

"Integrated Multichannel WGS Catalytic Membrane Reactor for Pre-combustion Carbon Capture," Phase II final review meeting presentation, August 2022.

"Integrated Multichannel WGS Catalytic Membrane Reactor for Pre-combustion Carbon Capture," Phase I final briefing/Phase II kickoff meeting, August 2019. *https://www.netl.doe.gov/projects/plp-download.aspx?id=12097&filename=Integrated+Multichannel+WGS+Catalytic+Membrane+Reactor+for+Pre-Combustion+Carbon+Capture.pdf*.

"Integrated Multichannel WGS Catalytic Membrane Reactor for Pre-combustion Carbon Capture," Phase I kickoff meeting presentation, July 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=12098&filename=Integrated+Multichannel+WGS+Catalytic+Membrane+Reactor+for+Pre-combustion+Carbon+Capture.pdf*.

US Provisional Patent Application No. 63/150,253, "Integrated multichannel membrane reactor," 2021.

Transformational Membranes for Pre-Combustion Carbon Capture

primary project goal

The Ohio State University's (OSU) goal was to develop cost-effective design and fabrication methods for a novel amine-containing membrane to capture carbon dioxide (CO_2) from coal gasification-derived syngas, using a single-stage membrane process utilizing modules in commercial spiral-wound configuration. Project scope of optimization and scale-up of transformational membranes with high CO_2/hydrogen (H_2) selectivity and CO_2 permeance, plus testing of spiral-wound membrane modules using simulated syngas, facilitated progress toward CO_2 capture with improved performance to meet U.S. Department of Energy (DOE) targets for cost of electricity (COE) and efficiency in advanced power generation plants.

technical goals

- Synthesize and characterize membranes, scale-up the best performing membrane using a continuous roll-to-roll fabrication method, and fabricate prototype membrane modules with approximate membrane area of 800 cm^2.
- Establish module stability by testing of the modules at 31.7 bar and 107°C for at least 200 hours on simulated syngas at 34 standard liter per minute (slpm) flowrate.
- Enable CO_2 capture at 95% CO_2 purity, with greater than 99% H_2 recovery from syngas.
- Optimize processes for integrating membrane modules into integrated gasification combined cycle (IGCC) with carbon capture, showing potential via techno-economic analysis (TEA) to reduce the COE by 30% relative to conventional/baseline approaches (Selexol).

technical content

Many common polymeric membranes for gas separations are based on a solution-diffusion mechanism, which makes these polymeric membranes simple to fabricate and low in cost. However, these membranes face considerable performance limitations, along with the inevitable trade-off between selectivity and permeability. Figure 1 illustrates this for polymer membrane separation of CO_2 and H_2. In order to exceed the upper bound, utilization of selective facilitated transport is essential.

OSU's technological approach for the membrane focuses on a CO_2-selective and permeable membrane layer on top of a polymer support, with amino groups added to facilitate CO_2 transport. The basic structure of the membrane is depicted in Figure 2. Because this membrane is to be deployed to remove CO_2 from coal-derived syngas, it is required to exhibit chemical stability to hydrogen sulfide (H_2S)

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Pre-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Amine-Containing Polymeric Membranes for CO_2 Capture from Coal Syngas

participant:
The Ohio State University

project number:
FE0031635

predecessor projects:
N/A

NETL project manager:
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partners:
American Electric Power;
Microdyn-Nadir US Inc.

start date:
10.01.2018

percent complete:
100%

gas, which is always present in at least trace amounts of coal syngas. Also, it is preferred that it can function at elevated temperature, which is characteristic of warm syngas cleanup regimes. The top layer of the membrane is the selective layer containing polymeric and small amines, while the support layer is made of nanoporous polysulfone, which is both highly permeable to gases and is mechanically robust. Some details of composition of the selective polymer layer are proprietary.

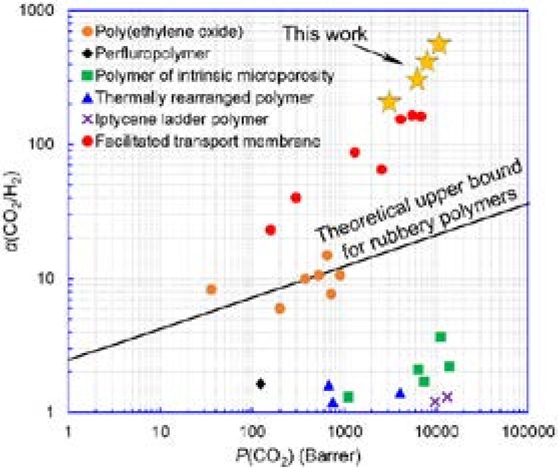

Figure 1: Typical performance of polymer membranes for CO_2/H_2 separations.

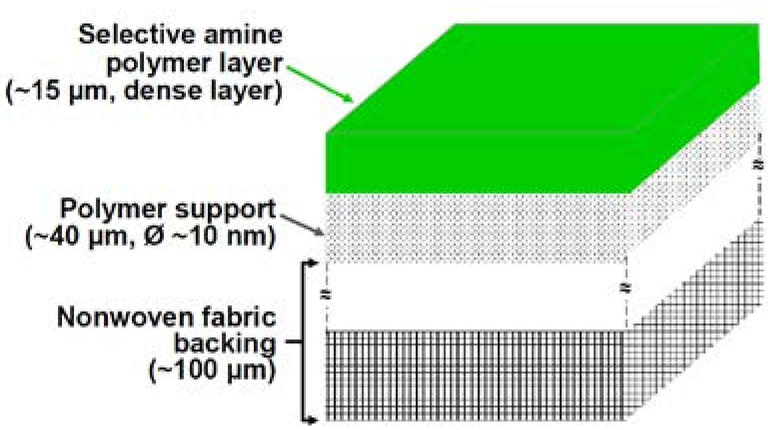

Figure 2: Membrane structure.

The facilitated transport mechanism involves enhancement of CO_2 transfer or flux through the membrane via chemical reaction with amino groups located in the selective layer. The reversible reaction of CO_2 with amino groups is as follows:

$$CO_2 + R\text{-}NH_2 + H_2O \rightleftharpoons R\text{-}NH_3^+ + HCO_3^-$$

The facilitated transport mechanism is depicted in Figure 3. Other non-acid gases, including H_2, carbon monoxide (CO), methane (CH_4), and nitrogen (N_2), are non-reactive with the membrane, and can therefore only slowly permeate through the membrane by a physical solution-diffusion mechanism. This results in high selectivities for CO_2 relative to these non-reactive gases. In contrast, the acid gas H_2S has an even higher rate of permeation through the membrane than CO_2. This means that high levels of sulfur removal from the syngas will be accomplished in a membrane separation module, with less than 10 parts per million (ppm) H_2S remaining in the syngas retentate on the feed side. The CO_2 permeate does require further treatment to remove the H_2S from the CO_2 before the latter could be stored or used.

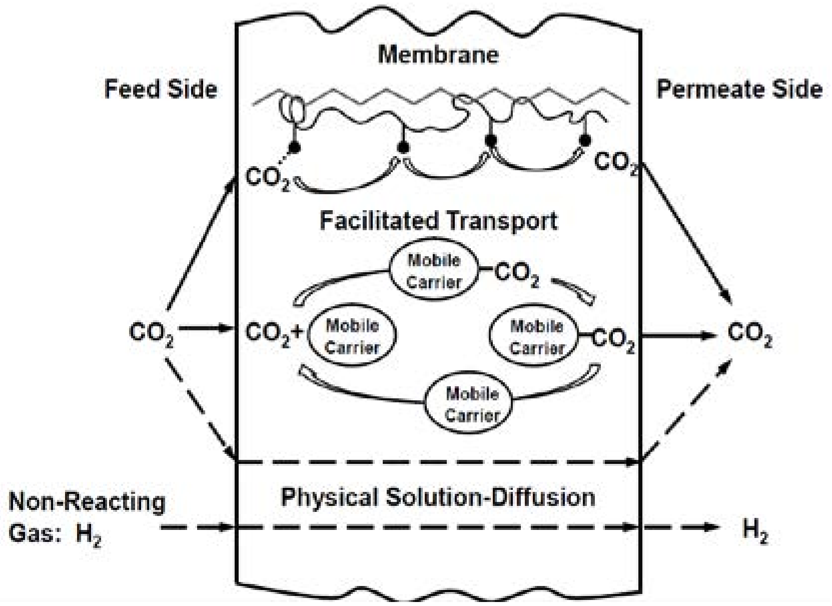

Figure 3: Mechanism of facilitated transport.

Process Scenario

One scenario for an overall plant process context is depicted in Figure 4. In order to enable 90% carbon capture in coal gasification-based IGCC processes, the preferred method is oxygen-based pressurized gasification resulting in low nitrogen content raw syngas. Syngas is shifted via the water-gas shift (WGS) reaction in a WGS unit, resulting in syngas containing large fractions of H_2 and CO_2. This shifted syngas is introduced at the high-pressure feed side of the membrane unit. Carbon dioxide and H_2S permeate to the low-pressure permeate side of the membrane unit; H_2S can be subsequently separated from the permeate mixture in a single-stage Selexol unit, while the purified CO_2 is compressed and sent to storage. The high-pressure syngas retentate serves as fuel gas for a combustion turbine.

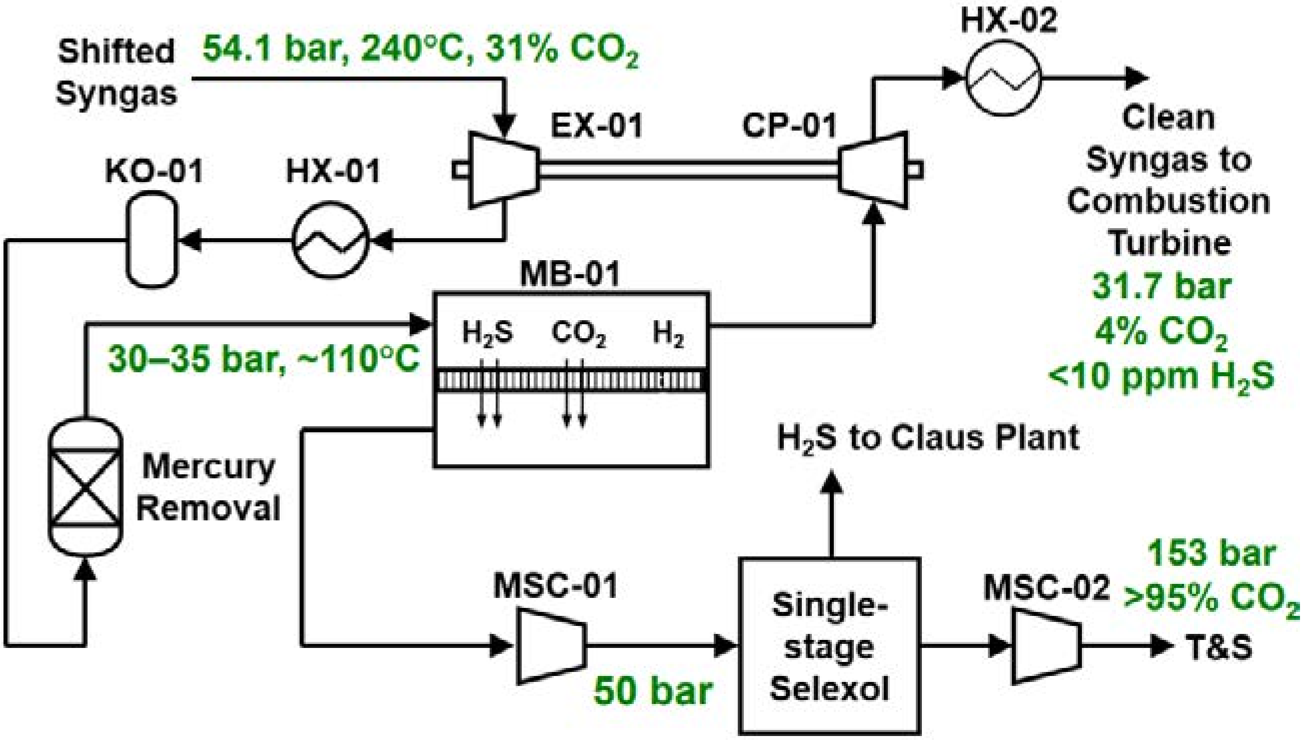

Figure 4: Process integration of membrane separation unit.

For industrial applications, it is intended that the polymeric membrane would be packed into spiral-wound membrane modules, a commonly used module design for current commercial membrane installations. Spiral-wound modules are robust, resistant to fouling, and economical; they are used in 95% of the reverse osmosis (RO) desalination industry and more than 60% of the membrane market for CO_2 removal from natural gas. Figure 5 shows the fabrication procedure and photos of the prototype spiral-wound element and assembled membrane module. The module consists of a permeate collection tube with a spiral formation of permeate spacers and feed spacers. OSU has continuously fabricated thin-film-coated membranes at 14-inch width, which were incorporated in prototype spiral-wound membrane modules used for testing and evaluation. Modules with membrane areas of 0.08 and 0.16 m^2 (Type I and Type II, see below) were fabricated.

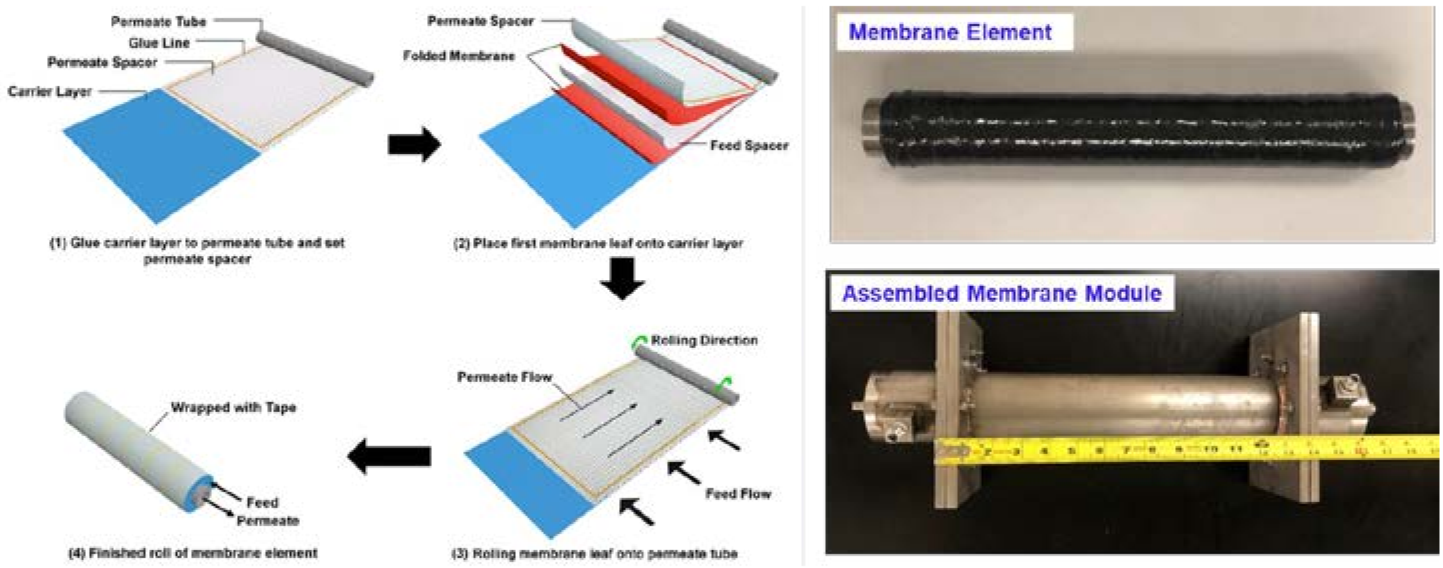

Figure 5: Procedure of single-leaf spiral-wound membrane element fabrication (left). Photos of an 0.08-m^2 prototype spiral-wound membrane element and assembled membrane module (right).

Membrane Optimization

A major technology development focus was improving performance of the membrane chiefly in terms of increasing CO_2 permeance (while maintaining CO_2/H_2 selectivity in the range of greater than 100). Approaches for improving permeance included the following:

- Using sterically hindered amines as CO_2 carriers: Comparing the mechanisms of reaction of CO_2 with both unhindered and hindered amines, the latter can double the CO_2 carrying capacity. Figure 6 shows the CO_2 permeance and CO_2/H_2 selectivity of a membrane incorporating the Type II carrier, which is a hindered amine. The hindered amine shows high selectivity at low CO_2 partial pressures (< 8 bar), while still maintaining acceptable permeance values. Also, H_2S/CO_2 selectivity of ~4 is attained, which allows a substantial degree of separation of H_2S resulting in 6 ppmv concentration of H_2S in the H_2 retentate.
- Incorporating certain molecular substituents or side chains in the membranes' molecular structure to improve facilitated transport: Also shown in Figure 6 is a membrane containing the Type I carrier, an amine-containing hydroxyethyl moiety. This membrane shows a CO_2/H_2 selectivity greater than 100 even at high CO_2 partial pressures (up to 14 bar).
- Tuning the composition of the membrane polymers: Different carrier structures in the membrane have effects on performance. It is possible to optimize membrane polymer composition for different ranges of CO_2 partial pressures.
- Incorporation of nanofillers: Linkages between molecular chains are not rigid in the polymer membrane. This means that at working temperatures (e.g., 107°C), the crosslinked polymer network is rubbery and compressible. At high syngas pressure, induced hydrostatic compression reduces the polymer free volume, causing reduced gas diffusivity through the polymer. In order to mitigate the membrane compaction, nanofillers can be dispersed in the polymer network as reinforcement. Nanofiller in the form of perforated carbon nanosheet has been economically synthesized in-house at OSU and utilized for this purpose.

Ultimately, targets for membrane fabrication and performance were met, with CO_2 permeance in the range of 275–350 GPU and CO_2/H_2 selectivity in the range of 120–140 achieved. Also, the targeted scale-up of fabricated membranes and size/capacity of the prototype spiral-wound modules were achieved.

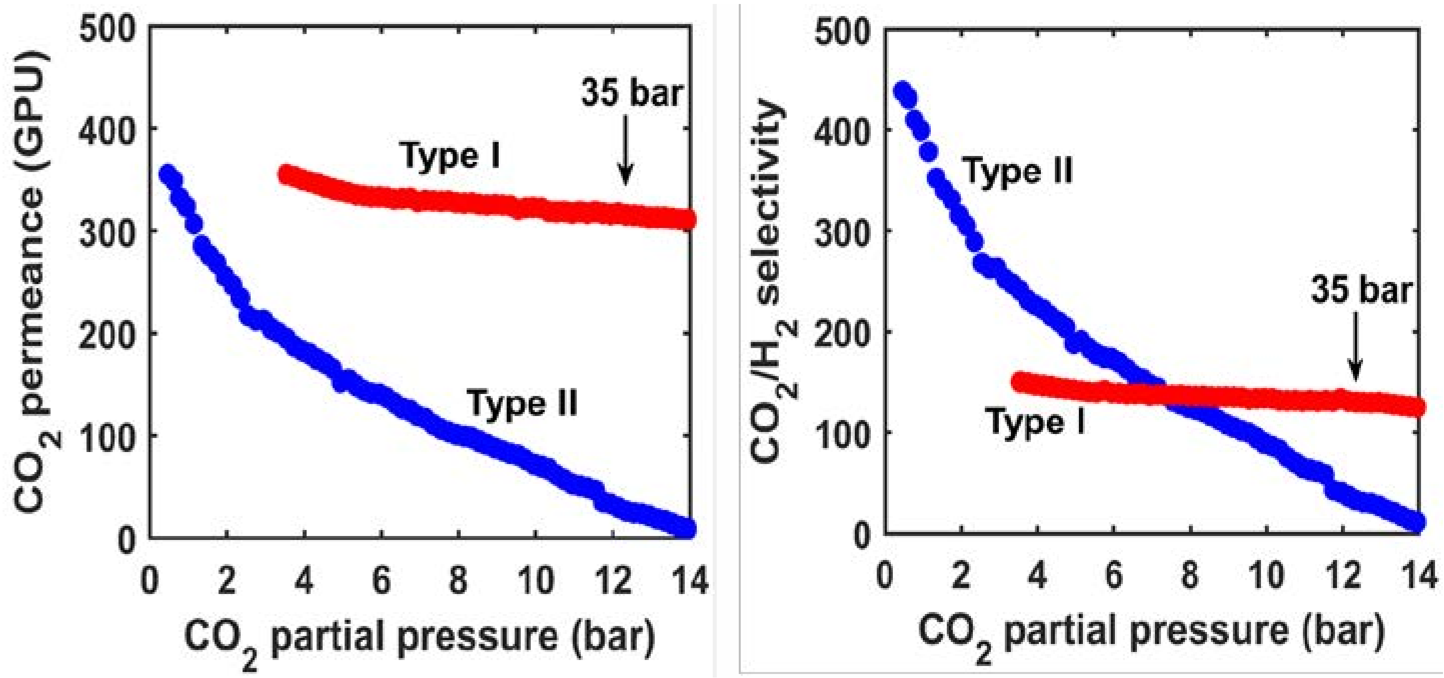

Figure 6: CO_2 permeances and CO_2/H_2 selectivities of membranes incorporating the Type I and Type II mobile carriers in simulated syngas at 107°C and 35 bar.

Spiral-wound modules incorporating optimized Type I and Type II membranes were tested in simulated syngas at 107ºC and 35 bar. The purity of CO_2 permeate and H_2 recovery were measured as functions of extent of CO_2 recovery, and the results are depicted in Figure 7. Note that the Type II modules with twice the membrane area of Type I enable higher purities and H_2 recovery for given CO_2 recoveries. Experimental results agree well with theoretical calculations.

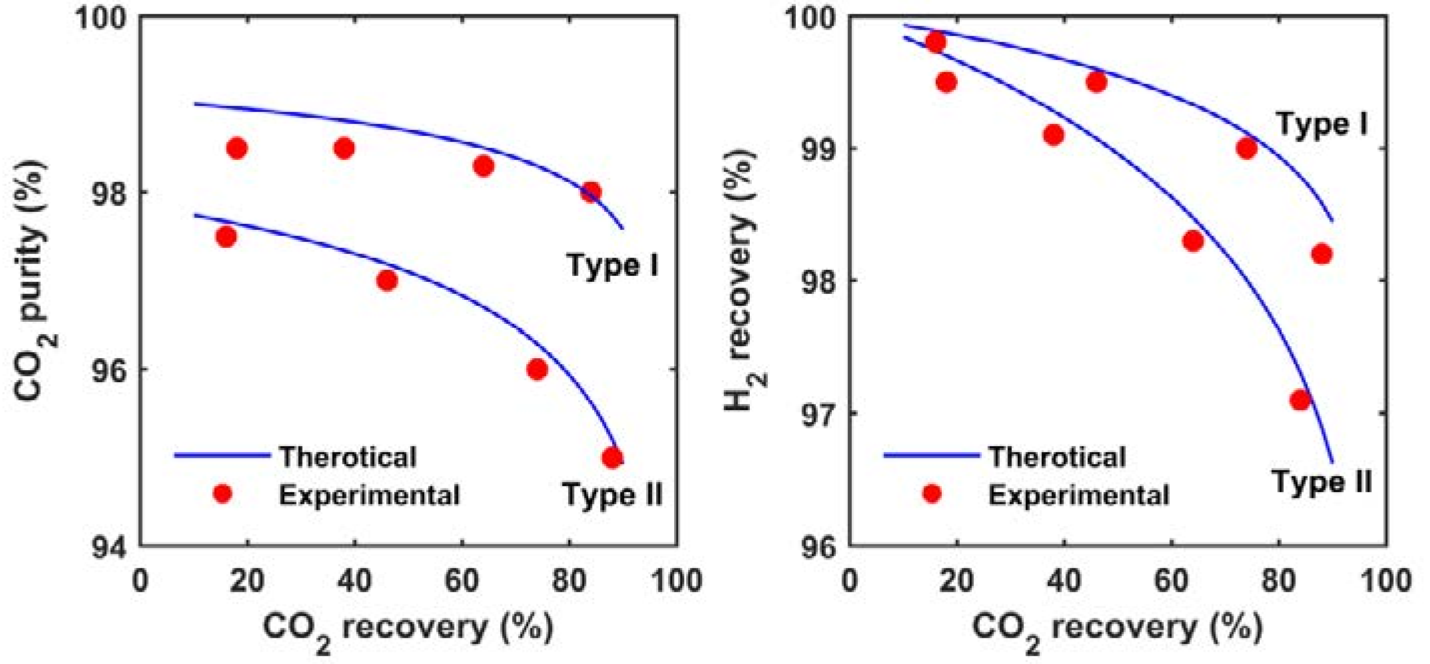

Figure 7: Spiral-wound module performance testing and evaluation.

The Type I and Type II modules OSU had developed were connected in a series and tested on simulated syngas for 200 hours. The membrane modules yielded an average CO_2 purity of 95.2% with a H_2 recovery of 99.3% and remained stable, with no discernable loss of separation performance to the end of the period of testing. The 200-hour stability demonstrated that the mobile carriers possess a negligible volatility in the polymeric membrane (which minimizes the possibility of loss through volatility), that the membranes are mechanically stable under the high syngas pressure, and that the polymer matrix is fully rubbery and not subject to a conformational relaxation (i.e., no physical aging is expected).

A TEA of a single-stage membrane process based on the OSU-facilitated transport membrane in an IGCC plant context was performed. This was based on an IGCC plant baseline as documented in the 2019 DOE Cost and Performance Baseline document (Revision 4). OSU found that implementation of the membrane-based capture results in a COE of \$124.4/MWh. This value corresponds to a COE increase of 15.3%, which is significantly lower (i.e., 54.5%) than the benchmark two-stage Selexol process given in the DOE baseline case B5B (i.e., COE increase of 33.6%). Figure 8 shows the COE values of the non-capture baseline IGCC plant B5A, the increased COE values for the capture case B5B, and the lower increased COE values of the OSU membrane process case (on the right side of the figure).

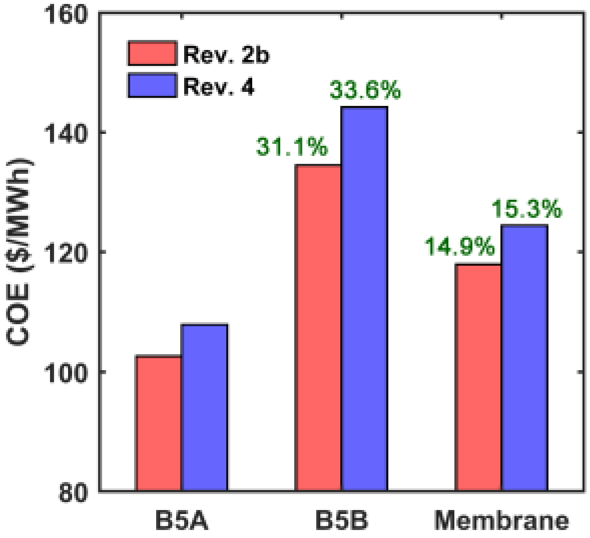

Figure 8: COE values comparison.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value *	Target R&D Value
Materials of Fabrication for Selective Layer	—	polymer with amino groups	polymer with amino groups
Materials of Fabrication for Support Layer	—	polysulfone	polysulfone
Nominal Thickness of Selective Layer	µm	~15 – 25	15 – 25
Membrane Geometry	—	spiral wound	spiral wound
Maximum Trans-Membrane Pressure	bar	35	35
Hours Tested without Significant Degradation	—	200	≥200
Manufacturing Cost for Membrane Material	\$/m^2	~54	≤54
Membrane Performance			
Temperature	°C	107	107
CO_2 Pressure Normalized Flux	GPU	355	275 – 350
CO_2/H_2O Selectivity	—	1	1
CO_2/H_2 Selectivity	—	150	120 – 140
H_2S/CO_2 Selectivity	—	4 – 7	3
Sulfur Tolerance	ppm	>6,000	>6,000
Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design			
Flow Arrangement	—	Counter-current	

Packing Density	m^2/m^3		2000	
Shell-Side Fluid	—		Retentate, H_2-rich flow	
Syngas Gas Flowrate	slpm		50	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90	95.2	1.1
H_2 Recovery, Purity, and Pressure	%/%/bar	99.3	94	35
Pressure Drops Shell/Tube Side	psi/m		1.5	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{m^2}$		87.2	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-10} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in desulfurized syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Facilitated transport mechanism.

Contaminant Resistance – Membrane is tolerant to greater than 6,000 ppm H_2S.

Syngas Pretreatment Requirements – Thermal expansion for mild syngas cooling, and filtration to remove any particulate matter.

Membrane Replacement Requirements – Spiral-wound membrane elements are expected to be replaced every five years.

Waste Streams Generated – Elemental sulfur recovered from the captured H_2S and CO_2 stream via the Claus process.

Proposed Module Design – See Figures 4 and 5. The pressure, temperature, and composition of the gas entering the membrane module are as follows:

Pressure	Temperature	Composition						
		vol%						ppmv
psia	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
507.6	224.6	39.6	—	—	—	56.1	3.7	6065

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	N/A	N/A
Cost of Carbon Avoided	\$/tonne CO_2	N/A	N/A
Capital Expenditures	\$/MWhr	73.4	78.7
Operating Expenditures	\$/MWhr	51.0	54.6
Cost of Electricity	\$/MWhr	124.4	133.3

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity, Revision 4.

Scale of Validation of Technology Used in TEA – Laboratory testing.

Qualifying Information or Assumptions –

- The membrane element cost is assumed as \$5/ft^2 membrane area based on the current market price for spiral-wound element in natural gas sweetening. A cost of \$0.5/ft^2 membrane area is used for the module housing according to RO applications with a feed pressure up to 60 bar.
- The membrane life is assumed as four years. Based on the membrane element cost of \$5/ft^2, the annual membrane replacement cost is \$1.25/ft^2. This cost is included in the variable cost.

technology advantages

- The simplicity of the amine-polymer membrane structure lowers its manufacturing cost.
- Membrane modules do not contain moving parts or involve chemical reaction, simplifying operation and maintenance.
- The membrane material has a high tolerance to acid gases and is inert to all primary syngas species.
- The membrane capture system has a compact footprint and low energy cost.
- Spiral-wound module configuration affords minimal pressure drop, helping energy efficiency.
- The membrane capture system can operate warm/hot to reduce the need for heat exchange (e.g., membrane modules operate at a higher temperature and pressure than conventional acid gas removal processes like Selexol, reducing the need for syngas cooling and lowering the energy and capital cost required to convert captured CO_2 to liquid).
- The membrane can remove H_2S simultaneously with CO_2, resulting in low-sulfur H_2 for combustion or chemical synthesis.

R&D challenges

- Increasing the CO_2 permeance of the membrane.
- Assuring polymer support performance and properties.

- Choice of spacer and glue for high-temperature membrane module fabrication.
- Scale-up and integration issues are possible given the large number of membranes needed to service a 550-megawatt-electric (MWe) plant.

status

The project was completed in March 2022. OSU was able to obtain successful levels of CO_2 permeance with the most advanced membrane synthesized measured at 314 GPU and CO_2/H_2 selectivity of 138 at ~110°C. Increased membrane performance was attained via a series of compositional improvements, including better amine carrier with optimal steric hindrance, optimized nanofiller geometry, and improved polymer matrix with high CO_2 uptake.

Membrane modules were successfully fabricated and tested; a hybrid configuration of two membrane modules in series demonstrated H_2 recovery of 99.3% at 90% CO_2 removal and a CO_2 purity of 95.2, exceeding recovery and purity requirements. The hybrid configuration of two membrane modules in series remained stable for 200 hours with the simulated syngas at 107°C. TEA results showed that a COE increase of no more than 15% over a baseline IGCC non-capture plant case could be attained with the OSU membrane system in a 90% CO_2 removal case.

available reports/technical papers/presentations

"FE0031635: Transformational Membranes for Pre-Combustion Carbon Capture," Project Final Technical Report (Draft), W,S, Winston Ho and Yang Han, Ohio State University, Submitted to the U.S. Department of Energy National Energy Technology Laboratory, June 11, 2022. *https://www.osti.gov/servlets/purl/1872189*.

Y. Han and W. S. W. Ho, "Facilitated Transport Membranes for H_2 Purification from Coal-Derived Syngas: A Techno-Economic Analysis," *J. Membr. Sci*., 636, 119549 (2021).

"Design of Amine-Containing CO_2-Selective Membrane Process for Carbon Capture from Flue Gas," Yang Han and W.S. Winston Ho, Industrial & Engineering Chemistry Research, 59, 5340–5350 (2020).

"Transformational Membranes for Pre-combustion Carbon Capture," presented by Winston Ho and Yang Han, The Ohio State University, 2021 NETL Carbon Management Research Project Review Meeting, August 16, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Ho.pdf*.

"Amine-Containing Membranes with Functionalized Multi-Walled Carbon Nanotubes for CO_2/H_2 Separation," Yutong Yang, Yang Han, Ruizhi Pang, and W.S. Winston Ho, Membranes, 10, 333 (2020).

"Transformational Membranes for Pre-combustion Carbon Capture," NETL Budget Period 1 Project Review Meeting (virtual), Pittsburgh, PA, February 18, 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10563&filename=Transformational+Membranes+for+Pre-combustion+Carbon+Capture.pdf*.

"Facilitated Transport Membranes with Tunable Amine-CO_2 Chemistry for Highly Selective CO_2/H_2 Separation," presentation by Yang Han and W.S. Winston Ho, 2019 AIChE (American Institute of Chemical Engineers) Annual Meeting. Orlando, FL, November 2019, Paper 750a.

"Transformational Membranes for Pre-combustion Carbon Capture," presentation by Winston Ho and Yang Han, The Ohio State University, 2019 NETL CCUS Integrated Project Review Meeting. Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/Y-Han-OSU-Transformational-Precombustion-Membranes.pdf*.

"Transformational Membranes for Pre-combustion Carbon Capture," project kickoff meeting presentation, November 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10567&filename=Transformational+Membranes+for+Pre-combustion+Carbon+Capture.pdf*.

"Transformational Membranes for Pre-combustion Carbon Capture," Poster presentation by Yang Han, The Ohio State University, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/Y-Han-OSU-Transformational-Membranes.pdf*.

Development of Carbon Molecular Sieves Hollow Fiber Membranes Based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties

primary project goal

The goal of this State University of New York (SUNY)–Buffalo project was to develop scalable membrane technology by engineering polymers to achieve superior hydrogen (H_2)/carbon dioxide (CO_2) separation properties in readily fabricated and easily deployed membranes for capture of CO_2 from coal-derived syngas. Specifically, the approach was to derive carbon molecular sieve (CMS) membranes from polybenzimidazole (PBI) doped with polyprotic acids, which were expected to offer high H_2 permeance and H_2/CO_2 selectivity while retaining robust chemical stability at elevated operating temperature.

technical goals

- Develop CMS hollow fiber membranes (HFMs) having a H_2 permeance of 1,000 gas permeation units (GPU) and an H_2/CO_2 selectivity of 40 at 200–300°C.
- Fabricate small membrane modules and demonstrate membrane performance and durability via testing of the modules under simulated syngas flow at 0.01 kilowatt-electric (kWe) equivalency for 120 hours.
- Characterize a CMS membrane-based system able to capture 90% CO_2 from coal-derived syngas with 95% CO_2 purity at a cost of electricity 30% less than baseline capture approaches (Selexol) in the context of an integrated gasification combined cycle (IGCC) plant scenario.

technical content

Conventional methods for pre-combustion carbon capture consist mainly of solvent-based processes such as Selexol and Rectisol. Although enabling high levels of capture at high gas purity, these processes have high capital and operating costs and result in severe energy penalties. Membrane-based carbon capture is of continued interest as an alternative, given its potential advantages in simplicity, lower costs, and potential for large savings in energy use. Among membranes for separation of CO_2 from syngas, inorganic membranes such as palladium alloys, ceramics, metal-organic frameworks (MOFs), and graphene oxide have been evaluated, given their excellent H_2/CO_2 separation properties. However, they are faced with challenges in cost and reliability, scale-up of membrane production, and module fabrication. In contrast, polymer-based membranes are much easier to implement than inorganic membranes, provided

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Pre-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Carbon Molecular Sieve Hollow Fiber Membranes With Coal Syngas

participant:
State University of New York–Buffalo

project number:
FE0031636

predecessor projects:
N/A

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partners:
Los Alamos National Laboratory; Trimeric Corporation

start date:
10.01.2018

percent complete:
100%

that the membrane materials demonstrate suitable separation properties. Production scale-up and module fabrication using polymeric membranes have been widely practiced, creating a substantial engineering knowledge base across the polymer membrane industry. Building on this foundation, this work targeted the development of scalable membranes by engineering polymers to achieve superior H_2/CO_2 separation properties.

Most work in H_2/CO_2 gas separations by polymeric membrane materials relies solely on strong size-sieving derived from the rigid polymer chains. Polymers available commercially in this class include examples like poly(p-phenylene oxide) (PPO), Matrimid, poly(bisphenol-A sulfone) (PSF), and cellulose acetate (CA). However, the commercially available polymers have low H_2 diffusivity and permeability, are limited by the permeability/selectivity trade-off, and are well below the Robeson upper bound, as illustrated in Figure 1.

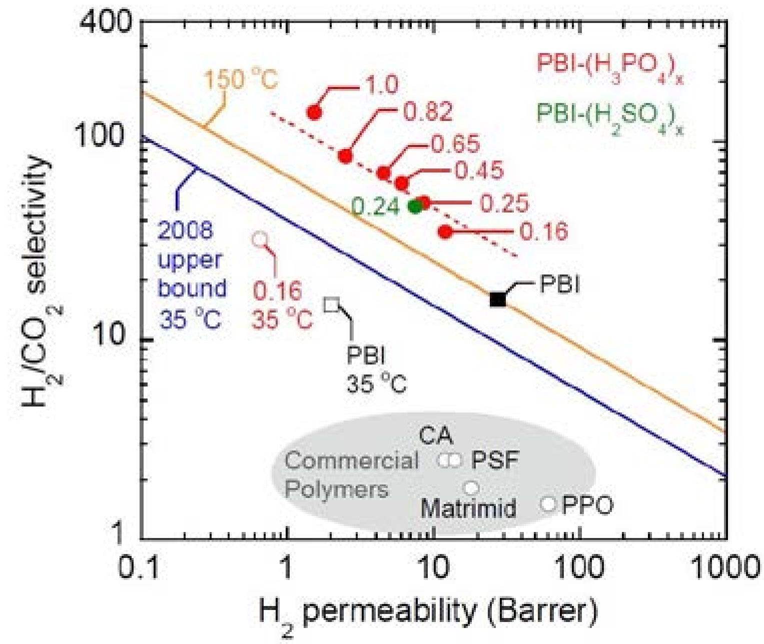


Figure 1: Pure-gas H_2/CO_2 separation performance of PBI-$(H_3PO_4)_x$ (x = 0.16-1.0) and PBI-$(H_2SO_4)_{0.24}$ at 150°C versus Robeson's upper bound at 35°C and 150°C.

The SUNY team has demonstrated considerable improvement in polymer membrane performance by doping PBI with polyprotic acids such as phosphoric acid (H_3PO_4) and sulfuric acid (H_2SO_4) to improve the size-sieving ability and H_2/CO_2 separation properties at 120–180°C. As shown in the upper part of Figure 1, increasing the H_3PO_4 doping level (defined as the molar ratio of H_3PO_4 to the PBI repeating units) decreases the pure-gas permeability and drastically increases the H_2/CO_2 selectivity at 150°C. For example, plain PBI shows an H_2/CO_2 selectivity of 16, while PBI-$(H_3PO_4)_{1.0}$ exhibits a remarkable selectivity of 140, which is much higher than that of any previously studied polymers. Phosphoric acid can strongly interact with multi-PBI chains via proton transfer from the acid to imidazole rings of PBI and hydrogen bonding, and thus it crosslinks the PBI. In comparison, a monoprotic acid such as hydrogen chloride (HCl) does not crosslink the PBI chains and has minimal effect on H_2/CO_2 separation properties.

SUNY's approach was to start with the already strongly size-sieving polymers (i.e., PBI doped with polyprotic acids [PPA]), and then carbonize them (by heating/pyrolysis at 500–800°C in inert nitrogen [N_2] for at least an hour) to increase both permeability and selectivity into a range suitable for commercial deployment. This approach is diagrammed in Figure 2, showing PBI being doped with the PPA, and then carbonized by pyrolysis. Carbonizing the acid-doped PBI results in microcavities increasing gas permeability and ultra-microporous necks increasing size-sieving ability.

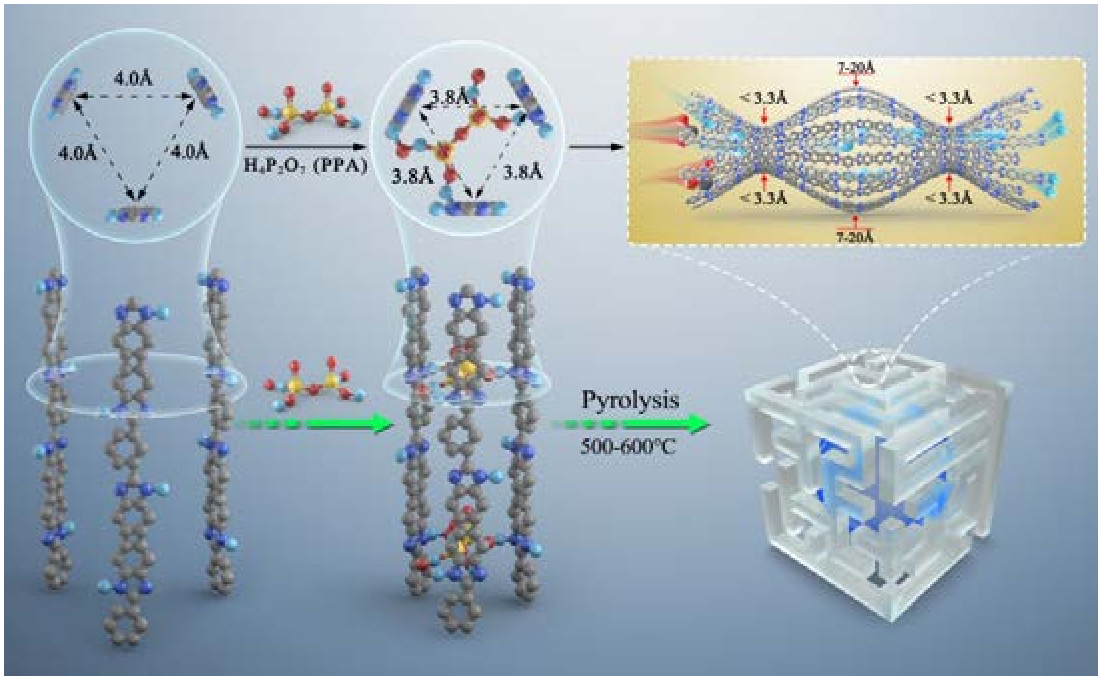


Figure 2: Steps to CMS membranes derived from PBI doped with polyprotic acids.

In past work, CMS membranes were made by carbonizing plain PBI. The pyrolysis increases the porosity and generates graphite-like structure. As shown in Figure 3 in blue, the carbonization of PBI substantially increases H_2 permeability while retaining or slightly increasing H_2/CO_2 selectivity at 100°C. All CMS samples have exhibited H_2/CO_2 separation properties above the upper bound. For example, pure PBI exhibits an H_2 permeability of 12 Barrer and an H_2/CO_2 selectivity of 14 at 100°C, while the CMS prepared by pyrolysis of PBI at 800°C shows an H_2 permeability of 670 Barrer (which is 50 times higher than pure PBI) and an H_2/CO_2 selectivity of 18 at 100°C.

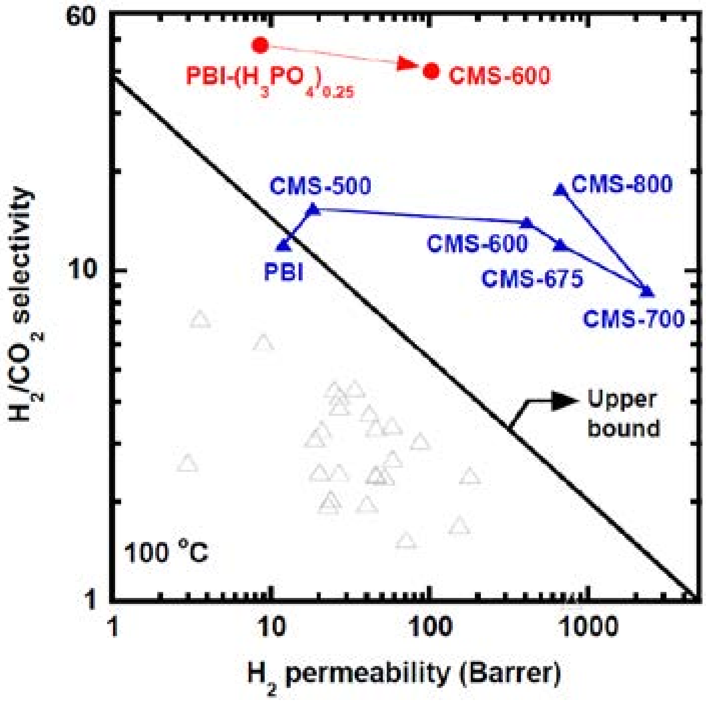


Figure 3: Improvement in membrane performance upon carbonization to CMS.

The SUNY team hypothesized that the CMS membranes would be able to meet targeted separation properties (H_2 permeance of 1,000 GPU and H_2/CO_2 selectivity of 40) if the starting polymers were PBI doped with polyprotic acids with strong size-sieving ability. For example, PBI-$(H_3PO_4)_{0.25}$ exhibits an H_2 permeability of 8.6 Barrer and an H_2/CO_2 selectivity of 48 at 150°C. The pyrolysis at 600°C increases the permeability to 100 Barrer while retaining an H_2/CO_2 selectivity of 40 at 100°C, as shown in red in Figure 3. During the pyrolysis, the H_3PO_4 gradually decomposes to polyphosphoric acid ($(HPO_3)_n$), retaining the rigid chains and strong molecular size-sieving ability.

Results of optimization of the acid type, composition, and pyrolysis temperature are depicted in Figure 4. The left side depicts results of doping with phosphoric acid at different proportions, while the right side shows results of doping with pyrophosphoric acid at different proportions, and before and after carbonization (respectively blue and red). A pyrolysis temperature of 600°C was found to be optimal. SUNY was able to achieve H_2 permeability of 200 Barrer with an H_2/CO_2 selectivity of 40 for pyrophosphic acid-doped, 600°C pyrolized PBI-PPA_x at x values of about 0.25.

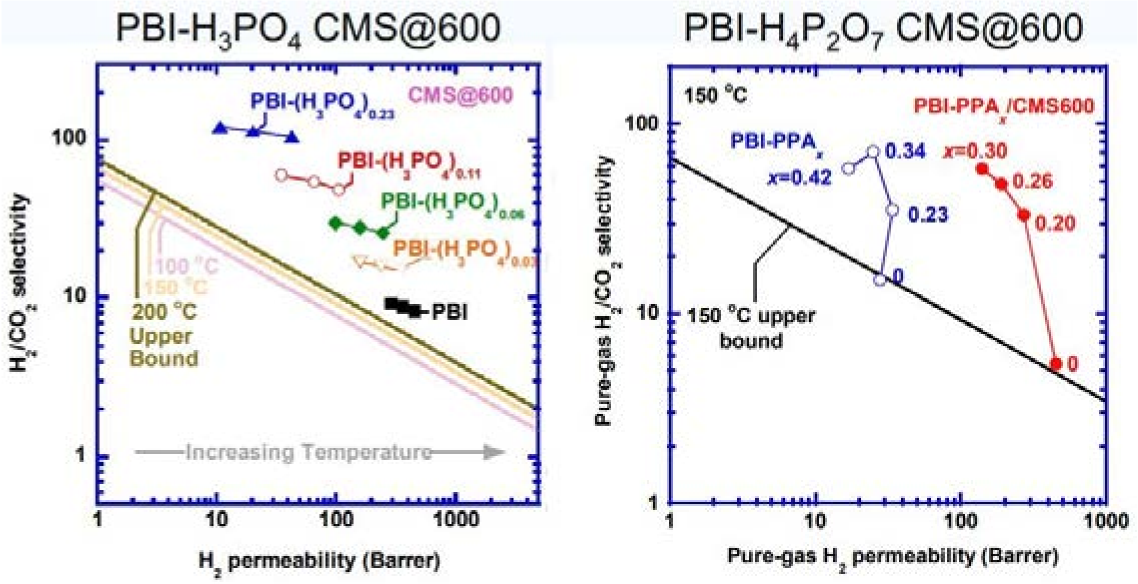


Figure 4: Improvement in membrane performance upon carbonization to CMS.

With this degree of permeability, HFMs with a selective layer thickness of 0.2 µm will achieve an H_2 permeance of 1,000 GPU and an H_2/CO_2 selectivity of 40. Los Alamos National Laboratory (LANL) has successfully fabricated nearly defect-free PBI HFMs with a 0.2 µm selective layer. Figure 5 shows images of (a) a base PBI HFM and (a′) carbonized hollow fiber. This illustrates that the carbonized fiber retains the porous support morphology of the starting fiber.

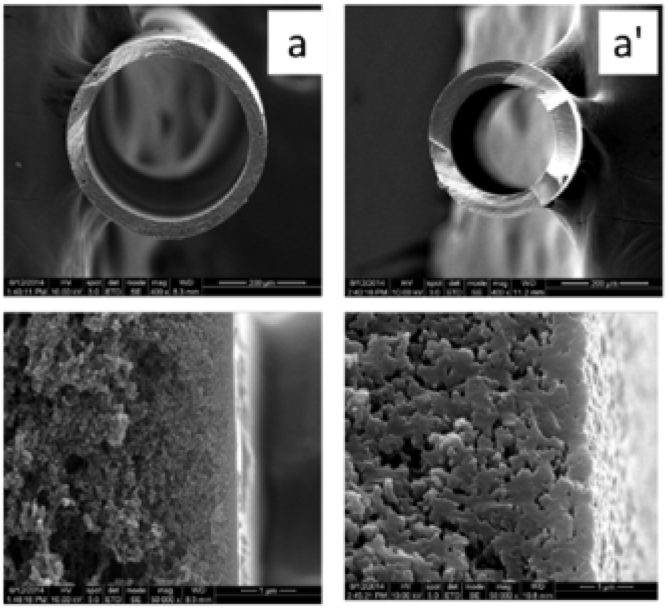


Figure 5: Scanning electron microscopy (SEM) images of PBI hollow fibers, before (left) and after (right) carbonization.

CMS membranes are intended for incorporation in hollow fiber modules for deployment in gas separation systems. LANL used the hollow fiber spinning system depicted in Figure 6 to fabricate the hollow fibers. A custom micro-machined spinneret forms the fiber. The steps resulting in CMS carbon fibers are also diagrammed.

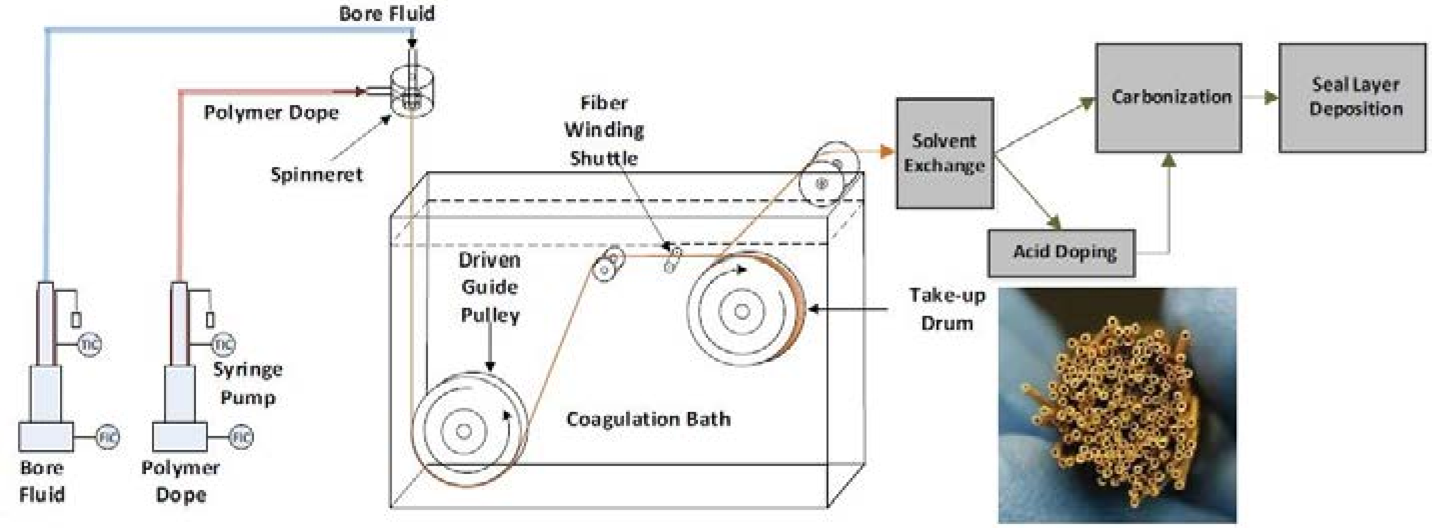


Figure 6: LANL lab-scale continuous hollow fiber spinning system.

SUNY manipulated the PBI-CMS HFM fabrication process to optimize HFM H_2/CO_2 separation performance. Figure 7a shows the H_2 permeance and H_2/CO_2 selectivity for a series of PBI-CMS HFMs fabricated under varied conditions. The project goal of 1,000 GPU H_2 permeance and H_2/CO_2 selectivity of 40 was definitively attained along the measured points under gas permeation testing at 250°C. Figure 7b shows the influence of temperature on the H_2/CO_2 separation performance of asymmetric PBI-CMS HFMs. The ideal H_2, CO_2, and N_2 permeance increases as the temperature increases from 150 to 300°C. The highest H_2 permeance of 1,090 GPU and H_2/CO_2 selectivity of 57 was measured at 300°C, which substantially exceeds the project goal.

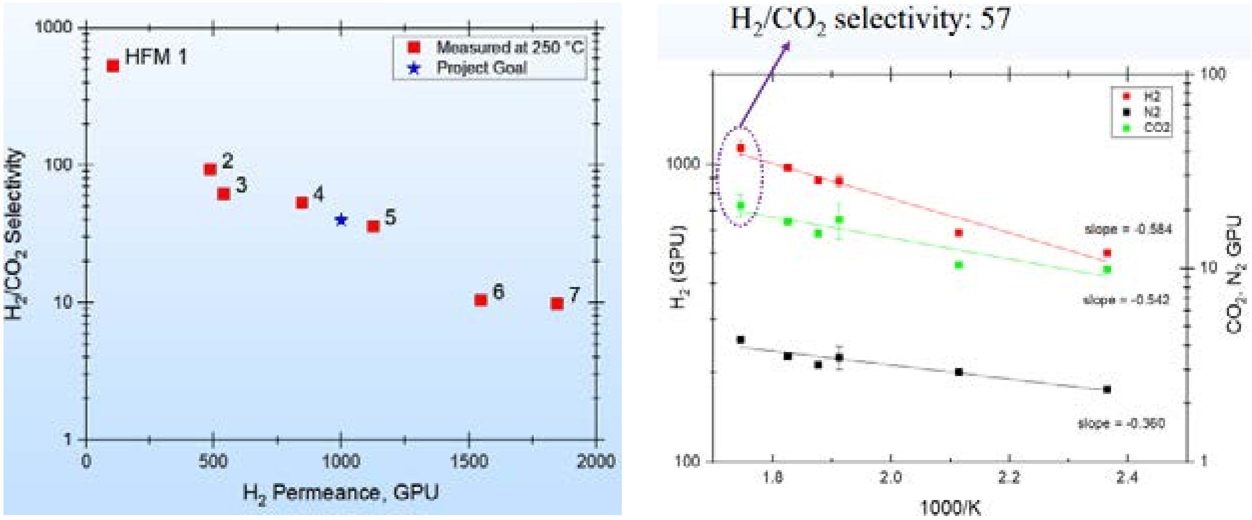


Figure 7a (left) and 7b (right): PBI-CMS HFM testing results.

Process implementation of CMS membrane modules would follow the basic flow diagram shown in Figure 8. Shifted syngas (1) containing mostly H_2 and CO_2 passes through membrane modules. Hydrogen selectively permeates and is swept away by N_2 (3), which is available in large quantities from the air separation unit producing oxygen for coal gasification (not shown on this figure). The H_2 and N_2 mixture comprises fuel gas (4) to be combusted in the power turbine. Retentate from the membrane modules is conditioned, dewatered, and compressed/pumped into liquid CO_2 for storage or use (2). With the CMS membranes able to withstand increased operating temperature of 200–300°C (as opposed to more conventional limit of 150°C), there is reduced cost of cooling syngas upstream of the membrane separation step, while improved permeability and selectivity afforded by the PBI-CMS HFMs reduces CO_2 processing costs downstream. These benefits combine to offer better economics for CO_2 capture than conventional approaches.

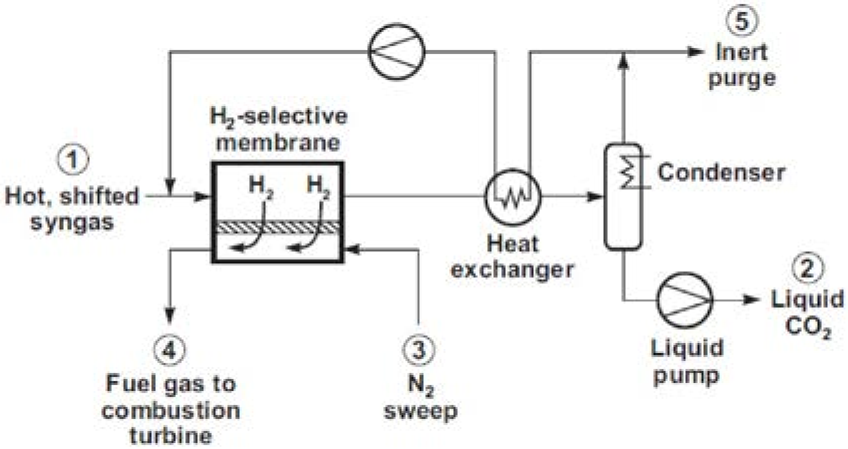
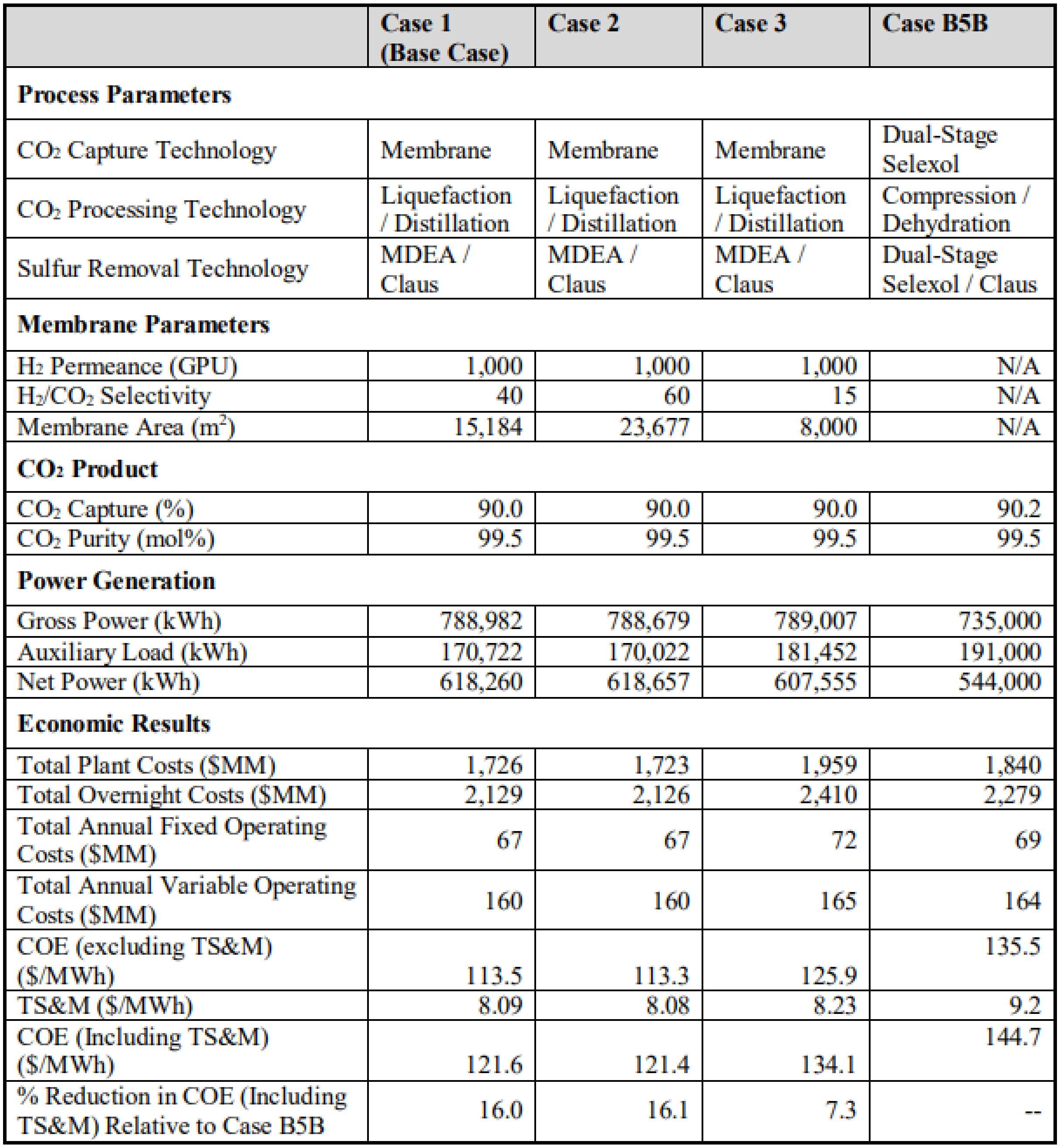


Figure 8: Membrane process integration in process cycle.

The SUNY team conducted a techno-economic analysis (TEA) to quantify costs for a membrane-based capture process and enable comparison to the NETL baseline cases (Case B5A IGCC without CO_2 capture, and Case B5B IGCC with CO_2 capture using a dual-stage Selexol unit), which are from the 2015 U.S. Department of Energy (DOE) Cost and Performance Baseline Report (Volume 1, Revision 2b). Although the baseline capture case uses dual-stage Selexol to remove all acid gases (CO_2 and H_2S), it was found that substituting a pairing of a methyldiethanolamine (MDEA) unit to remove sulfur with the membrane unit for CO_2 capture is a more efficient and cost-effective arrangement. Because target H_2/CO_2 selectivity of 40 to nearly 60 was attained in experimental evaluation (well above the original target of 25), this afforded an opportunity to perform a sensitivity study of varying selectivity in plant costs and cost of electricity (COE). These results are tabulated in Figure 9. Note that the NETL baseline capture case (Case B5B) has COE of 144.7$/Mhr, and for SUNY-developed membrane cases, improvements over the baseline COE were realized, with reduction in COE reaching 16% for the higher selectivity membranes of 40 and 60.



	Case 1 (Base Case)	Case 2	Case 3	Case B5B
Process Parameters				
CO_2 Capture Technology	Membrane	Membrane	Membrane	Dual-Stage Selexol
CO_2 Processing Technology	Liquefaction / Distillation	Liquefaction / Distillation	Liquefaction / Distillation	Compression / Dehydration
Sulfur Removal Technology	MDEA / Claus	MDEA / Claus	MDEA / Claus	Dual-Stage Selexol / Claus
Membrane Parameters				
H_2 Permeance (GPU)	1,000	1,000	1,000	N/A
H_2/CO_2 Selectivity	40	60	15	N/A
Membrane Area (m^2)	15,184	23,677	8,000	N/A
CO_2 Product				
CO_2 Capture (%)	90.0	90.0	90.0	90.2
CO_2 Purity (mol%)	99.5	99.5	99.5	99.5
Power Generation				
Gross Power (kWh)	788,982	788,679	789,007	735,000
Auxiliary Load (kWh)	170,722	170,022	181,452	191,000
Net Power (kWh)	618,260	618,657	607,555	544,000
Economic Results				
Total Plant Costs ($MM)	1,726	1,723	1,959	1,840
Total Overnight Costs ($MM)	2,129	2,126	2,410	2,279
Total Annual Fixed Operating Costs ($MM)	67	67	72	69
Total Annual Variable Operating Costs ($MM)	160	160	165	164
COE (excluding TS&M) ($/MWh)	113.5	113.3	125.9	135.5
TS&M ($/MWh)	8.09	8.08	8.23	9.2
COE (Including TS&M) ($/MWh)	121.6	121.4	134.1	144.7
% Reduction in COE (Including TS&M) Relative to Case B5B	16.0	16.1	7.3	--

Figure 9: Performance and economic summary for H_2/CO_2 selectivity sensitivity.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value *	Target R&D Value
Materials of Fabrication for Selective Layer	—	carbonized acid-doped PBI	carbonized acid-doped PBI
Materials of Fabrication for Support Layer	—	plain PBI	plain PBI
Nominal Thickness of Selective Layer	μm	0.2	0.2
Membrane Geometry	—	hollow fiber	hollow fiber
Maximum Trans-Membrane Pressure	bar	20	50
Hours Tested without Significant Degradation	h	120	500
Manufacturing Cost for Membrane Material	\$/m^2	20	20
Membrane Performance			
Temperature	°C	150	200-350
CO_2 Pressure Normalized Flux	GPU or equivalent	1000	1,000
CO_2/H_2O Selectivity	—	0.5	0.5
CO_2/H_2 Selectivity	—	0.025	0.017
CO_2/H_2S Selectivity	—	2	2
Sulfur Tolerance	ppm	20	20
Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design			
Flow Arrangement	—	Countercurrent	
Packing Density	m^2/m^3	~1,000	
Shell-Side Fluid	—	Permeate, CO_2-rich flow	
Syngas Gas Flowrate	kg/hr	~960,000	
CO_2 Recovery, Purity, and Pressure	%/%/bar	94.3 43.6 50.4	
H_2 Recovery, Purity, and Pressure	%/%/bar	72.8 41.9 32	
Pressure Drops Shell/Tube Side	bar	1/1	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	~4.0	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in desulfurized syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Physical solution-diffusion.

Contaminant Resistance – Membranes are resistant to chemicals in the syngas.

Syngas Pretreatment Requirements – Removal of particles.

Membrane Replacement Requirements – Module lifetime is three to five years.

Waste Streams Generated – Water vapor will permeate with H_2, and the water stream will be produced after the H_2 combustion.

Proposed Module Design – See Figure 8. The pressure, temperature, and composition of the gas entering the membrane module are as follows:

Pressure	Temperature	Composition						
psia	°F	vol%						ppmv
		CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
756	432	30.8	0.6	0.76	0.44	43.7	23.3	4700

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	43.01	—
Cost of Carbon Avoided	\$/tonne CO_2	60.74	—
Capital Expenditures	\$/MWhr	60.9[1]	60.9
Operating Expenditures	\$/MWhr	25.5/52.5[2]	52.5
Cost of Electricity	\$/MWhr	113.5/121.3[3]	—

[1] Capital Cost Factor*Total Overnight Capital/MWh-net

[2] without fuel / with fuel

[3] without transportation, storage and monitoring costs / with transportation, storage and monitoring costs

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – The cost of Carbon Captured and Carbon Avoided in Table 2 are based on the supercritical, pulverized coal reference plant Case B12A, found in the "Cost and Performance Baseline for Fossil Energy Plants Volume 1a: Bituminous Coal (PC) and Natural Gas to Electricity Revision 3" report (https://www.netl.doe.gov/energy-analysis/details?id=729). The Cost of Carbon Captured excludes the costs for transportation, storage, and monitoring. The Cost of Carbon Avoided includes the costs for transportation storage, and monitoring.

The costs for the current R&D case are based on Case B5B, found in the "Cost and Performance Baseline for Fossil Energy Plants Volume 1b: Bituminous Coal (IGCC) to Electricity Revision 2b – Year Dollar Update" report (https://www.netl.doe.gov/energy-analysis/details?id=1033).

Costs for the current R&D case and reference cases were adjusted to a cost basis of June 2011 US Dollars. Costs reported in Table 2 are in June 2011 US Dollars.

Scale of Validation of Technology Used in TEA – Laboratory scale experiments were conducted to assess the membrane technology performance. The TEA is a conceptual study on a full-scale power plant using the laboratory-measured performance metrics.

technology advantages

- The capability of CMS membranes with high permeance and selectivity to operate at high temperatures eliminates the need for syngas cooling and avoids water vapor loss, which improves the energy and cost efficiency of the carbon capture process.
- The simplicity of the membrane structure lowers its manufacturing cost.
- A membrane system does not contain moving parts or involve chemical reactions, conferring some operation and maintenance (O&M) advantages.
- The membrane material has a high tolerance to acid gases and is inert to all primary syngas species.
- Membrane capture systems (particularly those based on HFM modules) have a compact footprint.

R&D challenges

- Assuring polymer performance and properties.
- Feed and permeate side pressure drops may lead to excessive energy losses.
- Cost reductions for the membrane module materials will be needed if the technology is to become economically viable.
- Durability and integrity of membrane modules (gas seals, fouling).
- Scale-up and integration issues (and operational complications from multiple vacuum pumps and valves and complicated ductwork in multiple flow banks) likely given the large number of membranes needed to service a 550-megawatt-electric (MWe) plant.

status

The project was completed in April 2022. The SUNY team developed high-permeance hollow fiber polymer membranes based on polybenzimidazole doped with inorganic polyprotic acids, and refined the formulations to attain advanced carbon molecular sieving materials reaching H_2 permeance of 1,090 GPU and H_2/CO_2 selectivity of 57 at 300°C, exceeding targeted performance and best case separation reported in the literature. Membrane reactors were fabricated and evaluated for water-gas shift (WGS) reaction, demonstrating stability with simulated syngas and robust WGS potential. Sensitivity analysis on the impact of H_2/CO_2 selectivity on a membrane capture unit in IGCC context was evaluated, showing significant COE reductions compared to a baseline IGCC case.

available reports/technical papers/presentations

"Development of Carbon Molecular Sieves Hollow Fiber Membranes based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties (Final Report)," Haiqing Lin, July 17, 2022. *https://www.osti.gov/servlets/purl/1876358*.

"Development of Carbon Molecular Sieves Hollow Fiber Membranes Based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties," presented by Haiqing Lin and Leiqing Hu, University at

Buffalo, 2021 NETL Carbon Management Research Project Review Meeting, August 16, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Lin.pdf*.

"Development of Carbon Molecular Sieves Hollow Fiber Membranes Based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties," BP1 Project Review Meeting, March 27, 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10574&filename=+Development+of+Carbon+Molecular+Sieves+Hollow+Fiber+Membranes+Based+on+Polybenzimidazole+Doped+with+Polyprotic+Acids+with+Superior+H2%2fCO2+Separation+Properties.pdf*.

"Development of Carbon Molecular Sieves Hollow Fiber Membranes Based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties," presentation by Haiqing Lin, SUNY Buffalo, 2019 NETL CCUS Integrated Project Review Meeting. Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/H-Lin-UB-SUNY-Carbon-Hollow-Fiber.pdf*.

"Development of Carbon Molecular Sieves Hollow Fiber Membranes Based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties," project kickoff meeting presentation, November 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10570&filename=Development+of+Carbon+Molecular+Sieves+Hollow+Fiber+Membranes+Based+on+Polybenzimidazole+Doped+with+Polyprotic+Acids+with+Superior+H2%2fCO2+Separation+Properties.pdf*.

"Development of Carbon Molecular Sieves Hollow Fiber Membranes Based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties," presented by Haiqing Lin, State University of New York (SUNY) at Buffalo, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA. August 2018. *https://netl.doe.gov/sites/default/files/netl-file/H-Lin-SUNY-Carbon-Molecular-Sieves.pdf*.

"Unexpectedly Strong Size-Sieving Ability in Carbonized Polybenzimidazole for Membrane H_2/CO_2 Separation," M. Omidvar, H. Nguyen, L. Huang, C.M. Doherty, A.J. Hill, C.M. Stafford, X. Feng, M.T. Swihart, and H. Lin, ACS Appl. Mater. & Interfaces, 11 (50), 47365-47372 (2019).

"Ultraselective Carbon Molecular Sieve Membranes with Unprecedented Performance for H_2/CO_2 Separation for Pre-combustion CO_2 Capture," presented by Hien Nguyen, State University of New York (SUNY) at Buffalo, 2019 Materials Research Society, Boston, MA. December 2019.

Mitchell Cement Plant Carbon Capture FEED

primary project goal

Heidelberg Materials is conducting a site-specific front-end engineering design (FEED) study for retrofitting Mitsubishi Heavy Industries America Inc. (MHIA's) solvent carbon capture technology at the state-of-the-art Mitchell, Indiana, cement plant. The proposed project will capture approximately 2,000,000 tonnes of carbon dioxide (CO_2) per year, or 95% of the CO_2 emissions from the newly renovated cement facility and will ultimately store the CO_2 in a sandstone or dolomite formation within the Illinois Basin. The primary objective of the FEED study is to evaluate the cost and performance of the overall project, including site-specific considerations for full-scale implementation.

technical goals

- Evaluate the cost and anticipated performance of retrofitting the newly modernized Mitchell plant with CO_2 capture technology, designed for capturing 95% of the plant's CO_2 emissions, including flue gases from the aux-boiler, and site-specific considerations for full-scale implementation.

technical content

The Mitchell cement plant (Figure 1), located approximately 85 miles south of Indianapolis, has been in operation producing Portland cement since the early 1900s and has recently completed a modernization resulting in a capacity expansion more than three times the plant's previous nominal capacity. The modern plant has a nominal clinker production rate of 7,000 metric tons per day (mtpd) produced by a single kiln and also includes expanded cement finish grinding capacity to accommodate the additional production. The plant design incorporates features and technologies to minimize energy consumption, enable the future utilization of alternative fuels and raw materials, and reduce the plant's greenhouse gas (GHG) footprint, all in alignment with Heidelberg Materials' "Beyond 2020" sustainability strategy. Emissions from the plant meet industry New Source Performance Standards and employ best-available control technologies, including fabric filter baghouses for particulate control, SNCR for nitrogen oxide (NO_X) control, activated carbon injection (ACI) for mercury control and dry sorbent injection (DSI) for sulfur dioxide (SO_2) control. The entire flue gas stream will be routed to the future CO_2 capture facility.

MHIA's carbon capture technology has been installed at 13 commercial facilities worldwide, with two commercial facilities in progress. The technology was used in the Petra Nova Project to capture 90% of the CO_2 in a 240-megawatt (MW) flue gas slipstream of the WA Parish Station southeast of Houston, Texas. Having recently restarted after being temporarily offline, significant operating time has been achieved. At Petra Nova, a coal-fired application, the MHIA technology was designed to capture 4,776 tonnes/day of CO_2. Based on the previous commercial

program area:

Point Source Carbon Capture

ending scale:

FEED

application:

Post-Combustion Industrial PSC

key technology:

Solvents

project focus:

FEED Study to Retrofit Cement Plant with Carbon Capture Technology

participant:

Heidelberg Materials US Inc.

project number:

FE0032222

predecessor projects:

N/A

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partners:

Eide Bailly LLP, Mammoet Branch Rosharon, Mitsubishi Heavy Industries, Sargent and Lundy, Trimeric Corporation, Mostardi Platt

start date:

08.18.2023

percent complete:

56%

experience, the large-scale facility at Petra Nova and the KS-21™ solvent testing on cement flue gas, the developmental stage of the MHIA technology applied to a cement clinkerization process is at Technology Readiness Level (TRL) 7 because the technology has been demonstrated in a relevant environment. MHIA considers all coal-based experiences to be relevant. Apart from integrating lessons learned from the Petra Nova experience, MHIA's analysis shows that there are minimal deviations from the Petra Nova design.

Figure 1: Heidelberg Materials' newly modernized Mitchell cement plant, the site for this FEED study.

TABLE 1: SOLVENT PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Proposed Module Design			
Flue Gas Flowrate	Nm^3/hr	1,372,046	
CO_2 Recovery, Purity, and Pressure	% / % / bar	95 99	150
Absorber Pressure Drop	bar	—	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Flue Gas Assumptions – Flue gas pressure, temperature and composition entering the direct contact cooler (DCC; wet basis):

		Composition						
		vol%					Ppmv	
Pressure	Temperature	CO_2	H_2O	N_2	O_2	CO	SO_x	NO_x
13.7 psia	242°F	10.50	16.6	64.5	8.3	209	15	87

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – KS-21 is an amine-based solvent that reacts selectively with CO_2.

Solvent Contaminant Resistance – KS-21 has a higher resistance to forming heat-stable salts (HSS) formed from the reactions between amine and impurities than standard MEA. Impurities still need to be removed by solvent reclaiming otherwise the CO_2 capture performance is reduced.

Solvent Foaming Tendency– Amine-based solvents react with oxygen, sulfur oxide (SO_X) and NO_X in the flue gas and result in the accumulation of HSS, which would cause foaming of the solvent.

Flue Gas Pretreatment Requirements – The KM carbon dioxide recovery (CDR) process utilizes a flue gas quencher to remove residual SO_2 and particulate matters (PM) from the incoming flue gas. These impurities can lead to an increase in the amine consumption rate through degradation.

Solvent Make-Up Requirements – The replenishment of solvent due to operational losses caused by the impact of the contaminants in the cement kiln flue gas.

Process Design Concept– Flowsheet/block flow diagram, if not included above.

technology advantages

- High-Performing Amine Solvent KS-21: The solvent is a sterically hindered amine that offers several advantages as compared to the conventional MEA process.
- Reduced steam consumption for regeneration, lower required solvent/CO_2 ratios.
- Lower solvent degradation (no corrosion inhibitor required).
- Lower solvent consumption from volatile emission losses.

R&D challenges

- Polishing unidentified trace constituents in the flue gas at the carbon capture inlet may adversely impact carbon capture performance/costs.

Status

The project team has completed the process design review and the technology has been validated. The final engineering design package is planned to be completed as scheduled by February 2025, including AACE Class 3 cost estimate. The expectation from this FEED study would be that the project is confirmed to be viable and will move ahead into the demonstration phase. Stack testing has been completed for different modes of operation and the results have been analyzed. Studies are ongoing to evaluate utilities for the carbon capture facility for the aux-boiler and combined heat and power (CHP) case, options for different water-cooling arrangements, steam and power requirements, and natural gas as fuel. The design basis document is finalized. The design criteria document has been issued for use and several engineering activities are ongoing.

available reports/technical papers/presentations

Krishnamoorthy, Sathish and Ronczka, Greg, "Mitchell Cement Plant Carbon Capture FEED," Presented at the 2024 FECM/NETL Carbon Management Project Review Meeting, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_PSCC_5_Ronczka.pdf*.

Krishnamoorthy, Sathish, "Mitchell Cement Plant Carbon Capture Feed," 2024 Preliminary Process Design Review Meeting, March 2024. *https://netl.doe.gov/projects/files/Mitchell%20Cement%20Plant%20Carbon%20Capture%20Feed.pdf*.

Krishnamoorthy, Sathish, “FEED Studies for Carbon Capture System,” 2023 Project Kickoff Meeting Presentation, November 2023.

Carbon Capture Plant Front-End Engineering Design (FEED) Study for Cement Manufacturing

primary project goal

RTI International, with CEMEX Inc., SLB (formerly Schlumberger), and KBR Inc., is performing a front-end engineering design (FEED) study for carbon dioxide (CO_2) capture from cement flue gas using RTI's non-aqueous solvent (NAS) with 95% capture efficiency.

technical goals

- Complete a FEED study for a 1,600,000 tonne/year CO_2 capture system integrated with CEMEX's Balcones cement plant (New Braunfels, TX).
- Develop an AACE Class 3 cost estimate.
- Complete a techno-economic analysis (TEA) and life cycle analysis (LCA).

technical content

RTI International, in collaboration with CEMEX Inc., SLB, and KBR Inc., is performing the FEED study for integrating RTI's NAS solvent-based CO_2 capture system with the cement plant. RTI will lead the CO_2 capture process design and manage the overall project activities. CEMEX, one of the largest cement producers in the world and the project host site provider, will evaluate the integration of the novel CO_2 capture system at its New Braunfels (Texas) Balcones cement plant, which produces approximately 2.0 Mt/year of cement with approximately 1.5 Mt/year of CO_2 emissions. The cement industry contributes approximately one-third of the total CO_2 emitted from industries. Successful deployment of CO_2 capture technology in the cement industry will be impactful in lowering climate risk.

The project's goal is to complete a FEED study of an integrated 1,600,000 tonnes CO_2/year CO_2 capture system with 95% capture efficiency at CEMEX's Balcones cement plant to better understand the capital costs and cost of CO_2 capture of the commercial-scale system with an AACE Class 3 estimate. Leveraging its large customer base and deep understanding in the global cement industry, CEMEX will conduct a business case analysis to highlight the market gaps and opportunities in producing low-carbon intensity cement in this FEED study.

program area:
Point Source Carbon Capture

ending scale:
FEED

application:
Post-Combustion Industrial PSC

key technology:
Solvents

project focus:
Non-Aqueous Solvent (NAS) for Cement Plant CO_2 Capture

participant:
Research Triangle Institute (RTI)

project number:
FE0032220

predecessor projects:
N/A

NETL project manager:
Mariah Young
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principal investigator:
Vijay Gupta
Research Triangle Institute
vgupta@rti.org

partners:
Cemex Inc.; Kellogg Brown and Root (KBR) LLC; Schlumberger Technology Corporation

start date:
04.14.2023

percent complete:
92%

Figure 1: Balcones cement plant.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	g.mol^{-1}	95-115[a]	99
Normal Boiling Point	°C	185-243[a]	200
Normal Freezing Point	°C	-6 to -24[a]	-9.15
Vapor Pressure @ 15°C	bar	0.034[a]	0.034
Manufacturing Cost for Solvent	$/kg	14	5
Working Solution			
Concentration	kg/kg	0.5-0.6	0.55
Specific Gravity (15°C/15°C)	-	0.950	0.941
Specific Heat Capacity @ STP	kJ/kg-K	2.01	2.77
Viscosity @ STP	cP	4.9	1.03
Absorption			
Pressure	bar	0.133	0.133
Temperature	°C	35-45	38
Equilibrium CO_2 Loading	mol/mol	0.426	0.426
Heat of Absorption	kJ/mol CO_2	85-90	85
Solution Viscosity	cP	2.9-13.1	2.4

Desorption			
Pressure	bar	4.0-5.0	4.4
Temperature	°C	100-120	110
Equilibrium CO_2 Loading	mol/mol	0.122-0.224	0.122
Heat of Desorption	kJ/mol CO_2	80-85	85

[a] Calculated data for different concentrations and concentrations and conditions using standard mixing rules from pure component data.

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the industrial plant baghouse should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	250°F	14.59	12.00	62.59	10.41	0.41	2	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical mechanism with fast kinetics.

Solvent Contaminant Resistance – Reaction with sulfur oxide (SO_X) forms heat stable salts. Oxidative and thermal degradation appear to be lower than aqueous solvents.

Solvent Foaming Tendency – Less foaming than aqueous amine solvents.

Flue Gas Pretreatment Requirements – Temperature adjustments and SO_X control.

Solvent Make-Up Requirements – Proprietary.

Waste Streams Generated – The waste streams generated are similar to other post-combustion CO_2 capture processes. These include the waste water stream after treatment of the condensed water from the direct contact cooler, acid wash waste, and reclaimer waste from the solvent reclamation process.

Process Design Concept – RTI's CO_2 capture process is similar to conventional solvent-based CO_2 capture systems with a direct contact cooler for flue gas pre-treatment, flue gas blower, absorber and regenerator columns and rich/lean crossover heat exchanger, trim cooler, and associated pumps. The absorber column has two intercoolers to remove the heat of absorption. The capture system also has water-wash sections and an activated carbon bed and acid wash section for emissions control. Given the non-aqueous nature of the solvent with little water to drive the thermosyphon, the reboiler is a kettle reboiler. The non-aqueous nature of the solvent also allows the regenerator to be operated at elevated pressures, approximately 4–5 bar, reducing the cost of CO_2 compression. (See Figure 2 for flowsheet/block flow diagram.)

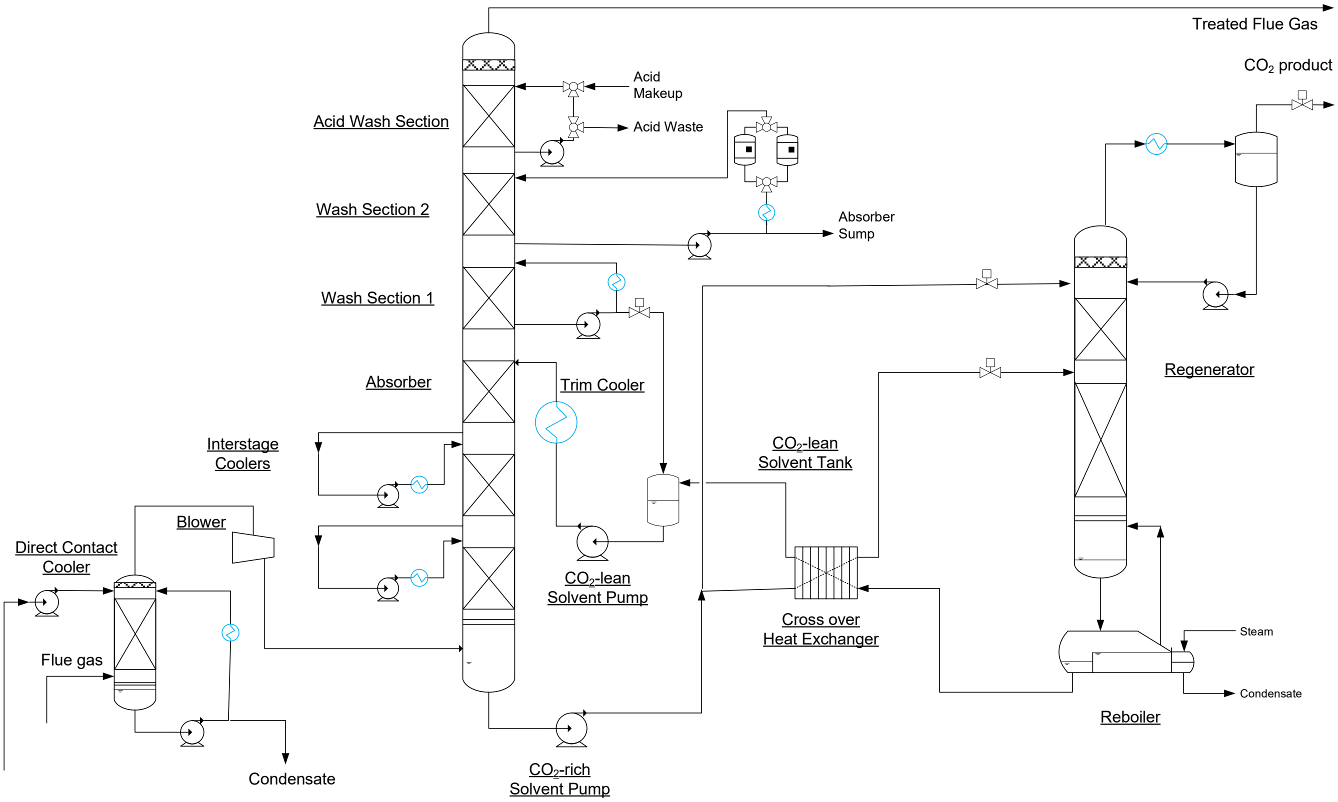

Figure 2: Schematic of the RTI's NAS process.

TABLE 2: INDUSTRIAL PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	63.2	
Cost of Carbon Avoided	\$/tonne CO_2	82.0	
Capital Expenditures	\$/tonne CO_2	25.8	
Operating Expenditures	\$/tonne CO_2	37.5	

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Calculations Basis – The numbers provided in the table are based on a TEA performed using the U.S. Department of Energy's (DOE) approach for power plants in its baseline studies (Rev 4), in which the capital expenditure (CAPEX) costs are annualized by using a DOE-designated fixed capital charge factor. The TEA was performed before the start of the project. The TEA assumed ready availability of water required for cooling, and used the electricity and natural gas prices as currently paid by CEMEX.

Scale of Validation of Technology Used in TEA – The process model used to generate the heat and materials balance was validated using pilot plant data at Tiller demonstration. The process models will be further validated using engineering-scale demonstration at TCM in the final TEA.

Qualifying Information or Assumptions – RTI used the Aspen Process Economics Analyzer to develop costs for the process equipment, and then selected installation factors of 2.34 and 1.45 to convert the purchased equipment cost to installed costs for the CO_2 capture and compression plants, respectively.

technology advantages

- Reduces the energy-consuming vaporization of water in the absorption-regeneration cycle.
- NAS has demonstrated low steam demand, 36% lower than aqueous solvents such as Econamine (30 wt.% MEA).
- Carbon dioxide is regenerated at 4.5 bar, reducing to lower costs for CO_2 compression.
- Lower corrosion rates that are two orders of magnitude lower than aqueous solvents such as Econamine (30 wt.% MEA).

R&D challenges

- Limited cooling water availability. The process uses hybrid cooling that includes available cooling water supplemented with use of condensed water from flue gas in the direct contact cooler, after treatment and air cooling.

status

RTI worked with CEMEX, Schlumberger, and KBR to develop a FEED package for CO_2 capture from the Balcones cement plant. Project and process design basis criteria have been finalized; piping and instrumentation drawings (P&IDs) have been developed and are currently under review. Current work is focused on finalizing the engineering design package and writing the final report.

available reports/technical papers/presentations

Vijay Gupta, "Carbon Capture Plant Front-End Engineering Design (FEED) Study for Cement Manufacturing," Presented at the 2024 FECM/NETL Carbon Management Project Review Meeting, Pittsburgh PA, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_PSCC_6_Gupta.pdf*.

Vijay Gupta, "Carbon Capture Plant Front-End Engineering Design (FEED) Study for Cement Manufacturing," Presented at the 2023 FECM/NETL Carbon Management Project Review Meeting, Pittsburgh PA, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC31_Gupta.pdf*.

Vijay Gupta, Carbon Capture Plant Front-End Engineering Design (FEED) Study for Cement Manufacturing, Project Kickoff Meeting, Pittsburgh PA, May 2023. *https://netl.doe.gov/projects/files/Carbon%20Capture%20Plant%20Front-End%20Engineering%20Design%20(FEED)%20Study%20for%20Cement%20Manufacturing.pdf*.

Front-End Engineering Design for Carbon Capture from Shell's Deer Park Chemical Complex

primary project goal

The project objective was to complete a front-end engineering design (FEED) study for retrofitting the Shell Chemical Complex in Deer Park, Texas, with Shell's CANSOLV post-combustion carbon dioxide (CO_2) capture technology. The capture unit was designed to capture more than 915,000 tonnes of carbon dioxide (CO_2) per year to reduce the overall facility CO_2 emissions by 95%.

technical goals

- Develop a project design basis.
- Develop an engineering design package for the carbon capture system (inside battery limits [ISBL]) and the balance-of-plant (outside battery limits [OSBL]).
- Develop a capital cost estimate consistent with an AACE Class 3 estimate.
- Prepare a comprehensive FEED study report, including the project design basis.
- Prepare a business case analysis, techno-economic analysis (TEA) and life cycle analysis (LCA).
- Prepare an environmental health and safety (EH&S) risk assessment.
- Prepare an environmental justice analysis (EJA) and economic revitalization and job creation outcomes analysis (ERJCOA).

technical content

The project is based on CANSOLV technology to capture CO_2 emitted from olefin units and a hydrotreater unit to reduce the overall facility CO_2 emissions by 95%. The CANSOLV CO_2 capture process has been proven at large scale (1 million tonnes of CO_2 per year) and operated at commercial scale for approximately 10 years. The CANSOLV solvent technology exhibits low energy consumption (less than 2.5 GJ/tonne CO_2), a low degradation rate (as low as 0.15–0.2 kg/tonne CO_2), and low emissions (less than 1 part per million [ppm] amines, 1 ppm ammonia).

The CANSOLV process generally consists of flue gas quenching/pre-scrubbing, CO_2 absorption, and solvent regeneration facilities. Hot flue gas at slightly above atmospheric pressure is routed via blowers to the pre-scrubber, which cools the flue gases to the required temperature for the capture process via direct contact with recirculating water over a bed of structured packing. Since water is condensed from the flue gas in the pre-scrubber packing, a continuous blowdown from the pre-scrubber water circulation loop is provided downstream of the pre-scrubber water cooler and is routed to wastewater treatment. Cooled flue gas is fed to the base of the CO_2 absorber, where CO_2 is captured from the flue gas by

program area:
Point Source Carbon Capture

ending scale:
FEED

application:
Post-Combustion Industrial PSC

key technology:
Solvents

project focus:
Shell CANSOLV Process at a Petrochemical Plant

participant:
Wood Environment & Infrastructure Solutions Inc.

project number:
FE0032142

predecessor projects:
N/A

NETL project manager:
Mariah Young
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principal investigator:
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Wood Environment & Infrastructure Solutions Inc.
brenda.clark2@woodplc.com

partners:
SAS Institute Inc.; Shell Chemical LP; Shell Global Solutions; Southern States Energy Board; Technip USA Corporation; University of Houston; Wood Group USA Inc.

start date:
02.15.2022

percent complete:
100%

counter-current contact with cooled lean solvent in a multi-level packed bed. The treated flue gas leaving the top of the CO_2 absorption section will pass through a water-wash section before being released to the atmosphere. The rich solvent collected in the sump of the CO_2 absorber is pumped through lean/rich exchanger(s) for heat recovery prior to feeding the rich solvent to the CO_2 stripper. The CO_2 bound in the rich solvent is liberated within the CO_2 stripper by the addition of heat, provided by low-pressure steam in the reboilers, which regenerates the solvent required for the absorption process in the CO_2 absorber. A mechanical vapor recompression (MVR) system is also included to optimize the regeneration energy requirements. The hot lean solvent from the bottom of the CO_2 stripper is cooled against cool rich solvent before partially filtering the solvent and further cooling the solvent feeding the CO_2 absorber. The process also includes a thermal reclamation unit (TRU) for the continuous reclamation of degraded amine generated within the process. The process diagram is shown in Figure 1.

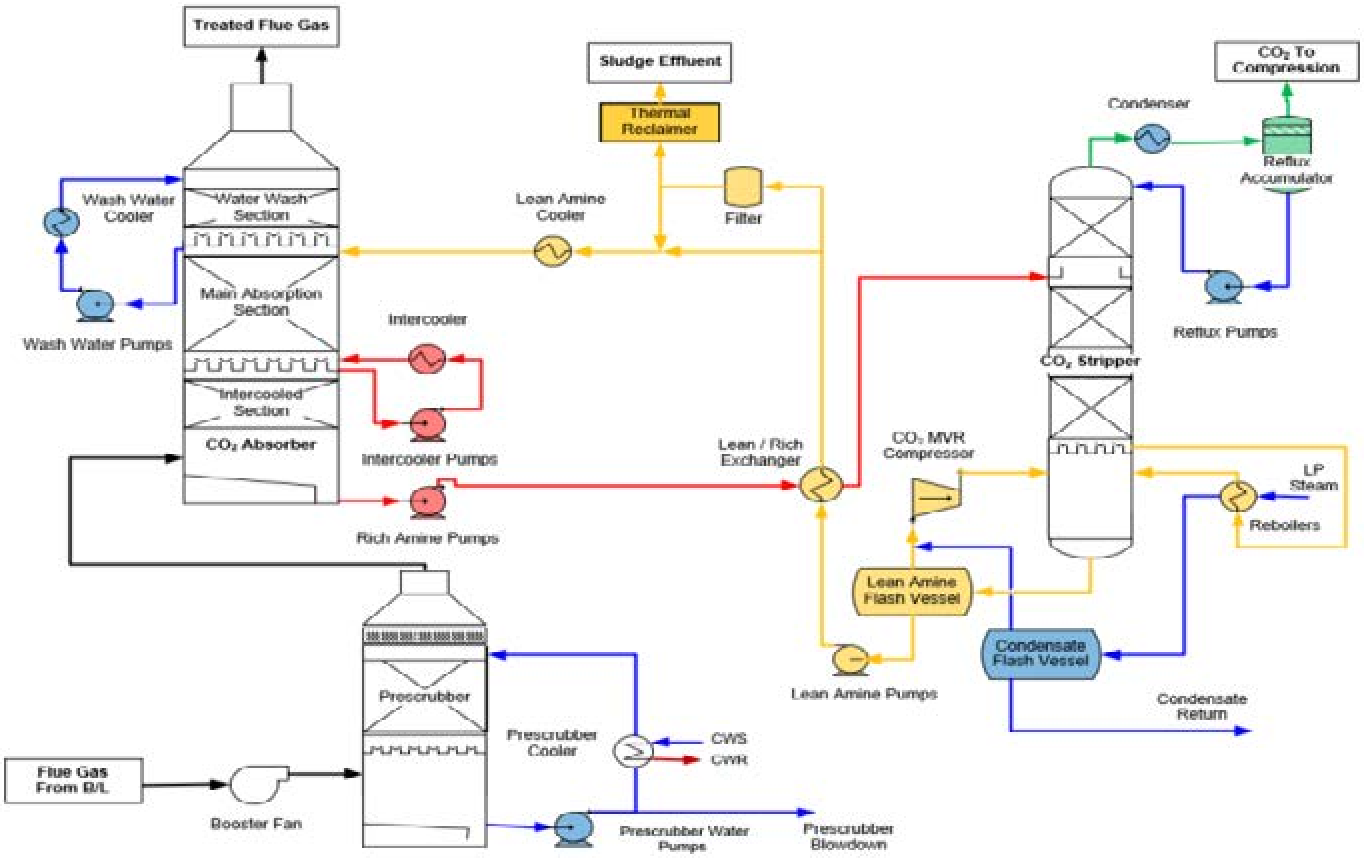

Figure 1: CANSOLV CO_2 capture process.

The carbon capture unit is designed to remove 98% of the CO_2 from 16 furnace stacks (olefins units OP3A/OP3B and hydrotreater unit HT2) to reduce the overall facility CO_2 emissions by 95%. The combined CO_2 emissions rate provided by Shell Chemicals is approximately 934,000 tonnes per year (annualized basis). The eight collection points for OP3A flue gases are combined and treated in one CO_2 absorber OP3A train. In addition, the eight collection points for OP3B and HT2 flue gases are combined and treated separately in a second CO_2 absorber OP3B train. This approach was selected in order to minimize the large ductwork required to collect the 16 furnace stack discharges that are essentially located in two separate areas.

Figure 2: Deer Park Chemical Complex — CO_2 emissions sources.

The CO_2-rich amine stream is treated and regenerated in a common amine regenerator unit located in the main ISBL area. A new cooling tower and cooling water system supplies dedicated cooling water for the project. Large cooling water lines are routed on a new pipe rack to/from the cooling tower and ISBL area. Cooling water lines were routed above grade, rather than underground, due to the large number of existing known and unknown obstructions present in an established plant. The primary steam supply for the site is currently from the adjacent Calpine facility. Calpine continues to supply steam for this project through the existing site distribution system. This project uses 1,250-pounds-per-square-inch (psi) and 650-psi steam tied into the existing site headers. Low-pressure steam is planned to come from a new steam turbine generator, which will use 1,250-psi inlet steam.

The Shell Chemical Complex in Deer Park, Texas, was the site chosen for the FEED study. The host site Shell Deer Park is located on the Houston Ship Channel near some of the nation's largest refineries and petrochemical complexes. The Houston Ship Channel provides ample opportunities for a sizable pipeline segment that could ultimately collect CO_2 and connect into the Denbury Green Pipeline.

The FEED study illustrates that it is possible to collect emissions from multiple sources at a site and remove up to 95% of the site CO_2 emissions. Following are findings and general drivers for a carbon capture project of this nature:

- When planning a carbon capture project, it is important to focus on the larger emissions sources at the site to provide maximum impact from the capital expenditure (CAPEX).
- Improved efficiencies with CO_2 absorbers should be targeted to reduce equipment sizes.
- Input from site operations and maintenance personnel is critical when routing and supporting the CO_2 collection ductwork. The ductwork should have removable sections or be routed to not interfere with operation and maintenance of the furnaces as much as practical. The large CO_2 collection ductwork can be a significant impact to project cost and routing is a major consideration. The current study was based on utilizing circular ductwork less than or equal to 12 feet in diameter and rectangular ductwork greater than 12 feet diameter. The large rectangular ductwork would be fabricated as flat panels to facilitate shipping and transported to the site for assembly at site.
- The best control method for flue gas ductwork pressure was determined to be variable speed motor drivers for the fans.

- The design requires a large quantity of cooling water with large supply/return lines. New cooling towers should be located as close as practicable to the ISBL users. Cooling water lines were routed above grade, rather than underground, due to the large number of existing known and potential unknown obstructions.
- Steam requirements are considerable, and a steam letdown turbine generator should be used to recover energy if steam is not available at the required pressure.
- Carbon dioxide compressor and stack noise abatement should be considered based on local area requirements.
- For similar future projects, consideration should be given to using one CO_2 absorber unit centrally located based on the existing facility emissions source layout. Note: This study utilized two flue gas CO_2 absorber units due to source dispersed geographic locations.

technology advantages

- Low volatile organic compound (VOC) emissions.
- More energy efficient than comparable technologies (Selexol, Rectisol, etc.).
- High capture rate (95%).

R&D challenges

- Noise abatement for CO_2 compressor.
- Availability of outside utilities and infrastructure.

status

The project was completed on August 14, 2023. The project scope included development of a project design basis that provides site characteristics, ambient conditions, fuel feedstock and flue gas characteristics, and host site environmental requirements. The design basis identified permits and environmental reviews necessary to initiate construction. All internal or corporate approvals required by the host site to initiate construction were identified. Piping and instrument diagrams (P&IDs) for ISBL/OSBL were developed and heat and material balances were issued. Development of utility usage summaries for ISBL and OSBL were issued for review. The progression of FEED study efforts ceased as of June 21, 2023, due to a fire incident at the Shell Chemical Complex. Due to early termination of the project, development of chemical usage summaries for ISBL and OSBL were not completed and the cost estimate, TEA, LCA, EH&S risk assessment, EJA and ERJCOA were not developed.

available reports/technical papers/presentations

Clark, B., "Front-End Engineering Design for Carbon Capture from Shell's Deer Park Chemical Complex." Final Technical Report, November 2023. *https://www.osti.gov/servlets/purl/2001054.*

Clark, B., "Front-End Engineering Design for Carbon Capture from Shell's Deer Park Chemical Complex." Final Presentation, July 2023.
https://netl.doe.gov/projects/files/Front%20End%20Engineering%20Design%20for%20Carbon%20Capture%20from%20Shells%20Deer%20Park%20Chemical%20Complex.pdf.

Clark, B., "Front-End Engineering Design for Carbon Capture from Shell's Deer Park Chemical Complex." Kickoff Meeting Presentation, May 2022.
https://netl.doe.gov/projects/files/Front%20End%20Engineering%20Design%20for%20Carbon%20Capture%20from%20Shells%20Deer%20Park%20Chemical%20Complex.pdf.

Combined Carbon Capture Solution on Air Liquide South Texas Steam Methane Reformer (SMR)

primary project goal

Electricore Inc. is completing a front-end engineering design (FEED) study for a commercial-scale carbon capture system to separate carbon dioxide (CO_2) emissions from Air Liquide's steam methane reformer (SMR) in South Texas. The carbon capture system is a combination of Air Liquide Cryocap^{TM} H_2 technology and BASF OASE® blue amine system.

technical goals

- Complete a FEED study for retrofitting the Air Liquide South Texas commercial-scale SMR facility with the carbon capture system.
- Perform design and optimization of the proposed plant, carbon capture calculations, mass and energy balances, technology integration, and possible process optimizations.
- Perform a techno-economic analysis (TEA) and life cycle analysis (LCA) outlining how the capture system achieves the 95% CO_2 capture rate.

technical content

Electricore Inc. and partners Air Liquide Global E&C Solutions US Inc. and Air Liquide Large Industries are completing a FEED study for a commercial-scale carbon capture system that would separate in excess of 95% of the total CO_2 emissions with 95% purity from the Air Liquide SMR H_2 production facility in Corpus Christi, TX. This plant has estimated annual CO_2 emissions of 490,000 metric tonnes at nameplate capacity. SMR produces hydrogen (H_2) from a fuel gas source (combination of natural gas and refinery fuel gas).

The retrofitted commercial-scale plant will utilize a unique combination of carbon capture technologies including Air Liquide's Cryocap^{TM} H_2 technology and BASF's OASE® blue amine-based solvent. CO_2 capture from the H_2 pressure swing adsorption (PSA) Tail Gas (~55% of overall CO_2 emissions) is done with the Cryocap^{TM} H2, integrating compression, cryogenic, and membrane "bricks" in an efficient and environmentally sustainable way, since it only requires electricity which can be supplied by renewables. CO_2 capture from the SMR flue gas stack (~45% of the overall emissions) occurs using an optimized amine setup leveraging a high level of heat integration and using the efficient BASF OASE® blue solvent. This combination minimizes the thermal energy required for the amine regeneration and uses the available heat from the SMR process without adding an extra boiler.

program area:
Point Source Carbon Capture

ending scale:
FEED

application:
Post-Combustion Industrial PSC

key technology:
Novel Concepts

project focus:
Cryogenic Carbon Capture

participant:
Electricore Inc.

project number:
FE0032181

predecessor projects:
N/A

NETL project manager:
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principal investigator:
Sara Odom
Electricore, Inc.
sara@electricore.org

partners:
Air Liquide Global E&C Solutions US Inc.; Air Liquide Large Industries

start date:
04.01.2023

percent complete:
64%

The FEED study will be conducted over 18 months and include the design and optimization of the proposed plant, carbon capture calculations, mass and energy balances, technology integration, and possible process optimizations. The project will also include several environmental, technical, and cost assessments that outline how this CCS project achieves DOE's capture targets and demonstrates zero net carbon emissions.

The results of the proposed project will provide a better understanding of the capital and operating costs of CCS, which will enable the broader implementation of these technologies in the H_2 production sector. Developing new technologies to lower the carbon footprint of existing and new H_2 production assets is critical to meeting the growing demand for clean H_2 and achieving the U.S. government's climate objectives.

Figure 1: Cryocap™ H_2 demonstration plant setup.

Figure 2: Air Liquide SMR plant host site.

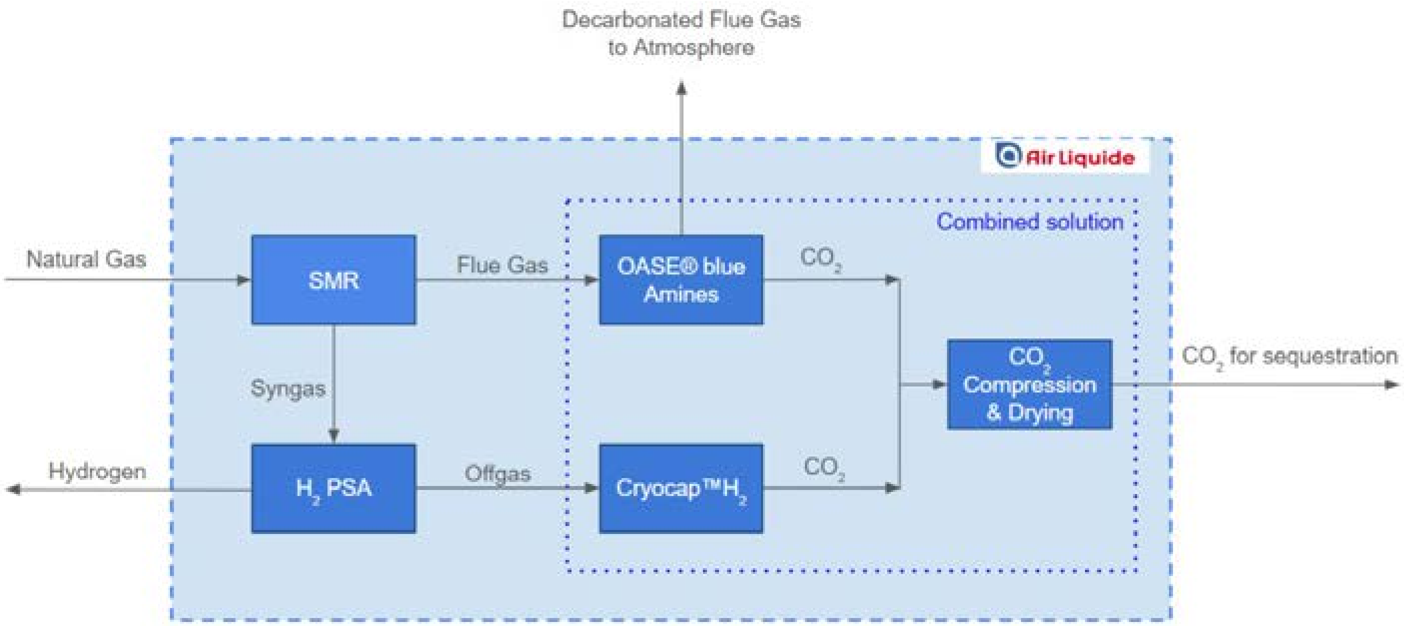

Figure 3: Process schematic.

technology advantages

- Configuration maximizes CO_2 capture rate (greater than 95%).
- Environmentally friendly technology, only requiring electricity that can be supplied with green energy.
- Minimizes the thermal energy required for regeneration and uses the available heat from the SMR process without adding an extra reboiler.

R&D challenges

- Meeting required quality of H_2.
- Meeting required quality of CO_2 for intended sequestration.
- Meeting 95% capture for total emissions.

status

The team has begun work on the FEED study, including the initial project scope and design basis. The first set of deliverables completed under this project have been submitted.

available reports/technical papers/presentations

A. Bonifacio, S. Odom, "Combined Carbon Capture Solution on Air Liquide South Texas Steam Methane Reformer", Presented at 2024 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_PSCC_6_Odom.pdf*.

A. Bonifacio, S. Odom, "Combined Carbon Capture Solution on Air Liquide South Texas Steam Methane Reformer", Presented at Kickoff Meeting, Pittsburgh, PA, June 2024. *https://netl.doe.gov/projects/files/Combined%20Carbon%20Capture%20Solution%20on%20Air%20Liquide%20South%20Texas%20Steam%20Methane%20Reformer%20(SMR).pdf*.

Carbon Capture on Air Liquide U.S. Gulf Coast Steam Methane Reformer Using the Cryocap™ Flue Gases Process

primary project goal

Dastur International Inc. and Air Liquide are performing a front-end engineering design (FEED) study for a commercial-scale carbon capture system integrated with a steam methane reformer (SMR) plant on the U.S. Gulf Coast, designed to capture approximately 900,000 metric tonnes of carbon dioxide (CO_2) per year using Air Liquide's Cryocap^{TM} Flue Gas technology combining pressure swing adsorption (PSA) and cryogenics.

technical goals

- Complete a FEED study for retrofitting a commercial-scale industrial facility with a carbon capture system that separates at least 95% of the total CO_2 emissions from an existing SMR facility on the U.S. Gulf Coast.
- Perform design and optimization of the proposed plant, carbon capture calculations, mass and energy balances, technology integration, and possible process optimizations.
- Perform environmental, technical, and cost assessments that outline how this carbon capture and storage (CCS) project achieves the U.S. Department of Energy's (DOE) goal of producing clean H2 from natural gas.

technical content

The objective of the project is to complete a FEED study to retrofit an existing commercial-scale SMR-based hydrogen plant owned and operated by Air Liquide, located along the U.S. Gulf Coast in La Porte, Texas. The host site is one of Air Liquide's largest SMR assets, and supplies hydrogen gas to the Air Liquide Gulf Coast Hydrogen System that serves refiners and petrochemical manufacturers through an existing hydrogen pipeline spanning more than 230 miles from Port Arthur, Texas, to Bay City, Texas. It is Air Liquide's longest hydrogen pipeline in the Americas. The host site produces up to roughly 120 million standard cubic feet per day (MMSCFD).

The proposed project will be based on Air Liquide's Cryocap^{TM} Flue Gas technology and will deliver a commercial-scale carbon capture system to achieve a net carbon capture efficiency of at least 95%. The captured CO_2 will be further purified to meet the CO_2 specifications for geologic storage. There will be a minimal impact on the levelized cost of hydrogen (LCOH), produced with a minimum of 99.97% purity. The FEED will be for a 900,000 metric tonnes per year CO_2 capture plant,

program area:
Point Source Carbon Capture

ending scale:
FEED

application:
Post-Combustion Industrial PSC

key technology:
Novel Concepts

project focus:
Cryogenic Capture Process for SMR

participant:
Dastur International Inc.

project number:
FE0032192

predecessor projects:
N/A

NETL project manager:
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partners:
Air Liquide Large Industries; Air Liquide Global E&C US; Air Liquide Capital; Implementation; Datsur Energy

start date:
04/01/2023

percent complete:

an adequate size to capture more than 95% of the selected SMR's annual CO_2 emissions. A Class 3 capital cost estimate for the CO_2 capture plant will also be developed. Additionally, the cost impact of carbon capture on the LCOH will also be determined.

Figure 1: Air Liquide steam methane reformer at the La Porte, Texas, host site on the Gulf Coast.

Feed Gas Pretreatment – The hot feed gas is brought to the Cryocap^{TM} unit using a blower, which is further cooled in the quench unit followed by compression and then the compressed gas is dried in the dryer units working as TSA bed before entering the PSA section.

PSA – The compressed, dehydrated gas is fed to the PSA unit, where the feed gas is split into a decarbonized stream that is vented to the atmosphere and a low-pressure CO_2-rich tail gas stream, which is compressed by the tail gas compressor before being fed to the cryogenic section for final purification.

Cryogenic Section – The cryogenic section purifies the PSA tail Gas and produces a high-purity CO_2 product ready for geologic storage.

Scale of Validation of Technology Used in TEA – The Cryocap^{TM} CO_2 capture technology has been developed by Air Liquide over the last 18 years. The figure below shows the development and progression of the technology, as well as the pilot-scale and industrial-scale CO_2 capture plants installed to test and validate the performance of the technology on various industrial feedstocks. The proposed technology is based on mature technology bricks that have already been individually deployed at a commercial scale.

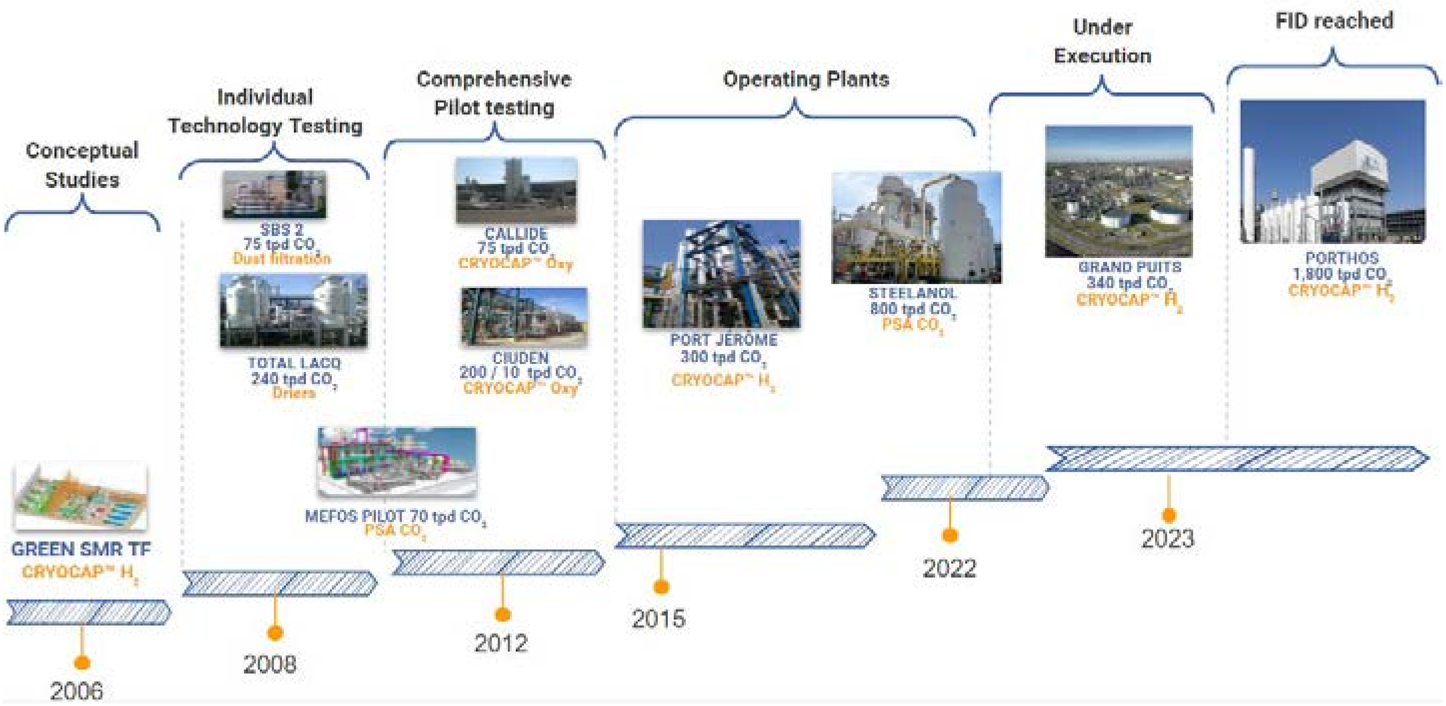

Figure 2: Cryocap^{TM}'s 18 years of legacy.

technology advantages

- Environmentally friendly technology, only requiring electricity that can be supplied with green energy.
- Does not require any large amount of heat (unlike an amine system), therefore avoiding the extra CO_2 emissions generated by a boiler burning hydrocarbons to provide the required heat in case waste heat is not available from the host site.
- Does not use any specialized chemicals subject to decomposition or formation of byproducts, such as those utilized in amine-based carbon capture systems.
- Does not require any hydrocarbons nor flammables.
- Reduces most of the direct nitrogen oxide (NO_X) emissions to the atmosphere.
- High potential for modularization, allowing for reduced construction costs/risks.
- Plot flexibility, with the possibility to locate the different modules (compression, PSA, and cryogenic separation) in different areas.
- Possibility to produce gaseous/supercritical or liquid CO_2.

R&D challenges

- Interconnection of the Cryocap^{TM} to the existing SMR to ensure a smooth operation of both plants.
- Optimizing the capital expenditures (CAPEX) and operating expenses (OPEX) of the CO_2 capture plant in order to reach the lowest CO_2 capture cost.

status

Dastur International Inc. and partner Air Liquide have begun their FEED study on retrofitting the SMR-based hydrogen plant hosted by Air Liquide at La Porte in Texas on the U.S. Gulf Coast with Air Liquide's Cryocap$^{\text{TM}}$ Flue Gas technology. The preliminary engineering package, technology maturation plan, process flow diagrams, piping and instrumentation diagrams, and the inside battery limits equipment list have been completed.

available reports/technical papers/presentations

Sarkar, Abhijit, Carbon Capture on Air Liquide U.S. Gulf Coast Steam Methane Reformer using Cryocap$^{\text{TM}}$ FG Process, 2024 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh PA, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_PSCC_6_Sarkar.pdf*.

Sarkar, Abhijit, Carbon Capture on Air Liquide U.S. Gulf Coast Steam Methane Reformer using Cryocap$^{\text{TM}}$ FG Process, 2023 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh PA, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC31_Sarkar.pdf*.

Sarkar, Abhijit, Carbon Capture on Air Liquide U.S. Gulf Coast Steam Methane Reformer using Cryocap$^{\text{TM}}$ FG Process, Kick-Off Meeting, Pittsburgh PA, July 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC31_Sarkar.pdf*.

Industrial Carbon Capture from an Existing Hot Briquetted Iron Manufacturing Facility Using the Cryocap™ FG Technology

primary project goal

The University of Illinois, partnering with Air Liquide Global E&C Solutions US Inc., Visage Energy Corporation, ArcelorMittal Texas HBI LLC, Hatch Associates Consultants Inc., and Midrex Technologies Inc., is working to complete a front-end engineering design (FEED) study to capture 95% of the carbon dioxide (CO_2) emitted through the main flue gas stack (1 million tonne CO_2/yr) at the largest Hot Briquetted Iron (HBI) plant in the world. The capture system is a pressure swing adsorption (PSA)-assisted Cryocap™ technology.

technical goals

- Complete a FEED study of an integrated cryogenic CO_2 capture system at an HBI plant that emits approximately 1 million tonne CO_2/yr.
- Develop business case analysis (BCA) outlining the current and projected volumes of the steel plant's point sources of CO_2 and the potential utilization of tax credits, including its projected revenue and duration.
- Complete a life cycle analysis (LCA) of the integrated cryogenic CO_2 capture system.

technical content

The project team is completing a FEED study to retrofit ArcelorMittal Texas HBI LLC's HBI plant in Portland, Texas with a carbon capture system. This plant, shown in Figure 1, is the largest HBI plant in the world, producing 2 million tonnes/year of MIDREX® HBI.

The design will employ Air Liquide's Cryocap FG carbon capture system combining PSA with cryogenic technologies to achieve high CO_2 capture rates with high CO_2 purity rates. Already demonstrated at facilities in France, Australia, and Spain, successful implementation of Cryocap FG will adapt carbon capture technology to an industrial application. The captured CO_2 emissions from this host site could readily be geologically stored at a location 10 miles from the project site.

program area:

Point Source Carbon Capture

ending scale:

FEED

application:

Post-Combustion Industrial PSC

key technology:

Novel Concepts

project focus:

Cryogenic Carbon Capture at HBI Plant

participant:

University of Illinois

project number:

FE0032221

predecessor projects:

N/A

NETL project manager:

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partners:

Air Liquide Global E&C Solutions US Inc., Visage Energy Corporation; ArcelorMittal Texas HBI LLC; Hatch Associates Consultants Inc.; Midrex Technologies Inc.

start date:

04.01.2023

percent complete:

15%

Figure 1: ArcelorMittal Texas HBI Facility in Portland, Texas.

Feed Gas Pretreatment—The hot feed gas is brought to the Cryocap unit using a blower, which is further cooled in the quench unit followed by compression; the compressed gas is then dried in the dryer units working as a temperature swing adsorption (TSA) bed before entering the PSA section.

PSA—The compressed, dehydrated gas is fed to the PSA unit, where the feed gas is split into a decarbonized stream that is vented to the atmosphere and a low-pressure CO_2-rich tail gas stream, which is compressed by the tail gas compressor, before being fed to the cryogenic section for final purification.

Cryogenic Section—The cryogenic section purifies the PSA tail gas and produces a high-purity CO_2 product ready for geologic storage.

Scale of Validation of Technology Used in Techno-Economic Analysis (TEA)—The Cryocap CO_2 capture technology has been developed by Air Liquide over the last 18 years. The figure below shows the development and progression of the technology, as well as the pilot-scale and industrial-scale CO_2 capture plants installed to test and validate the performance of the technology on various industrial feedstocks. The proposed technology is based on mature technology bricks that have already been individually deployed at a commercial scale.

Figure 2: Cryocap™'s 18 years of legacy.

technology advantages

- Environmentally friendly technology, only requiring electricity that can be supplied with green energy.
- Does not require any large amount of heat (unlike an amine system), therefore avoiding the extra CO_2 emissions generated by a boiler burning hydrocarbons to provide the required heat in case waste heat is not available from the host site.
- Does not use any specialized chemicals subject to decomposition or formation of byproducts, such as those utilized in amine-based carbon capture systems.
- Does not require any hydrocarbons nor flammables.
- Reduces most of the direct nitrogen oxide (NO_X) emissions to the atmosphere.
- High potential for modularization, allowing for reduced construction costs/risks.
- Plot flexibility, with the possibility to locate the different modules (compression, PSA, and cryogenic separation) in different areas.
- Possibility to produce gaseous/supercritical or liquid CO_2.

R&D challenges

- Interconnection of the Cryocap to the existing HBI plant to ensure a smooth operation of both plants.
- Optimizing the capital expenditures (CAPEX) and operating expenses (OPEX) of the CO_2 capture plant to reach the lowest CO_2 capture cost.

status

The University of Illinois and partners have begun the FEED study of the integrated cryogenic CO_2 capture system at an HBI plant that emits approximately 1 million tonnes CO_2/yr. Analyses of the capital and operating costs, business case, life cycle greenhouse gas emissions, and environmental health and safety risks are ongoing.

available reports/technical papers/presentations

Giardinella, S., "Industrial Carbon Capture from an Existing Hot Briquetted Iron Manufacturing Facility Using the Cryocap^{TM} FG Process," Presented at the 2024 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_PSCC_6_Giardinella.pdf.*

Industrial Carbon Capture from a Cement Facility Using the Cryocap™ FG Process

primary project goal

The University of Illinois and partners completed a front-end engineering design (FEED) study for the retrofit of the Holcim (U.S.) Ste. Genevieve cement manufacturing facility (largest single line kiln in the world) with a pressure swing adsorption (PSA)-assisted Cryocap™ carbon dioxide (CO_2) capture technology.

technical goals

- Complete a FEED study for retrofitting a commercial-scale industrial facility with a carbon capture system that separates 95% of the total CO_2 emissions.
- Perform a business case analysis outlining the anticipated revenue and credits if the project will be built and operated.
- Perform a techno-economic analysis (TEA) and life cycle analysis (LCA) outlining how the capture system achieves the 95% CO_2 capture rate.
- Perform an environmental justice analysis and economic revitalization and job creation outcomes analysis on the project.

technical content

The University of Illinois at Urbana-Champaign (UIUC) and partners have completed a FEED study for a commercial-scale carbon capture system that separates 95% of the total CO_2 emissions at Holcim's Ste. Genevieve cement plant in Missouri (Figure 1). The design employs Air Liquide's Cryocap technology (Figure 1) that utilizes a PSA unit to pre-concentrate the CO_2 in the feed stream combined with a cryogenic unit to produce a high-purity CO_2 product stream. The captured CO_2 will be stored at a site near the Prairie State Generating Company power plant in Illinois, within 80 miles of the CO_2 source. UIUC provides overall project management and has performed the TEA and LCA, business case analysis, and preliminary economic revitalization and job creation outcomes analysis. Air Liquide developed the design basis and the inside battery limits (ISBL) design and also performed the hazard and operability (HAZOP) study. Kiewit coordinated with Air Liquide for the ISBL design, performed the outside battery limits (OSBL) design, and led the constructability review and cost assessment. Visage Energy was responsible for the environmental justice analysis. Lastly, host site Holcim (U.S.) provided support in the form of site data and participated in engineering design decisions pertaining to host site and capture plant integration.

program area:

Point Source Carbon Capture

ending scale:

FEED

application:

Post-Combustion Industrial PSC

key technology:

Novel Concepts

project focus:

Cryogenic Carbon Capture

participant:

University of Illinois

project number:

FE0032136

predecessor projects:

N/A

NETL project manager:

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principal investigator:

Kevin O'Brien
University of Illinois
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partners:

Air Liquide Global E&C Solutions US Inc.; Visage Energy Corporation; Kiewit Engineering Group Inc.; Holcim

start date:

04.01.2022

percent complete:

100%

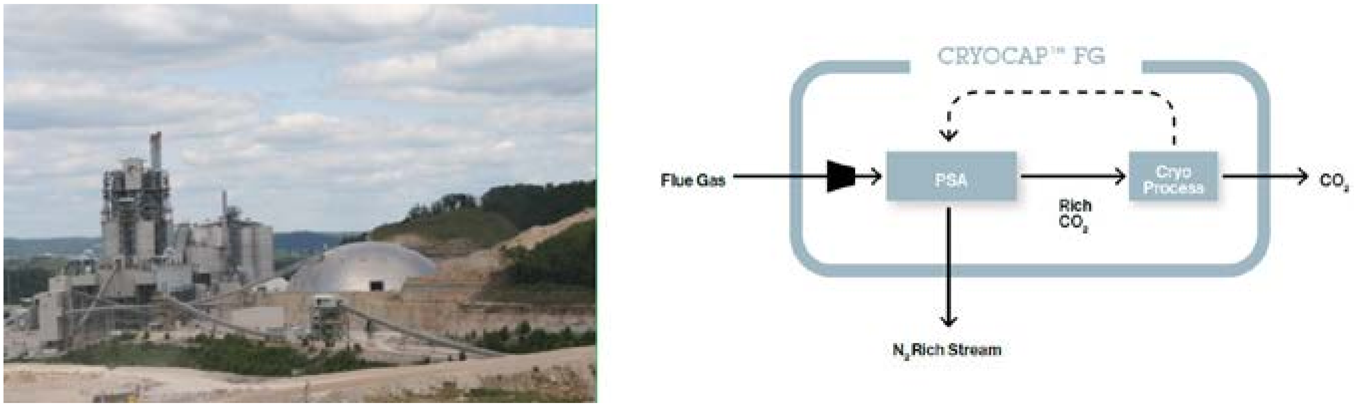

Figure 1: Holcim Ste. Genevieve cement plant and Air Liquide's Cryocap FG process.

Feed Gas Pretreatment—The hot feed gas is brought to the Cryocap unit using a blower, which is further cooled in the quench unit followed by compression; the compressed gas is then dried in the dryer units working as a temperature swing adsorption (TSA) bed before entering the PSA section.

PSA—The compressed, dehydrated gas is fed to the PSA unit, where the feed gas is split into a decarbonized stream that is vented to the atmosphere and a low-pressure CO_2-rich tail gas stream, which is compressed by the tail gas compressor, before being fed to the cryogenic section for final purification.

Cryogenic Section—The cryogenic section purifies the PSA tail gas and produces a high-purity CO_2 product ready for geologic storage.

Scale of Validation of Technology Used in Techno-Economic Analysis (TEA)—The Cryocap CO_2 capture technology has been developed by Air Liquide over the last 18 years. The figure below shows the development and progression of the technology, as well as the pilot-scale and industrial-scale CO_2 capture plants installed to test and validate the performance of the technology on various industrial feedstocks. The proposed technology is based on mature technology bricks that have already been individually deployed at a commercial scale.

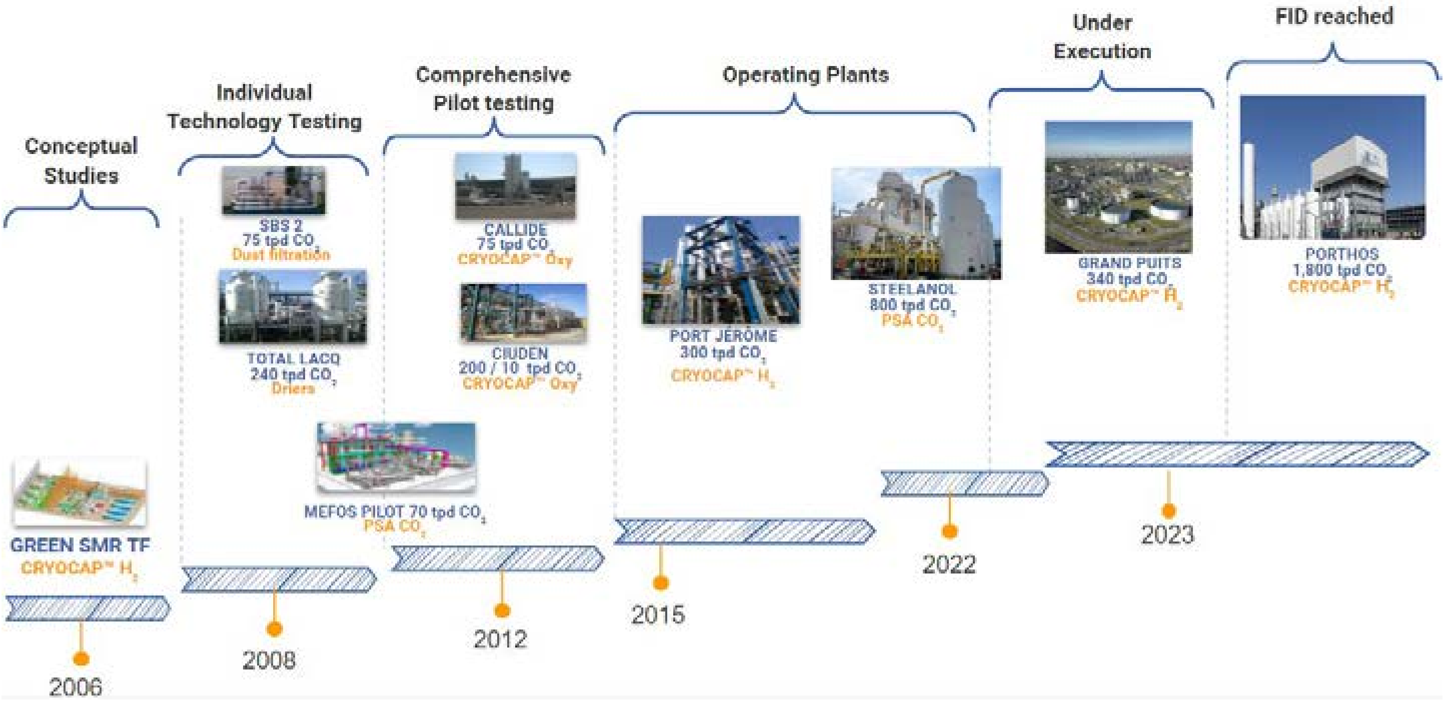

Figure 2: Cryocap's 18 years of legacy.

technology advantages

- Environmentally friendly technology, only requiring electricity that can be supplied with green energy.
- Does not require any large amount of heat (unlike an amine system), therefore avoiding the extra CO_2 emissions generated by a boiler burning hydrocarbons to provide the required heat in case waste heat is not available from the host site.
- Does not use any specialized chemicals subject to decomposition or formation of byproducts, such as those utilized in amine-based carbon capture systems.
- Does not require any hydrocarbons nor flammables.
- Reduces most of the direct nitrogen oxide (NO_X) emissions to the atmosphere.
- High potential for modularization, allowing for reduced construction costs/risks.
- Plot flexibility, with the possibility to locate the different modules (compression, PSA, and cryogenic separation) in different areas.
- Possibility to produce gaseous/supercritical or liquid CO_2.

R&D challenges

- Interconnection of the Cryocap to the existing cement plant to ensure a smooth operation of both plants.
- Optimizing the capital expenditures (CAPEX) and operating expenses (OPEX) of the CO_2 capture plant in order to reach the lowest CO_2 capture cost.

status

The project was completed on May 31, 2024. The project team established the design basis for the preliminary FEED study of the commercial-scale carbon capture project at the Holcim (U.S.) Ste. Genevieve cement manufacturing facility using the PSA system-assisted Cryocap technology. The TEA and LCA for the host site was initiated after the preliminary design was complete. The TEA, LCA, and final design of the carbon capture and storage (CCS) retrofit of the Genevieve cement plant will be included in the final report. The FEED is 100% complete.

available reports/technical papers/presentations

Salih, Hafiz, “Industrial Carbon Capture from a Cement Facility Using the Cryocap™ FG Process,” 2024 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_PSCC_6_Dreyer.pdf.*

Salih, Hafiz, “Industrial Carbon Capture from a Cement Facility Using the Cryocap™ FG Process,” 2023 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC31_Salih.pdf*.

Salih, Hafiz, “Industrial Carbon Capture from a Cement Facility Using the Cryocap™ FG Process,” 2022 Carbon Management Project Review Meeting, Pittsburgh, PA, August 2022.

O’Brien, Kevin C., “Industrial Carbon Capture from a Cement Facility Using the Cryocap™ FG Process,” Project Kickoff Meeting, Pittsburgh, PA, June 2022.

Enabling Production of Low-Carbon Emissions Steel Through CO_2 Capture from Blast Furnace Gases (BFGs)

primary project goal

Dastur International Inc. (Dastur) designed and engineered a solution to maximize decarbonization of available blast furnace gas (BFG) at Cleveland-Cliffs' 5-million-tonne/year integrated steel plant in Burns Harbor, Indiana. The project aim was to capture 2.8 million tonnes per annum (mtpa) of carbon dioxide (CO_2) emissions from the BFG by designing and integrating a BFG flow distribution system and an innovative BFG conditioning process, and by deploying a proven solvent-based carbon capture technology.

technical goals

- Design and engineer a cost-competitive, techno-economically viable, industrial-scale carbon capture system for Cleveland-Cliffs' Burns Harbor steel plant.
- Design and engineer a low-pressure water-gas shift (WGS) unit to maximize CO_2 capture from a single point source and increase the CO_2 concentration at the carbon capture unit.
- Optimize the WGS-based gas conditioning and reforming system to convert and extract hydrogen (H_2)-rich fuel and syngas from the BFG for use in existing combustion and conversion to pure H_2 in the future.
- Evaluate and validate the downstream combustion operations of converted H_2-rich fuel using computational fluid dynamics (CFD) and operating models.
- Evaluate the best possible strategy for sourcing the required steam and electricity and optimize the amount of sourced inputs for the lowest overall cost of capture, as well as the cost of CO_2 avoided (\$/tonne CO_2).
- Conduct a series of environmental and safety studies related to the project, namely solvent and CO_2 disposal/disposition studies, a wastewater treatment study, a permitting study and review, a hazard and operability (HAZOP) review, a constructability review, and an environmental health and safety (EH&S) risk assessment.
- Develop a techno-economic assessment (TEA) to determine the CO_2 capture costs.

technical content

Dastur completed the initial engineering design of a scalable carbon capture system for BFG at Burns Harbor, without impacting the competitiveness and

program area:
Point Source Carbon Capture

ending scale:
Pre-FEED

application:
Post-Combustion Industrial PSC

key technology:
Solvents

project focus:
Steel Blast Furnace Gas Conditioning Process

participant:
Dastur International Inc.

project number:
FE0031937

predecessor projects:
N/A

NETL project manager:
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principal investigator:
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Dastur International Inc.
Atanu.M@dastur.com

partners:
Cleveland-Cliffs Inc.;
ION Clean Energy Inc.;
University of Texas at Austin

start date:
10.01.2020

percent complete:
100%

techno-economics of the steelmaking process. The project was envisioned to extract low-carbon, H_2-rich fuels from the BFG for enhanced usage within the steel plant downstream operations. The goal was to engineer and design an industrial-scale CO_2 capture solution to capture 95% of the CO_2 in the BFG consisting of H_2, carbon monoxide (CO), and CO_2 before combustion, which equates to 75% of CO_2 emissions of the combusted BFG. This enables a competitive, environmentally friendly, and sustainable BFG-based process for producing low-carbon emissions steel.

The project proposed to capture 2.8 mtpa of CO_2 emissions from the available BFG at Burns Harbor by utilizing ION Clean Energy's solvent-based, state-of-the-art carbon capture technology, which has a proven carbon capture efficiency of more than 95%. To facilitate greater CO_2 capture, a compositional shift of the BFG was carried out using the WGS reactor. The initial engineering design system (Figure 1) used a WGS compositional shift of the CO and water (H_2O) mixture in the BFG to raise the CO_2 concentration, resulting in better capture efficiency and maximizing the CO_2 at a single point source of carbon capture. The BFG was also enriched to an H_2-heavy fuel gas, with H_2 content of up to 36%.

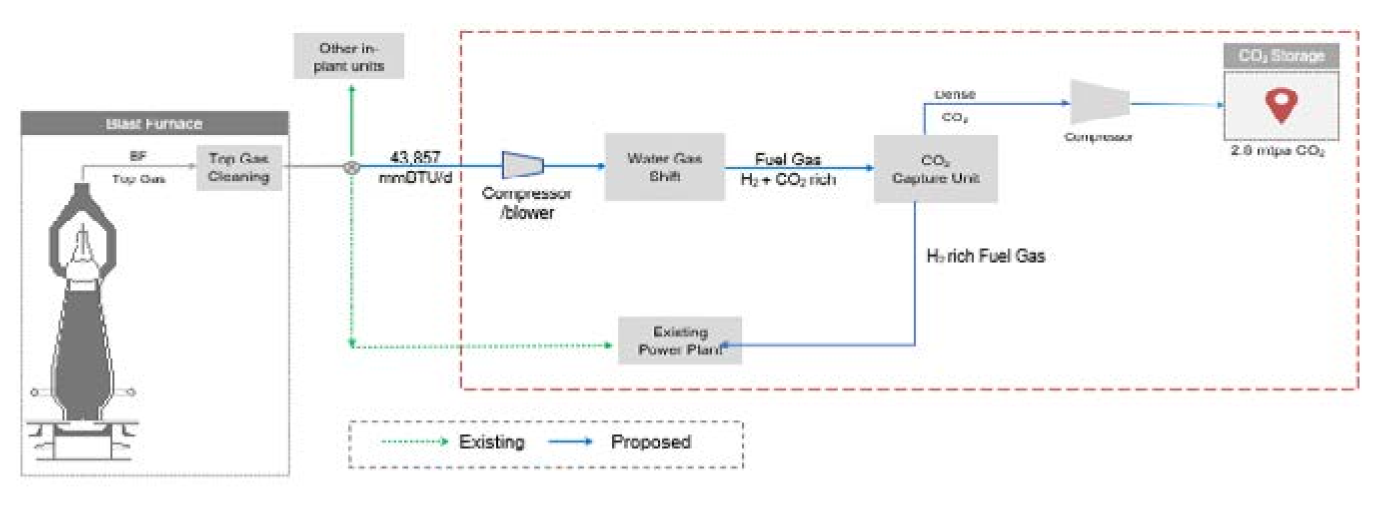

Figure 1: Flowchart of carbon capture system to be retrofitted to blast furnace.

Depending on the steam-to-dry-gas ratio required, external steam can be added to perform the shift reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$). Thereafter, the shifted gas from the WGS reactor can be passed through the carbon capture unit (CCU), which has a similar configuration to typical post-combustion amine-based CO_2 capture systems. In the CCU, the gas enters the absorber and interfaces with the carbon capture solvent, which absorbs the CO_2, leaving an H_2-rich gas. The solvent is routed to a stripper column where it is heated, releasing the captured CO_2. The captured CO_2 is compressed to pipeline pressure for transportation to locations for storage and/or utilization.

Input Gas Assumptions – BFG is considered as input. Unless noted, BFG pressure, temperature, and composition received at project area (dry basis) should be assumed as:

		Composition							
Pressure	Temperature	vol%						ppmv	
psia	°F	CH_4	CO_2	H_2	N_2	CO	Ar	SO_x	NO_x
16.7	86	0.5	22	9	45	23	0.5	-	-

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical absorption/desorption of CO_2 to/from working solution.

Flue Gas Pretreatment Requirements – As for any stable amine-based solvent.

A number of power and steam-sourcing options were investigated for this study. These include using a steam boiler, a combined heat and power system for supplementary power, and/or waste heat recovery (WHR) from coke-dry quenching at the coke oven plant. A summary of two such options that were evaluated is provided in Figure 2.

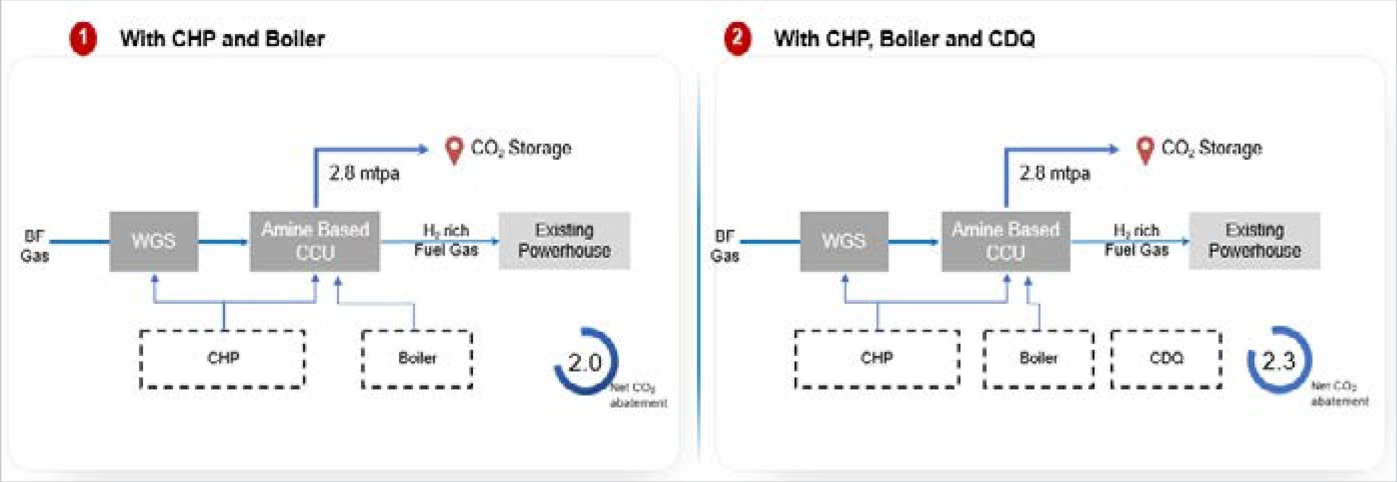

Figure 2: Steam and power-sourcing options.

The conditioned H_2-rich BFG had little to no CO_2. CFD models were used to evaluate and validate the use of multiple H_2-rich combustion stream options in the firebox of the furnace under varying operating conditions and the performance in terms of temperature distribution, flame profiles, flashback, and nitrogen oxide (NO_X) formation. The performance of the conditioned H_2-rich BFG has been evaluated as a boiler fuel against the unconditioned BFG, using CFD modelling of combustion characteristics. The base case corresponds to the current boiler operations, wherein suitable amounts of BFG, coke oven gas, natural gas, and preheated air are injected into the boiler in a non-premixed fashion. The H_2-rich cases consist of H_2-rich gas replacing the BFG in the current fuel mix, with varying H_2 content, 32% and 36% by volume, corresponding to 77% and 100% CO shift in the WGS, respectively. The developed CFD model was validated against velocity, temperature, and gas composition data obtained during a typical boiler operation.

The simulation results for the base and the H_2-rich cases were compared for the degree of combustion from the exit gas composition, velocity and temperature profiles, wall heat flux profiles, and exit NO_X flow rate. It was observed that the H_2-rich gases behave largely similar to the BFG. This similarity stems from the proximity of the calorific value of these gases and is due to the fact that the H_2-rich gas has a moderate volume fraction of H_2 (32% and 36%). Moreover, the lack of pre-mixed combustion eliminates the possibility of flashbacks in all cases. Thus, it can be concluded that the H_2-rich gas can safely replace the BFG in the boiler without the need for any design modifications to the boiler. This also enables the shifting of BFG all the way up to 100% in the WGS and therefore maximizes the CO_2 capture volume, based on the requirements.

Finally, a TEA was performed as a part of this study. Preliminary data at the onset of the project predicts an overall cost of capture of up to $60/tonne of CO_2 captured, as shown in Table 1. This cost of capture excludes the cost of transportation and storage (e.g., 10 $/tonne).

TABLE 1: INDUSTRIAL PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	NG @ 5 $/MMBtu	NG @ 3 $/MMBtu
Cost of Carbon Captured	$/tonne CO_2	60	50
Cost of Carbon Avoided	$/tonne CO_2	84	70

Capital Expenditures	\$/tonne CO_2	19	19
Operating Expenditures	\$/tonne CO_2	41	30

technology advantages

- No oxidative degradation.
- Low volatile organic compound and nitrogen emissions.
- Increased maximum train size.
- Significantly smaller absorber and ducting.
- Outlet CO_2 is supercritical (possibility for high byproduct power production/energy recovery).

R&D challenges

- Implementation of heat-integration strategies.
- Verification of long-term solvent performance in the BFG environment.
- Selection of proper CO_2 storage location. More geological surveying is required.

status

The project was completed on August 31, 2023. The design of the capture island and TEA were successfully completed. Various carbon capture options were investigated. In addition, due to a change in the project scope, several other items were investigated as part of the pre-front-end engineering design (pre-FEED), including the use of hot briquetted iron (HBI) in the blast furnace and the use of Coke dry quenching (CDQ) as part of the steam souring strategy. The specific results of the study are currently withheld as proprietary.

available reports/technical papers/presentations

Mukherjee, A. & Sarkar, A, 2023, “Enabling Production of Low Carbon Emissions Steel Through CO_2 Capture from BF Gases.” Presented at the 2023 NETL/FECM Carbon Management Research Project Review Meeting. Pittsburgh, PA.

Mukherjee, A. & Sarkar, A., 2021, “Enabling Production of Low Carbon Emissions Steel Through CO_2 Capture from Blast Furnace (BF) Gases (FE0031937).” Project Kickoff Meeting. Pittsburgh, PA. *https://netl.doe.gov/projects/plp-download.aspx?id=11014&filename=Enabling+Production+of+Low+Carbon+Emissions+Steel+through+CO2+Capture+from+Blast+Furnace+(BF)+Gases.pdf*.

Initial Engineering Design Study for Advanced CO_2 Capture from Hydrogen Production Unit at Phillips 66 Rodeo Refinery

primary project goal

Phillips 66, partnering with Worley Group Inc., performed an initial design of a commercial-scale, advanced carbon capture and storage (CCS) system that separates and stores approximately 190,000 tonnes per year net carbon dioxide (CO_2) with 90%+ carbon capture efficiency from an existing steam methane reforming (SMR) plant at the Phillips 66 Rodeo Refinery. The project goal was to analyze the technical results of three different carbon capture configurations and then select the one with the smallest predicted impact to the average levelized cost of hydrogen and produce an advanced engineering design for a commercial-scale unit based on the selected configuration.

technical goals

- Evaluate several proposed solvents for use in an absorption cycle and assess the performance of each, selecting one to utilize.
- Design and evaluate three different carbon capture configurations using a preliminary techno-economic analysis (TEA). Select the best option for minimum cost of hydrogen production.
- Design and create an initial engineering package for the selected solvent and configuration.
- Perform a final TEA on the complete system.
- Perform an environmental health and safety (EH&S) analysis.

technical content

Phillips 66, in collaboration with the Worley Group Inc., designed a commercial-scale carbon capture unit that could be installed onto the Phillips 66 Rodeo Refinery's SMR plant. The unit was designed to capture 90% of the CO_2 produced by the plant. The first part of the project consisted of a qualitative review of different commercially available technology providers' design packages. One licenser (Mitsubishi Heavy Industries [MHI]) was then chosen to proceed forward with the proposed three different carbon capture configurations.

The next phase of the project was focused on applying the selected technology to three separate CO_2 capture configurations: (1) capture from SMR flue gas and from the pressure-swing adsorption (PSA) tail gas; (2) capture from syngas before the PSA and from the SMR flue gas; and (3) capture from SMR flue gas only (post-combustion). By performing a TEA comparing these three options, the highest-

program area:
Point Source Carbon Capture

ending scale:
pre-FEED

application:
Post-Combustion Industrial PSC

key technology:
Solvents

project focus:
Solvent-Based Post-Combustion Carbon Capture System for NG Reforming

participant:
Phillips 66

project number:
FE0032109

predecessor projects:
N/A

NETL project manager:
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principal investigator:
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partners:
Worley Group Inc.

start date:
03.01.2022

percent complete:
100%

ranked CCS system configuration with the lowest impact to the levelized cost of hydrogen was selected. Consideration was also given to the project's capital cost estimate, ease of integration into the existing refinery, solvent cost and stability, and the expected reliability of the new systems. The study team further advanced engineering efforts for completing the initial engineering design for the selected CCS configuration, such that the next phase of engineering could proceed.

After selecting the most viable option, an initial engineering design package of the chosen system was created, including process flow diagrams (PFDs), piping and instrumentation diagrams (P&IDs), heat and mass balances, and equipment datasheets. Finally, a TEA was completed as a part of this study.

technology advantages

- Fast kinetics, coupled with low water content, enhances the carrying capacity and reduces regeneration energy.
- Environmentally benign (i.e., low parasitic load, near-zero emissions, and negligible solvent makeup).
- Low thermal and oxidative degradation rates result in good solvent stability, reducing solvent makeup rates and associated operating costs (OPEX).
- Low specific reboiler duty and solvent stability result in smaller capture plant equipment, reducing capital expenditure (CAPEX).

R&D challenges

- Implementation of heat-integration strategies.
- Verification of long-term solvent performance in natural gas-fired flue gas environment.

status

The project was completed on July 31, 2023. The project team selected the MHI amine-based solvent for the project. A complete draft design of the process was created, and both the TEA and EH&S studies were completed.

available reports/technical papers/presentations

N/A.

Initial Engineering and Design for CO_2 Capture from Ethanol Facilities

primary project goal

The University of North Dakota Energy and Environmental Research Center (UNDEERC) and project partners Red Trail Energy LLC (RTE), Trimeric Corporation, and KLJ have completed an initial engineering design and cost estimate for the installation of a hybrid system for the capture and compression of carbon dioxide (CO_2) generated from an ethanol production facility near Richardton, North Dakota. The hybrid capture system combined commercially available technologies of chemical absorption to process the CO_2 emissions associated with heat production (i.e., steam generated by firing a natural gas boiler) and liquefaction to process the CO_2 emissions associated with bioprocessing at RTE's ethanol plant.

technical goals

- Design a hybrid capture system using CO_2 emissions from both bioprocessing and heat production at the host site facility.
- Complete a pre-front-end engineering design (FEED) analysis of the hybrid capture system to include environmental health and safety (EH&S), a constructability report, identification of permits, and corporate approvals.
- Evaluation of performance and techno-economic analysis (TEA) in accordance with the U.S. Department of Energy's (DOE) methodology, as demonstrated by the bituminous baseline study.

technical content

The RTE carbon capture and storage (CCS) project constructed a CO_2 capture facility adjacent to the RTE ethanol plant near Richardton (Figure 1) to ultimately inject about 180,000 tonnes of CO_2 annually more than a mile below RTE property for permanent storage. The hybrid capture system combines chemical absorption to capture and compress CO_2 emissions associated with heat production (i.e., natural gas steam boilers, ~130,000 tonnes/year CO_2) and liquefaction to capture and compress CO_2 emissions associated with bioprocessing at the RTE operating ethanol facility (~180,000 tonnes/year CO_2). The resulting 310,000 tonnes/year CO_2 could then be destined for geologic injection and storage (Figure 2), or could be available for enhanced oil recovery (EOR) in the future because of the low oxygen (O_2) content of the CO_2 final product. This system was designed to use existing utilities to provide the required energy for potential hybrid capture operations. A conventional 30 wt.% monoethanolamine (MEA) absorber-stripper process was designed to capture the CO_2 from the boiler burner exhaust streams and to recover it as an essentially pure gas.

The liquefaction process was designed during the 2016–2017 study funded by DOE and the North Dakota Industrial Commission (NDIC) and conducted by

program area:
Point Source Carbon Capture

ending scale:
Pre-FEED

application:
Post-Combustion Industrial PSC

key technology:
Solvents

project focus:
Hybrid Absorption-Liquefaction CO_2 Capture System for Ethanol Production Plants

participant:
University of North Dakota Energy and Environmental Research Center (UNDEERC)

project number:
FE0031938

predecessor projects:
N/A

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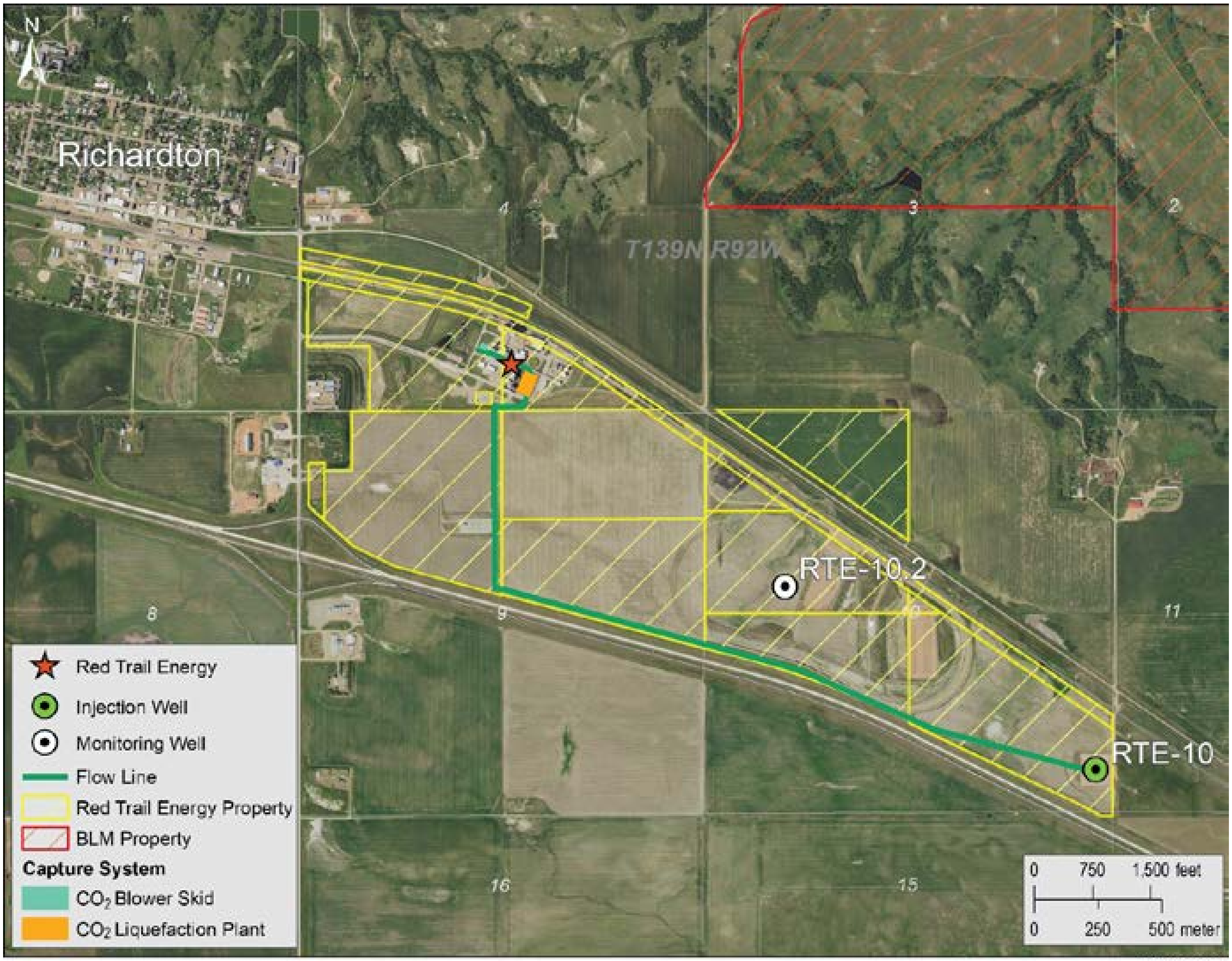
partners:
Red Trail Energy LLC; Trimeric Corporation

start date:
10.01.2020

percent complete:
100%

UNDEERC and RTE to assess the overall technical feasibility to remove CO_2 and perform subsurface injection onsite. A more rigorous design was conducted by Trimeric Corporation in 2019.



EERC KL59582.A.

Figure 1: RTE ethanol facility and CCS site.

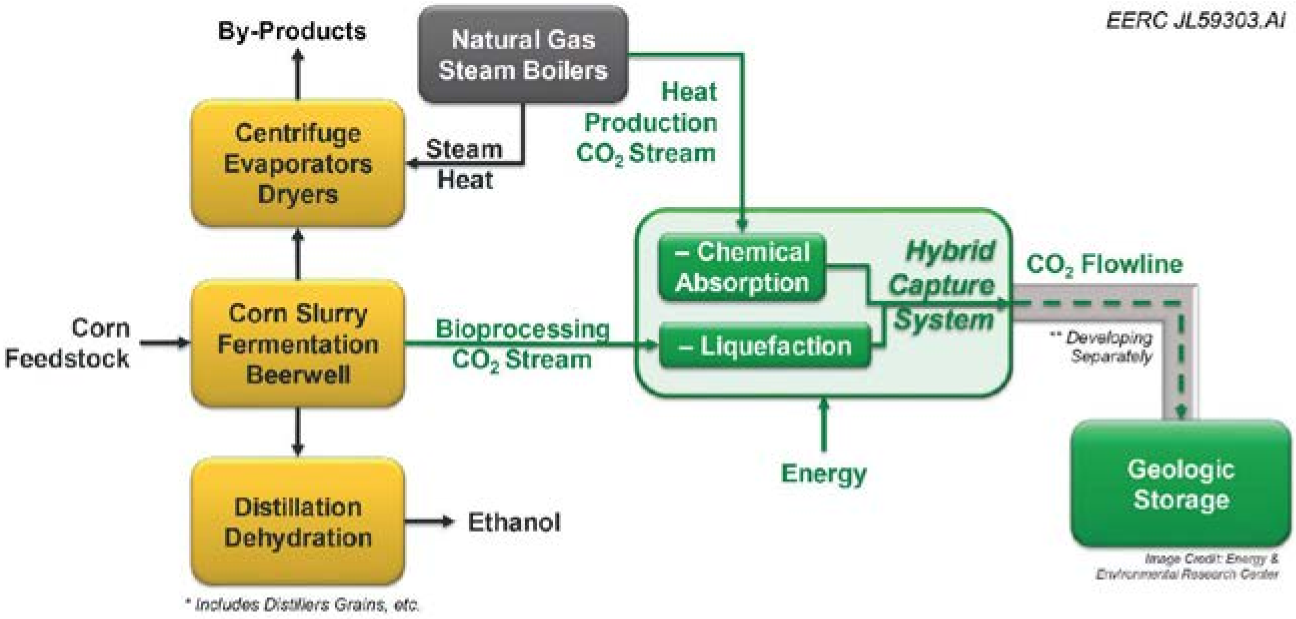


Figure 2: Block diagram of project process (*includes distillers' grains, etc.) at the RTE ethanol-CCS site; the hybrid capture system includes the required compression for geologic injection.

The hybrid capture system was designed to use RTE existing utilities to provide the required energy for potential operations. The liquefaction process captures the entirety of the nearly pure CO_2 (>99% dry) produced from RTE's fermentation process, compresses the CO_2 up to approximately 350 pounds per square inch gauge (psig), dehydrates the gas, and then liquefies it using a closed-loop ammonia refrigeration process. A conventional distillation column distills the liquid CO_2 to remove oxygen, in addition to other noncondensable gases. The chemical absorption process assumes 90% capture of the CO_2 from flue gas emitted by the two existing natural gas-fired boilers at the RTE facility, along with a potential new boiler, to provide the necessary steam for this portion of the hybrid capture process. The flue gas from the three boilers would contain a fraction of CO_2 (~4%) sufficient for capture and be fed to the absorption process, where CO_2 would be removed by employing MEA as a chemical solvent. The product CO_2 would be compressed and dehydrated, then combined with the CO_2 from the liquefaction process. The combined final CO_2 product stream could be then transported for geologic storage.

TABLE 1: SOLVENT PROCESS PARAMETERS*

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	68.0831	68.0831
Normal Boiling Point	°C	170.6	170.6
Normal Freezing Point	°C	10.4	10.4
Vapor Pressure @ 15°C	bar	<.001	<.001
Manufacturing Cost for Solvent	$/kg	—	—
Working Solution			
Concentration	kg/kg	0.3	0.3
Specific Gravity (15°C/15°C)	-	1.02	1.02
Specific Heat Capacity @ STP	kJ/kg-K	3.7	3.7
Viscosity @ STP	cP	2.5	2.5
Surface Tension @STP	dyn/cm	0.06	0.06
CO_2 Mass Transfer Rate [K_L]	m/s	—	—
CO_2 Reaction Rate	-	—	—

Thermal Conductivity	W/(m-K)	—	—
Absorption			
Pressure	bar	0	0
Temperature	°C	43	43
Equilibrium CO_2 Loading	mol/mol	2.1	2.1
Heat of Absorption	kJ/mol CO_2	1930	1930
Solution Viscosity	cP	1.8	1.8
Desorption			
Pressure	bar	0.7	0.7
Temperature	°C	115	115
Equilibrium CO_2 Loading	mol/mol	5.1	5.1
Heat of Desorption	kJ/mol CO_2	1930	1930

*Based on published commercial MEA data where available.

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

CO_2 Mass Transfer Rate – Overall liquid phase mass transfer coefficient.

CO_2 Reaction Rate – A characterization of the CO_2 absorption trend with respect to time, as complete in the range of time as possible.

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Absorption/desorption process as expected for 30 wt.% MEA.

Solvent Contaminant Resistance – Solvent is sensitive to exposure to sulfur dioxide (SO_2), halogen, nitrogen oxide (NO_X), and trace metals.

Solvent Foaming Tendency – Foaming tendency considered low for this application.

Air Feed-Gas Pretreatment Requirements – Pretreatment is not required.

Solvent Make-Up Requirements – Process preliminary design includes "bleed and feed" process for solvent makeup/reclaiming at a projected rate of 0.44 tonnes/day. Reclaiming will be conducted offsite.

Waste Streams Generated – 30 wt.% MEA to be taken offsite for reclaiming.

Process Design Concept – See description above.

Proposed Module Design – Amine-based system is typical absorption/desorption system.

TABLE 2: HYBRID PROCESS CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	55	55
Capital Expenditures	\$/tonne CO_2	30	30
Operating Expenditures	\$/tonne CO_2	25	25

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per unit of CO_2 captured.

Calculations Basis – Calculations taken from fundamental quotes for standard commercially available items. Capital cost levels utilized from the National Energy Technology Laboratory (NETL) quality guidelines for cost estimation methodology.

Scale of Validation of Technology Used in TEA – This technology is based on existing equipment and processes. Novel techniques are not being employed.

Qualifying Information or Assumptions – Assumes 97% online factor, which matches operation time of the ethanol plant. Water, natural gas, and electricity costs based on current rates at the ethanol facility.

technology advantages

- The 310,000 tonnes/year CO_2 from the fermentation process and steam boilers within the RTE ethanol facility can be stored using this technology.

R&D challenges

- Scale-up and variability of vendor estimates for operating costs of the supercritical carbon dioxide (sCO_2) loop process.

status

The project was completed on September 30, 2022. UNDEERC completed the pre-FEED design of a commercial-scale hybrid capture system. The TEA for the commercial-scale facility was also completed. The results of the initial engineering design showed the hybrid system to be technically viable, with a moderate estimated cost of \$55/tonne CO_2 captured for the hybrid system. The cradle-to-gate life cycle analysis (LCA) showed preliminary net-negative carbon emissions potential anticipated from implementing a hybrid CCS system at a commercial scale.

available reports/technical papers/presentations

Kay, J.P.; Leroux, K.M.; Laumb, J.D. Techno-Economic Assessment of Carbon Capture at the Red Trail Energy Ethanol Facility: Initial Engineering and Design for CO_2 Capture from Ethanol Facilities. Final Report for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FE0031938; EERC Publication 2022-EERC-03-12; Energy & Environmental Research Center: Grand Forks, ND, November 2022. *https://www.osti.gov/servlets/purl/1899941*.

Laumb, Jason, Leroux, Kerryanne, Kay, John, Beddoe, Christopher, and Crossland, Janet. Hybrid Capture for Net-Negative Emissions. United States: N. p., 2022. Web. doi:10.2139/ssrn.4280582. *https://www.osti.gov/servlets/purl/1960760*.

Jason Laumb, "Initial Engineering and Design for CO_2 Capture from Ethanol Facilities," NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 3, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CCUS_Laumb.pdf*.

Jason Laumb, "Initial Engineering and Design for CO_2 Capture from Ethanol Facilities," Project kickoff meeting presentation, Pittsburgh, PA, November 3, 2020. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11016&filename=Initial+Engineering+and+Design+for+CO2+Capture+from+Ethanol+Facilities.pdf*.

Engineering Design of a Linde-BASF Advanced Post-Combustion CO_2 Capture Technology at a Linde Steam Methane Reforming H_2 Plant

primary project goal

Linde Inc., in partnership with Linde Engineering and BASF, conducted an initial engineering design study (pre-front end engineering design [pre-FEED] equivalent) for a carbon dioxide (CO_2) capture plant based on Linde-BASF advanced aqueous amine-based OASE® blue technology installed at a Linde-owned, commercial-scale steam methane reforming (SMR) plant in the U.S. Gulf Coast. The plant was designed to capture 95% of the CO_2 from a flue gas stream produced by the SMR (approximately 3,700 tonnes of CO_2 per day or 1.4 million tonnes of CO_2 per year).

technical goals

- Complete an initial engineering design for the CO_2 capture plant, including the outside the battery limits (OSBL) equipment.
- Conduct a safety and environment analysis.
- Estimate total installed capital expense (CAPEX) and operating expense (OPEX).
- Conduct a techno-economic analysis (TEA) for CO_2 capture from the combustion flue gas of a commercial-scale SMR plant; develop accurate costs of CO_2 capture from SMR plants at the full commercial-scale.

technical content

The scope of the pre-FEED included process units for pre-conditioning of the supply flue gas, the CO_2 capture plant island, the CO_2 compression train, the OSBL equipment, and any necessary components for connection to and integration with the SMR plant. The design employs Linde-BASF post-combustion CO_2 capture technology that utilizes BASF's aqueous amine-based OASE blue solvent. Linde-BASF's technology has been tested on both coal-fired and natural gas combined cycle (NGCC)-derived flue gas under a wide range of flue gas compositions and impurities, in which the solvent has exhibited favorable kinetics and reduced steam energy requirements, enhanced chemical and thermal stability compared to monoethanolamine (MEA) with greater resistance to oxygen and flue gas impurities, and a lower solvent circulation rate. In addition to the benefits the OASE blue solvent provides, the key Linde-BASF process features include: (1) high-capacity structured packing, enabling a reduced absorber diameter and capital costs; (2) regeneration of CO_2 at elevated pressure (up to 2.5 bara) that reduces downstream compression costs and compressor CAPEX; (3) optimized heat

program area:
Point Source Carbon Capture

ending scale:
Pre-FEED

application:
Post-Combustion Industrial PSC

key technology:
Solvents

project focus:
Linde-BASF Amine Solvent-Based Technology Retrofit to SMR Plant

participant:
Linde Inc.

project number:
FE0031943

predecessor projects:
N/A

NETL project manager:
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principal investigator:
Minish Shah
Linde Inc.
minish.shah@linde.com

partners:
Linde Engineering America;
Linde Engineering Dresden;
BASF

start date:
10.01.2020

percent complete:
100%

transfer in the rich/lean exchanger and heat recovery through use of the stripper interstage heater; and (4) a fast-response reboiler design. The basic process schematic is shown in Figure 1.

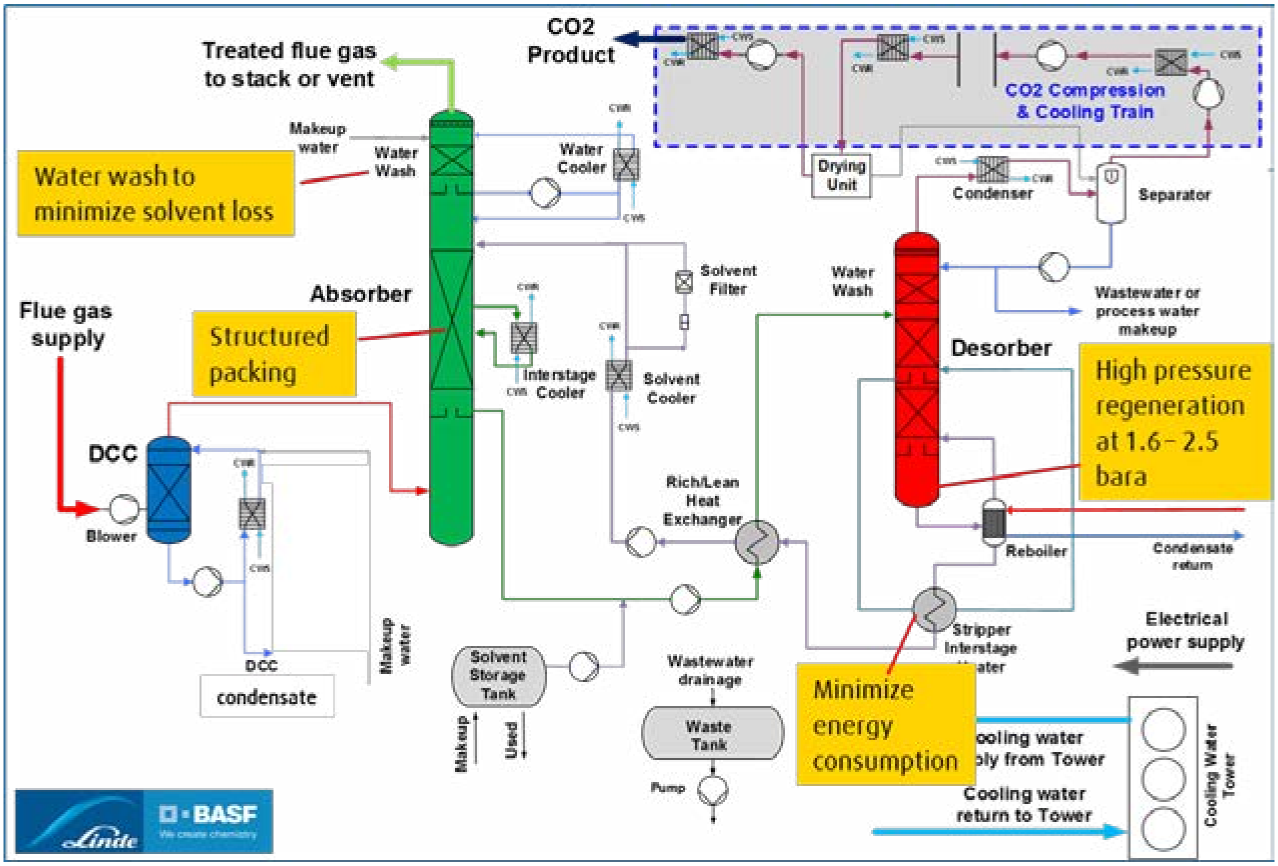

Figure 1: Process design with key features highlighted.

The use of an interstage cooler in the absorber suppresses a significant solvent temperature rise within the column from the exothermic chemisorption of CO_2 and increases the equilibrium content of CO_2 in the rich solution leaving the absorber. This increases the cyclic capacity of the solvent and decreases the reboiler duty. A water wash section is included above the absorber bed to promote a reduction of the solvent losses. A semi-CO_2 lean solvent reheater is added to the stripper column that heats up solvent taken from an intermediate position in the stripper using hot CO_2-lean solvent from the bottom of the stripper column reboiler and then injects this re-heated semi-CO_2 lean solvent back into the stripper column at an optimal packing location. Overall, this process modification significantly reduces the steam consumption per metric tonne of CO_2 captured.

The plant concept involves a single-train design with one direct contact cooler (DCC), an amine unit with one absorber and one regenerator, and one CO_2 compression train (Figure 2). Steam is available from the existing SMR to cover a portion of steam needed for the amine unit and an auxiliary boiler is included as part of the OSBL scope to generate additional steam needed for the amine unit. A reclaiming unit separates degradation products from the solvent, resulting in a reduction in amine consumption.

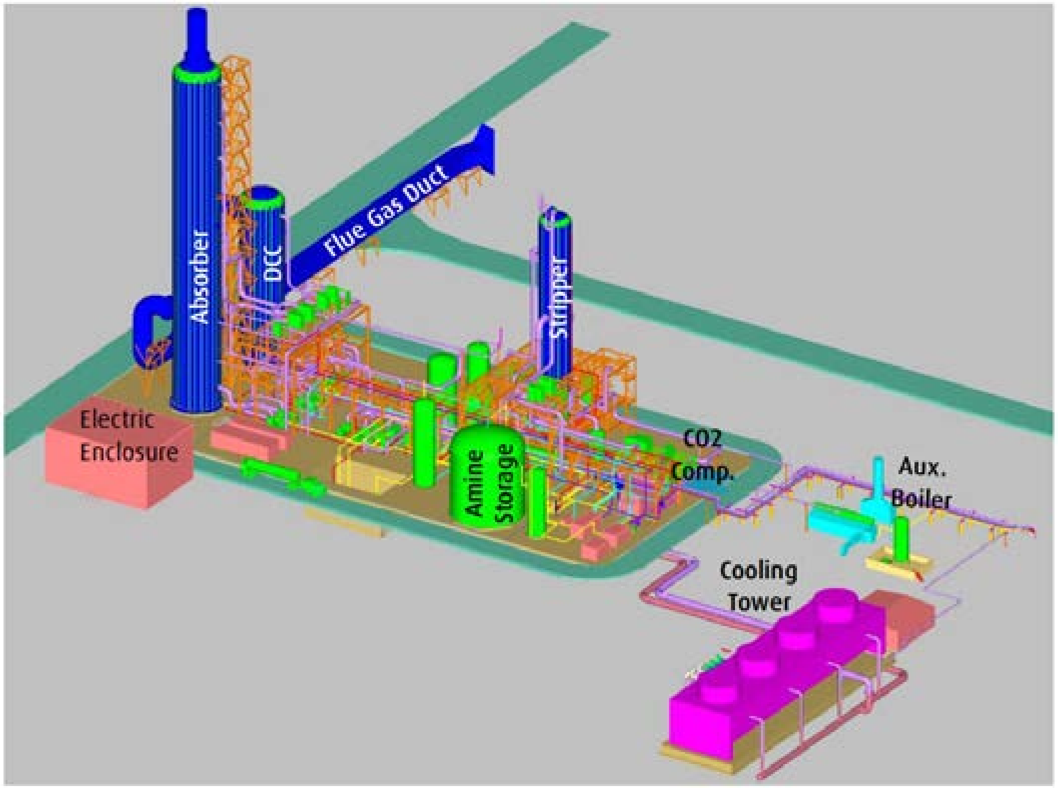

Figure 2: 3D layout of CO_2 capture plant.

The host site selected is one of the largest SMR plants in Linde's Gulf Coast fleet and is located in close proximity to saline aquifers and depleted oil and gas fields. Linde also owns and operates a large hydrogen (H_2) pipeline network and an H_2 storage cavern in the Gulf Coast.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	proprietary	proprietary
Normal Boiling Point	°C	proprietary	proprietary
Normal Freezing Point	°C	-5 to 25	-5 to 25
Vapor Pressure @ 15°C	bar	proprietary	proprietary
Manufacturing Cost for Solvent	$/kg	—	—
Working Solution			
Concentration	kg/kg	proprietary	proprietary
Specific Gravity (15°C/15°C)	-	1.0–1.2	1.0–1.2
Specific Heat Capacity @ STP	kJ/kg-K	proprietary	proprietary
Viscosity @ STP	cP	1.5–7.0	1.5–7.0
Absorption			
Pressure	bar	1.0	0.9–1.1
Temperature	°C	30–70	30–60
Equilibrium CO_2 Loading	mol/mol	proprietary	proprietary
Heat of Absorption	kJ/mol CO_2	proprietary	proprietary
Solution Viscosity	cP	—	—
Desorption			
Pressure	bar	1.6–2.5	1.6–2.5

Temperature	°C	proprietary		proprietary
Equilibrium CO_2 Loading	mol/mol	proprietary		proprietary
Heat of Desorption	kJ/mol CO_2	proprietary		proprietary
Proposed Module Design		*(for equipment developers)*		
Flue Gas Flowrate	kg/hr		—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	—	—	—
Absorber Pressure Drop	bar		—	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$		—	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.22 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical H_2 plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 22% (dry basis). Therefore, the partial pressure of CO_2 is roughly 0.22 atm or 0.217 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

		Composition				
		vol%			ppmv	
Pressure	**Temperature**	**CO_2**	**H_2O**	**$N_2 + O_2 + Ar$**	**SO_x**	**NO_x**
14.7 psia	320°F	18.00	20.00	62.00	trace	trace

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – CO_2 in the flue gas chemically binds to the OASE blue aqueous amine-based solvent via an exothermic absorption step and this chemical bond is broken in the endothermic desorption step via heat provided by steam in the reboiler of the regenerator column, generating pure CO_2.

Solvent Contaminant Resistance – The OASE blue solvent is highly resistant against many contaminants in the flue gas, as shown in both parametric and long-term continuous tests (see Electric Power Research Institute [EPRI] report[1] for additional information).

Solvent Foaming Tendency – Anti-foaming injection is included in the design as a safeguard. During the previous pilot plant tests, foaming was not an issue.

Flue Gas Pretreatment Requirements – Any trace sulfur oxide (SO_X) must be kept below 5 ppm (by volume). Since SMR flue gas contains SO_X at much lower concentrations than 5 ppm, no pretreatment is required.

Solvent Make-Up Requirements – The OASE blue solvent make-up rate is determined by the sum of the amine losses from the absorber column, the stripper column, filtration unit, and amine reclaimer unit, and the rate of solvent degradation during operation over time. Low make-up rates were observed during long-term testing well below an operationally manageable threshold. Low solvent makeup is expected at scale when processing flue gas from H_2 plants due to minimal aerosol.

Waste Streams Generated – Waste water from amine reclaimer unit will be sent to a treatment plant. A small amount of solid waste is removed using an activated carbon filter and mechanical cartridge filter that are replaced at regular intervals.

Proposed Module Design – See Figure 1 for process configuration and Figure 2 for 3D layout. Single-train arrangement is used for large equipment, such as DCC, absorber, and stripper. Modularization is used where practical (e.g., pumps, heat exchangers, small vessels).

TABLE 2: INDUSTRIAL PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	$/tonne CO_2	69	64
Cost of Carbon Avoided	$/tonne CO_2	75	70
Capital Expenditures	$/tonne CO_2	23	20
Operating Expenditures	$/tonne CO_2	46	44

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured. [Includes fixed O&M as well as transportation and storage costs.]

Calculations Basis – NETL's methodology as outlined in reference [1] and financial parameters from reference [2].

[1] Theis, Joel, 'Quality Guidelines for Energy Systems Studies – Cost Estimation Methodology for NETL Assessment of Power Plant Performance', NETL-PUB-22580, February 2021.

[2] Lewis, Eric et al., 'Comparison of Commercial, State-of-the Art, Fossil-Based Hydrogen Production Technologies', DOE/NETL-2022/3241, April 12, 2022.

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[1] BASF-Linde Post Combustion Carbon Capture Pilot Plant at the National Carbon Capture Center, 2016 Test Campaign Results, EPRI, February 2017.

Scale of Validation of Technology Used in TEA – Technology Readiness Level (TRL) 6.

Qualifying Information or Assumptions – Project life—30 years; financing – 38% debt and 62% equity; Natural Gas $4.42/MMBtu; Power $0.0717/kWh; CO_2 transportation and storage costs excluded.

technology advantages

- The Linde-BASF partnership covers the entire value chain (solvent development and manufacturing; process technology; engineering, procurement and construction [EPC]; and operations).
- The SMR host site offers favorable access to geological storage or use in enhanced oil recovery with low CO_2 injection costs.
- Higher CO_2 content in SMR flue gas (approximately 20 vol% dry basis) compared to coal- and natural gas-fired flue gases enables a smaller absorber diameter needed to achieve greater than 95% capture at ambient pressure, leading to lower CAPEX.
- Aerosol concentrations in SMR flue gas stream are much lower than in coal or NGCC flue gas streams.
- The CO_2 produced by the Linde-BASF post-combustion capture plant will contain greater than 99.9 mol% (dry) CO_2 and to as low as 10 parts per million by volume (ppmv) oxygen (O_2).

R&D challenges

- CAPEX for transportation and site installation of large size equipment and piping.

status

The project was completed on September 30, 2022. An initial comprehensive engineering design study was completed for retrofitting an existing SMR H_2 plant with Linde-BASF advanced post-combustion capture technology, based on a single-train design. A constructability review was conducted to review the preliminary plant layout and determine changes required for ease of plant construction and operation. A hazards and operability study (HAZOP) was conducted to qualitatively identify and address potential safety, health, environmental and asset risks. A TEA was completed, with the total cost of CO_2 capture estimated at $71/tonne for the base case scenario (assuming a low financing cost and 30-year project life).

available reports/technical papers/presentations

M. Shah, "Engineering Design of a Linde-BASF Advanced Post-Combustion CO_2 Capture Technology at a Linde Steam Methane Reforming H_2 Plant," Final Project Report, November 2022. *https://www.osti.gov/servlets/purl/1898038*.

M. Shah and B. McClean, "Engineering Design of a Linde-BASF Advanced Post-Combustion CO_2 Capture Technology at a Linde Steam Methane Reforming H_2 Plant," Closeout Meeting Presentation, September 2022.

M. Shah, "Engineering Design of a Linde-BASF Amine Technology for H_2 Plant Flue Gas," presented at the 2022 Carbon Management Project Review Meeting, August 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_PSC15_Shah.pdf*.

M. Shah, "Engineering Design of a Linde-BASF Advanced Post-Combustion CO_2 Capture Technology at a Linde Steam Methane Reforming H_2 Plant" presented at the Carbon Management and Natural Gas & Oil Research Project Review Meeting, Virtual Session – Integrated CCUS Projects and FEED Studies, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CCUS_Shah.pdf*.

M. Shah, et.al., "Engineering Design of a Linde-BASF Advanced Post-Combustion CO_2 Capture Technology at a Linde Steam Methane Reforming H_2 Plant" Kickoff meeting presentation, November 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11025&filename=Engineering+Design+of+a+Linde+BASF+Advanced+Post+Combustion+CO2+Capture+Technology+at+a+Linde+Steam+Methane+Reforming+H2+Plant.pdf*.

Engineering Study of Svante's Solid Sorbent Post-Combustion CO_2 Capture Technology at a Linde Steam Methane Reforming H_2 Plant

primary project goal

Linde Inc., with partners Linde Engineering Americas, Linde Engineering Dresden, and Svante Inc., conducted an initial engineering design of a commercial-scale carbon capture plant utilizing the Svante VeloxoTherm™ solid adsorbent carbon dioxide (CO_2) capture technology installed at an existing Linde-owned steam methane reforming (SMR) hydrogen (H_2) production plant in the U.S. Gulf Coast. The overall system was designed to capture approximately 1,435,000 tonnes/year net CO_2 with at least 90% reduction in direct CO_2 emissions (92% CO_2 capture efficiency) while producing "blue" H_2 with 99.97% purity from natural gas.

technical goals

- Develop an initial engineering design and overall process design package for the CO_2 capture process integrated with the H_2 production facility.
- Prepare a capital cost estimate, including the cost of capture in $/tonne CO_2 net captured from the H_2 plant, and the levelized cost of hydrogen.
- Generate a commercial-scale TEA of this post-combustion capture technology.
- Complete a Technology Maturation Plan (TMP) and Environment, Health, and Safety (EH&S) Risk Assessment.

technical content

The VeloxoTherm process developed by Svante is comprised of a rapid cycle thermal swing adsorption (TSA) process that uses a patented architecture of structured adsorbent beds (SABs) and a novel process design and embodiment to capture CO_2 from industrial and natural gas-fired flue gas streams. SABs possess unique physical and transport properties, which serve to greatly improve the performance of gas separation, enabling fast cycle times and small equipment sizes that deliver attractive capture economics. Figure 1 shows the rotary adsorption machine (RAM) design at the core of the technology. Svante uses solid adsorbents that have very high surface-to-volume ratios, instead of liquid chemicals (amines or potassium hydroxide), to capture CO_2. A new class of advanced sorbent materials, metal organic framework (MOF)-based sorbent material (CALF-20), has been developed by Svante and lab-tested under U.S. Department of Energy (DOE) Cooperative Agreement No. DE-FE0031732, and is being field-tested (since January 2021) at a cement plant in Vancouver, Canada.

program area:
Point Source Carbon Capture

ending scale:
pre-FEED

application:
Post-Combustion Industrial PSC

key technology:
Sorbents

project focus:
Svante VeloxoTherm™ CO_2 Capture Technology Applied to SMR Plant

participant:
Linde Inc.

project number:
FE0032113

predecessor projects:
N/A

NETL project manager:
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principal investigator:
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partners:
Linde Engineering Americas; Linde Engineering; Dresden GmbH; Svante Inc.

start date:
10.01.2021

percent complete:
100%

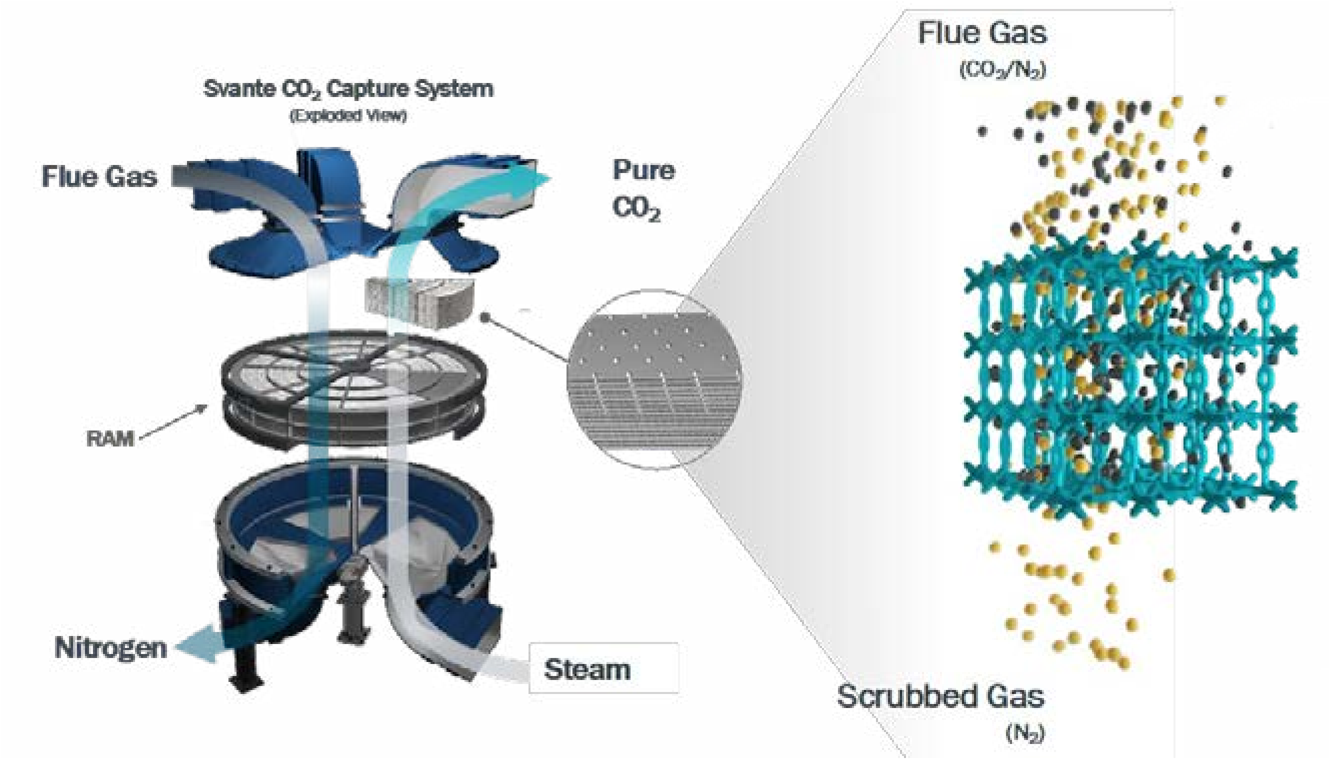

Figure 1: VeloxoTherm™ rotary adsorption machine.

CALF-20 was also tested at Chevron's oil field on a pilot scale under DOE Cooperative Agreement DE-FE0031944. This sorbent material exhibits unique resistance to sulfur oxide (SO_X), nitrogen oxide (NO_X), and oxygen impurities, as well as moisture swing. The team leveraged the learnings from the testing in the design of the capture plant in this study.

The project team developed an engineering design package comprised of the core technology; process units inside the battery limits (ISBL) of the CO_2 capture unit, such as flue gas conditioning and CO_2 product purification; and balance of plant components outside the battery limits (OSBL) of the capture plant.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Measured Performance
Weight/Bed Volume	kg/m^3	350-380
Bulk Density	kg/m^3	N/A
Adsorbent Particle Diameter	mm	0.31-0.35
Particle Void Fraction	m^3/m^3	N/A
Wetted sheet area/bed volume	m^2/m^3	2300-2500
Solid Heat Capacity @ STP	kJ/kg-K	1.4-1.6
Thermal Conductivity	W/m°K	0.25-0.35
Adsorption		
Pressure	Bar (a)	1–1.1
Temperature	°C	50
Equilibrium Loading – 20% CO_2	g mol CO_2/kg	1.7-1.9
Heat of Adsorption	kJ/mol CO_2	35-38
Desorption		
Pressure	Bar(a)	0.8-1.0
Temperature	°C	120-140

Equilibrium CO_2 Loading	g mol CO_2/kg	0.3-0.4		
Heat of Desorption	kJ/mol CO_2	35-38		
Proposed Module Design		*(for equipment developers)*		
Flow Arrangement/Operation		Rapid Cycle rotary valve moving bed		
Flue Gas Flowrate	kg/hr		596,000	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90-95	95	150

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the laminated sorbent composite sheet area/filter bed volume.

Equilibrium Loading – The basis for CO_2 loadings is mass of dry, sorbent measured with 20% CO_2 in N_2 mixture without moisture.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Physisorption.

Sorbent Contaminant Resistance – High oxidation resistance below 50 ppm SO_X and NO_X.

Sorbent Attrition and Thermal/Hydrothermal Stability – Very stable under direct steam regeneration.

Flue Gas Pretreatment Requirements – Conventional direct contact cooler.

Sorbent Make-Up Requirements – Three- to five-year year lifetime without bed replacement.

Waste Streams Generated – No chemicals in VeloxoTherm exhaust gas, water treatment system blowdown.

Process Design Concept – Flowsheet/block flow diagram shown in Figure 2.

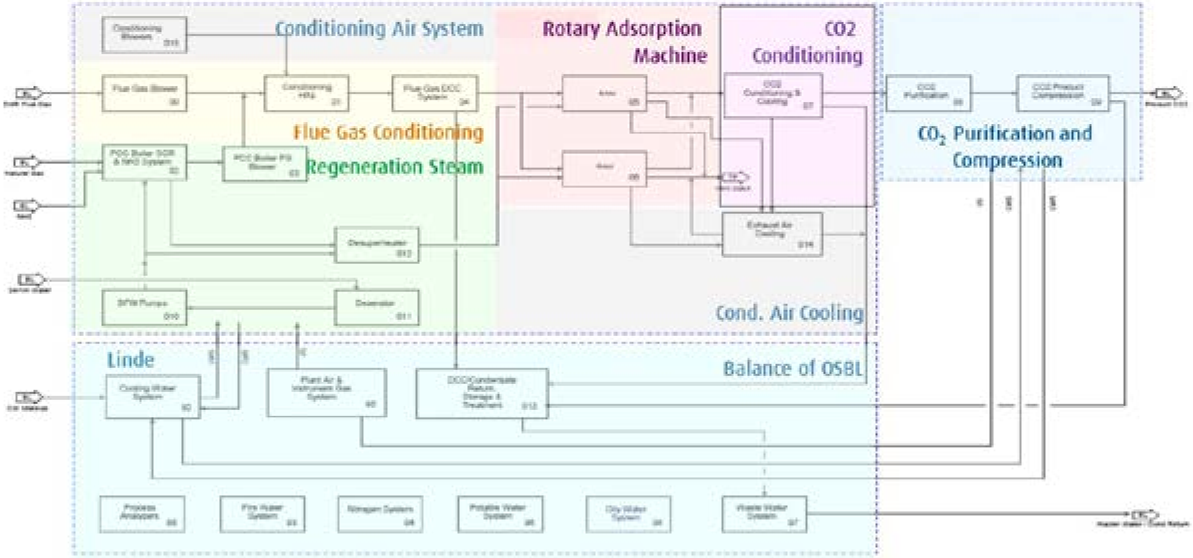

Figure 2: Flowsheet/block flow diagram of process.

TABLE 2: INDUSTRIAL CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	78	65
Cost of Carbon Avoided	\$/tonne CO_2	92	77
Capital Expenditures	\$/TPD	140,000 to 150,000	110,000 to 120,000
Operating Expenditures	\$/tonne CO_2	38	34

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided (scope 1 only) is site specific depending on the source of electricity and steam.

Capital Expenditures – Projected capital expenditures in dollars per tonne per day of capacity.

Operating Expenditures – Projected operating expenditures in dollars per unit of tonne of CO_2 produced including all the utilities and consumables and adsorbent bed replacement.

Scale of Validation of Technology Used in TEA – The technology numbers were validated for use in the preliminary TEA from pilot-scale data.

technology advantages

- Intrinsically lower regeneration energy compared to absorption.
- No secondary degradation products detected due to stability of the structured absorbent bed, reducing environmental impact to a minimum (emissions to air).
- Regeneration takes place at vacuum, allowing the use of low-value/waste heat for regeneration not usable by current state-of-the-art technologies.
- Rapid adsorption kinetics enables tight load-following and fast stop/start.

R&D challenges

- Integration with operations at the SMR plant.
- Engineering-scale testing and analysis.
- Further improvements needed for financial viability based on 45Q tax credits.

status

The project was completed on November 30, 2023. Linde Inc. has completed the site-specific engineering study for retrofitting Linde's SMR H_2 plant with Svante's PCC technology. The system was designed to reduce approximately 90% CO_2 emissions with a capture capacity of approximately 1.435 MM tonnes/yr. With energy optimization and simpler CO_2 purification, CCS cost was projected to be $88/tonne CO_2 for a 30-year project life and debt plus equity financing. For a 15-year project life and equity-only financing, the CCS cost is estimated to be $124/tonne CO_2. The study determined that further technology improvements are needed for financial viability based on 45Q tax credits.

available reports/technical papers/presentations

Minish Shah, "Engineering Study of Svante's Solid Sorbent CO_2 Capture Technology at a Linde's SMR H_2 Plant," Final Technical Report, Pittsburgh, PA, December 2023. *https://www.osti.gov/servlets/purl/2279036/*.

Minish Shah, "Engineering Study of Svante's Solid Sorbent CO_2 Capture Technology at a Linde's SMR H_2 Plant," 2023 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, September 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC1_Shah.pdf*.

Nicki Stuckert, Bill Chesser – "SMR CO_2 Capture Engineering Study." Project kickoff meeting presentation [WebEx meeting] October 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11229&filename=Engineering+Study+of+Svante%27s+Solid+Sorbent+Post-Combustion+CO2+Capture+Technology+at+a+Linde+Steam+Methane+Reforming+H2+Plant.pdf*.

LafargeHolcim CO_2MENT Colorado Project

primary project goal

Electricore Inc., with partners Kiewit Engineering Group and Svante, Inc., completed a pre-front-end engineering design (pre-FEED) study for installation of Svante's VeloxoTherm^{TM} carbon capture technology at the LafargeHolcim cement plant in Florence, Colorado.

technical goals

- Complete feasibility studies (FEL-1 and FEL-2) to estimate facility performance.
- Complete a hazard and operability (HAZOP) analysis to assess project risks and develop a risk management plan.
- Perform an energy cost optimization study and a complete techno-economic analysis (TEA).
- Complete a pre-front-end engineering design (pre-FEED) study.
- Complete the overall project execution strategy of carbon capture facility and surrounding infrastructure (pipeline connections, storage site facilities, renewable, etc.).

technical content

The VeloxoTherm process developed by Svante is comprised of a rapid-cycle temperature swing adsorption (RC-TSA) process that uses a patented architecture of structured adsorbent beds (SABs) and a novel process design and embodiment to capture carbon dioxide (CO_2) from industrial and natural gas-fired flue gas streams. SABs possess unique physical and transport properties that serve to improve the performance of gas separation, enabling fast cycle times and small equipment sizes. Figure 1 shows the commercial-scale rotary adsorption machine (RAM) design at the core of the technology. Svante uses metal organic framework (MOF) solid adsorbents that have very high surface-to-volume ratios, instead of liquid chemicals (amines or potassium hydroxide), to capture CO_2. This new class of advanced sorbent materials, MOF CALF-20, has been developed by Svante and lab-tested under U.S. Department of Energy (DOE) Cooperative Agreement No. DE-FE0031732 and field-tested at a LafargeHolcim cement plant in Vancouver, Canada. The material was used at an engineering-scale demonstration plant of about 25 tonnes per day (TPD) using natural gas post-combustion flue gases in Chevron's Kern River, California, under DOE Cooperative Agreement No. DE-FE0031944. The MOF CALF-20 sorbent material exhibits unique resistance to sulfur oxide (SO_X), nitrogen oxide (NO_X), and oxygen impurities, as well as moisture swing. The sorbent process parameters used for the FEL-1 and FEL-2 design studies are reported in Table1.

This pre-FEED study was for the integration of the VeloxoTherm adsorption system at LafargeHolcim's cement plant in Florence, Colorado, slated to capture

program area:
Point Source Carbon Capture

ending scale:
Pre-FEED

application:
Post-Combustion Industrial PSC

key technology:
Sorbents

project focus:
Rapid-Cycle Temperature-Swing Adsorption Process at Cement Plant

participant:
Electricore Inc.

project number:
FE0031942

predecessor projects:
N/A

NETL project manager:
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principal investigator:
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partners:
Svante Inc.; Kiewit Engineering Group; LafargeHolcim; Oxy Low Carbon Ventures; Total S.A.

start date:
11.09.2020

percent complete:
100%

more than 1.5 million tonnes of CO_2 per year. This location is near several ideal CO_2 storage locations, including a local saline aquifer and the Sheep Mountain natural CO_2 reservoir. The planned plant would utilize a solar energy and battery storage system power purchase agreement to provide supplemental energy to the plant, ensuring smooth operation without interruption during hours of high demand.

By completing the feasibility engineering study (FEL-2) for a fit-for-purpose design at the LafargeHolcim cement plant, this technology represents a step forward for large-scale deployment of carbon capture and storage. Given the near-term potential for increased 45Q tax credit pricing to $85/tonne and voluntary emissions credits, the business analysis pointed to significant potential realizable economic value for the project, as shown in Table 2.

Figure 1: Svante VeloxoTherm™ commercial-scale rotary adsorption machine.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m³	350-380	350-380
Bulk Density	kg/m³	NA	NA
Average Particle Diameter	mm	0.31-0.35	0.31-0.35
Particle Void Fraction	m³/m³	NA	NA
Packing Density	m²/m³	2300-2500	2300-2500
Solid Heat Capacity @ STP	kJ/kg-K	1.4-1.6	1.4-1.6
Thermal Conductivity	W/(m-K)	0.25-0.35	0.25-0.35
Manufacturing Cost for Sorbent	$/kg	30-35	20-25
Adsorption			
Pressure	bar	1-1.1	1-1.1
Temperature	°C	50	50
Equilibrium Loading (20% CO_2)	g mol CO_2/kg	1.7-1.9	1.7-1.9
Heat of Adsorption	kJ/mol CO_2	35-38	35-38
Desorption			
Pressure	bar	0.8-1.0	0.8-1.0
Temperature	°C	120-140	120-140
Equilibrium CO_2 Loading (20% CO2)	g mol CO_2/kg	0.3-0.4	0.3-0.4
Heat of Desorption	kJ/mol CO_2	35-38	35-38
Proposed Module Design			
Flow Arrangement/Operation	—	Rapid cycle rotary valves moving bed	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90-95 95	150

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the laminated sorbent composite sheet area/filter bed volume.

Equilibrium Loading – The basis for CO_2 loadings is mass of dry sorbent measured with 20% CO_2 in nitrogen (N_2) mixture without moisture.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Physisorption.

Sorbent Contaminant Resistance – High oxidation resistance below 50 parts per million (ppm) SO_X and NO_X.

Sorbent Attrition and Thermal/Hydrothermal Stability – Very stable under direct steam regeneration.

Flue Gas Pretreatment Requirements – Conventional Direct Contact Cooler (DCC).

Sorbent Make-Up Requirements – Three- to five-year lifetime without bed replacement.

Waste Streams Generated – No chemicals in depleted N_2 and typical cooling water blow-down.

TABLE 2: CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	50	30
Cost of Carbon Avoided	\$/tonne CO_2	Site specific	Site specific
Capital Expenditures	\$/TPD	70,000-80,000	60,000-70,000
Operating Expenditures	\$/tonnes CO_2	26-28	20-23
Cost of Electricity	\$/tonnes CO_2	12-18	12-18

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided is site specific depending on the source of electricity and steam.

Capital Expenditures – Projected capital expenditures in dollars per tonne per day of capacity for the capture unit.

Operating Expenditures – Projected operating expenditures in dollars per unit of tonne of CO_2 produced including filter bed replacement and compression cost.

Cost of Electricity – Projected cost of electricity per unit of tonne of CO_2 produced for a range of price of electricity of 3.5–6 cents per kWh.

Scale of Validation of Technology Used in TEA – The technology numbers were validated for use in the TEA from pilot-scale data.

technology advantages

- Svante's technology has the potential to enable a 50% reduction in capital costs of the capture unit compared to first-generation approaches.
- Novel technology replaces large chemical solvent towers (conventional approach) with a single piece of compact equipment, significantly reducing capital expenses (CAPEX).
- Advanced sorbent material exhibits sharper temperature and pressure swing absorption and desorption, which allows for lower energy loads and faster kinetic rates.
- The proprietary material also exhibits unique resistance to SO_X and NO_X, oxygen impurities, and moisture swings.

R&D challenges

- Technology scaling of filter manufacturing to commercial scale.
- Technology scaling of RAM to commercial-scale.
- Cost and schedule uncertainties of project execution.
- Access to water, carbon-free electricity, and storage options.

status

The project was completed on September 30, 2022. Both FEL-1 and FEL-2 were completed successfully. The project team also completed a HAZOP study, an EH&S risk assessment, and a TEA. For the pre-FEED study, more than 10,000 different financial scenarios were successfully simulated. Several key areas for action/further improvement were identified and set aside for the future full FEED study phase of the project. The overall results show that the CO_2 capture system takes up roughly 13% of the total plant cost (equivalent of $36,800/TPD). If the 45Q tax credits are increased to $85/tonne, the project results show that there are several scenarios in which the project becomes profitable.

available reports/technical papers/presentations

Jelen, D., 2023, "LH CO_2MENT Colorado Project." Final Report. DE-FE0031942. *https://www.osti.gov/servlets/purl/1907123*.

Letourneau, C. & Jelen, D., "LafargeHolcim CO_2MENT Colorado Project." 2021 NETL Carbon Management and Oil & Gas Research Project Review Meeting. Pittsburgh, PA. August 3, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CCUS_Jelen.pdf*.

Electricore, Inc., 2020, "LH CO_2MENT Colorado Project." Project Kickoff Meeting. U.S. Department of Energy: National Energy Technology Laboratory (DOE/NETL). FE0031942. Pittsburgh, PA. November 9, 2020. *https://netl.doe.gov/projects/plp-download.aspx?id=11020&filename=LH+CO2MENT+Colorado+Project.pdf*.

Engineering Design of a Polaris Membrane CO_2 Capture System at a Cement Plant

primary project goal

Membrane Technology and Research Inc. (MTR) partnered with Sargent & Lundy (S&L) and CEMEX to perform an initial engineering design of a full-scale Polaris membrane carbon dioxide (CO_2) capture system (approximately 1 million metric tonnes of CO_2 per day) applied to the CEMEX Balcones cement plant located in New Braunfels, Texas. This study produced estimates of the cost and performance of a first-of-its-kind industrial membrane capture plant at a cement plant. CEMEX is the owner and operator of the cement plant and provided plant-specific information on the Balcones facility for this study.

technical goals

- Complete an initial engineering design of the MTR membrane CO_2 capture process applied to the CEMEX Balcones cement plant located in New Braunfels, Texas.
- Complete a detailed engineering study for the membrane capture plant, including the process design with appropriate engineering drawings, system cost, constructability plan, and project execution schedule.
- Complete a techno-economic analysis (TEA) and Technology Maturation Plan (TMP) for the membrane capture system at the cement plant prepared per U.S. Department of Energy (DOE) guidelines.
- Complete an EH&S risk assessment and an environmental and permit review for the CEMEX host site.

technical content

MTR has developed a composite membrane called Polaris that sets the standard for post-combustion capture membranes. With an average CO_2 permeance of 1,000 gas permeation units (GPU) and a CO_2/N_2 pure-gas selectivity of 50, Polaris was a step-change improvement over typical commercial CO_2-selective membranes used for natural gas treatment. This improvement is illustrated in Figure 1, where membrane performance is compared in the form of a trade-off plot of CO_2/N_2 selectivity versus CO_2 permeance. Better membranes will have properties that move up and to the right on this plot.

In addition to showcasing the benefits of Polaris over conventional membranes, Figure 1 also shows some of the more recent improvements in the performance of Polaris membranes. A second-generation (Gen-2) version of the membrane has been scaled-up to pilot production, and an advanced Polaris membrane has been produced at the lab scale. These developments demonstrate that the Polaris membrane technology continues to improve.

program area:
Point Source Carbon Capture

ending scale:
Pre-FEED

application:
Post-Combustion Industrial PSC

key technology:
Membranes

project focus:
Membrane Technology for Cement Plant

participant:
Membrane Technology and Research Inc.

project number:
FE0031949

predecessor projects:
N/A

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partners:
CEMEX Inc.; Sargent & Lundy

start date:
10.01.2020

percent complete:
100%

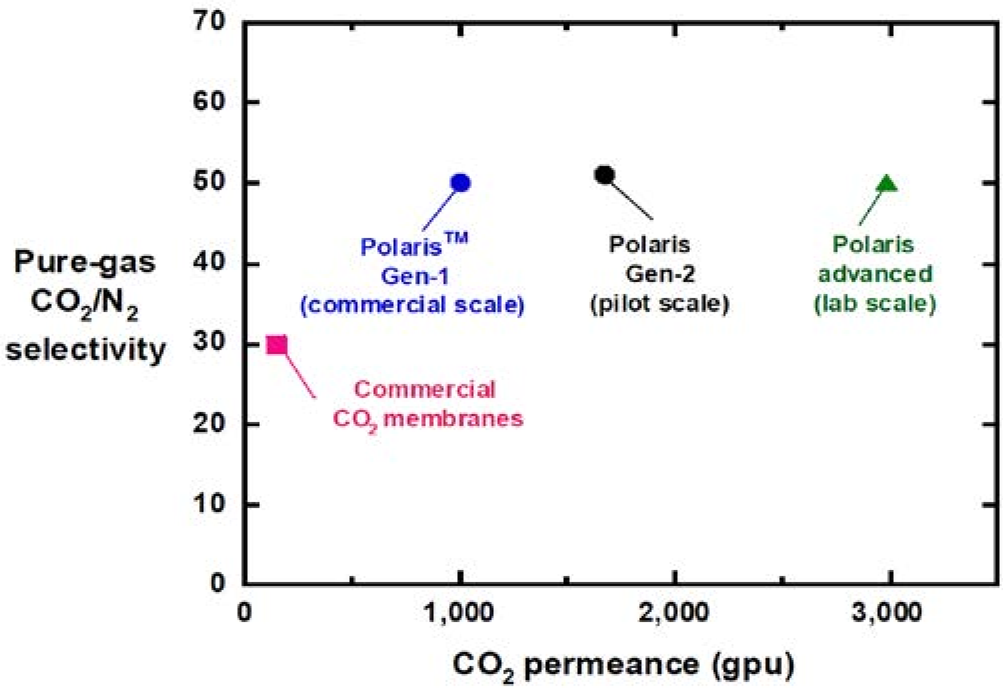

Figure 1: A CO_2/N_2 trade-off plot showing data for several generations of MTR Polaris, compared with the properties of the standard commercial natural gas membrane. Data are pure-gas values at room temperature.

The Gen-1 Polaris membranes were initially validated in field testing at the National Carbon Capture Center (NCCC), and are now being used in commercial natural gas and refinery membrane applications. The Gen-2 Polaris membrane has also been tested at the NCCC, and will be used on an upcoming engineering-scale field test at the Technology Centre Mongstad (TCM) in Norway (under DE-FE0031591).

As part of earlier MTR development programs, a low-pressure-drop membrane module specifically designed for a flue gas CO_2 capture process was created. Figure 2a shows a photo of a prototype of this planar module during testing at the NCCC. The simple straight-flow path of the new module results in a pressure-drop that is four-times lower than that measured for a conventional spiral-wound module (Figure 2b). This reduced pressure drop represents savings in fan power, equivalent to about 20–25 kWe/tonne of CO_2 capture. In addition to testing at the NCCC, the performance benefits of the planar module were verified in testing at Babcock & Wilcox and the University of Texas at Austin in separate DOE programs.

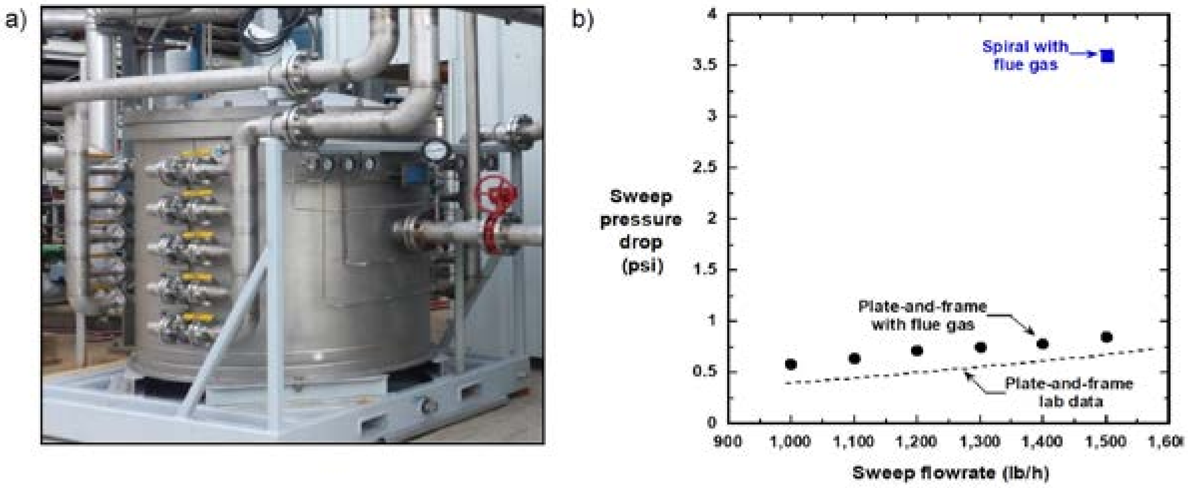

Figure 2: (a) Photo of the prototype planar module during testing at the NCCC, and (b) measured pressure drop in the module, compared to a conventional spiral-wound module.

The prototype planar module shown in Figure 2 was built in a local shop with machined parts and a stainless steel pressure vessel, resulting in relatively high costs. With the concept proven, the project team transitioned to a lower-cost design based on reusable aluminum or single-use injection-molded, fiber-reinforced thermoplastics to form a stackable membrane module complete with integrated internal gas distribution. These low-cost modules are being used at the TCM field test in Norway. The low-cost planar modules are designed to fit one on top of the other to create a module stack. The module stack has a pressure rating, which eliminated the need for a stainless steel pressure vessel and further reduced skid costs. A drawing of a standard shipping container housing several stacks is shown in Figure 3. This containerized skid will be assembled in the fabrication shop with all the required feed, residue, and permeate piping. The completed module skids were positioned onsite by a crane. Several skids can be stacked on top of one another to minimize capture plant footprint. The containerized skid is the final unit building block for the MTR membrane CO_2 capture process.

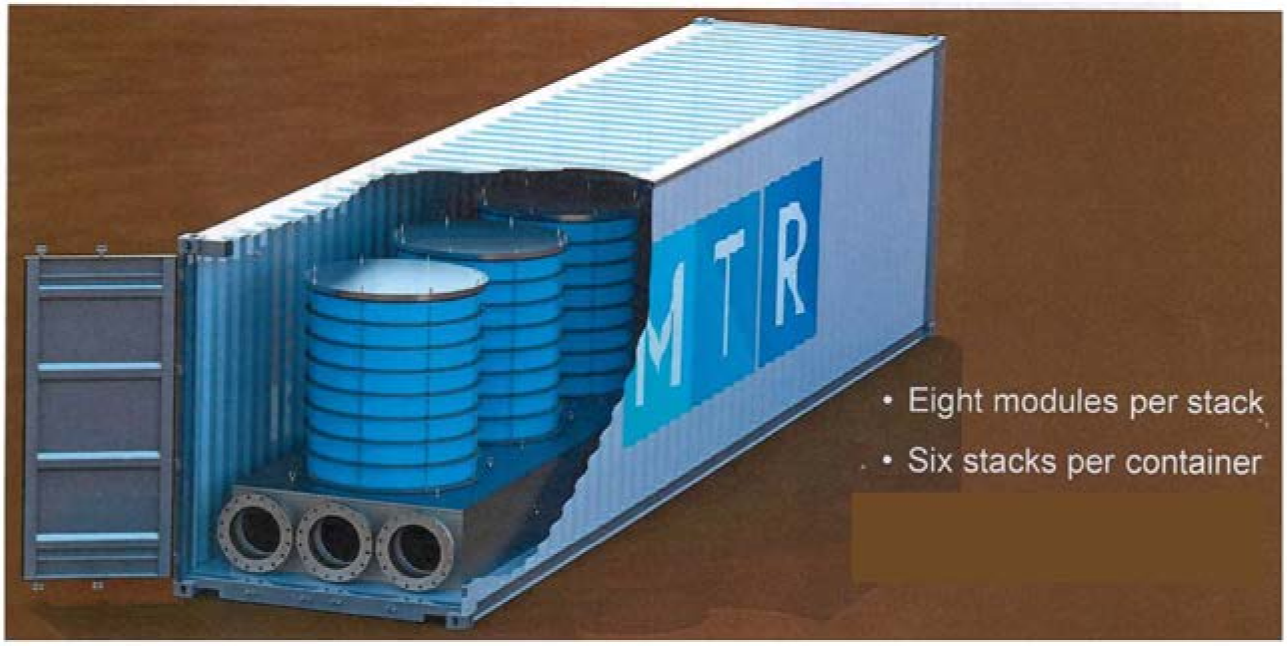

Figure 3: SolidWorks drawing showing the form of a containerized skid housing six membrane module stacks. Each stack is composed of eight modules.

technology advantages

- Capture cost is about 20% lower for cement compared to coal.
- Modular design membrane stacks ideal for scale-up for industrial CO_2 capture.
- High-purity CO_2 (greater than 99.5%) available for offtake at 150 bar.

R&D challenges

- Integration and testing of membrane stack at CEMEX testing site.

status

This project was completed on March 31, 2023. MTR completed the engineering study and membrane capture of 75% of CO_2 emissions from Kiln 2 at the CEMEX Balcones cement plant. The preliminary process design is completed, the capture plant location has been selected, and the design basis is set. The detailed design, costing, and environmental/permitting review has been completed. The TEA revealed an MTR membrane capture cost of \$76.10/tonne CO_2.

available reports/technical papers/presentations

Tim Merkel, Brice Freeman, Richard Baker, Pingjiao Hao, Paul St-Martin, Dana Pierik, "Engineering Design of a Polaris Membrane CO_2 Capture System at a Cement Plant," Final Technical Report, August 2024. *https://www.osti.gov/servlets/purl/2336740/*.

Brice Freeman, Pingjiao Hao, Tim Merkel, Paul St-Martin, Dana Pierik, Kevin Lauzze, Lucia Renau, and Nestor Mora, "Engineering Design of a Polaris Membrane CO_2 Capture System at a Cement Plant," 2023 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC31_Merkel.pdf*.

Alicia Breen, Brice Freeman, Pingjiao Hao, Tim Merkel, Dana Pierik and Kevin Lauzze, Lucia Renau and Nestor Mora, "Engineering Design of a Polaris Membrane CO_2 Capture System at a Cement Plant," Closeout Meeting, Pittsburgh, PA, March 2023.

Alicia Breen, Brice Freeman, Pingjiao Hao, Tim Merkel, Dana Pierik, Kevin Lauzze, Lucia Renau, and Nestor Mora, "Engineering Design of a Polaris Membrane CO_2 Capture System at a Cement Plant," 2021 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CCUS_Merkel.pdf*.

Brice Freeman and Tim Merkel, "Engineering Design of a Polaris Membrane CO_2 Capture System at a Cement Plant," Project kickoff meeting presentation, Pittsburgh, PA, November 2020. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11038&filename=Engineering+Design+of+a+Polaris+Membrane+CO2+Capture+System+at+a+Cement+Plant.pdf*.

Application of Transformational University of Kentucky 3 Tonne Per Day Carbon Dioxide Capture System at a Steel Process Plant

primary project goal

The University of Kentucky Research Foundation (UKRF), with partners Electric Power Research Institute, Emerson Cornerstone Controls, and Nucor Steel Gallatin, is performing engineering-scale testing of the University of Kentucky (UK) solvent-based carbon dioxide (CO_2) capture process at the Nucor Steel Gallatin sheet steel plant, treating electric arc furnace-evolved gas with a CO_2 concentration of approximately 1.5 volume percent (vol%).

technical goals

- Relocate and reconfigure an existing pilot CO_2 capture system for engineering-scale field testing at an industrial facility.
- Evaluate hazard and operability (HAZOP).
- Conduct parametric, dynamic and long-term test campaigns.
- Develop an initial Technology Maturation Plan (TMP).
- Perform a techno-economic analysis (TEA) and an environmental health and safety (EH&S) risk assessment.

technical content

UKRF and its teammates — the Electric Power Research Institute, Emerson Cornerstone Controls, and Nucor Steel Gallatin — are relocating and reconfiguring the E.W. Brown Generating Station pilot CO_2 capture system to the Nucor Gallatin steel plant in Ghent, Kentucky, for field testing at an industrial facility. The reconfiguration requires design work, site preparation, module erection and tie-in to the Nucor plant for engineering tests and evaluations.

The existing carbon capture system is a 3-tonne-CO_2/day system for an approximately 1.5 vol% CO_2 gas stream. It was developed to capture CO_2 in coal plant emissions in a previous U.S. Department of Energy (DOE)-funded project (FE0007395). The system was tested for more than 8,000 hours at a coal-fired generating power plant with flue gas containing greater than 10 vol% CO_2 concentration and for approximately 450 hours with flue gas containing approximately 4 vol% when diluted with air.

program area:
Point Source Carbon Capture

ending scale:
Small Pilot

application:
Post-Combustion Industrial PSC

key technology:
Solvents

project focus:
Solvent Process for Steel Plant CO_2 Capture

participant:
University of Kentucky Research Foundation

project number:
FE0032133

predecessor projects:
N/A

NETL project manager:
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principal investigator:
Kunlei Liu
University of Kentucky Research Foundation
kunlei.liu@uky.edu

partners:
Electric Power Research Institute, Emerson Cornerstone Controls, and Nucor Steel Gallatin

start date:
04.25.2022

percent complete:
60%

When applied to coal-fired flue gas with approximately 14 vol% CO_2, the UK system incorporates heat integration methods to utilize heat typically rejected to the environment via a two-stage, advanced solvent regeneration configuration, ultimately improving power plant efficiency. In the first stage, a steam-driven primary stripper removes most of the CO_2, followed by a secondary stage air stripper. The two-stage stripping reduces the carbon loading in the lean solvent to very low levels, and the exiting CO_2-laden air is fed into the boiler as supplementary combustion air to boost the CO_2 concentration at the absorber inlet. The system integration and heat recovery strategy has been demonstrated through small-pilot-scale experimentation and simulation. The secondary stripper also provides direct cooling to the lean solution returning to the absorber, significantly reducing the duty of the indirect-cooled lean solvent polishing exchanger; therefore, the additional capital cost of the second stripping column is offset by heat exchanger and cooling tower savings. Another advantage of the two-stage solvent regeneration scheme is that ion-free water carried by saturated air from the up-stream water evaporator is added to the solvent loop in the secondary stripper, eliminating the complexity, equipment, chemicals and power needed to produce de-ionized water for amine loop makeup. Results from DE-FE0007395 are comprehensively published and are listed in the available reports/technical papers/presentations section.

When applied at Nucor Steel Gallatin, this system is being reconfigured to treat evolving gas from an industrial steel galvanizing line with a much lower CO_2 concentration. UKRF will employ an absorber with temperature and absorption profile control, matched solvent physical properties and a split rich stripper feed (Figure 1). Researchers will also apply a model-based, feed-forward process control strategy with in-line solvent performance characterization. Together, these are expected to demonstrate 95% or greater carbon capture efficiency and 95% product CO_2 purity under actual flue gas conditions.

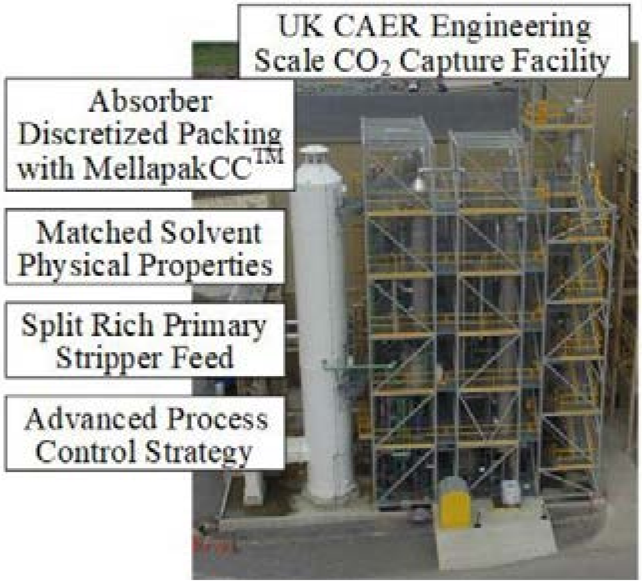

Figure 1: University of Kentucky's carbon capture system and process intensification techniques.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	g/mol	<90, Amine	<90, Amine
Normal Boiling Point	°C	160	160
Normal Freezing Point	°C	2	2
Vapor Pressure @ 15°C	bar	0.0007	0.0007
Manufacturing Cost for Solvent	$/kg (pure chemical)	6 (estimated in 2023)	6 (estimated in 2023)
Working Solution			

<table>
<tr><td>Concentration</td><td>kg/kg</td><td colspan="2"><0.45</td><td colspan="2"><0.45</td></tr>
<tr><td>Specific Gravity (15 °C/15 °C)</td><td>-</td><td colspan="2">~1.01</td><td colspan="2">~1.01</td></tr>
<tr><td>Specific Heat Capacity (30 °C, 1 bar)</td><td>kJ/kg-K</td><td colspan="2">3.3</td><td colspan="2">3.3</td></tr>
<tr><td>Viscosity (40 °C)</td><td>cP</td><td colspan="2">2.8</td><td colspan="2">2.8—</td></tr>
<tr><td colspan="6">Absorption</td></tr>
<tr><td>Pressure</td><td>bar</td><td colspan="2">1</td><td colspan="2">1</td></tr>
<tr><td>Temperature</td><td>°C</td><td colspan="2">35-55</td><td colspan="2">35-55</td></tr>
<tr><td>Equilibrium CO_2 Loading</td><td>gmol CO_2/kg solvent</td><td colspan="2">2.3</td><td colspan="2">2.3</td></tr>
<tr><td>Heat of Absorption</td><td>kJ/mol CO_2</td><td colspan="2">65-80</td><td colspan="2">65-80</td></tr>
<tr><td>Solution Viscosity</td><td>cP</td><td colspan="2">4.3 (rich condition)</td><td colspan="2">4.3 (rich condition)</td></tr>
<tr><td colspan="6">Desorption</td></tr>
<tr><td>Pressure</td><td>bar</td><td colspan="2">1.6-2.2</td><td colspan="2">1.6-2.2</td></tr>
<tr><td>Temperature</td><td>°C</td><td colspan="2">117-120</td><td colspan="2">117-120</td></tr>
<tr><td>Equilibrium CO_2 Loading</td><td>gmol CO_2/kg solvent</td><td colspan="2">1.1-1.4</td><td colspan="2">1.1-1.4</td></tr>
<tr><td>Heat of Desorption</td><td>kJ/mol CO_2</td><td colspan="2">65-80</td><td colspan="2">65-80</td></tr>
<tr><td colspan="2">Proposed Module Design</td><td colspan="4"><i>(for equipment developers)</i></td></tr>
<tr><td>Flue Gas Flowrate</td><td>cfm</td><td colspan="4">2000</td></tr>
<tr><td>CO_2 Recovery, Purity, and Pressure</td><td>% / % / bar</td><td>95</td><td colspan="2">99</td><td>1</td></tr>
<tr><td>Absorber Pressure Drop</td><td>psi</td><td colspan="4"><0.3</td></tr>
<tr><td>Estimated Absorber/Stripper Cost of Manufacturing and Installation</td><td>$\frac{\$}{kg/hr}$</td><td colspan="4">NA</td></tr>
</table>

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

		Composition						
		vol%					ppmv	
Pressure	**Temperature**	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.6 psia	80-100°F	≤1.5	<5	Balance	19-20	Balance	0.23-0.45	1.6-5.2

Chemical/Physical Solvent Mechanism – The UK solvent is an aqueous solution of a hindered primary amine. A carbamate species is formed upon CO_2 absorption. In a CO_2 capture absorber, the absorption rate, **R**, as a function of temperature, T, and carbon loading, **C/N**, can be expressed as: $R(T, C/N) = k_G \cdot a \cdot (P_{CO2} - P^*_{CO2})$ where k_G is mass transfer coefficient, **a** is effective wetted surface area, and $(P_{CO2} - P^*_{CO2})$ is the driving force, the difference in the concentration of CO_2 in liquid from the gas. Significant increase in **R**, via k_G and **a**, and corresponding reduction of capital cost comes from the mass transfer enhancement of the aqueous system compared to any second-generation technology because there is an order of magnitude greater effective wetted surface area in the top of the absorber.

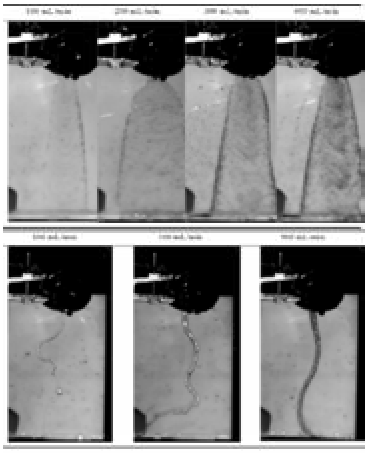

Figure 2: Liquid distribution on hydrophilic (top), hydrophobic (bottom) plate.

Solvent Contaminant Resistance – UK analysis shows the solvent is more resistant to degradation, 40–50% improvement than 30 wt% MEA. Accumulation of metals within the solvent is expected to be equivalent to that within 30 wt% MEA.

Solvent Foaming Tendency – Unstable froth formation (not persistent foaming) is a key aspect to the compact absorber. Surfactant is added to reduce the solvent surface tension and therefore control the frothing behavior. Initial CO_2 capture experiments on solvent physical properties were performed in a packed column (2-inch internal diameter [ID] mini-scrubber). Adding surfactant to change the solvent surface tension led to a CO_2 capture efficiency increase of 15–20% throughout the carbon loading range. The key reason for this enhancement is the presence of fine froth (bubbles) that increase surface area with the addition of surfactant. It was also found that as carbon loading increases, the tendency to form bubbles decreases due to increased viscosity and surface tension. For an unstable froth, the dispersion rate is also important. A surfactant was chosen with the faster dispersion rate compared to others considered.

Flue Gas Pretreatment Requirements – While the existing pretreatment system will be moved with the existing process and equipment it may not be used because the Nucor Steel flue gas contains low sulfur dioxide (SO_2) and water vapor content in a dilute oxyfuel combustion gas stream.

Solvent Makeup Requirements – Two factors contributing to solvent makeup rate are degradation and emission. UK analysis shows the solvent has degradation rates less than 30 wt% MEA and when the UK-developed solvent recovery technology is applied, the solvent emission will be about 0.5 parts per million (ppm). The anticipated solvent makeup rate is less than 0.6 kg/tonne CO_2 captured for routine transition state operation by following external load change for power generation. However, the anticipated solvent makeup rate could be less 0.3 kg/tonne CO_2 captured for industrial applications that are routinely operated at near-steady state.

Waste Streams Generated – The waste streams of the postcombustion CO_2 capture process using the compact absorber are the same as any other postcombustion CO_2 capture process. The wastewater stream is from the cooling towers and will be routed to the existing plant cooling tower sump. Nonhazardous liquid waste is generated when solvent is removed and the system is cleaned, with an annual average of 4,000 gallons being generated from 2016 to 2019. Thermal reclaiming is conducted to clean the solvent and restore alkalinity. The resulting reclaimer waste will likely also be nonhazardous due to lack of heavy metals in the proposed flue gas, but this will need to be verified.

Process Design Concept – Block diagram for the UK IDEA carbon capture and storage (CCS) for steel production flue gas:

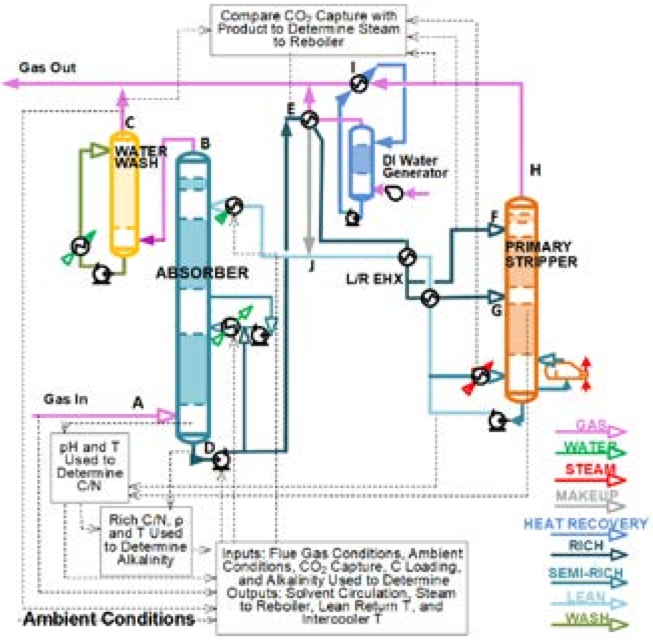

Figure 3: Process Flow for University of Kentucky's CO_2 capture process at Nucor Steel Gallatin.

Proposed Module Design – The existing heat-integrated 0.7-megawata-electric (MWe) postcombustion CO_2 capture (PCCC) facility (15 ton/day unit for 12 vol% CO_2 stream) will be reconfigured by removal of pretreatment system and air stripper to respond to the change in flue gas condition at a steel production plant: low SO_2 and water vapor content in a dilute oxyfuel combustion gas stream. The proposed technology includes an absorption/desorption loop and a heat recovery loop for in situ deionized (DI) water production as system makeup water. Flue gas enters the packing and is regenerated in an advanced stripper with split-rich feed to maximize the CO_2/water (H_2O) molar ratio in the exhaust producing a CO_2 product stream of 99+% purity after H_2O condensation. The absorber is operated at T=30–40°C, which is balanced between the driving force (CO_2 partial pressure [P]), liquid holdup (viscosity) and reaction kinetics. The T profile is controlled with a discretized packing arrangement for enhanced mass transfer and a reduced diameter. The treated flue gas then passes through a water-wash column equipped with an in-line cooler for amine entrainment and aerosol removal to less than 1 ppm prior emission. The carbon-rich solution exiting absorber passes through a cooler and two-stage lean/rich heat exchanger to recover the sensible heat and produce a warm liquid stream and two-phase stream entering the stripper for CO_2 liberation. Heat in the gaseous stream exiting stripper is recovered with a water loop producing DI water for amine loop makeup. During operation, the rich solution pH and density are measured and input to an energy optimization program to determine various control valve setpoints to maintain 95+% CO_2 capture while minimizing the solvent regeneration energy.

TABLE 2: INDUSTRIAL PLANT CARBON CAPTURE ECONOMICS

Economic Values Compared to 2019 B31B	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	$/tonne CO_2	49.9	49.9
Cost of Carbon Avoided	$/tonne CO_2	—	—
Capital Expenditures	2018$/MWh	18.9	18.9
Operating Expenditures	2018$/MWh	4.4	4.4

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Calculations Basis – The numbers provided in the table are based on the B31B reference plant provided by NETL for TEA, found in the "Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity" report Revision 4, September 24, 2019, $2018.

Scale of Validation of Technology Used in TEA – A unique process-oriented, process-intensified and heat-integrated PCCC technology has been developed and demonstrated at the 0.1 megawatt-thermal (MWth) bench-scale and 0.7 MWe engineering-scale in operation since 2008 and 2015. More than 10,000 operational hours and nearly 30 solvent campaigns treating gas streams with CO_2 concentration in the range of 4–14 vol% have been conducted, showing similar performance despite differences in solvent chemistry and physical properties.

Qualifying Information or Assumptions – An engineering adjustment was made for comparison with 2019 B31B. A bottom-up TEA will be conducted in the course of the project.

technology advantages

- Simple, solvent-independent process.
- UK hindered primary amine solvent with no known stable nitrosamine formation.
- Split rich stripper feed leading to reduced solvent regeneration energy requirement.
- Advanced, feed-forward process controls incorporating real-time solvent-quality knowledge and automatic set points for energy minimization.
- Repurposing existing equipment for new site and application.

R&D challenges

- The low CO_2 concentration (approximately 1.5 vol%) means a low liquid-to-gas ratio (L/G) and possible maldistribution on packing.
- Repurposing existing equipment for new site and application.

status

The host site agreement has been executed. The CO_2 capture island design is nearly complete by Koch Modular Process Systems (KMPS). Nucor Steel Gallatin has accepted responsibility for the balance of plant design upon reclassification as a subrecipient.

available reports/technical papers/presentations

Liu, K. and Nikolic, H., University of Kentucky, *“Application of Transformational University of Kentucky 3 Tonne Per Day Carbon Dioxide Capture System at a Steel Process Plant,”* 2024 FECM / NETL Carbon Management Research Project Review Meeting, August 2024. https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_PSCC_7_Nikolic.pdf.

Liu, K. and Nikolic, H., University of Kentucky, *“Application of Transformational University of Kentucky 3 Tonne Per Day Carbon Dioxide Capture System at a Steel Process Plant,”* 2023 FECM / NETL Carbon Management Research Project Review Meeting, Sep. 2023. https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC1_Liu.pdf.

Liu, K. and Nikolic, H., University of Kentucky, *“Application of Transformational UKy 3 Ton/Day CO_2 Capture System at a Steel Process Plant,”* 2022 Carbon Management Project Review Meeting – Point Source Carbon Capture, Aug. 2022. https://netl.doe.gov/sites/default/files/netl-file/22CM_PSC15_Liu.pdf.

Liu, K. and Nikolic, H., University of Kentucky, *“Application of Transformational UKy 3 Ton/Day CO_2 Capture System at a Steel Process Plant,”* Project Kickoff Meeting, May 31, 2022. *https://netl.doe.gov/projects/files/Application%20of%20Transformational%20UKy%203%20TonDay%20CO2%20Capture%20System%20at%20a%20Steel%20Process%20Plant.pdf.*

Liu, K., Nikolic, H., Thompson, J., Frimpong, R., Richburg, L., Abad, K., Bhatnagar, S., Irvin, B., Landon, J., Li, W., Matin, N. S., Pelgen, J., Placido, A., Whitney, C., Bhown, A., and Du, Y., "*Application of a Heat Integrated Post-combustion CO_2 Capture System with Hitachi Advanced Solvent into Existing Coal-Fired Power Plant (Final Technical Report)*". June 2020. *https://www.osti.gov/servlets/purl/1635102*.

Bhown, A. S., Schoff, R., Maxson, A., Du, Y., Jimenez, A., Liu, K., Neathery, J., Remias, J., Thompson, J., Richburg, L., Placido, A., Nikolic, H., Bartone, M., White, J., Eswaran, S., and Wu, S., *“Final Technical and Economic Feasibility Study on the Application of a Heat Integrated Post-Combustion CO_2 Capture System with Hitachi Advanced Solvent into Existing Coal-Fired Power Plant”*. May 2020. *https://www.osti.gov/servlets/purl/1634227*.

Frimpong, R., Nikolic, H., Pelgen, J., Ghorbanian, M., Figueroa, J., and Liu, K. *“Evaluation of different solvent performance in a 0.7 MWe pilot scale CO_2 capture unit.”* Chemical Engineering Research and Design. 148. 11-20. August 2019.

Li, W., Landon, J., Irvin, B., Thompson, J., Nikolic, H., and Liu, K. *“A Corrosion Inhibition Study of Carbon Steel in a 0.7 MWe Pilot CO2 Capture Process.”* Paper presented at the CORROSION 2018, Phoenix, Arizona, USA, April 2018.

Thompson, J., Nikolic, H., Combs, M., Bhatnagar, S., Pelgen, J., Abad, K., and Liu, K. *“Solvent Degradation and Emissions from a 0.7 MWe Pilot CO_2 Capture System with Two-stage Stripping.”* Energy Procedia. 114. 1297-1306. July 2017.

Thompson, J., Bhatnagar, S., Combs, M., Abad, K., Onneweer, F., Pelgen, J., Link, D., Figueroa, J., Nikolic, H., and Liu, K. *"Pilot Testing of a Heat Integrated 0.7 MWe CO2 Capture System with Two-stage Air-stripping: Amine Degradation and Metal Accumulation."* Internation Journal of Greenhouse Gas Control. 64. 23-33. September 2017.

Nikolic, H., Frimpong, R., and Liu, K. *"Trace Metals Accumulation in a Coal-fired Post Combustion CO_2 Capture Process with Amine-based Solvents."* International Journal of Greenhouse Gas Control. 42. 59-65. November 2015.

Bhown, A. S. Electric Power Research Institute. *"Implementation of a Rate-based Model to Analyze the Application of a Heat Integrated Post-combustion CO_2 Capture System with Hitachi Advanced Solvent into Existing Coal-fired Power Plant."* Submitted to U.S. Department of Energy National Energy Technology Laboratory. March 2015.

Fan, Z. and Nikolic, H. *"Applicability of the Liquid Desiccant Air Drying System on Power Plant Performance for the Application of a Heat-Integrated Post-Combustion CO_2 Capture System with Hitachi Advanced Solvent into Existing Coal-Fired Power Plant."* Submitted to U.S. Department of Energy National Energy Technology Laboratory. September 2014.

Cryogenic Carbon Capture from Cement Production

primary project goal

Sustainable Energy Solutions LLC (SES) is advancing a Cryogenic Carbon Capture™ (CCC) technology to engineering scale (30 tonnes of carbon dioxide [CO_2] captured/day). The carbon capture unit is being installed at the Eagle Materials Central Plains Cement Plant in Sugar Creek, Missouri.

technical goals

- Design and size all major process equipment.
- Finalize host site agreements and any required environmental or operational permits.
- Construct and commission the engineering-scale system.
- Operate the constructed system for at least two continuous months within a six-month testing period.
- Demonstrate that the system can achieve at least a 95% carbon capture rate with an exit CO_2 purity of 95% or more.
- Decommission the system and restore the host site to its pre-project state.

technical content

SES has developed a novel carbon capture process using cryogenic technology that exploits the different condensation/freezing points of the components of flue gases in order to separate and capture CO_2. A basic overview of the system is shown in Figure 1. The system works by first cooling the flue gas (state 1). The cooled gas is then sent to a separator (state 2), which removes the condensed CO_2 precipitate from the flue gases. Finally, the CO_2 is pressurized and helps cool the incoming flue gas before being shipped out and stored or utilized (state 3), while the flue gases vent out the stack (state 4). A more detailed view of this system can be seen in Figure 2. The system has been previously demonstrated at skid-scale (1 tonne/day) at power plants, cement plants, heating plants, and several other field locations around the world. The current efforts focus on scaling this system to 30 tonnes/day and operating it over a period of at least two months.

The host site is the Central Plains Cement Plant in Sugar Creek, Missouri, owned and operated by Eagle Materials. This plant operates in two different modes: "raw mill up" (80% of the time) and "raw mill down" (20% of the time). In raw mill up mode, the temperature and CO_2 concentration of the flue gas are lower (90°C versus 220°C and 18% versus 24%), so the CCC system needs to adapt accordingly.

program area:

Point Source Carbon Capture

ending scale:

Small Pilot

application:

Post-Combustion Industrial PSC

key technology:

Novel Concepts

project focus:

Cryogenic CO_2 Capture for Cement Production

participant:

Sustainable Energy Solutions LLC (SES)

project number:

FE0032148

predecessor projects:

N/A

NETL project manager:

Carl Laird
Carl.Laird@netl.doe.gov

principal investigator:

Larry Baxter
Sustainable Energy Solutions
l.baxter@sesinnovation.com

partners:

Chart Industries; Eagle Materials; FLSmidth

start date:

02.01.2022

percent complete:

50%

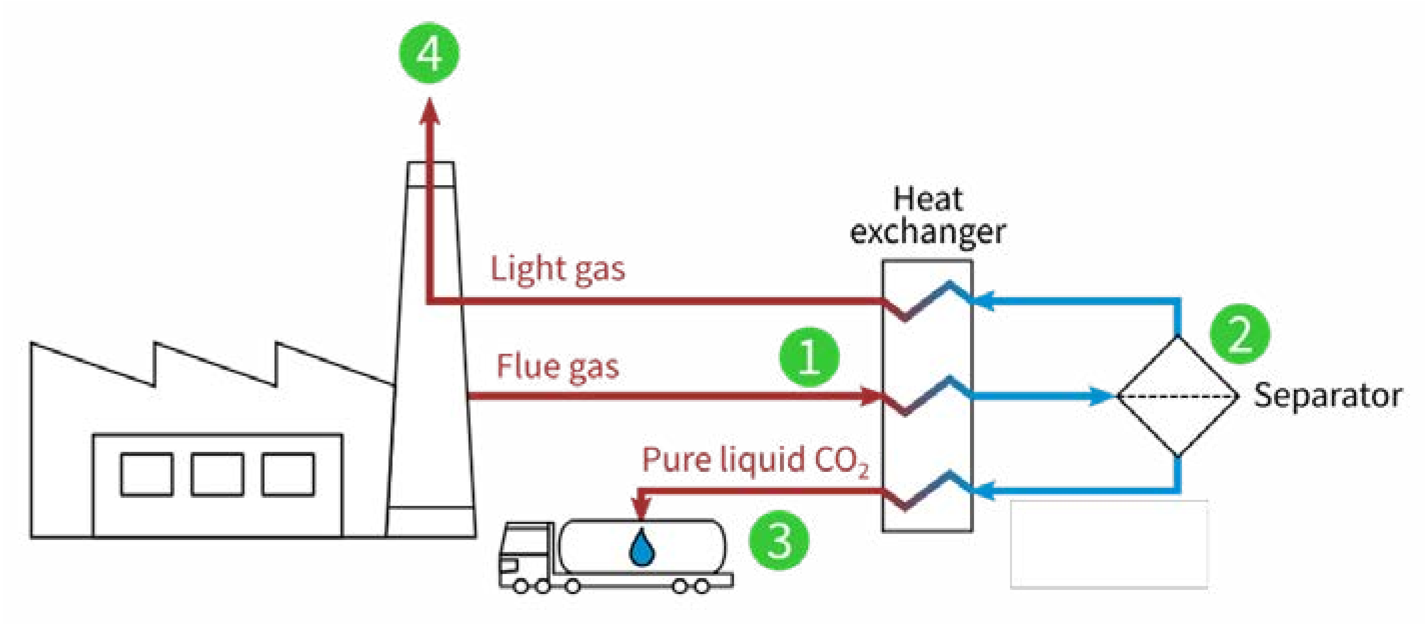

Figure 1: Simplified plant diagram.

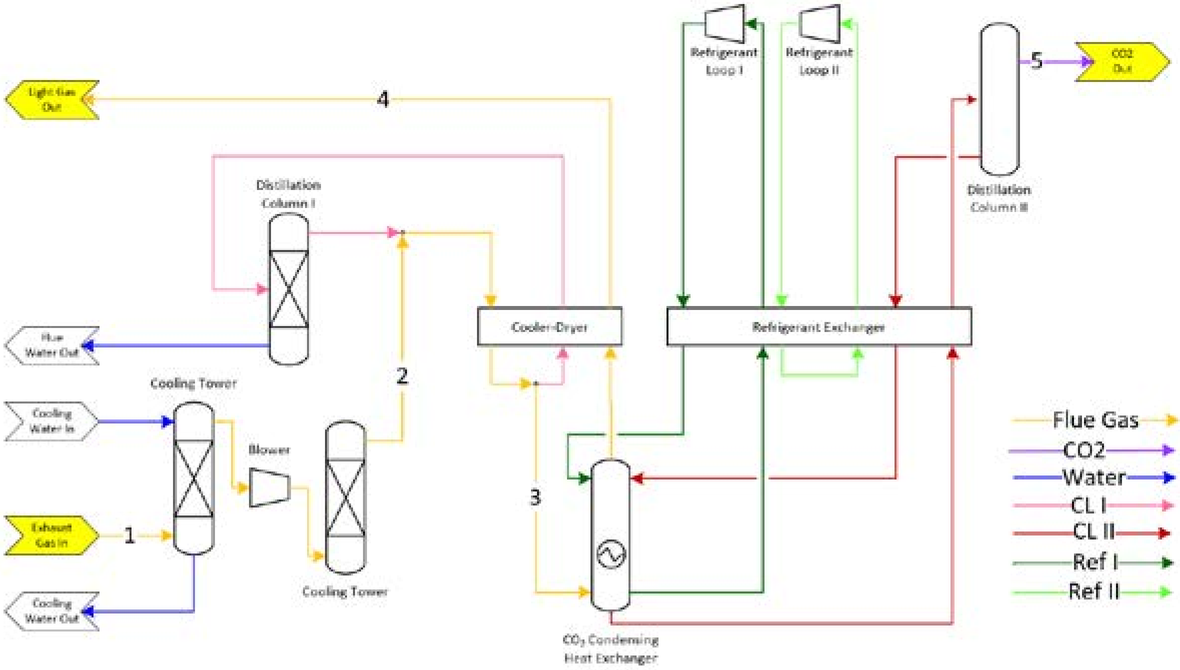

Figure 2: Schematic of CCC system.

Phase I project efforts include a hazard and operability (HAZOP) study and an environmental, health, and safety (EH&S) analysis following completion of the host site agreement. The purpose of these studies is to identify the environmental risks and safety of any future projects that plan to use the proposed capture system. Concurrent with these efforts is the initial design of the plant. Various process and instrumentation diagrams (P&IDs), as well as other detailed construction diagrams, are produced during this task. Finally, all necessary operating and environmental permits are secured in Phase I to ensure the construction phase can proceed.

Final products of Phase I work are: (1) the development of detailed flow simulations to ensure reliable performance and establish initial cost estimates, and (2) the sourcing of all major equipment to be used during the construction phase.

Simulations are carried out using commercial Aspen Plus® software. An initial techno-economic analysis (TEA) is also conducted in Phase I.

Project tasks planned for Phase II include finalizing design choices and necessary approvals, as well as initiating construction of the final system.

Project tasks planned for Phase III are to analyze the complete system over a six-month period and perform continuous operation for at least two of the six months; decommission the CCC system and restore the plant to its pre-project state; refine simulated models and TEA based on data obtained during testing; and compare and reconcile differences in observed and predicted process performance. The current estimated results and target research and development (R&D) values for the costs of capture are shown in Table 1.

TABLE 1: INDUSTRIAL PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	27	23
Cost of Carbon Avoided	\$/tonne CO_2	41	35
Capital Expenditures	\$/tonne CO_2	15	13
Operating Expenditures	\$/tonne CO_2	8	6

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Waste Streams Generated – There is no waste stream generation inherent to the CCC process. The water used to cool the inlet flue gas comes in direct contact with the flue gas and may become contaminated with pollutants or particulate matter, which would require water treatment. No other waste streams are expected.

Process Design Concept – The 30 tonnes/day process will be functionally the same and include a similar equipment list as a larger-scale process or system. The process as designed for this site-specific application has a minimum target carbon capture rate of 95%, and a CO_2 purity target of 99.97%.

Proposed Module Design – SES is using a skid-based system design for this project, which allows much of the equipment to be built offsite and minimizes construction onsite. This system is shown in 3. Chart Industries is supporting this skid-based design with both engineering support and in the construction of various coldboxes used in the system.

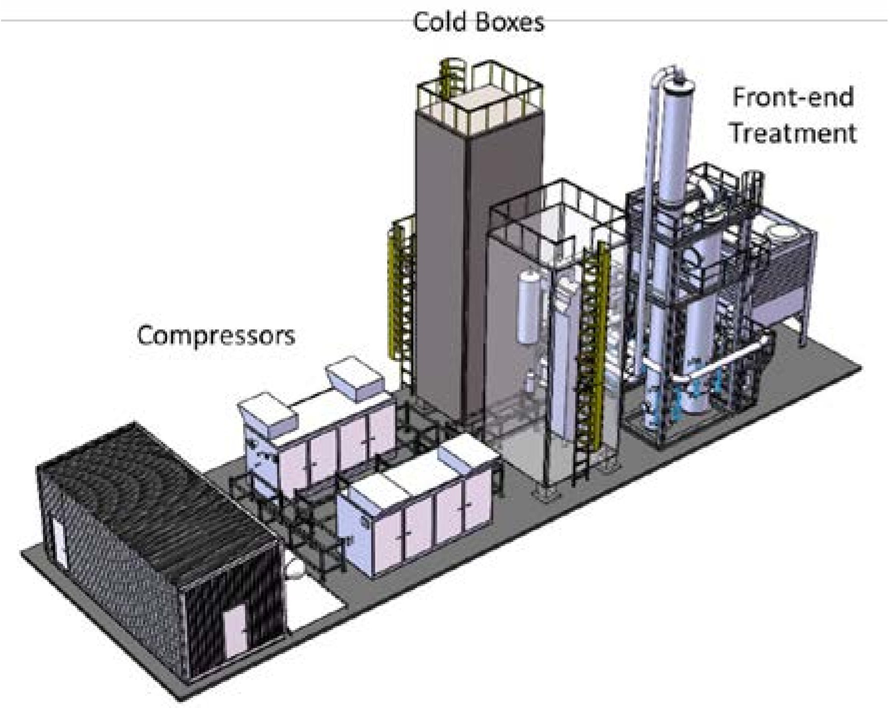

Figure 3: Preliminary design for skid-based CCC system.

technology advantages

- High carbon capture rate (99%+).
- Easy to retrofit onto existing plants.
- Integrated grid-scale energy storage.
- Lower cost than traditional amine sorbents.
- Lower water usage than traditional amine sorbents.
- Robust operation with pollutants such as nitrogen oxide (NO_X) and sulfur oxide (SO_X) and partial co-capture of these pollutants.
- Produces high-purity liquid CO_2.

R&D challenges

- Keeping energy usage low.
- Achieving continuous capture efficiency, even as cement plant changes operational modes.
- Scaling novel process equipment to small-industrial scale.

status

The main equipment designs have been finalized. An agreement with the Sugar Creek host site has been reached, including permits. SES is also working to develop potential offtake agreements.

available reports/technical papers/presentations

Hoeger, C., 2024, "Cryogenic Carbon Capture from Cement Production." Proceedings of the 2024 FECM/NETL Carbon Management Research Project Review Meeting. Pittsburgh, PA. August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_PSCC_7_Hoeger.pdf*.

Hoeger, C., 2023, "Cryogenic Carbon Capture from Cement Production." Proceedings of the 2023 FECM/NETL Carbon Management Research Project Review Meeting. Pittsburgh, PA. September 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC1_Hoeger.pdf*.

Stitt, K., 2023, "Cryogenic Carbon Capture from Cement Production." Project DE-FE0032148 – Phase II GO/NO-GO. Budget Period 1 Review Meeting Presentation. September 2023. *https://netl.doe.gov/projects/files/Cryogenic%20Carbon%20Capture%20from%20Cement%20Production.pdf*.

Stitt, K., 2022, "Cryogenic Carbon Capture from Cement Production." Project Kickoff Meeting. National Energy Technology Laboratory: Pittsburgh, PA. April 2022. *https://netl.doe.gov/projects/files/Cryogenic%20Carbon%20Capture%20from%20Cement%20Production.pdf*.

Blue Bison ATR Advanced CCUS System

primary project goal

Tallgrass MLP Operations LLC partnered with the University of Wyoming and Technip Energies to perform an initial engineering design of a commercial-scale carbon capture and storage (CCS) system installed at a hydrogen (H_2) production plant proposed to be installed in Douglas, Wyoming. The proposed plant would produce decarbonized H_2 from natural gas (or "blue" H_2), utilizing Haldor Topsøe's auto-thermal reforming (ATR) technology coupled with BASF's OASE® White carbon capture system.

technical goals

- Develop an initial engineering study of a commercial-scale carbon capture system that could be installed and fully integrated with a 220-million standard cubic feet per day (MMSCFD) blue H_2 facility utilizing ATR technology, producing 99.97% pure H_2 delivery pressure at or above 360 pounds per square inch absolute (psia).
- Establish system capability of meeting CO_2 capture requirements of 95% pure CO_2 with 90+% capture efficiency, CO_2 delivery pressure at or above 2,215 psia, and a goal for CO_2 transport and storage costs at or below $10 per tonne.
- Identify potential utilization pathways for CO_2 and H_2.
- Determine levelized cost of hydrogen and cost of carbon capture to help achieve the U.S. Department of Energy's (DOE) target for carbon-neutral blue H_2 production of less than $1 per kg.

technical content

The proposed site for the H_2 production plant with integrated capture is adjacent to Tallgrass' midstream gas processing plant in Douglas, Wyoming (see Figure 1). This location has multiple favorable characteristics:

- Immediate proximity to existing natural gas lines and existing gas processing plant with its infrastructure and utilities.
- Plausible regional market options for blue H_2 utilization in power generation, renewable diesel production, decarbonized ammonia production in the Midwest, and transportation uses.
- Options for CO_2 utilization with storage opportunities within 1 mile of the host site, enhanced oil recovery (EOR) fields in the regions, and the Wyoming CO_2 corridor initiative.

program area:

Point Source Carbon Capture

ending scale:

pre-FEED

application:

Pre-Combustion Industrial PSC

key technology:

Solvents

project focus:

BASF's OASE® White Carbon Capture System with Natural Gas Reforming

participant:

Tallgrass MLP Operations LLC

project number:

FE0032114

predecessor projects:

N/A

NETL project manager:

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principal investigator:

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partners:

University of Wyoming;
Technip Energies

start date:

10.01.2021

percent complete:

100%

Figure 1: Proposed project site.

The proposed H_2 production plant would leverage Haldor Topsøe's SynCOR™ ATR technology (see Figure 2). SMR is the most common natural gas reforming technology deployed, but SMR produces CO_2-loaded flue gas requiring post-combustion capture. However, in ATR, most of the CO_2 generated can be efficiently captured from the high-pressure raw synthesis gas (syngas) stream via amine scrubbing. Unlike SMR, ATR requires oxygen input, but for high CO_2 capture rates the ATR approach is preferred to SMR. The SynCOR ATR technology is oxygen-blown, featuring an adiabatic reformer upstream to convert heavy feedstocks to methane and a fired heater to preheat the feed natural gas, and a high-pressure steam byproduct is used to generate power in a steam turbine generator, which can offset the power demand of the air separation unit (ASU) needed for oxygen production.

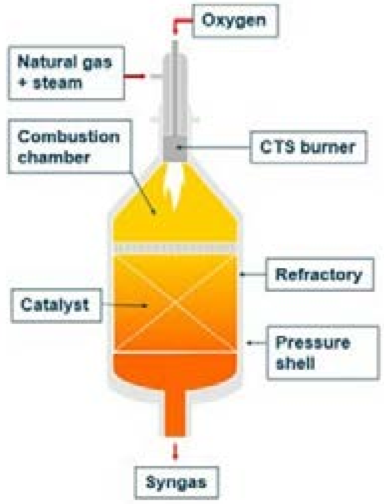

Figure 2: SynCOR™ autothermal reformer.

The integrated H_2 production plant would integrate the autothermal reformer with deep water-gas shift (WGS) and thorough CO_2 capture via BASF's OASE white carbon capture system. The overall process concept for the integrated plant is depicted in Figure 3.

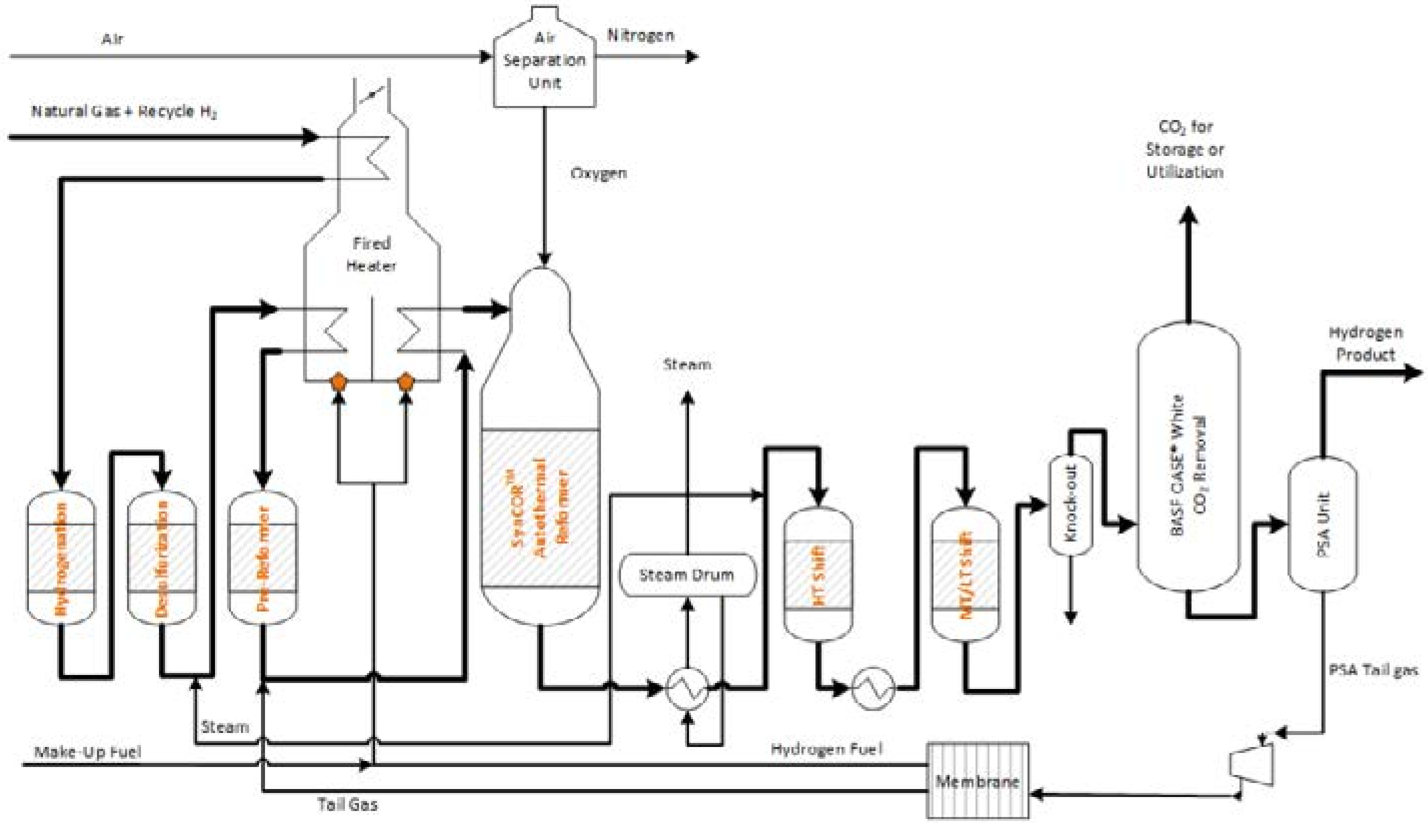

Figure 3: Process concept for integrated ATR with CO_2 capture.

BASF's OASE white is a state-of-the-art amine solvent-based technology for pre-combustion capture of CO_2 from syngas. It is a high-efficiency process, requiring low energy consumption per ton CO_2 captured.

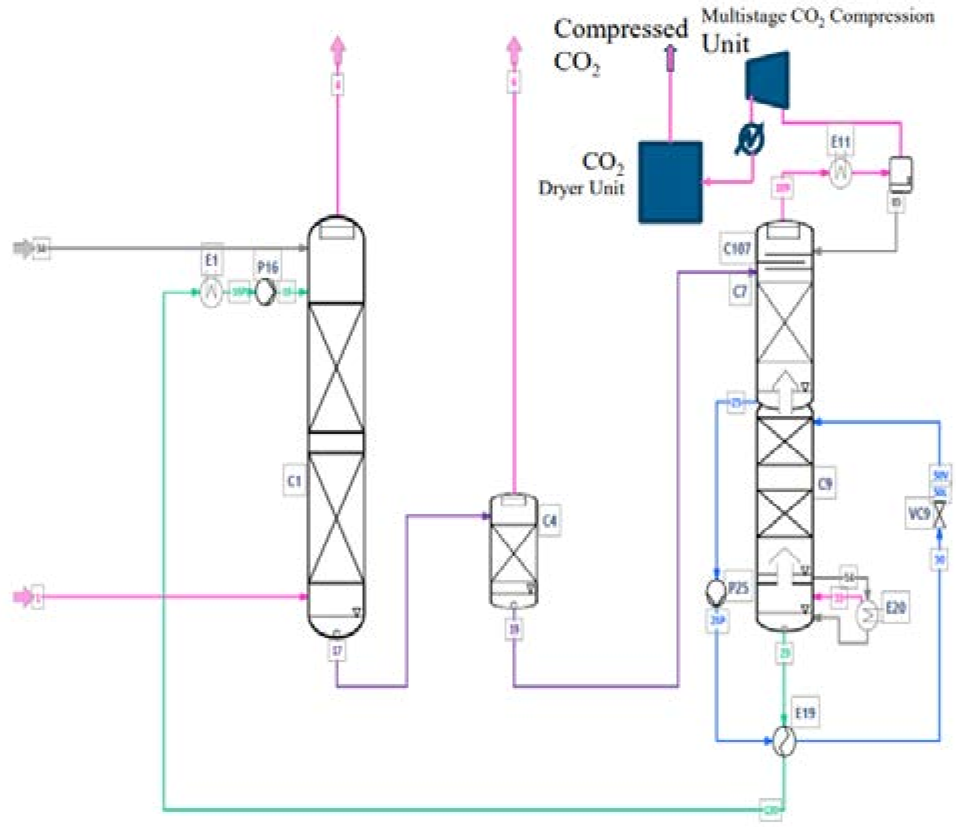

Figure 4: BASF OASE® White carbon capture technology.

Preliminary design involved developing the plant layout, specifying major process equipment items, developing utility flow diagrams, developing piping and instrumentation diagrams, and performing heat and material balances. As part of the preliminary design, a plot plan of the proposed hydrogen production facility was prepared, as shown in Figure 5. This occupies the area labeled “Proposed Facility” on the right side of the proposed host site satellite view in Figure 1. Figure 6 zooms in on the CO_2 capture unit located approximately in the middle of Figure 5, and is a 3D model that includes the main pieces of equipment comprising stripper and absorber columns, gas separator and flash drums, storage tanks, pumps, heat exchangers, and compressors.

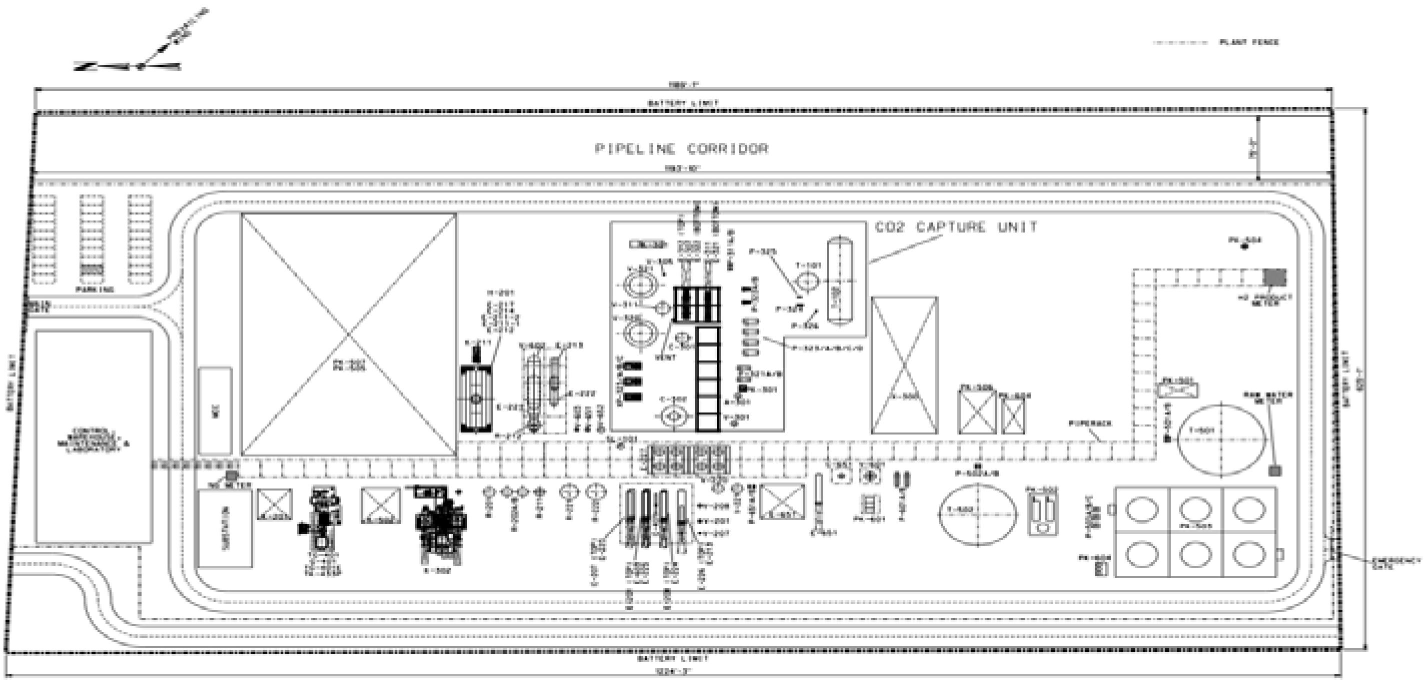

Figure 5: Plot plan.

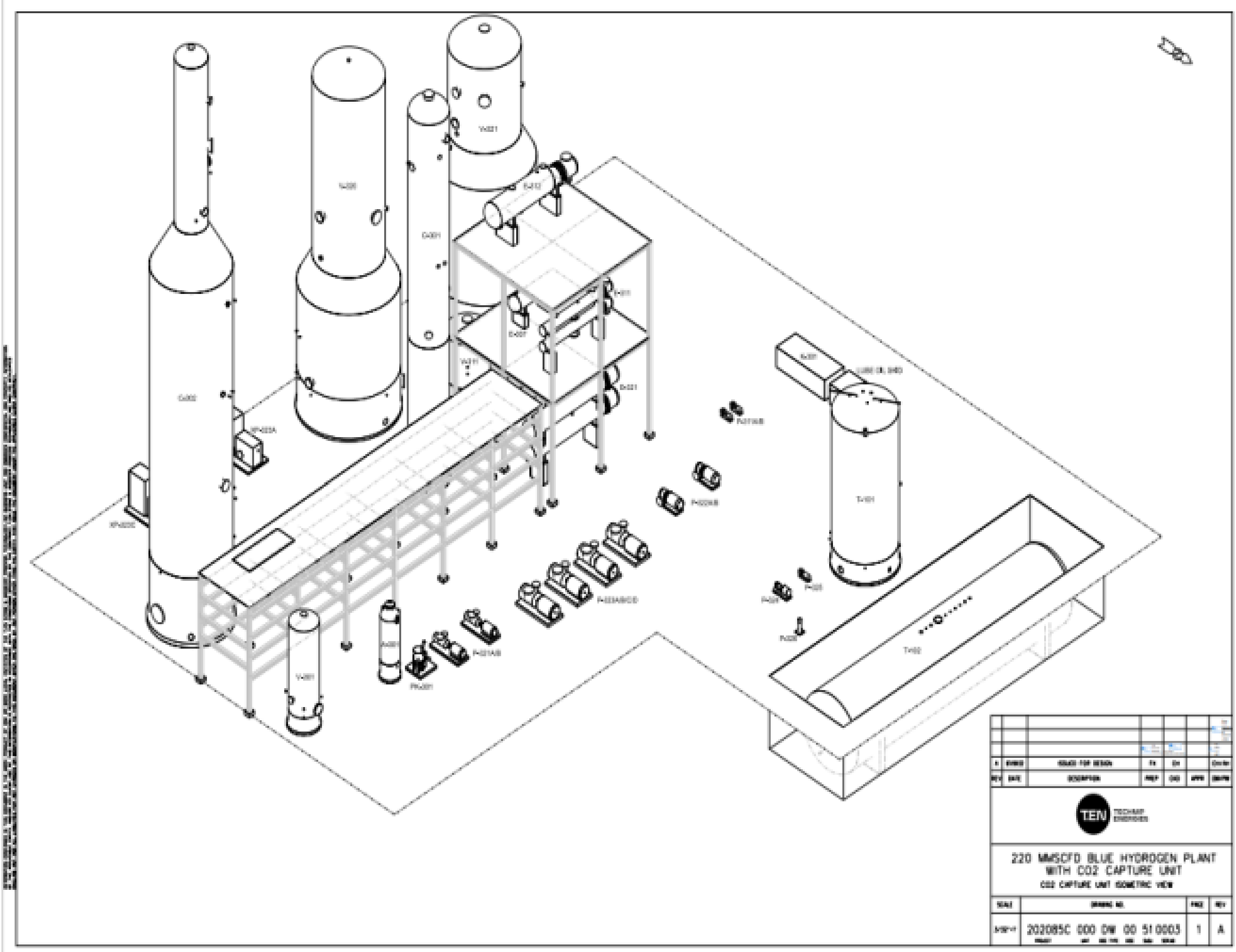

Figure 6: Isometric of carbon capture unit.

The Blue Bison Team developed an economic analysis of the ATR/CCUS plant per the preliminary design. It adhered closely to the “Quality Guidelines for Energy System Studies: Cost Estimation Methodology for NETL Assessments of Power Plant Performance” and capital costs as established in the National Energy Technology Laboratory’s (NETL) natural gas reforming baselines in “Cost and Performance Baseline for Fossil Energy Plants - Volume 1: Bituminous Coal and Natural Gas to Electricity (Rev 4, 2019).” For the ATR/CCUS plant, it was determined that the levelized cost of hydrogen (LCOH), taking into account the benefit of Section 45Q sequestration, would be $0.889 per kg for the first 12 years of plant operations. The required real LCOH after the initial 12 years (i.e., after the 45Q ends) increases to $0.945 per kg. Based on this analysis, it was concluded that blue H_2 production is feasible at a cost of less than $1.00/kg, per DOE’s ambitious decarbonized hydrogen cost target.

*TABLE 1: SOLVENT SYSTEM PROCESS PARAMETERS

Proposed Module Design			*(for equipment developers)*	
Syngas Flowrate	kg/hr		219,160	
CO_2 Recovery, Purity, and Pressure	% / % / bar	99.9	99.57	152
Absorber Pressure Drop	bar		0.2	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$		—	

*Numbers presented in this document represent best current information

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Combination of physical and chemical.

Solvent Contaminant Resistance – Currently unknown.

Solvent Foaming Tendency – Currently unknown.

Flue Gas Pretreatment Requirements – Currently unknown.

Solvent Makeup Requirements – Currently unknown.

Waste Streams Generated – Currently unknown.

Process Design Concept – See Figure 3.

Proposed Module Design – See Figure 4. The pressure, temperature and composition of the gas entering the module are as follows:

		Composition entering BASF module						
Pressure	**Temperature**	vol%						ppmv
psia	°F	**CO_2**	**CO**	**CH_4**	**Ar+N_2**	**H_2**	**H_2O**	**H_2S**
378	60	24.7	0.58	0.82	0.49	72.65	0.77	0

technology advantages

- State-of-the-art, commercially proven technologies for syngas generation and treatment.
- Application in carbon-neutral hydrogen production to allow a diversified clean energy portfolio.

R&D challenges

- Developing a mechanical design for the largest advanced heat exchanger reformer (TPR®), which can be integrated with the ATR to reduce O_2 consumption and minimize methane (CH_4) slip from the TPR.

- Verifying test data for use of pure blue H_2 as fuel in LSV® burners in the ATR preheater to minimize or eliminate CO_2 production in the fired heater.

status

The project was completed on February 28, 2023. This preliminary design/pre-front-end engineering design (FEED) study showed that the combination of ATR with carbon capture via BASF OASE® white carbon capture technology should allow carbon-neutral hydrogen production at competitive/targeted costs. The setting was in Wyoming with reasonable access to feedstock, plausible options for produced hydrogen utilization, and local carbon storage opportunity.

available reports/technical papers/presentations

Schaefer, Jeff. 2023. "Blue Bison ATR Advanced CCUS System (Final Report)". United States. https://doi.org/10.2172/1975500. *https://www.osti.gov/servlets/purl/1975500*.

FE0032114 Close Out Meeting, February 28, 2023.

"Blue Bison DE-FE0032114 Kickoff Meeting," Kickoff Meeting Presentation, October 19, 2021. *https://netl.doe.gov/projects/plp-download.aspx?id=11230&filename=Blue+Bison+DE-FE0032114+Kickoff+Meeting.pdf*.

The 8RH$_2$ Process for Producing Clean Hydrogen with Autothermal Reforming and Carbon Capture

primary project goal

8 Rivers Capital LLC is conducting a pre-front-end engineering design (pre-FEED) study for a new hydrogen production plant equipped with 8 Rivers Hydrogen (8RH$_2$) technology to produce 100 million standard cubic feet per day of clean hydrogen and capture 90–99% of carbon dioxide (CO$_2$) emissions, considering three design cases implementing the subsystems and equipment of the 8RH$_2$ autothermal reforming (ATR) technology and a CO$_2$ separation unit, with variations in the process.

technical goals

- Develop initial engineering design, including process flow diagram, piping and instrumentation diagrams, a plot plan, and heat and material balances based on host site integration data.
- Complete a techno-economic analysis (TEA).

technical content

8 Rivers Capital LLC is developing a pre-FEED for 8RH$_2$, an ATR carbon capture technology that can produce hydrogen from natural gas with carbon capture. The study will produce 8RH$_2$ designs to generate clean hydrogen with carbon captured for storage in Wyoming. The 8RH$_2$ technology could produce clean hydrogen for less than $1/kg with the §45Q tax credit.

The project aims to advance the engineering design of 8RH$_2$ technology for commercial-scale deployment. The 8RH$_2$ process utilizes subsystems and equipment that are commercially available today and have been deployed at various scales. Three cases are considered: (1) base case with ATR plus an air fired heater and cryogenic carbon capture, (2) ATR plus an air fired heater with a heat exchanger reformer and cryogenic CO$_2$ separation, and (3) ATR plus carboxy-fired heater with heat exchange reformer and cryogenic CO$_2$ separation.

The use of low-temperature CO$_2$ separation for CO$_2$ capture from pressure swing adsorption (PSA) tail gas has the potential to improve the efficiency of an ATR-based hydrogen plant compared to conventional CO$_2$ capture processes (the reference example uses a methyl diethanolamine [MDEA] process for CO$_2$ capture from high-pressure syngas). In addition, the recovery of CO$_2$ from PSA off-gas allows for additional hydrogen recovery from the waste gas leaving the CO$_2$ capture unit, bringing the total hydrogen recovery from crude hydrogen stream to about 98.5%. Furthermore, the use of a small oxy-fuel process heater in the

program area:
Point Source Carbon Capture

ending scale:
Pre-FEED

application:
Pre-Combustion Industrial PSC

key technology:
Novel Concepts

project focus:
Autothermal Reforming Technology with CO$_2$ Separation

participant:
8 Rivers Capital LLC

project number:
FE0032127

predecessor projects:
N/A

NETL project manager:
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partners:
Technip USA Corporation

start date:
02.07.2022

percent complete:
87.5%

system can increase the CO_2 capture rate to greater than 99%. The increase in the production cost due to marginal oxygen consumption in an oxy-fuel heater can be offset by using a heat exchanger reformer (HEXR), which would reduce the cost of natural gas feedstock.

The integration of low-temperature CO_2 capture and oxy-fuel heater/boiler system with ATR-based hydrogen production has not been developed and demonstrated before. This configuration promises the highest rate of CO_2 capture while keeping the levelized cost of hydrogen low. The project aims to leverage and integrate the existing knowledge for engineering, design and the operation of various equipment and subsystem, progressing the maturity of $8RH_2$ technology and reducing the technical risk of integration between various components.

Figure 1: Proposed brownfield site for clean hydrogen plant in Evanston, Wyoming.

technology advantages

- Low-energy cryogenic CO_2 separation system that maximizes hydrogen recovery while minimizing the carbon footprint of the operation.
- Integrating a heat exchange reformer (HEXR) with the ATR improves thermal efficiency through more effective heat utilization.
- Case 3 can handle high inert natural gas and offers high CO_2 capture (99%+).

R&D challenges

- Carboxy-fired process heater (for Case 3)
    - Challenges with novel kit and limited supply chain.
- CO_2 cold box - precise process control is required as equipment operates near the CO_2 freezing point.

status

The project was completed on September 30, 2024. The project team is preparing the pre-FEED report for the $8RH_2$ ATR carbon capture technology at the brownfield Painter Gas Complex in Evanston, Wyoming. The levelized cost of hydrogen and levelized cost of CO_2 capture as well as the carbon intensity were calculated for each of the three cases.

available reports/technical papers/presentations

Goff, Adam, "The 8RH$_2$ Process for Producing Clean Hydrogen," Closeout Meeting Presentation - Point Source Carbon Capture, September 2024. *https://netl.doe.gov/projects/files/The%208RH2%20Process%20for%20Producing%20Clean%20Hydrogen%20with%20Autothermal%20Reforming%20and%20Carbon%20Capture.pdf*.

Goff, Adam, "The 8RH$_2$ Process for Producing Clean Hydrogen," presented at 2024 NETL Carbon Management Project Review Meeting - Point Source Carbon Capture, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_PSCC_6_Patterson.pdf*.

Goff, Adam, "The 8RH$_2$ Process for Producing Clean Hydrogen," presented at 2023 NETL Carbon Management Project Review Meeting - Point Source Carbon Capture, September 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_PSCC1_Goff.pdf*.

Goff, Adam, "The 8RH$_2$ Process for Producing Clean Hydrogen with Autothermal Reforming and Carbon Capture," presented at 2022 NETL Kickoff Meeting, May 2022. *https://netl.doe.gov/projects/files/The%208RH2%20Process%20for%20Producing%20Clean%20Hydrogen%20with%20Autothermal%20Reforming%20and%20Carbon%20Capture.pdf*.

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CARBON CAPTURE TECHNOLOGY SHEETS

Carbon Dioxide Removal

Nuclear Direct Air Capture with Carbon Storage (NuDACCS)

primary project goal

Battelle Memorial Institute, in partnership with AirCapture LLC, Southern Company, the University of Alabama, Sargent and Lundy, and Carbonvert, is completing a front-end engineering design (FEED) study for an integrated direct air capture (DAC) system co-located at the Farley Nuclear Plant in Columbia, Alabama. The designed process will be capable of capturing a minimum of 5,000 tonnes/year net atmospheric carbon dioxide (CO_2) for subsequent storage while making use of waste heat and carbon-neutral electricity.

technical goals

- Further understand the DAC module and system design at the 5,000-tonnes per year level and the balance-of-plant requirements for this configuration.
- Understand the key contributors to the cost estimate and business case analysis (BCA) for the system and produce a robust life cycle analysis (LCA) for this system configuration.
- Determine the key inputs and outcomes of this system with environmental justice and economic revitalization lenses, including impacts on and requirements for potential future jobs.

technical content

The project's main goal is to determine the feasibility of integrating an established DAC sorbent process with an existing nuclear power plant in Columbia, Alabama, capable of providing waste heat for sorbent regeneration to remove CO_2 from the atmosphere for subsequent storage, as shown in Figure 1. The plant was chosen for its availability of waste heat and water resources, as well as its location for transport options following CO_2 removal. The project is led by Battelle, using DAC materials developed by Global Thermostat in a DAC process design provided by AirCapture LLC. The nuclear power plant providing the waste heat for regeneration is owned by Southern Company. Additional task support is being provided by the University of Alabama, Sargent and Lundy, and Carbonvert.

program area:
Carbon Dioxide Removal

ending scale:
FEED

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Integration of DAC with Nuclear Power Plant

participant:
Battelle Memorial Institute

project number:
FE0032160

NETL project manager:
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partners:
AirCapture LLC; Southern Company; University of Alabama; Sargent and Lundy; Carbonvert

start date:
09.01.2022

percent complete:
90%

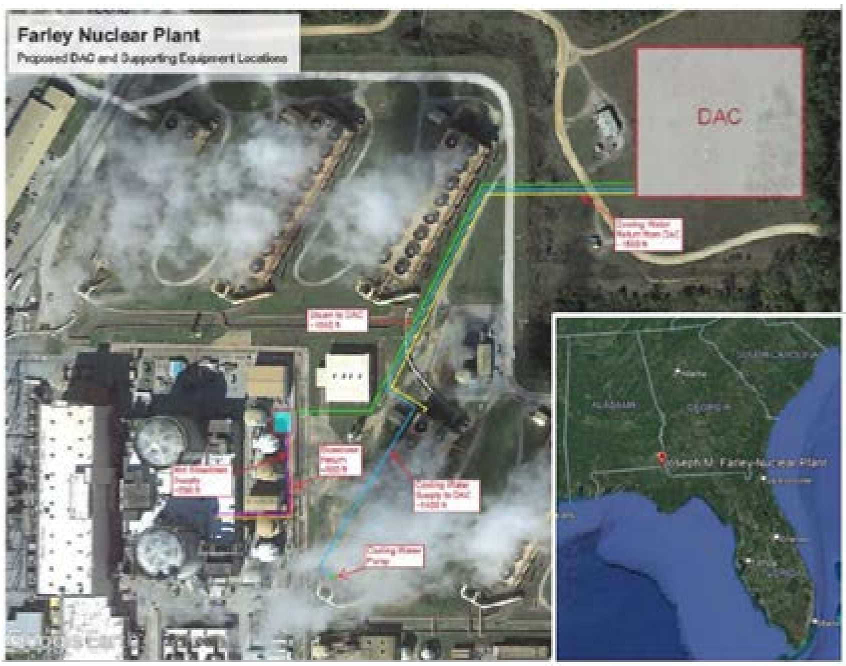


Figure 1: Satellite image of the Farley Nuclear Plant, including proposed locations for DAC site and key resources onsite. Inset: Geographic location of the Farley Nuclear Plant, the proposed host site for this project.

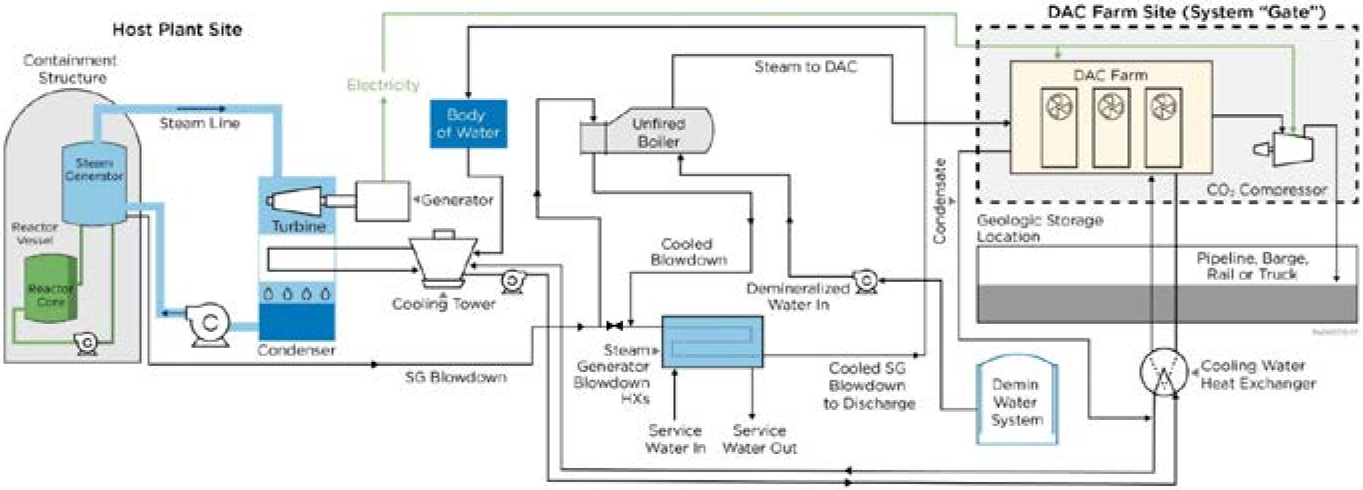
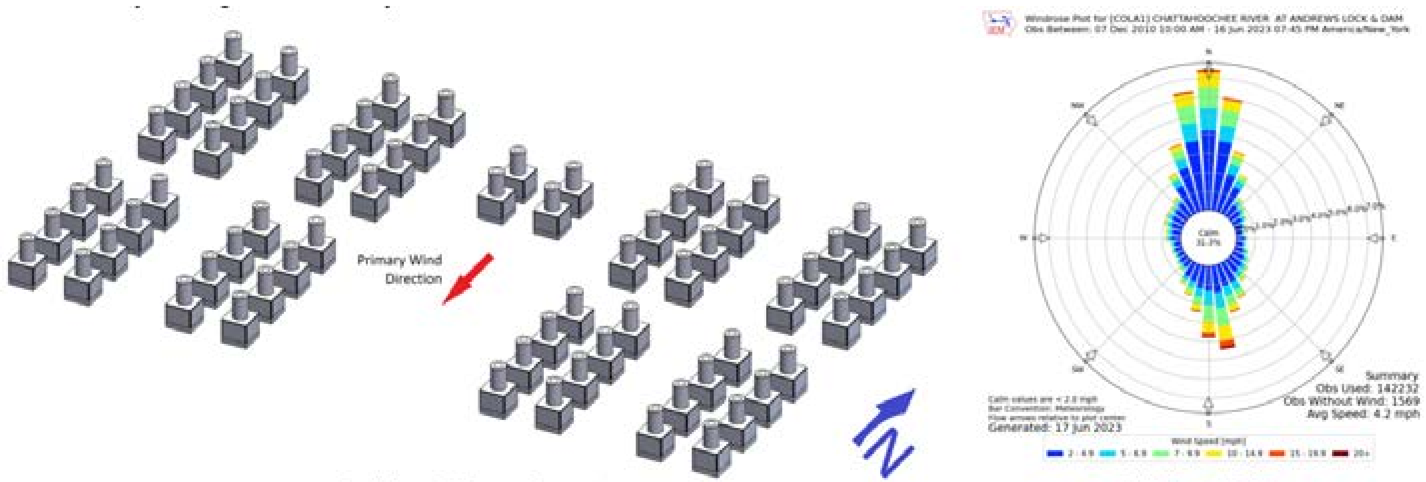


Figure 2: Overview of the integrated process, including critical inputs and outputs from the nuclear plant, the DAC farm site, product transportation and the proposed final storage location.

An overview of the process is shown in Figure 2. Air flows into a DAC process previously designed by AirCapture LLC, incorporating Global Thermostat's monolithic contactors with polymeric sorbents. This DAC system is designed to be modular and scalable, and it has demonstrated successful performance at the National Carbon Capture Center in Wilsonville, Alabama. A diagram of a preliminary DAC layout concept based on optimal wind direction is shown in Figure 3. The absorption step occurs when CO_2 is collected by moving air across the contactor, which takes approximately 900 seconds. To regenerate, the contactor is moved into a regeneration box where low-temperature steam flows across the contactor for approximately 90 seconds, removing CO_2 from the contactor, which is then collected for subsequent steps. The sorbent is regenerated using waste heat from the nuclear plant. The waste heat comes from the heated blowdown water, from which a portion is siphoned off to a heat exchanger in the DAC process that releases the CO_2 in a concentrated form. The cooled water is then returned back to the nearby water basin that serves as the source of blowdown water for the nuclear plant. The plant also provides carbon-free electricity for the DAC farm operation and for the compression step to prepare the CO_2 stream for transport by pipeline, railcar or barge to potential geologic storage locations.



Preliminary DAC Layout Concept

Preliminary Wind Data

Figure 3: Left: Preliminary DAC layout of modular systems at the proposed host site for optimal performance based on expected wind direction. Right: Windrose plot showing predominant north wind direction at the proposed project site.

The focus of this project is completion of a FEED study with cost estimate to evaluate feasibility of this DAC process in an integrated plant setting. These results are supported by the completion of a techno-economic analysis (TEA), LCA and BCA for the overall feasibility of the process. The project will leverage the results of the FEED study to quantify how deployment of the technology will promote and prepare a ready workforce for clean energy and manufacturing jobs and coordinate with community stakeholders to perform an environmental justice analysis and a preliminary economic revitalization and job creation outcomes analysis. The expected benefit of this project is to better understand system costs and performance specific to this process, as well as the business case options for the integration of DAC technologies with an existing industrial facility to remove CO_2 permanently from the atmosphere.

Results to date have produced important learnings from this study. An initial site visit provided crucial insight that was factored into the refined design of the integrated DAC system. Optimization of available resources (heat source, available land, cooling, etc.) is key to enabling the largest possible DAC capacity. There is high importance in developing infrastructure/equipment outside of restricted site areas in order to minimize impact to Farley operations and reduce project schedule risk. Pipeline transportation proved to be the most effective way of reaching potential CO_2 storage destinations, but other projects may have to consider shipping by barge, rail or truck if they cannot tap into a pipeline transport network. These types of smaller installations could be enabled by investments in common transport and injection infrastructure. Overall, the integration of DAC with a nuclear power plant has advantages due to the availability of low-carbon power, heat and cooling water.

technology advantages

- The DAC technology from Global Thermostat provides a monolith adsorbent that has been rigorously developed to ensure low pressure drop, low thermal mass, high geometric surface area, and compatibility with a variety of construction methods.
- The integration of the DAC system with existing operating infrastructure provides industrial waste heat for regeneration, as well as low-carbon power and cooling water, allowing for lowered costs of CO_2 removal for permanent storage.

R&D challenges

- Integration with an existing industrial plant for waste heat use and optimization of the process to achieve economically viable DAC operation.
- Securing the most economical offtake options for the removed CO_2 stream, and accounting for life cycle emissions across the entire chain of integrated systems from inputs to securely stored product CO_2.

status

Most of the tasks initially outlined for this project have been completed. Key deliverables, including LCA, EH&S risk analysis, Technology Maturation Plan, and BCA for the final FEED results, are in progress.

available reports/technical papers/presentations

Webster, B. et al., 2024, "Nuclear Direct Air Capture with Carbon Storage (NuDACCS)." *2024 NETL/FECM Carbon Management Project Review Meeting.* Battelle Memorial Institute. August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_CDR_7_Webster.pdf*.

Webster, B. et al., 2023, "Nuclear Direct Air Capture with Carbon Storage (NuDACCS)." *2023 NETL/FECM Carbon Management Project Review Meeting.* Battelle Memorial Institute. August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_CDR31_Webster.pdf*.

Young, M. et al., 2022, "Nuclear Direct Air Capture with Carbon Storage (NuDACCS)." *Project Kickoff Meeting*. Battelle Memorial Institute. December 2022. *https://netl.doe.gov/projects/files/Nuclear%20Direct%20Air%20Capture%20with%20Carbon%20Storage%20(NuDACCS).pdf*.

FEED Study of CarbonCapture Inc. DAC and CarbonCure Utilization Technologies Using U.S. Steel's Gary Works Plant Waste Heat

primary project goal

The University of Illinois worked with Visage Energy, CarbonCapture Inc., Ecotek Engineering, U.S. Steel Corporation, Ozinga and CarbonCure Technologies to perform a front-end engineering design (FEED) study on direct air capture (DAC) integrated with heating from an industrial plant. The project utilized CarbonCapture Inc.'s established sorbent-based DAC system to capture carbon dioxide (CO_2) from air using waste heat from U.S. Steel's Gary Works plant. The captured CO_2 is incorporated into concrete for permanent storage as a value-added product.

technical goals

- Establish feasibility of integration and operation of a DAC system powered by waste heat from the Gary Works steel plant, capable of capturing 5,000 tonnes CO_2/year.
- Demonstrate feasibility of offtake approach for the integrated DAC system using CO_2-loaded concrete as a value-added product, including transport logistics.
- Complete preliminary engineering and design work to support developing a detailed cost estimate for the integrated geothermal DAC process.
- Perform analyses for life cycle emissions, environmental justice and workforce readiness evaluation.

technical content

The project's main goal was to determine the feasibility of integration of an established DAC sorbent process with an existing steel plant in Gary, Indiana, capable of providing waste heat for sorbent regeneration to produce CO_2 for utilization in concrete. The plant was chosen for its quality and quantity of waste heat as well as its proximity to offtake options through cement plants in the region. The project was led by the University of Illinois using DAC technology developed by CarbonCapture Inc. The steel plant providing the waste heat for generation is owned by U.S. Steel, and the concrete plants where the CO_2 can be ultimately utilized are owned by Ozinga, who are all considered partners on this project.

program area:
Carbon Dioxide Removal

ending scale:
FEED

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Integration of DAC with Waste Heat from Steel Plant for Concrete Production

participant:
University of Illinois

project number:
FE0032154

NETL project manager:
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principal investigator:
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University of Illinois
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partners:
Visage Energy; CarbonCapture Inc.; Ecotek Engineering; U.S. Steel Corporation; Ozinga; CarbonCure Technologies

start date:
10.01.2022

percent complete:
100%

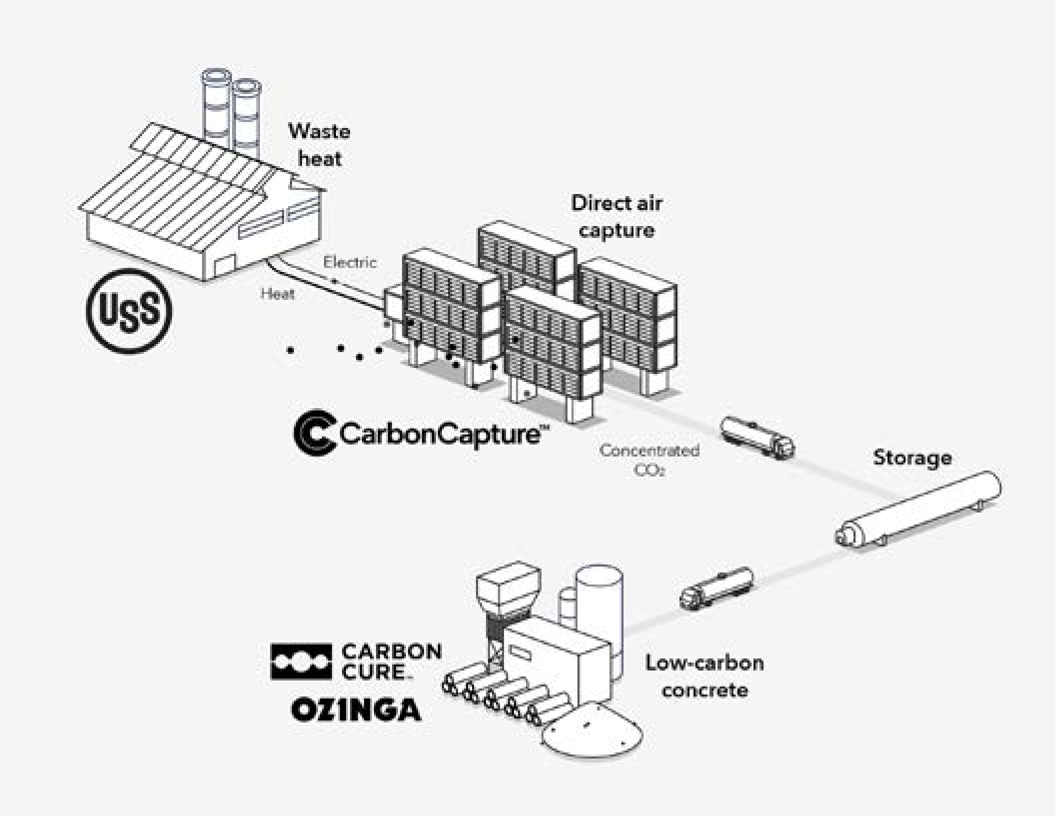

Figure 1: Overview of the integrated process, including waste heat and electricity from the Gary Works plant, DAC system installed at the same site, storage and transportation, and final utilization in low-carbon concrete products.

The overview of the process is shown in Figure 1. The process uses CarbonCapture's DAC technology, for which the core system is a modular temperature vacuum swing adsorption system capable of accepting multiple types of solid sorbents. The preferred sorbent type is an amine in a hydrophobic structure with high CO_2 adsorption capacity and robust cyclability. The typical desorption temperatures required for this type of sorbent are around 100°C, making it amenable to the use of waste heat from a steel facility, like the one at the Gary Works plant. This plant also provides electricity as needed for the DAC system. The modular DAC units are designed to be capable of combining into larger clusters of modular units that work in tandem and allow for appropriate sizing based on resources available and downstream product demand. Material balances for the process have been completed, while some facets of pricing are still being determined to provide the most accurate cost estimates for the total system. Much of the plant buildings have been digitally designed with appropriate piping and instrumentation diagrams (P&ID) established. The DAC system is located onsite with the steel plant and can produce sufficiently high-purity CO_2 for subsequent utilization.

Figure 2: Locations of proposed DAC site, nearby CO_2 storage locations, and cement plants owned by partnering organization.

The plant's location is ideal for partnership with Ozinga, which owns a fleet of cement plants in the region where CO_2 can be utilized, as shown in Figure 2. The CO_2 from the DAC system is trucked to one of two nearby storage locations, from which it can then be trucked to one of Ozinga's cement plants using Ozinga trucks fueled by renewable natural gas, which is considered in the LCA of the overall process. Concrete is considered as a desirable offtake option based on previous literature, which indicated significant CO_2 reduction is possible by curing concrete with captured CO_2. CarbonCure has developed a technology capable of being retrofitted into existing concrete production plants, which can utilize CO_2 in the production of ready-mix concrete. As shown in Figure 3, the use of this carbonization technology can reduce cement needs by more than 3% using the reclaimed water process technology, which decreases the high greenhouse gas (GHG) emissions from the cement production process. This can result in net-negative emissions for the entire process by both the removal of CO_2 from air and the decrease in emissions at the cement plant by use of the captured CO_2. Finalized estimates on the impact on GHG emissions are provided in the project's LCA. Community

Benefits Plans (CBPs) have been fleshed out through environmental justice analysis and stakeholder outreach.

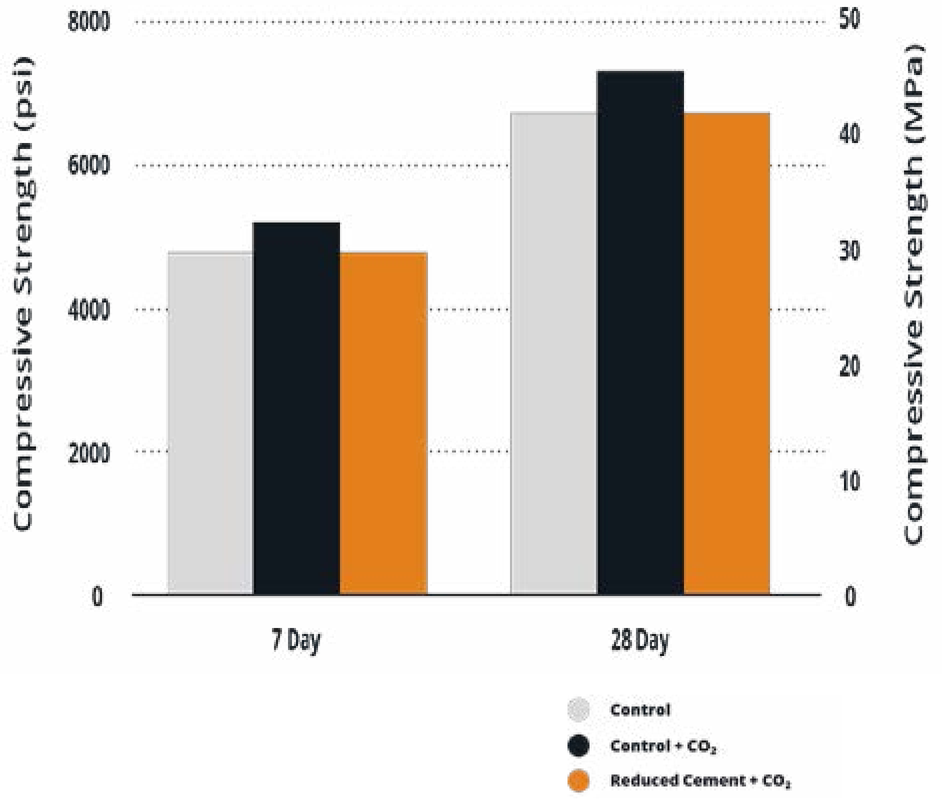

Figure 3: Materials performance test results from cement with incorporated CO_2.

technology advantages

- The DAC technology from CarbonCapture Inc. is a modular temperature vacuum swing adsorption system capable of accepting multiple types of solid sorbents, with desorption temperatures low enough to utilize sources of waste heat.
- Addition of produced CO_2 with concrete using CarbonCure's process provides an improved concrete product, a reliable market, and a decrease in net emissions for the concrete itself through decreased material use.

R&D challenges

- Accounting for life cycle emissions across the entire chain of integrated systems from inputs to final products.
- Integration with an existing industrial plant for waste heat use and optimization of the process in order to achieve economically viable DAC operation.

status

The project was completed on September 30, 2024. Deliverables that were submitted for the FEED study included a TMP, a hazard and operability analysis (HAZOP), final detailed design of the DAC system, cost estimates, constructability, LCA, BCA and EH&S reviews, a CBP, and a workforce Readiness plan.

available reports/technical papers/presentations

Gioja, L. et al., 2024, "FEED Study of Carbon Capture Inc DAC and CarbonCure Utilization Technologies Using United States Steel's Gary Works Plant Waste Heat." *Project Closeout Meeting.* September 2024.

https://netl.doe.gov/projects/files/FEED%20Study%20of%20CarbonCapture%20Inc.%20DAC%20and%20CarbonCure%20Utilization%20Technologies%20Using%20United%20States%20Steel%e2%80%99s%20Gary%20Works%20Plant%20Waste%20Heat.pptx.

Gioja, L. et al., 2024, "FEED Study of Carbon Capture Inc DAC and CarbonCure Utilization Technologies Using United States Steel's Gary Works Plant Waste Heat." *2024 FECM/NETL Carbon Management Project Review Meeting.* University of Illinois. August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_CDR_7_Gioja.pdf*.

Gioja, L. et al., 2023, "FEED Study of Carbon Capture Inc DAC and CarbonCure Utilization Technologies Using United States Steel's Gary Works Plant Waste Heat." *NETL Project Technical Presentation.* University of Illinois. December 2023. *https://netl.doe.gov/projects/files/FEED%20Study%20of%20Carbon%20Capture%20Inc%20DAC%20and%20CarbonCure%20Utilization%20Technologies%20Using%20United%20States%20Steel%e2%80%99s%20Gary%20Works%20Plant%20Waste%20Heat.pptx*.

Gioja, L. et al., 2023, "FEED Study of Carbon Capture Inc DAC and CarbonCure Utilization Technologies Using United States Steel's Gary Works Plant Waste Heat." *DOE/NETL 2023 Carbon Management Project Review Meeting*. University of Illinois. *https://netl.doe.gov/sites/default/files/netl-file/23CM_CDR30_Gioja.pdf*.

O'Brien, K. et al., 2022, "FEED Study of Carbon Capture Inc DAC and CarbonCure Utilization Technologies Using United States Steel's Gary Works Plant Waste Heat." *Project Kickoff Meeting*. University of Illinois. December 2022. *https://netl.doe.gov/projects/files/FEED%20Study%20of%20Carbon%20Capture%20Inc%20DAC%20and%20CarbonCure%20Utilization%20Technologies%20Using%20United%20States%20Steel%e2%80%99s%20Gary%20Works%20Plant%20Waste%20Heat.pptx*.

O'Brien, K. et al., 2022, "FEED Study of Carbon Capture Inc DAC and CarbonCure Utilization Technologies Using United States Steel's Gary Works Plant Waste Heat." *DOE/NETL 2022 Carbon Management Project Review Meeting*. University of Illinois. *https://netl.doe.gov/sites/default/files/netl-file/22CM_CDR17_OBrien_2.pdf*.

Low Carbon Intensity Formic Acid Chemical Synthesis from Direct Air Captured CO_2 Utilizing Chemical Plant Waste Heat (ChemFADAC)

primary project goal

Aircapture LLC, in partnership with OCOChem Inc. and the University of Alabama, prepared a front-end engineering design (FEED) study for an integrated direct air capture (DAC) and carbon conversion system, co-located at a Nutrien nitric acid production facility in Kennewick, Washington. The designed process is capable of capturing and converting a minimum of 5,000 tonnes/year net atmospheric carbon dioxide (CO_2) to low-carbon intensity formic acid using industrial waste heat and renewable electricity. The project aimed to better understand system costs and performance specific to this process, as well as the business case options for the integration of DAC technologies with an existing industrial facility to produce low-carbon products.

technical goals

- Conduct FEED study with Class 3 project cost estimate to evaluate feasibility of DAC conversion process using industrial waste heat from host site and renewable electricity.
- Perform a life cycle analysis (LCA) from the results of the FEED study, followed by business case analysis (BCA) based on results of the LCA, FEED study and cost estimate.
- Quantify socio-economic impact through environmental justice, economic revitalization, and job outcomes analysis.

technical content

The project's main goal was to determine the feasibility of integration of an established DAC sorbent process with an existing fertilizer production plant in Kennesaw, Washington, capable of providing waste heat for sorbent regeneration to capture CO_2 and convert it efficiently to chemicals, as shown in Figure 1. The Nutrien nitric acid production facility was chosen for its availability of waste heat and water resources, as well as its location for transport options following chemical production. The project was led by Aircapture LLC, using DAC materials developed by Global Thermostat. The fertilizer production plant providing the waste heat for generation is owned by Nutrien. The electrolyzer production was performed by OCOChem, and analysis task support provided by the University of Alabama, both of whom were subprime performers on this project.

program area:
Carbon Dioxide Removal

ending scale:
FEED

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Integration of DAC with Industrial Waste Heat to form Low-Carbon Products

participant:
Aircapture LLC

project number:
FE0032157

NETL project manager:
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partners:
University of Alabama; OCOChem; Nutrien

start date:
09.15.2022

percent complete:
100%

Figure 1: Location of Nutrien's Kennesaw Fertilizer Operations, the proposed host site for this project.

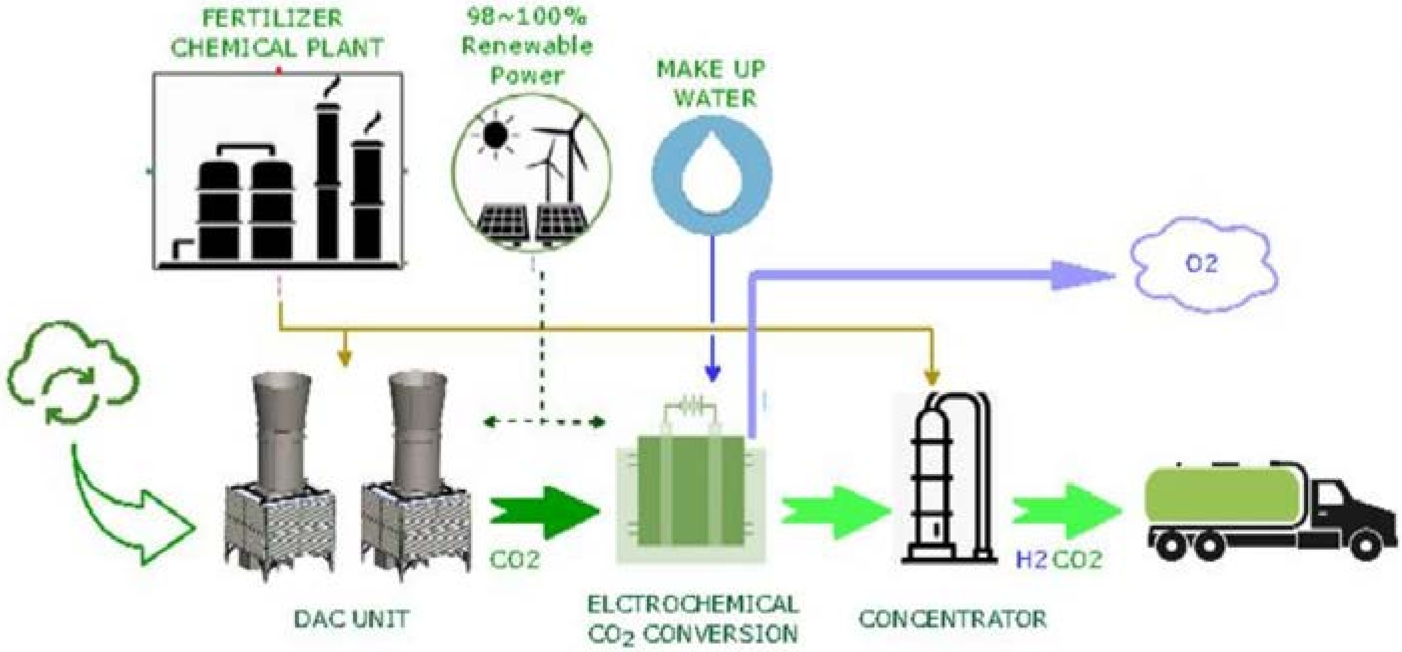

Figure 2: Overview of the integrated process, including critical inputs and outputs, the DAC step, conversion and processing, and final delivery of products.

An overview of the process is shown in Figure 2. Air flows into a DAC system that incorporates a monolithic contactor with polymeric sorbent contactors. This DAC system is designed to be modular and scalable, and it has demonstrated successful performance at the National Carbon Capture Center in Wilsonville, Alabama. The adsorption step occurs when CO_2 is collected by moving air across the contactor, which takes about 900 seconds. To regenerate, the contactor is moved into a regeneration box where low-temperature steam flows across the contactor for about 90 seconds, removing CO_2 from the contactor, which is then collected for subsequent steps.

The carbon conversion reaction takes place in the electrochemical conversion unit, displayed in Figure 3. The concentrated stream of CO_2 at more than 95% purity and less than 100 parts per million (ppm) oxygen is combined with a small amount of water in the formate electrolyzer, which is powered by 98–100% renewable electricity. At the cathode, formate ions are produced from the reaction of CO_2 with hydronium ions, while the anode regenerates hydronium ions and produces small amounts of oxygen gas as a byproduct. The formate ions enter the membrane-based electrodialysis unit where greater than 30% formic acid is produced. This stream then undergoes extractive distillation to produce formic acid with up to 85% purity for sale as product. The process has several advantages over conventional formic acid production, including:

- Operates at ambient pressure and temperature, rather than 80°C and 4.5 MPa.
- Net-negative consumption of -0.809 ton of CO_2 per 1 ton of formic acid produced, rather than generating 7.3 tons of CO_2 via traditional formic acid processes.
- Only three stages of reaction and separation, as opposed to eight stages of operation.
- 30% lower cost of production versus thermochemical production.

Following its concentration to product-level purity onsite, the formic can be ready for sale as a product. The overall process utilizes 100% of the waste heat available from the fertilizer plant and 98–100% renewable energy, with minimal make-up water requirements.

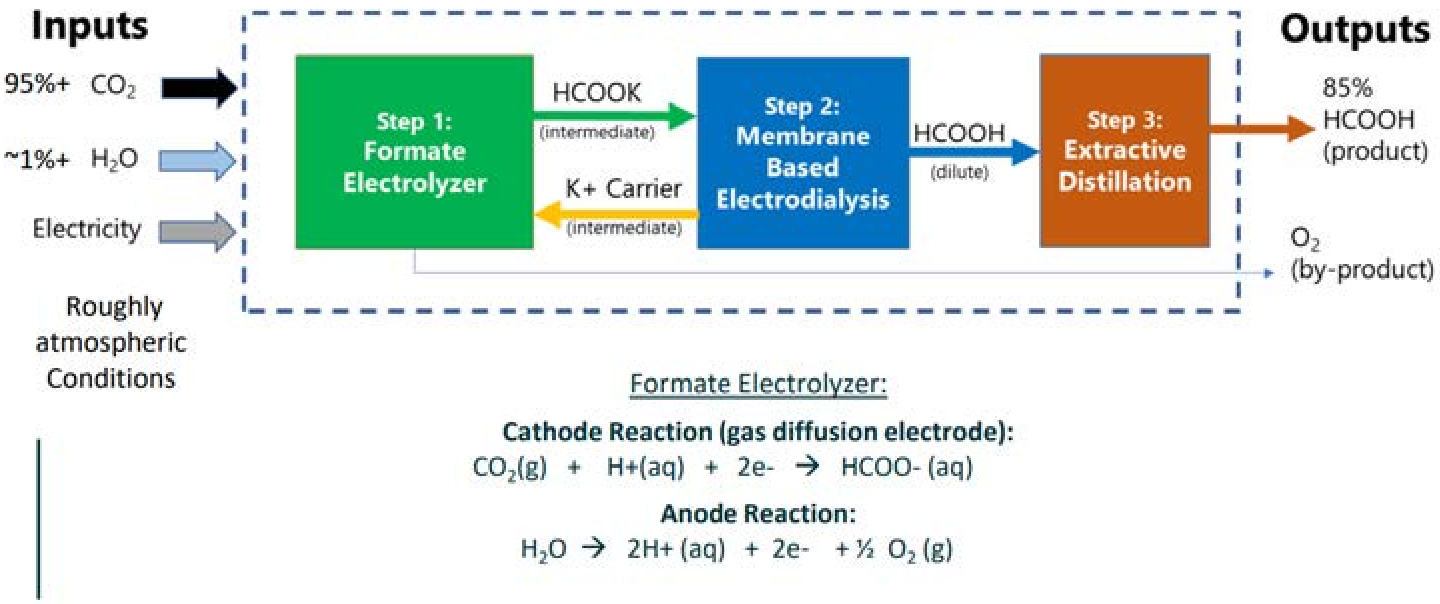

Figure 3: Overview of the inputs and outputs, main steps, and reaction mechanisms of the ChemFADAC process.

The focus of this project was completion of a FEED study with Class 3 project cost estimate to evaluate feasibility of this DAC and conversion process in an integrated plant setting. These results are supported by the completion of a techno-economic analysis (TEA), LCA and BCA for the overall feasibility of this process. The project leveraged the results of the FEED study to quantify how deployment of the technology will promote and prepare a ready workforce for clean energy and manufacturing jobs and coordinate with community stakeholders to perform an environmental justice analysis and a preliminary economic revitalization and job creation outcomes analysis. A benefit of this project was to better understand system costs and performance specific to this process, as well as the business case options for the integration of DAC technologies with an existing industrial facility to produce low-carbon products.

technology advantages

- The DAC technology from Global Thermostat provides a monolith adsorber that has been rigorously developed to ensure low pressure drop, low thermal mass, high geometric surface area, and compatibility with a variety of construction methods.
- The integration of the ChemFADAC system with existing infrastructure provides industrial waste heat for regeneration, allowing for production of chemicals for hard-to-abate sectors of the industry.

R&D challenges

- Accounting for life cycle emissions across the entire chain of integrated systems from inputs to final products.
- Integration with an existing industrial plant for waste heat use.
- Optimization of the process to achieve economically viable DAC operation.

status

The project was completed on September 14, 2024. The finalized FEED package included a Class 3 cost estimate for a process producing a low carbon intensity product from DAC utilizing waste heat from an industrial site. The LCA showed a net negative 84.6% reduction of CO_2e making this an attractive sustainable process to produce formic acid going forward compared to traditional formic acid processes. A BCA and environmental justice analysis were also completed.

available reports/technical papers/presentations

Atwood, M. et al., 2024 "Low Carbon Intensity Formic Acid Chemical Synthesis from Direct Air Captured CO_2 Utilizing Chemical Plant Waste Heat (ChemFADAC)." *2024 NETL/FECM Carbon Management Project Review Meeting.* Aircapture LLC. August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_CDR_7_Louwagie.pdf*.

Atwood, M. et al., 2023, "Low Carbon Intensity Formic Acid Chemical Synthesis from Direct Air Captured CO_2 Utilizing Chemical Plant Waste Heat (ChemFADAC)." *2023 NETL/FECM Carbon Management Project Review Meeting.* Aircapture LLC. *https://netl.doe.gov/sites/default/files/netl-file/23CM_CDR30_Louwagie.pdf*.

Atwood, M. et al., 2022, "Low Carbon Intensity Formic Acid Chemical Synthesis from Direct Air Captured CO_2 Utilizing Chemical Plant Waste Heat (ChemFADAC)." *Project Kickoff Meeting*. Aircapture LLC.

Scale-Up and Site-Specific Engineering Design for Global Thermostat Direct Air Capture Technology

primary project goal

Black & Veatch Corporation partnered with Global Thermostat (GT), Sargent & Lundy, ExxonMobil Research and Engineering, Southern Company Services, and Elysian Ventures LLC to execute an initial engineering design of a commercial-scale carbon capture, utilization, and storage direct air capture (CCUS-DAC) system that captures at least 100,000 net tonnes/year of carbon dioxide (CO_2) from the atmosphere. The lead system consists of a DAC unit utilizing GT's sorbent contactor technology coupled with a natural gas-fired combined heat and power (CHP) plant, with the effluent CO_2 in the CHP unit flue gas captured by a packaged post-combustion capture system using liquid amines.

technical goals

- Complete the baseline design of the commercial-scale DAC unit that captures CO_2 from the air, and the associated natural gas-fed CHP unit with packaged amine capture system, for a *net* removal of 100,000 tonnes of CO_2 per year from the atmosphere.
- Conduct site-specific studies for three proposed plant site locations: Odessa, Texas; Bucks, Alabama; and Goose Creek, Illinois.
- Conduct a comparative study of a CHP combined cycle power plant when outfitted with a DAC+ system versus the same plant with a post-combustion carbon capture system supported by a conventional DAC unit for at least one of the potential host sites.
- Develop a techno-economic analysis (TEA); life cycle analysis (LCA); and environmental, health, and safety (EH&S) analysis to compare the cost, emissions, and performance metrics between all three proposed site locations.

technical content

The project utilized a polymer-based adsorbent system developed by GT in 2009. The process container for the GT kilotonne-scale system, displayed in Figure 1, uses a temperature-vacuum swing adsorption (TVSA) regeneration cycle to remove CO_2 from both the air and flue gas. Steam was used as a direct phase-change heat transfer fluid to remove the CO_2 from the adsorbent. The proprietary adsorbent material uses a honeycomb geometry, which has been experimentally verified to have a very low pressure drop, helping to minimize energy cost. In this project, the kilotonne-scale system capacity was increased. The system was designed with cascading modularity: each module ring is about 120 feet in

program area:
Carbon Dioxide Removal

ending scale:
pre-FEED

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Sorbent-Based DAC System Integrated with Combined Heat and Power (CHP) Plant

participant:
Black & Veatch

project number:
FE0032101

predecessor projects:
N/A

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partners:
Global Thermostat; Sargent & Lundy; Southern Company; Elysian Ventures; ExxonMobil

start date:
10/01/2021

percent complete:
100%

diameter, with a four-pack of modules oriented around a shared process area. The four-packs were then numbered up to take advantage of centralized utilities and CO_2 compression.

Figure 1: Global Thermostat's kilotonne-scale DAC system as built in Colorado. The larger project module utilizes the same materials, process, and mechanical design as this functional unit.

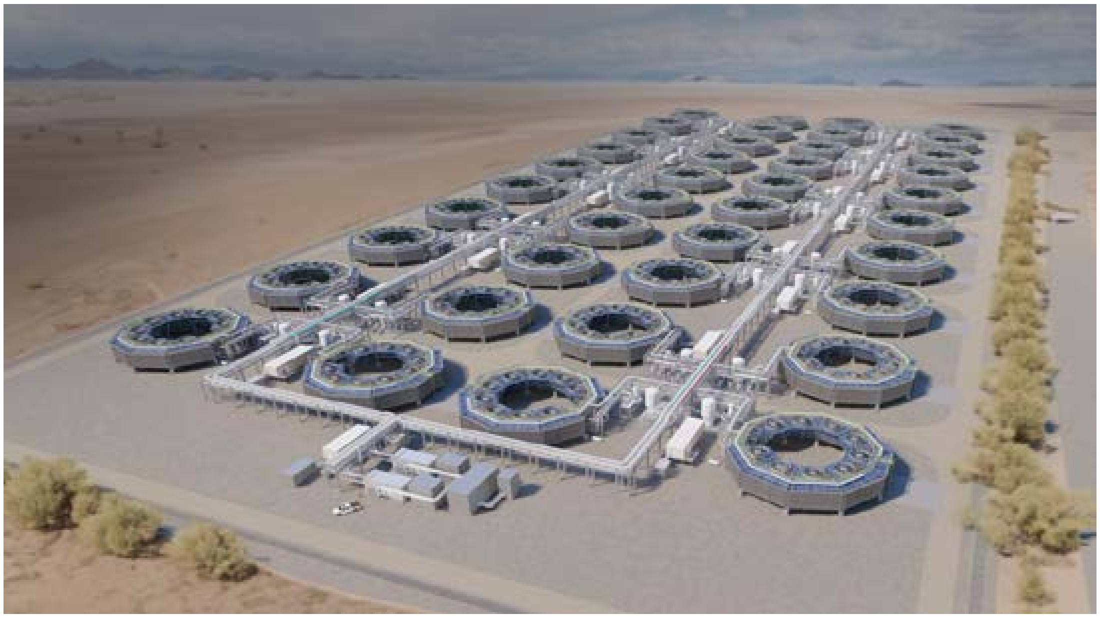

Figure 2: Rendering of ten four-packs of DAC modules

The proprietary adsorbent material's known properties and the operating parameters of the adsorption-regeneration system are shown in Table 1. The TVSA system works by manipulating the temperature and pressure of the adsorbent material in order to change the adsorptivity of the material to prioritize either adsorption or desorption at the right time, selectively removing CO_2 from the feed gas or releasing the CO_2 in order to transport it to the storage site.

A number of modules were installed at three specifically chosen locations in the continental United States: one in Odessa, Texas (warm, dry climate); one in Bucks, Alabama (warm, wet climate); and one in Goose Creek, Illinois (temperate climate). Each site's proposed plant design will utilize a natural gas-fired CHP plant to provide the energy to run the DAC unit. The resulting combined system was designed to capture more than 100,000 tonnes of CO_2 from the atmosphere (*after* accounting for the CO_2 produced by the CHP plant).

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Project Value**
True Density @ STP	kg/m^3	2,300
Bulk Density	kg/m^3	500
Average Particle Diameter	mm	0.23
Particle Void Fraction	m^3/m^3	0.78
Packing Density	m^2/m^3	1,800
Solid Heat Capacity @ STP	kJ/kg-K	0.81
Crush Strength	kg_f	4
Thermal Conductivity	W/(m-K)	0.4
Adsorption		
Pressure	bar	1.0
Temperature	°C	25
Equilibrium Loading	g mol CO_2/kg	2.5
Heat of Adsorption	kJ/mol CO_2	85-95
CO_2 Adsorption Kinetics	mol/kg-min	0.043
Desorption		
Pressure	bar	1.0
Temperature	°C	100
Equilibrium CO_2 Loading	g mol CO_2/kg	<0.05
Heat of Desorption	kJ/mol CO_2	85-95
CO_2 Desorption Kinetics	mol/kg-min	0.3
Proposed Module Design		
Flow Arrangement/Operation	—	Honeycomb Monolith
Air Feed Approach Velocity	m/sec	5
Space Velocity	hr^{-1}	120
Volumetric Productivity	$mol_{CO2}/(hr\text{-}kg_{sorbent})$	2.7
CO_2 Recovery, Purity, and Pressure	% / % / bar	50/95/1.0
Adsorber Pressure Drop	bar	0.002
Degradation	% capacity fade/yr	5%

**Development in materials properties is prohibited within this project area of interest (AOI) and therefore project-derived changes to these numbers is out of scope and not anticipated.

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

A complete TEA and LCA is being performed as a part of this study. Preliminary capture cost estimates for the DAC paired with CHP, post-combustion CO_2 capture, and compression facilities are shown in Table 2.

TABLE 2: DAC ECONOMICS

Economic Values	Units	Target Project Value
Cost of Carbon Captured	\$/tonne CO_2	90-150
Cost of Carbon Captured (Net Removal Basis)	\$/tonne CO_2	130-240
Capital Expenditures (annualized at 10%)	\$/tonne (net)	70-130
Operating Expenditures	\$/tonne (net)	60-110

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Captured (Net Removal Basis) – Projected cost of capture per mass of CO_2 under expected operating conditions for net removal from the atmosphere.

Capital Expenditures – Projected capital expenditures (CAPEX) in dollars per tonne on a net removal basis. Cost estimates use annualized values at 10% of CAPEX.

Operating Expenditures – Projected operating expenditures in dollars per tonne on either a total or a net removal basis.

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – The Global Thermostat DAC system employs a solid-sorbent system.

Sorbent Contaminant Resistance – Airborne contamination is mitigated with filters.

Flue Gas Pretreatment Requirements – Not established yet.

Sorbent Make-Up Requirements – Replacement after capacity loss tolerance level exceeded.

Waste Streams Generated – Waste gases contain mostly water.

technology advantages

- Modular design.
- Enables carbon-negative fossil power generation and carbon-neutral synthetic fuels.
- Low pressure drops.
- Future-proof—different adsorbent materials can be slotted into the units, allowing future generations of adsorbents to be used with the design to reduce cost of future upgrades.
- High selectivity—can capture CO_2 at incoming concentrations as low as 400 parts per million (ppm).

R&D challenges

- Integrating DAC system with commercial host sites.
- Completing the detailed TEA and LCA for all three sites.

status

The project was completed on June 30, 2024. The baseline DAC module design was successfully completed. The design parameters for the Alabama site were successfully characterized and modifications of the initial engineering design of the DAC system for the other two sites were completed. An LCA, TEA, benefit-cost analysis (BCA), and EH&S assessment were completed and are in included in the final report.

available reports/technical papers/presentations

Steutermann, M. and Ping, E., 2023, "Scaleup and Site-Specific Engineering Design for Air Capture Technology." Final Technical Report. Pittsburgh, PA. October 2024. *https://www.osti.gov/servlets/purl/2468628/*.

Steutermann, M. and Ping, E., 2023, "Scaleup and Site-Specific Engineering Design for Air Capture Technology." Project Closeout Meeting. Pittsburgh, PA. June 2024. *https://netl.doe.gov/projects/files/Scaleup%20and%20Site-Specific%20Engineering%20Design%20for%20Global%20Thermostat%20Direct%20Air%20Capture%20Technology.pdf*.

Steutermann, M. and Ping, E., 2023, "Scaleup and Site-Specific Engineering Design for Air Capture Technology." Presented at the 2023 NETL/FECM Carbon Management Research Project Review Meeting. Pittsburgh, PA. August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_CDR31_Steutermann.pdf*.

Steutermann, M. and Ping, E., 2023, "Scaleup and Site-Specific Engineering Design for Air Capture Technology." Presented at the 2022 NETL/FECM Carbon Management Research Project Review Meeting. Pittsburgh, PA. August 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_CDR17_Steutermann.pdf*.

Steutermann, M., "Scaleup and Site-Specific Engineering Design for Global Thermostat Direct Air Capture Technology." Project Kickoff Meeting. Pittsburgh, PA. December 2021. *https://netl.doe.gov/projects/plp-download.aspx?id=12682&filename=Scaleup+and+Site-Specific+Engineering+Design+for+Global+Thermostat+Direct+Air+Capture+Technology.pptx*.

Spatiotemporal Adaptive Passive Direct Air Capture

primary project goal

Carbon Collect Inc., along with the Electric Power Research Institute (EPRI), Arizona State University (ASU), Trimeric Corporation, and PM Group, performed an initial design of a commercial-scale, passive direct air capture (DAC) system termed "Carbon Trees" to capture, separate, and store or utilize a nominal capacity of 1,000 tonnes per day of carbon dioxide (CO_2) from air.

technical goals

- Prepare an initial engineering design package for carbon farms based on the Carbon Tree technology at each of three geographically diverse host sites throughout the United States to better understand the effect of local/regional ambient conditions on DAC system performance and project costs.
- Complete a techno-economic analysis (TEA), life cycle analysis (LCA), business case analysis, and an environmental, health, and safety risk assessment for each of the three geographically diverse host sites.

technical content

Passive DAC is unique among DAC technologies in that passive air delivery by wind avoids the energy penalty of forced convection. The passive DAC Carbon Tree system includes a passive collector that absorbs wind-delivered CO_2 and an integrated regenerator that releases CO_2 into a confined chamber. During CO_2 collection, the leaves of the Carbon Tree take the form of large horizontal disks arranged in a vertical column over a cylindrical regeneration chamber. For sorbent regeneration, the column lowers into the chamber; a combination of steam, low-grade heat, and vacuum releases the CO_2, which is extracted from the chamber and then purified and compressed.

Uniquely, this system readily accommodates alternative hybrid cycles—temperature vacuum swing absorption (TVSA), moisture vacuum swing absorption (MVSA), moisture temperature vacuum swing absorption (MTVSA), and their associated alternate sorbents—such that the collector system is adaptable to broadly different climate conditions. This study will illustrate and emphasize this unique advantage, employing both TVSA and MTVSA cycles as appropriate for the three study sites. For both of these cycles, the collector effluent gas is a mixture of CO_2 and water (H_2O) with trace residual air. The collector effluent is compressed and purified to storage-ready specifications by a compression and purification unit (CPU). The CPU comprises conventional unit operations that are configured to recapture nearly 100% of heat and water for a nearly closed cycle integration with the collector and optimal energy efficiency. The Carbon Tree design represents a radical departure from other forced-air DAC systems. Instead of using fans and blowers to force air, the contactor in its fully open position (Figure 1, right) stands in the native wind to capture CO_2 directly

program area:
Carbon Dioxide Removal

ending scale:
pre-FEED

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Dynamic Performance of Passive "Carbon Tree" DAC Technology

participant:
Carbon Collect Inc.

project number:
FE0032097

predecessor projects:
N/A

NETL project manager:
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principal investigator:
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partners:
Arizona State University; Electric Power Research; Institute; PM Group; Trimeric Corporation

start date:
10.01.2021

percent complete:
100%

from passing ambient air onto leaf-like structures containing sorbent. The system's vertical column incorporates a stack of 150 1.5-decimeter (dm) disks that hang freely on straps, forming a 7.5-meter column above the regenerator chamber. Wind flows freely through gaps between these disks while about 30% of the CO_2 is fractionally skimmed from the air stream.

Figure 1: Carbon Tree in capture (right) and regeneration modes (left).

The disk frames shown in Figure 2 provide support structure to hold a variety of sorbent materials and form factors with high surface area exposure. For regeneration, the column is lowered into the regeneration chamber, collapsing the disk stack. The chamber is pre-evacuated to rough vacuum to remove bulk air contamination and heated with sub-atmospheric steam to between 40–100°C, releasing CO_2 at a vapor pressure of about 5 kPa. The MTVSA cycle uses steam principally as a sweep gas to carry liquid water droplets as an aerosol to the MTVSA sorbent. In both TVSA and MTVSA cycles, the steam increases the total pressure during regeneration to significantly reduce the vacuum requirement. Steam is then condensed from the regeneration effluent for energy recovery and bulk water removal. The remaining gas comprising CO_2 with residual water and air is subsequently compressed and purified in the CPU as described below.

Figure 2: Top head and disks of Carbon Tree.

Starting with a durable sorbent that has been demonstrated in outdoor operation for more than a year, the temperature tolerance of the sorbent was increased to take better advantage of the heat of condensation of the water used to deliver these sorbents. The current sorbent receives a substantial boost from the increase in moisture, but by raising the temperature, this project can reach even higher concentrations and forgo the moisture boost in humid climates. ASU and, more recently Carbon Collect Limited (CCL), have worked over the past 10 years to build a library of sorbents and form factors to allow the fine-tuning of the Carbon Tree system for geographically diverse host sites. Without major hardware changes, sorbent selection, and the application of heat, vacuum and moisture can be optimized (patents pending). Detailed thermodynamic analyses of the role of water and heat in these sorbents have been developed. An MVTSA commercial system will require less than 70 kJe/mol or 440 kWh per tonne of final product CO_2.

Feed-Gas Assumptions –

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	- °F	0.04	variable	78.09	20.95	0.93	trace	trace

technology advantages

- Passive DAC uses wind delivery of air which lowers operating expenses (OPEX).
- Reduction in capital expenditure (CAPEX) using economies of mass production of inexpensive modular equipment.

R&D challenges

- Optimizing collector to minimize temperature, thermal mass, and void space.
- Cycle optimization for efficient water and thermal energy recovery.
- The original approach applied to the San Joaquin Valley, California, site was a moisture swing system. MTVSA technology is best suited for hot and dry climates; however, seasonal variability in California changed the preferred technology selection to TVSA.

status

Trimeric completed the process design basis and initial development of the engineering design of the process. This project advances commercialization by providing the analysis tools for site-specific evaluation of the CO_2 capture potential; evaluating and developing a supply chain for the various components of the subsystems for the complete PDAC carbon tree system; and mapping out the future subsystem developments to further reduce energy demands, manufacturing costs, and overall capital costs for the n^{th}-scale PDAC system. The DAC systems are modular and have the potential for scale-up to millions of tonnes per year per site.

available reports/technical papers/presentations

Michael Austell, "Spatiotemporal Adaptive Passive Direct Air Capture," Project Closeout Meeting, Pittsburgh, PA, June 2024. *https://netl.doe.gov/projects/files/Spatiotemporal%20Adaptive%20Passive%20Direct%20Air%20Capture%20(SAPDAC).pdf*.

Michael Austell, "Spatiotemporal Adaptive Passive Direct Air Capture," 2023 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_CDR31_Austell.pdf*.

Mike Austell, "Spatiotemporal Adaptive Passive Direct Air Capture (SAPDAC)," 2022 Carbon Management Project Review Meeting, Pittsburgh, PA, August 2022. *https://netl.doe.gov/projects/files/Spatiotemporal%20Adaptive%20Passive%20Direct%20Air%20Capture%20(SAPDAC).pdf*.

Mike Austell, "Spatiotemporal Adaptive Passive Direct Air Capture," Project kickoff meeting presentation, Pittsburgh, PA, November 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=12348&filename=Spatiotemporal+Adaptive+Passive+Direct+Air+Capture.pdf*.

Direct Air Capture-Based Carbon Dioxide Removal with U.S. Low-Carbon Energy and Sinks

primary project goal

The University of Illinois Urbana-Champaign led a team to develop preliminary designs for large-scale direct air capture (DAC) systems that separate and permanently store 100,000 tonnes/year net carbon dioxide (CO_2) from the air at each of the three different facilities located in Wyoming, Louisiana, and California. The project examined the effects that various climatic conditions and different low-carbon energy sources (i.e., geothermal, solar, wind, or waste heat) would have on the DAC system design and the overall costs. Further, this work aimed to tackle scale-up challenges related to construction, operation, and logistics, as well as gauge the technical and regulatory challenges at each site.

Technical goals

- Perform an initial engineering design, techno-economic analysis (TEA), life cycle analysis (LCA), business case analysis, and an environmental health and safety (EH&S) analysis for a commercial-scale carbon capture and storage (CCS)-DAC system to capture 100,000 tonnes/year net CO_2 from the air for each site studied.
- Prepare a capital cost estimate (Class IV) for a CCS-DAC system for each of the host sites. Use the capital and operating costs to estimate a cost of capture.

Technical content

Climeworks' DAC systems capture atmospheric CO_2 by applying a cyclic vacuum-temperature swing adsorption and desorption process, described below and schematically illustrated in Figure 1.

Phase I (Adsorption): Air is drawn into the system using fans and the CO_2 within the air is chemically bound to the sorbent, a highly selective filter material, henceforth also referred to as "filter." Carbon-dioxide-depleted air is released back into the atmosphere.

Phase II (Desorption): Once the filter is saturated with CO_2, it is heated under vacuum to around 100°C using low-grade heat as an energy source. The CO_2 is then released from the filter and collected as a concentrated gas and the continuous cycle is ready to start again. The filter material lasts for several thousand cycles (i.e., several years).

The filter material is arranged in a patented adsorber structure (called "contactor") optimized for low pressure drop and high air flow rates in order to maximize CO_2 capture at the lowest fan electricity cost. These contactors are

program area:
Carbon Dioxide Removal

ending scale:
pre-FEED

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Scale-up of Climeworks' Sorbent-Based DAC Technology

participant:
University of Illinois Urbana-Champaign

project number:
FE0032100

predecessor projects:
N/A

NETL project manager:
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principal investigator:
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partners:
Climeworks; Kiewit; LLNL; Ormat; GCS; SunPower; NSE

start date:
10.01.2021

percent complete:
100%

contained inside so-called "CO_2 collectors," where the filter is exposed to ambient air in Phase I and where the CO_2 is subsequently extracted from the filter in Phase II, as shown schematically in Figure 1.

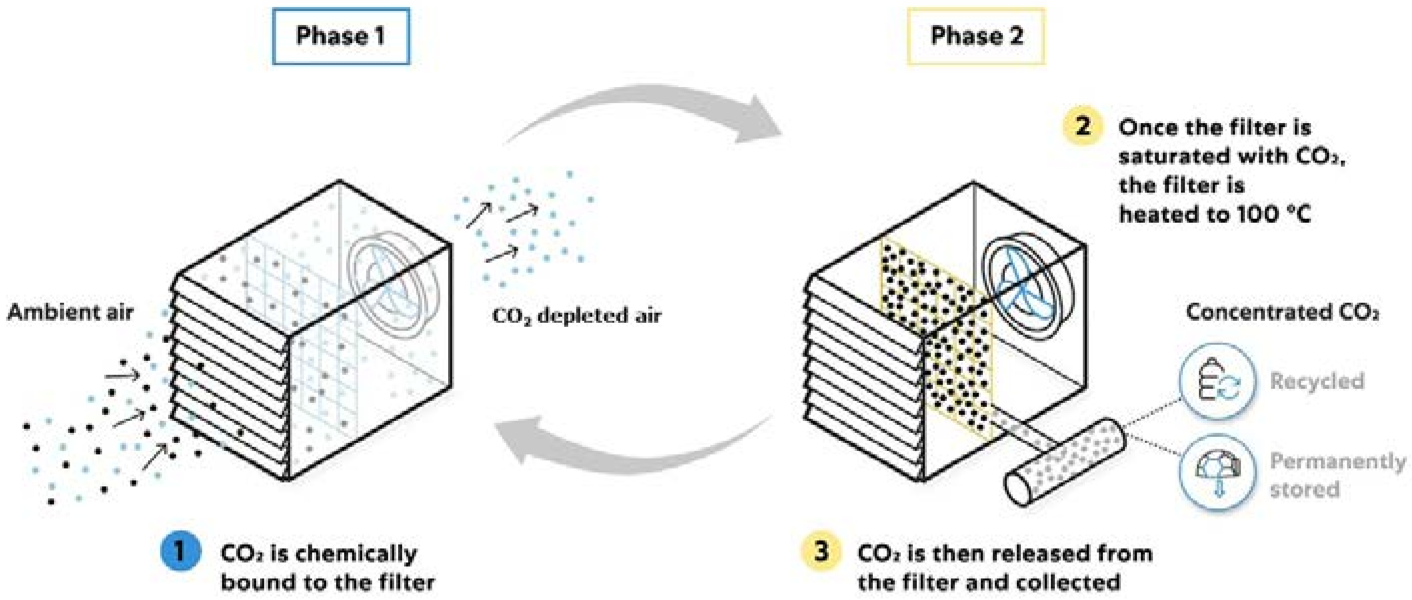

Figure 1: Working principle of Climeworks' DAC technology. Phase I produces CO_2-depleted air and binds the CO_2 on the filter. Phase II produces pure CO_2 and regenerates the sorbent.

Climeworks' technology has captured CO_2 from air at a pre-commercial scale for more than three years, at 24/7 operation, for a capacity of about 900 tonnes CO_2/year at Climeworks' Beta plant in Hinwil, Switzerland (Figure 2). Scale-up and further cost reductions are now the largest challenges for this technology to meet the increasing global demand for negative emissions. Currently, Climeworks has built the world's largest DAC facility (Orca plant, 4,000 tonnes CO_2/year, for storage) in Iceland, commissioned in September 2021.

	DAC only	DAC and geological storage for permanent CDR		
	Pre-commercial DAC plant ("Beta")	First CDR Pilot ("Arctic Fox")	First-of-a-kind demonstration ("Orca")	Commercial demonstration
Start of operation	2017	2017	2021	2025
CO_2 Collector design				
Arrangement of CO_2 Collectors	6 Collectors per container	1 Collector standalone	6 Collectors per container	1 Collector per container
Sealing of CO_2 Collectors	2 flaps per Collector	2 flaps per Collector	1 sliding door per container	1 sliding door per Table of containers
DAC Plant design				
Nominal CO_2 capacity of plant/per container [t/yr.]	900/300	50/50	4,000/500	100,000/750

Figure 2: Climeworks' development history.

Climeworks is advancing its scale-up roadmap to demonstrate large-scale commercial-size DAC at up to 100,000 tonnes CO_2/year with this project. In the current generation, the current cyclic adsorption/desorption technology generation is now mature; it has been optimized across collector geometry, adsorption settings, and desorption settings to result in a maximized output per DAC collector unit using current sorbent technology. The DAC collectors' modular nature and the flexibility of the integrated contactor structures ensure that future developments in sorbent technology can be easily integrated into existing hardware.

The case studies for this project represent different climatic conditions as well as a variety of environments for CO_2 storage from saline aquifers to depleted natural gas reservoirs for safe and permanent storage. Furthermore, the energy supply of the DAC plant differs in each case study and represents a broad variety of low-carbon energy solutions.

Atmospheric Air Feed-Gas Assumptions – Update values below to describe the air feed-gas pressure, temperature, and composition entering the capture system:

		Composition						
		vol%					ppmv	
Pressure	**Temperature**	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_X**	**NO_X**
ambient	ambient	0.04	variable	78.09	20.95	0.93	trace	trace

Chemical/Physical Sorbent Mechanism – Amine-based sorbent which binds CO_2 by chemisorption, as described in Phases I/II of Figure 2.

Sorbent Contaminant Resistance – Sorbent is highly resistant to expected contaminants found in the air. Sulfur oxide (SO_X) and nitrogen oxide (NO_X) at levels present in most air streams are not a key driver of degradation.

Sorbent Attrition and Thermal/Hydrothermal Stability – Stability of sorbent over thousands of cycles has been demonstrated by Climeworks' operating DAC plants.

Air Gas Pretreatment Requirements – N/A.

Sorbent Make-Up Requirements – Replacement of sorbent required every three years (equivalent to several thousand cycles).

Waste Streams Generated – Carbon-dioxide-depleted air is emitted from the compressors. Water is treated and reused in the plant (at full-scale).

Process Design Concept – A block flow diagram detailing the two phases of the project is shown in Figure 3.

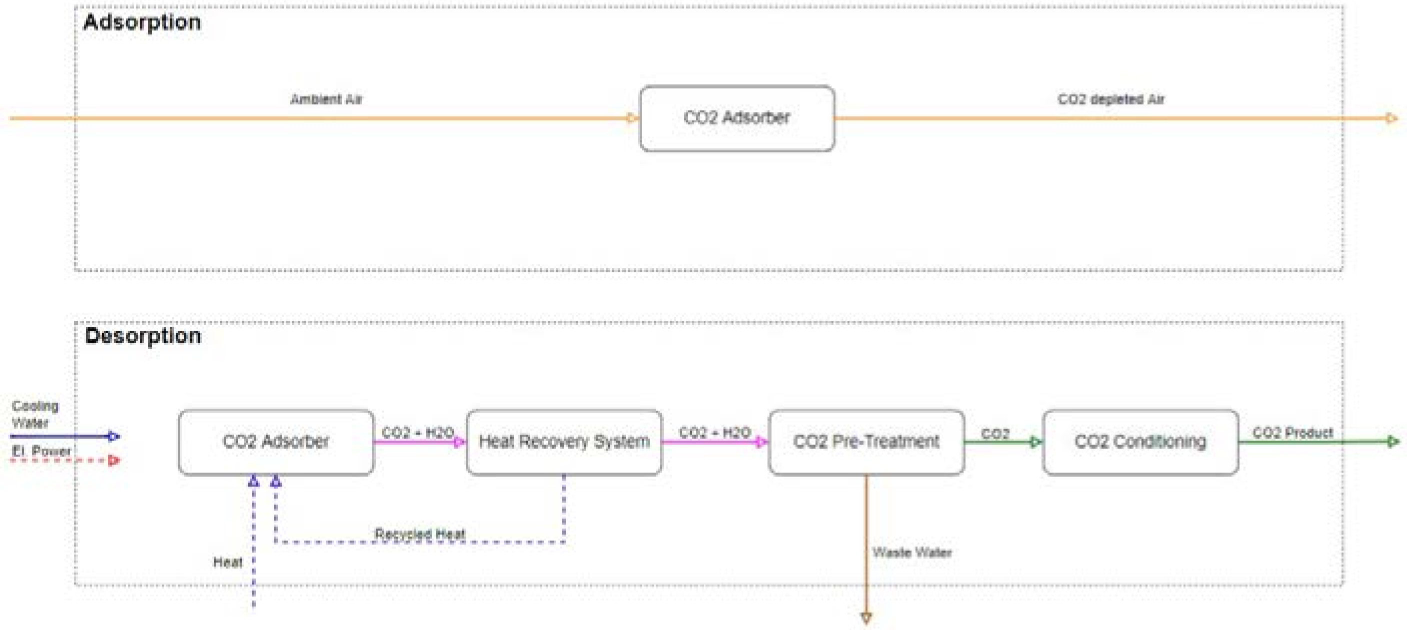

Figure 3: Block flow diagram.

Proposed Module Design – The sorbent is located inside a CO_2 Collector Container (CC). The concept of modular CCs was first developed in 2014 for the first generation of Climeworks plants. Its modularity allows for easy scale-up (the number of collectors can be adapted to match the required capacity per plant) and production can benefit from economies of scale. This CC has the external dimension of an ISO 668 40-foot container, to allow for simpler handling and shipping.

TABLE 1: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Estimate 2035**	Target long-term
Cost of Carbon Removed	\$/tonne CO_2	150-210	~100
Cost of Net Negative Emissions achieved*	\$/tonne CO_2	170-230	~110
Capital Expenditures	% of total	30-50%	
Operating Expenditures	% of total	50-70%	

* Including a full life cycle assessment from cradle-to-grave.

** At 1 $MtCO_2/y$ single plant scale, with a learning rate consistent with total installed volume of 100 $MtCO_2/y$ assumed.

Cost of Carbon Removed – Projected cost of capture and storage per mass of CO_2 under expected operating conditions.

Cost of Net Negative Emissions Achieved – Projected cost of capture and storage per mass of CO_2 when accounting for the associated grey emissions and system losses post adsorption.

Capital Expenditures – Projected capital expenditures in percentage of total costs.

Operating Expenditures – Projected operating expenditures in percentage of total costs.

Calculations Basis – Calculations above consider a 1 $MtCO_2$/year single plant, using capital cost values derived from Climeworks' current plants, with scaling factors in the range of 0.6–0.95 depending on the equipment type, with forecasted renewable electricity and heat prices, and with a learning rate assumed for future generations of plants equivalent to a total installed volume of 100 $MtCO_2/y$.

Scale of Validation of Technology Used in TEA – The Climeworks DAC systems consist of three major subsystems: the core technology (optimized sorbent/process combination); the full-scale modular CO_2 collectors, which house the core technology; and the process plant. This project focuses on the improvement of the process plant and optimization of a large-scale plant (layout and equipment optimization).

"Estimate 2035" costs are based on development improvements of the core technology, as well as incremental improvements of Climeworks' current systems for the collectors and process plant, based on field-proven enhancements of the Orca plant in Iceland.

Qualifying Information or Assumptions – A conservative 90% removal efficiency (net-negative emissions CO_2 achieved/CO_2 removed) is assumed, consistent with external LCAs performed of Climeworks' systems.

Technology advantages

- Mature system design, from the extensive experience in designing, constructing, and operating full-system prototypes, as well as up to 4,000 tonnes CO_2/year commercial units.
- Modular design of the CCS-DAC plants enables Climeworks to scale rapidly from a pre-commercial to commercial scale.
- DAC collector modular nature allows flexibility for future developments in sorbent technology, which can be easily integrated into existing hardware.

R&D challenges

- Engineering design of DAC systems at three different host sites with differing climates.
- Integrating different low-carbon energy sources to power and operate the systems.

Status

The project was completed on December 31, 2023. The research team concluded that Climeworks' technology can be used in different climates with minimal impact to performance. Wyoming had the highest CO_2 capture rate but also had the highest capital costs due to integration with plant waste heat systems. The heat integration with waste heat led to the lowest energy costs. The DAC facility is a modular and flexible design and therefore can be connected to different types of energy sources with minimal design changes. The co-location of the DAC system to energy and storage sites are an important selection criteria. The distance between energy source and storage site should be less than 35 miles. Access to low-cost, low-carbon energy is crucial to minimize operating expenses and grey emissions.

available reports/technical papers/presentations

Jason Dietsch, "Direct Air Capture-Based Carbon Dioxide Removal with United States Low-Carbon Energy and Sinks," Project Closeout Meeting, Pittsburgh, PA, October 2023. *https://netl.doe.gov/projects/plp-download.aspx?id=16406&filename=Direct+Air+Capture-Based+Carbon+Dioxide+Removal+with+United+States+Low-Carbon+Energy+and+Sinks.pptx*.

Jason Dietsch, Kevin O'Brien, "Direct Air Capture-Based Carbon Dioxide Removal with United States Low-Carbon Energy and Sinks," 2023 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_CDR31_Dietsch.pdf*.

Jason Dietsch, "Direct Air Capture-Based Carbon Dioxide Removal with United States Low-Carbon Energy and Sinks," Midpoint Review Meeting, Pittsburgh, PA, October 2022. *https://netl.doe.gov/projects/plp-download.aspx?id=14684&filename=Direct+Air+Capture-Based+Carbon+Dioxide+Removal+with+United+States+Low-Carbon+Energy+and+Sinks.pptx*.

Jason Dietsch, "Direct Air Capture-Based Carbon Dioxide Removal with United States Low-Carbon Energy and Sinks," 2022 Carbon Management Project Review Meeting, Pittsburgh, PA, August 2022. *22CM_CDR17_Dietsch.pdf*.

Kevin C. O'Brien, "Direct Air Capture Facility Development in the United States," presented at American University's Assessing Carbon Removal webinar series, February 21, 2022. *https://www.youtube.com/watch?v=HX5c3llo42w*.

Kevin C. O'Brien, "Direct Air Capture-Based Carbon Dioxide Removal with United States Low-Carbon Energy and Sinks," Project kickoff meeting presentation, Pittsburgh, PA, October 2021. *https://netl.doe.gov/projects/plp-download.aspx?id=11215&filename=Direct+Air+Capture-Based+Carbon+Dioxide+Removal+with+United+States+Low-Carbon+Energy+and+Sinks.pptx*.

3D-Printed Engineered Structures for High-Performance Direct Air Capture System

primary project goal

TDA Research Inc., with partners Schlumberger New Energy and the Missouri University of Science and Technology (MUST), is developing novel 3D-printed sorbent structures that can capture carbon dioxide (CO_2) from air via a rapid thermal swing adsorption (RTSA) process.

technical goals

- Prepare sorbent material and manufacture structures.
- Design a sorbent module.
- Scale-up structed sorbent size, fabricate a larger test unit, and demonstrate durability and performance through many cycles.
- Optimize the sorbent structure design through simulation and testing and conduct a sensitivity analysis.
- Complete detailed techno-economic analysis (TEA); technology gap analysis; and environmental, health and safety (EH&S) risk assessment.

technical content

TDA Research Inc. is developing novel 3D-printed sorbent structures that can capture CO_2 from air via an RTSA process, integrating thermally conductive additives (e.g., metal nanoparticles, carbon fibers) in between the sorbent layers assembled in a layer-by-layer printing process to develop sorbent structures with a continuous network of heat-conducting layers. The enhanced thermal conductivity and heat transfer rate in the sorbent structure will allow rapid and uniform heating of the sorbent. The layer-by-layer printing will also allow addition of integrated heat exchange tubes that can supply heat indirectly to the structure via conduction during the regeneration. Key metrics include improved volumetric CO_2 productivity; decreased pressure drop; reduced capacity fade; and a lower-cost, scalable fabrication process.

The project team will optimize and scale-up the dual head 3D-printing technique to prepare sorbent structures with integrated thermally conductive layers. They will optimize the sorbent paste properties based on their thermal conductivity, physical characteristics, mechanical stability, CO_2 adsorption properties and surface area. They will identify the best option to integrate the heat exchange tubes to indirectly heat the sorbent bed. Based on the experimental results, the team will design the gas-solid contactor using printed sorbent structures. The team will identify a unit cell size that can be printed using commercial additive

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Structured Sorbent for Carbon Dioxide Removal

participant:
TDA Research Inc.

project number:
FE0032260

predecessor projects:
N/A

NETL project manager:
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TDA Research Inc.
galptekin@tda.com

partners:
Schlumberger New Energy; Missouri University of Science and Technology (MUST)

start date:
07.24.2023

percent complete:
25%

manufacturing (AM) systems and assemble them into large modules. Scale-up of the printing process and printing larger test articles will also be conducted. Using the best material, the team will carry out multiple RTSA cycles to demonstrate the life and durability of the structured sorbent (1,000 cycles will be carried out under representative conditions). The team will complete the fabrication of a test module. The gas-solid contactor will be composed of multiple 3D-printed structures and a fully integrated heat loop to drive the direct air capture (DAC) process. The research team will also evaluate the prototype gas-solid contactor and demonstrate the efficacy of the contactor in achieving a high CO_2 uptake and productivity provided by rapid heating and cooling, while achieving a low pressure drop. In parametric tests, the team will optimize the operating conditions.

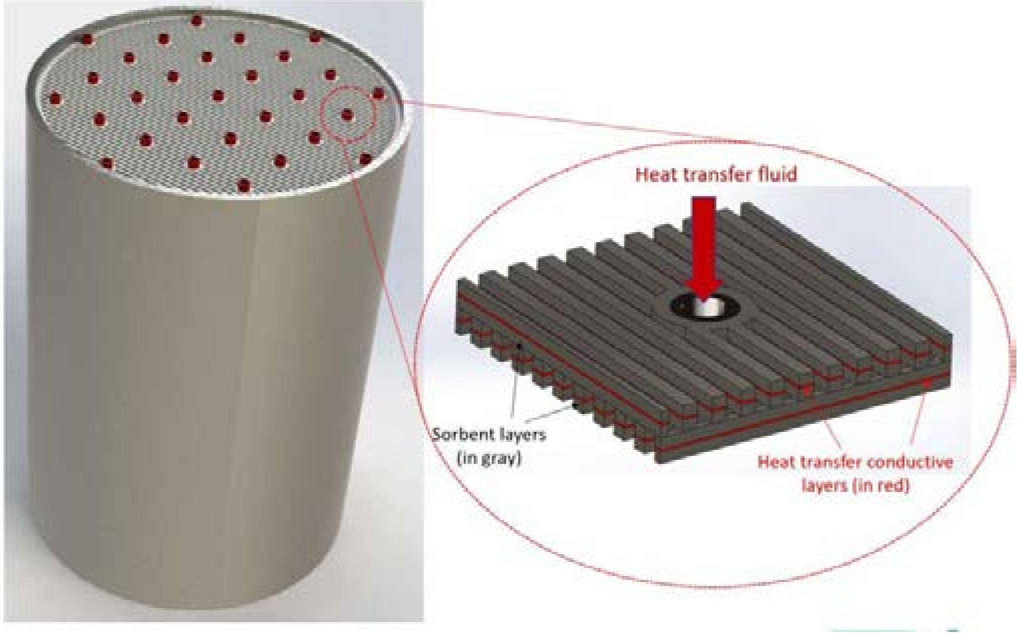

Figure 1: TDA's monolith.

technology advantages

- High sorbent stability during cycling.
- Low pressure drop.
- Enhanced heat transfer for rapid cycling.
- No release of byproducts at temperatures up to 150°C.
- Stable operation for approximately 800 cycles under DAC conditions.

R&D challenges

- Identify binders for 3D-printing structures with sorbent materials.

status

The project team has identified a list of binders to explore in their 3D-printing process. The structure embedded heater tests were successful, which resulted in better heat transfer characteristics compared to a packed bed. Preliminary computational fluid dynamics (CFD) results show that the conductive layer significantly enhances the heat transfer across the monolith. The project team has developed a new polymer sorbent for DAC and life support applications that has very high CO_2 uptake in dilute gas streams (e.g., 400 parts per million [ppm] CO_2 in air; 2,500 ppm spacecraft cabin; up to 5,000 ppm in submarines). The sorbent maintains its stability at high temperatures (up to 150°C). The sorbent has been prepared in the form of pellets, laminates and 3D-printed monoliths; in this project, it will be applied as a coating onto metal structures.

available reports/technical papers/presentations

Gökhan Alptekin, "3D Printed Engineered Structures for High Performance Direct Air Capture System," 2024 FECM/NETL Carbon Management Research Project Review Meeting, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_CDR_5_Alptekin.pdf*.

Gökhan Alptekin, "3D Printed Engineered Structures for High Performance Direct Air Capture System," 2023 Project Kickoff Meeting Presentation, October 2023. *https://netl.doe.gov/projects/files/3D%20Printed%20Engineered%20Structures%20for%20High%20Performance%20Direct%20Air%20Capture%20System.pdf*.

Gökhan Alptekin, "3D Printed Engineered Structures for High Performance Direct Air Capture System," 2023 FECM / NETL Carbon Management Research Project Review Meeting, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_CDR30_Alptekin.pdf*.

Integrated Bench-Scale Testing of a Structured Sorbent for Direct Air Capture

primary project goal

Susteon Inc. is developing a novel structured sorbent system with integrated electrical heating for regeneration on a low-pressure drop substrate for direct air capture (DAC) and conducting integrated bench-scale testing of the system.

technical goals

- Design, build and test an integrated bench-scale DAC system for continuous carbon dioxide (CO_2) production at greater than 2 kg/day (target greater than 3 kg/day, or nominally 1 tonne per year [TPY]).
- Complete more than 1,000 adsorption-desorption cycles to confirm sustained performance of structured material assembly (SMA) and integrated DAC system design.
- Process real, unconditioned air under multiple climate conditions to assess SMA performance.
- Perform a high-fidelity techno-economic analysis (TEA) and life cycle analysis (LCA) to develop a technology commercialization plan.

technical content

Susteon Inc. will conduct integrated bench-scale testing on a novel structured sorbent system with integrated electrical heating for regeneration on a low-pressure drop substrate for DAC. Previous work (FE0032118) demonstrated that the sorbent technology exhibits rapid CO_2 capture, high dynamic capacity under DAC conditions, excellent regenerability, and sustained multicycle performance with no degradation observed. The project team will conduct synthesis of the structured sorbent; finalize the design and commission of the integrated bench-scale DAC prototype system; perform extended parametric operation using ambient air from the real, outdoor environment under multiple weather conditions; and conduct transient operation of prototype system under startup, shutdown and trip recovery conditions. The existing process model, TEA and LCA will be updated based on the prototype operation. Sorbent synthesis will focus on scaling the current structured sorbent to produce the necessary amounts of SMAs with target performance. The integrated bench-scale prototype design will focus on validating sustained CO_2 productivity, CO_2 purity and energy required for regeneration.

The technical approach will be to design, build and demonstrate in an integrated DAC bench-scale prototype system by processing air from a real, outdoor environment and capturing >3 kg/day CO_2 (1 TPY). Prepare and synthesize sufficient SMAs coated with promoted sorbent and heating layer to complete integrated DAC prototype system operation (greater than 20 structured sorbents)

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Structured Sorbent with Integrated Heating

participant:
Susteon, Inc.

project number:
FE0032243

predecessor projects:
N/A

NETL project manager:
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principal investigator:
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partners:
N/A

start date:
07.01.2023

percent complete:
29%

with consistent heating and capture performance. Develop a robust gas seal design and purge operation capable of more than 1,000 cycle operation without loss in SMA or system performance. Design an efficient process cycle for adsorption, heating and desorption to maximize sorbent productivity and minimize the overall capital expenditures (CAPEX) and operating expenses (OPEX) for the technology. Cycle design will be validated in the integrated DAC bench-scale prototype system operation.

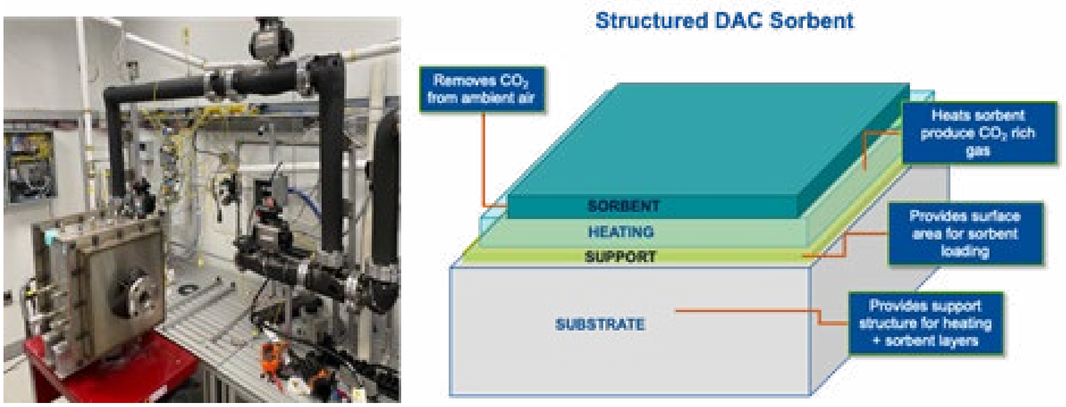

Figure 1: Integrated bench-scale testing on a novel structured sorbent system with integrated electrical heating.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Adsorption	Units	Current R&D Value	Target R&D Value
Pressure	Bar (abs)	1.01	1.01
Temperature	°C	22–25	5–40
Equilibrium Loading	g mol CO_2/kg	1.3	1.3
Heat of Adsorption	kJ/mol CO_2	68	68
CO_2 Adsorption Kinetics	gmol/min-kg	0.014	0.028
Desorption			
Pressure	bar	1.01	1.01
Temperature	°C	100	70
Equilibrium CO_2 Loading	g mol CO_2/kg	1.3	1.3
Heat of Desorption	kJ/mol CO_2	68	68
CO_2 Desorption Kinetics	gmol/min-kg	0.076	0.076
Proposed Module Design		*(for equipment developers)*	
Form Factor	—	Monolith	
Space Velocity (WHSV – Sorbent Basis)	hr^{-1}	300–800	
Volumetric Productivity	TPD_{CO2}/m^3_{SMA}	0.18–0.2	
CO_2 Recovery, Purity, and Pressure	% / % / bara	40 98 (Dry Basis) 1.2	
Adsorber Pressure Drop	inH_2O	0.5–1.5	

Definitions:

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Feed-Gas Assumptions –

		Composition						
		vol%					ppmv	
Pressure	Temperature	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	59°F	0.04	variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

Waste Streams Generated – Waste gases (mostly water).

TABLE 2: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	335	250
Capital Expenditures	\$/tonne CO_2	172	128
Variable Expenditures	\$/tonne CO_2	63	47
Operating Expenditures	\$/tonne CO_2	100	75

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Calculations Basis – The cost calculations are based on a facility with a nominal CO_2 capture rate of 100,000 TPY at a capacity factor of 85%. This facility is assumed to be at a generic greenfield site in the Midwest United States removing CO_2 from air at standard ISO conditions. The removed CO_2 is then transported and stored in a deep saline formation for which the cost is estimated using the U.S. Department of Energy (DOE) Office of Fossil Energy and Carbon Management (FECM)/National Energy Technology Laboratory (NETL) CO_2 Transport Cost Model (CO_2 Transport Cost Model) and the FECM/NETL CO_2 Saline Storage Cost Model (CO_2 Storage Cost Model).

The total cost of CO_2 capture was determined using key technical input parameters such as adsorption rate (0.014 gmol/min-kg), desorption/regeneration temperature, project contingencies, process contingencies, and capacity factor (85%), as well as and financial input parameters such as capital expenditure period (three years), operational period (30 years), debt (55%), equity (45%), debt cost of capital (5%), equity cost of capital (10%), after-tax weighted average cost of capital (ATWACC; 6.54%), capital depreciation period (20 years), escalation rate (3%), and a capital recovery factor of 7.69%. These parameters led to an AACE Class IV cost estimate with an expected accuracy range of -20% to +30%.

Scale of Validation of Technology Used in TEA – The technology numbers used in the TEA were derived via and validated through a combination of modeling, laboratory testing, bench scale testing.

technology advantages

- The SMA integrates the sorbent, regeneration method and substrate into an optimized form.
- Increases productivity by enabling fast CO_2 adsorption rate and rapid regeneration.
- Lowers the energy utilization by reducing pressure drop during adsorption and energy losses during desorption.
- Powered by low-carbon electricity for maximum net removal efficiency (no steam needed).

R&D challenges

- Stability of the integrated heating layer.
- Long-term stability of the structured sorbent layer.

status

The project team has completed the integrated SMA testing, and the structured sorbent was stable after more than 300 cycles of operation. The detailed integrated bench system design is currently in progress. The heating layer is stable and capable of rapid heating greater than 95°C/min. Long-term testing of SMA shows no degradation in CO_2 capture and heating performance over 250+ cycles.

available reports/technical papers/presentations

Tong, Andrew, Gupta, Raghubir, "Integrated Bench-Scale Testing of a Structured Sorbent for Direct Air Capture," 2024 FECM / NETL Carbon Management Research Project Review Meeting, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_CDR_5_Tong.pdf*.

Tong, Andrew, Gupta, Raghubir, "Integrated Bench-Scale Testing of a Structured Sorbent for Direct Air Capture," 2023 FECM / NETL Carbon Management Research Project Review Meeting, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_CDR30_Tong.pdf*.

Tong, Andrew, Gupta, Raghubir, "Integrated Bench-Scale Testing of a Structured Sorbent for Direct Air Capture," 2023 Project Kickoff Meeting Presentation, August 2023.

An Integrated and Continuous Bench-Scale Passive DAC Demonstration

primary project goal

RTI International is partnering with Creare, GE Research and Edare to design, fabricate and test a bench-scale contactor coated with advanced solid sorbents for direct air capture (DAC) of carbon dioxide (CO_2). The project is focused on the scale-up of materials production and the operation of a bench-scale CO_2 removal unit inside an environmental chamber that will maintain constant, controlled test conditions for long-duration life testing (e.g., 1,000 cycles) and parametric testing.

technical goals

- Scale-up DAC materials production to 10 kg; optimize coating formulations; and design and fabricate a wind-driven, bench-scale DAC-integrated process.
- Measure key performance metrics under simulated environmental conditions (air speed, ambient temperature, relative humidity) to observe performance conditions over 1,000 cycles.
- Conduct a detailed TEA and LCA using all experimental data collected.

technical content

The project's focus is on a DAC system that incorporates RTI's high-performance, high-durability amine sorbents in an innovative air contactor design that is optimized for wind-driven operation. Utilization of Creare's hybrid additive manufacturing technology enables the low-cost fabrication of high-performance, compact structures that exhibit efficient heat and mass exchange transfer and that are ideally suited for integration with sorbent materials. The sorbent/contactor design enables high CO_2 sorption, low regeneration temperature, and excellent tolerance for oxygen and water. The unique environmental chamber that was built for the predecessor project (FE0032099) for testing purposes enables rapid, automated temperature-swing sorption cycling of DAC contactors under conditions that simulate operation in a wind-driven system. Testing in the chamber with constant, controlled test conditions allows for long-term cyclic and parametric testing. Ducted fans provide specified air flow rates to simulate constant wind speed throughout the test. Two modules operate 180°C out of phase to maintain steady CO_2 concentration during simultaneous adsorption and desorption operation.

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Testing Continuous Operation of an Integrated Bench-Scale DAC Contactor

participant:
Research Triangle Institute

project number:
FE0032241

predecessor projects:
FE0032099

NETL project manager:
Erika Bittner
erika.bittner@netl.doe.gov

principal investigator:
Mustapha Soukri
Research Triangle Institute
msoukri@rti.org

partners:
Creare; GE Research; Edare

start date:
06.05.2023

percent complete:
30%

Figure 1: Left: Image of a DAC contactor, shown here with 50 plate pairs, 10 coated with 100 g of RTI sorbent on each plate. Center: Exterior of the test chamber for long-term testing of contactor modules. Right: Interior of the test chamber.

During this project, DAC sorbent material production will scale-up to 10 kg with simultaneous optimization of the sorbent coating. A wind-driven contactor performance model will be developed and tested to better understand and predict DAC performance. A wind-driven bench-scale contactor system will then be designed, fabricated and commissioned using these DAC materials. The system will undergo continuous long-term testing for more than one month to observe performance and assess durability over 1,000 cycles of operation. A complete LCA and TEA will be performed using the results of these tests to validate the technology's potential for CO_2 removal and its economic feasibility.

Feed-Gas Assumptions –

		Composition						
		vol%					ppmv	
Pressure	**Temperature**	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.7 psia	- °F	0.04	variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

Waste Streams Generated – Waste gases (mostly water).

technology advantages

- Rapid and simple temperature-swing sorption cycling.
- Highly efficient mass transfer and low flow resistance of contactor enables low-power, wind-driven operation.
- Low-cost additive manufacturing process for fabrication of contactor.
- High surface area contactor designed with parallel-plate micro-channels.
- This project leverages the knowledge and experience gained through the Advanced Research Projects Agency–Energy (ARPA-E) efforts to complete the development of a bench-scale DAC process by optimizing the sorbent binder composite coating and enabling long-term cyclic testing to prove performance and durability.

R&D challenges

- Sorbent coating durability and CO_2 sorption and regeneration performance during long-term cycling under relevant DAC conditions.
- Achieving a uniform sorbent coating layer with a thickness less than or equal to 10 mil (e.g., 0.254 mm) and strong film adhesion to the stainless steel plate surface.
- Achieving efficient CO_2 capture under minimal wind conditions.

status

The project team has optimized the sorbent-integrated contactor and completed wind-driven contactor performance modeling. Design preparation has occurred for the testing module to be constructed and subsequently tested under realistic DAC conditions.

available reports/technical papers/presentations

Soukri, M., "An Integrated and Continuous Bench-Scale Passive DAC Demonstration," Presented at the 2024 FECM/NETL Carbon Management Project Review Meeting, August 2024. *An Integrated and Continuous Bench-Scale Passive DAC Demonstration*.

Soukri, M. "An Integrated and Continuous Bench-Scale Passive DAC Demonstration," Budget Project 1 Review Meeting Presentation, May 2024. *https://netl.doe.gov/projects/files/An%20Integrated%20and%20Continuous%20Bench-Scale%20Passive%20DAC%20Demonstration.pdf*.

Soukri, M. "An Integrated and Continuous Bench-Scale Passive DAC Demonstration," Kickoff Meeting Presentation, August 2023. *https://netl.doe.gov/projects/files/An%20Integrated%20and%20Continuous%20Bench-Scale%20Passive%20DAC%20Demonstration.pdf*.

Amine-Infused Expanded Polytetrafluoroethylene (ePTFE)/Silica Laminate Structured Sorbents as an Advanced Direct Air Capture System

primary project goal

Georgia Tech Research Corporation is partnering with W.L. Gore and Associates to optimize polyethyleneimine (PEI)-infused expanded polytetrafluoroethylene (ePTFE)/silica sorbent material and to scale-up production of sorbent-infused laminates for direct air capture (DAC). The project team will also work on computational modeling and the design, fabrication and testing of a bench-scale contactor for efficient carbon dioxide (CO_2) removal under ambient and sub-ambient conditions.

technical goals

- Develop solid-supported amine materials for efficient DAC with enhanced mass transfer.
- Fabricate laminate modules for bench-scale testing with low-temperature steam stripping desorption and test sorbent material across a wide range of temperature and humidity conditions.
- Advance from technology readiness level (TRL) 2 to TRL 3 for PEI-infused ePTFE/silica sorbents, progressing toward achieving $100/net tonne CO_2 removed in DAC systems.

technical content

The project is centered around the development of a DAC system that utilizes solid-supported amine materials for efficient separation of CO_2 from air. The sorbent materials are being developed early in the project and are utilized in structured gas-solid contactors with ePTFE/silica laminates to enhance CO_2 mass transfer, as shown in Figure 1. The material is designed to overcome challenges such as managing low CO_2 concentrations in ambient air and heat/mass transfer limitations. Laminate modules are being fabricated for bench-scale testing, designed to efficiently manage a variety of conditions while retaining minimal pressure drop. The technology will advance from TRL 2 to TRL 3 for PEI-infused ePTFE/silica sorbents, and analysis of costs will be performed to determine progress toward achieving DAC operation with less than $100/net tonne CO_2 removed.

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Bench-Scale Testing of Amine-Infused Structured DAC Sorbents

participant:
Georgia Tech Research Corporation

project number:
FE0032278

predecessor projects:
N/A

NETL project manager:
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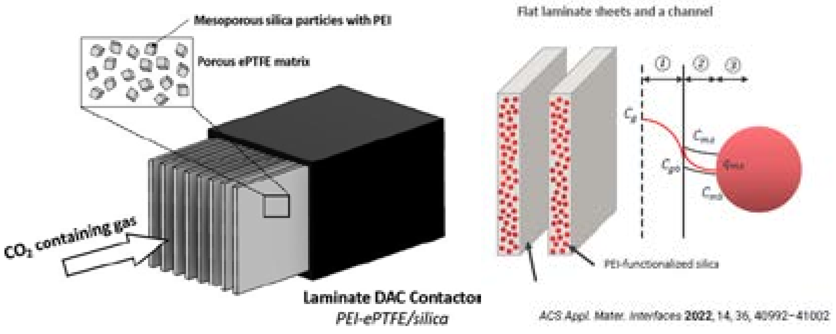
principal investigator:
Christopher Jones
Georgia Tech Research Corporation
cjones@chbe.gatech.edu

partners:
W.L. Gore and Associates

start date:
09.01.2023

percent complete:
40%



ACS Appl. Mater. Interfaces 2022, 14, 36, 40992−41002

Figure 1: Left: Diagram of the PEI/ePTFE/silica laminate and contactor. Right: Sample figure from process modeling showing the concentration of CO_2 in the gas phase, in the PTFE matrix, and at the PEI-functionalized silica particle surface.

During this project, DAC sorbent material is being further optimized and studied in testing. The material is designed to overcome key challenges such as low CO_2 concentrations in ambient air and heat/mass transfer limitations. Sorption experiments for this material provided key metrics that accurately describe its CO_2 sorption, which are used to guide kinetic and thermodynamic modeling of CO_2 sorption in laminate materials. The research team has previously set up bench-scale housing for laminate module and scale-up synthesis of laminate, as shown on the left in Figure 2. A modified bench-scale housing for the laminate module for this project has been designed and constructed for testing material performance under ambient and sub-ambient DAC process conditions. The constructed housing is integrated into the DAC system and tested to demonstrate cyclic capture of CO_2 from simulated air at ambient conditions. During testing, air at a controlled temperature and humidity will enter the laminate housing to allow sorption to occur, followed by the flow of steam to release the sorbed CO_2, as shown on the right in Figure 2. The process conditions will then be optimized for ambient DAC operation, and a range of process parameters will be established for effective CO_2 adsorption and desorption under ambient DAC conditions. A similar approach will be taken for sub-ambient conditions as well. Subsequent tasks for the project are focused on structural and oxidative stability testing, updated simulations, and techno-economic analysis (TEA) and life cycle analysis (LCA).

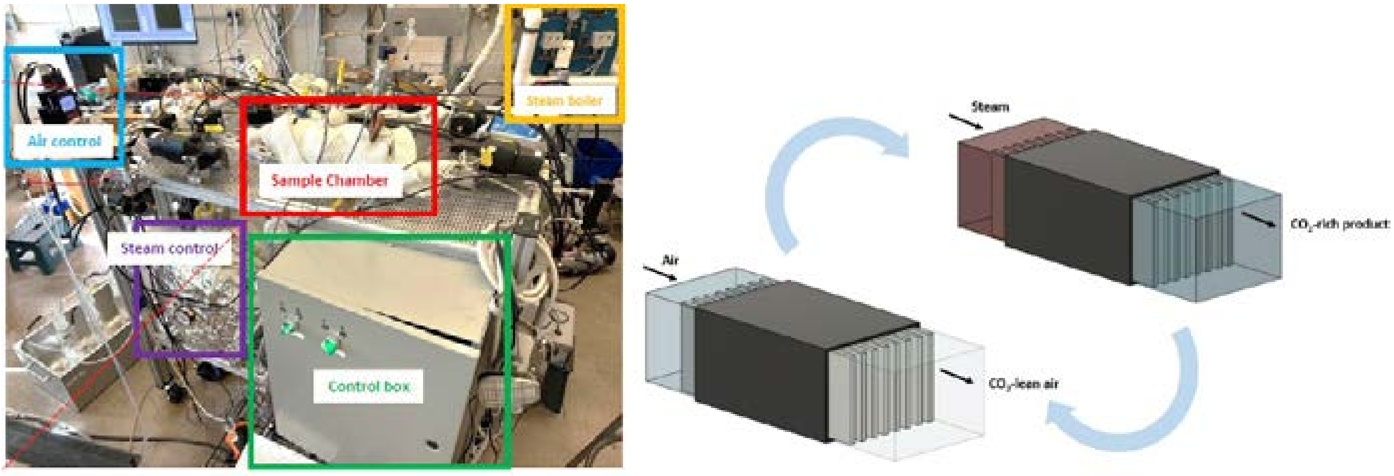


Figure 2: Left: Image of the testing setup previously constructed at this lab for evaluation of this material. Right: Diagram showing the cyclical process of CO_2 removal from flowing air switching with CO_2 release by flow of steam.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m³	—	—
Bulk Density	kg/m³	460	540
Average Particle Diameter	mm	0.004	0.012

Particle Void Fraction	m^3/m^3	0.3	0.3
Packing Density	m^2/m^3	—	—
Solid Heat Capacity @ STP	kJ/kg-K	1.14	1.14
Crush Strength	kg_f	—	—
Attrition Index	-	—	—
Thermal Conductivity	W/(m-K)	—	—
Manufacturing Cost for Sorbent	$/kg	—	—
Adsorption			
Pressure	bar	1.01	>1.01
Temperature	°C	35	-20 -35
Equilibrium Loading	g mol CO_2/kg	0.9	1.5
Heat of Adsorption	kJ/mol CO_2	95	84
CO_2 Adsorption Kinetics	gmol/time	0.015 gmol/min	>0.025 gmol/min
Desorption			
Pressure	bar	1.1	0.6 – 1.2
Temperature	°C	102	85 - 105
Equilibrium CO_2 Loading	g mol CO_2/kg	<0.1	< 0.3
Heat of Desorption	kJ/mol CO_2	95	84
CO_2 Desorption Kinetics	gmol/time	0.33 gmol/min	0.33 gmol/min

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Feed-Gas Assumptions –

		Composition						
		vol%					ppmv	
Pressure	Temperature	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	-4 — 95 °F	0.04	variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

Waste Streams Generated – Waste gases (mostly water).

TABLE 2: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	295	205
Cost of Carbon Avoided	\$/tonne CO_2		
Capital Expenditures	\$/tonne CO_2	173	123
Operating Expenditures	\$/tonne CO_2	122	83

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

technology advantages

- Efficient heat and mass transfer with reduced pressure drop using parallel-plate micro-channels.
- Reduced energy penalty via steam stripping desorption step at low temperatures.
- Project team has experience with designing, constructing and operating testing apparatus capable of testing under diverse DAC conditions.
- Sorbent material demonstrated efficient DAC performance in laboratory-scale testing.

R&D challenges

- Determining optimal PEI loading amount and synthesis method for composite laminate adsorbents with ideal distribution of PEI.
- Measuring and minimizing cyclic and oxidative degradation of DAC sorbent material.
- Low CO_2 concentrations in ambient air and heat/mass transfer limitations.

status

The project team is setting up bench-scale housing for the laminate module for integration into the DAC system for testing. Modeling is occurring concurrently to establish kinetic and equilibrium parameters for CO_2 adsorption on materials under ambient and sub-ambient conditions. Follow-up work will continue to establish a range of process parameters for efficient DAC under both conditions and analyze process feasibility through LCA and TEA.

available reports/technical papers/presentations

Jones, C., et al. "Amine Infused ePTFE/SiO_2 Laminate Structured Sorbents as an Advanced Direct Air Capture System," *2024 NETL/FECM Carbon Management Project Review Meeting*, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_CDR_5_CJones.pdf*.

Jones, C., et al. “Amine Infused ePTFE/SiO_2 Laminate Structured Sorbents as an Advanced Direct Air Capture System,” *Kickoff Meeting Presentation*, October 2023.

Realff, M., et al. “Amine Infused ePTFE/SiO_2 Laminate Structured Sorbents as an Advanced Direct Air Capture System,” *2023 NETL/FECM Carbon Management Project Review Meeting*, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_CDR28_Realff.pdf*.

Advanced Engineered Structures for High-Performance Direct Air Capture System

primary project goal

TDA Research Inc. is designing and constructing an engineered sorbent structure for capturing carbon dioxide (CO_2) from ambient air via a temperature swing adsorption (TSA) process. The unit cell will be a tube-in-plate heat exchanger, coated with an active sorbent phase.

technical goals

- Design and construct a structured cell for direct air capture (DAC) of CO_2 where the active sorbent phase will be coated on the surfaces of tube-in-plate heat exchangers that can be economically produced in large-scale.
- Demonstrate durability and performance through bench-scale testing.
- Design full scale sorbent module.
- Complete detailed techno-economic analysis (TEA); life cycle analysis (LCA); technology GAP analysis; and environment, health and safety (EH&S) risk assessment.

technical content

TDA Research Inc., in collaboration with GE Research, proposes to develop a structured cell for DAC of CO_2 where the active sorbent phase will be coated on the surfaces of tube-in-plate heat exchangers that can be economically produced in large-scale. The sorbent layer thickness, plate spacing and geometry will be optimized to reduce the pressure drop and improve the heat transfer rate (and hence the CO_2 productivity). The structured gas-solid contactor design will also reduce the associated parasitic energy loss for circulating large volumes of air to the system. While the adsorbent was developed in an earlier project and the proposed heat exchangers are commercially available, the use of sorbent-coated heat exchangers for CO_2 removal in a thermal swing application has not been demonstrated. Key metrics include improved volumetric CO_2 productivity; decreased pressure drop; reduced capacity fade; and a lower-cost, scalable fabrication process. The material system will demonstrate significant progress toward meeting the goal of $100/net tonne CO_2 removed.

The research team will optimize the sorbent paste to make it suitable for printing (e.g., viscosity, binder content). GE will coat the plates using TDA's sorbent formulations. The coated test plates (1 by 1 by 1 inch) will be evaluated individually or as stacks at the bench scale under representative conditions. The paste

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Sorbent on Tube-in-Plate Heat Exchanger Design for Carbon Dioxide Removal

participant:
TDA Research Inc.

project number:
FE0032261

predecessor projects:
N/A

NETL project manager:
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principal investigator:
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TDA Research Inc.
galptekin@tda.com

partners:
General Electric (GE) Company

start date:
09.01.2023

percent complete:
38%

properties will be optimized based on their physical characteristics, mechanical stability, CO_2 adsorption, pressure drop and surface area. Three types of fin structure plates will be tested at the individual coupon level. One baseline and one alternative fin structure will be down-selected as a result of optimization. The baseline and alternative fin structure will be tested at sub-bench scale (sub-bench scale can be defined as achieving DAC CO_2 removal productivity of 0.5 to 1.0 g CO_2/hr). An initial TEA and LCA will also be completed.

The coating paste will be further optimized at the sub-bench scale. Two sub-bench-scale heat exchangers and one larger heat exchanger (bench scale can be defined as achieving a DAC CO_2 removal productivity of 10 to 50 g CO_2/hr) will be coated using the optimized paste formula and coating process. The contactors' performance will be tested under DAC conditions in TDA's automated test rigs. A minimum of 5,000 cycles will be carried out to demonstrate the life of the structured sorbent in a sub-bench-scale contactor with compressed air. A minimum of 500 cycles will also be carried out with the bench-scale contactor to demonstrate the concept at ambient conditions. Based on the results, a full-scale gas-solid DAC contactor will be designed, identifying key parameters such as the tube size, length and spacing, plate type, spacing and depth, and material selection. The final TEA and estimate of the cost of CO_2 captured with the new technology will be completed with an LCA to fully quantify the carbon footprint reduction with the new technology.

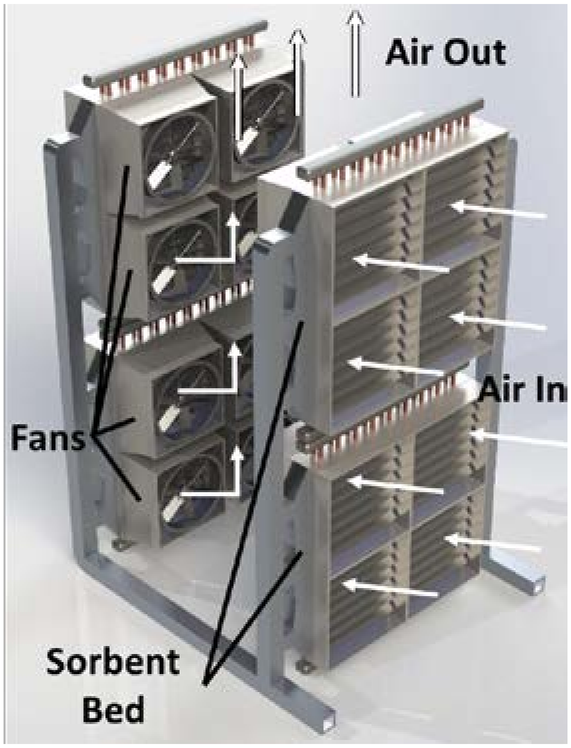

Figure 1: DAC sorbent towers.

technology advantages

- A rapid cycle sequence increases the CO_2 productivity (ton CO_2 removed per ton sorbent per hour).
- High surface area contactor.

R&D challenges

- Identify binders for adhesion for heat exchanger tube-in-plate adhesion.

status

The project team has produced the active sorbent phase at the bench scale and has optimized binder formulation, sorbent coating thickness and porosity to improve CO_2 capacity and uptake kinetics, and the adhesion and heat transfer performance. The research team has evaluated different types of enhanced performance tube-in-plate structures, wavy fins, offset fins and grooved fins, and has tested coat coupons for bench-scale performance testing.

available reports/technical papers/presentations

Gökhan Alptekin, "Advanced Engineered Structures for High Performance Direct Air Capture System," 2023 Project Kickoff Meeting Presentation, November 2023.

Gökhan Alptekin, "Advanced Engineered Structures for High Performance Direct Air Capture System," 2023 FECM / NETL Carbon Management Research Project Review Meeting, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_CDR28_Alptekin.pdf*.

Bench-Scale Development of Promoted High-Capacity Structured Sorbents

primary project goal

The overall objective of the project is to develop a high-capacity structured sorbent (HCSS) material system for direct air capture (DAC) of carbon dioxide (CO_2) to make significant progress toward reaching the U.S. Department of Energy's (DOE) Carbon Negative Shot target of less than \$100/net tonne CO_2.

technical goals

- Selection of structured materials and promoters to enhance the rate of CO_2 adsorption and working capacity.
- Optimization of the HCSS to maximize CO_2 working capacity and capture rate.
- Design and build of a bench-scale test unit to evaluate the HCSS to determine engineering factors and scale-up parameters.
- Development of a process design that utilizes the HCSS to estimate techno-economic analysis (TEA) and life cycle analysis (LCA) studies associated with the DAC process.

technical content

Susteon Inc. will conduct bench-scale research and development (R&D) to advance a novel HCSS comprised of a highly dispersed sorbent with a low-pressure drop substrate for DAC. The project team will test and select materials and form factors of the structured substrates to support the DAC sorbent. Structured substrate will be selected to provide a high surface area for loading sorbent, increasing the mass transfer rate, while minimizing pressure drop and energy loss. The team will perform sorbent optimization, preparation, testing and characterization to achieve a highly dispersed sorbent with maximum capacity, adsorption rate and adsorbent stability under process conditions that yield rapid CO_2 adsorption rate, high CO_2 capacity, and low desorption energy. The team will design and fabricate a system for bench-scale testing that can operate full process cycles under various adsorption and desorption conditions. Process data will be used for constructing and validating a process model, which in turn will be used to develop a process design, obtain process heat and material balances, determine optimal sizing of process equipment, TEA and LCA, and estimate overall process efficiency.

The technology to be assessed is a polyethyleneimine (PEI)/silica-promoted sorbent system for DAC applications. The PEI/silica sorbent is the key CO_2 adsorbing material used in the DAC process. Susteon has developed a promoted DAC sorbent with enhanced adsorption and desorption kinetics to lower the cost of DAC. The improved desorption kinetics allows for lowering the energy required

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Structured CO_2 Sorbents for Direct Air Capture

participant:
Susteon Inc.

project number:
FE0032254

predecessor projects:
N/A

NETL project manager:
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principal investigator:
James Zhou
Susteon Inc.
sjz@susteon.com

partners:
N/A

start date:
07.01.2023

percent complete:
46%

for releasing CO_2 from the capture agents. Improvement in absorption kinetics also allows for reducing the size of the air contactor, thus lowering the capital costs. R&D efforts also minimized the pressure required to move the air through the capture device. The sorbent is an amine-based solid sorbent promoted by proprietary promoters. The promoted sorbent has higher CO_2 adsorption and desorption rates than the unpromoted sorbents. In laboratory tests, these promoters are effective at parts per million (ppm) levels and demonstrate a 100% increase in sorbent CO_2 working capacity and a 40% increase in adsorption rate. Susteon has focused on (1) synthesizing the promoted amine-based sorbents for improved desorption and adsorption kinetics, (2) evaluating the promoted amine-based sorbents for direct CO_2 capture process to determine CO_2 adsorption and desorption rates and energy requirements, and (3) developing a conceptual process design based on the experimental results to perform a preliminary economic assessment to evaluate the potential for DAC process cost-reduction using the promoted sorbents.

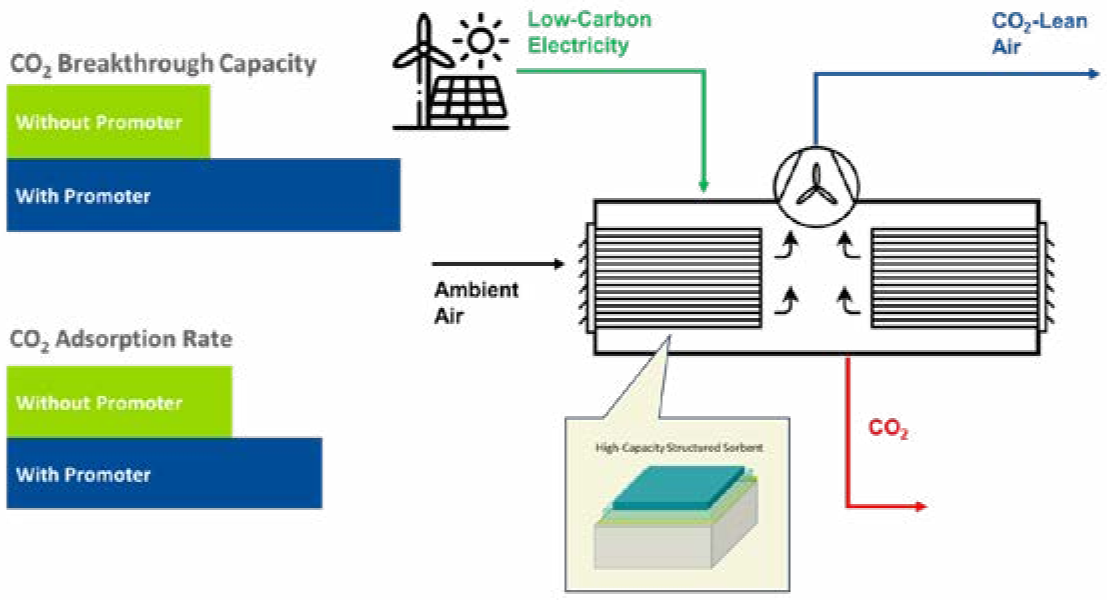

Figure 1: Highly dispersed sorbent with a low-pressure drop substrate for direct air capture.

technology advantages

- Reaction of CO_2 with sorbent is fast and not limiting, demonstrating greater than 40% increase in adsorption rate as compared to the state-of-the-art DAC sorbents.
- Approximately 100% increase in DAC sorbent CO_2 working capacity compared to the state-of-the-art DAC sorbents.

R&D challenges

- Long-term stability of the structured sorbent layer.
- Sorbent selection and optimization that achieves maximum capacity, adsorption rate and adsorbent stability over process conditions.

status

The project team has demonstrated DAC sorbents that have enhanced CO_2 adsorption rate and working capacity as compared with the current state-of-the-art sorbents. There was a greater than 40% increase in adsorption and desorption rate for their DAC sorbent technology. The team developed a bench-scale testing apparatus for high-capacity structured sorbents for DAC applications. Future work will focus on preforming parametric cyclic testing at the bench-scale to determine the CO_2 capacity, adsorption/desorption rate, pressure drop, and extent of CO_2 removal from air as a function of temperature, along with long-term cyclic testing for 100 to 500 cycles to determine long-term performance parameters.

available reports/technical papers/presentations

Zhou, James, "Bench-Scale Development of Promoted High-Capacity Structured Sorbents," 2024 FECM / NETL Carbon Management Research Project Review Meeting, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_CDR_5_Zhou.pdf*

Zhou, James, "Bench-Scale Development of Promoted High-Capacity Structured Sorbents," BP1 Project Briefing, May 2024. *https://netl.doe.gov/projects/files/Bench-Scale%20Development%20of%20Promoted%20High-Capacity%20Structured%20Sorbents.pdf*

Zhou, James, "Bench-Scale Development of Promoted High-Capacity Structured Sorbents," 2023 FECM / NETL Carbon Management Research Project Review Meeting, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_CDR28_Zhou.pdf*.

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Dual-Function Materials for Direct Air Capture of CO_2

primary project goal

Susteon Inc., with partners Columbia University and Kiewit Engineering, are developing a reactive direct air capture (DAC) process that is capable of capturing and converting carbon dioxide (CO_2) from air into valuable products. The reactive DAC process involves selective chemisorption of CO_2, followed by sorbent regeneration through reversible desorption or, optionally, catalytic conversion of adsorbed CO_2 into methane (CH_4; also referred to as renewable natural gas [RNG]), using waste or renewable hydrogen (H_2).

technical goals

- Develop optimum dual-function material (DFM) washcoat formulation on commercial monolith support through lab- and bench-scale testing.
- Develop an efficient method of heating the DFM layer on the monolith using Joule heating.
- Develop a commercial manufacturing process for DFM structures by working with a commercial catalyst manufacturer.
- Design and build a bench-scale unit capable of 1.0 kg/day of CO_2 capture.
- Conduct parametric testing in the bench-scale unit to determine optimum DAC-DFM process conditions for CO_2 adsorption, RNG production, and optimum process cycle design.
- Conduct long-term testing to establish DFM aging and performance degradation.
- Refine and validate the current process model using bench-scale data to develop a high-level process design for a pilot-scale (50 kg CO_2/day) system scale-up and testing in the next phase.
- Perform a TEA and LCA.

technical content

Susteon is advancing the development of a reactive DAC system that is capable of capturing, as well converting, CO_2 from air into valuable products. Susteon has successfully demonstrated the process-intensified reactive DAC process using DFMs for capture of CO_2 from air and its subsequent conversion into CH_4 using renewable/waste hydrogen for regeneration. The DFM porous solid material, consisting of a novel combination of an adsorbent and a catalyst, has shown high CO_2 capacity under DAC conditions, and even greater capacity in the presence of atmospheric moisture, in laboratory experiments. Regeneration can be achieved using mild temperatures (200–300°C), minimizing the temperature difference between chemisorption and sorbent regeneration and mitigating the need for heating and cooling of the reactor beds, which are typically needed in most adsorption-based processes. The "green" CH_4 formed in this process can be sold

program area:

Carbon Dioxide Removal

ending scale:

Bench Scale

application:

Direct Air Capture

key technology:

Sorbents

project focus:

Dual Function Materials for Capture and Conversion of CO_2 into Methane

participant:

Susteon Inc.

project number:

SC0020795

predecessor projects:

N/A

NETL project manager:

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Susteon Inc.
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partners:

Columbia University; Kiewit Engineering Group Inc.

start date:

06.29.2020

percent complete:

78%

as RNG, which qualifies for various carbon credits and incentives, similar to biogas, landfill gas, etc. This reactive DAC process is designed to intensify both the capture and utilization of atmospheric CO_2, creating a platform technology for production of a variety of green hydrocarbon products from air (i.e., CH_4, methanol, dimethyl ether, olefins, diesel, aviation fuel, etc.). As shown in Figure 1, air is fed into an adsorption reactor containing DFM, which rapidly captures CO_2 from ambient air. Once the bed is saturated with CO_2, it is heated to about 170°C and regenerated with an H_2-containing gas stream to directly react CO_2 to produce CH_4 using the Sabatier reaction ($CO_2 + 4H_2 = CH_4 + 2H_2O$). This project is aimed at demonstrating the production of RNG at a cost comparable or better than the current RNG prices in California with low-carbon fuel standards (~$15/MM British thermal units [Btu]), creating a business opportunity for further development and deployment of this DAC technology.

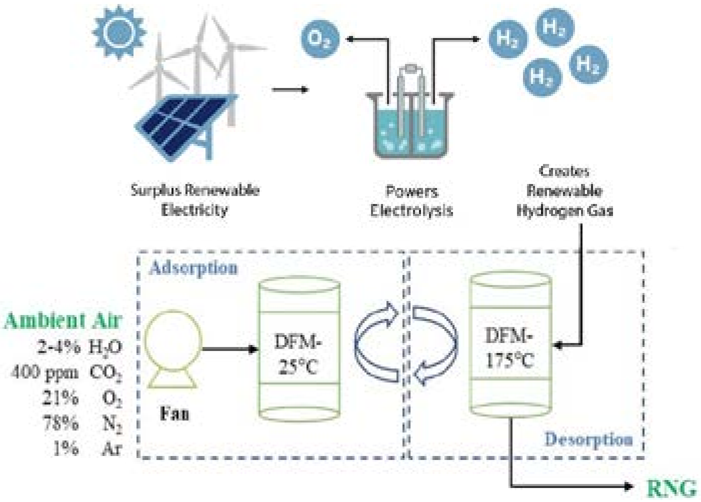

Figure 1: Block flow diagram for the overall DAC-DFM process using renewable H_2.

Working with research institute partner Columbia University, Susteon identified, synthesized, and tested a ruthenium (Ru)-promoted sodium oxide dispersed on alumina as the DFM for this process. DFM optimization led to identification of 0.25% Ru + 10% Na_2O supported on a high-surface area Al_2O_3 DFM, which exhibited a high CO_2 adsorption capacity and capture kinetics in ambient air. The extent of CO_2 capture (% removal of 400 parts per million [ppm] CO_2 in air) was significantly higher in the presence of atmospheric moisture (relative humidity in air), unlike physical sorbents like zeolites, aluminas, metal organic frameworks (MOFs), and even amine-based CO_2 capture sorbents. This DFM also showed a very fast mass transfer rate during adsorption and desorption/methanation without any noticeable aging/degradation. The preliminary techno-economic analysis (TEA) of the DFM-based DAC system (Figure 2) with 1 tonne CO_2/day basis indicated a combined power and heat requirement of 2,300 kWh/tonne CO_2, which involves (a) CO_2 capture under ambient conditions without needing to heat or pressurize air followed by (b) heating the DFM for initiating methanation to 120–200°C. The methanation reaction being significantly exothermic (-164 kJ/mol) creates opportunities to utilize and integrate this heat to further lower the overall energy need. The DFM material is used on a structured support (e.g., cordierite monoliths used in automobile catalytic converters) to minimize pressure drop.

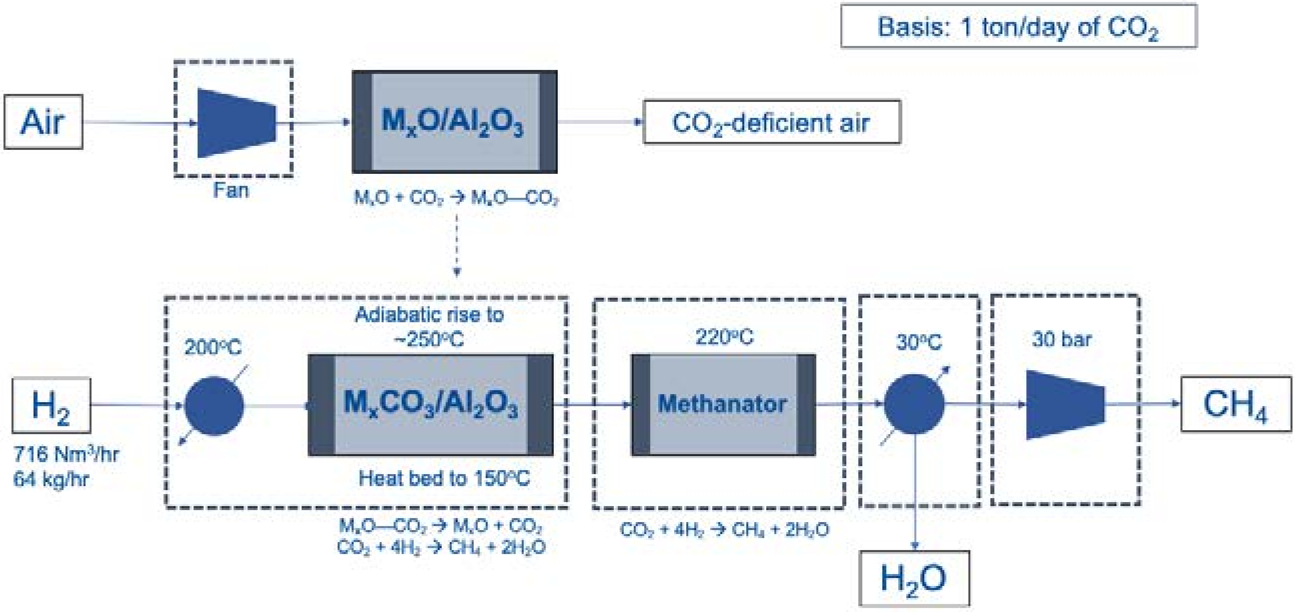

Figure 2: DAC-DFM with CO_2 capture at ambient conditions (25°C).

The project is aimed at further optimizing the DFMs and process cycle and building a high-fidelity bench-scale prototype unit to demonstrate this process and obtain engineering data needed for a pilot system design in a follow-on phase. DFM optimization focuses on the formulation and dispersion of DFM on the commercially available structured supports to achieve maximum DFM stability, CO_2 adsorption capacity, and rapid kinetics of CO_2 adsorption and methanation reactions. This work involves further reducing the Ru loading to lower overall cost of CO_2 capture. A novel Joule heating method is being integrated in the structured support to selectively heat the DFM layer between adsorption and regeneration steps. Bench-scale testing is being conducted to determine DFM process conditions that yield the fastest CO_2 adsorption rate, highest CO_2 capacity, maximum CH_4 production, and lowest-energy consumption for reactive DAC. The process model is validated using lab- and bench-scale data and employed to develop a high-level process design for a 50-kg/day engineering-scale reactive DAC system, as well as TEA and life cycle analysis (LCA) studies on a commercial-scale system. Lab- and bench-scale test results are used to further refine the process model.

Definitions:

Atmospheric Air Feed-Gas Assumptions – Update values below to describe the air feed-gas pressure, temperature, and composition entering the capture system:

Pressure	Composition						
	vol%					ppmv	
	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	0.04	variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Both chemisorption and physisorption occur during the adsorption step.

Sorbent Contaminant Resistance – To be determined.

Sorbent Attrition and Thermal/Hydrothermal Stability – To be determined.

Flue Gas Pretreatment Requirements – N/A.

Sorbent Make-Up Requirements – To be determined.

Waste Streams Generated – N/A.

Process Design Concept – See Figure 1 for block flow diagram and Figure 2 for more detailed DAC-DFM reaction scheme.

Proposed Module Design – To be determined.

TABLE 1: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	312	205
Produced RNG	tonne/day	18.2	32.4
Net Cost of Carbon Captured[i]	\$/tonne CO_2	197	0
Capital Expenditures	\$/tonne CO_2	187	86.1
Operating Expenditures	\$/tonne CO_2	125	115

[i] Projected cost of capture less revenue from RNG sales based on the current RNG price of \$15/MMBtu (including carbon credits), and a renewable hydrogen price of \$2/MMBtu.

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Net Cost of Carbon Captured – Projected cost of capture less revenue from RNG sales per mass of CO_2

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Calculations Basis – The economic values in Table 2 result from a process model on a 100 tonne/day captured CO_2 basis. The model developed in Aspen Plus was used to generate process material and energy balances, equipment sizing, and costs with the following assumptions:

- 25°C ambient temperature.
- 101.325 kPa ambient pressure.
- 60% relative humidity air.
- 1 kPa pressure drop in shell and tube heat exchangers.
- Compressor/blower specification: Polytropic with 70% efficiency and 90% drive motor efficiency.
- 10°C approach to cooling water on aftercooler heat exchanger.
- RGibbs reactor model for all reactions, including adsorption, desorption, and methanation.

Scale of Validation of Technology Used in TEA – The DAC economic values in Table 2 result from analysis of fundamental lab-scale data gathered at Technology Readiness Level (TRL) 3, implying a significant level of uncertainty in the process design and cost for a commercial system. This analysis is undertaken in the early stages of the technology development cycle to establish the feasibility of this novel technology with respect to technical soundness, operational flexibility, and economic viability.

Qualifying Information or Assumptions – Initial preliminary TEA results are based on the current RNG price of \$15/MMBtu (including carbon credits), and hydrogen price of \$2/MMBtu.

technology advantages

- Provides a saleable product from CO_2 with a strong market demand; for this project, it is RNG, which is in heavy demand to meet the low-carbon standards for CH_4 and power.
- Eliminates the need for CO_2 disposition infrastructure; compression, pipelines, storage sites, and long-term monitoring as CO_2 is directly converted into a saleable product, which can be distributed in existing natural gas infrastructure.

- Provides a platform for delivering renewable methane (RNG) from atmospheric CO_2 (Power-to-Gas) for downstream utilization to produce “green” hydrocarbons like methanol, Fischer-Tropsch fuels, olefins, etc. This could be accomplished by incorporating appropriate catalysts during the regeneration.
- Provides a market mechanism by utilizing current subsidies/incentives for low/negative carbon products (so called “Green Premiums”) for offsetting the cost of DAC by revenue generated by selling the products manufactured from CO_2.

R&D challenges

- Designing an efficient process cycle for adsorption, heating, desorption, methanation, and cooling to maximize capital productivity and minimize the overall capital expenses (CAPEX) and operating expenses (OPEX) for the technology.

status

Susteon has demonstrated a robust DFM washcoated monolith formulation with stable performance (greater than 450 hours of testing) that is enhanced with humidity achieving up to 1.2 mmol CO_2/gDFM capacity. The research team learned that CO_2 preferentially adsorbs on strong sites on DFM in the beginning of the adsorption step followed by weaker sites toward the end of the adsorption step. This led to operating near 50% capacity via 75% shorter adsorption step, resulting in greater than 90% conversion of CO_2 into CH_4. The TEA and LCA demonstrate commercial viability while maintaining net-negative carbon emissions on a cradle-to-gate basis.

available reports/technical papers/presentations

Jonathan Peters, “Dual Function Materials for Direct Air Capture of CO_2,” 2024 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_CDR_6_Peters.pdf*.

Jonathan Peters, “Dual Function Materials for Direct Air Capture of CO_2,” 2023 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_CDR30_Peters.pdf*.

Raghubir Gupta, “Dual Function Materials for Direct Air Capture of CO_2,” Phase II Project kickoff meeting presentation, Pittsburgh, PA, September 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=12122&filename=Dual+Function+Materials+for+Direct+Air+Capture+of+CO2.pdf*.

Demonstration of a Continuous-Motion Direct Air Capture System

primary project goal

Global Thermostat LLC (Global), in partnership with Zero Carbon Partners, VADA LLC, Georgia Institute of Technology, and the National Renewable Energy Lab, will develop a prototype continuous motion direct air capture (DAC) system that will capture carbon dioxide (CO_2) from the air through an adsorption process and produce a greater than 95% purity CO_2 product. The process employs honeycomb monolith contactors with a solid amine sorbent incorporated into the pores of the monolith, resulting in high CO_2 adsorption capacities at very low CO_2 partial pressures.

technical goals

- Develop the mechanical component and process equipment prototype engineering design.
- Develop a phenomenological flow model and a systems-level Aspen model that will refine process step development, estimate monolith lifetime, and key performance tradeoffs. Validation of models from experimental data will be used to supplement the basic engineering design for component capital expenditure (CAPEX) estimation and scaling analysis.
- Perform initial techno-economic analysis (TEA) and life cycle analysis (LCA) to evaluate purge-step tradeoffs, cost sensitivity to key parameters, and scale-up versus scale-out cost projections.
- Generate operational data from the DAC prototype, including a prolonged period of continuous operation, to feed into and refine the Aspen model to inform the prescreening TEA and LCA deliverables.
- Following the process conditions optimization, the unit will be operated continuously for one month to collect onstream data and demonstrate operability and reliability.

technical content

The project team is designing and validating the mechanical components of the system and completing detailed engineering and sizing of the process equipment. Global Thermostat is leveraging the phenomenological model to inform experimental work while assessing the impacts on sorbent lifetime. The process equipment is being fabricated, delivered, and integrated with the mechanical system to form an integrated DAC system. The prototype DAC unit will be commissioned and operated at the Global Thermostat Technology Center to collect onstream data that will inform the TEAs and LCAs. A primary challenge for DAC is low-cost, high-efficiency air contact. The Global DAC process employs relatively shallow honeycomb monolith contactors (~15 cm deep) that permit low

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Honeycomb Contactor with Amine-Based Sorbent for DAC

participant:
Global Thermostat LLC

project number:
FE0031957

predecessor projects:
N/A

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principal investigator:
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partners:
Georgia Institute of Technology; VADA LLC; Zero Carbon Partners LLC

start date:
10.01.2020

percent complete:
77%

pressure drops (100s of Pa) at gas approach velocities of 3–5 meters per second (m s^{-1}) while still maintaining a high geometric surface area per unit volume (Figure 1). This approach minimizes costs for gas processing by allowing the use of draft fans for gas movement upstream of the capture process.

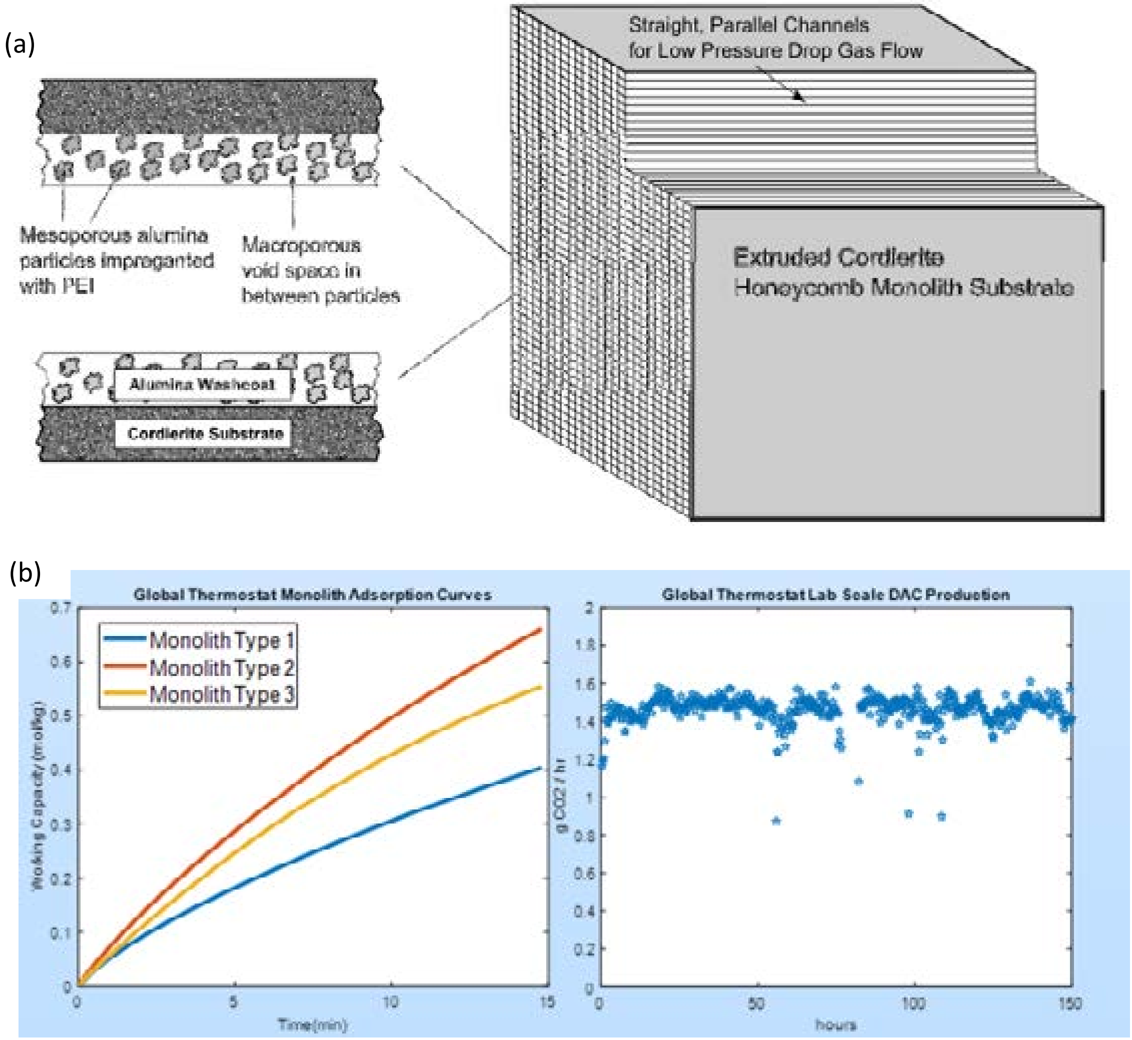

Figure 1: (a) Honeycomb monolith; (b) 15-minute DAC working capacities for Global monoliths developed.

Monolith contactors are already made on a commercial scale for numerous applications, and the technology to wash coat them with porous oxide films is mature. Global has active Joint Development Agreements (JDAs) with three global monolith manufacturers that have resulted in several production generations of advanced DAC material technology. The adsorbent itself is critical to the efficacy of the process, as it sets the productivity levels and regeneration requirements. Global has worked with Georgia Tech for several years on sorbents specifically designed for DAC. The current sorbent material is low molecular weight (~800 Dalton), highly branched poly(ethyleneimine) (PEI) that is incorporated into pores within a monolith. This allows for high volumetric amine loadings (i.e., amine sites/adsorbent volume). Solid amine adsorbents interact with CO_2 via a chemisorptive mechanism, resulting in high CO_2 adsorption capacities at very low CO_2 partial pressures and high selectivity to CO_2 over other components in air, including water. It is well established that the presence of humidity in air improves the efficiency of the adsorbent. Working capacities up to approximately 0.65 mol CO_2 per kg sorbent have been demonstrated under the standard Global adsorption process conditions of 5 m s^{-1} air approach velocity and a 15-minute duration (Figure 1b).

A drawback of the current PEI sorbent is a limited lifetime, primarily due to oxidation and polymer leaching. Global has done extensive prior research in both of these areas to establish lifetime targets. Figure 1b shows cyclic onstream data at laboratory scale for approximately 150 continuous hours of operation. PEI leaching rates and oxidation rates have been measured and it is estimated that the sorbent can maintain 80% of its capacity over approximately 100,000 cycles.

Desorption of CO_2 is performed by a temperature swing delivered by condensation of saturated steam directly onto the monolith surface, raising the temperature to approximately 70–100°C. Steps are performed before and after this to maintain sorbent lifetime and achieve high CO_2 purity. The core sequence of the Global regeneration process cycle is as follows:

1. Reduction in O_2 concentration surrounding the monolith.
2. Direct contact condensation of steam to heat the monolith and desorb CO_2.
3. Cooling of the monolith by evaporation of condensed water on its surface.

Internal heat integration may be performed by recycling the stream, resulting from Step 3 and including it in Step 1. In the current first-generation Global batch process, Step 1 and Step 3 are performed using vacuum. In the second-generation continuous process described here, these steps are performed with inert gas or a recycled product CO_2 stream. Critically, CO_2 is being neither adsorbed nor desorbed in Step 1 or Step 3, so minimizing their cumulative step times is important for maximizing productivity. Step 3 is conducted at constant pressure and CO_2 is removed as it is evolved by a vacuum pump or blower. This approach produces a steam/CO_2 mixture that, after passing through a condenser/separator, gives a 95+% CO_2 product.

technology advantages

- Rapid cycles (less than 20 minutes) enabled by monolith contactor (adsorption) and steam regeneration (desorption); reduced amortized CAPEX.
- High capital utilization efficiency (improved CAPEX) while maintaining low pressure drop, improved operation expenses (OPEX) via panel movement.
- High uptakes enabled by amine dense sorbent (improved CAPEX and OPEX).

R&D challenges

- Physical movement of large components can be mechanically challenging, particularly in a batch process (start/stop).
- Maintaining adequate sorbent life over many cycles.
- Requires careful consideration of movement and sealing methodologies to maximize adsorbent lifetime.

status

Global Thermostat continued to develop their continuous DAC prototype based on the Gas Technology (GT) platform and has completed the mechanical design, fabrication, and commissioning of the mechanical movement system, and conducted a 30-day field test campaign. Researchers learned the wiper seals were not adequate to maintain product purity and sorbent lifetime. The GT contactors were mechanically robust enough to utilize direct contact rollers with high contact area to maximize effectiveness, and the optimization of the evaporative cooling in inert flow is more complex than optimizing the air purge. Future testing and development in will include finishing testing and process commissioning of the DAC system. The testing campaign will generate data demonstrating the reliability of the dynamic sealing methodology, the effectiveness of purge and cooling steps, and the overall impact on the DAC TEA and LCA analysis.

available reports/technical papers/presentations

Eric W. Ping, Stephanie Didas, "Demonstration of a Continuous-Motion Direct Air Capture (DAC) System," 2023 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_CDR29_Ping.pdf*.

Miles Sakwa-Novak, "Demonstration of a Continuous Motion Direct Air Capture System," 2022 Carbon Management Project Review Meeting, Pittsburgh, PA, August 2022. *https://netl.doe.gov/projects/files/Demonstration%20of%20a%20Continuous%20Motion%20Direct%20Air%20Capture%20System.pdf*.

Eric W. Ping, "Demonstration of a Continuous Motion Direct Air Capture System," 2022 Budget Period 1 Review Meeting, Pittsburgh, PA, July 2022. *https://netl.doe.gov/projects/files/Demonstration%20of%20a%20Continuous%20Motion%20Direct%20Air%20Capture%20System.pdf*.

Miles Sakwa-Novak, "Demonstration of a Continuous Motion Direct Air Capture System," NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Novak.pdf*.

Eric W. Ping, "Demonstration of a Continuous Motion Direct Air Capture System," Direct Air Capture Kickoff Meeting Presentation, Pittsburgh, PA, February 2021. *https://netl.doe.gov/sites/default/files/netl-file/21DAC_Ping.pdf*.

A Combined Water and CO_2 Direct Air Capture System

primary project goal

IWVC LLC is developing a transformational hybrid direct air capture (HDAC) technology that simultaneously captures carbon dioxide (CO_2) and water from the air using highly specialized solid sorbents developed together with the Pacific Northwest National Laboratory (PNNL). In HDAC, a combination of high-performance desiccant and CO_2-selective sorbents are used to remove both water vapor and CO_2 from the air in a single pass through the HDAC system.

technical goals

- Conduct a detailed design for a 3,000-cubic-feet-per-minute (CFM) HDAC unit to validate the initial electrical, heat, mass, and fluid flow requirements for the system.
- Procure components and fabricate the complete HDAC unit.
- Execute field-testing of the HDAC unit and prepare a final report on the testing, results, conclusions, and recommendations.

technical content

Producing commercially significant amounts of CO_2 from a DAC system requires movement of a large volume of air through the device. Because the emerging field of atmospheric water extraction (AWE) similarly requires movement of large volumes of air, integration of these two technologies into a single overall process has the potential to become more economically and environmentally attractive than if pursued separately. Figure 1 shows the process flow diagram for IWVC's pilot plant consisting of a pair of chambers with a water capture bed (AWE) and CO_2 capture bed (DAC). The operating principles are simple. First, humid air flows over a desiccant bed that removes moisture. A parallel desiccant bed is isolated from the air stream and simultaneously regenerated under a vacuum. The AWE section of the unit utilizes a temperature and pressure swing regeneration cycle. The desiccant beds can be thermally controlled. This thermal control optimizes desiccant capacity both during uptake, when the heat of water vapor adsorption is generated in the active desiccant bed, and during regeneration, when the endothermic heat of desorption is consumed in the desiccant bed. Air exiting the desiccant bed can be kept within a desired temperature and humidity window. The vacuum system provides suction on the desiccant bed during its regeneration cycle.

The low relative humidity air stream then enters the second set of sorbent beds that are selective for CO_2 removal and are designed for optimum removal of CO_2 from the air stream at low relative humidities. Carbon dioxide regeneration occurs within the same chamber as the AWE bed, where both are exposed to vacuum and the increase in water vapor pressure facilitates the release of CO_2. The product gases are compressed to ambient by the vacuum system and separated

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Combined Desiccant and CO_2 -Selective Sorbent in DAC System

participant:
IWVC LLC

project number:
FE0031970

predecessor projects:
N/A

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partners:
Barr Engineering; University of North Texas

start date:
10.01.2020

percent complete:
95%

by the condensation of water vapor. In commercial systems, the heat recovered from compression and condensation can be supplemented with an external low-grade heat source (waste heat, solar, or resistance heating) to thermally regenerate the beds. The warm/dry air stream is exhausted to ambient conditions. Using this design approach, the system can capture CO_2 and water with a low-energy requirement.

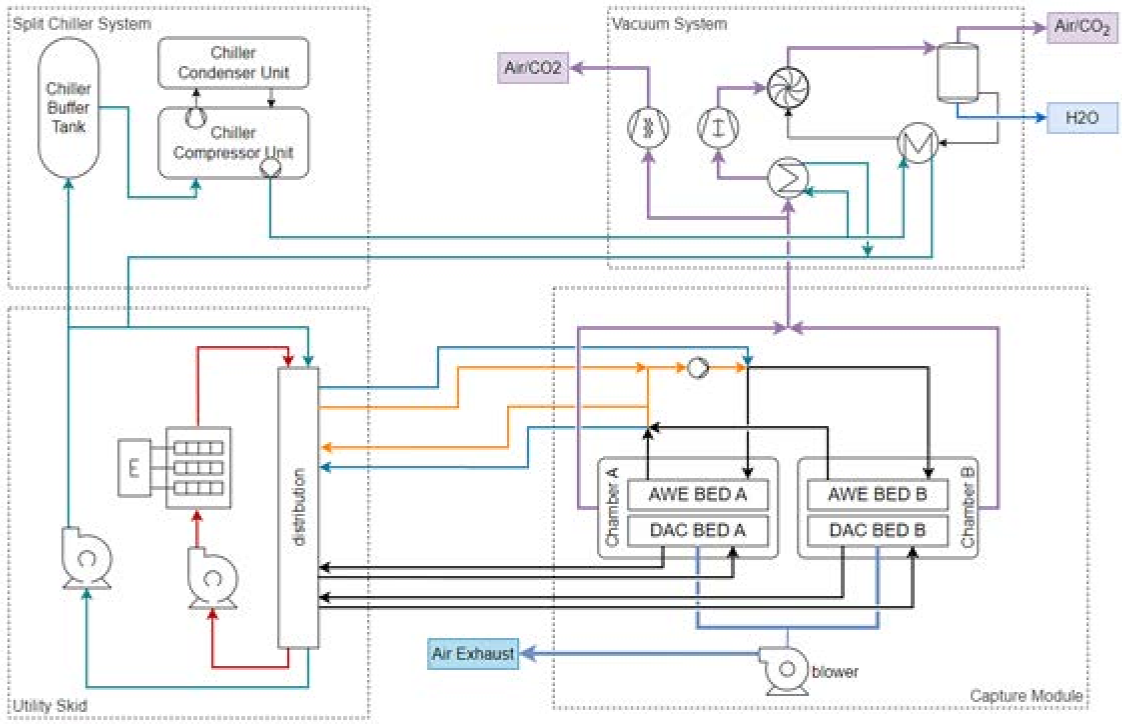

Figure 1: Process flow diagram of IWVC LLC's Bakersfield pilot plant.

The project tasks included conducting a detailed design of the HDAC pilot unit sufficient to provide specifications to individual component manufacturers and parts suppliers for the HDAC unit build; optimizing the CO_2 sorbent bed cycling; and evaluating energy savings potential for incorporation of multiple sorbents in the AWE and DAC section of the design. The implementation of multiple sorbents would potentially stagger the release of CO_2, thus providing CO_2 mass flow earlier in the regeneration cycle and optimizing compressor use. The beds can also be heated to different regeneration temperatures, thus reducing thermal energy input required to achieve the same CO_2 production rate. The energy savings potential for this second sorbent was quantified using data on University of South Florida's (USF) SIFSIX CO_2 sorbent and a recommendation was provided on whether to include this option in the HDAC pilot unit.

Initial CO_2 sorbent considerations included self-assembled monolayers on mesoporous supports (SAMMS) that had been previously developed by PNNL. These were supplemented by the aforementioned class of SIFSIX materials following detailed testing. Various AWE desiccant materials have been considering, starting at MOF-303 desiccant. IWVC has conducted extensive investigations into several lower-cost and higher-capacity alternatives, for both the AWE desiccant and DAC sorbents, and will be testing these on the pilot facility.

The sorbent surface coating (both desiccant and DAC) on aluminum fins of heat exchange contactors is a critical step in achieving the uniform sorbent thin film for high diffusive flux of water as well as CO_2 molecules. The aluminum fin supports with sorbents bonded have been assembled into desiccant beds by incorporating the heat pipes/heat supply tubes with the fin supports. Final assembly included end caps and structural supports for mounting the desiccant beds in their respective housings. The complete assemblies were shipped to Barr Engineering for incorporation in the HDAC pilot unit. The unit has been constructed and commissioned in Bakersfield, California.

TABLE 1: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	600	284
Cost of Carbon Avoided	\$/tonne CO_2	—	—
Capital Expenditures	\$/tonne CO_2	342	112
Operating Expenditures	\$/tonne CO_2	258	172

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Calculations Basis – Values are derived from the techno-economic analysis (TEA) previously employed to obtain values for the initial application and technology maturation plan for project no. FE0031970 and will be updated with current system configurations and confirmed values for sorbent and system performance for the pilot plant described in the scope of the project.

Scale of Validation of Technology Used in TEA – Current values for sorbent performance have been obtained by laboratory testing by PNNL. Overall system performance has been modelled by IWVC. The pilot plant is currently in operation to evaluate the newest sorbents and processes.

Qualifying Information or Assumptions –

- Sorbent cyclical performance in application is estimated at 50% of successful laboratory-scale testing.
- Sorbent and plant life cycle analysis (LCA) are to be determined and will be reported at a later stage of the project.

technology advantages

- System engineering eliminates large thermodynamic inefficiencies with pure thermal swing regeneration cycles performed in typical AWE designs.
- Combining potable water generation and CO_2 capture in a single device with the unique energy conserving features of the design enables a competitive cost of capture to be achieved with much smaller plant capacities and capital costs than required by conventional DAC systems.
- The integrated DAC and AWE system makes DAC technology deployable in more locations with limited water resources.
- Fast kinetics, coupled with low water content, enhances the carrying capacity and reduces regeneration energy.

R&D challenges

- Fabrication of HDAC unit.
- Installation and operation of the HDAC unit at the host site.
- Development and selection of materials.

status

IWVC LLC has completed the HDAC detailed design and manufacturing of the unit. Testing was completed to evaluate coating performance with the desiccant and sorbent materials. The coating tests showed no reduction in water (H_2O) and CO_2 capacity due to the coating procedure. The pilot facility has been constructed and commissioned in Bakersfield, California. Process and materials development is being implemented to finalize operational parameters for long-term testing.

available reports/technical papers/presentations

Neel Rangnekar, Alexander Spiteri, "A Combined Water and CO_2 Direct Air Capture System," 2024 Carbon Management Project Review Meeting, Pittsburgh, PA, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_CDR_6_Rangnekar.pdf*.

Will Kain, "A Combined Water and CO_2 Direct Air Capture System," 2022 Carbon Management Project Review Meeting, Pittsburgh, PA, August 2022. *https://netl.doe.gov/projects/plp-download.aspx?id=13809&filename=A+Combined+Water+and+CO2+Direct+Air+Capture+System.pdf*.

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Energy-Efficient Direct Air Capture System for High-Purity CO_2 Separation

primary project goal

The University of Cincinnati (UC) is developing a revolutionary carbon dioxide (CO_2) capture system optimized for direct air capture (DAC). The technology utilizes an adsorption-regeneration cycle with a proprietary aminopolymer-silica hybrid adsorbent. UC is being assisted by BASF Catalysts in developing the sorbent-washcoated monolith structure and Trimeric for the economic analysis.

technical goals

- Perform a computational fluid dynamics (CFD) analysis to model fluid mechanics and adsorption kinetics to establish baseline adsorbent geometry.
- Manufacture sorbent in-house. Establish long-term lab-scale performance criteria.
- Manufacture sorbent-washcoated monolith structure.
- Design, construct, and test air contactor structure.
- Design, construct, and test full DAC system.
- Evaluate performance of adsorbent-washcoated monolith in air contactor/DAC system.
- Perform a techno-economic analysis (TEA) and life cycle analysis (LCA) and construct a state-point data table for the whole system.

technical content

UC is developing a new adsorbent material with a proprietary hybrid blend of aminopolymer and silica with a washcoated monolith structure. The new adsorbent is slated to be used in a DAC system that constructed in partnership with BASF Catalysts. Trimeric is assisting in carrying out a full-scale TEA and LCA for the complete DAC system. The scope of work for this project consists of the determination of CO_2 adsorption kinetics (via process modeling through a CFD study); sorbent manufacturing; development of the sorbent-washcoated monolith structure; the design, fabrication, and operation of a passive air contactor; performance evaluations; and TEAs and LCAs. The DAC system design makes use of a novel air contactor system that is slated to maximize CO_2 throughput with minimal external energy requirements (less than 50 kJ/mol CO_2 for desorption). The sorbent is being designed to be resistant to both oxidative and thermal degradation with cost-effective scalability. The air contactor is being designed for high air throughput with minimum pressure drop. The process parameters of the complete DAC sorbent system are shown in Table 1, while a schematic of the air contactor system is shown in Figure 1.

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Sorbent-Washcoated Monolith in Air Contactor System

participant:
University of Cincinnati

project number:
FE0032128

predecessor projects:
N/A

NETL project manager:
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University of Cincinnati
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partners:
BASF Catalysts LLC; Trimeric

start date:
10.01.2021

percent complete:
70%

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,371	1,371
Bulk Density	kg/m^3	941	941
Average Particle Diameter	mm	0.02-0.04	0.02-0.04
Particle Void Fraction	m^3/m^3	0.31	0.3-0.4
Packing Density	m^2/m^3	470,000	TBD
Solid Heat Capacity @ STP	kJ/(kg-K)	1.30	1.30
Crush Strength	kg_f	Not applicable	TBD
Attrition Index	-	~7-10	~7-10
Thermal Conductivity	W/(m-K)	Not available	TBD
Manufacturing Cost for Sorbent	$/kg	4-8	4-8
Adsorption			
Pressure	bar	1.013	1.013
Temperature	°C	0-40	0-40
Equilibrium Loading	g mol CO_2/kg	1.1-1.7	1.1-1.7
Heat of Adsorption	kJ/mol CO_2	~66	~66
CO_2 Adsorption Kinetics	gmol/(kg sorbent×min)	~0.01-0.1	~0.01-0.1
Desorption			
Pressure	bar	0.3-1	0.3-1
Temperature	°C	70-90	70-90
Equilibrium CO_2 Loading	g mol CO_2/kg	~0.1	~0.1
Heat of Desorption	kJ/mol CO_2	<~50	<~50
CO_2 Desorption Kinetics	gmol/(kg sorbent×min)	~0.2-0.3	~0.2-0.3

Proposed Module Design		(for equipment developers)		
Flow Arrangement/Operation	—	Flow though monolith in air contactor, adsorption-desorption cycles		
Air Flowrate	kg/hr	<~780		
Space Velocity	hr^{-1}	<80,000		
Volumetric Productivity	$gmol_{CO2}/(hr \times V(L)_{absorber\ bed})$	<~1		
CO_2 Recovery, Purity, and Pressure	% / % / bar	>90%	>95%	1.0325 (without compression)
Adsorber Pressure Drop	bar	<0.002		
Degradation	% capacity fade/cycle	<0.007		
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	Not available		

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

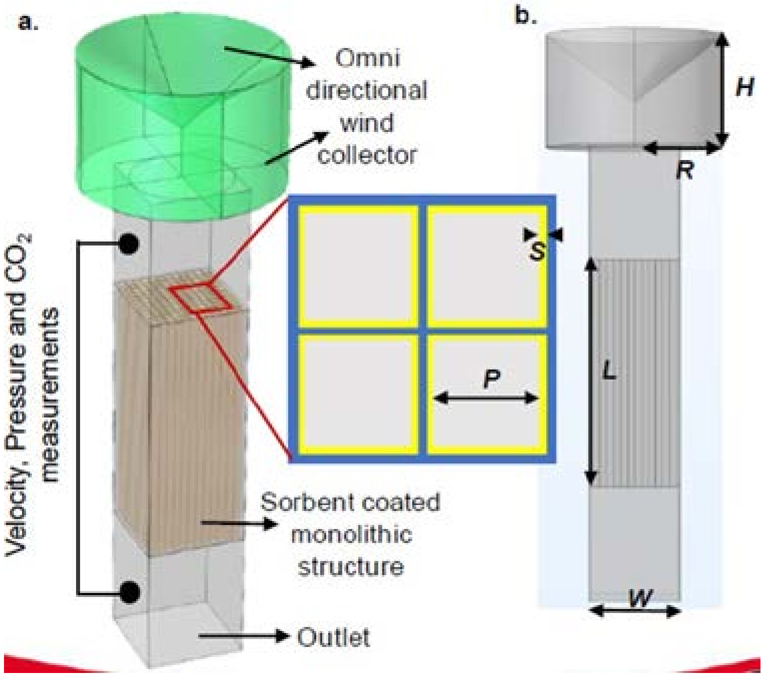

Figure 1: Passive air contactor (a) isometric view and (b) side view.

One of the core strengths of the new adsorbent mixture is the resistance to oxidative and thermal degradation. Figure 2 highlights the performance of the proposed sorbent compared to that of a conventional one of similar chemical makeup. The modified aminopolymer/silica blend suffers significantly less weight loss over time and is able to maintain high performance for more than 30 times longer than the conventional sorbent blend.

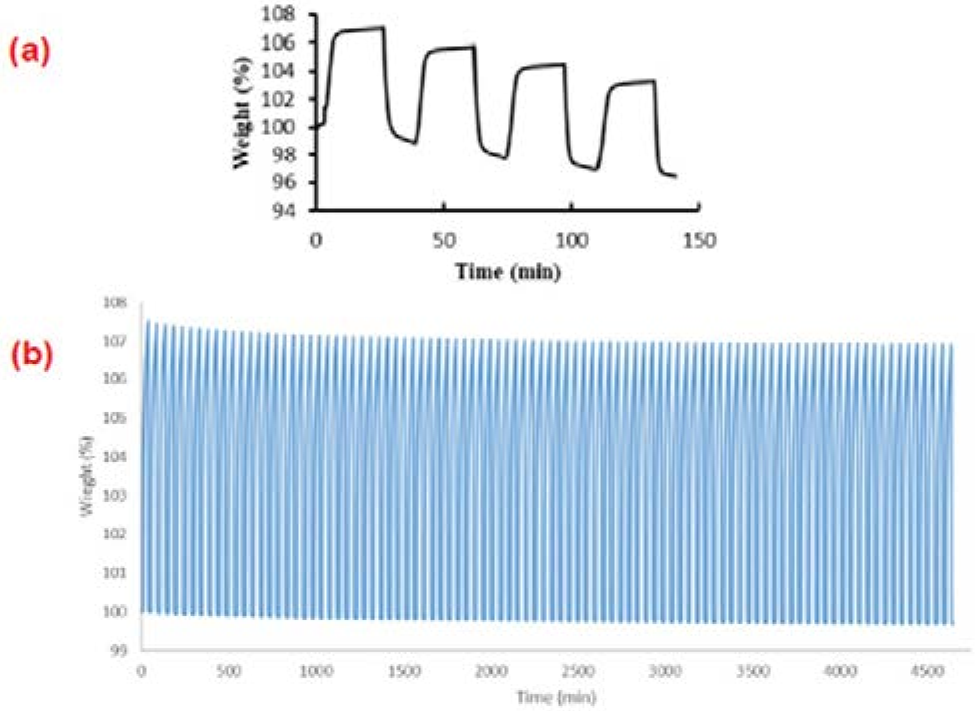

Figure 2: Degradation performance (@ 25°C, 400 ppm CO_2 in dry air) of (a) conventional aminopolymer/silica and (b) modified aminopolymer/silica.

A TEA is being performed as a part of this study. Predicted and target economics results are shown in Table 2.

TABLE 2: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	150	100
Cost of Carbon Avoided	\$/tonne CO_2	n/a	n/a
Capital Expenditures	\$/tonne CO_2	n/a	n/a
Operating Expenditures	\$/tonne CO_2	n/a	n/a

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Feed Gas Assumptions –

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	50-105 °F	0.04	variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Chemical adsorption by complex formation.

Sorbent Contaminant Resistance – Selectivity toward CO_2 over H_2O and resistance to O_2.

Sorbent Attrition and Thermal/Hydrothermal Stability – Sorbent attrition is dependent on sorbent coating onto monolith and the monoliths are being prepared using the proprietary formulations of BASF. Thermal stability is warranted by controlling temperature and pressure conditions for desorption.

Flue Gas Pretreatment Requirements – N/A.

Sorbent Make-Up Requirements – Sorbent make-up rate is determined from long-term cyclic evaluations of the sorbent.

Waste Streams Generated – Waste gases (mostly water).

technology advantages

- Lower degradation rate: longer lifespan.
- Low required desorption energy input (<80 kJ/mol).
- Air contactor requires no external energy input.
- High CO_2 purity (>95%).
- High CO_2 adsorption selectivity.
- Low air-side pressure drop.

R&D challenges

- Development of the sorbent-washcoated monolith structure.
- Establishing the CO_2 adsorption kinetics.

status

The project team successfully completed preliminary CFD studies of the passive air contactor for the complete capture system. Small-scale and larger-scale monoliths were constructed and successfully tested using various sorbent coating amounts. The performance of these structures has been successfully tested, pending implementation in the full-scale DAC system.

available reports/technical papers/presentations

Lee, J., 2024, "Energy-Efficient Direct Air Capture System for High-Purity CO_2 Separation." Presented at the 2024 Carbon Management Project Review Meeting. Pittsburgh, PA. August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_CDR_5_Youp.pdf*.

Akinjide, J.; Lee, J.-Y.; Priye, A. Harnessing Wind with a Passive Direct Air Capture System for CO_2 Capture, *Ind. Eng. Chem. Res.*, 2023, *62*, 18780.

Akinjide, J.; Priye, A.; Lee, J.-Y. "CO_2 Adsorption Kinetic Model for Direct Air Capture," Paper # 130f, *AIChE Annual Meeting*, Orlando, FL, November 5-10, 2023.

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Ummireddi, A.; Payra, S.; Akinjide, J.; Lee, J.-Y. "Scale-up of CO_2 Capture from Powdered Sorbent to Sorbent-Washcoated Monolith for Direct Air Capture," Paper # 156e, *AIChE Annual Meeting*, Orlando, FL, November 5-10, 2023.

Lee, J., 2023, "Energy-Efficient Direct Air Capture System for High-Purity CO_2 Separation." Presented at the 2023 Carbon Management Project Review Meeting. Pittsburgh, PA. August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_CDR28_Lee.pdf*.

Akinjide, J.; Priye, A.; Lee, J.-Y. "Adsorption Kinetic Model for Direct Air Capture," Paper # 628d, *AIChE Annual Meeting,* Phoenix, AZ, November 13-18, 2022.

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Ma, Y.; Lee, J.-Y. "Epoxide-Modified Amine-Based CO Adsorbent for Direct Air Capture," Paper # 371h, *AIChE Annual Meeting,* Phoenix, AZ, November 13-18, 2022.

Lee, J., 2022, "Energy-Efficient Direct Air Capture System for High-Purity CO_2 Separation." Presented at the 2022 Carbon Management Project Review Meeting. Pittsburgh, PA. August 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_CDR17_Lee.pdf*.

Lee, J., 2022, "Energy-Efficient Direct Air Capture System for High-Purity CO_2 Separation." Project Kickoff Meeting. DOE/NETL. Pittsburgh, PA. March 2022.

Advanced Integrated Reticular Sorbent-Coated System to Capture CO_2 Using an Additively Manufactured Contactor

primary project goal

General Electric Research (GE), with partners University of California at Berkeley (UCB) and the University of South Alabama, is developing an advanced integrated reticular sorbent-coated system to capture carbon dioxide (CO_2) using an additively manufactured contactor (AIR2CO2 Contactor) and testing a bench-scale (1 kg CO_2/day) direct air capture (DAC) system that consists of two low-pressure drop AIR2CO2 Contactors that alternate adsorption/desorption cycles for continuous CO_2 removal from ambient air.

technical goals

- Scale-up synthesis of the optimized MOF-808-Lys for sorbent integration and refinement of the sorbent cost model.
- Perform systems engineering and computational fluid dynamics (CFD) modeling for bench-scale AIR2CO2 Contactor system.
- Construct and test contactor components for pressure drop and adapt sorbent-binder composite coatings onto these components to evaluate CO_2 capture performance under DAC conditions.
- Fabricate a bench-scale (up to 1 kg CO_2/day) AIR2CO2 Contactor system and evaluate performance.
- Perform a techno-economic analysis (TEA) and life cycle analysis (LCA).

technical content

The AIR2CO2 Contactor combines UCB's metal-organic framework (MOF) sorbents (Figure 1) for CO_2 capture and GE's sorbent-binder composite formulation and coating process in an additively manufactured, low pressure drop contactor (Figure 2). Operation of the integrated system will allow for continuous removal of CO_2 from air via alternating temperature vacuum swing adsorption/desorption cycles. The coated component performance characteristics and process conditions are summarized in Table 1, along with target performance metrics for an optimized sorbent-coated contactor.

A major focus of the program is to evaluate various prototype contactor (e.g., hydraulic diameter) and sorbent coating (e.g., coating thickness) properties as a function of gas flow rate to understand the effects on pressure drop across the contactor. CFD modelling is performed to reach an understanding of the CO_2/H_2O

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Novel Additively Manufactured Air Contactor with Integrated Sorbent

participant:
General Electric Research

project number:
FE0032126

predecessor projects:
FE0031956

NETL project manager:
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principal investigator:
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General Electric
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partners:
University of California Berkeley; University of South Alabama

start date:
10.01.2021

percent complete:
95%

transport process at relevant length scales (micropore and macropore scales) and complimented by experiments to understand the impact of the coating on sorbate diffusion resistances.

The project tasks are to: (1) produce a bench-scale contactor by scaling the contactor fabrication and sorbent-coating processes; (2) validate the CFD model and pressure drop predictions; (3) fabricate a second bench-scale contactor and combine with the relevant balance of plant components (e.g., fans, steam generator, vacuum pump, etc.); (4) evaluate the contactor system against the performance criteria detailed in Table 1 under DAC conditions; perform iterate experimentation with varying process conditions to understand the operating envelope of the AIR2CO2 Contactor system for removal of up to 1 kg CO_2/day from ambient air; and (5) utilize outputs of the sorbent scaling efforts, the CFD modelling, and CO_2 capture experiments to develop a TEA and LCA of the full AIR2CO2 Contactor system.

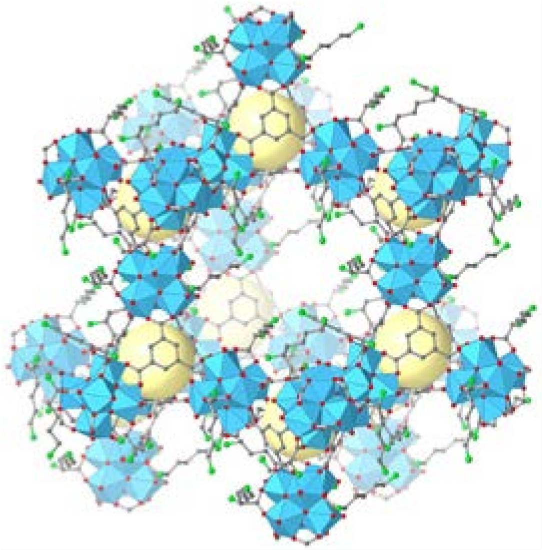

Figure 1: MOF-808-Lys sorbent.

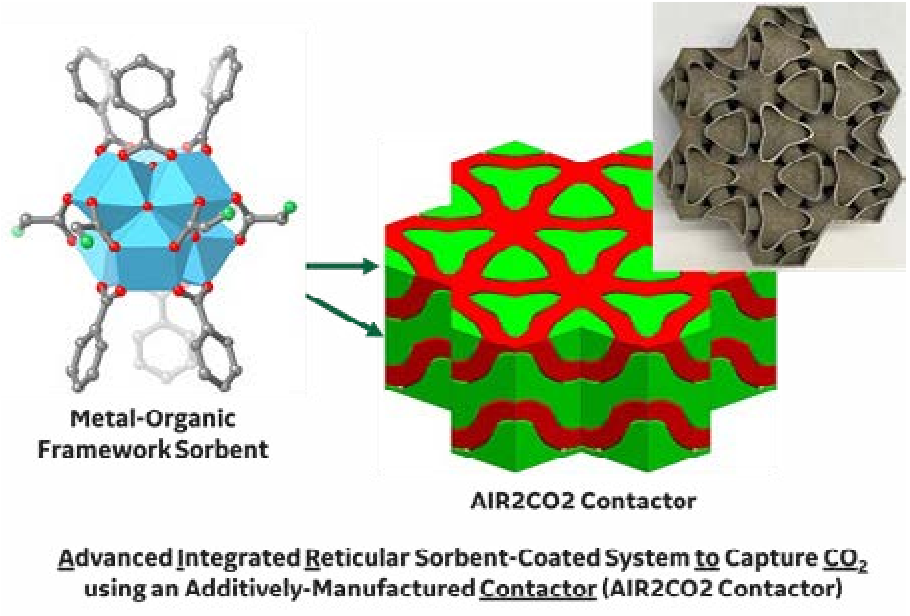

Figure 2: AIR2CO2 Contactor project (FE0032126). Sorbent-coated contactor design showing sorbent-integrated channels (green) and hot air channels for desorption (red).

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	520	520
Bulk Density	kg/m^3	350	350
Average Particle Diameter	mm	0.002-0.01	0.002-0.01
Particle Void Fraction	m^3/m^3	0.3	0.3
Packing Density	m^2/m^3	$\sim 2.7 \times 10^5$	$\sim 5.6 \times 10^5$
Solid Heat Capacity @ STP	kJ/kg-K	0.866	—
Crush Strength	kg_f	Not applicable	Not applicable
Attrition Index	-	Not applicable	Not applicable
Thermal Conductivity	W/(m-K)	0.125	—
Manufacturing Cost for Sorbent	$/kg	—	—
Adsorption			
Pressure	bar	0.0004	0.0004
Temperature	°C	25	25
Equilibrium Loading	g mol CO_2/kg	0.07	2.3
Heat of Adsorption	kJ/mol CO_2	72	72
CO_2 Adsorption Kinetics	gmol/kg·min	5.5×10^{-4}	0.2
Desorption			
Pressure	Bar	<0.0004	<0.0004
Temperature	°C	100-120	80-110
Equilibrium CO_2 Loading	g mol CO_2/kg	0.01	0.25
Heat of Desorption	kJ/mol CO_2	72	72
CO_2 Desorption Kinetics	gmol/kg·min	1.1×10^{-4}	0.2
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	—	
Flue Gas Flowrate	kg/hr	—	
Space Velocity	hr^{-1}	150,000	
Volumetric Productivity	$gmol_{CO2}/(hr\ l_{absorber\ bed})$	2	
CO_2 Recovery, Purity, and Pressure	% / % / bar	70 95 —	
Adsorber Pressure Drop	Pa	150	
Degradation	% capacity fade/cycle	0.0001	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Feed-Gas Assumptions –

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	-70 °F	0.04	variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Fundamental process by which the sorbent materials adsorb or react with gases of interest. At high CO_2 partial pressures, both chemisorption and physisorption of CO_2 occurs. At DAC conditions (0.04 kPa CO_2), only chemisorption of CO_2 occurs.

Sorbent Contaminant Resistance – Ability for the solid sorbent materials to perform under direct air conditions despite the presence of volatile components coming in contact with the sorbent-integrated contactor system. Nitrogen oxide (NO_X) is not expected to have a significant impact on sorbent performance; however, reaction of amine-based sorbents with sulfur oxide (SO_X) to form heat-stable salts is a known issue that will slowly decrease sorbent capacity.

Sorbent Attrition and Thermal/Hydrothermal Stability – Evaluation of the performance and life of the solid sorbent materials as a result of exposure to temperature and relative humidity. Long-term thermal/hydrothermal stability of the sorbent-binder composite under operating conditions is being investigated.

Waste Streams Generated – Waste gases that are produced as a result of CO_2 capture and release.

technology advantages

- A compact, low pressure drop, sorbent agnostic contactor design that can only be fabricated using additive manufacturing
- Lower energy potential compared to conventional solvents.
- Tailored reticular sorbent-binder structured material composite with the potential for high capacities, rapid sorption kinetics, and robust cycle performance.
- Modular and scalable contactor system that enables alternating capture and release of atmospheric CO_2.

R&D challenges

- Ability to achieve 1 kg CO_2/day bench-scale testing of coated additively printed parts.
- Achieving the desired energetics and cost of capture.
- Scale-up potential: demonstration scale with full-size additive contactor.
- Understanding the mass transfer mechanisms of the integrated sorbent/contactor system.
- Lack of sorbent coating uniformity and hysteresis result in rapid system degradation.
- Insufficient sorbent-binder composite capacity and slow CO_2 capture/release kinetics.

status

The project completed an optimized contactor design in order to achieve pressure drop target values. The GE-115 sorbent was successfully integrated into the AIR2CO2 system with coatings that allow the sorbents to retain more than 80% of their normal CO_2 capacity. The system has successfully met several performance targets, including achieving 67.5% capture efficiency (50% target), a space velocity of 86,000/hour (50,000/hour target), and a pressure drop of 235 Pa (less than 500 Pa target).

available reports/technical papers/presentations

Moore, D., 2024, “AIR2CO2 Contactor: Advanced Integrated Reticular Sorbent-Coated System to Capture CO_2 using an Additively-Manufactured Contactor.” Presented at the 2024 Carbon Management Project Review Meeting. Pittsburgh, PA. August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_CDR_5_Moore.pdf*.

Moore, D., 2023, “AIR2CO2 Contactor: Advanced Integrated Reticular Sorbent-Coated System to Capture CO_2 using an Additively-Manufactured Contactor.” Presented at the 2023 Carbon Management Project Review Meeting. Pittsburgh, PA. August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_CDR28_Moore.pdf*.

Moore, D., 2021, “AIR2CO2 Contactor Kick-Off: Advanced Integrated Reticular Sorbent-Coated System to Capture CO_2 Using an Additively-Manufactured Contactor.” NETL/DOE Kickoff Meeting Presentation. December 6, 2021. *https://netl.doe.gov/projects/plp-download.aspx?id=12536&filename=Advanced+Integrated+Reticular+Sorbent-Coated+System+to+Capture+Carbon+Dioxide+(CO2)+Using+an+Additively-Manufactured+Contactor+(AIR2CO2+Contactor).pdf*.

Direct Air Capture of Energy for Carbon Capture, Utilization, and Storage Partnership (DAC RECO$_2$UP)

primary project goal

Southern States Energy Board (SSEB) led efforts, with AirCapture LLC, to advance a solid amine sorbent-based technology for direct air capture (DAC) through field testing in a commercially relevant environment. The primary goal of the DAC RECO$_2$UP project was to decrease the cost of DAC through the testing of existing DAC materials in integrated field units that produce a concentrated carbon dioxide (CO_2) stream of at least 95% purity. This project focused on engineering design of an integrated DAC system utilizing energy recovery and support services at the National Carbon Capture Center (NCCC).

technical goals

- Conduct applied research and development (R&D) to decrease the cost of DAC from atmospheric air and mixtures of air and simulated industrial gases available in a test bay at the NCCC.
- Develop and scale-up an integrated system utilizing energy recovery at the NCCC.
- Increase the integrated system's fidelity by validating and demonstrating operations in a simulated commercial environment by maximizing capital efficiency and energy efficiency.
- Identify and address key technical barriers, within a representative operating environment, in support of DAC technology commercialization.
- Perform a pre-screening TEA and LCA to determine the environmental sustainability (amount of carbon negativity) and economic viability (cost impacts) of the integrated DAC system.

technical content

The DAC technology, previously developed by Global Thermostat, employs a solid-amine CO_2 adsorption-desorption cycle using a honeycomb-type monolithic contactor impregnated with a solid polyethylenimine polymer that forms agglomerations of polymeric amine capture sites within the mesopores of the contactor. A fan draws air or mixtures of air and CO_2-rich gas streams through the contactor in a laminar flow regime wherein CO_2 is adsorbed by the contactor via diffusion into the contactor walls perpendicular to the airflow. The ultra-low pressure drop monoliths maximize the efficiency of air flow, increasing mass transfer of CO_2 for adsorption. Once the sites bind sufficient quantities of CO_2, the monoliths are then exposed to vacuum and steam heat to desorb the CO_2 from the solid sorbent. The latent heat and hydration from the steam liberates the CO_2

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Monolith Contactor with Amine-Based Sorbent for DAC

participant:
Southern States Energy Board

project number:
FE0031961

predecessor projects:
N/A

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principal investigator:
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Southern States Energy Board
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Kimberly S. Gray
Southern States Energy Board
gray@sseb.org

partners:
AirCapture LLC; Crescent Resource Innovation;

start date:
10.01.2020

percent complete:
100%

from the amine capture sites and acts as a sweep gas pushing the CO_2 out of the contactor towards a condenser, which condenses the steam back into water for recycle, leaving greater than 98.5% CO_2 gas. The CO_2 is collected and the contactor is cooled via thermal recovery and evaporative heat loss and cycled back to adsorption mode, repeating the cycle.

The technology employs a desorption mechanism that leverages a combination of vacuum and low-temperature steam, which together provide a rapid and efficient mechanism of CO_2 desorption while reducing the primary deactivation mechanism of amine oxidation at regeneration temperatures. Laboratory testing has demonstrated the technology's highest efficiency of CO_2 adsorption-desorption mass transfer ratio 10:1 with 900:90 second adsorption-desorption for air concentrations of CO_2. Increasing the technology fidelity in a system capable of continuously cycling 10 contactor assemblies, wherein nine positions are in CO_2 capture mode and one position is in regeneration mode, with integrated system architecture and robust operations, is required to advance the design. Engineering principles of airflow dynamics, movement of contactors through a cyclically sealed regeneration system, and efficient thermal transfer of low-temperature steam are all well understood.

Detailed laboratory-scale research has been conducted with pre-prototypical configurations using integrated unit operations achieving Technology Readiness Level (TRL) 4. Figure 1 shows a laboratory-scale system used to test and validate monolith adsorption performance, desorption performance, and cycle times. Various tests were carried out on air concentrations of CO_2, along with higher feed concentrations of CO_2, both within co-fed air streams and simulated air streams.

Figure 1: GT's laboratory-scale system used to test and validate monolith adsorption performance, desorption performance, and cycle times.

The laboratory system used the following primary process steps and time/control targets: airflow (5–20 minutes); drain (drain water, 5 seconds); pump down (remove air/O_2 from chamber to prevent oxidation and increase pressure, 10 seconds, 0.2 bar); pressurize (increase pressure in chamber, 10 seconds, 0.6–1.5 bar); regen/CO_2 collection (regenerate monolith, collect CO_2, 30–240 s); and cool (reduce pressure, flash off steam, 0.3–0.6 bar).

Figure 2: DAC and heat treatment skid installed at the NCCC.

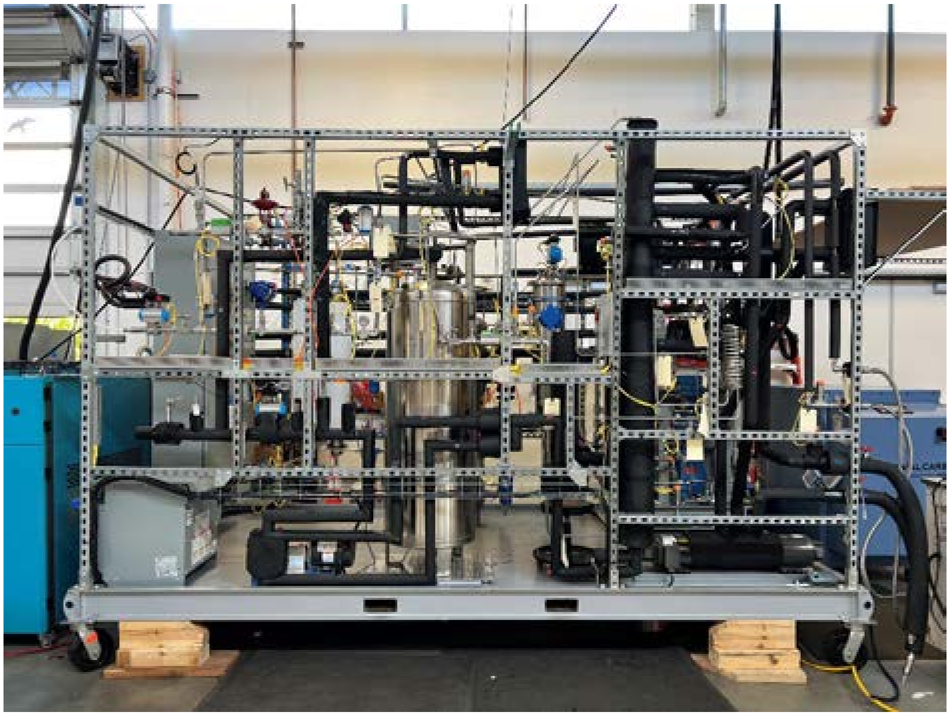

Figure 3: CO_2 compression, storage, and upgrading skid before being installed at the NCCC.

This project involved a three-phased testing campaign being conducted in an integrated system environment at the NCCC. A DAC skid capable of adsorbing/desorbing CO_2 using GT's solid-amine sorbent monolithic contactors and an energy recovery integration skid that uses process control and heat exchangers to produce the required steam for the DAC process were constructed and installed at the NCCC (Figure 2). AirCapture also provided an existing third skid capable of compressing, liquifying, and purifying the CO_2 (Figure 3).

TABLE 1: PERFORMANCE PARAMETERS AND TARGETS

Performance Attribute	Performance Target	Current Status/ Test Range	Comments/Justification for Performance Requirement
Capture Efficiency	>50%	30–60%	Dependent on contactor, airspeed, environmental conditions. Ideal economic case may be below 50% depending on environmental conditions and local energy costs.
Gas CO_2 Purity	>95%	>97%	Purity ranges between 95–99% have been achieved. Depends on process control set points for desorption rough down.
Liquefaction Efficiency	>95%	TBD	Liquefaction efficiency should be above 95% to avoid excessive product losses, which increase overall cost (95% is a suitable target based on preliminary TEA work).
Liquid CO_2 Purity	99.9%	TBD	Liquid CO_2 purity should exceed the proposed target to achieve minimum purity required by various industries. Greater than 99.9% has been achieved at Berkeley.
Desorption Temperature	80–110°C	80–95°C	Acceptable range for desorption given the technology. Waste heat available from a large number of industrial sources in this temperature range. Utilization of low-grade waste heat in this range will reduce overall CO_2 production costs.
Adsorption: Desorption Cycle Time	900s:90s	Achieved, Various	An adsorption to desorption ratio of 9:1. Timing model flexible due to system design. Efficiency maximization depends on contactor performance.
Remote Operations	Uninterrupted Remote Operations	Remote Operations Achieved	No specific performance targets for uninterrupted performance stated for FOAK. Aspirational target of approximately one month uninterrupted operations at the NCCC. From commissioning start, current interrupts have been due to planned downtime of heat availability from thee NCCC and BOP maintenance issue (chiller).

Definitions:

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Atmospheric Air Feed-Gas Assumptions – Update values below to describe the air feed-gas pressure, temperature, and composition entering the capture system:

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	Ambient	0.04	variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Solid-sorbent system.

Sorbent Contaminant Resistance – Airborne contamination mitigated with filters.

Sorbent Attrition and Thermal/Hydrothermal Stability – Targeted sorbent lifetime: approximately three years.

Flue Gas Pretreatment Requirements – N/A.

Sorbent Make-Up Requirements – Replacement as needed, drop-in.

Waste Streams Generated – Mostly water.

Proposed Module Design – 100 tonne/year DAC modular nameplate design together with heat integration skid module and scale-matched CO_2 upgrading/liquefaction module.

technology advantages

- Monolithic contactor provides low pressure drop, low thermal mass, high geometric surface area, and compatibility with various construction methods.
- Adsorption cycle capable capturing CO_2 in 900 seconds.
- Desorption cycle releases CO_2 via saturated steam in less than 90 seconds.
- Modular system design enables commercial application in a wide variety of applications.
- Integrated system design for production of high-grade CO_2 from DAC increases overall system exergy.

R&D challenges

- Construction and testing of integrated high-fidelity system in an operational test environment.

status

This project was completed on July 31, 2024. CFD modelling provided insight in system design and architecture and validated preliminary design concepts. Iterative design based on CFD analysis supported design to maximize overall system energy efficiency and performance. The system design completed 90,000 desorption cycles across both operating units and long-term testing at NCCC was completed, which demonstrated the mechanical reliability and operational parameters in the real-world environment. The modular system platform design was optimized for cost reduction through heat recovery integration to decrease the thermal energy demand.

available reports/technical papers/presentations

Joshua Miles, “DAC RECO2UP - Direct Air Capture Recovery of Energy for CCUS Partnership,” 2024 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_CDR_6_Miles.pdf*.

Joshua Miles, “DAC RECO2UP - Direct Air Capture Recovery of Energy for CCUS Partnership,” 2023 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_CDR29_Miles.pdf*.

Matthew Atwood, “Direct Air Capture of Energy for Carbon Capture, Utilization, and Storage (CCUS) Partnership (DAC RECO$_2$UP),” 2022 Budget Period 2 Review Meeting Presentation, Pittsburgh, PA, September 2022. *https://netl.doe.gov/projects/files/Direct%20Air%20Capture%20of%20Energy%20for%20Carbon%20Capture,%20Utilization,%20and%20Storage%20(CCUS)%20Partnership%20(DAC%20RECO2UP).pdf*.

Patricia Berry, Matt Atwood, "Direct Air Capture of Energy for Carbon Capture, Utilization, and Storage (CCUS) Partnership (DAC RECO$_2$UP)," Budget Period 1 Review Meeting Presentation, Pittsburgh, PA, October 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11078&filename=Direct+Air+Capture+of+Energy+for+Carbon+Capture%2c+Utilization%2c+and+Storage+(CCUS)+Partnership+(DAC+RECO2UP).pptx*.

Matt Atwood, Bran Raskovic, "Direct Air Capture of Energy for Carbon Capture, Utilization, and Storage (CCUS) Partnership (DAC RECO$_2$UP)," Project kickoff meeting presentation, Pittsburgh, PA, April 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11080&filename=Direct+Air+Capture+of+Energy+for+Carbon+Capture%2c+Utilization%2c+and+Storage+(CCUS)+Partnership+(DAC+RECO2UP).pdf*.

Transformational Sorbent-Based Process for Direct Air Capture

primary project goal

InnoSepra LLC further advanced their adsorption-based direct air capture (DAC) process. The overall goals of the project were to generate data to confirm that the process can provide significant cost and parasitic power savings compared to state-of-the-art DAC processes and to utilize process models to produce a conceptual design of a large-scale DAC system.

technical goals

- Construct bench-scale unit test unit.
- Install and test at the National Carbon Capture Center (NCCC) and validate the process simulation model.
- Estimate capital cost (CAPEX), operating cost (OPEX), and CO_2 capture cost for approximately 250-tonne-per-day (tpd) CO_2 capture from air.

technical content

The project was based on utilizing physical sorbents in particulate form for capturing CO_2 from the air and further upgrading it to purities needed for pipeline transport. In contrast to amine-based systems, the heats of adsorption of CO_2 on physical sorbents range between 30–40 kJ/mole of CO_2—about a fifth of the total energy needed for amine-based absorption systems. Even after adding the heat needed for vessel and sieve heating, and the sensible heat for heating CO_2, the total energy required is significantly lower than that for amine-based solvents and reactive sorbents. This can lead to significantly lower parasitic power consumption. InnoSepra discusses the use of physical sorbents for CO_2 capture from power plants. The sorbents used in the InnoSepra process have a much higher surface-to-volume ratio (greater than $1x10^6$ m^2/m^3) compared to structured packings used in absorption processes (less than 1,000 m^2/m^3) and membranes (250–5,000 m^2/m^3 for plate-and-frame, spiral-wound, and hollow fiber modules, respectively), which allows a five-foot tall adsorption bed to provide the same or better separation of CO_2 as a 200-foot tall absorption column. The technical and economic feasibility of the technology has been demonstrated through laboratory testing, process modeling, and a preliminary techno-economic analysis (TEA).

In the InnoSepra process, the CO_2 in ambient air, about 400 parts per million (ppm), is concentrated to a stream containing greater than 95% CO_2, which can be transported through a CO_2 pipeline for storage or enhanced oil recovery (EOR). DAC plants can be standalone plants or they can be part of CO_2 capture at a power plant and utilize the power from the plant for capture. This can be particularly

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Physical Sorbent-Based
Process for DAC

participant:
InnoSepra LLC

project number:
SC0020740

predecessor projects:
N/A

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partners:
N/A

start date:
06.29.2020

percent complete:
100%

advantageous during times when the power demand from the fossil-fuel-based power plant is low and the power prices are very low or even negative during high renewables penetration.

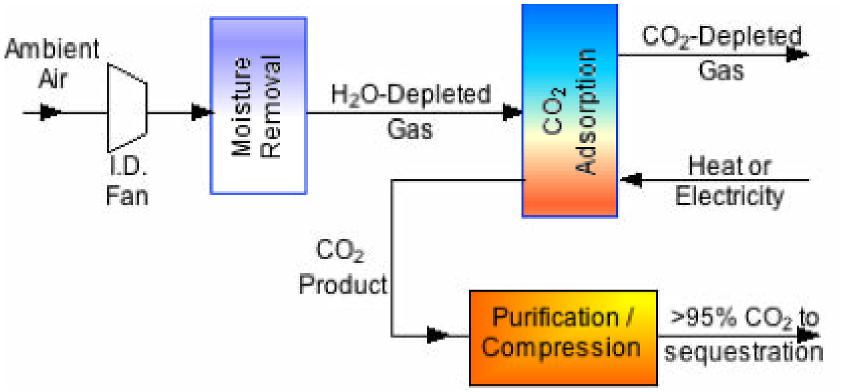

Figure 1. Process schematic for the InnoSepra process.

The DAC process schematic is shown in Figure 1. The pressure of ambient air is raised by 0.1–0.2 pounds per square inch (psi) in an induced draft (ID) fan and the compressed air is sent to a rotating bed moisture adsorption unit for removing moisture and a CO_2 adsorption unit in sequence. Because of the very large gas volumes involved with DAC, the system pressure drop for CO_2 capture needs to be minimized and structured sorbents are used in both stages for this to be accomplished. The pressure drop in each of these stages is expected to be less than 0.05 psi. Depending on the fabrication method, the costs of the structured sorbents are not significantly higher than the cost of particulate sorbents.

The purpose of the moisture adsorption system is to reduce the relative humidity of the feed gas to below 1% to minimize the moisture adsorption on the CO_2 sorbent. The rotating bed configuration for moisture removal is shown in Figure 2. The entire structure is housed inside a duct. The typical wheel depth is eight to 16 inches. Short bed height coupled with a large open area, greater than 75%, leads to a very low pressure drop. One rotation of the wheel takes six to 12 minutes, during which time the entire wheel undergoes adsorption (in the adsorption zone) and regeneration (in the regeneration zone). A rotating seal is used to separate the adsorption and regeneration zones. The wheel areas used for adsorption and desorption steps are nearly equal. For this dehumidification process, the adsorbent volumes needed are reduced by a factor of more than 10 compared to the particulate sorbents. Flue gas dehumidification using rotating wheel adsorbers provides very significant process intensification and is very important for DAC.

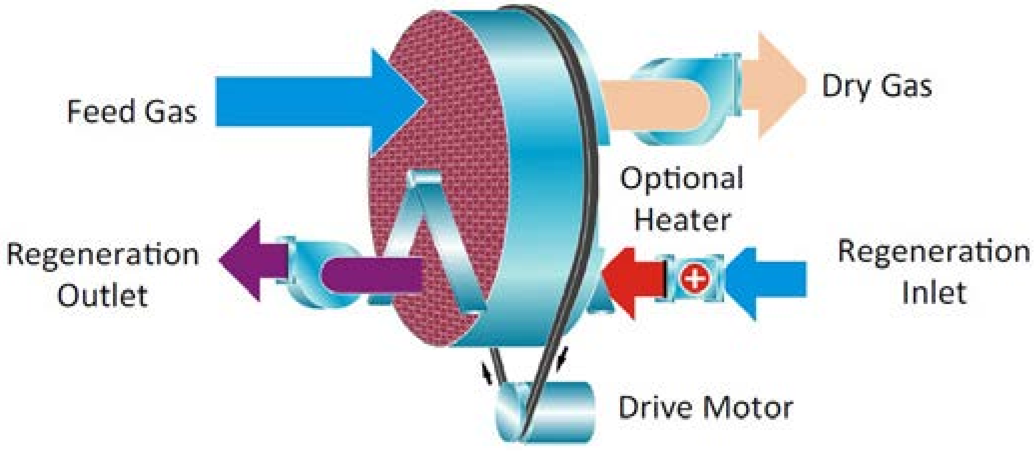

Figure 2. Rotating wheel dryer for feed dehumidification.

The moisture-depleted gas is sent to a CO_2 adsorber containing a sorbent that has a high CO_2 capacity at low CO_2 partial pressures. These sorbents can be thermally regenerated to produce a first CO_2 product stream that can be further purified and compressed to produce a CO_2 stream suitable for pipeline transport (Figure 1). The process operates continuously and does not require any switching valves, unlike the fixed bed adsorption processes.

The CO_2 adsorber is a rotating bed (similar to that in Figure 2) or a parallel passage contactor. Again, the pressure drop in this step is less than 0.03 psi. The regeneration of CO_2 sorbents is done at 100–110°C and typically requires low pressure steam. Where possible, the steam for regeneration is generated by solar heating and is stored during non-daylight hours. The dry, CO_2-product stream is further concentrated to a purity (greater than 95% CO_2) suitable for pipeline transport in another stage. If the DAC system is sited at a power plant, synergies between post-combustion capture and DAC can be utilized to significantly reduce the cost of CO_2 capture using DAC. The power plant can be utilized to provide steam and electrical power needed for capture.

The second key element of the system is the adsorption of CO_2 on structured sorbents with very high capacities at low CO_2 partial pressures. Whereas typical physical sorbents have CO_2 capacities below 1 wt% for typical CO_2 concentrations in air, the InnoSepra materials have a CO_2 capacity of more than 4.0 wt% for 400-ppm CO_2 in air. These materials also have low heats of adsorption (less than 42 kJ/mol of CO_2). These high CO_2 capacities and low heats of adsorption significantly reduce the regeneration energy needed for DAC. The regeneration energy requirement for this system is significantly lower compared to other DAC technologies. The use of structured sorbents for moisture removal and CO_2 capture allows the equipment to be shop-fabricated and field-assembled, significantly reducing fabrication and transportation costs.

The third key element of the system is the regeneration of the CO_2-containing sorbent to produce a pipeline-quality CO_2 product in two stages. The final CO_2 product is compressed to a pressure of approximately 2,200 pounds per square inch gauge (psig) for pipeline transport. A cooling water stream is heated to 50–70°C in the CO_2 compressor train, utilizing the CO_2 heat of compression, and provides some of the process heating needs. The estimated energy required for the CO_2 capture for an air feed containing 400-ppm CO_2 is given in Table 1. This assumes feed compression to 0.1 psig, a heat of adsorption of 42 kJ/mol of CO_2, and a net adsorption capacity of 3.5 wt%. The energy consumption to capture CO_2 at a pressure of 1 bara is approximately 550 kJ/mol of CO_2 (4.6 GJ/tonne). This number is significantly lower than the 1,000 kJ/mol of CO_2 (less than 8.5 kJ/mol) needed for amine-based sorbents for DAC.

TABLE 1: ENERGY REQUIRED FOR CO_2 AND MOISTURE REMOVAL SECTIONS

Heat of Desorption	1.0 GJ/tonne of CO_2
Sensible Heat for CO_2	0.1 GJ/tonne of CO_2
Sensible Heat for the Sorbent	3.0 GJ/tonne of CO_2
Dehydration Energy	0.1 GJ/tonne of CO_2
Mechanical Energy	0.4 GJ/tonne of CO_2
TOTAL	**4.6 GJ/tonne of CO_2**

TABLE 2: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,600	1,600
Bulk Density	kg/m^3	690	690
Average Particle Diameter	mm	<0.1	<0.01
Particle Void Fraction	m^3/m^3	0.45	0.45
Packing Density	m^2/m^3	1e+8	1e+8
Solid Heat Capacity @ STP	kJ/kg-K	1.00	1.00
Crush Strength	kg_f	>10	>10
Attrition Index	-	<0.01%	<0.01%
Thermal Conductivity	W/(m-K)	—	—
Manufacturing Cost for Sorbent	$/kg	15	10

Adsorption			
Pressure	bar	1.01	1.005
Temperature	°C	25-35	25-35
Equilibrium Loading	g mol CO_2/kg	0.9	1.2
Heat of Adsorption	kJ/mol CO_2	44	44
CO_2 Adsorption Kinetics	gmol/time	0.2	0.5
Desorption			
Pressure	bar	0.2-1.0	0.2-1.0
Temperature	°C	100-150	90-105
Equilibrium CO_2 Loading	g mol CO_2/kg	0.2	0.1
Heat of Desorption	kJ/mol CO_2	44	44
CO_2 Desorption Kinetics	gmol/time	0.4	0.6

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is the market price of material, if applicable; "Target" is the estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Atmospheric Air Feed-Gas Assumptions – Update values below to describe the air feed-gas pressure, temperature, and composition entering the capture system:

Pressure	Composition						
	vol%					ppmv	
	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	0.04	variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Physical.

Sorbent Contaminant Resistance – No impact of oxygen and moisture in feed air, acid gas impurities are not relevant to DAC.

Sorbent Attrition and Thermal/Hydrothermal Stability – Very stable.

Flue Gas Pretreatment Requirements – N/A.

Sorbent Make-Up Requirements – At least five-year life before any make-up is needed.

Waste Streams Generated – N/A.

Proposed Module Design – N/A.

TABLE 3: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	175-200	150-175
Cost of Carbon Avoided	\$/tonne CO_2	—	—
Capital Expenditures	\$/tonne CO_2	100-115	80-100
Operating Expenditures	\$/tonne CO_2	75-85	70-75

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Calculations Basis – No U.S. Department of Energy (DOE) reference case for DAC.

Scale of Validation of Technology Used in TEA – Lab-scale.

Qualifying Information or Assumptions – N/A.

technology advantages

- Very low pressure drops (typically one-fifth to one-tenth used for particulate sorbents for the same flow rate).
- Not subject to fluidization constraints or attrition issues.
- Very small effective particle size (less than 80 µm), leading to very short mass transfer zones.
- Can process significantly higher flows for a given bed volume.
- The materials are low cost and can be produced in very large quantities fairly quickly.
- Can be fabricated with virtually any sorbent.
- Equipment is commercially available up to 10 feet in diameter.

R&D challenges

- Identifying pathways for materials fabrication at large scale and further process scale-up.

status

The project was completed on March 31, 2024. The InnoSepra LLC DAC process utilizing low-cost InnoSepra DAC materials has the potential for a significant reduction in the energy required for DAC. Process modeling indicates that the process has the potential to reduce the energy required by more than 50% over current DAC processes. The low energy requirement coupled with low material cost can lead to a CO_2 removal cost below $200/tonne.

available reports/technical papers/presentations

Ravi Jain, Norberto Lemcoff, "Transformational Sorbent-Based Process for Direct Air Capture," 2023 FECM / NETL Carbon Management Research Project Review Meeting, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_CDR30_Jain.pdf*.

Ravi Jain, Norberto Lemcoff, "Transformational Sorbent-Based Process for Direct Air Capture," Project kickoff meeting presentation, Pittsburgh, PA, October 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=12451&filename=Transformational+Sorbent-Based+Process+for+Direct+Air+Capture.pdf*.

Accelerated Life Cycle Testing of Advanced Structured Material Systems for Direct Air Capture

primary project goal

RTI International partnered with Creare to design, fabricate and test, at bench scale, a contactor coated with advanced solid sorbents for direct air capture (DAC) of carbon dioxide (CO_2). The project focused on the operation of a bench-scale CO_2 removal unit inside an environmental chamber that will maintain constant, controlled test conditions for long-duration life testing (e.g., 1,000 cycles) and parametric testing.

technical goals

- Develop a robust sorbent binder composite coating onto contactor structure.
- Identify the best coating thickness while maximizing the diffusivity and kinetics under optimal sorption and desorption conditions.
- Demonstrate high CO_2 capacity and excellent mechanical durability of coating, and assess the flow versus the pressure drop performance.
- Build a unique test system that will enable rapid, automated cycling of DAC contactors under conditions that simulate operation in a wind-driven system.
- Demonstrate performance and durability in parametric tests across a range of simulated environmental conditions (air speed, ambient temperature, relative humidity).
- Demonstrate long-term performance of the contactor using a controlled air stream (known flow rate, composition, temperature and pressure) to ensure controlled test conditions over 1,000 cycles.
- Conduct a detailed techno-economic analysis (TEA) and life cycle analysis (LCA) using all experimental data collected.

technical content

The system incorporates RTI's high-performance, high-durability amine sorbents in an innovative air contactor design that is optimized for wind-driven operation. Utilization of Creare's hybrid additive manufacturing technology enables the low-cost fabrication of high-performance, compact structures that exhibit efficient heat and mass exchange transfer and that are ideally suited for integration with sorbent materials. RTI's design employs an amine-based phosphorous dendrimer (*P*-dendrimer) sorbent coated onto a stainless steel plate surface. The sorbent/contactor design enables high CO_2 sorption, low regeneration temperature, and excellent tolerance for oxygen and water. The contactor module was designed so that one unit cell adsorbs CO_2 as the other is heated and

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Life Cycle Testing of Passive Sorbent/Contactor for DAC

participant:
Research Triangle Institute

project number:
FE0032099

predecessor projects:
N/A

NETL project manager:
Andrew O'Palko
Andrew.OPalko@netl.doe.gov

principal investigator:
Mustapha Soukri
Research Triangle Institute
msoukri@rti.org

partners:
Creare LLC

start date:
10.01.2021

percent complete:
100%

evacuated for desorption. Each unit cell has steam ports on the top and bottom plates and a sealing door that rotate to seal alternating unit cells. Contactor modules are combined to form an array.

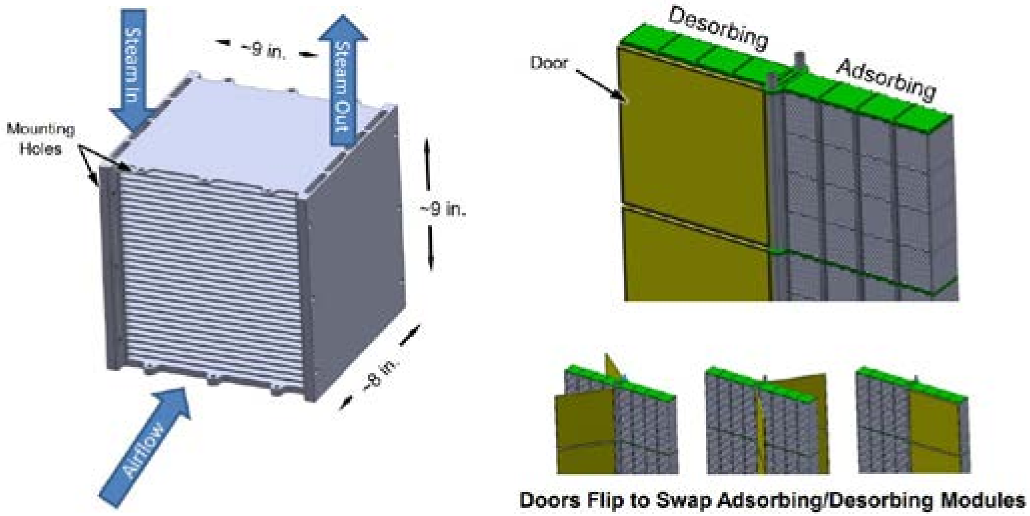

Figure 1: Contactor module (left); adsorption/desorption modules (right).

The unique environmental chamber built for testing purposes enables rapid, automated temperature-swing sorption cycling of DAC contactors under conditions that simulate operation in a wind-driven system. Testing in the chamber with constant, controlled test conditions allows for long-term cyclic testing and parametric testing. Ducted fans provide specified air flow rates to simulate constant wind speed throughout the test. Two modules operate 180°C out of phase to maintain steady CO_2 concentration during simultaneous adsorption and desorption operation.

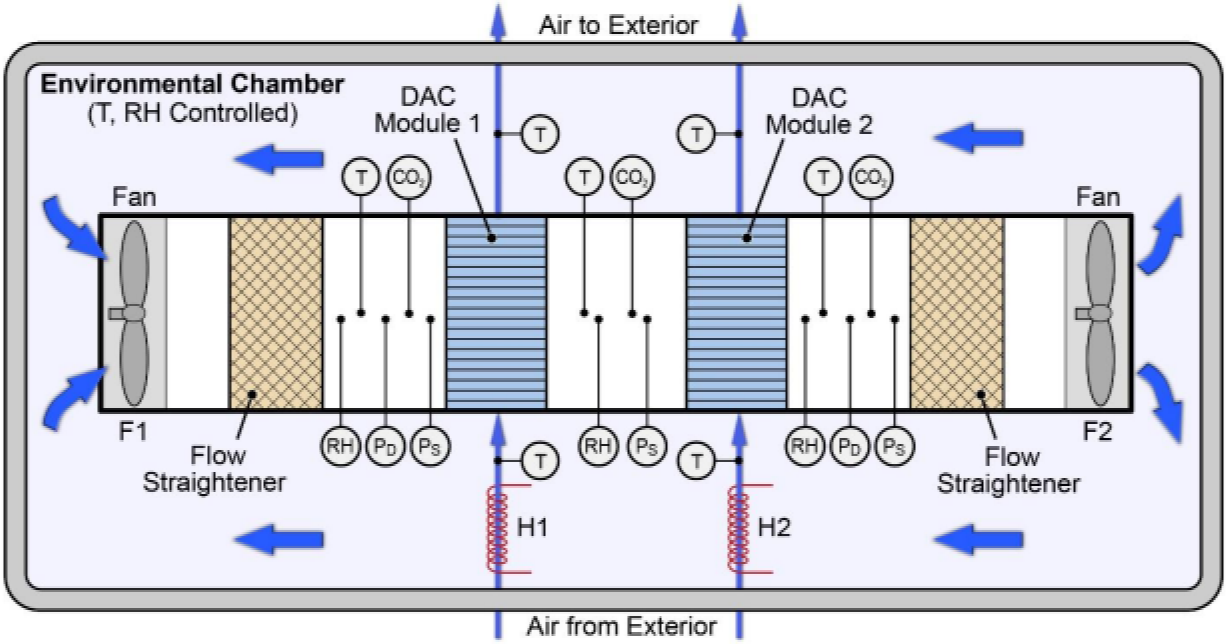

Figure 2: Test chamber for long-term testing of contactor modules.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	220	220
Bulk Density	kg/m^3	220	220

Average Particle Diameter	mm	≥0.35	≥0.35
Particle Void Fraction	m^3/m^3	0.5	0.5
Packing Density	m^2/m^3	$75\text{x}10^6$	$75\text{x}10^6$
Solid Heat Capacity @ STP	kJ/kg-K	0.25	0.25
Crush Strength	kg_f	—	—
Attrition Index	-	—	—
Thermal Conductivity	W/(m-K)	≥1.0	≥1.0
Manufacturing Cost for Sorbent	$/kg	—	—
Adsorption			
Pressure	bar	1	1
Temperature	°C	25	25
Equilibrium Loading	g mol CO_2/kg	1.25	1.0
Heat of Adsorption	kJ/gmol CO_2	90	90
CO_2 Adsorption Kinetics	gmol CO_2/g/min	>0.06	>0.06
Desorption			
Pressure	bar	1	1
Temperature	°C	80	80-85
Equilibrium CO_2 Loading	g mol CO_2/kg	0.01	0.01
Heat of Desorption	kJ/gmol CO_2	90	90
CO_2 Desorption Kinetics	gmol CO_2/g/min	>0.3	>0.3
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	—	
Flue Gas Flowrate	kg/hr	—	
Wind Velocity	m/s	4	
Space Velocity	s^{-1}	39.0	
Volumetric Productivity	$\text{gmol}_{CO_2}/(\text{hr } l_{\text{absorber bed}})$	0.532	
CO_2 capture efficiency (single pass)	%	22.5	
Adsorber Pressure Drop	Pa	21.3	
Degradation	% capacity fade/cycle	—	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	—	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Atmospheric Air Feed-Gas Assumptions – Update values below to describe the air feed-gas pressure, temperature and composition entering the capture system:

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
ambient	ambient	0.04	variable	78.09	20.95	0.93	trace	trace

technology advantages

- Rapid and simple temperature-swing sorption cycling.
- Highly efficient mass transfer and low flow resistance of contactor enables low-power, wind-driven operation.
- Low-cost additive manufacturing process for fabrication of contactor.
- High surface area contactor designed with parallel-plate micro-channels.
- This project leverages the knowledge and experience gained through the Advanced Research Projects Agency–Energy (ARPA-E) efforts to complete the development of a bench-scale DAC process by optimizing the sorbent binder composite coating and enabling long-term cyclic testing to prove performance and durability.

R&D challenges

- Sorbent coating durability and CO_2 sorption and regeneration performance during long-term cycling under relevant DAC conditions.
- Achieving a uniform sorbent coating layer with a thickness ≤ 10 mil (e.g., 0.254 mm) and strong film adhesion to the stainless steel plate surface.
- Achieving efficient CO_2 capture under minimal wind conditions.

status

The project was completed on March 31, 2024. The project team prepared an optimum sorbent coating formulation that exhibits excellent CO_2 capacity, adhesion and mechanical durability. RTI has scaled up sorbent production to kg scale and has coated more than 100 contactor plates with the amine-based sorbent for Creare to use for testing. Parametric testing has been performed on 20 contactor plates and the project team has determined that the optimal operation condition is 75% relative humidity, regeneration at 90°C for 10 minutes, and adsorption at 30°C for 50 minutes. Long-term testing was conducted at the optimal conditions for approximately 1,000 cycles, with humidity conditions being altered during the test. Additionally, Creare has conducted computational fluid dynamics analysis on the contactor array design to study the air flow characteristics.

available reports/technical papers/presentations

Mustapha Soukri, "Accelerated Life Cycle Testing of Advanced Structured Material Systems for Direct Air Capture," Final Technical Report, July 2024. *https://www.osti.gov/servlets/purl/2382722/*.

Mustapha Soukri, "Accelerated Life Cycle Testing of Advanced Structured Material Systems for Direct Air Capture," presented at the 2023 FECM/NETL Carbon Management Research Project Review Meeting, August 2023.

Mustapha Soukri, "Accelerated Life Cycle Testing of Advanced Structured Material Systems for Direct Air Capture," Kickoff Meeting Presentation, December 2021. *https://netl.doe.gov/projects/plp-download.aspx?id=12664&filename=Accelerated+Life+Cycle+Testing+of++Advanced+Structured+Material++Systems+for+Direct+Air+Capture.pdf*.

Hybridizing Heat-Integrated 3D-Printed Modules with Mass Manufacturable, Low Pressure Drop Fiber Sorbents

primary project goal

Georgia Tech Research Corporation (GTRC) and project partners Oak Ridge National Laboratory (ORNL), ReactWell LLC, and Trimeric Inc. advanced a fiber sorbent technology for direct air capture (DAC) through optimization of a contactor design to enhance productivity and lower cost. Polyethyleneimine (PEI)-infused cellulose acetate (CA)/silica fiber sorbents previously developed for DAC applications are being housed in 3D-printed modules that provide heat integration and flow control for adsorption of carbon dioxide (CO_2).

technical goals

- Fabricate the 3D-printed modules and fiber sorbents.
- Experimentally evaluate the performance of the assembled hybrid modules and further optimize the design.
- Complete modeling and a full techno-economic analysis (TEA) and update the model with experimental results.
- Test the hybrid modules in a long-term cycling study.

technical content

The overall objective was to research, develop, and evaluate a modular DAC system that is simple and scalable. This system is based on the adsorption of CO_2 into commercial polyamines supported by porous fiber sorbents, which can be produced at kilometer-per-hour scales using the project's pre-pilot spinning line. The project goal was to increase the already-high productivity of these fiber materials via novel 3D-printed modular housing systems that provide easy-to-manufacture and localized heat integration and flow control (Figure 1). This hybridization of fiber sorbent technology with modular housing provides several advantages that lead to lower air pressure drops and higher sorbent productivity, as well as an ease of manufacturing and assembly that is unrivaled by existing and emerging heat-integrated contactor designs.

The design of the modular housing is one of the key enabling features of this new DAC approach, as the manufacturing of the fiber sorbents is a routine practice in the project's facility. The modular housing was fabricated with the following features, at a minimum: (i) a tapered air intake to reduce pressure drop related to entrance effects; (ii) a structured network of heat transfer channels to enable localized cooling and heating during adsorption and desorption, respectively; and (iii) low pressure drop supports for the fiber sorbents (Figure 1). This hybrid

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
3D-Printed Modules Integrated with Fiber Sorbents

participant:
Georgia Tech Research Corporation

project number:
FE0032129

predecessor projects:
N/A

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partners:
Oak Ridge National Laboratory (ORNL);
ReactWell LLC;
Trimeric Corporation

start date:
10.01.2021

percent complete:
100%

manufacturing approach provides a facile method for taking fiber sorbents from lab scale to pilot scale as it dramatically simplifies the fabrication of heat-integrated contactor structures.

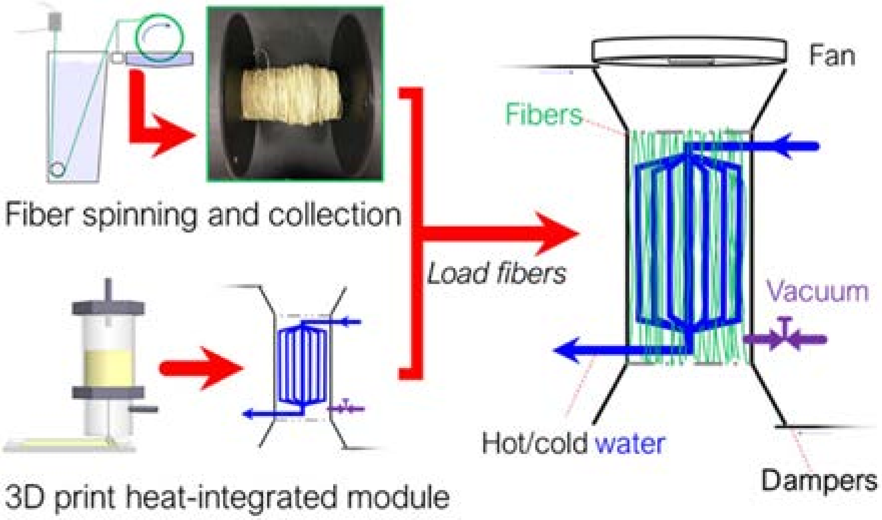

Figure 1: Schematic of proposed technology. The scalability of fiber sorbent spinning (top) is leveraged via novel 3D-printed contactors with internal heating and cooling elements (bottom). The fibers are easily loaded into the contactor without need of glue or epoxy, simplifying manufacturing and driving down costs (right).

This combination of fiber sorbent spinning, re-infusible polyamines, and 3D-printed modular housing provides several advantages that accelerate the translation of DAC materials out of the lab and into the field. Three scalable and modular components are combined into a system that is straightforward to build: (i) the contactor, which provides mechanisms for delivering air, removing/adding heat, and enabling vacuum; (ii) the fiber support, which provides high surface areas and low pressure drops via fiber alignment; and (iii) the active amine adsorbent that is infused into the fiber post-spinning, which enables geography-specific customization in terms of the amine composition and loading. Key challenges in the fabrication of heat-integrated hollow fiber sorbents are avoided, as are difficulties associated with 3D-printing high integrated module devices. Indeed, decoupling the adsorption contactor into two components (the fiber and the novel housing) captures advantages of an all-fiber or an all-3D-printed contactor, but with significant improvements in scalability.

are three major cost barriers that are often associated with DAC systems: the fans, the sorbent, and the heat input. Fan costs can be reduced via the creation of low pressure drop structures, which is an objective of this project. The sorbent costs can be reduced by rapidly cycling the adsorption system; beyond this, using commodity-scale materials wherever possible and ensuring that the materials have a lifetime of at least one year can further drive down costs. Both of these approaches are being pursued over the course of this project. The final major cost associated with DAC systems is the energy input to desorb the captured CO_2. These are ultimately bounded by the sorption or reaction enthalpy of the adsorbate-adsorbent systems. In the case of heating-induced desorption, avoiding losses associated with poor heat transfer, high thermal masses of contactor materials, and other inefficiencies can reduce the energetic requirements for the CO_2 desorption step. Monoliths are solid contactors composed of parallel channels resembling a honeycomb structure. Monoliths have several advantages over packed beds, such as higher mass transfer rates, good attrition properties, and lower pressure drop, but this is typically balanced against a lower loading of sorbent per unit volume. Monoliths can either be made entirely of the sorbent material, as when the sorbent material is directly extruded with no binder, or with some fraction of sorbent dependent on ratios of binder/sorbent/monolith body, as is the case with many deposition or growth methods (the latter is most common). Laminate-style contactors are essentially simpler forms of monoliths comprised of 1D slits. However, laminates are difficult to make reproducibly. The precision in manufacturing must be quite high to avoid slit bypass effects (less than 5% differences in channel size is required for uniform flow). This level of precision is difficult to scale, and thus laminate-style adsorbents are not often used in gas-separation processes. From a scalability perspective, monoliths are essentially made from high-quality ceramic materials one at a time using high-precision, multi-step robotic equipment. This process has been commercialized, but the fundamentals of processing ceramics suggest that upper limits on manufacturing rates are being reached and that these rates are likely too low to drive down adsorption contactor costs by an order of magnitude.

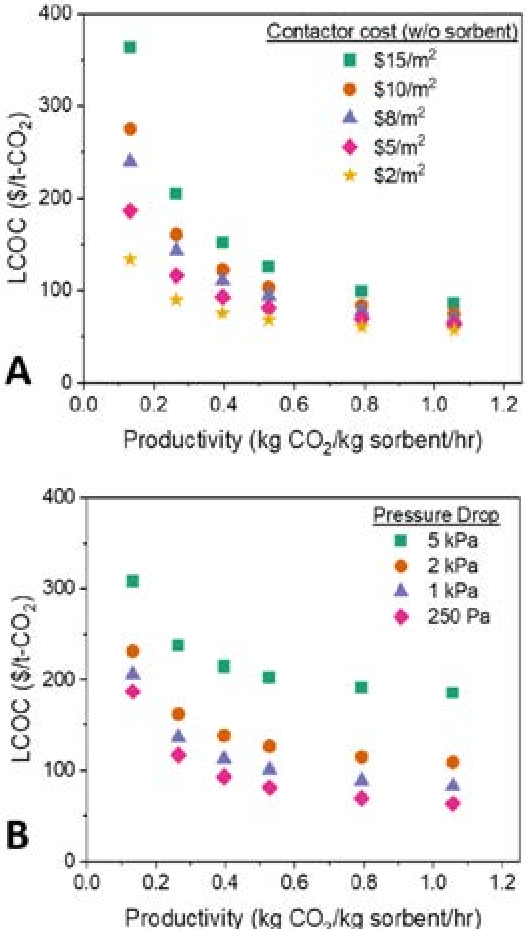

Figure 2: Pre-screen TEA results. Levelized cost of CO_2 capture as a function of productivity and (A) contactor cost or (B) pressure drop. Other parameters are held constant, including one-year sorbent lifetime, -65 kJ/mol heat of adsorption, 300 seconds cycle time, and 100,000 tonne CO_2/year captured.

The project team initially developed polymeric hollow fiber contactors that supported high loadings of CO_2 adsorbents. These materials are highly scalable and facilitated heat-integrated process configurations for post-combustion CO_2 capture. These "hollow fiber sorbents" have several important features that provide solutions to deleterious issues typically associated with post-combustion CO_2, and these solutions have proven to be transferrable to DAC technologies. For instance, CA fiber sorbents containing mesoporous silica impregnated with polymeric amines have been previously developed for DAC applications. In the case of fiber sorbents, the polymeric amines are added to the fibers in a simple, scalable post-spinning infusion step. The porous fiber support allows rapid gas access to the high loadings (~55 wt% without the polyamine infused, ~75 wt% with the polyamine infused) of sorbent particles within the fiber wall. Moreover, the fibers themselves act as structured packing elements, thus allowing for low gas pressure drops (~0.1 pounds per square inch [psi]/foot; Figure 3). This prior work demonstrated the ease at which these materials can be made in large quantities (400 g–1 kg scale per day), and desorption experiments highlighted the ability of these fibers to create CO_2 products that have purities in excess of 98 mol%. The adsorption and desorption chemistry, kinetics, and thermodynamics of the PEI-infused CA/silica sorbents are well understood. Carbon dioxide chemically binds to the PEI located in the silica pores within the CA matrix, and a temperature vacuum swing can be used to desorb the CO_2.

Traditionally, a dense barrier layer is installed on the bore-side of fiber sorbents, preventing mass transport from the shell side of the fibers to the bore, transforming the fibers into integrated "adsorbing heat exchangers." The fibers are capable of rapid thermal cycles on the order of one to four minutes and have excellent heat management properties (Figure 4). However, the barrier layer addition is the most time-intensive and tedious step of the fiber sorbent fabrication process and prone to defect formation. The contactors proposed here entirely eliminate the need for a barrier layer through advanced 3D-printing technology, thus reducing the time, complexity, and fragility of the contactor manufacturing and assembly process.

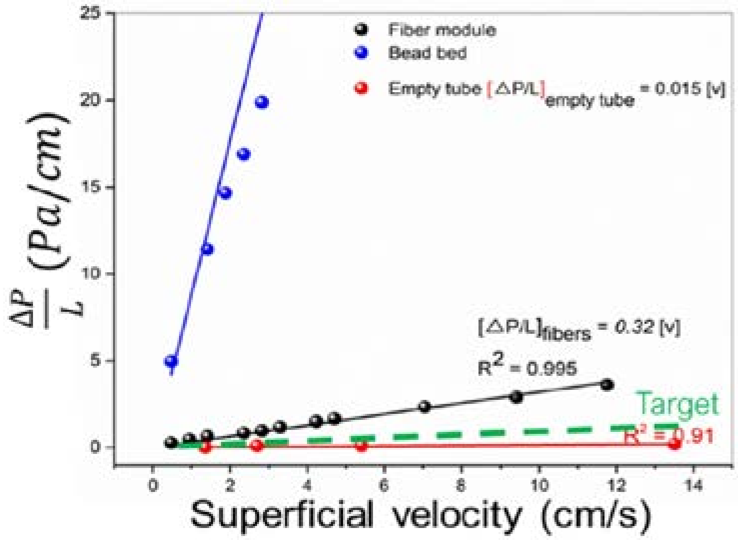

Figure 3: Pressure drop comparison and targets. Target pressure drop for this work is 250 Pa at 3 m/s air speed and is shown by the green line.

In recent years, 3D printing has been used as a method to directly print sorbent-containing monoliths. However, creating internal porosity inside the polymer-adsorbent structure and maintaining high sorbent loadings is a complex task, and the technology is further from scale-up than fiber sorbents. Importantly, printing commercially available polymers is a technologically mature process that has already been scaled up. By hybridizing fiber sorbents and 3D-printed contactors, the most complex aspects of each technology (barrier layer addition of fiber sorbents and internal porosity of 3D printing) are eliminated. Other limitations, including entrance pressure drop, sorbent degradation from direct steam contact, and low productivity due to inefficient heat management, can also be overcome via contactor design.

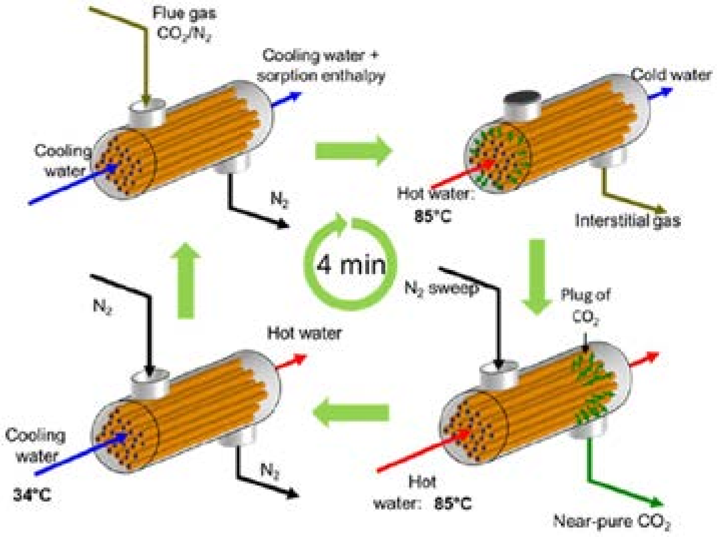

Figure 4: Rapid thermal swing adsorption cycle originally demonstrated for post-combustion CO_2 capture. Cycle times of 2.5–4.0 minutes have been demonstrated experimentally for 10% CO_2.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	—	—
Bulk Density	kg/m^3	600-700	—
Average Particle Diameter	mm	0.3	0.3 – 0.5
Particle Void Fraction	m^3/m^3	—	—
Packing Density	m^2/m^3	—	—
Solid Heat Capacity @ STP	kJ/kg-K	0.86	0.8-1.2
Tensile Strength	kPa	8723	> 5000
Crush Strength	kg_f	—	—
Attrition Index	-	—	—
Thermal Conductivity	W/(m-K)	0.005	NA
Manufacturing Cost for Sorbent	$/kg	$3.00	$1.50
Adsorption			
CO_2 Pressure	bar	0.0004	0.0004
Temperature	°C	22°C	22°C
Equilibrium Loading	g mol CO_2/kg	1.2	1.4
Heat of Adsorption	kJ/mol CO_2	-65	-65
CO_2 Adsorption Kinetics	gmol/time	0.16	—
Desorption			
Pressure	bar	0.003 bar CO_2	0.3 bar CO_2
Temperature	°C	70°C	80°C
Equilibrium CO_2 Loading	g mol CO_2/kg	<0.1	0.2
Heat of Desorption	kJ/mol CO_2	65	65
CO_2 Desorption Kinetics	gmol/time	0.48	—
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	laminate or shell-tube	
Gas Flowrate	kg/hr	75.8	
Space Velocity	hr^{-1}	60,000	
Volumetric Productivity	$gmol_{CO2}/(hr\ l_{absorber\ bed})$	1.25	
CO_2 Recovery, Purity, and Pressure	% / % / bar	N/A ; 95%, 0.003 50%, 95%, 0.3	
Adsorber Pressure Drop	bar	1,000 Pa <500 Pa	
Degradation	% capacity fade/cycle	0.1 - 0.0005	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

STP – Standard Temperature and Pressure (0°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Atmospheric Air Feed-Gas Assumptions – Values below describe the air feed-gas pressure, temperature, and composition entering the capture system:

Pressure	Composition						
	vol%					ppmv	
	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	0.04	variable	78.09	20.95	0.93	trace	trace

TABLE 2: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	$/tonne CO_2	>300	<200
Cost of Carbon Avoided	$/tonne CO_2	418	—
Capital Expenditures	$/tonne CO_2	251	—
Operating Expenditures	$/tonne CO_2	227	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

technology advantages

- High sorbent loading in hybrid fibers reduces cycle time.
- Low-pressure drop design.
- 3D hybrid fibers are easy to manufacture and assemble, making these suitable for large-scale production.
- Reduce material costs and regeneration heat duty via the use of all-plastic components.

R&D challenges

- Develop sorbent with half-life target equal to one year via non-oxidative internal cooling.

status

This project was completed on December 31, 2023. GTRC developed fiber fabrication, weaving, and integration into DAC contactors. The project also conducted fiber bed and woven laminate modeling and validation work. Researchers fabricated the fiber-loaded 3D-printed structures (1 foot x 1 foot nonwovens were fashioned into 3 inch x 4 inch sheets) with internal heat management and pressure drops less than 250 Pa at 3 m/s flow. The system demonstration of the product purity was greater than 95% CO_2, with productivity of 0.2 kg/kg-hr, and pressure drop less than 250 Pa at 3 m/s flow.

available reports/technical papers/presentations

Ryan P. Lively, David S. Sholl, Matthew J. Realff, Joshua A. Thompson, Anne I. Ryan, Brandon J. Iglesias, "Hybridizing Heat-Integrated 3D Printed Modules with Mass Manufacturable, Low Pressure Drop Fiber Sorbents," Final Technical Report, April 2024. *https://netl.doe.gov/projects/files/Final%20Technical%20Report.pdf*.

Ryan P. Lively, David S. Sholl, Matthew J. Realff, Joshua A. Thompson, Anne I. Ryan, Brandon J. Iglesias, "Hybridizing Heat-Integrated 3D Printed Modules with Mass Manufacturable, Low Pressure Drop Fiber Sorbents," Project Closeout Meeting, Pittsburgh, PA, February 2024. *https://netl.doe.gov/projects/files/Hybridizing%20Heat-Integrated%203D%20Printed%20Modules%20with%20Mass%20Manufacturable,%20Low%20Pressure%20Drop%20Fiber%20Sorbents.pdf.*

Ryan P. Lively, David S. Sholl, Matthew J. Realff, Joshua A. Thompson, Anne I. Ryan, Brandon J. Iglesias, "Hybridizing Heat-Integrated 3D Printed Modules with Mass Manufacturable, Low Pressure Drop Fiber Sorbents," 2022 Budget Period 1 Review Meeting, Pittsburgh, PA, July 2022. *https://netl.doe.gov/projects/files/Hybridizing%20Heat-Integrated%203D%20Printed%20Modules%20with%20Mass%20Manufacturable,%20Low%20Pressure%20Drop%20Fiber%20Sorbents.pdf.*

Ryan P. Lively, David S. Sholl, Matthew J. Realff, Joshua A. Thompson, Anne I. Ryan, Brandon J. Iglesias, "Hybridizing Heat-Integrated 3D Printed Modules with Mass Manufacturable, Low Pressure Drop Fiber Sorbents," Project kickoff meeting presentation, Pittsburgh, PA, December 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=12554&filename=Hybridizing+Heat-Integrated+3D+Printed+Modules+with+Mass+Manufacturable%2c+Low+Pressure+Drop+Fiber+Sorbents.pdf*.

Bench-Scale Testing of Monolithic Poly(Propyleneimine) Structured Contactors for Direct Air Capture of Carbon Dioxide

primary project goal

CORMETECH Inc., in partnership with Global Thermostat LLC and Georgia Institute of Technology, developed and tested a novel sorbent-air contactor with low pressure drop optimized for carbon dioxide (CO_2) removal from ambient air. The project focused on optimizing a monolith contactor to support a next-generation sorbent composition, linear poly(propyleneimine) (l-PPI), for direct air capture (DAC).

technical goals

- Perform experimental and simulation studies of the novel CO_2 sorbent/gas contactor system based on l-PPI sorbents at DAC-relevant conditions.
- Measure isotherm, kinetic, and transport behaviors of the powder and slab materials.
- Develop a single channel monolith model to optimize the geometry and the meso/macro-porosity of monoliths specifically tuned for l-PPI.
- Develop a transport model based on l-PPI supported on monolith slabs.
- Build and evaluate a single brick sorption tester (SBST) for the bench-scale evaluation of extruded monoliths loaded with l-PPI, enabling the CO_2 sorption performance to be optimized.
- Measure the resistance of the sorbent/contactor composition to oxidation under relevant dry and humid conditions.
- Perform a techno-economic analysis (TEA) utilizing the process model incorporating the novel sorbent/contactor combination.

technical content

Global Thermostat's baseline DAC process employs monolithic, low pressure drop contactors loaded with organic amine molecules or macromolecules to allow for high throughput gas/solid contacting with high volumetric CO_2 sorption productivity. The Global Thermostat DAC process employs relatively shallow honeycomb monolith contactors (~15 cm deep) that permit low pressure drops (hundreds of Pa) at gas approach velocities of 3–5 m s^{-1} while still maintaining a high geometric surface area per unit volume (Figure 1).

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Monolith Contactor Impregnated with Novel Sorbent for DAC

participant:
CORMETECH Inc.

project number:
FE0032094

predecessor projects:
N/A

NETL project manager:
Elliot Roth
elliot.roth@netl.doe.gov

principal investigator:
Christopher Bertole
CORMETECH Inc.
bertolecj@cormetech.com

partners:
Georgia Institute of Technology; Global Thermostat LLC

start date:
09.15.2021

percent complete:
100%

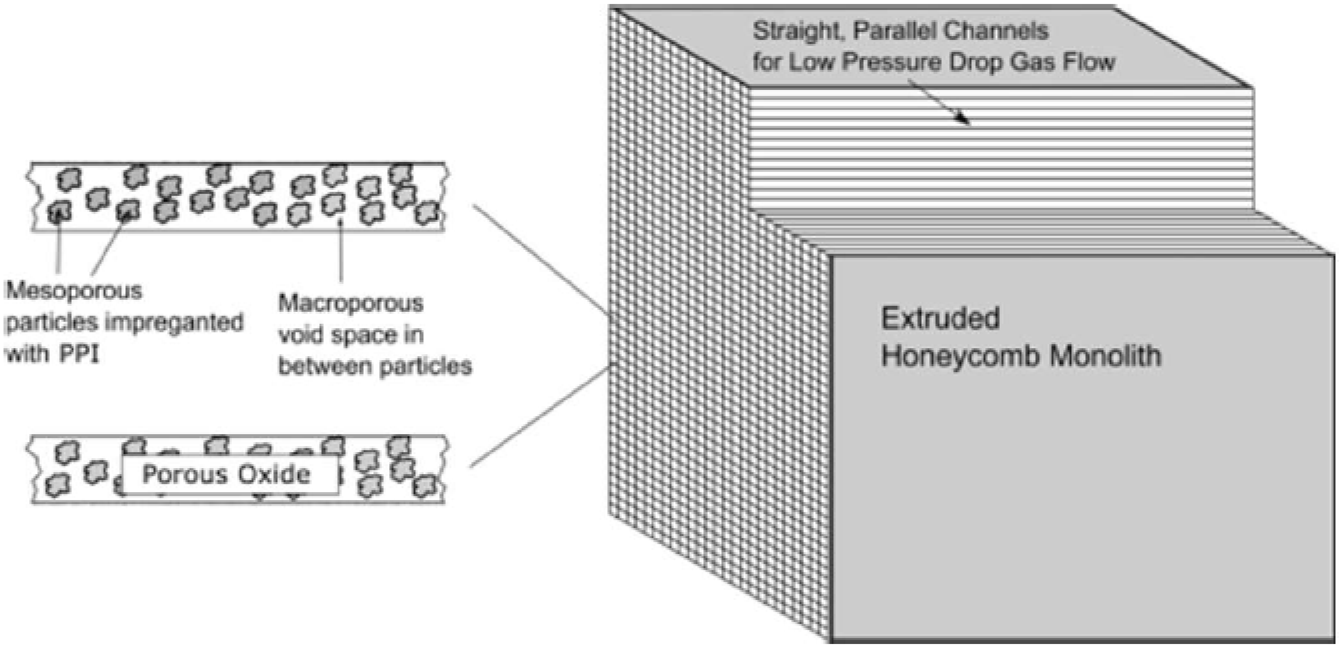

Figure 1: Monolith system used in Global Thermostat process.

After CO_2 adsorption, CO_2 is desorbed and collected by combined temperature-vacuum swing desorption employing steam-stripping, producing a concentrated CO_2 product (Figure 2). Early generations of Global Thermostat's technology used commercially available components that were initially designed and optimized for other applications (e.g., [i] nonporous monolithic contactors with porous oxide washcoats designed for high-temperature catalytic applications and [ii] known commercially available amine compositions). Whereas commercially available materials were leveraged in early development, this project is focused on design and optimization of a gas/solid contactor specifically formulated for DAC.

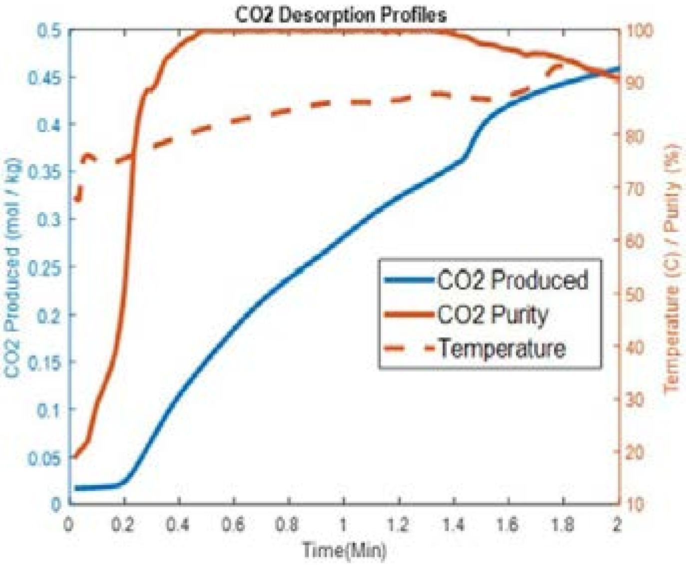

Figure 2: CO_2 desorption using steam regeneration.

Recently, Global Thermostat has developed several generations of amine sorbents with improved properties for DAC in collaboration with Georgia Tech, relative to a baseline commercial amine composition, PEI. Global Thermostat also has collaborated closely with CORMETECH to design and formulate new porous monolith contactors specifically engineered to support PEI amine compositions for DAC. The purpose of this project was to advance the design of a new monolithic air/solid contactor by developing designs optimized specifically for DAC by tailoring the properties of the monolith contactor to fit synergistically with the next-generation amine composition, l-PPI. The benchmark amine polymer, PEI, is deployed as a branched oligomer. In contrast, the selected next-generation polymer is linear in structure (l-PPI). Given the different structure of the macromolecule (PEI: branched with ethyl linkers, versus l-PPI: linear with propyl linkers), the new polymer is expected to interface with the porous monolith support differently from the baseline PEI case. In powder tests (data are shown in Figure 3), l-PPI has similar CO_2 sorption properties as PEI, yet superior oxidative stability and water sorption properties (more hydrophobic), making it a promising next-generation amine polymer for DAC. Furthermore, l-PPI was scaled up to the 100-gram quantity levels by project partner Celares GmbH, who provided sufficient quantities of the polymer needed for monolith-scale testing. Given the promise of l-PPI as a sorbent composition, the focus of this project was to customize a monolith formulation for this next generation sorbent. The project was directed at conducting experimental measurements and formulating a sorption/diffusion/transport model of the adsorption process, which can be used to advance process models and inform process TEAs.

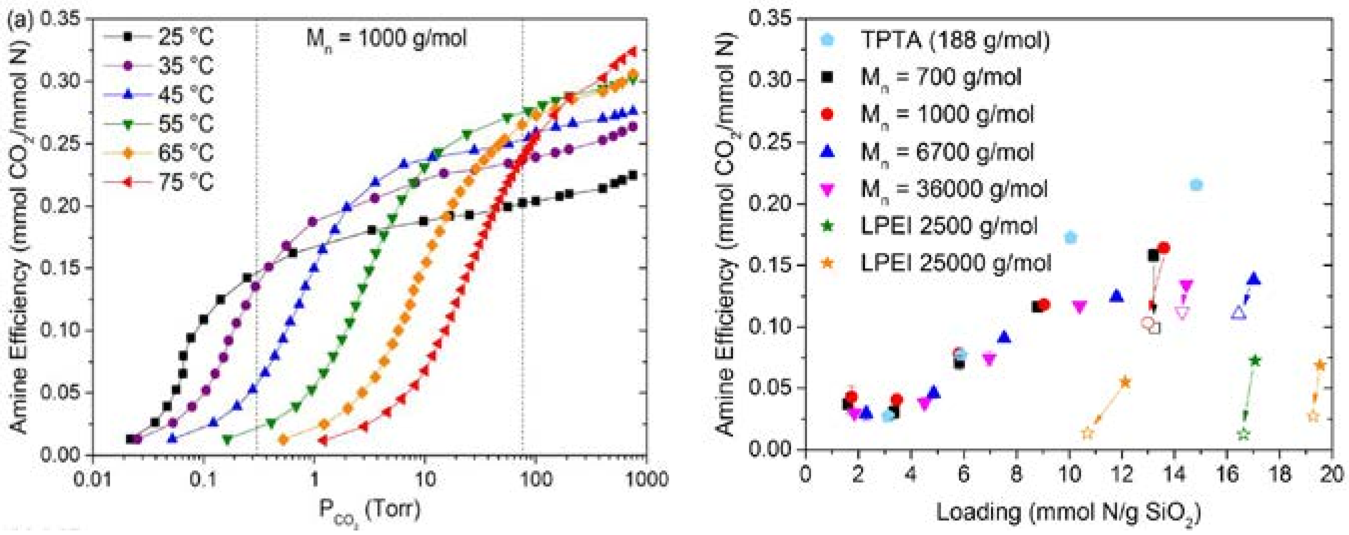

Figure 3. Left: Isotherms at varied temperatures for PPI/SBA-15 sorbents. Right: Amine efficiency versus amine loading for l-PPI versus PEI (closed shapes), 400 ppm CO_2 at 35°C, showing loss after treatment in oxidative environment (open shapes), 21%O_2/N_2, 110° C for 24 hours.

technology advantages

- Monolithic contactor achieves low pressure drop CO_2 capture capability.
- New sorbent with enhanced oxidative stability will improve the on-steam sorbent lifetime in the base Global Thermostat DAC process.
- Utilizes cost-effective fabrication technique from CORMETECH for CO_2 contactor development using porous monolith substrate that can be impregnated with the amine.

R&D challenges

- Synthesis of l-PPI sorbent at kg-scale for full-size optimized monolith brick impregnation and SBST validation testing.
- Development of single-channel monolith with combined momentum, mass, and heat transfer, incorporating porous wall flow and the multi-phase regimes that arise from the use of steam as a desorbing medium, to optimize the monolithic substrate's textural properties for l-PPI and maximize DAC performance.
- Measurement of fundamental transport properties of CO_2 through amine-loaded porous materials and adsorption/desorption equilibria, for model development and incorporation into the single channel monolith model.
- Confirmation of the enhanced oxidative stability of the scaled-up l-PPI sorbent.

- Impregnation protocol requires non-aqueous solvents.
- Structure of the l-PPI solid domains in the porous solid monolith structure impacts performance.
- Humidity either promotes or inhibits CO_2 adsorption, depending on the l-PPI loading and the pore size distribution.

status

The project was completed on December 14, 2023. The project team designed, built, and commissioned the bench-scale SBST unit, along with manufacturing, validation, and bench-scale testing of l-PPI (at kg-scale) using a standard monolithic substrate and the SBST. Development of a single channel model to optimize the geometry and the meso/macro-porosity of monoliths specifically tuned for l-PPI was conducted. L-PPI supported on an optimized monolithic substrate has been synthesized and tested on the bench-scale, exceeding the anticipated CO_2 adsorption capacity target.

available reports/technical papers/presentations

Christopher Bertole, "Bench-Scale Testing of Monolithic Poly Propyleneimine Structured Contactors for Direct Air Capture of Carbon Dioxide," Final Technical Report, Pittsburgh, PA, July 2024. *https://www.osti.gov/servlets/purl/2371863*.

Christopher Bertole, "Bench-Scale Testing of Monolithic Poly Propyleneimine Structured Contactors for Direct Air Capture of Carbon Dioxide," Budget Period 2 Review Meeting, Pittsburgh, PA, December 2023. *https://netl.doe.gov/projects/files/Bench-Scale%20Testing%20of%20Monolithic%20Poly%20Propyleneimine%20Structured%20Contactors%20for%20Direct%20Air%20Capture%20of%20Carbon%20Dioxide.pdf*.

Christopher Bertole, "Bench-Scale Testing of Monolithic Poly Propyleneimine Structured Contactors for Direct Air Capture of Carbon Dioxide," 2023 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_CDR28_Bertole.pdf*.

Christopher Bertole, "Bench-Scale Testing of Monolithic Poly Propyleneimine Structured Contactors for Direct Air Capture of Carbon Dioxide," Budget Period 1 Review Meeting, Pittsburgh, PA, August 2022. *https://netl.doe.gov/projects/files/Bench-Scale%20Testing%20of%20Monolithic%20PPI%20Structured%20Contactors%20for%20Direct%20Air%20Capture%20of%20CO2.pdf*.

Christopher Bertole, "Bench-Scale Testing of Monolithic Poly Propyleneimine Structured Contactors for Direct Air Capture of Carbon Dioxide," 2022 Carbon Management Project Review Meeting, Pittsburgh, PA, August 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_CDR16_Bertole.pdf*.

Christopher Bertole, "Bench-Scale Testing of Monolithic Poly Propyleneimine Structured Contactors for Direct Air Capture of Carbon Dioxide," Project kickoff meeting presentation, Pittsburgh, PA, October 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=12444&filename=Bench-Scale+Testing+of+Monolithic+Poly+Propyleneimine+Structured+Contactors+for+Direct+Air+Capture+of+Carbon+Dioxide.pdf*.

Direct Air Capture Using Novel Structured Adsorbents

primary project goal

Electricore Inc. advanced a direct air capture (DAC) technology that combines a vacuum-temperature swing carbon dioxide (CO_2) adsorption process with structured adsorbent beds (SABs). The process employs Svante's novel solid sorbent laminate filter technology integrated with Climeworks' DAC technology in which CO_2 from air is chemically bound to a solid sorbent material and the sorbent is regenerated using vacuum- and temperature-swing desorption.

technical goals

- Design, build, and operate a 30-kg/day integrated field test unit capable of producing a concentrated CO_2 stream of at least 95% purity.
- Conduct a 12-month field test of the DAC system to capture operational data on the novel process and material combination under real conditions.
- Perform a full characterization of first-, second-, and third-generation sorbent materials after at least 1,000 cycles of operation, with a goal of understanding failure modes to increase lifetime. The different sorbent generations have the goal of optimizing the sorbent structure geometry, reducing the amount of water uptake during adsorption, and improving CO_2 uptake.
- Use test data to advise techno-economic and life cycle assessments of the technology.
- Validate current state-of-the-art DAC systems and sorbent materials and achieve cost reductions through the use of advanced sorbents and energy optimization realized via reduced pressure drop in sorbent beds.

technical content

This project, led by Electricore, combined Climeworks' DAC process technology with Svante's SAB technology and was demonstrated at a test facility in California. Climeworks' DAC process technology adsorbs CO_2 from air on a solid adsorbent encased in a collector, and then regenerates using vacuum- and temperature-swing desorption (Figure 1). During adsorption, air is drawn into the collector with a fan. Carbon dioxide is captured on the surface of a selective sorbent, or "filter," that sits inside the collectors. Once saturated with CO_2, the filter is heated (using a low-grade heat energy source) to ~100°C. The CO_2 then releases from the filter and this continuous cycle begins again. In a standard Climeworks collector, sorbent is contained as a packed bed of particles, arranged in a patented geometry to minimize pressure drop in adsorption and heat demand in desorption.

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Structured Sorbent Bed Process for DAC

participant:
Electricore Inc.

project number:
FE0031959

predecessor projects:
N/A

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partners:
Climeworks; Svante Inc.

start date:
10.01.2020

percent complete:
100%

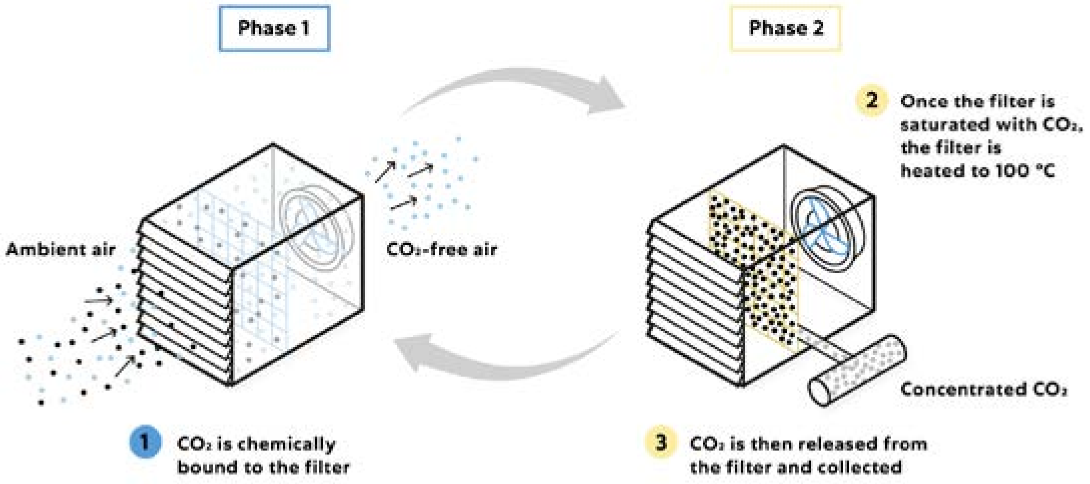


Figure 1: Schematic representation of Climeworks' adsorption and temperature-vacuum swing desorption processes for DAC.

Climeworks plants consist of modular CO_2 collectors. At full-scale, these modular collectors can be seen in Figure 2 at Orca, the world's largest DAC plant, commissioned in Iceland in 2021 and operated with geothermal energy. The modular concept is scalable through "numbering-up." Collectors are designed for mass-production, enabling deployment on the large scale required for climate change mitigation.

Figure 2: Climeworks' Orca plant, the world's largest direct air capture and storage plant, commissioned in Iceland in September 2021, with a capture capacity of up to 4,000 t_{CO2}/year.

The project team's approach was to construct, operate, and test an integrated DAC system, combining Climeworks' contactor with Svante's novel solid sorbent laminate filter (Figure 3) under real conditions. Svante's sorbent technology consists of a patented architecture of structured adsorbent laminate (spaced sheets), containing tailor-made nano-materials (solid adsorbents) with very high storage capacity for CO_2. This geometry enables very fast CO_2 uptake kinetics without incurring high pressure drops nor significant parasitic thermal mass, which keeps energy demand low.

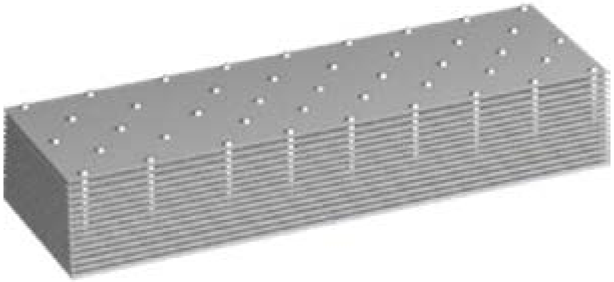


Figure 3: Svante's structured adsorbent bed structure.

Previously verified to Technology Readiness Level (TRL) 4 in the laboratory, performance targets for the combination of Climeworks' DAC process with Svante's structured adsorbent structure (Figure 4) were validated in the field at a test facility built in California. Three generations of sorbent-structure combinations were developed and tested to improve upon current performance. The sorbent filter lifetime was estimated at several thousand cycles (approximately two to three years); process parametric testing as well as durability studies were conducted to study the lifetime. The team extrapolated collected data to estimate performance for a one-million-tonne-per-year plant and beyond, to confirm cost targets and to advise techno-economic and life cycle assessments of the DAC technology. Climeworks' collectors filled with novel solid sorbent materials produced by Svante enable an efficient adsorption-desorption process, allowing CO_2 extraction from diluted gas streams (such as air) at minimal energy demand, which is vital for implementation.

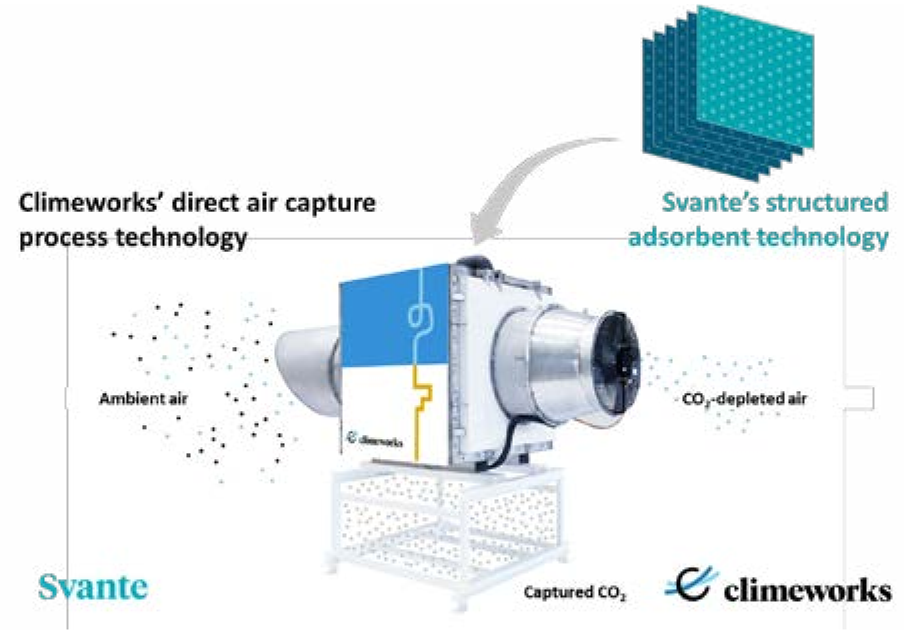


Figure 4: Climeworks' DAC technology with Svante's structured adsorbent technology.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current* R&D Value	Target R&D Value
True Density @ STP	$kg_{laminate}/m^3{}_{bed}$	100-270	80-150
Bulk Density	kg/m^3	N/A	N/A
Average Particle Diameter	mm (laminate thickness)	0.24-0.28	0.24-0.36
Particle Void Fraction	m^3/m^3	N/A	N/A
Packing Density (wetted sheet area/bed volume)	m^2/m^3	1700-3000	1000-1700
Solid Heat Capacity @ STP	kJ/kg-K	1.4	1.4
Crush Strength	kg_f	N/A	N/A

Attrition Index	-	N/A	N/A
Thermal Conductivity	W/(m-K)	0.14-0.18	0.14-0.18
Adsorption			
Pressure	bar	ambient	ambient
Temperature	°C	ambient	ambient
Equilibrium Loading	g mol CO_2/kg	>1	>1
Heat of Adsorption	kJ/mol CO_2	70-80	70-80
CO_2 Adsorption Kinetics	gmol//$kg_{sorbent}$/min	0.05-0.07	0.08-0.1
Desorption			
Pressure	bar	0.2-0.3	0.2-0.3
Temperature	°C	<100	<100
Equilibrium CO_2 Loading	g mol CO_2/kg	<0.1	<0.1
Heat of Desorption	kJ/mol CO_2	70	70
CO_2 Desorption Kinetics	gmol/$kg_{sorbent}$/min	N/A	N/A
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	cyclic fixed bed	
Air Flowrate**	kg/hr	1000 - 2800	
Space Velocity	hr^{-1}	7200 - 18000	
Volumetric Productivity	$gmol_{CO2}$/(hr $l_{absorber\ bed}$)	0.1 - 0.3	
CO_2 Recovery, Purity, and Pressure	% / % / bar	>70% >95% (adaptable depending on use) 1 (adaptable depending on use)	
Adsorber Pressure Drop	bar	0.007-0.01	0.005-0.007
Degradation	% capacity fade/cycle	long-term target is 20% in 2-3 years	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	N/A (no absorber/stripper)	

*"Current" taken to mean "today in this project" at 40% completion, and is therefore already a significant improvement on the status quo.

**Module flowrate here refer to a single module in the test plant to be built as part of this project.

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Atmospheric Air Feed-Gas Assumptions:

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
ambient	ambient	0.04	variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Amine-based sorbent which binds CO_2 by chemisorption.

Sorbent Contaminant Resistance – The sorbent is highly resistant to expected contaminants found in the air. Sulfur oxide (SO_X) and nitrogen oxide (NO_X) at levels present in most air are not a key driver of degradation.

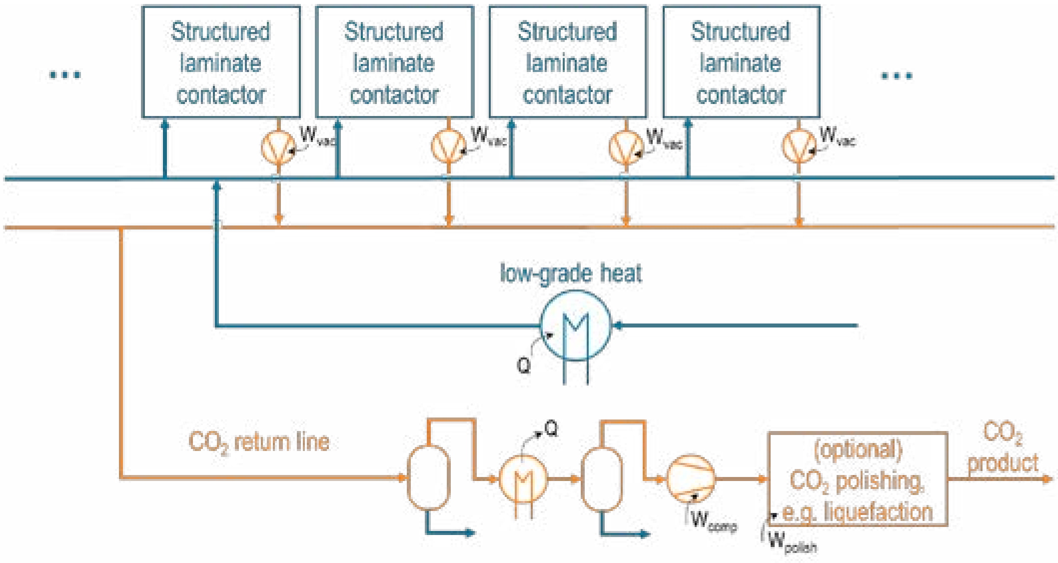
Sorbent Attrition and Thermal/Hydrothermal Stability – The sorbent's basic stability to DAC process had been demonstrated prior to this project; the stability of the sorbent and laminate combination over more than 1,000 cycles is a research focus of this project.

Air Pretreatment Requirements – None.

Sorbent Make-Up Requirements – Unknown as of now; the stability of the sorbent + laminate combination over several thousand cycles is one research focus of this project, and this will inform the make-up requirements. The target is to replace the sorbent every two to three years.

Waste Streams Generated – Air depleted in CO_2 is emitted from the contactors. Water is treated and reused in the plant (at full-scale).

Process Design Concept – A block-flow diagram for a full-size plant concept is shown below.



Proposed Module Design – The full-scale plant design will integrate Climeworks' modular DAC "collectors" with Svante's modular structured adsorbent beds. This is a fixed-bed, structured sorbent (laminates) approach. The flowrates in Table 1 above are for individual modules for the test plant being built in California for this project.

TABLE 2: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Estimate 2035*	Target long-term
Cost of Carbon Removed	\$/tonne CO_2	150-210	~100
Cost of Net Negative Emissions Achieved**	\$/tonne CO_2	170-230	~110
Capital Expenditures	% of total	30-50%	
Operating Expenditures	% of total	50-70%	

* At 1 Mt$_{CO2}$/y single plant scale, with a learning rate consistent with total installed volume of 100 Mt$_{CO2}$/y assumed.

** Including a full cradle-to-grave life cycle assessment (LCA).

Definitions:

Cost of Carbon Removed – Projected cost of capture and storage per mass of CO_2 under expected operating conditions.

Cost of Net Negative Emissions Achieved – Projected cost of capture and storage per mass of CO_2 under expected operating conditions, when accounting for the associated grey emissions.

Capital Expenditures – Projected capital expenditures in percentage of total costs.

Operating Expenditures – Projected operating expenditures in percentage of total costs.

Calculations Basis – Calculations above are done for a 1 Mt$_{CO2}$/y single plant basis, using capital cost values derived from Climeworks' current plants, with scaling factors in the range of 0.6–0.95 depending on the equipment type, with forecasted renewable electricity and heat prices, and with a learning rate assumed for future generations of plants equivalent to a total installed volume of 100 Mt$_{CO2}$/y.

Scale of Validation of Technology Used in TEA – The Climeworks DAC systems consist of three major subsystems: the core technology (optimized sorbent/process combination), the full-scale modular CO_2 collectors which house the core technology, and the process plant. This project focuses on the improvement of the core technology (optimized sorbent/process combination). "Estimate 2035" costs are based on the "Current R&D" technical information for the core technology, validated at lab scale over 1,000 cycles of operations. The rest of the plant (collector and process plant) will include incremental improvements of Climeworks' current systems, based on and field proven with the Orca plant in Iceland.

Qualifying Information or Assumptions – A conservative 90% removal efficiency (net-negative emissions achieved/CO_2 removed) is assumed, consistent with external life cycle assessments performed of Climeworks' systems.

technology advantages

- Modular design for easy scale-up.
- Sorbent stability well over 1,000 cycles.
- Good performance due to fast CO_2 uptake in structured adsorbent beds.

R&D challenges

- Work on Gen3 sorbents for improved sorbent lifetime.
- New design geometry of SABs for lower pressure drop.
- Complete optimization of sorbent structure and process for DAC.

- Demonstrate and study structured sorbent's lifetime to estimate costs based on measured data.
- Beyond this project: scale-up sorbent structure to standard module size; number-up collector units; scale-up plant.

status

This project was completed on September 30, 2023. Gen1 sorbent design and testing of more than 1,000 cycles has been completed, demonstrating sorbent stability and reasonable performance at low relative humidity. The Gen2 sorbent, which uses Climeworks' sorbent with Svante's laminate structure, demonstrated significant improvement of performance over Gen1 in wet air, and met or exceeded Gen2 targets. The project designed, built, and commissioned an integrated DAC test facility ("IDS") and operated it successfully for more than one year. Focus was on Gen2 results and Gen3 sorbent development and analysis was completed. Durability testing to more than 3,000 cycles was completed for Gen2, and to more than 5,000 cycles for Gen3, and the project achieved both TRL 5 and significant technology improvement.

available reports/technical papers/presentations

Kathy Fagundo, Electricore, Inc., "Direct Air Capture Using Novel Structured Adsorbents," Project Closeout Meeting, Pittsburgh, PA. September 2023. *https://netl.doe.gov/projects/files/Direct%20Air%20Capture%20Using%20Novel%20Structured%20Adsorbents.pdf*.

Kathy Fagundo, Electricore, Inc., "Direct Air Capture Using Novel Structured Adsorbents," 2023 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA. August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_CDR29_Fagundo.pdf*.

Adelaide Calbry-Muzyka, Climeworks, "Direct Air Capture Using Novel Structured Adsorbents," 2022 Carbon Management Project Review Meeting, Pittsburgh, PA. August 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_CDR16_Calbry-Muzyka.pdf*.

Deborah Jelen, Adelaide Calbry-Muzyka, "Direct Air Capture Using Novel Structured Adsorbents," 2022 Budget Period 1 Review Meeting, Pittsburgh, PA, April 2022. *https://netl.doe.gov/projects/files/Direct%20Air%20Capture%20Using%20Novel%20Structured%20Adsorbents.pdf*.

Deborah Jelen, Adelaide Calbry-Muzyka, "Direct Air Capture Using Novel Structured Adsorbents," presented at the 2021 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Jelen.pdf*.

Deborah Jelen, "Direct Air Capture Using Novel Structured Adsorbents," Project kickoff meeting presentation, Pittsburgh, PA, March 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11073&filename=Direct+Air+Capture+Using+Novel+Structured+Adsorbents.pdf*.

Bench-Scale Development of a Novel Direct Air Capture Technology Using High-Capacity Structured Sorbents

primary project goal

Susteon Inc., in partnership with Cormetech Inc. and Columbia University, conducted bench-scale testing on a novel structured sorbent system for direct air capture (DAC). The project team developed a structured material system (SMS) that integrates a highly dispersed sorbent with in situ desorption by direct electric heating and a low pressure drop structured support in order to reduce the overall cost of DAC by lowering energy consumption by approximately 50%.

technical goals

- Advance the novel SMS from the current Technology Readiness Level (TRL) 3 to TRL 4 to justify its scale-up and pilot test in a subsequent program.
- Optimize the sorbent and structured support to maximize CO_2 working capacity, capture/adsorption rate, and adsorbent stability.
- Design and build a bench-scale test unit to evaluate the SMS and determine CO_2 working capacity, adsorption and desorption rates, desorption energy requirements, and cycle times.
- Evaluate desorption method and refine the current COMSOL-based desorption heating method model to design an energy-efficient, facile, and cost-effective means to integrate desorption energy into the SMS.
- Develop and validate a process model using lab- and bench-scale data.
- Perform techno-economic analysis (TEA) and life cycle analysis (LCA) studies.

technical content

DAC is a potentially scalable negative CO_2 emissions technology. Beyond the benefit of negative emissions, DAC technologies can use CO_2 for a wide variety of applications, ranging from CO_2 conversion to value-added products to geologic storage without expensive pipelines. A majority of DAC technologies are based on solid adsorbents, primarily containing amine (e.g., polyethylene imine [PEI]) as a reactive chemical agent for CO_2, and almost all of them are supported on a high surface area support material, like a silica and/or a metal organic framework (MOF).. This project's technology uses alkali sorbents, primarily sodium-based materials on an alumina support. The CO_2 in this process is captured by the synergistic combination of physical adsorption by high surface area alumina support followed by chemisorption by sodium carbonate (Na_2CO_3).

At ambient temperatures, CO_2 chemisorption on Na_2CO_3 is highly favorable, bringing CO_2 concentration in air down from 415 to less than 25 parts per million-

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Structured Sorbent System with Direct Electric Heating for Desorption in DAC Process

participant:
Susteon Inc.

project number:
FE0032118

predecessor projects:
N/A

NETL project manager:
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principal investigator:
Raghubir Gupta
Susteon Inc.
rg@susteon.com

partners:
Cormetech Inc.;
Columbia University

start date:
10.01.2021

percent complete:
100%

volume (ppmv), while at higher temperatures the reverse reaction is favored, decomposing sodium bicarbonate ($NaHCO_3$) into Na_2CO_3 and CO_2.

Susteon has been working with Columbia University to develop dual-function materials for reactive CO_2 capture, both from flue gas and for reactive DAC applications (Small Business Innovation Research [SBIR] grant DE-SC0020795). This collaboration has led to the identification of unique sorbent materials that exhibit very desirable characteristics for DAC applications. It was found that moisture in the air significantly enhanced the performance and stability of the sorbent, unlike MOF-based sorbents, which selectively adsorb H_2O over CO_2. A high degree of dispersion of Na_2CO_3 on high surface area alumina allows rapid adsorption and desorption rates. Using the sorbent compositions identified, a structured DAC sorbent system capable of capturing CO_2 from air at a rapid rate and high dynamic capacity was developed by washcoating a low pressure-drop monolithic structure while minimizing heat/energy needed to desorb the captured CO_2. In this project, the sorbent was incorporated on commercially available monolith supports (for low-cost fabrication) to minimize pressure drop.

The major cost contributor to DAC is the high regeneration temperature and energy input requirement for CO_2 desorption. In the case of Susteon's DAC technology, favorable sorbent characteristics enable CO_2 to be desorbed below 120°C with heat generated using renewable electricity. Relying purely upon temperature-swing adsorption, this technology does not require partial pressure difference as a driving force for desorption, as is the case with other amine-based DAC sorbents that use steam to lower the CO_2 partial pressure. This enables energy savings via lowered temperature requirements for sorbent regeneration and a reduction in auxiliary energy requirements such as vacuum and steam generation.

One of the key components of the SMS in Susteon's DAC technology is an electrical heating component that enables selective heating of the sorbent to facilitate CO_2 desorption. Selective heating leads to minimal wasted heat and high energy efficiency, while the overall low temperature requirement for sorbent regeneration enables Susteon's engineered DAC solution to be powered entirely by carbon-free energy (e.g., solar, wind). Other advantages of the SMS relative to other leading DAC sorbents include high sorbent working capacity (~3 wt%) and long-term stability, sorbent resistance to atmospheric oxygen and humid conditions, fast adsorption and desorption rates, and the environmentally benign nature of the sorbent materials.

Figure 1 shows a process flow diagram for a fully engineered DAC technology, which includes both the sorbent-containing SMS and supporting downstream systems. During the adsorption step at ambient conditions, CO_2 is adsorbed onto the sorbent contained within channels in the SMS, with air drawn into the system using a fan. The SMS is then closed to the air, and a fan evacuates CO_2-lean air from the system. Renewable electricity is used to selectively heat the sorbent whereupon the CO_2 is desorbed, regenerating the sorbent. A vacuum pump pulls high-concentration CO_2 (containing some water vapor) from the system. Water is condensed out and the pure CO_2 is compressed and sent for storage.

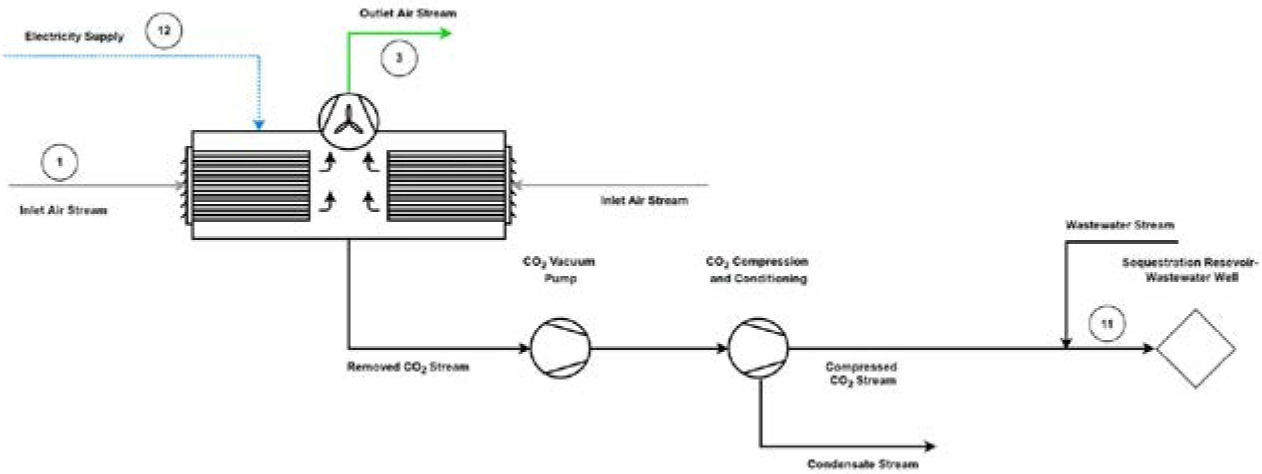

Figure 1: Process flow diagram for the Susteon DAC technology.

Feed-Gas Assumptions –

		Composition						
		vol%					ppmv	
Pressure	**Temperature**	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.7 psia	- °F	0.04	variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Chemisorption with temperature swing.

Sorbent Contaminant Resistance – High.

Sorbent Attrition and Thermal/Hydrothermal Stability – Proprietary.

Flue Gas Pretreatment Requirements – N/A.

Sorbent Make-Up Requirements – Proprietary.

Waste Streams Generated – N/A.

Process Design Concept – Figure 1 (above) illustrates the process design concept for Susteon's DAC technology.

Proposed Module Design – The key components of Susteon's DAC module include: (i) a solid sorbent, consisting of an alkali carbonate as a CO_2 getter; (ii) a monolith to support the sorbent and allow air flow through the module; (iii) a layer of resistive material to selectively heat the sorbent; (iv) an enclosure to house the supported sorbent; (v) mechanical components such as fans and louvers to draw air into the module and enable a product stream of pure CO_2; (vi) necessary gas handling and process control systems. The module operates by temperature-swing adsorption principles.

TABLE 1: KEY TECHNOLOGY METRICS FOR DIRECT AIR CAPTURE

Values	Units	Current R&D Value	Target R&D Value
Carbon Capture Capacity	w/w % sorbent	2.5	3.5
Heating Rate	°C/min	10	75
Energy Intensity	kWh/tonne CO_2	3,335	<2,500
Capital Expenditure Intensity	\$/tonne CO_2	1,050	<800

Definitions:

Calculations Basis – Susteon performed a preliminary engineering and TEA on its DAC technology at multiple scales, including the present lab scale (~1 kg/day CO_2 removal), 100 tonnes/day CO_2 removal, and 1,000,000 tonnes/year CO_2 removal. Based on this TEA, Susteon believes that there is a reasonable pathway to achieve \$100 per tonne of CO_2 capture cost at 1 million tonnes/yr scale assuming electricity price of ~3 cents/kWh and capital intensity of ~\$600/tonne-year.

Scale of Validation of Technology Used in TEA – Susteon validated the key innovations of the proposed DAC technology at the laboratory scale, corresponding roughly to TRL 3.

Technology advantages

- Novel electrical heating subsystem to minimize heat losses, lowering regeneration energy penalty.
- Low cost of sorbent and higher CO_2 capture rate and capacity compared to amine-based sorbents.
- Sodium carbonate sorbent has favorable impact of moisture compared to MOF sorbents, and easy regenerability at less than 120°C.

R&D challenges

- Implementation of integrated electrical heating technology in the structured support material.

Status

This project was completed on September 30, 2023. Susteon Inc. performed sorbent development, optimization, and characterization work, all of which focused on high surface area sorbent dispersed on the selected support structure to achieve maximum capacity, sorption rate, and adsorbent stability. Susteon Inc. completed at least 100 cycles on the bench-scale system, and continuous testing of the DAC process cycle demonstrated less than 5% decrease in system CO_2 capacity, and there was less than 1% capacity fade achieved with greater than 300 cycles completed. The TEA showed \$346/tCO_2 cost under current design conditions. The pathway to less than \$250/tCO_2 is feasible with further Structured Material Assembly (SMA) and process optimization.

Available reports/technical papers/presentations

Raghubir P. Gupta, "Bench-Scale Development of a Novel Direct Air Capture Technology Using High-Capacity Structured Sorbents," Final Technical Report, Pittsburgh, PA, March 2024. *https://www.osti.gov/servlets/purl/2324585/*.

Raghubir P. Gupta, "Bench-Scale Development of a Novel Direct Air Capture Technology Using High-Capacity Structured Sorbents," 2023 Project Closeout Meeting, Pittsburgh, PA, September 2023. *https://netl.doe.gov/projects/files/Bench-Scale%20Development%20of%20a%20Novel%20Direct%20Air%20Capture%20Technology%20Using%20High-Capacity%20Structured%20Sorbents.pdf*.

Raghubir P. Gupta, Andrew Tong, "Bench-Scale Development of a Novel Direct Air Capture Technology Using High-Capacity Structured Sorbents," 2023 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_CDR28_Gupta.pdf*.

Cory Sanderson, "Bench-Scale Development of a Novel Direct Air Capture Technology Using High-Capacity Structured Sorbents," 2022 Carbon Management Project Review Meeting, Pittsburgh, PA, August 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_CDR17_Sanderson.pdf*.

Cory Sanderson, "Bench-Scale Development of a Novel Direct Air Capture Technology Using High-Capacity Structured Sorbents," 2021 Project Kick Off Meeting, Pittsburgh, PA, November 2021. *https://netl.doe.gov/projects/files/Bench-Scale%20Development%20of%20a%20Novel%20Direct%20Air%20%20Capture%20Technology%20Using%20High-Capacity%20%20Structured%20Sorbents.pdf*.

Demonstration of Direct Air Capture of CO_2 with Building Air-Handling Equipment

primary project goal

Oak Ridge National Laboratory (ORNL) evaluated the feasibility of integrating carbon capture technologies with existing heating, ventilation, and air conditioning (HVAC) systems in buildings to remove carbon dioxide (CO_2) directly from ventilated air streams. The use of existing air handling infrastructure can enable the deployment of distributed direct air capture (DAC) systems that are modular and scalable. The project assessed specific types of buildings and associated equipment in order to identify the major opportunities and challenges associated with DAC incorporation into representative building HVAC systems. To execute this multi-faceted project, an integrated project team from ORNL's Energy and Transportation Science Division was tasked with applying capabilities and technologies associated with HVAC equipment, advanced materials, and system integration.

technical goals

- Perform a preliminary assessment of utilizing existing building equipment infrastructure for DAC.
- Characterize adsorbent materials and modules for this application.
- Assess various approaches for regeneration of sorbents.
- Evaluate system integration options and assess the impact on equipment performance due to additional power requirements.
- Perform a techno-economic assessment (TEA) of DAC in buildings and conduct a feasibility analysis based on building processes and occupant comfort.

technical content

Centralized DAC is an expensive technology requiring logistics support, large-scale air-moving technology, and sorbent regeneration capability where the levelized costs are in the range of 94–232 $USD/tonne-$CO_2$, as shown in Figure 1. A distributed approach may be more feasible and lead to lower-cost DAC. There are more than 120 million buildings across the United States (114 million residential and 6 million commercial). Existing building HVAC equipment is capable of moving large amounts of air using installed blowers and fans. The air-handling infrastructure may be able to be retrofitted with a distributed DAC system. The approach to this technology is to develop a highly modular and scalable technology for CO_2 capture, enabling distributed deployment in residential and commercial HVAC systems with minimal capital and operational costs.

The primary objectives of this project were to conduct a preliminary assessment of HVAC systems to ascertain what kind of system design is needed, perform a

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Building HVAC Retrofit with DAC System

participant:
Oak Ridge National Laboratory (ORNL)

project number:
FWP-FEAA156

predecessor projects:
N/A

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partners:
N/A

start date:
08.01.2020

percent complete:
100%

demonstration of DAC using existing building equipment, and quantify the techno-economic impact of this distributed approach to DAC technology.

Figure 1: Centralized DAC technology.

A preliminary assessment of the technology regeneration approaches revealed that the building exhaust air is 30–35°C. Condenser heat at approximately 50°C can be used to pre-heat a liquid sorbent for regeneration. The onsite gas-fired furnace can be modulated to provide ancillary heat for sorbent regeneration at approximately 100°C. The form of the sorbent can be chosen to minimize pressure drop while keeping a high surface area. The adsorbent module consists of modules with several CO_2 filters in series in order to achieve a large enough CO_2 capture breakthrough period. The test plan for adsorbent materials is to consider both physisorption and chemisorption materials. Physisorption materials have lower CO_2 capacity but are easily regenerated. Chemisorption materials have higher CO_2 capture capacity, but also need higher temperatures for sorbent regeneration.

System integration is shown in Figure 2.

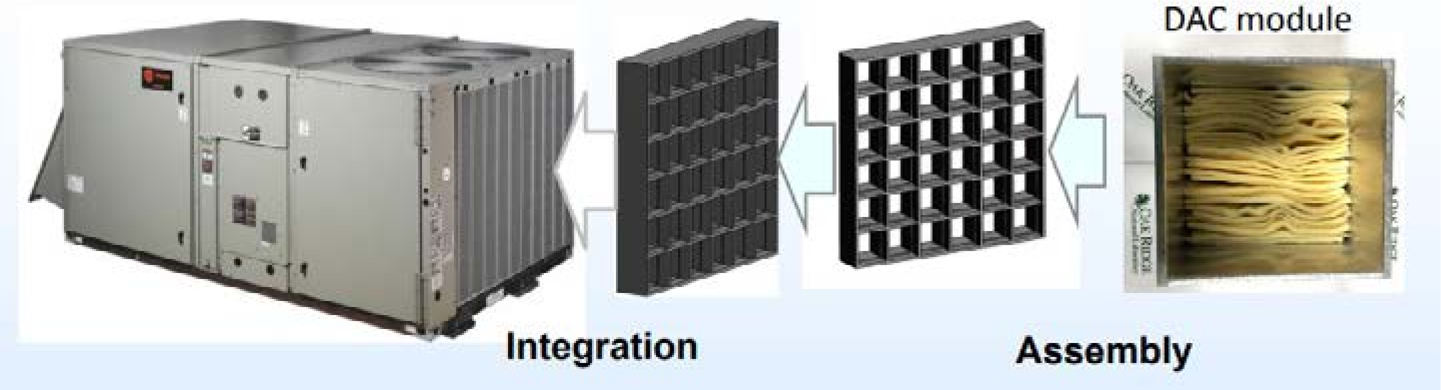

Figure 2: System integration (HVAC-DAC).

Different sorbent materials were developed and the most promising were down-selected for further evaluation and deployment. Adsorbents were configured in different ways (parallel channels vs. packed bed) for testing. Different types of DAC systems for demonstration of ambient DAC and non-ambient DAC (Figure 3).

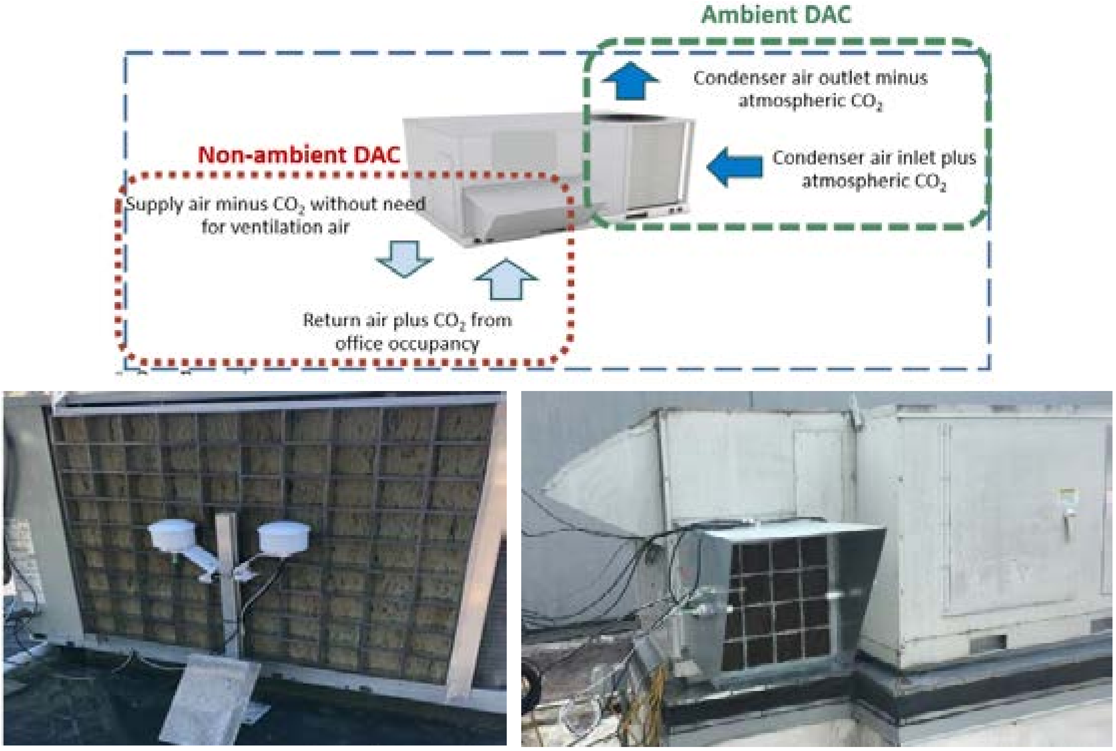

Figure 3: (top): DAC framework; (bottom left): Demonstration of ambient DAC; (bottom right): Demonstration of non-ambient DAC – make-up air unit with capture device installed.

Atmospheric Air Feed-Gas Assumptions:

		Composition						
		vol%					ppmv	
Pressure	**Temperature**	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.7 psia	°F	0.04	variable	78.09	20.95	0.93	trace	trace

technology advantages

- Existing HVAC equipment may be used, lowering both capital and operating costs for DAC technology.
- DAC can lead to improved indoor air quality in buildings (schools, restaurants).

R&D challenges

- Developing a highly modular and scalable technology for CO_2 capture for distributed application.
- Development of compatible materials and system configurations are critical.
- CO_2 storage or transmission and utilization.

status

This project was completed on April 30, 2023. The ORNL project team evaluated the feasibility of integrating carbon capture technologies with existing HVAC systems to understand the materials behavior and process control, and aspects of integrating the CO_2 capture system into existing facilities. The activated carbon-amine sorbent materials developed maintained the absorption capacity around 2–2.5 mmol CO_2/g-sorbent and also adsorbed moisture from air at 125–175 mg H_2O/g-sorbent.

available reports/technical papers/presentations

Kai Li, Kashif Nawaz, "Demonstration of Direct Air Capture (DAC) of CO_2 with Building Air Handling Equipment," 2022 Carbon Management Project Review Meeting, Pittsburgh, PA, August 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_CDR15_Nawaz.pdf*

Kashif Nawaz, "Demonstration of Direct Air Capture (DAC) of CO_2 with Building Air Handling Equipment," DAC Kickoff Meeting, February 2021. *https://netl.doe.gov/sites/default/files/netl-file/21DAC_Nawaz.pdf*.

Negative-Emissions-Enabled Direct Air Capture with Coupled Electro-Production of Hydrogen at a 5 kg/Hour Scale

primary project goal

The University of Kentucky Research Foundation (UKRF) is developing a 5 kg/hr carbon dioxide (CO_2)-intensified and -simplified direct air capture (DAC) process that simultaneously produces hydrogen (H_2) using an electrochemically regenerated solvent carbon capture system to offset the process cost.

technical goals

- Scaling-up the University of Kentucky's (UK) capture technology while reducing system-boundary carbon emissions and reducing the cost of capture through leveraging low-carbon footprint power source and H_2 credit.
- Develop a two-unit process operation with facile CO_2 capture at mild- to high-pH conditions and low gaseous pressure drop in the CO_2 absorber while regenerating CO_2 at less than 3 Volts in the electrochemical reactor by using catalytic electrodes and mist eliminator for bicarbonate formation.
- Demonstrate a continuous and reliable electrochemical-regenerated solvent DAC process at the air flow rate of higher 4,000 cubic feet per minute (CFM) with capture efficiency greater than 70% for one or more months to collect data for the next-scale development.
- Data collection to support techno-economic assessment (TEA); life cycle assessment (LCA); and environmental, health and safety (EH&S) assessment.

technical content

The UKRF, in partnership with the Electric Power Research Institute (EPRI), will develop a 5 kg/hour CO_2 DAC process. Three objectives are targeted: (1) the scale-up of an electrochemical reactor to simultaneously produce H_2 and CO_2 at a low-electric potential of less than 3 volts with collaboration from a commercial water electrolyzer developer; (2) the design and construction of an open-tower absorber for low gas pressure drop, including a spray section with a multifunctional mist eliminator to provide reaction surface area for CO_2 capture, while minimizing the liquid droplet loss; and (3) reducing the energy consumption for CO_2 release by 50% by immobilizing a catalyst on the absorber demister to enhance bicarbonate formation and total CO_2 loading in the solvent. The research team will design and test the hybrid absorber (HA) and electrochemical reactor. The research team will also focus on scale-up with parametric and long-term testing, with a particular focus on CO_2 capture efficiency, gas-liquid contact effectiveness, and energy

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Electrochemical

project focus:
Electrochemically Regenerated Solvent DAC System

participant:
University of Kentucky Research Foundation

project number:
FE0032255

predecessor projects:
N/A

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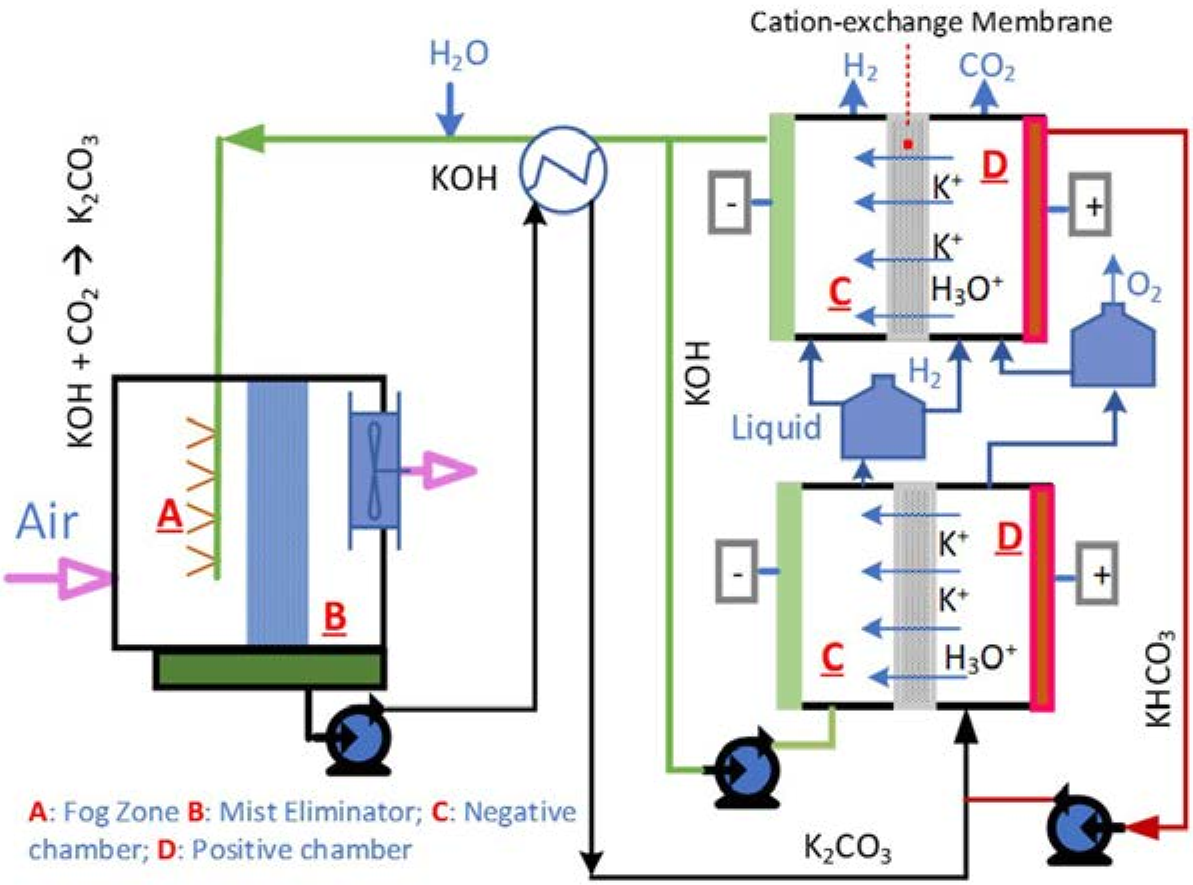
partners:
Electric Power Research Institute (EPRI)

start date:
08.01.2023

percent complete:
28%

requirement, coupled with the performance of the electrochemical reactor targeting, minimizing the power requirement, along with data collection to support TEA, LCA, and EH&S assessment.



A: Fog Zone **B**: Mist Eliminator; **C**: Negative chamber; **D**: Positive chamber

Figure 1: University of Kentucky's negative emissions DAC process with electrochemical solvent regeneration.

TABLE 1: DAC SOLVENT PROCESS PARAMETERS

Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	g mol-1	56	56
Normal Boiling Point	°C	1,327	1,327
Normal Freezing Point	°C	360	360
Vapor Pressure @ 15°C	bar	~0	~0
Concentration	kg/kg	0.05-0.5	0.05-0.5
Specific Gravity (15°C/15°C)	-	~1	~1
Specific Heat Capacity @ STP	kJ (kg K)$^{-1}$	4.02	4.02
Viscosity @ STP	cP	~1	~1
Surface Tension @ STP	dyn cm^{-1}	51	51
CO_2 Mass Transfer Rate [K_L]	m s^{-1}	0.001 – 0.003	0.01 – 0.003
Thermal Conductivity	W (m K)$^{-1}$	0.6	0.6
Absorption			
Pressure	bar	~1	~1
Temperature	°C	20-30	10-45
Equilibrium Loading	g mol CO_2/kg	0.4	0.4
Heat of Adsorption	kJ/mol CO_2	144	144

Solution Viscosity	gmol/time	143	143
Desorption			
Pressure	bar	~1	2-5
Temperature	°C	30-40	30-50
Equilibrium CO_2 Loading	g mol CO_2/kg	0	0
Heat of Desorption	kJ/mol CO_2	144	144
Degradation	% capacity fade/cycle	-	-
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	cross-flow	
Flue Gas Flowrate	kg/hr	25,438	
Space Velocity	hr^{-1}	1,234	
Volumetric Productivity	g mol CO_2/kg	~0.024	
CO_2 Recovery, Purity, and Pressure	% / % / bar	80 99.5	15
Absorber Pressure Drop	bar	<1	
Degradation	% capacity fade/cycle	N/A	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	31,177 (based on present project cost)	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine monoethanolamine MEA in an aqueous solution).

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

CO_2 Mass Transfer Rate – Overall liquid phase mass transfer coefficient.

CO_2 Reaction Rate – A characterization of the CO_2 absorption trend with respect to time, as complete in the range of time as possible.

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Feed-Gas Assumptions –

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	50-113°F	0.04	variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

Waste Streams Generated – Waste gases (mostly water).

TABLE 2: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	-	281
Cost of Carbon Avoided	\$/tonne CO_2	-	300
Capital Expenditures	\$/tonne CO_2	-	212
Operating Expenditures	\$/tonne CO_2	-	457

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Calculations Basis – The capital costs for the UK DAC + H_2 process are major equipment (ME) factored estimates. ME, material and labor costs are developed from equipment sizes, quantities and design parameters defined by the conceptual DAC + H_2 process design described in reference to Figure 1. Bulk material and labor costs are factored from the ME costs. The sum of the ME and bulk material costs, including shipping costs, forms the total direct cost. Construction indirect cost, factored from total direct labor cost, is added to the total direct cost to estimate the bare erected cost (BEC). Engineering construction management (eng CM), home office (HO) fees, and process/project contingencies were calculated using percentages from the U.S. Department of Energy (DOE)/National Energy Technology Laboratory (NETL) Solvent DAC Report. Cost estimates in this analysis represent neither first-of-a-kind (FOAK) nor nth-of-a-kind (NOAK) costs, since cost estimates for plant components that are not yet fully mature (e.g., air contactors, electrochemical regenerator at the scale required by this system, etc.) use the same cost estimation methodology as for mature plant components, which does not account for the unique cost premiums associated with the initial complex integrations of emerging technologies in a commercial application. Process contingencies are anticipated to cover only part of these cost premiums, and it is anticipated that initial deployments of this plant may incur higher costs than those resulting from this analysis. The DOE/NETL Solvent DAC Report provides capital costs for liquid solvent DAC technology that uses a potassium hydroxide (KOH) solvent to absorb CO_2 from air with a calcium caustic recovery loop to regenerate the solvent and produce a concentrated CO_2 stream. Modifications were made to DOE/NETL's solvent DAC capital costs either by capacity factoring (i.e., cost scaling) or by direct replacement with the project team's own estimates to obtain the total project cost (TPC) for UK's DAC + H_2 process.

Scale of Validation of Technology Used in TEA – Costs scaled from the DOE/NETL Solvent DAC Report were first escalated to 2022 dollars, using Chemical Engineering Plant Cost Index (CEPCI) values. Systems that remain unchanged from the DOE/NETL Solvent DAC Report (e.g., balance of plant systems) are factored based on the cost-scaling guidelines included in the report, as well as from DOE/NETL's "QGESS: Capital Cost Scaling Methodology: Revision 4" report, where applicable. For scaling parameters that fall outside of the applicable ranges outlined in the DOE/NETL solvent DAC and

QGESS scaling guidelines, the project team's in-house scaling exponents were used. The DAC system evaluated in the DOE/NETL Solvent DAC Report includes an integrated natural gas combined cycle (NGCC) plant to provide power to the DAC process. Since the UK DAC + H_2 system is powered exclusively by grid electricity, cost adjustments were made to specific subsystems to account for the different power sources used in the two systems.

Qualifying Information or Assumptions – Assumptions used in the estimates include (1) 2022 Base Hourly Labor Rate \$40.46 hr^{-1}; (2) Labor Burden, Base Salary 30%; (3) Administrative/Support Labor, Operations and Maintenance (O&M) Labor 25%; (4) Maintenance Material + Labor, % TPC 1.60%; (5) Maintenance Labor Only, % Maintenance Material + Labor 40%; (6) H_2 Sale Value, \$6 kg^{-1}; (7) Current U.S. Grid Mix at 546 kg CO_2e/MWh; (8) 2050 U.S. Grid Mix (U.S. Energy Information Administration [EIA] Annual Energy Outlook [AEO]) at 434 kg CO_2e/MWh; (9) Fossil Power with Carbon Capture and Storage (CCS) at 220 kg CO_2e/MWh; (10) 100% Renewables at 23 kg CO_2e/MWh.

technology advantages

- The chloride-based catalyst immobilized on the absorber de-mister led to a more than 90% enhancement in the CO_2 capture rate and a more than 100% improvement in the carbon removal amount.
- Use of catalyst-coated de-misters increases droplets' suspension time and improves performance.

R&D challenges

- Low catalyst enhancement for absorber.
- Water losses during carbon capture.

status

The project team has demonstrated, using an inorganic-based catalyst, a 175% improvement in carbon capture capacity (e.g., bicarbonate formation) and a greater than 90% improvement in carbon capture rate. A catalytic electrode, dimensional stable anode (DSA), was sustained in a solvent regeneration process for at least 140 hours. The preliminary TEA indicates that the expense of capturing 1 ton of CO_2 may fall below \$300 when factoring in proceeds from H_2 sales (at \$6/kg) and catalyst cost. The preliminary LCA shows that improved carbon capture using their catalyst can reduce global warming potential. In addition, the process design package is completed, including computer-aided design (CAD) for the absorber and solvent regenerator, the piping and instrumentation diagram (P&ID), etc.

available reports/technical papers/presentations

Xin Gao, Jesse Thompson, and Kunlei Liu, "Negative-Emissions Enabled Direct Air Capture with Coupled Electro-Production of Hydrogen at a 5 kg-per-hour Scale," 2024 FECM / NETL Carbon Management Research Project Review Meeting, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_CDR_5_Gao.pdf*.

Xin Gao, Jesse Thompson, and Kunlei Liu, "Negative-Emissions Enabled Direct Air Capture with Coupled Electro-Production of Hydrogen at a 5 kg-per-hour Scale," 2024 Budget Period 1 Review Meeting, May 2024. *https://netl.doe.gov/projects/files/Negative-Emissions%20Enabled%20Direct%20Air%20Capture%20with%20Coupled%20Electro-Production%20of%20Hydrogen%20at%20a%205%20kg-per-hour%20Scale.pdf*.

Xin Gao, Ayokunle Omosebi, Aron Patrick, Kunlei Liu, "Optimizing Direct Air Capture Solvents to Minimize Energy Consumption of CO_2 Release in a Carbonate Electrolyzer" ECS Advances 3 (2), 024501, April 2024. *https://iopscience.iop.org/article/10.1149/2754-2734/ad3928/meta*.

Ayo Omosebi, Xin Gao, Jesse Thompson, Kunlei Liu, "Negative-Emissions Enabled Direct Air Capture with Coupled Electro-Production of Hydrogen at a 5 kg-per-hour Scale," 2023 Project Kickoff Meeting Presentation, September 2023. *https://netl.doe.gov/projects/files/Negative-Emissions%20Enabled%20Direct%20Air%20Capture%20with%20Coupled%20Electro-Production%20of%20Hydrogen%20at%20a%205%20kg-per-hour%20Scale.pdf*.

Ayo Omosebi, Xin Gao, Jesse Thompson, Kunlei Liu, "Negative-Emissions Enabled Direct Air Capture with Coupled Electro-Production of Hydrogen at a 5 kg-per-hour Scale," 2023 FECM / NETL Carbon Management Research Project Review Meeting, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_CDR30_Omosebi.pdf*.

Electrochemically Regenerated Solvent for Direct Air Capture with Co-Generation of Hydrogen at Bench Scale

primary project goal

The University of Kentucky Institute for Decarbonization and Energy Advancement (UK IDEA), Vanderbilt University, the Electric Power Research Institute (EPRI), and Louisville Gas and Electricity and Kentucky Utilities (LG&E and KU) developed an intensified, cost-effective, and easily scalable process using aqueous potassium hydroxide (KOH) as a solvent for direct air capture (DAC). The process features the use of a hybrid membrane absorber (MA) coupled with an electrochemical solvent regenerator (ER) that is capable of extracting carbon dioxide (CO_2) from the atmosphere and pre-concentrating the potassium carbonate (K_2CO_3) solvent followed by regenerating the solvent to release CO_2 in the ER, simultaneously refreshing the capture solvent while producing hydrogen (H_2) to offset the DAC cost.

technical goals

- Design and fabricate a hybrid bench-scale MA and ER with suitable electrode material and the flow channel pattern.
- Perform system integration, installation, and commissioning.
- Pursue parametric studies of the bench-scale system through long-term operation, focusing on:
  - Performance of the MA with a focus on CO_2 capture efficiency, gaseous pressure drop, and gas-liquid contact effectiveness.
  - Performance of the ER with the target of minimizing both the operating voltage and H^+ transport through the cation-exchange membrane.
  - Leveraging long-term operation to investigate the degradation mechanisms of both the electrode and membrane materials.
- Develop a techno-economic assessment (TEA) and life cycle analysis (LCA) to compare against commercial technologies.

technical content

The two-unit operation employs a hybrid MA that extracts CO_2 from air, enriching carbon content in the solvent solution after capture, coupled with an ER that releases the CO_2 and simultaneously produces H_2 as a saleable coproduct. The process operates in a loop with a chemically stable and non-toxic potassium (K+) solvent that offers both fast absorption kinetics and near-zero vapor pressure. The

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Novel Concepts

project focus:
Hybrid Membrane Absorber Coupled with Electrochemical Solvent Regenerator for DAC

participant:
University of Kentucky

project number:
FE0032125

predecessor projects:
N/A

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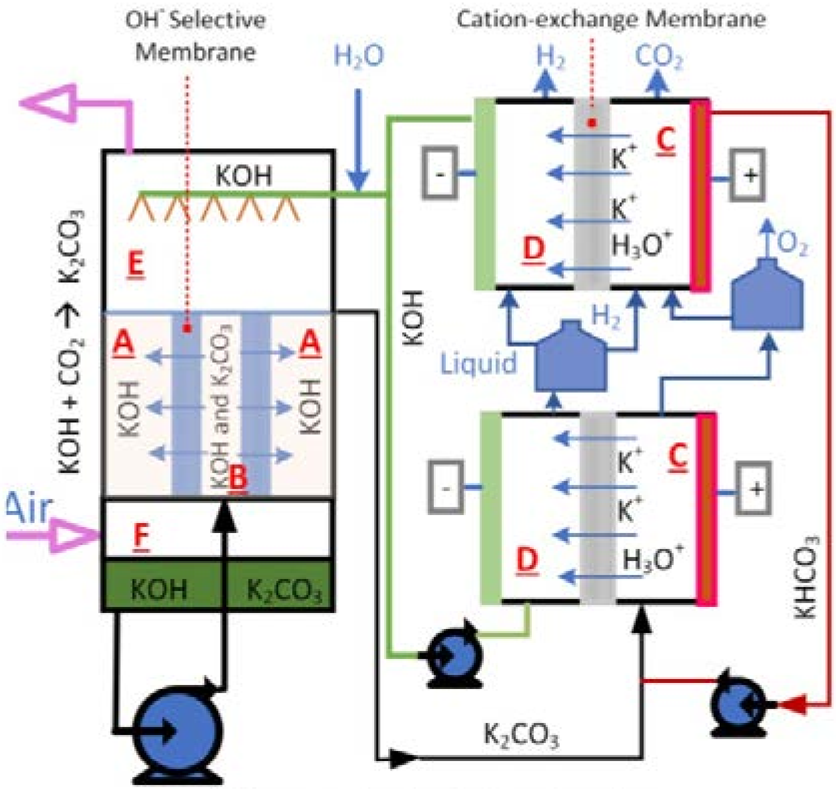
partners:
Electric Power Research Institute; Louisville Gas & Electric and Kentucky Utilities; Vanderbilt University

start date:
10.01.2021

percent complete:
100%

system in Figure 1 shows: (1) a hybrid MA to capture CO_2 from the atmosphere to form carbonate (CO_3^{2-}), and (2) an ER to regenerate hydroxide (OH^-) while producing H_2 at the negative chamber.



A: Permeate chamber for CO_2 absorption
B: Feed chamber for mixture of KOH and K_2CO_3
C: Positive chamber **D**: Negative chamber
E: Open-tower for CO_2 absorption
F: Air entrance and liquid sump

Figure 1: Solvent–based DAC process.

Key features of the process include: (1) utilizing a KOH solution as the capture solvent in a hybrid absorber; (2) using an OH^- selective nanofiltration membrane to concentrate carbon content in the rich solvent prior to regeneration to reduce the parasitic reactions in the ER; (3) producing saleable H_2 to offset the CO_2 capture cost; and (4) leveraging the mature technologies of nanofiltration and the alkaline electrolyzer to make the process easily scalable.

In addition to the solvent spray at the open tower (E) for CO_2 capture and air entrance above the liquid sump (F), the middle of MA has two chambers divided by an OH^- selective membrane acting as structured packing for gas-liquid contact, in which, at the permeate chamber (A) with large cross-sectional area (to maintain the gas velocity below 1.5 m/s) under ambient conditions, CO_2 from air is effectively captured using a KOH liquid. The majority of CO_2 is captured in the open tower section, while the wetted membrane surface provides the additional gas-liquid interface for reactions to boost the carbon loading. At the feed chamber (B) under a moderate operating pressure (e.g., less than 200 pounds per square inch gauge [psig]), K_2CO_3 collected from the prior CO_2 capture process from the sump is separated from the unreacted KOH. Furthermore, similar to a conventional alkaline electrolyzer, the ER is a compact electrochemical cell equipped with an ion-exchange membrane and catalytic positive and negative electrodes. At the chamber with the positive electrode, CO_2 is liberated along with O_2, and at the chamber with the negative electrode, H_2 gas is produced via typical water electrolysis.

Aqueous KOH produced from the negative chamber of the ER (D) enters the open tower of the MA from the top via liquid spray while air enters near the sump. Under such a countercurrent configuration, KOH reacts extensively with CO_2 from air to form K_2CO_3 via $2KOH + CO_2 = K_2CO_3 + H_2O$ under ambient pressure in the open tower, along with the permeated KOH in permeate chamber (A) flowing downward against the membrane surface. Subsequently, the unreacted KOH and K_2CO_3 are transferred from the sump to the feed chamber of the membrane, where the KOH gets selectively transported across the OH^- selective membrane, leading to the concentrated CO_3^{2-} solution (e.g., K_2CO_3) prior to regeneration in the ER. The solution exiting the MA is first pumped to the positive chamber (C) of the ER, in which CO_3^{2-} is converted to carbon dioxide (CO_2) via a three-step reaction of $4OH- + 4e- = O_2 + 2H_2O$, $CO_3^{2-} + H^+ = HCO_3^-$ followed by $HCO_3^- + H^+ = CO_2 + H_2O$. Meanwhile, K^+ is repulsed by electrostatic forces through the K^+ selective membrane to the negative chamber (D) to balance the electronic charge along with a portion of H^+. In the negative chamber with the liquid recirculation, H_2 is produced via $2H_2O + 2e- = H_2 + 2OH^-$ while forming KOH for the next CO_2 capture cycle in the MA. In the UK IDEA process, the concentration of the K^+-based solvent is adjustable with internal recirculation and make-up water (H_2O) to satisfy both the CO_2 capture performance in the MA, the ER operating voltage, and water balance maintenance.

To produce a high-purity CO_2 stream, a two-stage ER is utilized in which two ERs with the same physical structure and functionality are connected in series. The bottom ER converts aqueous CO_3^{2-} to HCO_3^- and releases O_2 in the positive chamber. The HCO_3^- solution can then be flashed for CO_2 release or H_2 released in the negative chamber of the bottom ER is purged into the liquid fed to the positive chamber in the top ER, thereby biasing the positive electrode. Under such configuration, in the top ER, O_2 evolution at the positive chamber can be minimized via a depolarization technique to facilitate the acidification process of $KHCO_3$ via $HCO_3^- + H^+ = CO_2 + H_2O$ towards producing high-purity CO_2. Alternatively, for a more simplistic ER configuration, a conventional cryogenic CO_2 distillation technique can be applied for CO_2 recovery and purification at anode outlet.

Process Features:

(1) Hybrid membrane absorber for CO_2 capture using KOH solution. The low CO_2 concentration in air generates a significant challenge on the gas/liquid contact surface if a concentrated KOH solution is used. Compared to a liquid/gas mass ratio of 1 for the application of 5 M solvent to capture CO_2 from natural gas combustion flue gas (~4 vol% CO_2), applying the same solvent for air capture (~0.04 vol% CO_2) will result in the liquid/gas mass ratio as low as 0.01, which is too low to produce an effective gas-liquid contact interface on any commercially available packing. One effective way to solve the challenge is to use a solvent (e.g., 0.5–1 M). However, the lower the solvent concentration, the higher the energy needed to regenerate the solvent after capturing CO_2. The hybrid MA (a) effectively absorbs CO_2 via spraying the solvent onto the mist in the open-tower, thereby reducing the overall capital cost of the absorber while enhancing CO_2 capture by hydroxide permeate on the membrane surface; and (b) reduces parasitic reactions by removing OH- and pre-concentrating the capture solution's carbon content for the ER. The removal of OH^- prior to the solvent regeneration at the ER bottom eliminates the electron/charge transfer spent on the parasitic KOH neutralization toward non-CO_2 liberation at the positive chamber of the ER. For instance, when KOH enters the positive chamber of the ER, H^+ reacts with OH^- forming H_2O; in contrast, when K_2CO_3 enters the positive chamber of the ER, H^+ reacts with CO_3^{2-} leading to the CO_2 product.

(2) Besides producing KOH as a highly effective CO_2 capture solvent, the ER simultaneously generates a ≥99.9% pure H_2 stream as a saleable carbon-free energy carrier, thereby offsetting the overall DAC process cost. In the demonstrated process, H_2 is produced at the negative chamber of the ER by accepting two electrons while liberating CO_2 at the positive chamber of the ER by giving away two electrons to produce H^+, which means that for each mole of CO_2 captured from air, one mole of H_2 coproduct is produced through electrolysis. Furthermore, since H_2O is the only electrochemically active species at the negative chamber of the ER, 100% of electronic charge efficiency is expected toward H_2 coproduction. In addition, internally recirculating the liquids help retain a high level of ionized species, therefore stabilizing the ER overall electrical conductivity. Such an operating configuration will further lead to H_2 production at a reliable operating voltage, thereby mitigating the voltage variation, which may be detrimental to the equipment lifespan.

(3) The process is easily scalable to a larger scale, as both the MA and ER are built upon mature technologies. The MA is built upon liquid atomization and the nanofiltration technology, utilizing the membrane with either enhanced chemical surface charge or size-exclusion to selectively separate monovalent ions from divalent ions under a moderate operating pressure. For this case, OH^- is separated from CO_3^{2-}. Moreover, the design of the MA will leverage

the physical structure of the commercialized membrane contactors and spray towers, thereby providing a convenient pathway for modulation. The ER is slightly modified with respect to the conventional alkaline electrolyte. For this case, instead of using an anion-exchange membrane, a cation-exchange membrane is utilized to attain a high quality of KOH for efficient CO_2 capture from air while producing H_2.

In this project, the team designed and fabricated a bench-scale unit (10 cubic feet per minute air flowrate) and conducted parametric and long-term studies to inform next-scale process development.

TABLE 1: PROCESS PARAMETERS

Performance Attributes	Units	Initial R&D Value	Final R&D Value
Carbonate Rejection/Hydroxide Rejection	%/%	50/<10	80/<10
Nanofiltration Membrane Fade	%/hr	N/A	0.02
ER K^+ Transport Efficiency	%	65	80
Membrane K^+ Transport Fade	%/hr	0.06	0.02
CO_2 Capture Efficiency	%	60	>90
Space Velocity	Hr^{-1}	1200	3600
Pressure Drop	Pa	N/A	1000
Regenerator Operating Potential	Volts	4	2.4
Regeneration Energy (55% thermal/electric)	kJ/mole	880	533
Overall Volumetric Productivity	gmol CO_2/ hr	0.001	2

Definitions:

Absorber Geometry – Hybrid absorber integrating nanofiltration stacking and liquid atomization in open tower architecture.

Atmospheric Air Feed-Gas Assumptions – Update values below to describe the air feed-gas pressure, temperature, and composition entering the capture system:

		Composition						
		vol%					ppmv	
Pressure	Temperature	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	68-72°F	0.04	variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

CO_2 Capture Mechanism – The driving force for capture is the partial pressure difference between CO_2 in air and the capture solvent on the nanofiltration face and in the open tower section. The electrochemical cell regenerates the solvent after CO_2 is absorbed to preserve the driving force.

Flue Gas Pretreatment Requirements – N/A

Product Streams Generated – Hydrogen for sale.

Process Design Concept – See Figure 1.

TABLE 2: DIRECT AIR CAPTURE ECONOMICS WITHOUT H_2 SALE CREDIT @ 49,000 T CO_2/Y SCALE

Economic Values	Units	Initial R&D Value	Final R&D Value
Cost of Carbon Captured	\$/tonne CO_2	852	683

The current market price of water electrolysis grade green H_2 is \$7–14/kg H_2. This process coproduces H_2 at 67.3 kg H_2/tonne CO_2 captured. Assuming the sale of H_2 at \$8/kg H_2 for economic analysis, the CO_2 capture cost will be \$145/tonne.

Definitions:

Cost of Carbon Captured – The capture cost is estimated assuming approximately 2.4 V operation of the electrochemical regenerator, regenerator cost is 90% capture cost, 7 cents/kWh electricity cost.

technology advantages

- The process is easily scalable to a large-scale, as both the MA and ER are built upon mature technologies.
- Simplified (two-unit operation) capture process with a significant reduction (greater than 25%) in both the capital and operating cost while producing H_2 as a saleable byproduct.
- Provide easy integration with renewable power sources for remote operation and reducing CO_2 emissions.

R&D challenges

- Design of anode-cathode to minimize corrosion and voltage loss due to sluggish kinetics.
- Design of flow channel for rapid degassing.
- Electrochemical regeneration performance and energy requirement of the ER are strongly dependent on inter-electrode spacing and loading factor, solvent concentration, flow rate, and current.

Status

This project was completed on February 29, 2024. UK IDEA designed and fabricated the CO_2 capture technology consisting of a hybrid MA that extracts CO_2 from air, enriching carbon content in the solution after capture, coupled with an ER for solvent regeneration. UK IDEA has performed parametric evaluation for membrane integrity, transmembrane pressure, and OH^-/CO_3^{2-} selectivity for the MA, as well as cell development for the ER. The project demonstrated that the hybrid absorber, including spray absorber and selective membrane, is an effective absorber for DAC with capture facilitated by the KOH solvent. The NFX and NF270 nanofiltration membranes show capability to concentrate carbon loading by removing OH^- prior to sending ER for regeneration toward reducing energy consumption. Even though the reaction between CO_2 and hydroxide is instantaneous, the air and liquid contact time is still critical and the low gas-side pressure drop is the key to minimizing the capture cost.

available reports/technical papers/presentations

Ayo Omosebi, Xin Gao, Kunlei Liu, "Electrochemically Regenerated Solvent for Direct Air Capture with Cogeneration of Hydrogen at Bench-Scale," Final Technical Report, Pittsburgh, PA, April 2024. *https://www.osti.gov/servlets/purl/2349461/*.

Ayo Omosebi, Xin Gao, Kunlei Liu, "Electrochemically Regenerated Solvent for Direct Air Capture with Cogeneration of Hydrogen at Bench-Scale," Final Briefing Presentation, Pittsburgh, PA, February 2024.

https://netl.doe.gov/projects/files/Electrochemically%20Regenerated%20Solvent%20for%20Direct%20Air%20Capture%20with%20Cogeneration%20of%20Hydrogen%20at%20Bench-Scale.pdf.

Kunlei Liu, "Electrochemically Regenerated Solvent for Direct Air Capture with Cogeneration of Hydrogen at Bench-Scale," 2022 Carbon Management Project Review Meeting, Pittsburgh, PA, August 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_CDR17_Liu.pdf*.

Kunlei Liu, "Electrochemically Regenerated Solvent for Direct Air Capture with Cogeneration of Hydrogen at Bench-Scale," Project kickoff meeting presentation, November 2012. *https://www.netl.doe.gov/projects/plp-download.aspx?id=12447&filename=Electrochemically+Regenerated+Solvent+for+Direct+Air+Capture+with+Cogeneration+of+Hydrogen+at+Bench-Scale.pdf*.

Experimental Demonstration of Alkalinity Concentration Swing for Direct Air Capture of Carbon Dioxide

primary project goal

Harvard University conducted experimental verification of a novel approach for direct air capture (DAC) of carbon dioxide (CO_2) that employs an alkalinity concentration swing (ACS) process concentrating an aqueous alkaline solution (that has equilibrated with air) using commercially available technologies such as reverse osmosis (RO) or capacitive deionization (CDI). The concentrated solution has a higher partial pressure of CO_2 relative to the initial solution, allowing the CO_2 to be separated and stored.

technical goals

- Adapt the design of RO and CDI from their traditional desalination uses and tune each for a specific target concentration factor (10-times for RO; 100-times for CDI) necessary to extract CO_2 from alkaline solution.
- Assemble a calibrated system to measure CO_2 extracted from solution and build a subsystem to extract CO_2 from concentrated solution using either a vacuum on a fluid reservoir and/or using gas permeable membrane technology.
- Use CO_2 measurement and extraction systems to test the solution's equilibrium and kinetic properties key to the ACS, including how dilution and re-equilibration with air proceed.
- Demonstrate system integration and energy quantification coupled to the ability to extract CO_2 from solution concentrated by RO or CDI and measure the energy necessary to operate the process per quantity of CO_2 captured.
- Develop an understanding of breakdown pathways and confirm the revolutionary stability of the new solvent using various laboratory techniques.

technical content

The concentration of dissolved inorganic carbon (DIC)—the sum of carbonate ion, bicarbonate ion, and dissolved CO_2—in equilibrium with air ($pCO_2 \approx 415$ parts per million [ppm]) depends on the alkalinity of a solution (i.e., the charge difference between the sum of the conservative cations and anions in solution). As the alkalinity of a solution increases, the amount of DIC, when equilibrated with air, increases, but at a decreasing rate. This is due to the transition from bicarbonate as the dominant species of DIC (at an intermediate pH range from 6.5–10) to carbonate ion as pH increases. At higher alkalinity and higher pH, the charge balance required is now accommodated primarily by carbonate ions, which are divalent. Consider any basic solution in equilibrium with air—if pure water is removed from this solution in a closed system with respect to the dissolved

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Solvents

project focus:
Alkaline Concentration Swing Process for DAC

participant:
Harvard University

project number:
FE0031964

predecessor projects:
N/A

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partners:
N/A

start date:
02.09.2021

percent complete:
100%

components (including CO_2), both the DIC and the alkalinity increase in proportion to their relative concentrations in the solution, while the partial pressure of CO_2 steadily increases, due to the change in speciation of carbon from bicarbonate to carbonate. This creates an opportunity for collection of CO_2 in concentrated form. The solution can be recycled simply by recombining the concentrated solution with the freshwater produced from the RO or CDI modules and then allowing it to re-equilibrate with air, returning the system to the initial point. The cycle is illustrated in Figure 1, which shows the first two steps (concentration and outgassing) of the ACS.

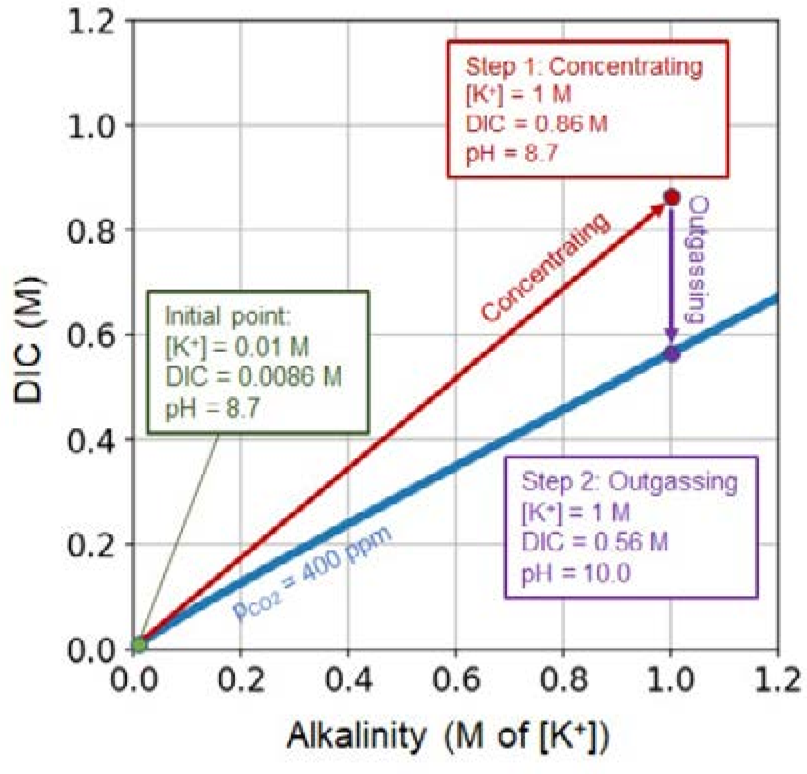

Figure 1. The ACS cycle (concentrating and outgassing steps).

Figure 1 plots a representative example of a solution at 0.01 M alkalinity (K+), equilibrated at pCO_2 of 400 ppm, concentrated by a factor of 100 to 1 M alkalinity. At these values, the solution will outgas 3 mM of CO_2 with respect to the feed. In Figure 1, the blue line plots the relationship between DIC concentration at a fixed partial pressure of CO_2 (400 ppm) as a function of alkalinity. The red arrow indicates the concentration step of the ACS and plots the trajectory in DIC and alkalinity space if a solution that was equilibrated at 0.01 M alkalinity (green point) was concentrated by a factor of 100 times to an alkalinity of 1 M. In the concentrated state (red point), the solution has an excess DIC to the amount of alkalinity in solution. When exposed to a pressure of 400 ppm, the purple arrow indicates the amount of CO_2 that would outgas as the system reaches a new equilibrium at high alkalinity. This figure does not show the remaining step of the ACS, dilution and atmospheric CO_2 re-equilibration, which would return the system to the initial point.

This basic approach will work with any strong base. Potassium hydroxide solutions are the solvent of choice due to the very high solubility of potassium bicarbonate. Sodium bicarbonate is less soluble, and the concentration step may drive precipitation of solids, which would complicate the process; calcium carbonate is even less soluble. There are multiple tradeoffs to consider in terms of what concentrations to use for optimization of the ACS process. Starting with more dilute solutions (e.g., 0.01 M), and then concentrating by a factor of 100, can produce a higher CO_2 outgassing pressure from the concentrated solution, but requires more energy for the concentration step and a larger initial feed solution volume. On the other hand, starting with a more concentrated initial solution (e.g., 0.6 M) can result in a significantly lower ACS energy requirement and, at this higher initial alkalinity, ingassing kinetics (i.e., re-equilibration with air following dilution) are also significantly faster, based on estimates using the literature.

It is difficult to make detailed calculations of the energy demand of DAC without experimental demonstration of the full cycle as is being performed in this project. However, using standard numbers for energy use in RO desalination plants and at similar concentration ranges, a rough estimate of 1.7 megawatt-hours (MWh) of electricity per tonne of CO_2 was obtained, which suggests there is potential for improvement on the 2.28-MWh minimum energy requirement in published estimates of solvent-based DAC energy requirements. Another important advantage of the ACS approach to DAC is that, because it makes use of existing technologies for water purification and desalination that are widely deployed at commercial scale around the world (such as RO), the capital costs of this approach to DAC are likely to be extremely low. High capital approaches to DAC require steady power supply and continuous operation to reduce costs; ACS has the potential to harness very inexpensive but intermittent energy sources (such as wind) that would be impossible if capital costs for the system were high.

This project's approach to experimental demonstration of ACS was to first test each step of the system independently before integrating them into a full cycle. The process was divided into three subsystems (shown in Figure 2).

1. Concentration of an alkaline solution.
2. Carbon dioxide extraction.
3. Dilution and re-equilibration with air.

For the concentration step, which is at the heart of the ACS process, the project team conducted experiments on two parallel approaches. First, to use a laboratory-scale RO desalination system; second, to use a CDI system that has advantages at lower concentration ranges. One experimental range of concentrations for the ACS was used in both systems to allow for direct comparisons. Two approaches for CO_2 extraction—one applying a vacuum on a fluid reservoir and another making use of gas permeable membrane technology—were also evaluated.

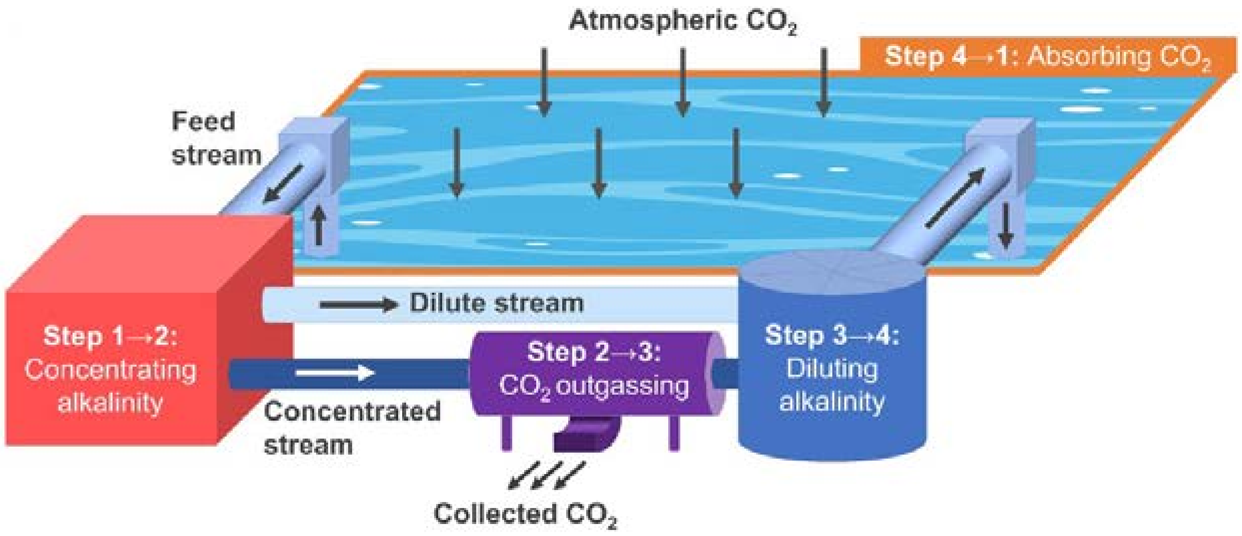

Figure 2. System schematic for ACS implementation. Flow diagram indicating the three steps of the ACS: (1) concentration; (2) CO_2 extraction; (3) dilution and re-equilibration with air.

Concentration Step Using RO

RO is a membrane-based separation process where pressure is applied against a solvent-filled solution, overcoming the solution's osmotic pressure, to create a concentrated and purified stream. RO technology has a wide range of applications, from wastewater treatment and home water purification to seawater desalination. Desalination plants are designed to produce a stream of freshwater from an input feed of about 0.6 M of sodium chloride (NaCl)-equivalent salt (i.e., seawater), yielding a brine of roughly double the original salinity. This exact process can be used to demonstrate the carbon capture approach of the ACS, but different membranes need to be tested, in particular with respect to rejection of DIC and the alkalinity carrier (K+), as well as water permeability—both factors that contribute to the maximum reachable concentration factor. Unlike in traditional desalination processes, higher permeability may be tolerated since minimizing the salinity of the permeate stream is not a necessary optimization goal for the ACS. Initially, a range of commercially available polyamide thin-film composite membranes and cellulose acetate membranes are being tested, deploying different membrane performance parameters testing salt rejection between 95–99% and permeabilities between 28.9–68 $L/m^2/h$, over a range of applied pressures, between 5–80 bar. In order to reach higher concentration factors, more advanced membrane geometries, such as spiral-wound membranes, could be tested to increase the surface area of the membrane in the RO cell. The RO module used in this experimental system consisted of two main components: the pressure pump driving the alkaline feed solution and the RO cell. Prior to the integration of all three subsystems, the initial feed solution was a 0.6-M potassium hydroxide solution equilibrated with air by bubbling air with a controlled CO_2 partial pressure through a reservoir. The pressure pump can reach up to 80 bar (typical seawater desalination pressures), allowing for an osmotic separation of more than 1 M of NaCl equivalent ions across the RO membrane and reaching a concentration factor of 2. A lower feed concentration of 0.1 M—concentrated by a factor of 10 reaching 1 M—is also being tested and compared to CDI experiments.

Concentration Step Using CDI

CDI provides an alternative mechanism for concentrating the alkaline solution. CDI is a method of concentrating and removing anions and cations from solution by applying voltage across two electrodes, adsorbing anions to the positive electrode and cations to the negative electrode to dilute the solution. When the voltage is switched off, the release of the adsorbed ions creates a high-alkalinity brine, which constitutes the concentrating step of the ACS.

CDI systems operate best in brackish water conditions, with salt concentrations below 200 mM, and early-stage CDI systems have been commercialized for desalination, wastewater remediation, and water softening. The effective operation of CDI in this range makes it a candidate for optimal implementation of the ACS at lower salinity. The ability to work at lower initial concentrations enables larger concentration swings that have a larger yield and can thus result in significantly lower energies per unit CO_2 outgassed, as shown in Figure 1. Furthermore, CDI may enable outgassing directly within the concentration module, using gas diffusion electrodes, providing an option for continuous cycling by avoiding the need for a separate outgassing chamber.

Unlike RO systems, commercial CDI systems are less mature and are not designed to be gas-tight, so most commercially available systems are not appropriate for experiments. Because CDI systems do not require high pressure for operation, it is straightforward to create customized test cells at the lab scale and at relatively low cost. The CDI module, at its most basic, consists of a chamber in which the alkaline, air-equilibrated feed solution can come into contact with two electrodes. A type of “sandwich" CDI device is being used, in a “flow-by” configuration, to allow for continuous cycling and reproducible experiments with controllable electrode size, surface area, and cell geometries.

System Integration: Full Demonstration of ACS Cycle

After independently testing each of the three components of the ACS approach—(1) concentration of an alkaline solution, (2) CO_2 extraction, and (3) dilution and re-equilibration with air—the combined system was tested to demonstrate the full ACS cycle. Testing of the full system involved verifying that the carbon removed by the integrated system matched the predicted values for each swing from the theoretical ACS predictions. The energy required for each swing is also measured to determine an overall energy requirement per mole of captured CO_2. This integration of the three modular components of the experimental system achieves a Technology Readiness Level (TRL) of 3. Based on estimates of the energy requirement for RO in standard saltwater conditions, estimates suggest the ability to achieve CO_2 capture at an energy below 2.0 MWh per tonne of captured CO_2 (265 kilojoule [kJ]/mol). Beyond TRL 3, this requirement could be improved upon by implementing pressure-retarded osmosis, enabling energy recovery when concentrated and diluted solution streams are recombined. Based on estimates of the energy requirement for CDI in standard brackish water conditions, it is estimated to achieve CO_2 capture at an energy of 1.9 MWh per tonne of captured CO_2 (300 kJ/mol). Because electricity flows in the reverse direction when the electrodes are switched off, CDI enables energy recovery; the literature commonly reports energy recovery of 50%, with some studies approaching 80%.

technology advantages

- Process utilizes well-established, commercially available technologies, including RO and CDI.
- In the RO method, higher feed concentration outgasses more CO_2 for the same concentration factor and higher concentration factor outgasses more CO_2 for the same feed concentration.

R&D challenges

- Assembling a crossflow RO system.
- Prototyping CDI cells with a larger electrode mass-to-cell volume ratio.
- Building a fully operational CDI model with small volume handling.
- Implementing bicarbonate selectivity with anion exchange membranes.
- Assembling an integrated system and conducting a full demonstration of the ACS cycle.
- High DIC-to-alkalinity regimes have high aqueous CO_2 concentrations, which results in CO_2 being permeated through the membrane.
- The capacitive deionization is selective for carbonate ions over bicarbonate ions, lowering efficiency of the concentration step.
- Promoters (substances used to modify the selectivity of the membrane) are needed to bring the ACS unit to a competitive rate because of its reliance on bicarbonate ions to operate.

status

This project was completed on August 8, 2023. Harvard University has developed and assembled a dead-end RO system and achieved operating conditions comparable to published systems. The project: demonstrated that RO can be used to concentrate alkalinity, blocking more than 99% of sodium bicarbonate and bicarbonate ions; demonstrated that the CO_2 permeated through the membrane; and showed that an extraction module placed on the permeate line would increase cycle capacity and lower process energy. The researchers also demonstrated that capacitive deionization preferentially selects on carbonate ions over bicarbonate ions, lowering the efficiency of the concentration step. Gas-liquid exchange membranes appear to be a promising CO_2 extraction technology for potassium and sodium bicarbonate solutions.

available reports/technical papers/presentations

Daniel P. Schrag, Toly Rinberg, Andrew Bergman, "Experimental Demonstration of Alkalinity Concentration Swing for Direct Air Capture of Carbon Dioxide," Final Technical Report, Pittsburgh, PA, December 2023. *https://www.osti.gov/servlets/purl/2248073/*.

Toly Rinberg, Andrew Bergman, "Experimental Demonstration of Alkalinity Concentration Swing for Direct Air Capture of Carbon Dioxide," 2023 Final Project Briefing Meeting, Pittsburgh, PA, July 2023. *https://netl.doe.gov/projects/files/Experimental%20Demonstration%20of%20Alkalinity%20Concentration%20Swing%20for%20Direct%20Air%20Capture%20of%20Carbon%20Dioxide.pdf*.

Toly Rinberg, "Alkalinity Concentration Swing for Direct Air Capture of Carbon Dioxide," 2022 Carbon Management Project Review Meeting, Pittsburgh, PA, August 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_CDR15_Rinberg.pdf*.

Daniel P. Schrag, Michael J. Aziz, Andrew Bergman, Anatoly Rinberg, "Experimental Demonstration of Alkalinity Concentration Swing for Direct Air Capture of CO_2," kickoff meeting presentation, Pittsburgh, PA, November 2021. *http://www.netl.doe.gov/projects/plp-*

download.aspx?id=12414&filename=Experimental+Demonstration+of+Alkalinity+Concentration+Swing+for+Direct+Air+Capture+of+CO2.pdf.

Daniel P. Schrag, Michael J. Aziz, "Experimental Demonstration of Alkalinity Concentration Swing for Direct Air Capture of CO_2," Direct Air Project kickoff meeting presentation, Pittsburgh, PA, February 2021. *https://netl.doe.gov/sites/default/files/netl-file/21DAC_Schrag.pdf*.

Direct Air Capture Using Trapped Small Amines in Hierarchical Nanoporous Capsules on Porous Electrospun Fibers

primary project goal

The State University of New York (SUNY)-Buffalo is teaming with Arizona State University (ASU) and Gas Technology Institute (GTI) to develop an innovative sorbent comprised of trapped small amines in hierarchical nanoporous capsules (HNCs) embedded in porous electrospun fibers (PEFs) for direct air capture (DAC). The effective encapsulation of amines in HNCs will enable high sorbent stability and the innovative PEF macroscopic scaffold will allow for fast exposure of sorbent material to air. Research efforts involve the tailoring of both sorbent and PEF materials to achieve a compact system for DAC with high capacities for carbon dioxide (CO_2) at concentrations typically available in air and at near-ambient conditions.

technical goals

- Develop HNCs with trapped small amines sorbents (SUNY-Buffalo).
- Incorporate the sorbent material into PEFs (Arizona State University).
- Test the PEFs with the embedded sorbent material to collect data on CO_2 working capacity and adsorption/desorption rates (SUNY-Buffalo).
- Utilize the experimental data obtained to perform high-level process design/analysis.
- Develop an understanding of breakdown pathways; confirm the revolutionary stability of the new solvent using various laboratory techniques.

technical content

An innovative sorbent structure is being designed to directly capture CO_2 from the air using trapped small amines (Figure 1). This technology differs from the sorbents for CO_2 capture at higher CO_2 partial pressure by physical adsorption, in that approximately 400 parts per million (ppm) CO_2 in the air is adsorbed into the HNCs and reacts with trapped amines, following the reactions below:

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Amine Sorbent Embedded in Porous Electrospun Fibers for DAC

participant:
State University of New York (SUNY)-Buffalo

project number:
FE0031969

predecessor projects:
N/A

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partners:
Arizona State University; Gas Technology Institute (GTI)

start date:
02.01.2021

percent complete:
70%

Dry condition

$$CO_2 + 2RNH_2 \leftrightarrow RNH_3^+ + RNHCOO^-$$

$$CO_2 + 2R_1R_2NH \leftrightarrow R_1R_2NH_2^+ + R_1R_2NHCOO^-$$

Moisture condition

$$CO_2 + R_1R_2NH + H_2O \leftrightarrow \underset{\text{bicarbonate}}{\underline{R_1R_2NH_2{}^+HCO_3{}^-}} \leftrightarrow \underset{\text{carbonate}}{\underline{R_1R_2NH_2{}^+CO_3{}^{2-}}}$$

$$CO_2 + R_1R_2R_3N + H_2O \leftrightarrow R_1R_2R_3NH^+HCO_3{}^- \leftrightarrow R_1R_2R_3NH^+CO_3{}^{2-}$$

Therefore, theoretically, two amine groups can bond with one CO_2 molecule under dry conditions and one amine group with one CO_2 under wet conditions. Small amines enable high amine efficiency (molar ratio of the adsorbed CO_2 to the total amine groups, CO_2/nitrogen [N]) and thus high CO_2 adsorption capacity from the air, while HNCs prevent amine loss and drastically extend amine lifetime. Small-sized (2–5 mm), macroscopic scaffold PEFs allow fast external mass transfer rates and minimize CO_2 adsorption capacity loss via high porosity. In addition, optimized packing of PEFs in a mat (Figure 1) ensures high sorbent packing density while balancing the air flow rate with the energy consumption from the blower.

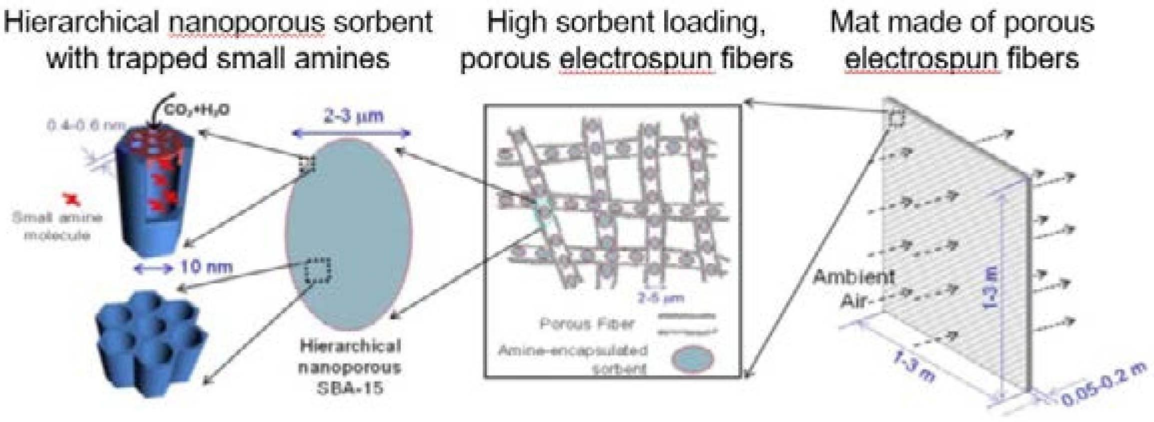

Figure 1: Diagram of the transformational adsorbent for direct capture of CO_2 from air.

These mats are effectively utilized in a process for direct CO_2 capture from the air, as shown in Figure 2. For each operation unit, there are two components: a blower and a sorbent mat equipped with heat exchanger, heating wires, and a hinged cover for mat sealing. Each unit has three operational modes: adsorption, preheat, and desorption. During the process, each unit finishes one operational mode and enters another operational mode. Note that depending on the available sources of energy input, desorption energy can be provided by either electricity or waste heat.

Amine-functionalized sorbents and ion-exchange resins are the promising sorbents reported in the literature for DAC; the former can achieve much higher CO_2 purity (greater than or equal to 98 vol.%) than the latter (less than 5 vol.%). In amine-based sorbents, large surface-area porous substrates are usually used to increase the loading of amines and thus the amine group density; amines with different molecular structures are also used to increase efficiency. The combination of the amine group density and amine efficiency leads to a high CO_2 adsorption capacity. Depending on the interaction between the amines and substrates, three types of sorbents (Types I: physical impregnation; Type II: covalent tethering via silane linkage; Type III: direct covalent tethering via in situ polymerization) can be prepared, as shown in Figure 3.

Figure 4 plots the CO_2 equilibrium capacity versus amine efficiency of the sorbents described above. As shown, the efficiencies are lower than 0.2, far below the theoretical 0.5 (dry condition) and 1 (moisture condition). In the sorbent structure being designed in this project, small amines are featured with fast reaction kinetics and high concentration of amine groups and are expected to have high CO_2 capacity and fast adsorption rate, making them ideal amines for DAC. In addition, small amines typically show high amine efficiency (e.g., diethanolamine [DEA] shows an efficiency of 0.407, very close to the theoretical value [0.5]). In the technology for this project, small amines are loaded and trapped in SBA-15 (a mesoporous form of silica with approximately 10 nm pores and a high surface area of 600–1,000 m^2/g). Assuming 30–50 wt.% amine loading, 0.4–0.6 amine efficiency (in humid air), and four amine groups in one amine molecule (molecular weight: 200 g/mol), the estimated CO_2 capacity of the sorbent is in the range of 3.4–13.3 mmol CO_2/g (Figure 4). This is much higher than reported results, demonstrating the great potential of small amines for DAC.

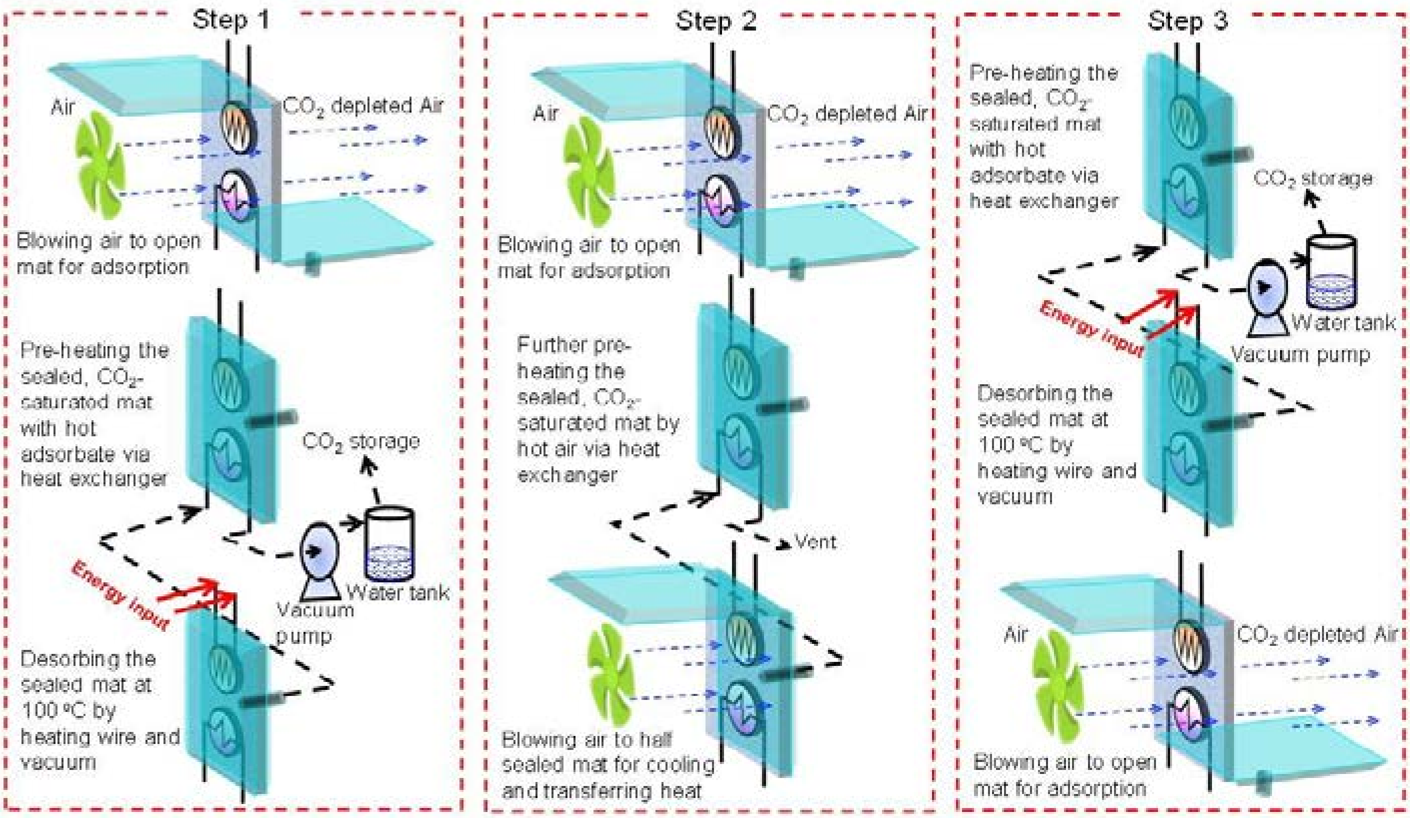

Figure 2: Diagram of the process for DAC.

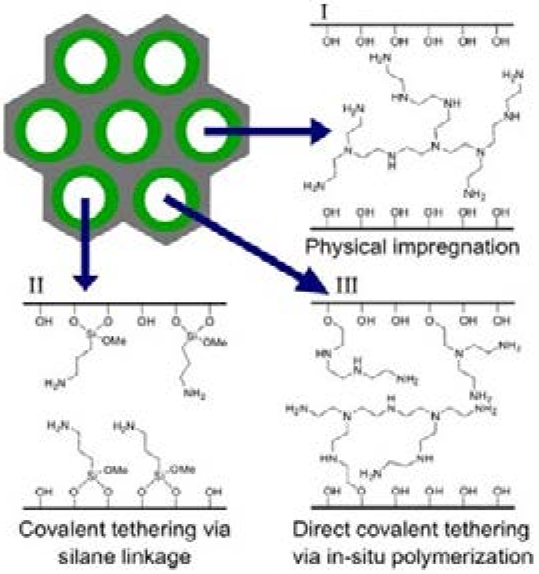

Figure 3: Schematic of three types of amine-based sorbents for DAC.

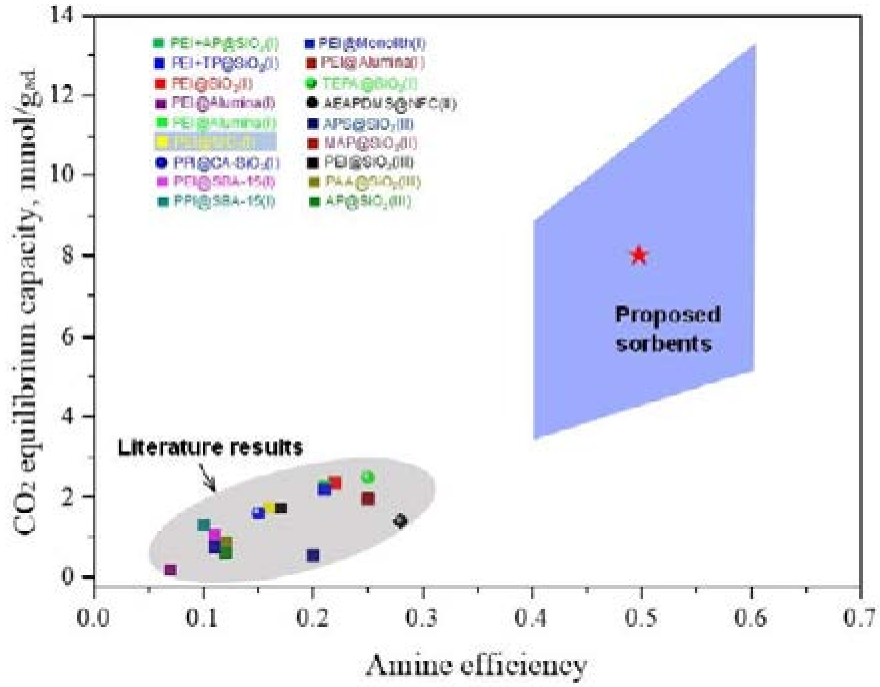

Figure 4: Comparison of reported sorbent materials and projected performance of the proposed sorbent for DAC. Red star represents the average performance of the proposed sorbent.

Small amines, such as monoethanolamine (MEA) and DEA, have been widely used for solvent-based CO_2 capture/removal due to their fast reaction rate with CO_2 and high CO_2 capacity. Small amines on porous substrates exhibited excellent CO_2 adsorption performance: fast CO_2 uptake rate, high amine efficiency (e.g., 0.4–0.6 for DEA), high CO_2 adsorption capacity resulting from the high nitrogen to carbon (N/C) ratio, high primary amine concentration, and low viscosity. However, high volatility of small amines led to severe loss during the sorbent regeneration at high temperature, which significantly restricted their application in sorbent materials. Physically trapped small amines in porous structure using an innovative interfacial reaction process is expected to resolve the amine loss issue.

SUNY-Buffalo recently developed a facile and scalable interfacial reaction process to deposit ultra-thin, microporous coatings on nanoporous substrates for trapping/encapsulating functional species. A mesoporous silica, SBA-15, was used as the porous substrate, and a microporous coating layer of titanium dioxide (TiO_2) was deposited by the liquid-liquid interfacial reaction between ethylene glycol (EG) and titanium chloride ($TiCl_4$) and subsequent calcination to remove the organic compound. Microporous coating pore size can be adjusted by adding different amounts of water in EG and by changing calcination conditions. The microporous TiO_2 coating on SBA-15 was characterized by transmission electron microscopy (TEM), which showed that a continuous, ultra-thin TiO_2 layer (30–50 nm) can be seen on SBA-15 after the coating process. Thermogravimetric analysis (TGA) showed the material was thermally stable to at least 300°C (data not shown). These results clearly showed that hierarchical SBA-15 can be formed by facile interfacial reaction process and can effectively trap functional species. To trap small amines with molecular size of 0.5–0.8 nm, a well-designed interfacial reaction process is applied to form coatings with pores larger than CO_2 (0.33 nm) and H_2O (0.26 nm), but smaller than the amine molecules. Because of the strong affinity of CO_2 with small amines, the adsorption selectivity of CO_2 over N_2 is expected to be high. Studies have shown the CO_2 working capacity is much higher than the amount of N_2 adsorbed. Therefore, very high CO_2/N_2 selectivity can be achieved, and CO_2 purity higher than 99% can be obtained after sorbent regeneration.

HNCs can be fabricated by utilizing interfacial reactions followed by calcination. Depending on metal precursors and organic precursors, a hybrid dense layer with different composition can be formed and subsequently converted into microporous coatings by removal of the organic compound upon calcination. The team fine-tuned coating pore size by changing the calcination conditions and adding different amounts of H_2O into EG; coating pore size was characterized by N_2 adsorption at 77K.

Recently, ASU developed PEFs embedded with various sorbent materials (metal-organic frameworks [MOFs], zeolites, and resin particles) and applied them for separation applications, including DAC. Matrimid (glass transition point: 320°C) and polystyrene (glass transition point: 100°C) with excellent thermal, mechanical, and chemical stabilities have been used as the PEF materials. PEFs with different porosity, morphologies, and post-synthetic modifications have been prepared. The technique to controllably create porosity on PEFs, called solvothermal polymer additive removal (SPAR), has been demonstrated in a preliminary study of uniaxial electrospinning technique. The mechanical and chemical strength of PEFs embedded with sorbent materials can also be improved by a cross-linking process that has been previously demonstrated. In previous work, PEFs embedded with ion-exchange resin have been demonstrated for DAC application by moisture swing adsorption and showed the highest cycle capacity with an uptake rate of 1.4 mmol CO_2.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,050-1,740	1,050-1,740
Bulk Density	kg/m^3	—	600-800
Average Particle Diameter	mm	0.002-0.005	0.002-0.005
Particle Void Fraction	m^3/m^3	—	0.4-0.5
Packing Density	m^2/m^3	—	600,000-800,000
Solid Heat Capacity @ STP	kJ/kg-K	—	1.4-1.6
Crush Strength	kg_f	—	>5
Attrition Index	-	—	N/A
Thermal Conductivity	W/(m-K)	—	<1.2
Manufacturing Cost for Sorbent	$/kg	—	—
Adsorption			
Pressure	bar	1.01-1.10	1.01-1.10
Temperature	°C	20-40	20-40
Equilibrium Loading	g mol CO_2/kg	3.8	5-8
Heat of Adsorption	kJ/mol CO_2	—	50-80
CO_2 Adsorption Kinetics	gmol/kg/h	4	3.5-5
Desorption			
Pressure	bar	0.2-0.3	0.05-0.2
Temperature	°C	90-100	85-110
Equilibrium CO_2 Loading	g mol CO_2/kg	0.1	0.1
Heat of Desorption	kJ/mol CO_2	—	50-80
CO_2 Desorption Kinetics	gmol/kg/h	8	8-10

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

TABLE 2: ATMOSPHERIC AIR FEED-GAS CONDITIONS

Pressure	Composition						
	vol%					ppmv	
	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	0.04	variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Trapped amines inside the hierarchical nanoporous capsules react with low concentration of CO_2 (~400 ppm) in the air for high-capacity CO_2 capture.

Sorbent Contaminant Resistance – Resistance of the sorbent to trace sulfur oxide (SO_X) and nitrogen oxide (NO_X) is not clear at this stage, but resistance to other components is expected to be good.

Sorbent Attrition and Thermal/Hydrothermal Stability – Sorbent attrition is not clear at this stage. The thermal/hydrothermal stability of the sorbent is expected to be excellent under DAC operation.

Flue Gas Pretreatment Requirements – Particulate removal from air using filters is required to prevent sorbent mat from plugging.

Sorbent Make-Up Requirements – There are no sorbent make-up requirements for the process. The sorbent is expected to have a lifetime of five years before it needs to be replaced.

Waste Streams Generated – Depleted air stream and condensed liquid water.

Proposed Module Design – Refer to Figure 2.

TABLE 3: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	311	—
Cost of Carbon Avoided	\$/tonne CO_2	—	—
Capital Expenditures	\$/tonne CO_2	24	—
Operating Expenditures	\$/tonne CO_2	259	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

TABLE 4. COST ASSESSMENT OF THE SORBENT TECHNOLOGY

Line	Items	Units	Value
1	**Major Equipment (blower, heat exchanger, vacuum pump, and compressors) Cost**	$	506,921
2	**Projected Lifetime of the Equipment**	years	15
3	**Major Equipment Annual Costs (= line 1/line 2)**	$/year	33,795
4	**Utility Costs for Major Equipment (compressor, heater, vacuum)**	$/year	776,480
5	**Total Major Equipment and Utility (= line 3+line 4)**	$/year	810,275
6	**CO_2 Capture Rate**	tonne/hr	0.3425
7	**Major Equipment and Utility Cost Per Tonne CO_2 Produced**	$/tonne CO_2	270
8	**Cost of PEF Embedded with HNC Sorbent Particles**	$/tonne CO_2	13.0
9	**Total Capital Costs (total of lines 7 and 8)**	$/tonne CO_2	283
10	**Total Operating & Maintenance Costs (10% of line 9)**	$/tonne CO_2	28.3
11	**Total CO_2 Production Costs (total of lines 9 and 10)**	$/tonne CO_2	311

Table 4 indicates that the estimated sorbent DAC cost of $311/tonne of CO_2 captured is only 44% of Climeworks' sorbent technology (~$700/tonne). Note that the lower cost is mainly due to the high CO_2 adsorption capacity[1,2] of this project's sorbent, as Sholl et al.[3] also reported that the CO_2 capture cost in DAC would decrease by 43–46% when the CO_2 adsorption capacity of the sorbent is doubled. Further analysis indicates this project's CO_2 capture cost could decrease to $169/tonne if waste heat is used for desorption instead of electricity. A more comprehensive cost assessment will be performed at the end of the project during the high-level design and analysis based on the experimental data and kinetic parameters collected.

1. Wurzbacher, J. A., Gebald, C., Piatkowski, N. & Steinfeld, A. Concurrent Separation of CO_2 and H_2O from Air by a Temperature-Vacuum Swing Adsorption/Desorption Cycle. *Environ. Sci. Technol.* **46**, 9191–9198 (2012).
2. Wurzbacher, J. A., Gebald, C. & Steinfeld, A. Separation of CO_2 from air by temperature-vacuum swing adsorption using diamine-functionalized silica gel. *Energy Environ. Sci.* **4**, 3584–3592 (2011).
3. Kulkarni, A. R. & Sholl, D. S. Analysis of Equilibrium-Based TSA Processes for Direct Capture of CO_2 from Air. *Ind. Eng. Chem. Res.* **51**, 8631–8645 (2012).

Calculations Basis – The operational process (Figure 2) was translated into a compact process design (Figure 5) and modeled in ASPEN using the project team's preliminary experimental data, projected sorbent performance, and literature data for capital cost and energy calculation.[4,5] Three groups of sorbent mats are included in the design, and each group has six steps to finish one cycle.

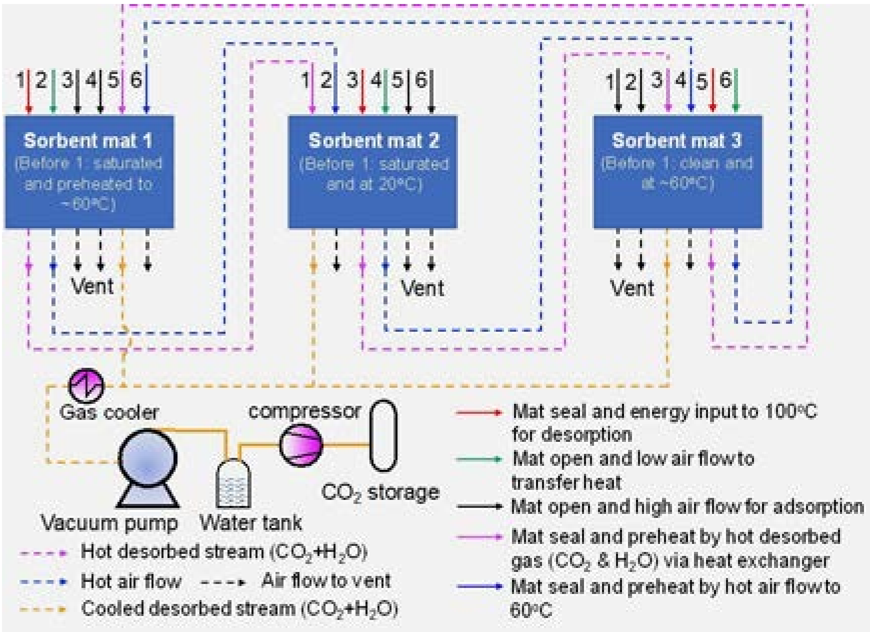

Figure 5: Proposed process flow for DAC.

4. Wurzbacher, J. A., Gebald, C., Brunner, S. & Steinfeld, A. Heat and mass transfer of temperature–vacuum swing desorption for CO_2 capture from air. *Chem. Eng. J.* **283**, 1329–1338 (2016).
5. Peters, M. S. & Timmerhaus, K. D. *Plant design and economics for chemical engineers*. (McGraw-Hill Press, 1991).

Scale of Validation of Technology Used in TEA – The basis for the cost assessments is 3,000 tonnes captured CO_2/year (3,000 tonne/year was selected for this preliminary cost assessment to be compared to published data on the Climeworks technology[4]).

Qualifying Information or Assumptions – In the assessments, the lifetime for the PEF fiber sorbent was assumed to be five years. The other capital equipment was assumed to have a 15-year operating life. The total annual operating and maintenance costs were assumed to be 10% of the total capital costs.

technology advantages

- Small amines with molecular weight less than or equal to 200 g/mol trapped in HNCs enable fast reaction kinetics, high amine efficiency, and high CO_2 sorption capacity for dilute CO_2 (~400 ppm) in the air.
- Thin coating with molecular-sized pores (0.4–0.6 nm pores) effectively prevents small amines from leaking during the heat regeneration process and thus achieving good sorbent stability.
- Innovative macroscopic scaffold with small fiber size (2–5 mm) and porous features allows high sorbent loading and fast and effective exposure of sorbent material to the air.

R&D challenges

- Amine Loading and Sealing: Developing effective amine loading and sealing processes on samples with microporous coating; conducting amine loss evaluation.
- PEFs Loaded with Sorbent: Optimizing electrospinning conditions to incorporate sorbent materials; characterizing composite sorbent structure.

status

SUNY-Buffalo has prepared amine-coated SBA-15 by pore filling and precursor loading via vapor condensation and liquid-phase preparation methods. The highest dry CO_2 uptake capacity obtained for amine loading before coating development and amine loading post coating development was 0.61 and 2.38 mmol/g, respectively. In the humid gas adsorption system, the same coated sorbent showed a humid CO_2 capacity of 4.43 mmol CO_2/g with no capacity loss after 10 simulated thermal cycles and 24 hours of heating at 100°C. The SBA-15+50 wt.% amine samples were coated with Pebax using vacuum filtration. These sorbents exhibited the highest CO_2 uptake performance of 3.33 mmol/g for SBA-15/Pebax mass ratio of 2. Pebax coated samples showed impressive thermal stability in humid conditions with no apparent performance loss even after 24-hour thermal treatment at 100°C in an N_2 environment.

available reports/technical papers/presentations

Miao Yu, Bin Mu, "Direct Air Capture Using Trapped Small Amines in Hierarchical Nanoporous Capsules on Porous Electrospun Hollow Fibers," NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Yu.pdf*.

Miao Yu, Bin Mu, Shiguang Li "Direct Air Capture Using Trapped Small Amines in Hierarchical Nanoporous Capsules on Porous Electrospun Hollow Fibers," Project kickoff meeting presentation, Pittsburgh, PA, April 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11099&filename=Direct+Air+Capture+Using+Trapped+Small+Amines+in+Hierarchical+Nanoporous+Capsules+on+Porous+Electrospun+Fibers.pptx*.

Miao Yu, "Direct Air Capture Using Trapped Small Amines in Hierarchical Nanoporous Capsules on Porous Electrospun Hollow Fibers," Direct Air Capture kickoff meeting presentation, Pittsburgh, PA, February 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11097&filename=Direct+Air+Capture+Using+Trapped+Small+Amines+in+Hierarchical+Nanoporous+Capsules+on+Porous+Electrospun+Hollow+Fibers.pdf*.

Novel, Efficient, Low-Cost Technology for Direct Air Capture of CO_2 and its Removal from Low Concentration Streams

primary project goal

Emissol LLC designed, modeled, prototyped, and tested a novel honeycomb contactor smaller than typical honeycomb contactors. Emissol plans to optimize their novel contactor for an even higher capture rate, as well as for greater direct air capture (DAC) cost savings.

technical goals

- Reduce contactor thermal mass in order to minimize thermal energy and lower its associated costs (operating expenses [OPEX]).
- Study sorbent loading in mesopores of the contactor for enhanced, internal mass diffusion, further increasing carbon dioxide (CO_2) transport rate.
- Optimize the geometry of the contactor at unit level (e.g., to minimize pressure drop) and at system level (e.g., to meet the capture target at lowest cost).
- Develop a low-cost, scalable, cost-competitive manufacturing method to produce the novel honeycomb.
- Perform a techno-economic analysis (TEA) to assess the impact of the resulting contactor on reducing the total DAC cost.
- Develop a process model for parametric studies and data feeding into the TEA.

technical content

Honeycomb monolith substrates have found successful use in DAC. The primary reason for using honeycomb-type contactors is that they provide plenty of surface area ideal for CO_2 adsorption/desorption while yielding very low pressure drop and, hence, low pumping power energy cost for air flow to pass through contactors. However, such honeycombs have one major limitation: in their straight channels, CO_2 species travel to the sorbent-coated wall (or to the solvent) via diffusion, an inherently slow process (i.e., the channel's base flow, the convection, has no role in CO_2 transport to the sorbent). Removing this major barrier, Emissol has invented a proprietary honeycomb contactor replacing the slow CO_2 diffusion with the much faster convective transport, hence dramatically increasing the rate of CO_2 transport to the sorbent (wall). Further, since the channel mass transfer increases faster than its friction force does, it yields a "net gain" in performance versus its pressure drop increase. The contactor makes available faster CO_2 adsorption/desorption rates (i.e., grams/seconds) and thus higher capture frequency. Therefore, the potential exists to replace mainstream

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Monolith Amine-Based Sorbent for CO_2 Capture

participant:
Emissol LLC

project number:
SC0020860

predecessor projects:
N/A

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partners:
N/A

start date:
06.29.2020

percent complete:
98%

contactors, some discussed above, with this project's transformational contactor, markedly reducing DAC cost. A block flow diagram of the overall DAC process is shown in Figure 1.

The contactor was tested, both experimentally and in mathematical models. Good agreement was observed between the project's test data and math-modeling results. It was observed that the novel contactor captures and removes CO_2 at a high rate while also requiring approximately 40% less sorbent than typical honeycomb contactors. Particularly, Emissol's results indicate that, given its markedly faster capture rate, the contactor can also be downsized by approximately 40% (relative to a typical, baseline contactors) without impacting the captured CO_2 target (tonnes/unit time), in turn enabling a major sorbent reduction by about the same ratio (40%).

Continuing research and development (R&D) focuses on key tasks to further enhance the contactor impact on the total DAC cost reduction (i.e., above and beyond the current cost-saving that has been achieved).

Task 1. Reduce contactor thermal mass, to reduce thermal energy for desorption and its associated costs.

Task 2. Sorbent loading in mesopores of the contactor: sorbent-contactor optimization.

Task 3. Optimizing the contactor geometry, first at the honeycomb scale (local unit), and next at the system scale. Both efforts target maximizing cost savings for DAC.

Task 4. Developing a low-cost, scalable, manufacturing method.

Task 5. Develop a TEA.

Proposed Module Design – Honeycomb contactor with switching between adsorption and desorption modes.

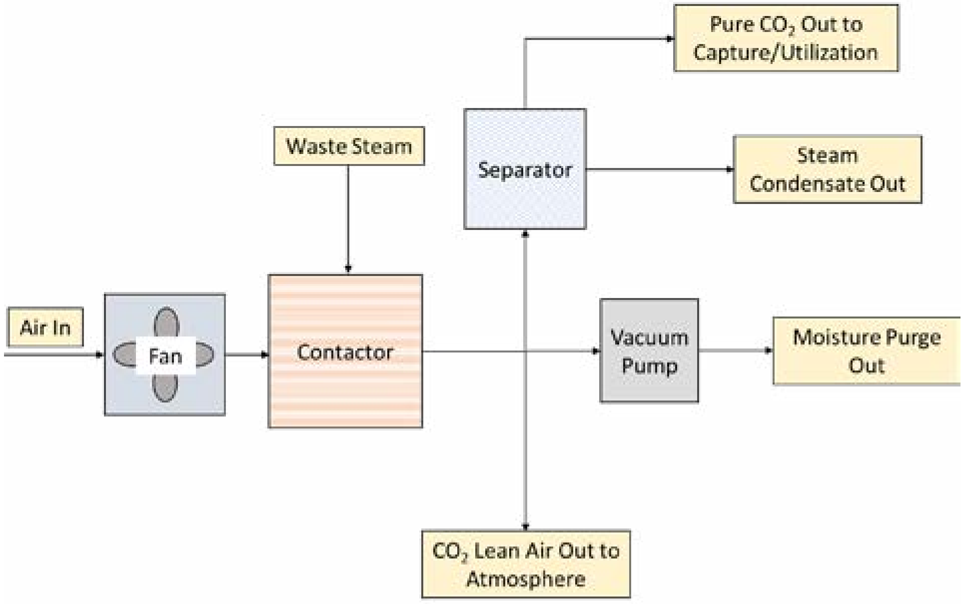

Figure 1: Block flow diagram of DAC system.

technology advantages

- Novel contactor design.
- Reduced contactor size to roughly half the size of conventional honeycomb contactors.
- Reduced sorbent use (by approximately half).
- Enables faster capture cycles, hence accelerated capture/release cycle, and increases the net capture amount (tonne CO_2/day).
- Lowers thermal energy required for sorbent regeneration and low pressure drop.

R&D challenges

- Engineering-enhanced pore diffusion of CO_2 in the solid sorbent; managing the intricacy between support's pore size and powder (sorbent) pore size in a manufacturing process aiming at faster pore diffusion.
- Optimizing the contactor geometry at the honeycomb scale and at the system level.

status

Emissol has developed its own coating process for applying the sorbent to a structured support. The Emissol contactor reduces sorbent use by 40% and lowers the DAC cost by approximately 30% to \$105.24/tonne CO_2. Emissol is currently working on further contactor optimization to reduce DAC capture costs beyond the 30% already achieved, and is developing manufacturing techniques to reduce contactor production costs.

available reports/technical papers/presentations

Mansour Masoudi, "A Novel Contactor for Reducing the Cost of Direct Air Capture of CO_2," 2023 FECM / NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, September 2023.

Mansour Masoudi, "Novel, Efficient Contactor Technology to Substantially Lower the Cost of Direct Air Capture of CO_2," 2022 Carbon Management Project Review Meeting, Pittsburgh, PA, August 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_Posters_Masoudi2.pdf*.

Masoudi, M. "Novel, Efficient, Low Cost Technology for Direct Air Capture of CO_2 and its Removal from Low Concentration Streams." NETL Direct Air Capture Kickoff Meeting. February 2021. *https://netl.doe.gov/sites/default/files/netl-file/21DAC_Masoudi.pdf*.

Transformational Sorbent Materials for a Substantial Reduction in the Energy Requirement for Direct Air Capture of CO_2

primary project goal

InnoSepra LLC, with partners Missouri University of Science and Technology, Arizona State University, Adroitech Enterprise, and RJF Consultants, developed transformational structured sorbents for direct air capture (DAC).

technical goals

- Perform computational simulations, materials characterization, and lab-scale testing to optimize the performance of materials under DAC conditions.
- Develop a high-level process design to provide an estimate of electrical and thermal energy requirements, equipment sizing, and cost and carbon footprint.
- Demonstrate the effectiveness of InnoSepra's DAC materials and technology for pipeline-quality CO_2 with an energy consumption of less than 4 GJ/tonne.
- Demonstrate the potential of the transformational materials to reduce the energy required for DAC compared to current state-of-the-art technologies by up to 50%.
- Identify means to scale-up the materials to thousands of tonnes per year needed for commercial scale-up of DAC.

technical content

The technology utilizes physical sorbents in structured forms for capturing CO_2 directly from air. It leverages InnoSepra's past work on CO_2 capture from flue gas, as well as from low-concentration sources (1–1.5% CO_2), and adapts them to materials and processes developed for DAC. The use of structured sorbents minimizes the pressure drop associated with handling the very large volumes of air in DAC. While the driving force for DAC is significantly smaller due to a very low CO_2 partial pressure (about 0.04 kPa compared to a CO_2 partial pressure of about 15 kPa in the flue gas), the equipment size for the process per unit amount of CO_2 captured is minimized due to the use of high surface area sorbent materials and high CO_2 capacity of the materials under DAC conditions. Additionally, the materials have low heats of adsorption for CO_2 (40–45 kJ/mole) compared to amine-based sorbents (>100 kJ/mole) used for DAC. The combination of low-pressure drop, low heat of adsorption, very high surface-to-volume ratio for materials, and high CO_2 capacity at DAC conditions leads to a process with significantly lower energy requirements for DAC.

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Structure Sorbents for DAC

participant:
InnoSepra LLC

project number:
FE0031953

predecessor projects:
N/A

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partners:
Missouri University of Science and Technology; Arizona State University; Adroitech Enterprise; RJF Consultants

start date:
10.01.2020

percent complete:
100%

The schematic in Figure 1 shows the DAC process. The pressure of ambient air is raised by 0.1–0.2 pounds per square inch (psi) in an induced draft (ID) fan and the compressed air is sent to a rotating bed moisture adsorption unit for removing moisture and a CO_2 adsorption unit in sequence. Because of the very large gas volumes involved with DAC, the system pressure drop for CO_2 capture needs to be minimized and structured sorbents are used in both stages for this to be accomplished. The pressure drop in each of these stages is expected to be less than 0.05 psi.

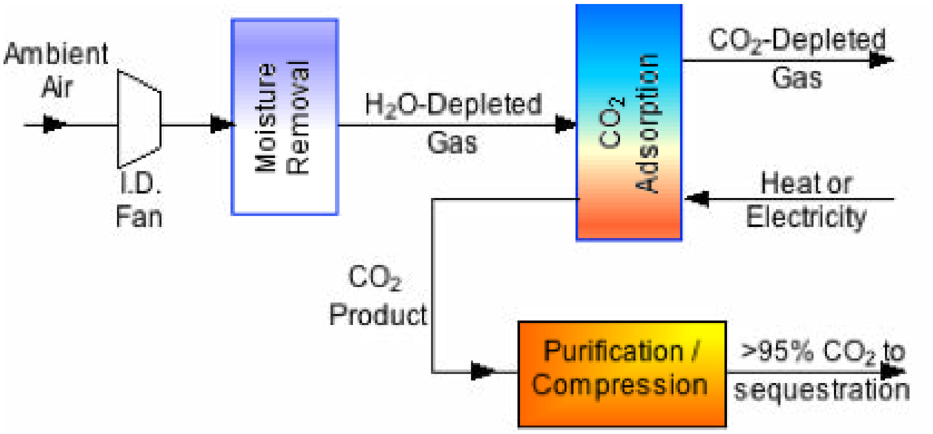

Figure 1: InnoSepra DAC process schematic.

The structured sorbents have significant advantages over particulate sorbents, including:

- Very low pressure drops (typically one-fifth to one-tenth of the particulate sorbents).
- Not subject to fluidization constraints or attrition issues.
- Very small effective particle size (less than 80 microns), leading to very short mass transfer zones.
- Ability to process significantly higher flows for a given bed volume.
- Can be fabricated with virtually any adsorbent, commercially available up to 10 feet in diameter.

A physical sorbent with high moisture capacity and very low CO_2 adsorption capacity is used during the dehumidification step. The rotating bed configuration for moisture removal is shown in Figure 2. Short bed depths coupled with a large open area (greater than 75%) lead to a very low pressure drop. One rotation of the wheel takes six–12 minutes, during which time the entire wheel undergoes adsorption (in the adsorption zone) and regeneration (in the regeneration zone). The drying process operates continuously. A rotating seal is used to separate the adsorption and regeneration zones. The moisture-depleted gas is sent to a CO_2 adsorber containing a sorbent that has a high CO_2 capacity at low CO_2 partial pressures.

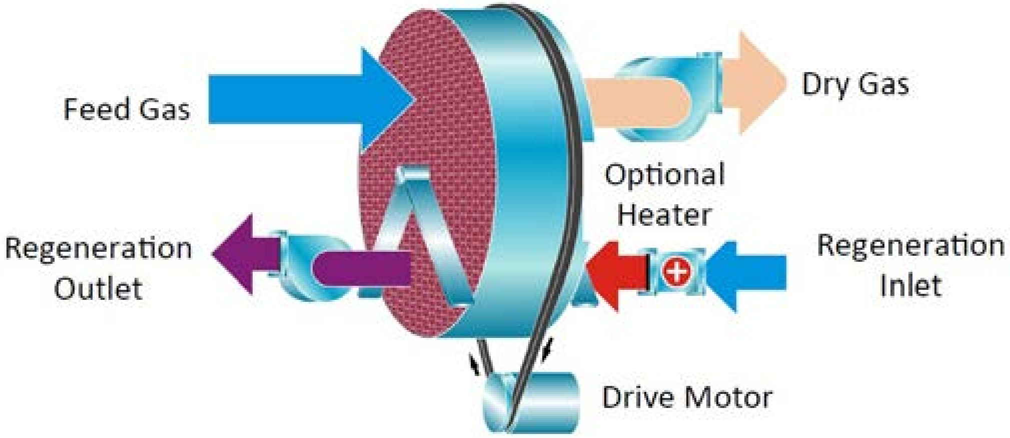

Figure 2: Rotating wheel dryer for feed dehumidification.

The CO_2 adsorber also contains structured sorbents. These sorbents can be thermally regenerated to produce a first CO_2 product stream that can be further purified and compressed to produce a CO_2 stream suitable for pipeline transport (Figure 1).

The breakthrough innovation is the use of a novel sorbent that leads to a significantly lower energy requirement for DAC compared to all known DAC technologies. It has a CO_2 capacity of more than 5 wt% at a CO_2 partial pressure of 400 parts per million (ppm) (0.04 kPa) and a temperature of 25°C. The heat of adsorption is approximately 44 kJ/mol of CO_2. The high CO_2 capacity and low heat of adsorption significantly reduce the regeneration energy needed for DAC. The sorbents are also very stable and exhibit no degradation in presence of any of the components in air.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,600	1,600
Bulk Density	kg/m^3	690	690
Average Particle Diameter	mm	<0.1	<0.01
Particle Void Fraction	m^3/m^3	0.45	0.45
Packing Density	m^2/m^3	1e+8	1e+8
Solid Heat Capacity @ STP	kJ/kg-K	1.00	1.00
Crush Strength	kg_f	>10	>10
Attrition Index	-	<0.01%	<0.01%
Thermal Conductivity	W/(m-K)	—	—
Manufacturing Cost for Sorbent	$/kg	15	10
Adsorption			
Pressure	bar	1.01	1.005
Temperature	°C	25-35	25-35
Equilibrium Loading	g mol CO_2/kg	0.9	1.2
Heat of Adsorption	kJ/mol CO_2	44	44
CO_2 Adsorption Kinetics	gmol/min	0.2	0.5
Desorption			
Pressure	bar	0.2-1.0	0.2-1.0
Temperature	°C	100-150	90-105
Equilibrium CO_2 Loading	g mol CO_2/kg	0.2	0.1
Heat of Desorption	kJ/mol CO_2	44	44
CO_2 Desorption Kinetics	gmol/min	0.4	0.6

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – “Current” is market price of material, if applicable; “Target” is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Atmospheric Air Feed-Gas Assumptions:

		Composition						
		vol%					ppmv	
Pressure	**Temperature**	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.7 psia	77 °F	0.04	variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Physical.

Sorbent Contaminant Resistance – No impact of oxygen and moisture in feed air, acid gas impurities are not relevant to DAC.

Sorbent Attrition and Thermal/Hydrothermal Stability – Very stable.

Sorbent Make-Up Requirements – At least five years life before any make-up is needed.

TABLE 2: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	N/A	N/A
Cost of Carbon Avoided	\$/tonne CO_2	N/A	N/A
Capital Expenditures	\$/tonne CO_2	N/A	N/A
Operating Expenditures	GJ/tonne CO_2	4.6	<4.0

Definitions:

Cost of Carbon Captured – The projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – The projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Calculations Basis – No U.S. Department of Energy (DOE) reference case for DAC.

The Scale of Validation of Technology Used in TEA – Since this is a materials project, only power consumption numbers are provided in the techno-economic analysis (TEA).

technology advantages

- High CO_2 capacities at a CO_2 concentration of 400 ppm (greater than 4 wt%).
- Very long sorbent life (more than five years).

- Regenerable at low temperatures (less than 125°C).
- Can be quickly scaled-up to very large quantities for commercial-scale DAC.
- Potential for up to 50% reduction in the energy needed for DAC (less than 4 GJ/tonne).
- Potential for up to 50% reduction in the capture cost (less than $200/tonne).

R&D challenges

- Fabrication of large quantities of structured sorbent and process demonstration at a commercially relevant scale.

status

This project was completed on September 30, 2023. InnoSepra Inc. has demonstrated CO_2 sorbent capacities between 3.5–4.5 wt% is possible from dilute source absorption 400-ppm CO_2 in the air at 25°C. Carbon dioxide breakthrough capacities between 2.5–3 wt% CO_2 have also been demonstrated. Fabrication, testing, identification, and downselection to two sorbent materials in structured form with a minimum 3.5 wt% CO_2 capacity was completed. The project showed the selected sorbent material has at least 50% lower energy requirements for DAC when compared to the current state-of-the-art technologies. The materials are low cost and can be produced in very large quantities quickly. There is the potential for a significant reduction in the CO_2 removal cost with the ability for quick deployment after pilot-scale validation.

available reports/technical papers/presentations

Ravi Jain, Norberto Lemcoff, "Transformational Sorbent Materials for a Substantial Reduction in the Energy Requirement for Direct Air Capture of CO_2," Final Technical Report, January 2024. *https://www.osti.gov/servlets/purl/2315076/*.

Ravi Jain, Norberto Lemcoff, "Transformational Sorbent Materials for a Substantial Reduction in the Energy Requirement for Direct Air Capture of CO_2," 2022 Carbon Management Project Review Meeting, Pittsburgh, PA, August 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_CDR15_Jain.pdf*.

Ravi Jain, Norberto Lemcoff, "Transformational Sorbent Materials for a Substantial Reduction in the Energy Requirement for Direct Air Capture of CO_2," Project kickoff meeting presentation, Pittsburgh, PA, September 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=12367&filename=Transformational+Sorbent+Materials+for+a+Substantial+Reduction+in+the+Energy+Requirement+for+Direct+Air+Capture.pdf*.

Ravi Jain, "Transformational Sorbent Materials for a Substantial Reduction in the Energy Requirement for Direct Air Capture of CO_2," Direct Air Capture kickoff meeting presentation, Pittsburgh, PA, February 2021. *http://www.netl.doe.gov/projects/files/Transformational%20Sorbent%20Materials%20for%20a%20Substantial%20Reduction%20in%20the%20Energy%20Requirement%20for%20Direct%20Air%20Capture.pdf*.

TRAPS: Tunable Rapid-Uptake AminoPolymer Aerogel Sorbent for Direct Air Capture of CO_2

primary project goal

The Palo Alto Research Center Inc. (PARC), in collaboration with Lawrence Livermore National Laboratory (LLNL), developed a novel solid sorbent for direct air capture (DAC) of carbon dioxide (CO_2). The innovative sorbent, Tunable Rapid-uptake AminoPolymer Aerogel Sorbent (TRAPS), builds on PARC's proprietary polymer aerogel synthesis platform, which was adapted to produce a polyamine aerogel with a combination of high CO_2 capacity, rapid uptake kinetics, resistance to degradation, and low cost. During the project, PARC developed the novel TRAPS sorbent and LLNL tested the performance of the sorbent under DAC-relevant conditions in a lab-scale fixed-bed reactor. TRAPS will yield substantial improvements to process cost, energy consumption, and sorbent lifetime, drastically improving the economic viability of DAC.

technical goals

- PARC: Develop a synthesis process to produce polyamine aerogels achieving, at 400 parts per million (ppm) CO_2 in air, high equilibrium CO_2 capacity, rapid uptake rate, and oxidative stability greater than benchmark silica-supported poly(ethylenimine) (PEI).
- PARC: Produce sorbent at scales required for fixed-bed performance evaluation and characterize its physical properties to inform the future design of a DAC contactor.
- LLNL: Demonstrate the performance of the sorbent under DAC-relevant conditions (400 ppm CO_2) in a lab-scale fixed-bed reactor.
- LLNL: Develop a high-level model to assess the performance and cost of a notional DAC process incorporating the sorbent.
- Develop a techno-economic assessment (TEA) to compare against commercial technologies.

technical content

PARC's development of TRAPS solid sorbent for DAC technology delivers simultaneous advances in all areas identified by the National Academy of Sciences (NAS), with the potential to achieve a disruptive process cost below $100/tonne CO_2, using estimates from the NAS report. The aerogel structure (Figure 1) that results from PARC's proprietary polymerization process provides numerous benefits to the TRAPS sorbent for DAC applications, including:

1. High equilibrium-loading of CO_2 (4 mmol/g) due to minimization of inert content in the aerogel.

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Polyamine Aerogel Sorbent for DAC

participant:
Palo Alto Research Center Inc.

project number:
FE0031951

predecessor projects:
N/A

NETL project manager:
Naomi O'Neil
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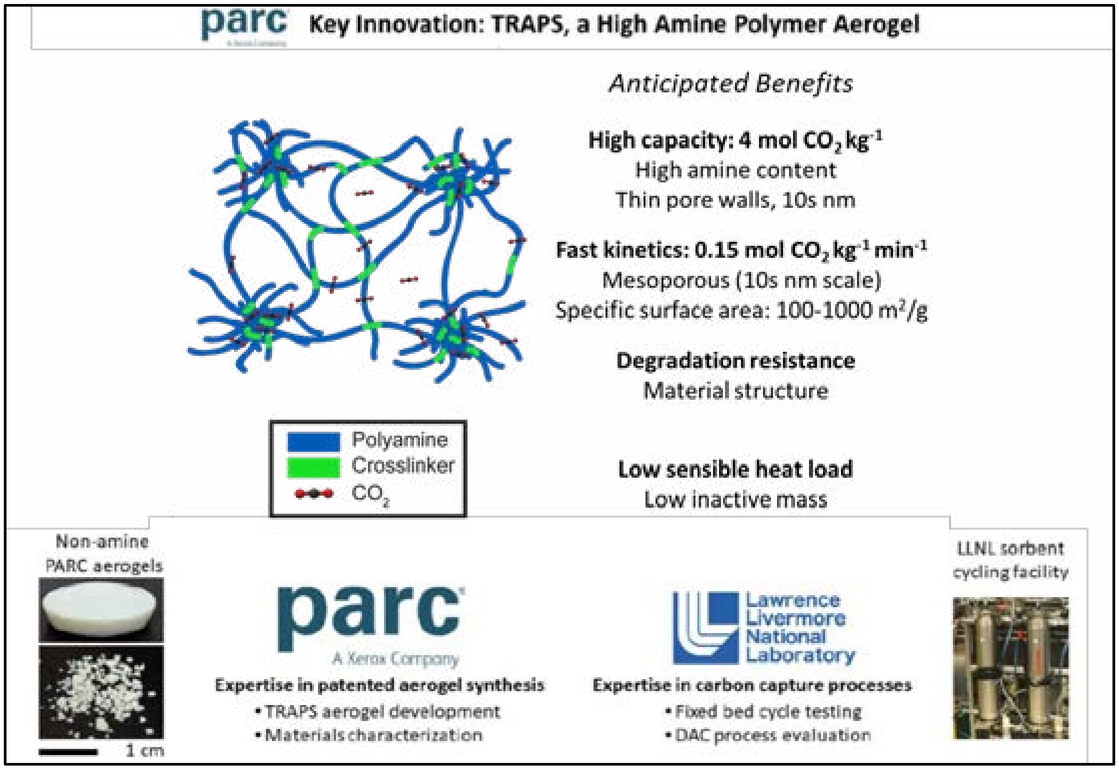
principal investigator:
Jonathan Bachman
Palo Alto Research Center
jonathan.bachman@sri.com

partners:
Lawrence Livermore National Laboratory

start date:
02.16.2021

percent complete:
100%

2. High uptake rate (45-minute full cycle) achieved by controlling aerogel structure through synthesis. High specific surface area combined with high amine incorporation provides a large number of accessible surface sites for sorption. Porosity in the mesopore size regime enables efficient gas transport.
3. Improvement in oxidative stability over conventional ceramic-supported PEI sorbents is expected due to the covalent integration of amines and control of chemical environment.
4. Low sorbent cost due to use of commodity precursors and scalable processes. In the NAS study, the sorbent budget, \$50/kg, is higher than the expected cost of the sorbent. The expected long-term cost of TRAPS is in line with cost models that use a carbon price of \$100/tonne CO_2.
5. Low minimum sensible heat load due to low content of inert materials.
6. System-integration benefits—the sorbent is compatible with a variety of schemes for heat integration and regeneration.



Key Innovation: TRAPS, a High Amine Polymer Aerogel

Anticipated Benefits

High capacity: 4 mol CO_2 kg^{-1}
High amine content
Thin pore walls, 10s nm

Fast kinetics: 0.15 mol CO_2 kg^{-1} min^{-1}
Mesoporous (10s nm scale)
Specific surface area: 100-1000 m^2/g

Degradation resistance
Material structure

Low sensible heat load
Low inactive mass

Expertise in patented aerogel synthesis
- TRAPS aerogel development
- Materials characterization

Expertise in carbon capture processes
- Fixed bed cycle testing
- DAC process evaluation

Figure 1. TRAPS concept overview.

Sorbents for DAC are deployed in a variety of contactor designs. PARC's polymerization process has been used to produce aerogels in a variety of form factors ranging from 25–100 µm particles to 0.3 x 10 x 10 cm^3 monoliths. TRAPS could be produced as binder-free pellets, fluidizable particles, or cast onto macroporous substrates. Due to the intrinsic toughness of polymers, TRAPS particles are advantaged in crush- and attrition-resistance over brittle ceramic sorbents.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	970	1000
Bulk Density	kg/m^3	450	450
Average Particle Diameter	mm	0.36	Controllable
Particle Void Fraction	m^3/m^3	0.76	0.3
Packing Density	m^2/m^3	0.04 x 10^9	0.24 x 10^9
Solid Heat Capacity @ STP	kJ/kg-K	1.23	1.2

Crush Strength	kg_f	—	2
Attrition Index	-	—	0.4
Thermal Conductivity	W/(m-K)	0.5	0.14
Manufacturing Cost for Sorbent	$/kg	—	—
Adsorption			
Pressure	bar	0.004 CO_2	.0004 CO_2
Temperature	°C	25	25
Equilibrium Loading	g mol CO_2/kg	4	4
Heat of Adsorption	kJ/mol CO_2	45	90-45
CO_2 Adsorption Kinetics	gmol/time	0.15	0.15 mmolCO_2/g/min
Desorption			
Pressure	bar	0.5	0.5
Temperature	°C	80	110
Equilibrium CO_2 Loading	g mol CO_2/kg	0	0.4 (remaining)
Heat of Desorption	kJ/mol CO_2	45	90-50
CO_2 Desorption Kinetics	gmol/time	0.4	0.3 mmol CO_2/g/min

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Atmospheric Air Feed-Gas Assumptions:

		Composition						
		vol%					ppmv	
Pressure	Temperature	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	—	0.04	variable	78.09	20.95	0.93	trace	trace

TABLE 2: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	$/tonne CO_2	170	—
Cost of Carbon Avoided	$/tonne CO_2	170	—
Capital Expenditures	$/tonne CO_2	17	—
Operating Expenditures	$/tonne CO_2	152	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Calculations Basis – The DAC facility included 12 contactors per bank, with the number of banks being calculated based on the amount of adsorbent mass needed to achieve 100,000 ton/year capture rate. Each contactor contained 633 kg of adsorbent and had a volume of 2.8 m^3. Each contactor was equipped with an individual fan. A single steam generation unit was used to supply steam to the contactor banks. A hot oil system was envisioned to provide the sensible heat that brings the system to the desorption temperature. This is helpful to minimize water usage in the system, and supplies the heat needed to bring the non-sorbent contactor mass to the desorption temperature. Following desorption, the steam and desorbed CO_2 are flowed through a condenser and knockout drum, which separates the water from the gaseous CO_2. Finally, the CO_2 is flowed through the vacuum pump, which exhausts the CO_2 at ambient pressure.

Scale of Validation of Technology Used in TEA – Laboratory testing.

Qualifying Information or Assumptions – Assumed a cost of electricity of $0.10/kWh, a steam cost of $2.03/GJ, and a plant uptime of 95%.

technology advantages

- Enable cost less than $200/tonne CO_2, leveraging unique pore characteristics to improve lifetime capture capacity of sorbent.
- Significantly lower energy consumption due to reduced sensible heat load.
- Enable cycle life greater than 10,000 by tuning the chemical environment around amine sites in the aerogel.
- High equilibrium loading is achieved by minimizing inert material in the aerogel.
- High uptake rate 15-minute full cycle is achieved by controlling aerogel structure through synthesis.
- Improvement in oxidative stability over conventional ceramic-supported PEI sorbents.
- Low sorbent cost is enabled by using a demonstrated, scalable polymerization process; high-volume, low-cost precursors; and rapid ambient drying of the aerogel.

R&D challenges

- Adapting synthesis to incorporate amine.
- Maximizing amine content without sacrificing pore structure.
- Achieving long cycle life is a challenge for solid sorbents, in general.

status

This project was completed on March 31, 2023. PARC demonstrated a new state-of-the-art adsorbent material for temperature swing adsorption, meeting the ambitious target of 4 mmol CO_2/g equilibrium capacity. The project demonstrated a 43% reduction in capture cost relative to the current state of the art, due to improvements in the sorbent performance. PARC also developed a novel approach to fabricating structure sorbents using the TRAPS aerogel process that can be scaled into a continuous benchtop process. The physical properties of the sorbents were studied, including preliminary multi-cycle sorbent stability using thermogravimetric analysis. The materials exhibit CO_2 uptake at low CO_2 partial pressures. PARC manufactured the sorbent material at the ~5-g-scale for packed-bed testing at LLNL; the porosity was robust for pelletization and handling.

available reports/technical papers/presentations

Mahati Chintapalli, PARC, "TRAPS: Tunable Rapid Uptake AminoPolymer Aerogel Sorbent for Direct Air Capture of CO_2," Final Technical Report, June 2023. *https://www.osti.gov/servlets/purl/1987516/*.

Mahati Chintapalli, PARC, "TRAPS: Tunable Rapid Uptake AminoPolymer Aerogel Sorbent for Direct Air Capture of CO_2," 2023 Final Project Briefing Presentation, Pittsburgh, PA, March 2023.

Mahati Chintapalli, PARC, "TRAPS: Tunable Rapid Uptake AminoPolymer Aerogel Sorbent for Direct Air Capture of CO_2," 2022 Carbon Management Project Review Meeting, Pittsburgh, PA, August 2022.

Mahati Chintapalli, "TRAPS: Tunable Rapid Uptake AminoPolymer Aerogel Sorbent for Direct Air Capture of CO_2" PARC, A Xerox Company, 2021 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Chintapalli.pdf*.

Mahati Chintapalli, "TRAPS: Tunable Rapid Uptake AminoPolymer Aerogel Sorbent for Direct Air Capture of CO_2" Project kickoff meeting presentation, Pittsburgh, PA, April 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11043&filename=Tunable+Rapid+Uptake+Amino+Polymer+Aerogel+Sorbent+for+Direct+Air+Capture+of+CO2.pdf*.

Mahati Chintapalli, "TRAPS: Tunable Rapid Uptake AminoPolymer Aerogel Sorbent for Direct Air Capture of CO_2" Direct Air Capture kickoff meeting presentation, Pittsburgh, PA, February 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11045&filename=TRAPS%3a+Tunable+Rapid+Uptake+AminoPolymer+Aerogel+Sorbent+for+Direct+Air+Capture+of+CO2.pdf*.

Development of Advanced Solid Sorbents for Direct Air Capture

primary project goal

RTI International partnered with Creare and Mohammed VI Polytechnic University to develop two types of advanced adsorbent materials—metal-organic frameworks (MOFs) and phosphorous dendrimers (P-dendrimers)—for direct air capture (DAC) of carbon dioxide (CO_2). Incorporation of the novel sorbents into a low pressure drop multichannel monolith-type reactor can result in capturing CO_2 from air at a cost of approximately \$70/tonne of CO_2.

technical goals

- Develop MOF- and P-dendrimer-based sorbents for high durable DAC sorbent, to achieve high CO_2 capacity (in excess of 7–9 wt%) at low CO_2 partial pressures observed in air.
- Investigate the mass and heat transfer characteristics of select high CO_2 capacity solid sorbents when incorporated in a multichannel monolith-type reactor configuration.
- Develop computational fluid dynamics (CFD) model of the MOF and P-dendrimer sorbent to help understand the adsorber reactor design and optimize sorbent-absorber integration.
- Demonstrate long-term chemical and mechanical stability of select high CO_2 capacity sorbents (more than 100 cycles). The multicycle performance testing for both sorbents will be used for CFD model validation, including diffusion of gases into the porous sorbent materials.
- Evaluate the impact of sorbent contaminants present in air, such as oxygen (O_2) and water (H_2O), on these advanced solid sorbents at different temperatures and humidity levels.
- Perform a preliminary process design for DAC with a qualitative assessment of sorbent properties affecting the critical process design choices.
- Select sorbents that have high CO_2 capacity, have long-term stability, are low cost (less than \$15/kg of sorbent), are contaminant resistant, and can be scaled rapidly in one to two years for future testing.

technical content

The RTI team developed, studied, and compared the performance of two novel materials, MOFs and P-dendrimers, for DAC that have the potential of significantly reducing the capital cost of the adsorbent while demonstrating high CO_2 working capacity at extremely low CO_2 concentrations (~400 parts per million [ppm]) and high CO_2 selectivity over moisture, oxygen, and nitrogen, which are major constituents of air. The sorbents were synthesized, characterized, and optimized

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Metal-Organic Framework and Phosphorous Dendrimer Sorbents for DAC

participant:
Research Triangle Institute

project number:
FE0031954

predecessor projects:
N/A

NETL project manager:
Mariah Young
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principal investigator:
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Research Triangle Institute
msoukri@rti.org

partners:
Creare; Mohammed VI Polytechnic University

start date:
10.01.2020

percent complete:
100%

to achieve high CO_2 capacity at very low CO_2 partial pressures, high swing capacity, improved mass and heat transfer, and long operational life at low cost. The project team tested two selected sorbents (one MOF adsorbent and one amine-P-dendrimer adsorbent) over 100 adsorption-desorption cycles in a laboratory-scale packed-bed reactor (PBR) and evaluated sorbent performance in the presence of contaminants (e.g., oxygen and water). The best performing sorbent was evaluated for commercial production cost and scalability.

RTI's MOF-Based Sorbent for DAC

RTI's MOF-based sorbent NbOFFIVE-Ni ($[Ni(NbOF_5)(C_4H_4N_2)_2 \cdot 2H_2O]$) has been very recently considered as an ideal MOF material for trace CO_2 capture. This MOF displayed square-like channels with contracted pore-aperture sizes ranging from 3.5–3.9 Å (Figure 1) and apparent specific Brunauer–Emmett–Teller (BET) surface area of around 250–300 m^2/g. As stated earlier, these fluorinated MOF platforms show very interesting carbon capture performances, explained by the combined synergetic effect of thermodynamics and kinetics associated with the small pore size of the 1-D channels aligned with a periodic array of fluorine moieties.

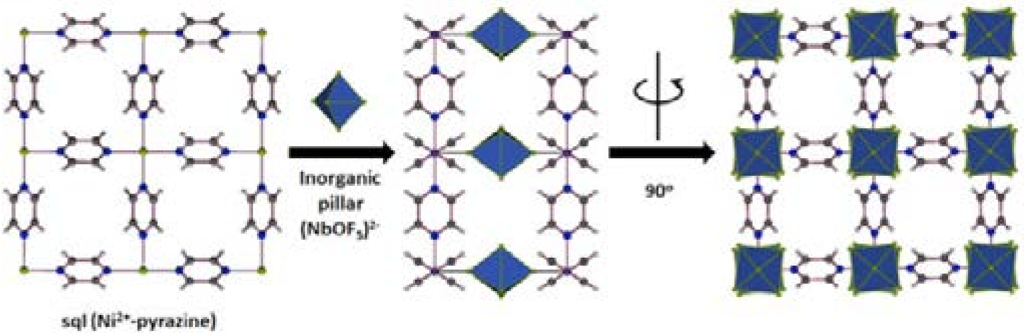


Figure 1: Structural representation of the NbOFFIVE-1-Ni (left), the 2-periodic square grid layer constructed by linking Ni(II) with pyrazine ligands, (middle), pillaring of square-grid layers by the (NbOF5)2- inorganic pillars, (right), square-shaped channels in the resultant 3-periodic pcu-MOF, NbOFFIVE-1-Ni.

RTI's partner Mohammed VI Polytechnic University has studied the CO_2 adsorption performance of NbOFFIVE-1-Ni at different conditions and has shown that this MOF exhibits 5.7 and 9.6 wt% at 400 ppm and 10 vol% CO_2, respectively (Figure 2), which surpasses the performance of the SIFSIX family and the Mg-MOF-74, one of the best MOFs for low-pressure CO_2 adsorption. In addition, RTI has prepared and tested this MOF in thermogravimetric analysis (TGA) at 1,000 ppm CO_2 and in RTI's lab-scale PBR at 500 ppm CO_2. Fluorinated MOF, NbOFFIVE-1-Ni, exhibits the highest CO_2 gravimetric uptake (ca. 7.2 wt% at 1,000 ppm CO_2 and 6.5 wt% at 500 ppm CO_2) for a physical adsorbent at low partial pressures of CO_2.

The contracted square channels decorated with proximal fluorine moieties were believed to confer this MOF with the observed exceptional CO_2/nitrogen (N_2) selectivity. Moreover, NbOFFIVE-1-Ni presented an exceptional chemical stability especially toward water; hence, NbOFFIVE-1- Ni stands as the best physical adsorbent material for CO_2 capture from atmospheric air with a CO_2 gravimetric uptake (at 400 ppm), 300% higher than the reference physical adsorbent, namely SAPO- 34(Sr^{2+}). The RTI team further evaluated the performance of NbOFFIVE-1-Ni as an advanced sorbent for DAC, in particular, the long-term cycling characteristics and the effect of contaminants.

The competition of CO_2 adsorption with water vapor is a significant challenge for physisorbent materials in CO_2 capture, either from DAC or from flue gas. However, fluorinated MOFs with high uniform charge density and small pore sizes such as MFFIVE-1-Ni will enhance the affinity of MOFs for water molecules in the highly confined pore system without affecting CO_2 adsorption. For example, these characteristics permitted water and CO_2 to adsorb at distinct sites. In particular, water will preferentially adsorb to the open metal coordination sites, and CO_2 will preferentially adsorb via interactions with the fluorine moieties.

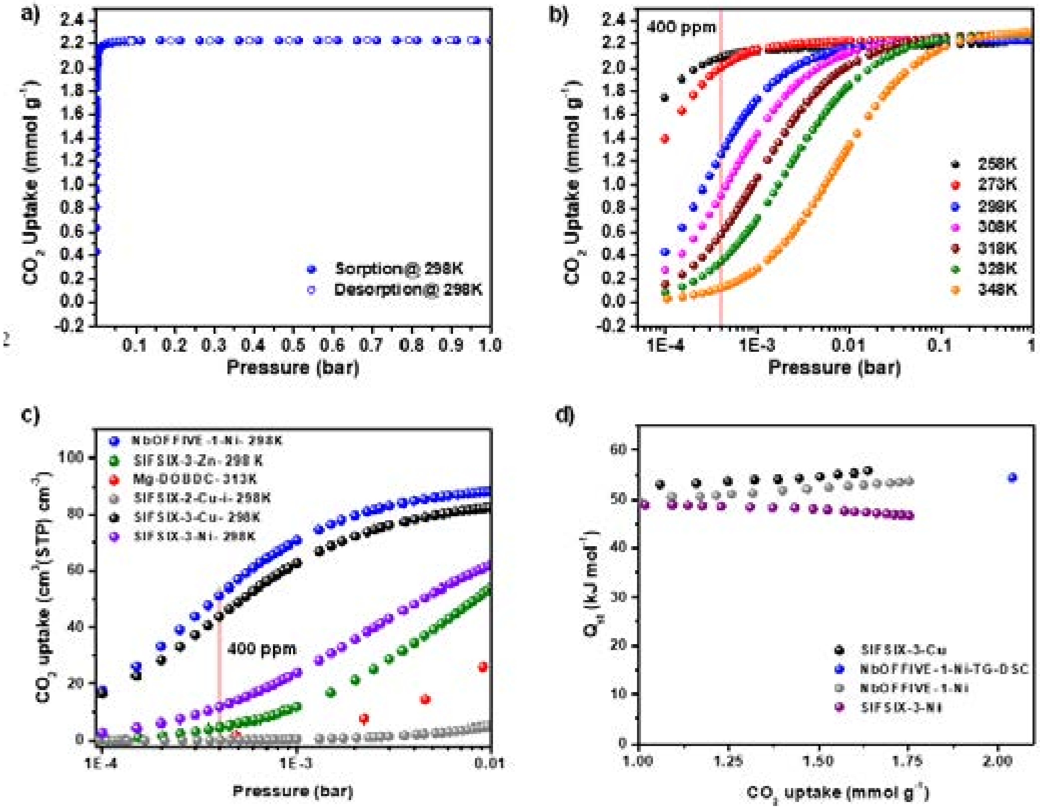


Figure 2: (a) CO_2 adsorption isotherm for NbOFFIVE-1-Ni up to 1 bar and 298 K. (b) CO_2 adsorption isotherms for NbOFFIVE-1-Ni at different temperatures. (c) Comparison of the CO_2 uptake at low pressures between the NbOFFIVE-1-Ni and the SIFSIX family and the Mg-MOF-74, one of the best MOFs for low-pressure CO_2 adsorption. (d) CO_2 heat of adsorption for NbOFFIVE-1-Ni as compared to SIFSIX-3-Ni and SIFSIX-3-Cu, determined using multiple CO_2 adsorption isotherms and TG-DSC measurements.

RTI's P-Dendrimer-Based Sorbent for DAC

Under a U.S. Department of Energy/National Energy Technology Laboratory (DOE/NETL)-funded project (DE-FE0026432), RTI developed a novel water stable solid sorbent that was produced in 91% yield by crosslinking polyethyleneimines (PEIs) with polyaldehyde P-dendrimers (Figure 3), capturing on average 13.1 wt% CO_2 from simulated flue gas over 350 cycles (700 continuous hours running with no degradation or loss of CO_2 observed). The sorbent shows excellent thermal and chemical stabilities when operating under simulated flue-gas conditions with rapid kinetics for both adsorption and regeneration. This sorbent was also tested, after two years stored in the bench at 25°C, for CO_2 capture at 500 ppm of CO_2 in RTI's PBR. For the adsorption condition, the sorbent was exposed to 150 standard cubic centimeters (sccm) of 500 ppm-CO_2 in air at 25°C in the presence of 40% relative humidity (RH). The sorbent regeneration was performed by heating the sorbent to 80°C with 40% RH while monitoring the CO_2 desorbed from the sorbent at the reactor outlet. The CO_2 loading was determined from both the adsorption and regeneration steps for comparison. This adsorbent has demonstrated a CO_2 capacity of 7.45 wt% with 100% regeneration (80°C) and no degradation or capacity loss over eight cycles.

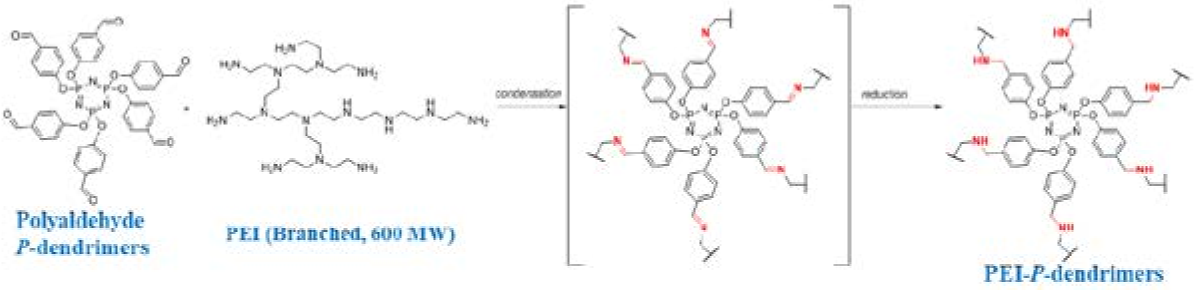


Figure 3: Synthesis of PEI-P-dendrimer.

The RTI team has prepared new sorbents with different textural properties and functionalized by grafting three polyamines: short chain ethylenediamine, 600 MW PEI, and 10,000 MW PEI and a polyaldehyde P-dendrimer crosslinker. To improve the capacity of the sorbent for DAC, RTI optimized the material's pore size, pore volume, and surface area through a neutral templating cycle route and disrupted the hydrogen bonding between dendrimers for improved CO_2 uptake.

Feed-Gas Assumptions –

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	77 °F	0.04	variable	78.96	21.00	0.0	0	0

Other Parameter Descriptions:

Waste Streams Generated – Waste gases (mostly water).

technology advantages

- High-capacity, fast kinetics, robust cycling, facile/cheap synthesis procedures, and easy scalability.
- Low-cost sorbents.
- Selective binding for CO_2.
- Ultra-microporous fluorinated MOFs offer fast sorption kinetics to enable selective capture of CO_2 over both N_2 and H_2O (low % RH), effective for trace CO_2 capture under both dry and humid conditions.
- The P-dendrimer amine-based sorbents perform very well under DAC conditions regardless of concentration of water vapor in air.

R&D challenges

- Improve performance under the presence of contaminants.
- Demonstrate the scale-up of selected candidate sorbents.

status

This project was completed on March 31, 2023. MOF synthesis and characterization of three different MOFs were accomplished in collaboration with Mohammed VI Polytechnic University. The CO_2 capture and kinetics under optimal conditions were determined and one MOF was evaluated using thermogravimetric analysis and packed bed reactor (PBR) for CO_2 capture uptake under relevant DAC conditions. The P-dendrimer amine sorbents were prepared using different amines ranging from short (ethylene diamine) to branched (polyethyleneimine) and tested in the PBR to determine their CO_2 capture uptake under the optimal conditions. One hundred cycles of 400 ppm CO_2 capture at 75% RH was completed on the P-Dendrimer using the PBR with a five-hour cycle, the P-dendrimer material captured 5–7 wt.% CO_2 at 25℃ and was completely regenerated after one hour at 120℃. The presence of H_2O aided the adsorption of CO_2 in the P-Dendrimer sorbent, whereas in the MOF materials H_2O competed with the CO_2 capture performance.

available reports/technical papers/presentations

Mustapha Soukri, "Development of Advanced Solid Sorbents for Direct Air Capture," Final Technical Report, June 2023. *https://www.osti.gov/servlets/purl/1987759/*.

Mustapha Soukri, "Development of Advanced Solid Sorbents for Direct Air Capture," NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Soukri.pdf*.

Mustapha Soukri, "Development of Advanced Solid Sorbents for Direct Air Capture," Direct Air Capture kickoff meeting presentation, Pittsburgh, PA, February 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11052&filename=Development+of+Advanced+Solid+Sorbents+for+Direct+Air+Capture.pdf*.

Mustapha Soukri, "Development of Advanced Solid Sorbents for Direct Air Capture," Project kickoff meeting presentation, Pittsburgh, PA, November 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11053&filename=Development+of+Advanced+Solid+Sorbents+for+Direct+Air+Capture.pdf*.

Gradient Amine Sorbents for Low Vacuum Swing Carbon Dioxide Capture at Ambient Temperature

primary project goal

The University of Akron, in partnership with Aspen Aerogels Inc., developed novel solid sorbent materials that can be regenerated in a low vacuum swing adsorption (VSA) process with greater performance than current state-of-the-art materials for the capture of carbon dioxide (CO_2) from air.

technical goals

- Prepare amine-functionalized aerogel.
- Fabricate and test a hierarchical structure of gradient amine sorbent on carbon fiber.
- Construct a VSA test apparatus.
- Conduct sorbent characterization and performance testing.
- Conduct high-level process design and analysis to evaluate feasibility of applying the new sorbents in a direct air capture (DAC) system.

technical content

A hierarchical structure of gradient amine sorbent, which allows CO_2 to adsorb in the form of weakly adsorbed CO_2, was constructed in bead form. The weakly adsorbed CO_2 was then regenerated from the sorbent by applying a low vacuum. The novel sorbent allows VSA to be operated at ambient temperature without a significant energy demand, eliminating the energy-intensive heating and cooling cycle in temperature swing adsorption (TSA) processes. Operation at ambient temperature also eliminates the possibility of thermal degradation of sorbents, leading to a prolonged lifetime of the sorbent and minimizing maintenance costs to provide a cost-effective approach for DAC.

To mitigate the corrosive nature of liquid amine sorbents and solvent loss, and to enhance the rate of adsorption/desorption, immobilization of organic amine on high surface area/porous solid has been shown to hold a great promise for replacing the liquid amine process. Many studies have suggested the mechanism of CO_2 adsorption/desorption on solid amines resembled that of CO_2 adsorption in liquid amines. The overall reactions involved in the adsorption/desorption process can be described by the following:

$$2\ R_1R_2NH + CO_2 \leftrightarrow R_1R_2NH_2^+ + R_1R_2NCOO^- \text{ (carbamate ion) (1)}$$

$$R_1R_2NH + H_2O + CO_2 \leftrightarrow R_1R_2NH_2^+ + HCO_3^- \text{ (bicarbonate) (2)}$$

$$R_1R_2NH + CO_2 \leftrightarrow R_1R_2NCOO^-H^+ \text{ (carbamic acid) (3)}$$

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Amine-Based Aerogel Sorbents for DAC

participant:
The University of Akron

project number:
FE0031958

predecessor projects:
N/A

NETL project manager:
Carl Laird
carl.laird@netl.doe.gov

principal investigator:
Steven Chuang
University of Akron
schuang@uakron.edu

partners:
Aspen Aerogels Inc.

start date:
01.01.2021

percent complete:
100%

In absence of water (H_2O) vapor, one mole of CO_2 reacts with two moles of amine to form carbamate by reaction (1); in presence of H_2O vapor, one mole of CO_2 reacts with one mole of amine to form bicarbonate by reaction (2). Recently infrared spectroscopic studies conducted by the University of Akron (Akron), as well as a number of in-depth spectroscopic studies, have shown that CO_2 adsorbs on the immobilized amine (i.e., solid amine) as carbamic acid and ammonium carbamate ions (i.e., the same type of carbamate ion as the liquid organic amine in the aqueoussolution). Because of an insufficient amount of adsorbed H_2O and the lack of mobility of amine sites, bicarbonate was produced at a negligible level on immobilized amine.

Development of Pellets for TSA with Fixed Bed and Fluidized Bed

Akron has developed a number of immobilized amine sorbents for TSA processes. Collaboration with Aspen Aerogels (Aspen) led to the development of a robust sulfur-resistance sorbent for TSA. Akron has also developed a sorbent for fixed and fluidized beds. The infrared spectra in Figure 1 shows these sorbents containing primary amine at 3,297 and 3,355 cm^{-1}. The secondary amine at 3,297 cm^{-1} capture of these sorbents and their CO_2 binding energy, as well as their resistance to degradation, are strongly dependent on many factors, such as the type of amine (i.e., primary, secondary, and tertiary) and their loading, overlapped with the asymmetric vibration of the primary amine. The sulfur resistant amine (KD-SRE) sorbent containing Aspen's hydrophobic aerogel produced a smaller water band in the 3,100–3,700 cm^{-1} region. These results show Aspen's amine-functionalized aerogel is able to impart hydrophobicity to the amine sorbent. The carbon dioxide adsorbed in the form of ammonium ions at 1,668 cm^{-1} and carbamate ion at 1,510 cm^{-1}. Evacuation of adsorbed CO_2 at 8 pounds per square inch (psi) at 25℃ for three minutes by vacuum led to a decrease in the infrared intensity of adsorbed CO_2, indicating a weakly adsorbed CO_2, which may be removed without heating. More than 60% of adsorbed CO_2 has to be removed from the temperature program desorption (TPD). The sorbent was then returned to the initial state, as shown by its infrared spectra, which exhibited the same feature as the initial spectra. The key feature of TSA sorbents was the requirement of heating to desorption temperature for sorbent regeneration.

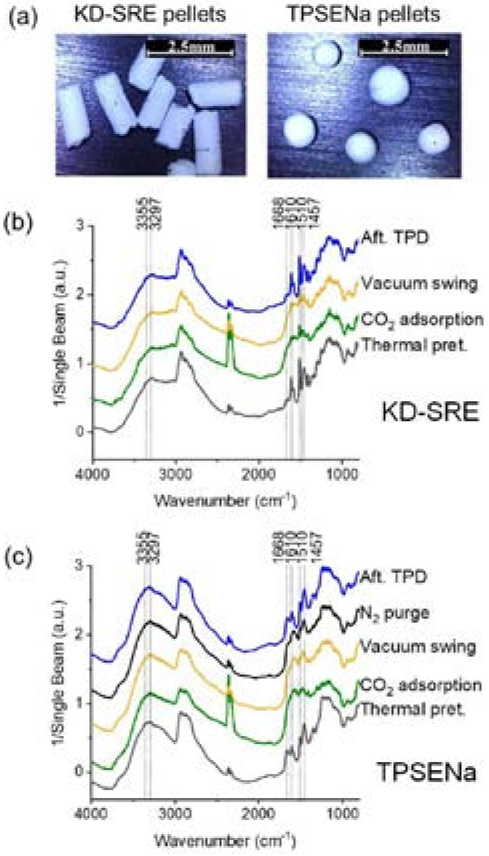


Figure 1: (a) KD-SRE pellets: a sulfur-resistant amine sorbent prepared by incorporation of TPSENa with Aspen's aerogels; TPSENa pellets: a high attrition-resistance sorbent that contains tetraethylenepentamine (TEPA), polyethylene glycol (PEG), epoxy, Na_2CO_3, and SiO_2; (b) (c) infrared spectra.

Vacuum Swing Adsorption

Akron devised a vacuum swing CO_2 capture process for the sorbent that allows CO_2 to adsorb in the form of weakly adsorbed CO_2. Figure 2 compares Akron's VSA process with the TSA process. VSA significantly simplifies the process by eliminating the highly energy-intensive heating and cooling process. Operation at ambient temperature further eliminates the possibility of thermal degradation of the amine sorbents.

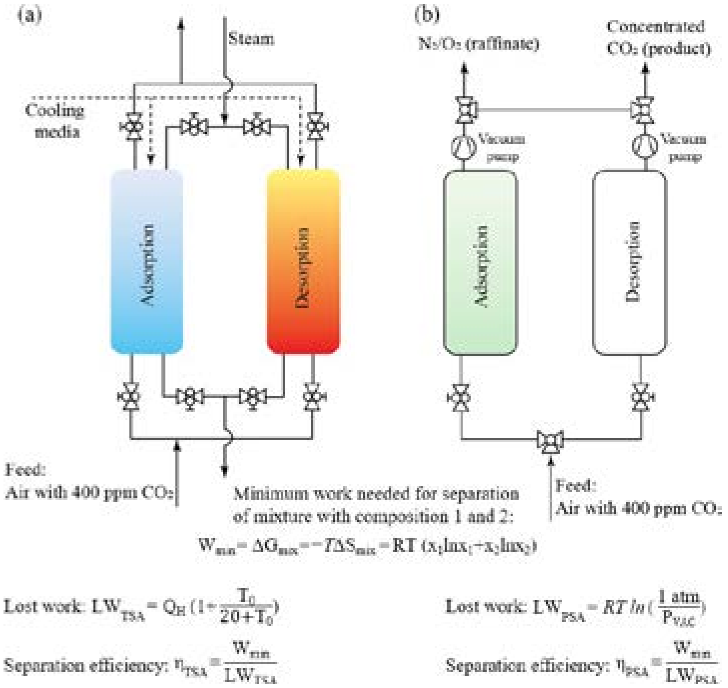
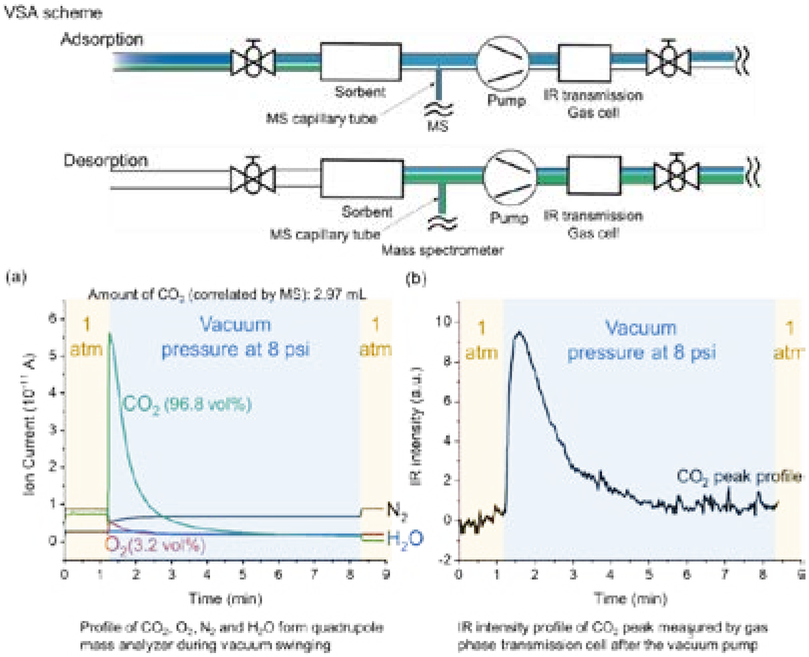


Figure 2: Temperature swing adsorption versus vacuum swing adsorption. (T_0 = heating temperature).

Thermodynamics for TSA and VSA

Minimum work (Wmin) for separation of CO_2 from air is the same for both TSA and PSA. The thermodynamic efficiency of the processes are determined by lost work temperature swing adsorption (LW_{TSA}) and lost work pressure swing adsorption (LW_{PSA}). The absence of thermal energy term (Q_H) in the separation efficiency of the pressure swing adsorption (ηPSA) equation leads to lost work being greater than that of the TSA (ηPSA > ηTSA). LW_{PSA} is a result of using a mechanical pump to evacuate gaseous species to drive the desorption of weakly adsorbed CO_2. Lowering the pressure from 1 atm (760 torr) to 8 psi (413 torr), LW_{PSA} = 1,563 kJ/mol of gas, the operation efficiency can vary from more than 90% to less than 80%, depending on the level of vacuum. Therefore, decreasing the solid volume (i.e., the amount of gas to be evacuated) in the VSA unit can increase the efficiency of the VSA system; however, it will affect the kinetics of adsorption and desorption, as well as the pressure drop of the air flow during CO_2 adsorption. The research team has also observed a 2–3°C drop in temperature during CO_2 desorption of weakly adsorbed CO_2 and then a return to the initial sorbent bed temperature under argon purge, revealing the sorbent bed adsorbs the energy from the ambient. Thus, it is essential to incorporate highly thermal co-conductive materials in the sorbent to facilitate the heat transfer and desorption.

Figure 3 illustrates the VSA results on previous TSA sorbents that were selected for their high capacity of weakly adsorbed CO_2 for the preliminary study. In a typical VSA, CO_2 adsorption was carried out by flowing CO_2-containing stream over the sorbent bed. Instead of heating for sorbent regeneration and collection of both weakly and strongly adsorbed CO_2 with steam or purge gas, VSA removes weakly adsorbed CO_2 at ambient temperature with low pressure. In this specific experiment, closing the inlet valve of the sorbent bed and applying the low pressure at 8 psi led to the removal of weakly adsorbed CO_2. (Note that 1 atm=14.7 psi) Figure 3(a) shows the mass spectrometer (MS) composition profile of the gaseous stream during evacuation of weakly adsorbed CO_2 on a KD sorbent (an amine-functionalized aerogel prepared by Aspen Aerogels Inc.). Figure 3(b) shows the infrared profile of gaseous CO_2 emitted from the vacuum pump. The infrared profile of CO_2 is broader than the MS profile of CO_2 because of the transportation lag resulting from the gaseous line and the vacuum pump. The MS profile showed a highly concentrated CO_2 mole fraction of 96.8%, with a low concentration of nitrogen (N_2) and oxygen (O_2), as determined by the areas under their corresponding MS profiles in Figure 3(a), demonstrating the technical feasibility of VSA using sorbent with weakly adsorbed CO_2.



Profile of CO_2, O_2, N_2 and H_2O form quadrupole mass analyzer during vacuum swinging

IR intensity profile of CO_2 peak measured by gas phase transmission cell after the vacuum pump

Sample	Capture capacity (mmol/g)	Weakly adsorption percentage	
		Vacuum swinging	N_2 purge
TPSENa	3.4	18.84%	24.76%
KD-240-24-9B sorbent	2.0	55.55%	/

Figure 3: VSA Scheme—Adsorption by flowing a 0.04% CO_2 stream over a sorbent bend; desorption of weakly adsorbed species by vacuum. The concentration profiles of the effluent form adsorption bed under 8 psi vacuum determined by (a) MS before vacuum pump, (b) infrared gas cell after vacuum pump. (1 atm=14.7 psi)

CO_2 Capture VSA Unit

The need for processing a large volumetric flow of air with a dilute concentration of CO_2 around 420 parts per million (ppm) presents a monumental challenge to the development of a sustainable and cost-effective CO_2 capture process. The current liquid monoethanolamine (MEA) technology is cost-effective for separation of CO_2 from natural gas in liquefaction and ammonia synthesis processes because of the value of their end products. This technology, when applied for capture of CO_2 from coal-fired power plants, increases the cost of electricity by more than 70%. Application of MEA technology to a dilute stream is not economically feasible in the foreseeable future. In spite of extensive research and development on immobilized (i.e., solid) amines and their attractive features, the employment of solid amines in TSA CO_2 capture has not been successful because of sorbent degradation and low CO_2 capture capacity. In addition, the cost of energy-intensive heating and cooling in TSA is nearly insurmountable.

Recent studies conducted by Akron have shown that amine sorbents aiming at TSA CO_2 capture consists of strongly and weakly adsorbed CO_2. The availability of weakly adsorbed CO_2 to be removed under a purge gas flow and vacuum at ambient temperature for sorbent regeneration provides a unique opportunity to utilize low vacuum for a VSA CO_2 capture process.

Figure 4 illustrates the approach to develop a cost-effective VSA CO_2 capture process. Figure 4(a) show a cascade VSA process consisting of two VSAs in a series, which allows concentrated CO_2 from the first VSA to be further concentrated in the second VSA. Air stream was diverted to parallel VSA units for semi-continuous processing, where one VSA unit was operated at the adsorption stage and the other unit was operated at the desorption stage (i.e., under vacuum). Preliminary estimation showed that a 1-kg VSA unit will be able to process 200 liters per minute for five minutes for CO_2 adsorption to saturate amine sites at ambient condition (room temperature and one atm).

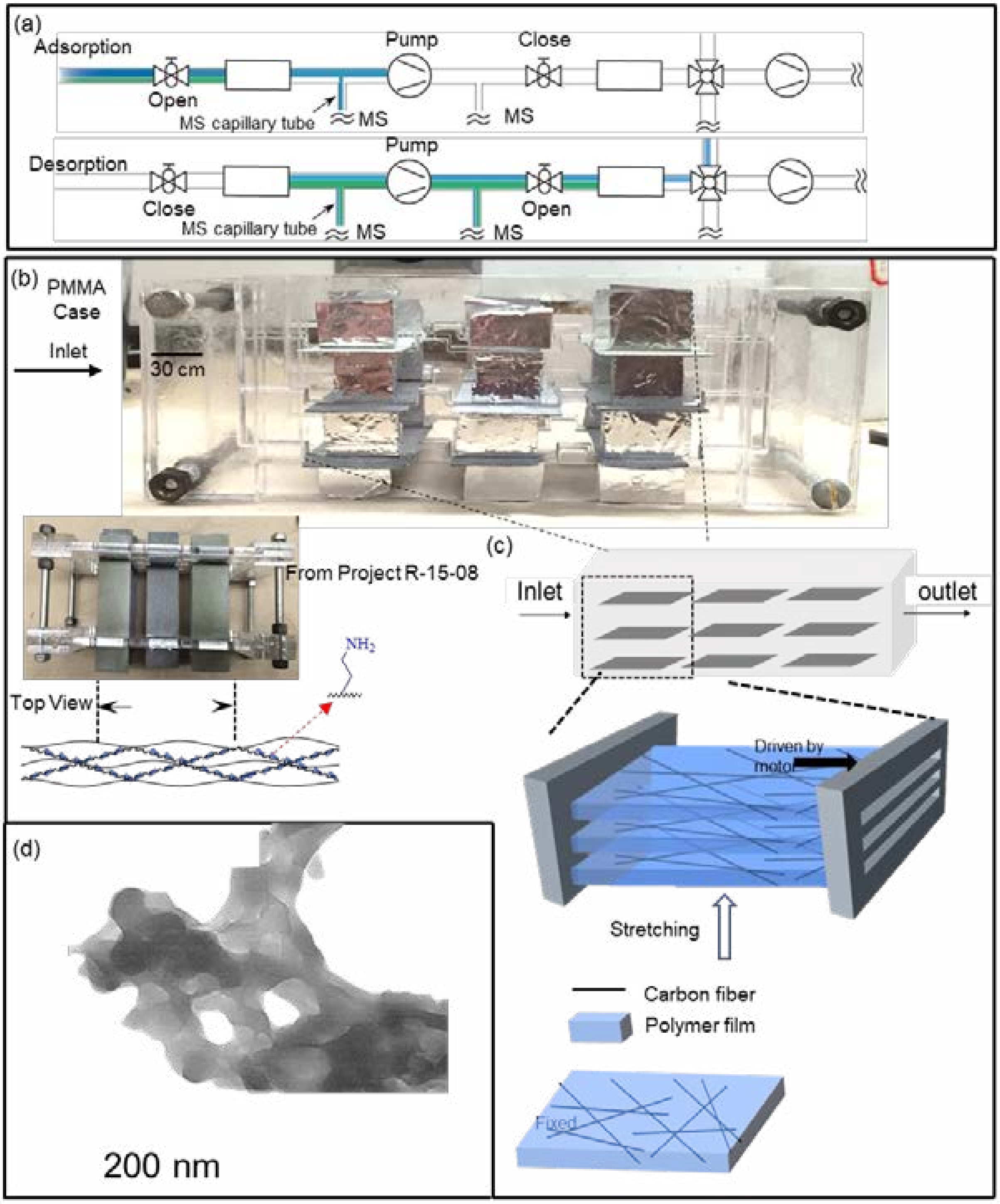


Figure 4: Vacuum swing adsorption for CO_2 capture from air (a) VSA scheme, (b) a VSA unit with sorbent plates in a plexiglass (i.e., PMMA) case, (c) the arrangement of sorbent plates in a parallel configuration, (d) the structure of amine sorbent functional groups.

Figure 4(b) shows the CO_2 VSA unit Akron has designed and built on plexiglass (i.e., Poly(methyl methacrylate): PMMA). This unit was previously built for an electrically heated TSA process and consists of a set of monolithic rectangular plates of sorbent with dimensions of 20 cm x 10 cm x 0.1 cm, shown in Figure 4(c)/(d). The new sorbent plates manufactured with a low-cost carbon fiber provides mechanical strength. Amine sorbent particles were adhered on the carbon fiber with a porous adhesive. The use of parallel sorbent plates allows for the processing of a large volume of air flow with a minimum pressure drop and diffusion limitation. Porous polymer with a surface area greater than 350 m^2/g will be used to support the amine sites, shown in Figure 4(d). Akron has prepared sorbent pellets at kg-scale for previous TSA CO_2 capture processes. This preparation method, which was tuned for mechanical strength for a fluidized bed operation, are being tuned for high surface area since the sorbents in VSA are stationary. Immobilized amine and specific additives will eliminate the migration of amine sites during long-term VSA operation. In summary, the VSA process will allow use of low energy air blower to bring air to contact with VSA sorbent and allow use of low vacuum for collecting weakly adsorbed CO_2.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	910	900
Bulk Density	kg/m^3	270	280
Average Particle Diameter	mm	0.32	0.5
Particle Void Fraction	m^3/m^3	073	0.6
Packing Density	m^2/m^3	0.5	0.5
Solid Heat Capacity @ STP	kJ/kg-K	2.36	2.3
Crush Strength	kg$_f$	NA	NA
Attrition Index	-	NA	NA
Thermal Conductivity	W/(m-K)	NA	—
Manufacturing Cost for Sorbent	\$/kg	20	15
Adsorption			
Pressure	bar	1.013	1.013
Temperature	°C	25-40	25-35
Equilibrium Loading	g mol CO_2/kg	2.6	1.2
Heat of Adsorption	kJ/mol CO_2	80	40-60
CO_2 Adsorption Kinetics	gmol/time	0.01	0.1
Desorption			
Pressure	bar	0.5	0.1
Temperature	°C	25	25
Equilibrium CO_2 Loading	g mol CO_2/kg	0.05	0.1
Heat of Desorption	kJ/mol CO_2	51	40-45
CO_2 Desorption Kinetics	gmol/time	0.01	0.1
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	Vacuum Swing Adsorption	
Flue Gas Flowrate	kg/hr	27	
Space Velocity	hr^{-1}	NA	
Volumetric Productivity	gmol$_{CO2}$/(hr l$_{absorber\ bed}$)	0.3	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90	
Adsorber Pressure Drop	bar	0.05	
Degradation	% capacity fade/cycle	0.05	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	3,700	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – “Current” is market price of material, if applicable; “Target” is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Feed-Gas Assumptions –

		Composition						
		vol%					ppmv	
Pressure	**Temperature**	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.7 psia	- °F	0.04	variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

Waste Streams Generated – Waste gases (mostly water).

TABLE 2: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	580	60
Cost of Carbon Avoided	\$/tonne CO_2	NA	NA
Capital Expenditures	\$/tonne CO_2	—	—
Operating Expenditures	\$/tonne CO_2	480	40

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Calculations Basis – Basis for estimation: capture of 1 kg CO_2. Adsorption time = 100 minutes and desorption time = four minutes. The volume of adsorption/desorption column = 600 liter (0.6 m3) filled with 300 kg of sorbent; flow rate of air = 100 liter/minute = 4.46 mol/min with a 2% H_2O vapor. A 1-hp (0.735 Joule/sec) vacuum pump was operated for four minutes for the desorption (i.e., sorbent regeneration) process and used 220 KJ, which costs $0.48. The estimate cost of electricity = 0.10 $/kWh. The cost of electricity for capture of one tonne CO_2 = $480.

Scale of Validation of Technology Used in TEA –

- Materials and energy balances around the complete process, including electric power requirements, heating and/or cooling requirements, were used in the TEA calculation.
- The unique advantage of the VSA technology investigated in this project is that the process is operated at ambient condition without heating and cooling. Thus, no thermal energy balance was required and conducted. The main energy input needed for the VSA operation is electricity needed for operating vacuum pumps.
- System performance summary. The preliminary estimation for capture of one tonne of CO_2 could cost up to $480/tonne. The performance could be significantly enhanced by improving sealing of the VSA unit (i.e., minimizing the leakage) and the selectivity of weakly adsorbed CO_2.

Qualifying Information or Assumptions – The data obtained from 1-gram scale could be extended to estimate and simulate CO_2 capture performance in pilot scale and commercial scale.

technology advantages

- Amine-functionalized aerogels have high CO_2 working capacity, low energy sorbent regeneration, high moisture resistance, and long stability over 500 adsorption-desorption cycles.
- Operates at ambient temperature.
- Scalable and modular design.

R&D challenges

- Identification of amine sites for weakly adsorbed CO_2.
- Production of high-purity CO_2 (greater than 99%).
- Fabrication of hierarchical sorbents with a high density of weakly adsorbed CO_2 sites.
- Construction of low leakage vacuum swing unit.

status

This project was completed on March 31, 2023. The project team developed an amine-functionalized aerogel that was tested in multiple adsorption/desorption cycles in a laboratory-scale (5–10 cm^3) VSA unit. The simultaneous monitoring of the aerogel sorbent using in situ infrared and MS was completed to understand the adsorption and desorption kinetics for both the strongly and weakly adsorbed CO_2. The project team fabricated and scaled-up a 1-liter VSA unit and prepared impregnated amine-based aerogel into monolith structures.

available reports/technical papers/presentations

Aderinsola A Oduntan, Steven S. C. Chuang, "Weakly Adsorbed CO_2 and H_2O Species on Monoethanolamine Films in a Room-Temperature CO_2 and Direct Air Capture Cycle: An In Situ Infrared Study," 63, 7, 3245–3255, Industrial & Engineering Chemistry, 2024. *https://doi.org/10.1021/acs.iecr.3c03771*.

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FNU Huhe, J King, Steven Chuang. “Amine-based sorbents for CO_2 capture from air and flue gas—a short review and perspective,”- Research on Chemical Intermediates, 2023 – Springer (2023) 49:791–817 *https://doi.org/10.1007/s11164-022-04902-7*.

Steven Chuang, “Gradient Amine Sorbents for Low Vacuum Swing CO_2 Capture at Ambient Temperature,” Final Technical Report, July 2023. *https://www.osti.gov/servlets/purl/1992922/*.

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Steven Chuang, “Gradient Amine Sorbents for Low Vacuum Swing CO_2 Capture at Ambient Temperature,” 2022 Carbon Management Project Review Meeting, Pittsburgh, PA, August 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_CDR15_Chuang.pdf*.

Steven Chuang, “Gradient Amine Sorbents for Low Vacuum Swing CO_2 Capture at Ambient Temperature,” NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Chuang.pdf*.

Steven Chuang, “Gradient Amine Sorbents for Low Vacuum Swing CO_2 Capture at Ambient Temperature,” Direct Air Capture Kickoff Meeting Presentation, Pittsburgh, PA, February 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11068&filename=Gradient+Amine+Sorbents+for+Low+Vacuum+Swing+CO2+Capture+at+Ambient+Temperature.pdf*.

Next Generation Fiber-Encapsulated Nanoscale Hybrid Materials for Direct Air Capture with Selective Water Rejection

primary project goal

Columbia University, along with project partners Cornell University and Oak Ridge National Laboratory, developed an intelligently tailored sorbent material using a state-of-the-art anhydrous nanofluid solvent and electrospinning technology to form a hybrid coaxial-fiber system for direct air capture (DAC) of carbon dioxide (CO_2).

technical goals

- Develop novel NOHMs while tuning the CO_2-binding energies that are suitable for DAC; optimize the chemistries of CO_2-binding sites for the minimum parasitic energy consumption.
- Develop the innovative support system based on the fiber-encapsulation technology.
- Design and develop air filter DAC systems consisting of fibers to allow use as an open system, as well as a closed system, with minimum pressure drop.
- Develop an understanding of degradation pathways and confirm the revolutionary stability of the new solvent using various laboratory techniques.

technical content

There is a need for CO_2 capture materials in DAC systems to be further improved to provide better CO_2 capture capacity and long-term durability. The hybrid fiber system developed in this project employs Columbia University's well-studied, liquid-like nanoparticle organic hybrid materials (NOHMs) embedded in a permeable, hydrophobic, CO_2-selective ceramic or polymeric shell to form a viscosity-controlled sorbent material with improved CO_2 capture kinetics, long-term stability, and reduced energy requirement for sorbent regeneration. The nanofiber-encapsulated sorbent has the ability to selectively reject water while allowing facile CO_2 diffusion, which can lead to a reduction in parasitic energy consumption during pressure/temperature swing desorption. The nanofibers embedded with NOHMs are being used to fabricate air filters, affording the low pressure drop and improved chemical and physical stability that is needed for DAC systems.

The notion of encapsulated NOHMs follows Columbia University's earlier work where encapsulation of NOHMs in polymeric microcapsules (Figure 1) was investigated. While the initial capture kinetics were fast, it was found that mass

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Hybrid Coaxial-Fiber System for DAC

participant:
Columbia University

project number:
FE0031963

predecessor projects:
N/A

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partners:
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start date:
01.01.2021

percent complete:
100%

transfer limitation does exist at a higher CO_2 loading. Thus, this project focused on other novel carrier designs that can provide greater interfacial areas.

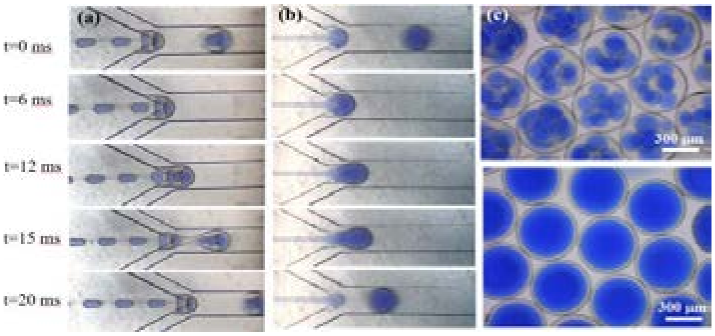

Figure 1: Encapsulated CO_2 capture solvent (NOHMs) produced using a microfluidic device.

The fiber-encapsulation system studied herein, carrying nanoscale and micronscale droplets of NOHMs in a gas permeable fiber, is highly innovative and has great potential. A fixed-bed CO_2 capture experiment that was recently performed using the encapsulated NOHMs showed that the selection of polymer fiber materials is as important as the NOHMs themselves for DAC with high capacity and high selectivity. Thus, this project focused on systematically designing NOHM-based hybrid sorbent systems. The approach of encapsulating NOHMs or embedding them in polymer and ceramic fiber matrix provided a transformative multifaceted solution to DAC. The polymer shell provided mechanical strength of NOHM-based sorbents, and can be chemically tuned to selectively reject water. They can also protect NOHMs and reduce the overall parasitic energy consumption of DAC. The design of the DAC unit is flexible (both open and closed systems), allowing potential reduction in the capital and operating costs.

The tunable nature of the grafted polymeric canopy of hybrid nanomaterials allows for enhanced CO_2 capture capacity and selectivity. The presence of primary and tertiary amines in the polymeric canopy significantly enhances the CO_2 capture capacity ([polyethylene imine (PEI)]-SiO_2 hybrid versus polyetheramine [PEA]-SiO_2 hybrid). In experiments, the amine functional sites of PEI-SiO_2 hybrid reacted with CO_2 to form carbamate species, whereas protonated quaternary amines (as in PEA-SiO_2 hybrid) could not react with CO_2 since they were involved in ionic bonding with the silica nanoparticles (NPs). Overall, a promising CO_2 capture capacity was obtained, exceeding the level commonly reported for monoethanolamine (MEA) solvents.

Solvent impregnated polymers (SIPs) were also considered for the NOHM encapsulation. With this technique, the project was able to encapsulate the pure NOHMs-I-PEI (polyethylenimine functionalized silica nanoparticles) inside a continuous gas permeable polymer matrix (TEGO Rad 2650) as an emulsion phase via shear emulsification and thin polymer film (1-mm thickness) containing microdroplets of NOHMs-I-PEI was produced (Figure 2). Multiple SIP films with different NOHMs-I-PEI loading (9.8–49 wt%) were successfully synthesized and it was observed that the NOHMs-I-PEI droplets (less than 10 μm) are well distributed inside the emulsion phase. Because of the small size of the microdroplets, NOHMs-I-PEI has high interfacial areas enhancing its CO_2 capture kinetics.

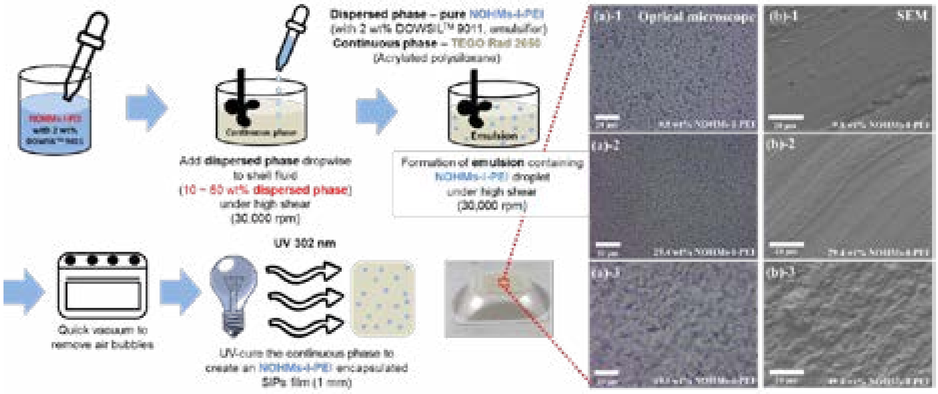

Figure 2: Synthesis of SIPs with NOHMs-I-PEI. (a) Optical microscope images of SIPs and (b) SEM images of the cross-section area of cross-linked SIPs film with different NOHMs loading: 9.8, 29.4, and 49.0 wt%. (Rim, G. et al. *Advanced Functional Materials*, 2021, *31*(21), 2010047)

The CO_2 capture using the SIP films containing 49 wt% NOHMs-I-PEI greatly improved; a remarkable 50-fold increase in CO_2 capture was observed in the SIP films compared to the bulk NOHMs-I-PEI where 5.55 mmol/g of CO_2 uptake capacity was achieved. The combination of liquid-like NOHMs, which has high CO_2 binding energy and highly CO_2 permeable polymer matrix, has a synergetic effect on the absorption of CO_2 by the extremely viscous solvents. Although the slow CO_2 capture kinetics of NOHMs-I-PEI was dramatically enhanced in the SIP films, it was found that its capture kinetics are much slower than particle sorbent systems, which have higher gas-to-solid interfacial area. Therefore, a cryogenic grinding method was used to grind the SIP films and SIP particles (average diameter ($\bar{d}^*$) = 430 μm) resulting in a 49.0 wt% NOHMs-I-PEI powder. The CO_2 absorption performance of the ground SIP particles was evaluated at different temperature conditions (25–100°C) upon exposure to 1 atm CO_2 and compared with the SIP films. The CO_2 uptake kinetics were significantly enhanced by grinding, showing a potential for encapsulation of NOHMs-I-PEI as a solid sorbent. The electrospinning process was proposed as a synthesis route for nanofibers for the encapsulation of NOHMs. Amine-based CO_2 capture materials including NOHMs-I-PEI are typically regenerated at 120°C to break the carbamate bond, which is formed by a rapid chemical reaction between amine groups and CO_2. Stable absorption/desorption behaviors of SIPs containing NOHMs-I-PEI over multiple thermal swing cycles are essential for DAC. As shown in Figure 3, the NOHMs-I-PEI/SIPs showed a great thermal stability over 20 temperature swing (50°C ↔ 120°C) cycles when compared to encapsulated pure PEI (PEI/SIPs) due to the strong ionic bond between the silica nanoparticles and PEI polymer chains. Consequently, the project was able to achieve long-term thermal stability by encapsulating highly viscous NOHMs-I-PEI inside the SIPs.

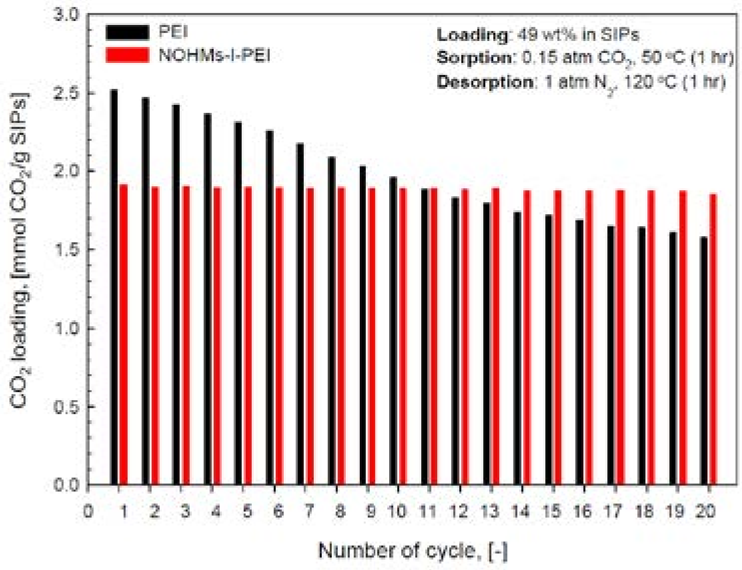

Figure 3: Recyclability of NOHMs-I-PEI/SIPs. (Rim, G. et al. *Advanced Functional Materials*, 2021, *31*(21), 2010047)

Simultaneous CO_2 and moisture capture are inevitable during the DAC process since the water concentration in ambient air is generally about 1%, which is 25-times greater than the CO_2 concentration in ambient air. The co-absorption of moisture along with CO_2 led to the breakthrough time being much longer under the wet condition, leading to increased working CO_2 capture capacity. The theoretical capture capacity of primary and secondary amines was enhanced up to twofold due to bicarbonate formation and the tertiary amines in PEI being able to react with CO_2 forming the bicarbonate in the presence of water.

Cornell has developed scalable, nanomanufacturing processes in advanced materials processing, including nanofiber formation via electrospinning. Based on the understanding of the electrospinning process, a gas-assisted electrospinning (GAES) system was designed to overcome many shortcomings of the conventional electrospinning setup. Utilizing the concentric, coaxial nozzle configuration to synergistically combine high electric field and high-speed air, GAES allows for cost-effective, facile production of polymer, metallic, and ceramic nanofibers and their hybrids and has also been successful in tailoring the placement of nanomaterials in nanofibers. The electrospun nanofibers were collected as randomly oriented non-woven mats on the collector and have been applied in air filtration application. Due to the large surface area of nanofibers and residual electric charges in electrostatically active nanofibers, a significantly enhanced filtration efficiency without increasing pressure drop was observed.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,000	1300
Bulk Density	kg/m^3	660	300
Average Particle Diameter	mm	0.4	0.0001 - 0.005
Particle Void Fraction	m^3/m^3	0	0.25
Packing Density	m^2/m^3	$9x10^3$	$2x10^6$
Solid Heat Capacity @ STP	kJ/kg-K	1.75	1.75
Crush Strength	kg_f	140 MPa	<< 140 MPa
Attrition Index	-	0.05	< 0.1
Thermal Conductivity	W/(m-K)	0.15	15
Manufacturing Cost for Sorbent	$/kg	1,398	1300
Adsorption			
Pressure	bar	1	1
Temperature	°C	25	10 - 40
Equilibrium Loading	g mol CO_2/kg sorbent	1.66	2
Heat of Adsorption	kJ/mol CO_2	-85	-85
CO_2 Adsorption Kinetics	gmol/time	0.08 gmol/kg/hr	1.0 gmol/kg/hr
Desorption			
Pressure	bar	0	0
Temperature	°C	120	<100
Equilibrium CO_2 Loading	g mol CO_2/kg	0.02	0.04
Heat of Desorption	kJ/mol CO_2	60	85
CO_2 Desorption Kinetics	gmol/time	-12 gmol/kg/hr	-20 gmol/kg/hr
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	Air filtration media	
Flue Gas Flowrate	kg/hr	n/a	
Space Velocity	hr^{-1}	n/a	
Volumetric Productivity	$gmol_{CO2}/(hr\ l_{absorber\ bed})$	n/a	
CO_2 Recovery, Purity, and Pressure	% / % / bar	— n/a	—
Adsorber Pressure Drop	bar	Negligible	
Degradation	% capacity fade/cycle	n/a	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	n/a	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Atmospheric Air Feed-Gas Assumptions – Update values below to describe the air feed-gas pressure, temperature, and composition entering the capture system:

	Composition						
Pressure	vol%					ppmv	
14.7 psia	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
	0.04	variable	78.09	20.95	0.93	trace	trace

Chemical/Physical Sorbent Mechanism – Chemisorption of CO_2 onto amine-functionalized silica nanoparticles (NOMHs).

Sorbent Contaminant Resistance – Hydrophobic polymeric and ceramic encapsulation materials provide water-rejection while maintaining high CO_2 permeability and selectivity. The hydrophobic surface also allows easy removal of any particles collected onto fibers by washing.

Sorbent Attrition and Thermal/Hydrothermal Stability – PEI-tethered silica (e.g., NOHMs) has been demonstrated to possess enhanced oxidative thermal stability at elevated temperatures with lower capacity loss across multiple cycles, compared to neat PEI. Since the filter design does not require the movement of sorbent, there are no concerns related to sorbent attrition.

Process Design Concept – See Figure 4.

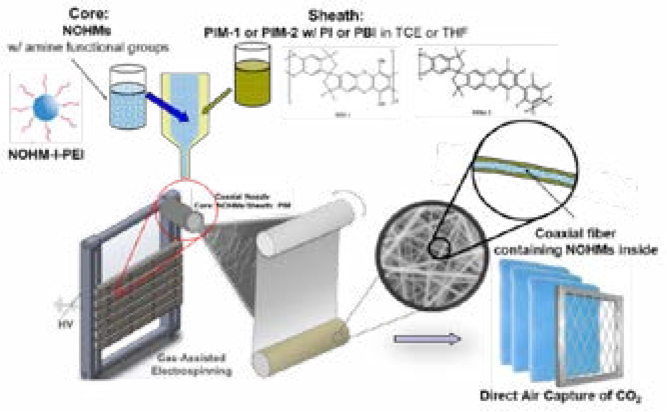

Figure 4: Proposed module design.

TABLE 2: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	148.12	120
Cost of Carbon Avoided	\$/tonne CO_2	21.5 ~ 124 (vary by source)	20 – 100 (vary by source)
Capital Expenditures	\$/tonne CO_2	825	1,000
Operating Expenditures	\$/tonne CO_2	-	93.8

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured. Current R&D value is the total capital for a DAC system with PIM/NOHM nanofibers.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured. The target R&D value is from work by Wilcox et.al (2019) for solid sorbent DAC system.

Calculations Basis – Current R&D values are obtained using the Technoeconomic Assessment Tool for Direct Air Capture (Wilcox, J. et al, March 2020), which is based on the main assumptions outlined in NASEM 2019 Sorbent Mid-Range (https://doi.org/10.17226/25259).

Scale of Validation of Technology Used in TEA – Modeling.

technology advantages

- NOHMs embedded in polymeric nanofibers will offer enhanced capture kinetics and improve the long-term recyclability with minimized sorbent regeneration energy due to hydrophobicity of the polymeric nanofibers.
- NOHMs do not suffer from solvent loss in air streams due to their negligible vapor pressure.
- NOHM-encapsulated nanofibers have a greater interfacial area for enhanced air-NOHM interactions to overcome mass transfer-related issues associated with high viscosity and more flexibility for the reactor design with minimum pressure drop.
- Novel tailored material that incorporates the desirable properties of both liquid-like NOHMs and solid nanofiber sorbents enables ease of deployment, while addressing the challenges with both.

R&D challenges

- Incorporation of NOHM-based hybrid sorbents with electrospun fibers.
- Moving to large-scale production while maintaining higher capture capacity and selectivity, and improved water tolerance.

status

This project was completed on October 31, 2022. Columbia University successfully synthesized NOHMs with oxidative thermal stability and optimized techniques to successfully electrospin PIM-1 and PIM-2 fibers in the 0.8-2-micron dimensional range. Encapsulated NOHMs have been tested and have shown promising thermal cyclability and CO_2 capture performance across multiple loading/regeneration cycles. High-level techno-economic analysis (TEA) estimates show a large manufacturing plant (30 tonne/yr) for electrospun fiber sorbents would yield \$226/kg sorbent.

available reports/technical papers/presentations

Ah-Hyung Park, "Next Generation Fiber-Encapsulated Nanoscale Hybrid Materials for Direct Air Capture with Selective Water Rejection," 2022 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_CDR15_Park.pdf*.

Ah-Hyung (Alissa) Park, "Next Generation Fiber-Encapsulated Nanoscale Hybrid Materials for Direct Air Capture with Selective Water Rejection," 2021 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Park.pdf*.

Ah-Hyung (Alissa) Park, "Next Generation Fiber-Encapsulated Nanoscale Hybrid Materials for Direct Air Capture with Selective Water Rejection," Direct Air Capture Kickoff Meeting presentation, Pittsburgh, PA, February 2021. *https://netl.doe.gov/sites/default/files/netl-file/21DAC_Park.pdf*.

MIL-101(Cr)-Amine Sorbents Evaluation Under Realistic Direct Air Capture Conditions

primary project goal

Georgia Tech Research Corporation investigated the use of hybrid sorbents based on metal-organic framework (MOF, MIL-101(Cr)) materials functionalized with amine groups for the direct air capture (DAC) of carbon dioxide (CO_2) at sub-ambient conditions. The primary goal of the project was to tailor MIL-101(Cr)-based sorbents to overcome technical barriers associated with their application at sub-ambient temperatures/conditions and validate their amenability to practical DAC application.

technical goals

- Develop powder MIL-101(Cr) amine sorbents and baseline testing.
- Study of the influence of amine molecular weight on sorbent performance in air feeds containing 400 parts per million (ppm) CO_2 at sub-ambient conditions (in the range of -20°C and 25°C) and varied humidity.
- Investigate the incorporation of MIL-101(Cr) into fibers and monoliths.
- Complete computational studies to model adsorption and desorption equilibrium and kinetics of MIL-101(Cr)-amine material.
- Develop adsorption/desorption models used to predict DAC system parameters, including energy consumption, sorbent efficiency, and system size.
- Develop of three-dimensional printing procedure for MIL-101(Cr) monoliths.
- Develop an understanding of breakdown pathways and confirm the revolutionary stability of the new solvent using various laboratory techniques.

technical content

MOFs are two- or three-dimensional crystalline structures composed of metal nodes coordinated by organic linkers. These hybrid materials have demonstrated great potential for the capture of CO_2, with promising applications, either as CO_2 sorbents themselves or as supports for amine-based CO_2 capture. The use of MOFs, as compared to other commonly used supports (e.g., silica), provides a range of advantages, including:

i. High Brunauer–Emmett–Teller (BET) surface areas.
ii. Tunable pore characteristics.
iii. High pore volume.
iv. High density of open metal sites.
v. Stability under a wide range of conditions.

The last three features are highly desirable for functionalization of the support with amines. MIL-101(Cr) and $Mg_2(dobpdc)_2$ are two MOFs that offer potential to

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Metal-Organic Framework-Based Sorbent for DAC

participant:
Georgia Tech Research Corporation

project number:
FE0031952

predecessor projects:
N/A

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partners:
N/A

start date:
06.01.2019

percent complete:
100%

be a tunable platform for practical DAC. However, Mg_2(dobpdc) has been reported to be unstable under humid conditions, and amine-ligated Mg_2(dobpdc) has unsuitable sorption kinetics under DAC conditions. Contrary to this behavior, MIL-101(Cr) has been reported to possess good stability in boiling water, over a variety of pH conditions, and to exposure to sulfur dioxide (SO_2) and nitric oxide (NO). Thus, in this proposed work, the aim is to develop MIL-101(Cr)-based sorbents tailored for deployment under specific DAC conditions. MIL-101(Cr) is a three-dimensional framework with open chromium metal sites that, together with the open space within the porous framework, can provide “loading sites” for various amine species designed for CO_2 capture (Figure 1). The capabilities of this amine-functionalized MOF for CO_2 capture at varied CO_2 concentrations have been demonstrated, with reported CO_2 capacities under DAC conditions as high as 1.35 mmol/g (polyethyleneimine [PEI]-MIL-101(Cr)) and 2.8 mmol/g (TREN-MIL-101(Cr)). Although promising candidates as DAC sorbents, prior work evaluating the performance of these materials has focused on CO_2 adsorption at temperatures ranging from 25–100°C and studies of the effect of humidity have been minimal.

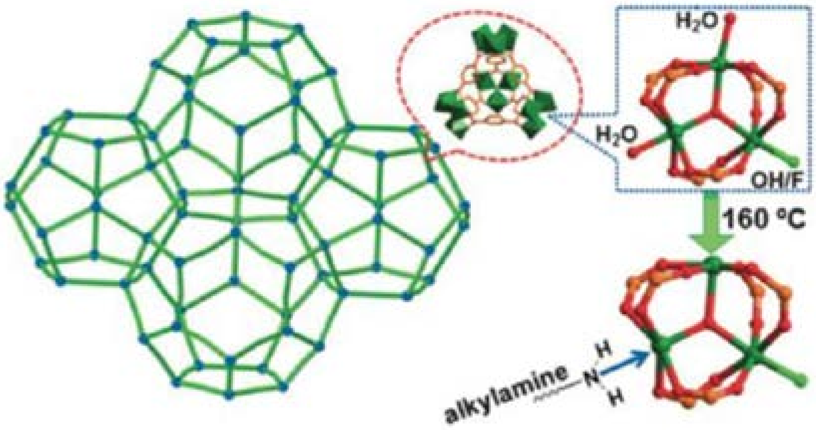

Figure 1: Schematic of amine functionalization of MIL-101(Cr).

The effective removal of carbon from the atmosphere by an air capture technology is known to depend on the specific climate (e.g., temperature and relative humidity [RH]) at a given location, so currently available data are only relevant to hot desert climates. If one considers the temperature spectrum for all the climate regions of the United States in 2019 (Figure 2), the variations in the temperature profiles are noticeable. Furthermore, sub-ambient temperatures (defined herein as temperatures below 20°C) are predominant among these regions for a large portion of the year. From a DAC deployment perspective, the diversity in the profiles reported in Figure 2 would lead to distinct temperatures for CO_2 capture at each of these locations. This would cause significant performance inconsistencies if an identical DAC technology were implemented across these locations. In the proposed work herein, the aim is to investigate the CO_2 adsorption capabilities of MIL-101(Cr)-amine sorbents focusing on the overlooked temperature range: (-20 to 20°C).

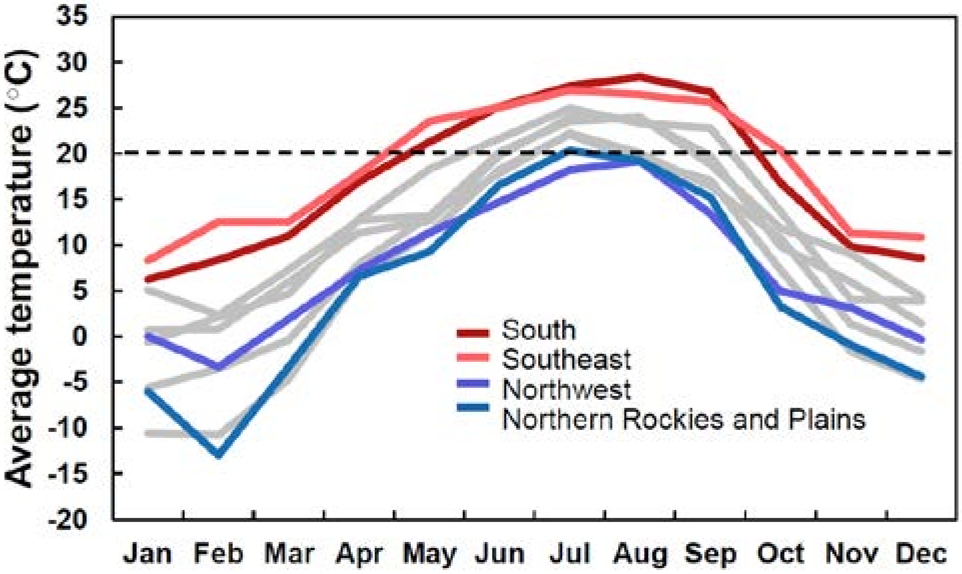

Figure 2: Summary of 2019 average monthly temperatures for U.S. climate regions. Data from the National Climatic Data Center. The gray lines include the following climate regions: Southwest, Ohio Valley, West, Northeast, Upper Midwest.

Separation Mechanism of MIL-101(Cr)/amine [FOA MRC1(b)]

The MIL-101(Cr)-amine hybrid materials follow the zwitterionic mechanism of CO_2 capture. This is the most common mechanism for solid adsorbents, where a zwitterion is formed via the interaction between CO_2 and an amine (process 1 in Figure 3). In the presence of a base, the zwitterion deprotonates to produce a carbamate (process 2 in Figure 3). In dry sorption conditions, a second amine species acts as the base, while in humid conditions, the water or hydroxide group may play this role. In humid conditions, one amine is able to capture up to one CO_2 molecule, improving the theoretical maximum CO_2/N ratio (i.e., amine efficiency) from 0.5 to 1. Under dry conditions, the placement of amines in close proximity (i.e., at high loading) is often used to achieve high amine efficiencies. For both sorption conditions (dry or humid), a sorbent that facilitates the access of CO_2 to the amine sites is required. In this direction, it is anticipated that for CO_2 capture under sub-ambient conditions, the decrease in temperature will increase the rigidity of polymeric amines, leading to high diffusional resistances and therefore compromising the reaction kinetics of CO_2 adsorption. To tackle this challenge, the project proposed a design of the MOF-amine hybrid sorbents where the effect of low molecular weight (LMW) aminopolymers on the CO_2 adsorption capacity and kinetics at sub-ambient conditions will be evaluated. Furthermore, the hypothesis is that the open Cr coordination sites in the MIL-101(Cr) will allow retention of LMW amines (e.g., TREN and tetraethylenepentamine [TEPA]), circumventing issues related to amine losses due to volatility. These losses will also be alleviated by the use of mild desorption temperatures (e.g., as low as 50°C). This approach introduces the idea of sorbent optimization based on DAC deployment location, where the use of LMW amine-based sorbents will be more favorable at ultra-low temperature, while the use of high molecular weight amine-based sorbents would be targeted for elevated temperature operation. The choice of MOF supports is crucial in this design as the absence of open metal coordination sites in silica, alumina, and related supports would preclude use of volatile LMW amines.

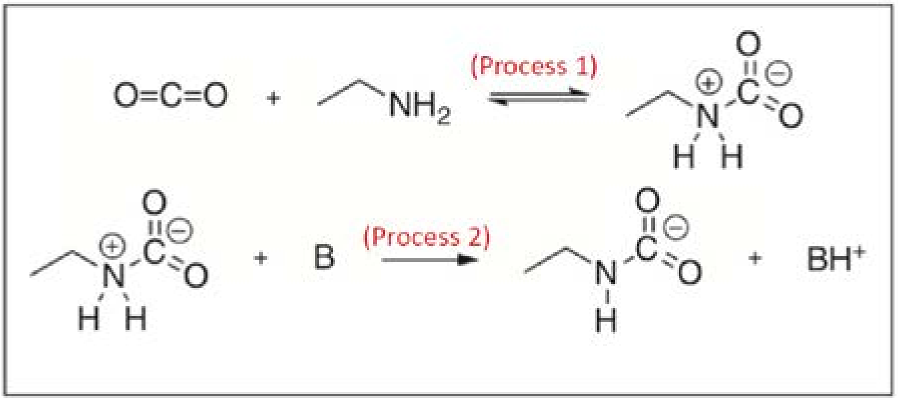

Figure 3: Mechanism of CO_2 capture involving (1) interaction between CO_2 and an amine followed by (2) deprotonation of resulting zwitterion in presence of a base.

Material Compatibility with DAC Conditions

The deployment of solid adsorbents for DAC applications offers a lower energy penalty during the adsorption-desorption process compared to aqueous sorbents, with the sorbents categorized as physisorbents or chemisorbents. At room temperature, physisorbent materials, such zeolite-based adsorbents, have shown appealing CO_2 capacities in pure CO_2 (~135 mg CO_2/g sorbent at 25°C in pure CO_2). However, given the physisorption nature of the uptake and consequential low selectivity between gases, these materials perform poorly at low CO_2 partial pressures, as demonstrated by the isotherms in Figure 4a. In this direction, chemical adsorption of CO_2 to the solid sorbent is more appropriate for DAC application, as it has been shown to be more efficient at extremely low CO_2 concentrations (ca. 400 ppm) (Figure 4a). Chemisorbents can be created by the functionalization of a solid support (e.g., silica, alumina, or MOF) by amines. Moreover, functionalizing the support with amines that exhibit optimum adsorbate-adsorbent interaction strength, such as PEI (-65 kJ/mol), provided near-ideal separation efficiency for DAC concentrations in temperature swing adsorption (TSA). In fact, in previous studies using MIL-101(Cr) as CO_2 sorbents at 25°C, it was demonstrated that the CO_2 adsorption performance of MIL-101(Cr) is greatly benefited by functionalization with amines, such as PEI and TREN (Figure 4b).

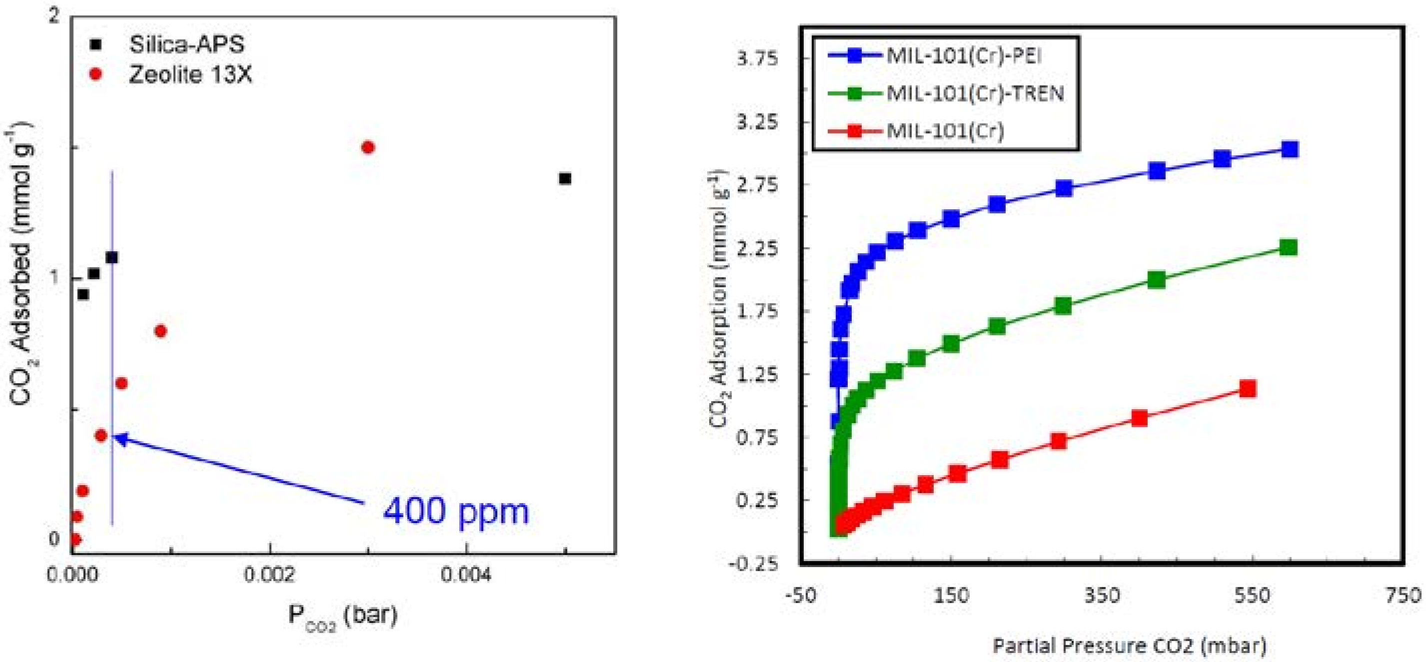

Figure 4: CO_2 adsorption as function of CO_2 partial pressure for: (a) physisorbent (zeolite) versus chemisorbent (silica-APS). (b) Bare MIL-101(Cr), MIL-101(Cr)-TREN (grafted), and MIL-101(Cr)-PEI.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	500 (estimated)	500
Bulk Density	kg/m^3	350 (measured)	350
Average Particle Diameter	mm	Crystal size: 1.5 – 8 x 10^{-4} Fiber diameter: 0.3 – 1.2 Monolith channel opening: 1 -6 (measured)	No change
Particle Void Fraction	m^3/m^3	Fibers: 0.35 (within fiber wall)	No change
Packing Density	m^2/m^3	Fibers: 5,000 – 10,000 (for bundle of fibers in shell and tube configuration)	No change
Solid Heat Capacity @ STP	kJ/kg-K	Crystals: 0.892 Fibers: 0.47 Monolith: 0.84	No change
Crush Strength	kg_f	N/A	N/A
Attrition Index	-	N/A	N/A
Thermal Conductivity	W/(m-K)	N/A	N/A
Manufacturing Cost for Sorbent	$/kg	15	15
Adsorption			
Pressure	bar	0.0004 bar CO_2, 1 bar total	0.0004 bar CO_2, 1 bar total
Temperature	°C	-20 to 20°C	-20 to 20°C
Equilibrium Loading	g mol CO_2/kg	1.8 (PEI_MIL-101(Cr)) 2.1 (TEPA_MIL-101(Cr)) (Measured at 25°C)	1 – 4 (at -20°C)
Heat of Adsorption	kJ/mol CO_2	-90	-60
CO_2 Adsorption Kinetics	gmol/time	0.016 mmol/g/min (initial adsorption rate, measured at 25°C)	0.02 mmol/g/min (at -20°C)
Desorption (temperature swing adsorption)			
Pressure	bar	0.005 bar CO_2	0.1 – 1 bar CO_2
Temperature	°C	25 – 60°C	25 – 60°C
Equilibrium CO_2 Loading	g mol CO_2/kg	<0.2 (at 25 – 60°C)	<0.2 (at 25 – 60°C)
Heat of Desorption	- kJ/mol CO_2	40 - 95	60
CO_2 Desorption Kinetics	gmol/time	0.045 mmol/g/min (estimated)	0.1 mmol/g/min (at 25°C) 0.2 mol/g/min (at 60°C)

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Atmospheric Air Feed-Gas Assumptions:

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	-4 °F	0.04	variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Amines in PEI or TEPA react with CO_2 to form ammonium carbamate under the dry condition and potentially also bicarbonate or carbonate in the presence of water.

Sorbent Contaminant Resistance – In the targeted ambient air gas stream, oxygen and water can be the contaminants deteriorating the performance of the developed sorbent, However, the effect of the oxygen is assumed to be negligible due to the low operating temperature (from -20°C to 25°C). Under 70% relative humidity at -20°C, TEPA-impregnated MIL-101(Cr) showed promising stability to humidity with ~0.8 mmol of CO_2/g of working capacity.

Sorbent Attrition and Thermal/Hydrothermal Stability – Developed amine-MIL-101(Cr) materials were stable for 15 cycles of temperature swing adsorption and desorption process (from -20 to 25°C or 60°C) under dry conditions. Also, during five cycles of the breakthrough experiment at -20°C 70% relative humidity with the same temperature swing process, TEPA-impregnated MIL-101(Cr) showed stable working capacity with ~0.8 mmol of CO_2/g of sorbent.

Flue Gas Pretreatment Requirements – Targeted air gas stream is directly from the ambient atmosphere.

Sorbent Make-Up Requirements – MIL-101(Cr) synthesis requires chromium precursor and terephthalic acid as an organic linker. PEI and TEPA are used to functionalize MIL-101(Cr) for enhanced CO_2 capture performance. To incorporate MIL-101(Cr) into contactors such as fiber and monolith, cellulose acetate (CA) is used as a typical polymer matrix.

Waste Streams Generated – During the sorbent and contactor synthesis steps, chemical solvents such as methanol, hexane, N-methyl-2-pyrrolidone are generated as waste streams. In the CO_2 adsorption process, CO_2 depleted air, high purity CO_2, and water are generated.

Process Design Concept – Process flowsheet shown in Figure 5. Temperature vacuum swing adsorption using fiber or monolith contactor.

Proposed Module Design – Fiber and monolith.

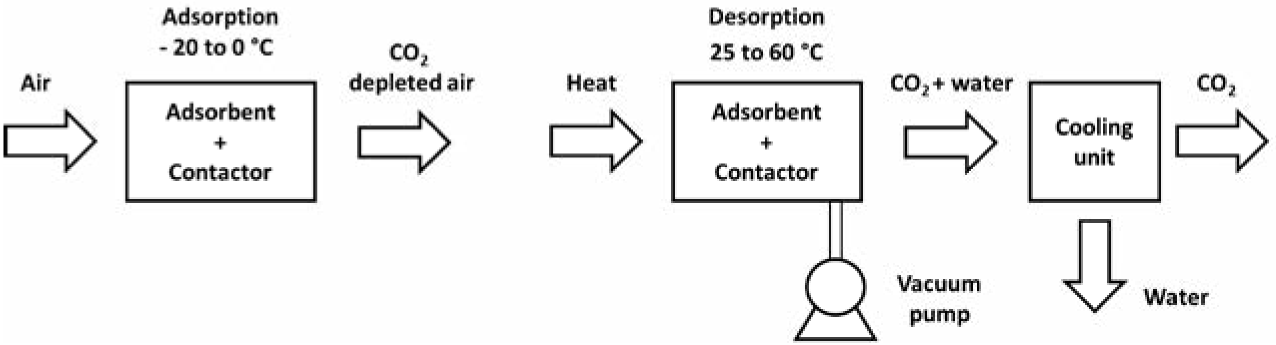

Figure 5: Process Flowsheet/block diagram.

Calculations Basis – Current R&D values for process parameters sometimes refer to estimates from the paper below, whereas sorbent performance parameters refer to new data generated in this project. Sinha, Anshuman, et al. "Systems design and economic analysis of direct air capture of CO_2 through temperature vacuum swing adsorption using MIL-101 (Cr)-PEI-800 and mmen-Mg_2 (dobpdc) MOF adsorbents." Industrial & Engineering Chemistry Research 56.3 (2017): 750-764.

technology advantages

- Chemical adsorption of CO_2 to the solid sorbent more efficient at extremely low CO_2 concentrations (ca. 400 ppm).
- Carbon dioxide adsorption performance of MIL-101(Cr) is greatly benefited by functionalization with amines.
- Carbon dioxide uptake at sub-ambient temperatures as low as -20°C enables operation in the temperature range of -20°C to 20°C will cover a wide range of deployment locations.
- Regeneration of sorbent occurs at ambient 25°C.

R&D challenges

- Carbon dioxide capture under sub-ambient conditions will increase the rigidity of polymeric amines, leading to high diffusional resistances and challenges in the reaction kinetics of CO_2 adsorption.

status

This project was completed on September 30, 2022. Georgia Tech Research Corporation completed preparation of MOF MIL-101(Cr) powder sorbents. The amine-impregnated MIL-101(Cr) powder show promising CO_2 uptake at -20°C due to enhanced physisorption at cold temperatures. The sorbents' sub-ambient capture capacity of 1.1 mmol/g at -20°C and low regeneration temperature of 25°C is believed to be a physisorption-dominant mechanism. The MIL-101(Cr)-based fiber sorbents were also manufactured and tested, showing 400 ppm CO_2 uptake of 1.2 mmol/g at -20°C. The CA/MIL-101/PEI monoliths were prepared using 3D-printing solvent-based additive manufacturing technique. Direct air CO_2 capture performance under both dry and wet sub-ambient conditions were evaluated by breakthrough experiments. The CO_2 uptake capacities were boosted by pre-adsorbed H_2O, but the sorption kinetics decreased relative to the base case. The MOF MIL-101(Cr) with 30% TEPA had a higher capacity and production rate compared to the sorbent with 30% PEI.

available reports/technical papers/presentations

Christopher W. Jones, Ryan P. Lively, Matthew J. Realff, "MIL-101(Cr)-Amine Sorbents Evaluation Under Realistic Direct Air Capture Conditions," Final Technical Report, December 2022. *https://www.osti.gov/servlets/purl/1907464/*.

Christopher W. Jones, Ryan P. Lively, Matthew J. Realff, "MIL-101(Cr)-Amine Sorbents Evaluation Under Realistic Direct Air Capture Conditions," 2022 Project Closeout Meeting, Pittsburgh, PA, September 2022. *https://netl.doe.gov/projects/plp-download.aspx?id=14174&filename=MIL-101+(Cr)-Amine+Sorbents+Evaluation+Under+Realistic+Direct+Air+Capture+Conditions.pptx*.

Christopher W. Jones, Ryan P. Lively, Matthew J. Realff, "MIL-101(Cr)-Amine Sorbents Evaluation Under Realistic Direct Air Capture Conditions," 2022 Carbon Management Project Review Meeting, Pittsburgh, PA, August 2022.

Christopher W. Jones, Ryan P. Lively, Matthew J. Realff, "MIL-101(Cr)-Amine Sorbents Evaluation Under Realistic Direct Air Capture Conditions," NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Jones.pdf*.

Ryan P. Lively, "MIL-101(Cr)-Amine Sorbents Evaluation Under Realistic Direct Air Capture Conditions," Direct Air Capture Kickoff Meeting presentation, Pittsburgh, PA, February 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11046&filename=MIL-101(Cr)-Amine+Sorbents+Evaluation+Under+Realistic+Direct+Air+Capture+Conditions.pdf*.

Christopher W. Jones, Ryan P. Lively, Matthew J. Realff, "MIL-101(Cr)-Amine Sorbents Evaluation Under Realistic Direct Air Capture Conditions," Project Kickoff Meeting presentation, Pittsburgh, PA, December 2020. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11047&filename=MIL-101(Cr)-Amine+Sorbents+Evaluation+Under+Realistic+Direct+Air+Capture+Conditions.pdf*.

Guanhe Rim, Fanhe Kong, Mingyu Song, Cornelia Rosu, Pranjali Priyadarshini, Ryan P. Lively, and Christopher W. Jones," Sub-Ambient Temperature Direct Air Capture of CO_2 using Amine-Impregnated MIL-101(Cr) Enables Ambient Temperature CO_2 Recovery," JACS Au 2022, 2, 2, 380–393, *https://doi.org/10.1021/jacsau.1c00414*.

Low Regeneration Temperature Sorbents for Direct Air Capture of CO_2

primary project goal

Susteon Inc., in partnership with the University of Wyoming (UWy), developed solid sorbents with fast kinetics and low regeneration temperature catalyzed by an ionic liquid for direct air capture of carbon dioxide (CO_2) to reduce energy consumption for sorbent regeneration and lower the cost of DAC.

technical goals

- Develop amine-doped solid sorbents catalyzed by an IL that have the potential to increase the CO_2 desorption rates significantly at desorption temperatures of approximately 80°C.
- Evaluate the catalyzed amine-based sorbents to determine CO_2 desorption and adsorption kinetics.
- Based on the experimental results, develop a conceptual process design for the sorbents applied in a DAC system and conduct a preliminary cost analysis to assess the potential of the novel sorbent to reduce the cost of DAC.

technical content

Sorbents for DAC application must have several characteristics: (i) high selectivity for CO_2 adsorption over the other components present in the air (such as water [H_2O], nitrogen [N_2] and oxygen [O_2]), (ii) high cyclic CO_2 working (adsorption) capacity, (iii) mild conditions for regeneration (usually induced by pressure or temperature swings), (iv) high stability and resistance against impurities and moisture, and (v) fast CO_2 adsorption and desorption kinetics. Amine-doped solid sorbents have been proven effective for DAC and can be regenerated by heat or by a combination of heat and steam. Lowering the regeneration temperature, and hence opening a way to use waste heat for sorbent regeneration, can significantly lower the cost of DAC. The IL catalysts can be easily added to amine-doped solid sorbents because the IL is not volatile and can be easily mixed with possible amine molecules such as polyethyleneimine (PEI), polypropyleneimine (PPI), etc.

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Amine-Doped Sorbent Catalyzed by Ionic Liquid for Direct Air Capture of CO_2

participant:
Susteon Inc.

project number:
FE0031965

predecessor projects:
N/A

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James Zhou
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partners:
University of Wyoming

start date:
10.01.2020

percent complete:
100%

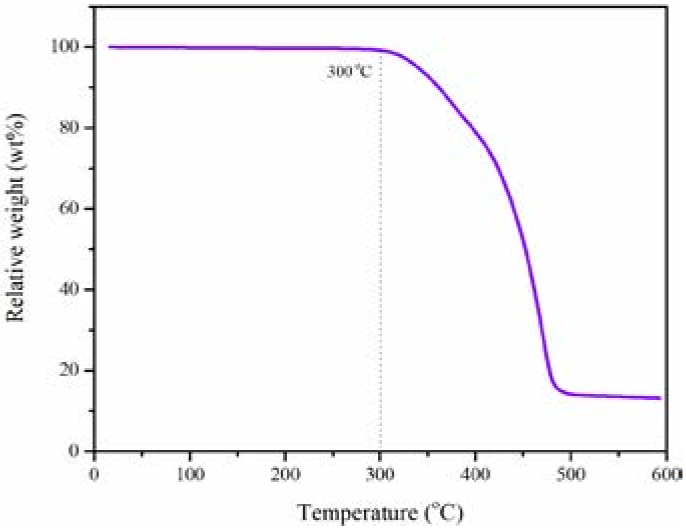

Figure 1: TGA confirming catalyst thermal stability at 300°C.

This project was aimed at using the IL as catalyst in amine-based direct air capture (DAC) sorbents to enhance adsorption and desorption kinetics and to lower the cost of DAC. The key to lower the cost of DAC rests on three factors: (1) the energy required for releasing CO_2 from the capture agents; (2) reduce the size of the air contactor, thus lowering the capital costs; and (3) the pressure required to move the air through the capture device.

The project developed amine-doped solid sorbents catalyzed by the IL with increased CO_2 adsorption and desorption rates. In laboratory tests, the proprietary IL catalyst was shown to increase the CO_2 desorption rate by up to 60 times at 85°C when added in parts per million (ppm) levels as a catalyst to a monoethanolamine (MEA) solvent. Similar results for a different solvent have been peer-reviewed and published in the Nature Communications journal in mid-2018. This transformational discovery enables solvent regeneration at much lower temperatures to dramatically reduce energy consumption, amine degradation, and solvent emissions.

This project successfully scaled up the catalyst synthesis process from gram quantities to kilogram quantities. The large batch catalyst was characterized and compared with small laboratory synthesized samples and no difference was found in the chemical and physical properties between the two samples. The produced batch of IL catalyst was characterized with TGA, ^{1}H-NMR, ^{13}C-NMR, FT-IR, and ESI-MS; ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker spectrometer (400 MHz). Thermogravimetric analysis (TGA) of the IL was obtained using a TA Instruments SDT Q600 apparatus with a heating ramp of 10°C min^{-1} at the temperature of 20–600°C with a nitrogen flow rate of 100 mL min^{-1}. The characterization results showed that the IL batch met all chemical specifications. The TGA results, shown in Figure 1, indicate that the IL catalyst is stable up to 300°C.

The impact of IL catalyst concentration in the sorbent was studied. The team prepared 50 wt% PEI on fumed silica with 0, 100, 200, and 300 ppm by weight of IL catalyst and measured their CO_2 breakthrough behavior. The data from these measurements are shown in Figure 2. As seen in this figure, fumed silica (FS)-PEI-50 with 100 ppm catalyst showed the best adsorption performance with the longest breakthrough time. Carbon dioxide adsorption performance declined slightly when the catalyst loading was increased from 100 ppm to 200 ppm. As the catalyst loading further increased to 300 ppm, CO_2 adsorption performance showed no improvement as compared with that of the sorbent without catalyst. Therefore, catalyst loading needs to stay within 100 to 200 ppm range. Through optimization and testing, 200 ppm was selected as the final catalyst loading and 35 wt% PEI on fumed silica was selected as the final sorbent composition. The selection of 35 wt% PEI resulted from testing of sorbents with 20, 35, and 50 wt% PEI and from consideration of PEI loading on PEI accessibility.

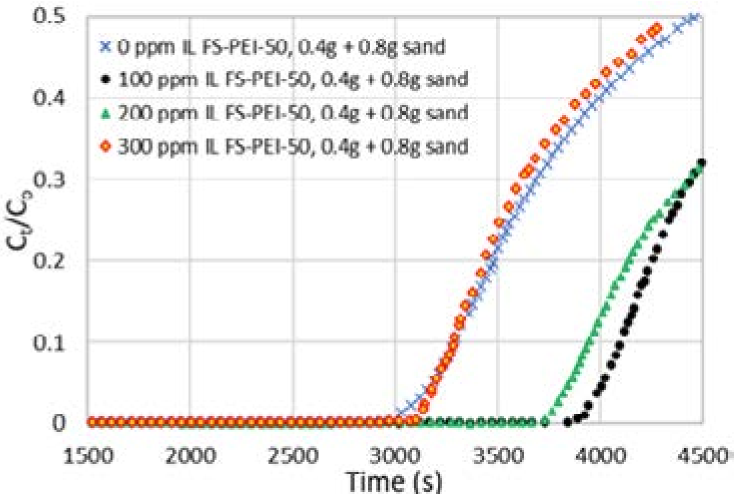

Figure 2: Effect of catalyst concentrations.

The cyclic stability of sorbent in both dry and humid air was also investigated. These cyclic studies consisted of an adsorption step in 400 ppm CO_2 with 0% or 100% relative humidity (RH) followed by a heating step to 110°C in flowing N_2 to facilitate endothermic desorption of CO_2. The cycle results for 100 ppm IL catalyzed FS-PEI with 35 wt% PEI loading are shown in Figure 3. Carbon dioxide breakthrough capacity remained stable with minor variations under both dry and humid conditions. The breakthrough times and hence breakthrough CO_2 capacity were significantly greater in the presence of humidity. Fewer cycles were run under humid conditions due to the long breakthrough time. The data shown in Figure 3 confirm that the IL catalyzed sorbents have good cyclic stability and high cycle capacity.

The IL catalyzed FE-PEI sorbent has shown high rates of CO_2 adsorption (as high as 0.1 mol/kg/min) as seen in Figure 4, which shows that higher inlet air space velocity leads to higher rate of CO_2 adsorption, indicating that the adsorption is mass transfer limited and not limited by reaction kinetics.

The project demonstrated the IL catalyzed FS-PEI sorbents for DAC application and provided proof that these sorbent compositions have been successfully developed on commercially available fumed silica support. Furthermore, the IL catalyst was scaled up to a kilogram scale. The team produced about 20 kg of this catalyst at a commercial manufacturer for several testing campaigns. The best sorbent composition identified was PEI on fumed silica with 200 ppm IL catalyst.

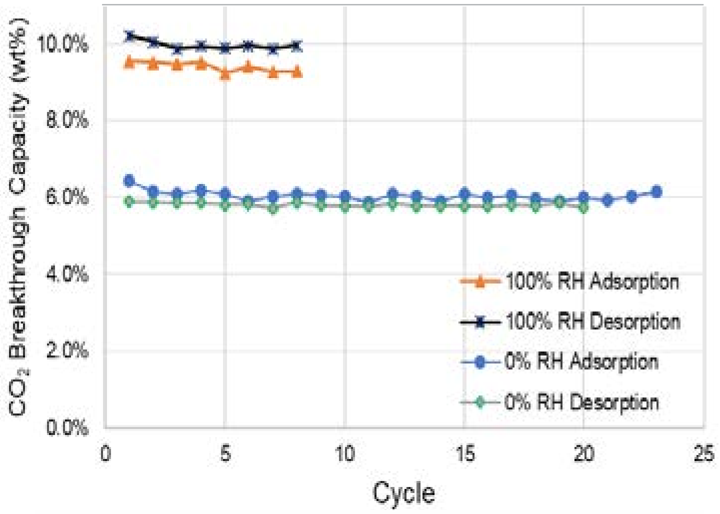

Figure 3: Cyclic stability of 100 ppm IL catalyzed sorbent.

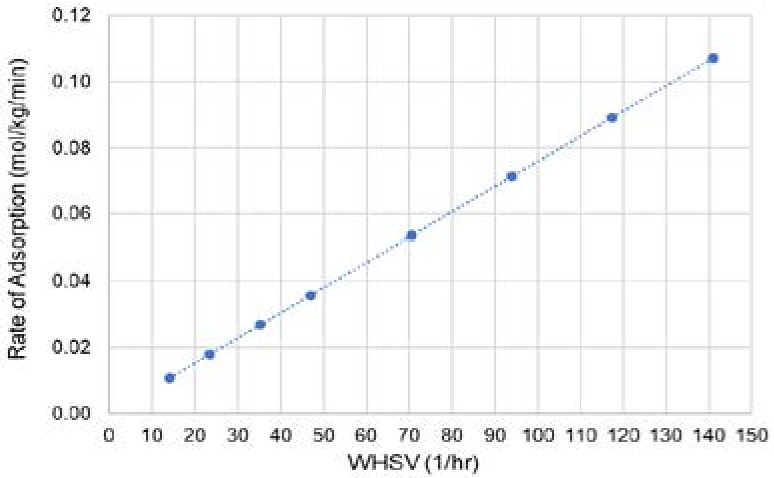

Figure 4: CO_2 adsorption rate as a function of gas weight hourly space velocity (WHSV).

The IL catalyzed amine-doped solid sorbents are proven effective for DAC applications and can be regenerated by heat or by a combination of heat, steam, and vacuum. The best sorbent formulation was shown (see Figure 5) to have a CO_2 breakthrough capacity twice that of the non-catalyzed sorbent, in laboratory tests with air at 75% RH. The CO_2 adsorption rate was also 40% higher than that of the non-catalyzed sorbent. This type of sorbent has the attributes required for lowering the overall cost of DAC with high CO_2 capacity and high rate of adsorption and desorption.

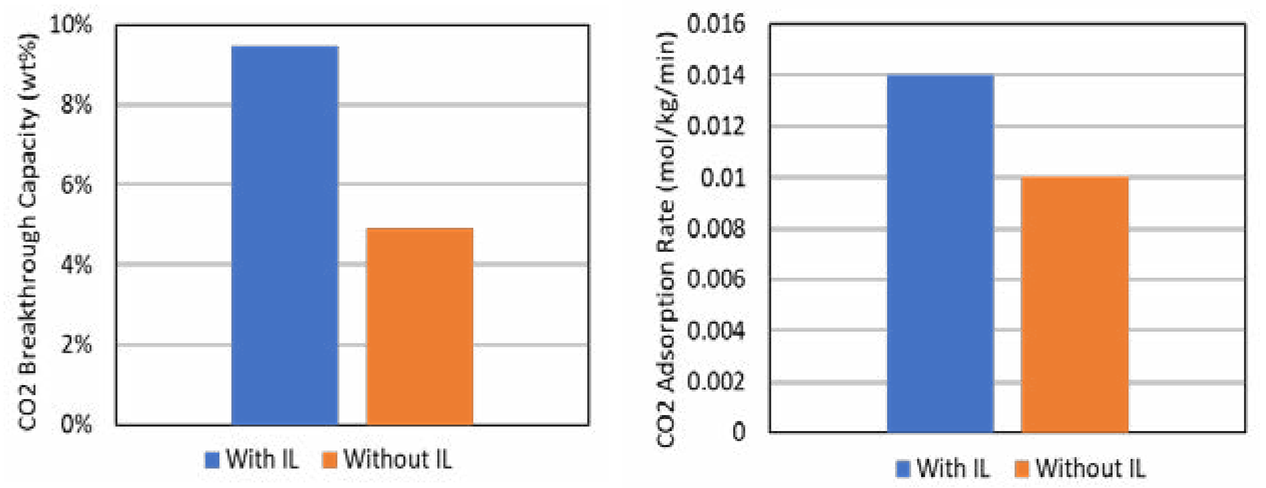

Figure 5: Performance comparison of FS-PEI sorbents with and without IL catalyst.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,700	1,700
Bulk Density	kg/m^3	380	<200[a]
Average Particle Diameter	mm	00.25	0.1[b]
Particle Void Fraction	m^3/m^3	N/A	0.46[c]
Packing Density	m^2/m^3	2,000 – 3,000	2,000 – 2,400[d]
Solid Heat Capacity @ STP	kJ/kg-K	1.15	0.83
Crush Strength	kg$_f$	N/A	N/A
Attrition Index	-	9%	N/A
Thermal Conductivity	W/(m-K)	0.045	0.045
Manufacturing Cost for Sorbent	\$/m^3	20,000	10,000

Adsorption			
Pressure	bar	1 – 1.1	1 – 1.1
Temperature	°C	25	Ambient
Equilibrium Loading	g mol CO_2/kg	1.6 – 2.5	1.6 – 2.5
Heat of Adsorption	kJ/mol CO_2	80	80
CO_2 Adsorption Kinetics	gmol/time	1.0	2.0
Desorption			
Pressure	bar	0.9	0.9
Temperature	°C	100 – 120	85
Equilibrium CO_2 Loading	g mol CO_2/kg	0.1	0.1
Heat of Desorption	kJ/mol CO_2	80	80
CO_2 Desorption Kinetics	gmol/time	10	20

[a] Bulk density of monolith

[b] Sorbent washcoat thickness

[c] Porosity of the monolith

[d] Packing density calculated as the surface area of the active sorbent divided by the overall monolith volume, including voidage.

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – “Current” is market price of material, if applicable; “Target” is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Atmospheric Air Feed-Gas Assumptions – Update values below to describe the air feed-gas pressure, temperature, and composition entering the capture system:

	Composition						
	vol%					ppmv	
Pressure	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.7 psia	0.04	variable	78.09	20.95	0.93	trace	trace

TABLE 2: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	143	100
Cost of Carbon Avoided	\$/tonne CO_2	—	—
Capital Expenditures	\$/tonne CO_2	52	52
Operating Expenditures	\$/tonne CO_2	91	48

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

technology advantages

- Platform technology for enhancing performance of all amine-based CO_2 DAC systems.
- Catalyst can be added to any amine-based sorbents or solvents for improved sorption and desorption kinetics.
- Low-risk technology that can be applied to existing low-pressure-drop contactor designs.
- The sorbent-based process enables a reduction in the energy required for sorbent regeneration and increased sorbent lifetime/stability due to operation at lower desorption temperatures.

R&D challenges

- Developing an IL catalyst that can be added to amine-doped DAC sorbents to increase desorption kinetics.
- Developing sorbents with low regeneration temperature and low regeneration energy for direct air capture of CO_2.

status

This project was completed on September 30, 2022. Susteon's patented IL catalyst enhanced cyclic CO_2 adsorption capacity of DAC sorbents by two to four times with much longer breakthrough times. The IL has been successfully scaled up to the kilogram scale and the IL catalyzed DAC sorbent showed stable performance in multi-cycle testing. IL catalyst can improve performance of amine-based sorbents and solvents for CO_2 capture, can be added to any amine-based sorbents or solvents for improved adsorption and desorption kinetics, and can reduce the overall CO_2 capture cost by 5% to 20%.

available reports/technical papers/presentations

James Zhou, "Low Regeneration Temperature Sorbents for Direct Air Capture of CO_2," Final Technical Report, Pittsburgh, PA, December 2022. *https://www.osti.gov/servlets/purl/1906132/*.

James Zhou, "Low Regeneration Temperature Sorbents for Direct Air Capture of CO_2," 2022 Carbon Management Project Review Meeting, Pittsburgh, PA, August 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_CDR15_Zhou.pdf.*

James Zhou, Maohong Fan, "Low Regeneration Temperature Sorbents for Direct Air Capture of CO_2," NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Zhou.pdf.*

James Zhou, "Low Regeneration Temperature Sorbents for Direct Air Capture of CO_2," Direct Air Capture Kickoff Meeting Presentation, Pittsburgh, PA, February 2021. *https://netl.doe.gov/sites/default/files/netl-file/21DAC_Zhou.pdf*.

James Zhou, "Low Regeneration Temperature Sorbents for Direct Air Capture of CO_2," Project kickoff meeting presentation, Pittsburgh, PA, October 2020. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11092&filename=Low+Regeneration+Temperature+Sorbents+for+Direct+Air+Capture+of+CO2.pdf*.

AIR2CO2: Advanced Integrated Reticular Sorbent-Coated System to Capture CO_2 from the Atmosphere

primary project goal

General Electric Research (GE) partnered with the University of California, Berkeley (UCB) to develop an advanced integrated reticular sorbent-coated system to capture carbon dioxide (CO_2) from the atmosphere ("AIR2CO2"). The system integrates pioneering metal-organic framework (MOF) sorbents and sorbent-binder composite coatings to capture and release atmospheric CO_2. UCB built on their benchmark MOF sorbent to synthesize, test, downselect, and sufficiently scale a next-generation sorbent with optimized overall CO_2 adsorption capacity and thermal and chemical stability. GE developed a robust MOF sorbent-binder formulation and coating process and integrated the advanced sorbent into an additively manufactured substrate. Component and system modeling of the AIR2CO2 process was performed based on laboratory-scale experimental results and used to develop a techno-economic model that will inform future development of the sorbent material and AIR2CO2 contactor.

technical goals

- Integrate UCB's CO_2-capture MOF sorbents and GE's sorbent-binder coating technology into a viable AIR2CO2 material system.
- Build on benchmark MOF-808-Gly to synthesize, test, downselect, and sufficiently scale a next-generation sorbent.
- Conduct AIR2CO2 lab-scale component and process modeling, including mass-energy balancing and techno-economic modeling.
- Develop a robust MOF sorbent-binder formulation and coating process and integrate the advanced sorbent into an additively manufactured substrate.

technical content

The National Academies of Sciences, Engineering, and Medicine established that commercial viability of sorbent-based direct air capture (DAC) technologies requires the development of sorbents with higher capacities and faster reaction kinetics, as well as process intensification, including more effective mass and thermal transport and a lower pressure drop in the contactor. To address these challenges, GE and UCB developed:

1) Advanced sorbents that build on UCB’s promising benchmark Technology Readiness Level 2 (TRL 2) MOF sorbents.
2) A robust MOF-binder composite that yields greater than 90% enriched CO_2 directly from the atmosphere.

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Metal-Organic Framework-Based Sorbent for DAC

participant:
General Electric Research

project number:
FE0031956

predecessor projects:
N/A

NETL project manager:
Nicole Shamitko-Klingensmith
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principal investigator:
David Moore
General Electric Research
moored@research.ge.com

partners:
University of California, Berkeley

start date:
10.01.2020

percent complete:
100%

3) A conceptual design based on sorbent material and system modeling for an AIR2CO2 contactor that integrates the advanced sorbent with a high surface area, additively manufactured heat exchanger.

The AIR2CO2 contactor vision capitalizes on the unique capabilities of additive manufacturing to enable the fabrication of and sorbent integration into structures with larger surface area/weight ratios and lower pressure drops than conventional "honeycomb" designs. The robust coating of a thin sorbent layer on the structured walls is critical to realize an advanced AIR2CO2 contactor (Figure 1). Figure 1a conceptualizes the AIR2CO2 system, which undergoes alternating adsorption/desorption cycles for continuous CO_2 removal from air.

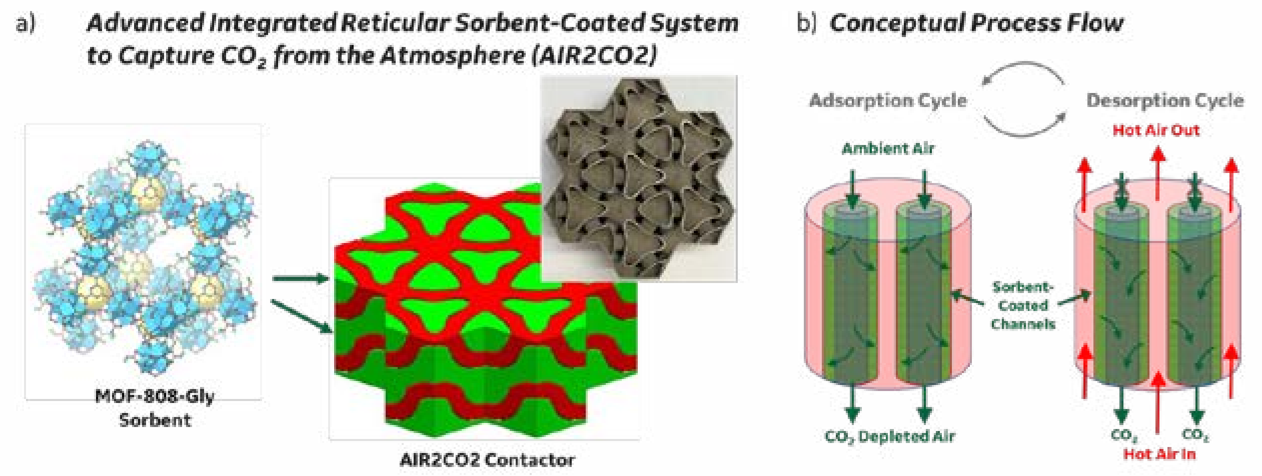

Figure 1: (a) Sorbent-coated contactor design showing sorbent-integrated channels (green) and hot air channels for desorption (red). (b) Conceptual process flow within alternating adsorption/desorption cycles.

Figure 1b shows a process flow rendering of the AIR2CO2 contactor design. The first contactor undergoes an adsorption cycle as ambient air flows through it, while the second contactor experiences a high-temperature (110°C) desorption cycle to release CO_2 and regenerate the sorbent. When the sorbent in the first contactor approaches its full adsorbent capacity, the air flow through the contactor is shut down and directed to the second contactor. MOFs, a class of porous, crystalline materials composed of metal ions joined by organic linkers, are the enabler materials for the AIR2CO2 material system. MOF sorbents demonstrate promising CO_2 sorption capacities and, more importantly, have the potential for significantly better performance than the current state of the art. MOF-808-Gly has been identified as a benchmark sorbent for CO_2 adsorption under DAC conditions. Figure 2a shows MOF-808-Gly and the CO_2 binding site consisting of five glycinate ligands coordinated to the $Zr_6O_4(OH)_4$ secondary building units in a bidentate fashion, which results in an amine loading of 3.3 mol/kg MOF. These amine groups enable chemisorption of CO_2 to occur at low partial pressures and in the presence of water, as evidenced by the dry (black) and humid (red) CO_2 adsorption isotherms (Figure 2b). Carbon dioxide reacts with the pendant amine groups to form bicarbonate (top), carbamate (middle), or carbamic acid (bottom), depending on the water content of the airstream examined. Covalent attachment of amine groups to the organic linker, rather than ionic attachment at a hydrolytically unstable metal site, allows for increased amine density (i.e., increased CO_2 capacity) and increased framework stability. Additionally, control of amine nucleophilicity and steric properties will reduce the heat of desorption of CO_2, facilitating faster CO_2 desorption kinetics and reducing the energy required to desorb CO_2.

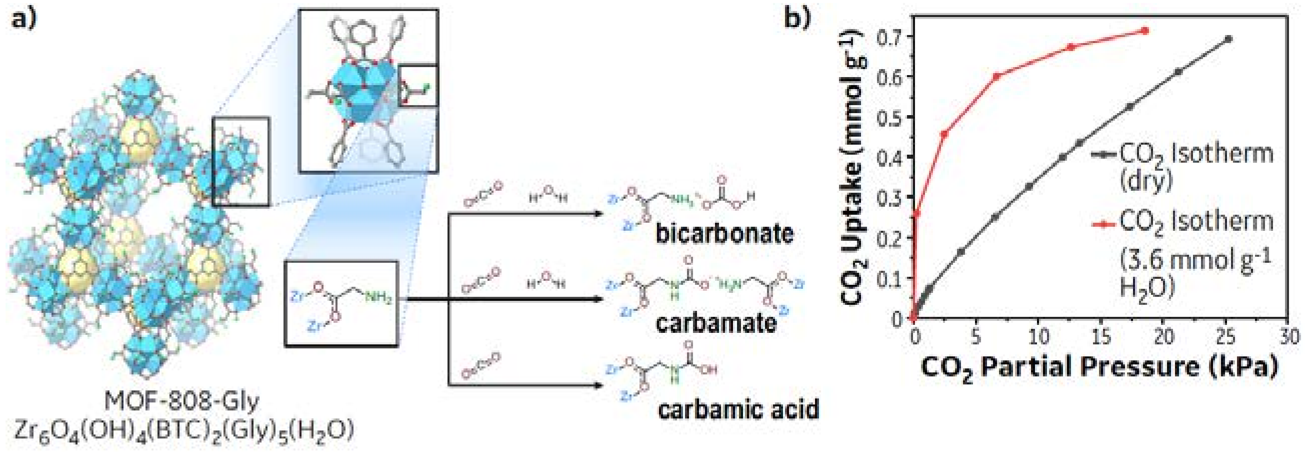

Figure 2: MOF-808-Gly benchmark MOF: (a) molecular structure and CO_2 adsorption mechanisms and (b) dry and humid CO_2 isotherms.

The two key innovations of the AIR2CO2 program include advanced sorbent architectures with high capacity and rapid sorption kinetics, and a sorbent-binder slurry and coating process that enables integration into an additively manufactured contactor that will ultimately reduce equipment size and pressure drop.

The currently available benchmark MOF-808-Gly (Figure 2) was designed for and performs well for post-combustion CO_2 capture, in which physisorption of CO_2 is responsible for the majority of the CO_2 captured. At low CO_2 concentrations, physisorption of CO_2 has a lower driving force, and chemisorption is the predominant capture mechanism. MOF-808-Gly exhibits low CO_2 capacity because of poor utilization of the amine groups required for chemisorption of CO_2, which translates to a higher thermal cycling energy penalty. Consequently, a large potential to improve CO_2 capacity of the benchmark MOF at DAC conditions exists. MOF capacity was improved by increasing utilization of amine groups, accomplished by more efficient amine deprotonation during post-synthetic activation. Further enhancements were achieved by increasing the density of amine groups loaded into the sorbent framework and by decreasing the heat of CO_2 desorption through incorporation of secondary amines into the structure. Integration of next-generation MOF sorbents into the AIR2CO2 contactor resulted in an additional 40% lower energy consumption as a result of lower pressure drop across the contactor. Overall energy requirements for the AIR2CO2 concept are projected to be 60–70% lower than amine-functionalized zeolites. Moreover, initial projections show next-generation MOFs have greater than 40% lower energy requirements than aqueous amines for post-combustion CO_2 capture.

The advanced MOFs and sorbent-binder coating process that were developed in the project have the potential to dramatically reduce DAC costs to \$20–80/ton CO_2. This conclusion incorporates the assessment by the National Academies of Sciences, Engineering, and Medicine of DAC CO_2 capture costs using sorbent technologies. The study evaluated sorbent and contactor performance for a generic sorbent across a range of parameters and assumptions, and concluded that CO_2 costs were \$18–\$1,076/ton CO_2. Furthermore, the successful completion of this project was a groundbreaking step in decarbonization efforts, as the technology is competitive with post-combustion CO_2 capture costs.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	950	950
Bulk Density	kg/m^3	450	450
Average Particle Diameter	mm	0.002-0.01	0.005
Particle Void Fraction	m^3/m^3	0.3	0.3
Packing Density	m^2/m^3	~7.4 x 10^5	~5.6 x 10^5
Solid Heat Capacity @ STP	kJ/kg-K	0.7	0.7
Crush Strength	kg$_f$	Not determined	Not determined
Attrition Index	-	Not determined	Not determined

Thermal Conductivity	W/(m-K)	Not determined	Not determined
Manufacturing Cost for Sorbent	\$/kg	—	<10
Adsorption			
Pressure	bar	0.0004	0.0004
Temperature	°C	25	25
Equilibrium Loading	g mol CO_2/kg	0.34	2.3
Heat of Adsorption	kJ/mol CO_2	~72	72
CO_2 Adsorption Kinetics	gmol/g·min	~0.14 (meas. at 15% CO_2)	0.2
Desorption			
Pressure	bar	<0.0004	<0.0004
Temperature	°C	90-120	80-110
Equilibrium CO_2 Loading	g mol CO_2/kg	~0.03	0.25
Heat of Desorption	kJ/mol CO_2	~72	72
CO_2 Desorption Kinetics	gmol/g·min	~0.13 (meas. at 15% CO_2)	0.2
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	—	
Flue Gas Flowrate	kg/hr	—	
Space Velocity	hr^{-1}	150,000	
Volumetric Productivity	gmol CO_2/(hr $l_{absorber\ bed}$)	2	
CO_2 Recovery, Purity, and Pressure	% / % / bar	— — —	
Adsorber Pressure Drop	bar	0.0015	
Degradation	% capacity fade/cycle	0.0001	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Atmospheric Air Feed-Gas Assumptions:

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	77 °F	0.04	variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – At high CO_2 partial pressures both chemisorption and physisorption of CO_2 occurs. At DAC conditions (0.04 kPa CO_2) only chemisorption of CO_2 occurs as described in Figure 2 and accompanying text.

Sorbent Contaminant Resistance – Nitrogen oxide (NO_X) is not expected to have a significant impact on sorbent performance; however, reaction of amine-based sorbents with sulfur oxide (SO_X) to form heat stable salts is a known issue that will slowly decrease sorbent capacity.

Sorbent Attrition and Thermal/Hydrothermal Stability – Attrition is not anticipated to be a concern because the sorbent is integrated into a polymeric coating on the surface of the heat exchanger. Long-term thermal/hydrothermal stability of the sorbent-binder composite under operating conditions is unknown; however, the sorbent has been cycled approximately 80 times with no detectable decrease in CO_2 capacity.

TABLE 2: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	185	88
Cost of Carbon Avoided	\$/tonne CO_2	NA	NA
Capital Expenditures	\$/tonne CO_2	50	48.3
Operating Expenditures	\$/tonne CO_2	100	39.7

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Calculations Basis – The calculation basis for the TEA was from “Quality Guidelines for Energy System Studies: Performing a Techno-Economic Analysis for Power Generation Plants,” National Energy Technology Laboratory (NETL), DOE/NETL-2015/1726, July 2015. The approach follows the guidelines for the aspirational performance of a new technology.

Scale of Validation of Technology Used in TEA – The numbers in the TEA were validated using the scaled model.

technology advantages

- Two contactors operate in alternating adsorption and desorption modes to continuously remove CO_2 from air.
- High amine loading of MOFs (3.3 gmol/kg).
- High thermal stability inherent to MOFs.

- MOFs can be designed to exhibit high hydrolytic stability.
- High CO_2 capacity, fast sorption kinetics, and novel contactor designs would reduce energy requirements by 60–70% versus state-of-the-art DAC systems (liquid solvent and solid sorbents).

R&D challenges

- Evaluation of new MOF-binder composite coatings, cyclability, thermal stability.
- Post-AIR2CO2: Bench-scale testing of coated additively printed parts; techno-economics; 1 kg CO_2/day demo.
- Scale-up potential: demonstration scale with full-size additive contactor.

status

This project was completed on March 31, 2022. The AIR2CO2 lab-scale test apparatus was designed and assembled at GE for evaluation of MOF-binder composite formulations under DAC-relevant conditions. The 1-kg benchmark MOF was successfully scaled. Several contactor coating formulations were developed and exhibited excellent adhesion to contactor substrates and maintained 70–80% of the native sorbent CO_2 capture performance over 50 cycles. The learnings in these three areas—MOF design, DAC system design, and coatings formulations—will be instrumental in advancing the AIR2CO2 technology toward demonstration scale, pilot scale, and eventual commercial deployment.

available reports/technical papers/presentations

David Moore, et al. "AIR2CO2: Advanced Integrated Reticular Sorbent-Coated System to Capture CO_2 from the Atmosphere," Final Technical Report, June 2022 *https://www.osti.gov/servlets/purl/1874532/*.

David Moore, Omar Yaghi, "AI O2: Advanced Integrated Reticular Sorbent-Coated System to Capture CO_2 from the Atmosphere," 2021 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. R2C*https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Moore.pdf*.

David Moore, "AIR2CO2: Advanced Integrated Reticular Sorbent-Coated System to Capture CO_2 from the Atmosphere," Direct Air Capture Kickoff Meeting Presentation, Pittsburgh, PA, February 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11060&filename=AIR2CO2%3a+Advanced+Integrated+Reticular+Sorbent-Coated+System+to+Capture+CO2+from+the+Atmosphere.pdf*.

David Moore, "AIR2CO2: Advanced Integrated Reticular Sorbent-Coated System to Capture CO_2 from the Atmosphere," Project kickoff meeting presentation, Pittsburgh, PA, November 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11061&filename=AIR2CO2%3a+Advanced+Integrated+Reticular+Sorbent-Coated+System+to+Capture+CO2+from+the+Atmosphere.pdf*.

Electrochemically Driven Carbon Dioxide Separation

primary project goal

The University of Delaware developed an electrochemically driven carbon dioxide (CO_2) separator (EDCS) using poly(aryl piperidinium) (PAP) ionomers that performs near-continuous CO_2 separation from air under ambient conditions. The novel EDCS process is distinct from thermal separation technologies for direct air capture (DAC) by use of an electrochemical driving force across a membrane to perform both capture and release of CO_2 within a single electrochemical cell.

technical goals

- Fabricate structured membranes with porosity and internal air flow channels to provide high interfacial area for CO_2 uptake and low air pressure drop.
- Characterize dense PAP membranes to determine the fundamental kinetic, thermodynamic, and transport properties as a function of temperature, relative humidity (RH), and degree of carbonation.
- Test porous and structured membranes for through-plane conductivity and volumetric CO_2 mass transfer coefficient.
- Fabricate EDCS cells (25 cm^2) using composite electrodes and a flow-through membrane and test for CO_2 separation over a range of simulated conditions.
- Optimize electrode composition using electrochemical cycling without CO_2.
- Develop an electrochemically driven CO_2 separator with a final performance level of ≥ 0.4 mol/m^2-hr CO_2 capture rate at 235 kJ/mol CO_2 electricity consumption.
- Characterize PAP properties to support future development.

technical content

The EDCS concept can be applied with different cell configurations and different electrode reactions. The EDCS cell is shown in Figure 1. A pair of nickel hydroxide ($Ni(OH)_2$) electrodes generate a flux of hydroxide (OH^-) anions through a flow-through membrane with air channels. Nickel hydroxide electrodes are used in rechargeable nickel metal hydride (NiMH) and nickel–cadmium (NiCd) batteries. The electrodes are identical and alternate roles as anode and cathode as the cell is cycled, with cycle times of one to four hours. Nickel hydroxide electrodes are durable, with 30,000 cycle lifetimes demonstrated in nickel-hydrogen (Ni-H_2) batteries. Air is blown through the air channels inside the membrane. OH^- passing through the membrane reacts with CO_2 in air to make carbonate (CO_3^{2-}). The membrane is a hydroxide exchange ionomer (HEI) and transports OH^-, CO_3^{2-}, and bicarbonate (HCO_3^-) along a potential gradient. At the anode, consumption of OH^- lowers the pH, decomposing CO_3^{2-} and releasing pure CO_2. Each electrode will produce CO_2 for the half cycle, during which it serves as anode. Although the current is cycled, air follows a single flow path through the membrane, and a pair

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Membranes

project focus:
Electrochemical CO_2 Separator for DAC

participant:
University of Delaware

project number:
FE0031955

predecessor projects:
N/A

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partners:
N/A

start date:
10.01.2020

percent complete:
100%

of check valves at electrode outlets collect CO_2 from anode and prevent backflow to the cathode.

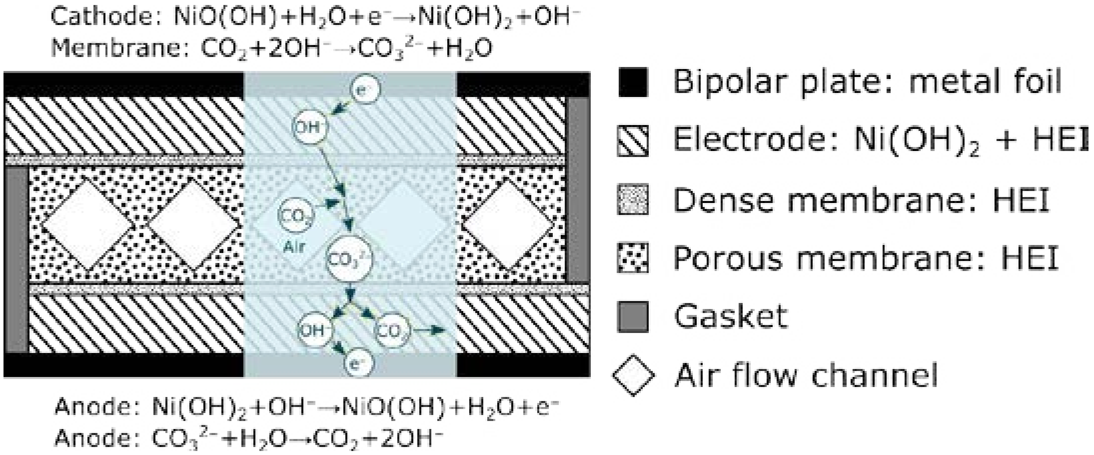

Figure 1: Schematic of EDCS showing the cross section of a single cell.

In Figure 1, air enters through the air flow channels in the membrane. Hydroxide is generated at the cathode by the reduction of nickel oxyhydroxide and electrochemically driven through the membrane. Carbon dioxide reacts with hydroxide to make carbonate. At the anode, the oxidation of $Ni(OH)_2$ causes the pH to drop until decomposition of carbonate occurs, releasing pure CO_2.

The entire process of CO_2 capture, transport, and release in the EDCS occurs under ambient conditions. Dry conditions may require a supply of water to the cathode flow channels for humidification because HEI conductivity depends on water content. However, for a range of RH conditions to be determined in this project, humidification is not necessary and the cell does not consume water.

The project team focused on PAP, which was recently developed for fuel cells and electrolyzers and offers very high conductivity, good mechanical properties, and excellent chemical stability. The structure of PAP is shown in Figure 2.

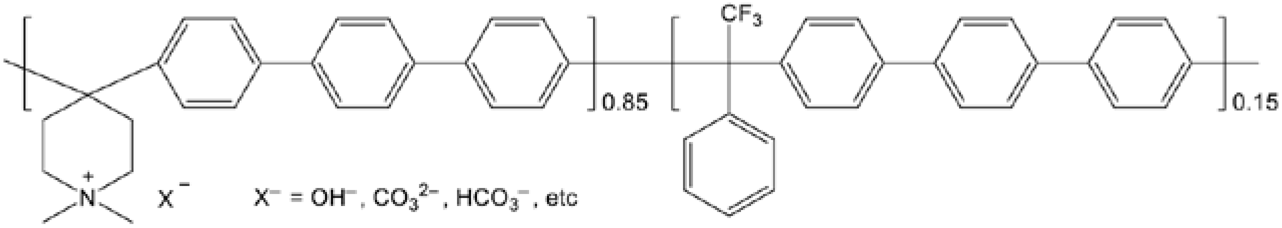

Figure 2: Structure of PAP-TP-x membrane.

A comparison of the EDCS to competing thermal technologies is made in Figure 3. Scenarios A–D show simplified energy balance calculations for amine-based sorbents, using vacuum or steam regeneration. Scenario E shows the aqueous potassium hydroxide (KOH) process piloted by Carbon Engineering, for which a rigorous process analysis has been published. In comparison, the EDCS performance targeted in this project and after more extensive process development and optimization is shown in Scenarios F and G. For vacuum regeneration of amine sorbents, coadsorbed water represents a major issue, as illustrated with Scenarios A–C. Studies have reported $H_2O:CO_2$ ratios of 2.4, 3.9, 5.4, and 7.3 for 20, 40, 60, and 80% RH, respectively. Even in the desert conditions of Las Vegas, Nevada, the annual average RH of 30% corresponds to an $H_2O:CO_2$ ratio of 3.1 and 358 kJ/mol total thermal energy demand. In the steam regeneration scenario (Scenario D), the thermal energy requirement, 169 kJ/mol, is comparable to the most optimistic case. However, Scenario D limited analysis to thermal energy requirement and did not calculate the minimum steam sweep for desorption near 100°C.

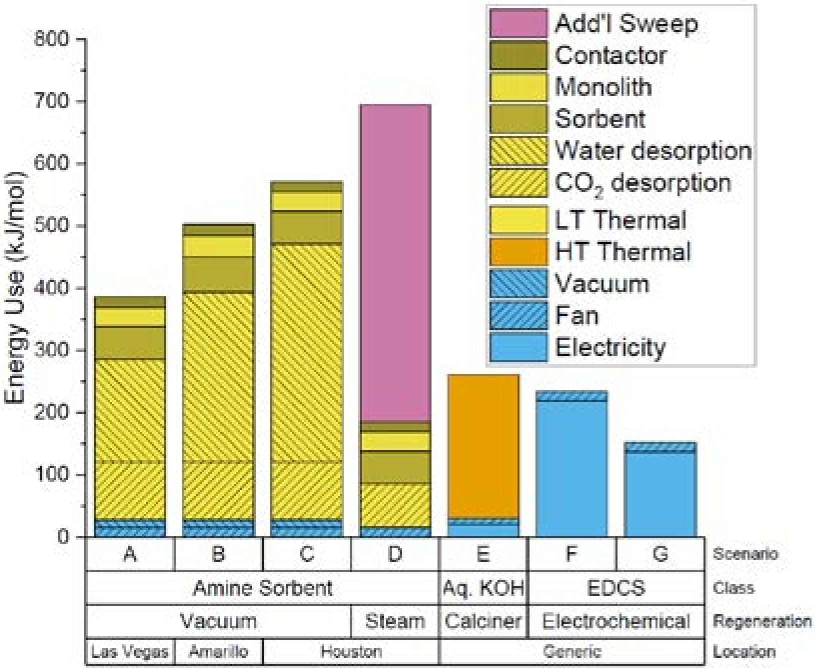

Figure 3: Energy use comparison of DAC technologies.

In Figure 3, Scenarios A, B, and C are based on vacuum desorption of a supported amine sorbent with CO_2 and water desorption energy following the calculations of Wurzbacher et al. Scenario D is steam regeneration of a supported amine sorbent, TRI-PE-MCM-41, as in Kulkarni and Sholl, with the addition of a steam minimum sweep constraint as discussed in the text. Scenario E represents Carbon Engineering's process, net of CO_2 compression. Finally, Scenarios F and G represent the proposed EDCS, with current project and long-term targets, respectively. For Scenarios A–D, location considers average temperature and RH (Las Vegas, Nevada—21°C, 30% RH; Amarillo, Texas—14°C, 57% RH; Houston, Texas—21°C, 70% RH). The sensible heat requirement has been harmonized for a configuration with 2 mmol/g sorbent capacity, 1:1 monolith to sorbent weight ratio, 0.5:1 contactor to sorbent weight ratio, and heat capacities of 1.4, 0.84, and 0.9 kJ/kgºC for sorbent, monolith, and contactor, respectively. Heats of desorption are 80 kJ/mol for CO_2 and 47 kJ/mol for H_2O in Scenarios A, B, and C, and 67.3 kJ/mol for CO_2 in Scenario D. Regeneration is assumed to occur at 95ºC in Scenarios A–D.

EDCS technologies have been reported in the literature for flue gas CO_2 capture. These cells were powered by "oxygen pump" chemistry, with oxygen reduction reaction (ORR) as the source of hydroxide and oxygen evolution reaction (OER) the sink. Two major disadvantages are the slow electrode kinetics, requiring high cell voltage, and the oxygen product of OER, which is mixed with product CO_2. Electrodialysis has been proposed as a technique to regenerate alkaline solvents for DAC. In electrodialysis, acid and alkaline solutions are regenerated from a neutral salt using bipolar membranes to dissociate water into H^+ and OH^-. The cycles vary, but generally, electrodialysis wastes energy by generating strong acid and base solutions and a pH swing of 14 units requiring 0.83 Volts (V). Some cycles have reduced current efficiency and high energy consumption if strong OH^- solutions are generated. In contrast, the EDCS cell uses the solid-state redox couple of $Ni(OH)_2$ and $NiO(OH)$ with favorable kinetics and no gaseous coproducts. While a charge storage electrode must be cycled, increasing process complexity, a new EDCS has been designed where air is fed through flow channels in the membrane and does not need to be redirected as the cell reverses polarity. Hydroxide ion enters from either electrode to capture CO_2, and the product CO_2 is collected from either electrode using check valves to prevent backflow.

technology advantages

- Lower energy consumption.
- Powered by lower-cost renewables.

- No added emissions.
- No flue gas capture.
- Continuous separation.
- Modular design.

R&D challenges

- Regeneration using vacuum; determination the experimental tradeoff between vacuum and temperature.
- Performance metrics using steam regeneration, co-adsorbed water may increase heat requirement.
- Difficult to generate a large equilibrium swing, which may result in excess sweep steam requirement and implementation of heat-integration strategies.

status

This project was completed on September 30, 2023. The University of Delaware has improved their the $Ni(OH)_2$ EDCS cell; the energy requirement 3 GJ/t and the EDCS module flux 580 kg/m^2-yr exceeds the proposed target requirments. Conductivity tests and pH monitoring have demonstrated a strong relationship between humidity and carbonate ion conductivity through the membrane. The performance of EDCS was tested using various membranes and it was found that performance can be improved by increasing the resistance of the membrane to reduce backdiffusion of bicarbonate from anode to cathode.

available reports/technical papers/presentations

Brian Setzler, "Electrochemically-Driven Carbon Dioxide Separation," 2022 Carbon Management Project Review Meeting, Pittsburgh, PA, August 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_CDR15_Setzler.pdf*.

Yushan Yan, "Electrochemically-Driven Carbon Dioxide Separation," NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Yan.pdf*.

Brian P. Setzler, "Electrochemically-Driven Carbon Dioxide Separation," Direct Air Capture Kickoff Meeting Presentation, Pittsburgh, PA, February 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11059&filename=Electrochemically-Driven+Carbon+Dioxide+Separation.pdf*.

Brian P. Setzler, Yushan Yan, "Electrochemically-Driven Carbon Dioxide Separation," Kickoff Meeting Presentation, Pittsburgh, PA, November 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11057&filename=Electrochemically-Driven+Carbon+Dioxide+Separation.pdf*.

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High-Performance, Hybrid Polymer Membrane for Carbon Dioxide Separation from Ambient Air

primary project goal

InnoSense LLC developed a direct air capture (DAC) system for carbon dioxide (CO_2) separation from ambient air using a highly CO_2-selective, ultra-thin, functionalized hybrid polymer membrane (HypoMem) integrated with carbon materials such as graphene oxide (GO).

technical goals

- Fabricate ultra-thin (<100 nm) robust HypoMem and evaluate its properties and performance to establish selection/acceptance criteria for use in a novel CO_2 separation system.
- Conduct lab-scale CO_2 capture experiments to understand the effects of membrane performance (thickness, permeability, selectivity, etc.) and processing conditions (temperature, pressure, humidity, gas compositions, flow rate, etc.) for process optimization on CO_2 capture capacity.
- Integrate the optimized bench-scale CO_2 capture system in the recipient's lab at InnoSense.

technical content

In current DAC processes, sorbents and solvents are commonly used as CO_2 capture media. The disadvantages of sorbents and solvent systems include the need to build a very large structure, the cost and complexity of regenerative systems, and the loss of moisture in dry environments.

Carbon dioxide separation using membrane technology offers energy efficiency, lower cost and simple operation, and is an environmentally friendly process. Deficiencies of polymer membranes still remain, which include low gas permeability and selectivity, high temperature instability, and low flexibility and robustness. In this project, HypoMem is being utilized to overcome these deficiencies. Improvements to polymer membrane separation properties have been achieved by adding GO into the polymer matrix. Improving CO_2 separation performance using mixed matrix membranes has been demonstrated in prior studies where different levels and concentrations of inexpensive GOs were used to improve CO_2 selectivity of membranes. A variety of HypoMems have been created, embedding GO in polymer matrices, such as polyaniline (PANi), Polybenzimidazole (PBI), and Pebax® MH 1657, to improve CO_2 selectivity.

Figure 1 shows the thin-film liftoff (T-FLO) technique for HypoMem fabrication. Here, the active layer, which determines the membrane properties, is cast

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Membranes

project focus:
Hybrid Polymer Membrane for DAC

participant:
InnoSense LLC

project number:
FE0031968

predecessor projects:
N/A

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partners:
University of Utah

start date:
01.01.2021

percent complete:
100%

separately from the support layer. The support layer determines active layer perm-selectivity and morphology. The physical and chemical properties of the active layer can be investigated independently from the entire membrane composite. The T-FLO technique shows potential for scaling the HypoMem for real-world applications.

Carbon Dioxide Permeability and Selectivity of HypoMem: HypoMem has demonstrated potential for high CO_2 permeability (up to 1,279 Barrers with pure CO_2) by controlling polymer and GO content. The addition of GO increased not only the free volume between the polymer chains, but also the stability of the membranes.

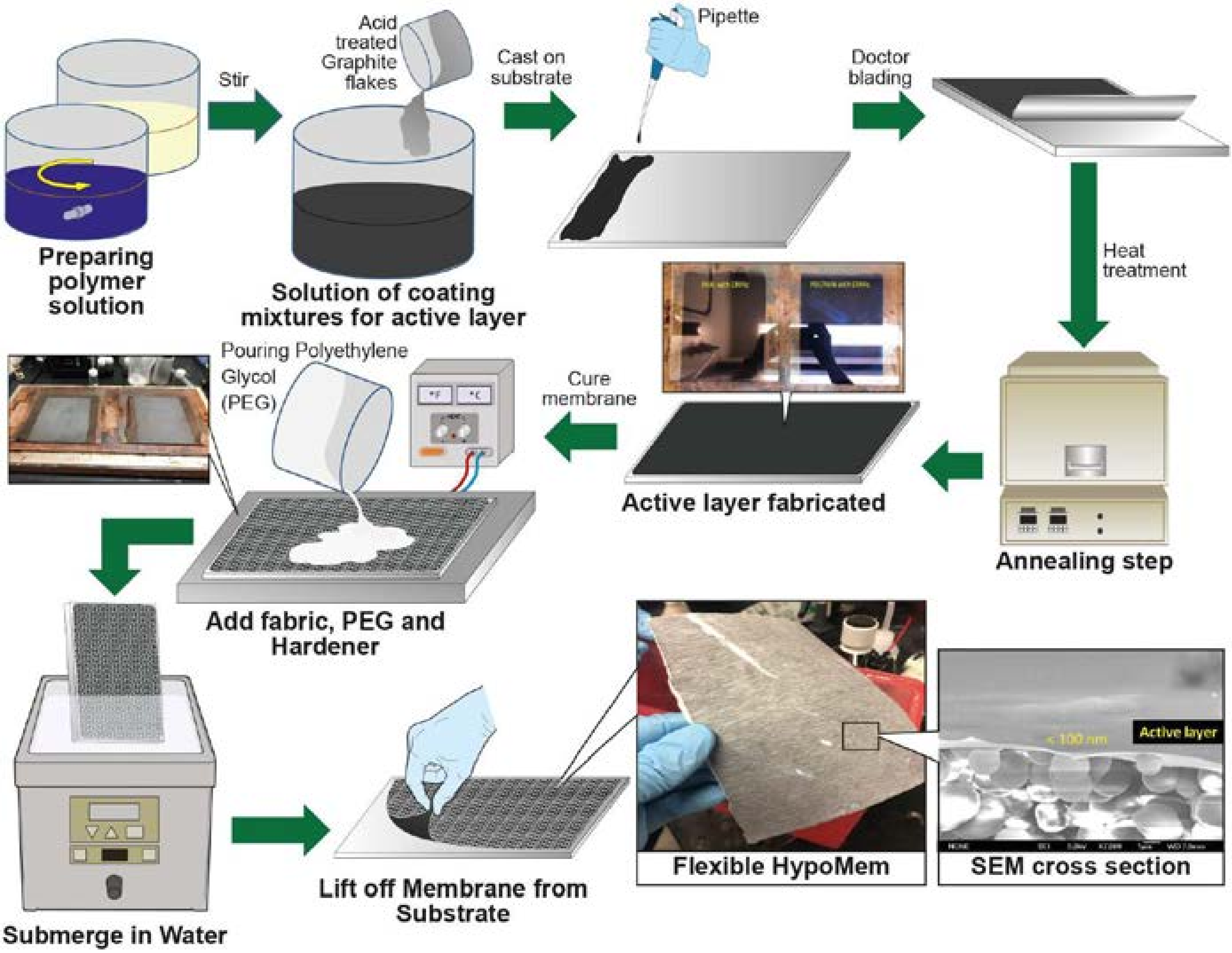

Figure 1: Schematic (follow the arrow from upper left corner) for fabricating HypoMem with functionalized additives.

These morphological changes primarily influence the permeant diffusivity and gas selectivity. The CO_2 permeability and selectivity of HypoMem samples made using the T-FLO technique were demonstrated using pure CO_2 and nitrogen (N_2) gases along with mixtures (15% CO_2, 5% oxygen [O_2], balance N_2) for CO_2 separation tests and compared with other membranes in Figure 2 (A). In earlier work performed, the selectivity and permeability were tuned by employing various polymers and different oxidation levels of carbon materials. Further, HypoMem CO_2 permeability and selectivity were tuned by doping, de-doping, and re-doping with selected acids (e.g., hydrochloric acid [HCl]) and bases (e.g., ammonium hydroxide [NH_4OH]) as reported in literature. HypoMem exhibits excellent CO_2 separation performance and is also flexible and mechanically robust. In this project, HypoMem was formed into spiral-wound configurations for an alpha demonstration. The transport and separation in membranes involves molecular-scale interactions of the permeating gas component with the active layer. More importantly, the extremely thin and defect-free active layer requires a highly porous non-selective support layer. Also, permeability is a pressure- and thickness-normalized flux of a desired gas component. Figure 2 (B) presents the effect of active layer thickness on CO_2 permeability and selectivity in earlier studies.

Since the pore size of both the fabric and epoxy layers can be controlled with the T-FLO technique, the molecular transport mechanism can be optimized to further develop HypoMems.

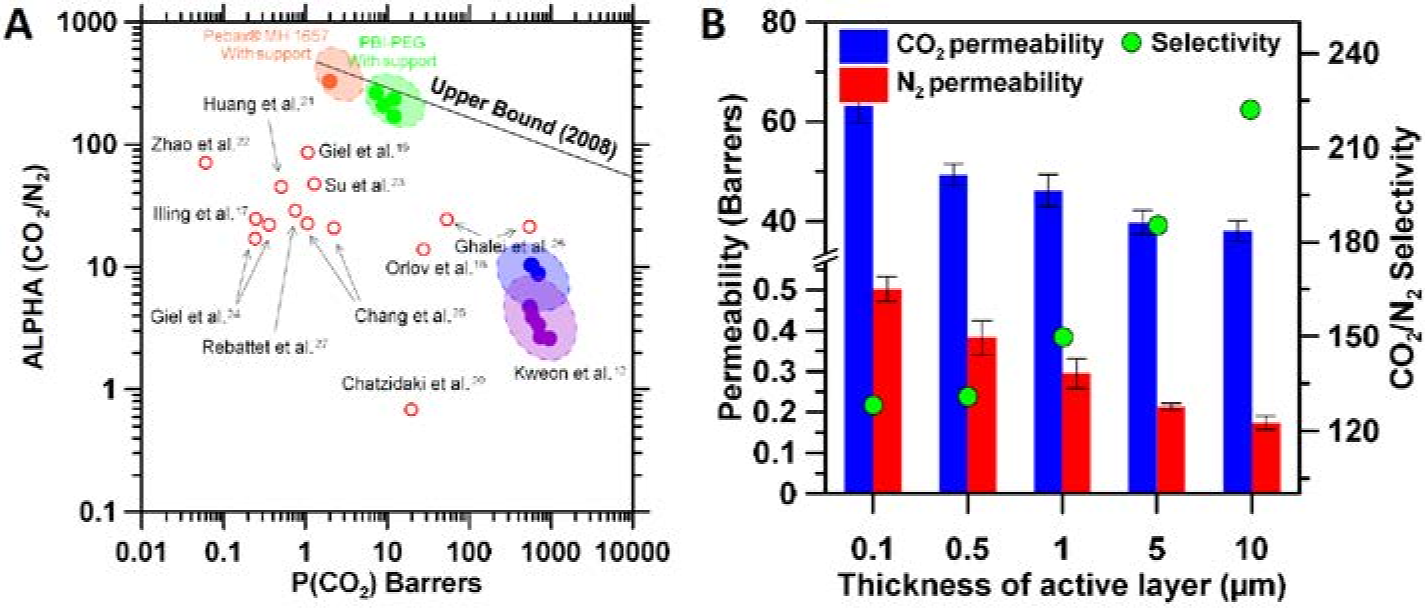

Figure 2: (A) A Robeson plot comparing the performance of the developed HypoMem against other polymer composite membranes for CO_2/N_2 gas separations. (B) Permeability and ideal selectivity data for different thicknesses of active layers with pure CO_2 and N_2.

For gas molecules (e.g., CO_2, N_2, and O_2) smaller than 4 Å, HypoMem combined with functionalized GOs improves gas transport properties with thermal and chemical stability since the gaps of individual GO sheets are slightly bigger than feed gas molecules. Functional groups such as amine and ethylene oxide attached on the active layers have a strong affinity to CO_2 molecules in the presence of N_2 and O_2. However, freestanding polymer membranes tend to crystallize, swell, and break, especially at high water content. To overcome this limitation, different molecular weights of polyethylene glycol (PEG), diglycidyl resin, and diamine hardener have been used in the T-FLO technique. Therefore, in the current scenario, by adding support layer separately, more stable membranes can be generated without changing properties of the active layer. Different molecular weight PEGs are now being employed to control the permeability of crosslinked networks in the support layer. These membranes rely on reversible chemical reactions between the target CO_2 gas and specific functional groups attached to the polymer matrix. Therefore, only the reacting species (CO_2) are transported across the membrane by this mechanism, theoretically increasing both permeability and selectivity. Amines are able to bind CO_2 selectively through different possible chemical mechanisms, such as those shown in Figure 3. The membranes contain amine groups that are considered a convenient medium to selectively transport CO_2 in the presence of humidity. Another important parameter to consider is pH, as it influences amine protonation equilibrium, which in turn affects CO_2 interaction with the active layers. Thus, to exploit the facilitated transport mechanism presented, a neutral amine form is needed to maintain high pH values during material purification and membrane preparation.

Cycle and Operating Conditions: Figure 4 is an overall process schematic of the HypoMem system. First, an ultra-thin active layer is fabricated individually, and then support layers are added to form mechanically robust HypoMem (Figure 4 [2]). Next, HypoMem is formed and packed into the spiral-wound membrane module. If necessary, use of a hollow-fiber module will be examined (Figure 4 [3]). Then, the CO_2 separation system is sealed, and simulated air is injected, passing first through a gas pre-conditioning unit to control humidity and temperature (Figure 4 [1]). Following CO_2 separation, the permeate gas (high-purity CO_2) and rejected gases (N_2, O_2, sulfur dioxide [SO_X], nitrogen dioxide [NO_X], etc.) are collected and exhausted safely (Figure 4 [4]), and, if necessary, additional post treatments can be added. Following a sufficient duration of simulated air injection (one day ≤ t ≤ 30 days), the membrane modules are characterized for any performance degradation.

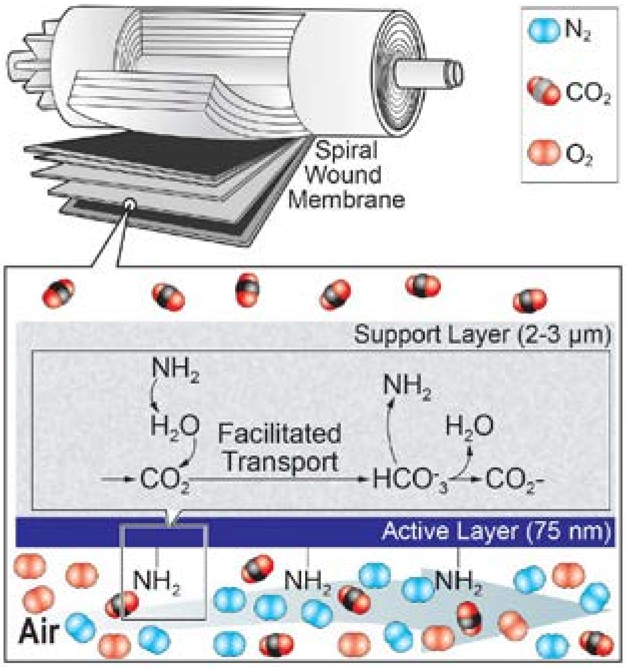

Figure 3: Schematic of facilitated transport mechanism for CO_2 separation from ambient air.

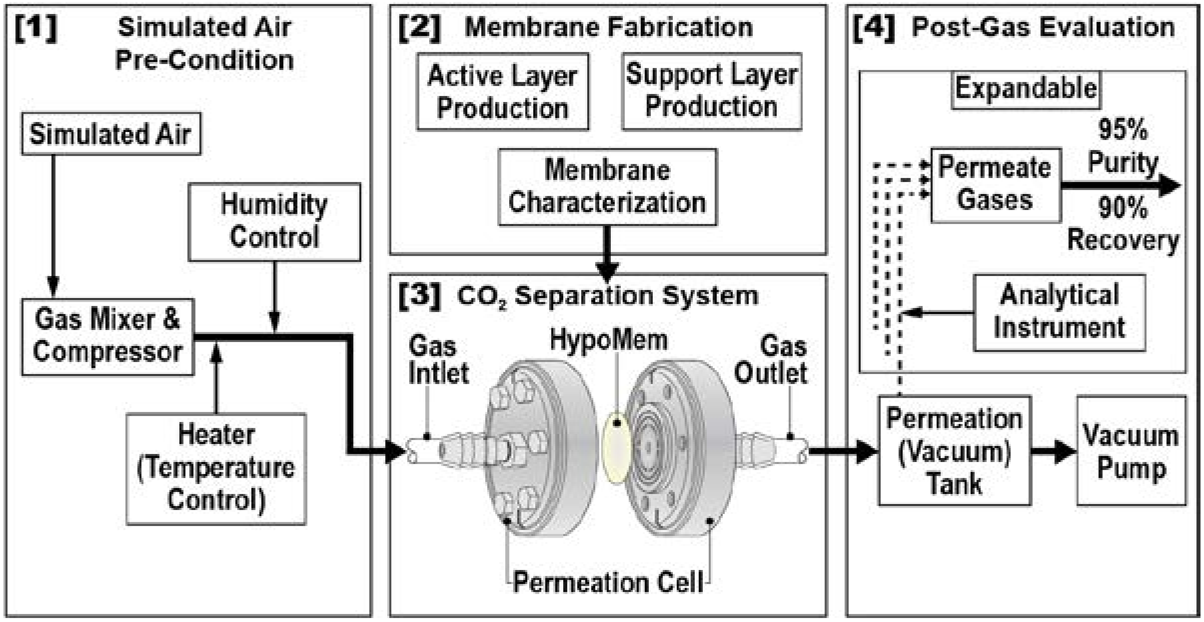

Figure 4: An illustration of the HypoMem CO_2 separation system.

Also, in an earlier study, a multi-stage membrane separation process was considered to improve CO_2 purity and energy efficiency. Final CO_2 purity obtained was 82.1% with 90.7% overall recovery with the use of three stages.

Different compositions of ultra-thin robust HypoMem are a pioneering approach to a cost-effective process for CO_2 separation from a low concentration of CO_2. Through active and support layer modification and chemical treatments, (doping, de-doping, and re-doping), the CO_2 permeability and selectivity can be tuned as needed. The CO_2 separation system's robustness were demonstrated in terms of CO_2 permeability and selectivity with CO_2 and N_2 mixed gases, and the impact of active layer modification and thickness control on mass transfer resistance were revealed. Because membrane gas separation is pressure-driven, the thickness of the active layer is the key to maximizing the permeation rate. Using the T-FLO technique, a high-permeance membrane was fabricated with processability that enables scale-up for commercial applications.

Atmospheric Air Feed-Gas Assumptions

Pressure	Composition						
	vol%					ppmv	
	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	0.04	variable	78.09	20.95	0.93	trace	trace

Simulation and Modeling: A commercial module (MEMSIC) integrated with a process simulator (ASPEN Plus, version 12.0) was used to investigate the impact of various factors, such as: (1) membrane selectivity; (2) area; (3) pressure ratio; and (4) feed flow rates on separation performance (CO_2 of 400 parts per million [ppm] with nitrogen), such as purity and recovery of CO_2 in permeate, stage cut, and energy requirements. A numerical simulator is also developed simultaneously to solve four flow patterns: (1) co-current, (2) counter-current, (3) fully mixed, and (4) crossflow with constant permeability flux model. For co-current flow, a higher CO_2 concentration in the permeate (e.g., approximately 700 ppm for a selectivity of 2 and 13,600 ppm for a selectivity of 200) is achieved while keeping the CO_2 concentration in retentate to 300 ppm. However, the CO_2 recovery factor does not change much for selectivity values above 20. A trade-off between purity and recovery factor is observed, and achieving high purity in permeate requires high concentration in the retentate. The vacuum power depends on the permeate flow rate and pressure ratio.

Computer Simulation and Modeling Based on Experimental Data to Optimize HypoMem Performance: Simulations are conducted for single- and multi-stage with membrane selectivity values of 2 to 20, which are achieved using the HypoMem. At a selectivity of 2, the recovery factor was found to be 40%, and the purity of CO_2 in permeate was about 700 ppm using a single-stage co-current flow and constant permeability flux model. In comparison, a selectivity of 20 resulted in a recovery factor of 27% and a purity of about 5,000 ppm. The concentration of CO_2 in retentate was maintained at 300 ppm. In the multi-stage co-current flow, the study found that the concentration of CO_2 reached 1.6% (mole) using three stages with a selectivity of 20, while it was low at 0.2% using five stages with a selectivity of 2. The crossflow pattern, however, increased the purity monotonically with increasing numbers of stages for higher selectivity. The CO_2 purity was only 0.18% for a selectivity of 2, but it increased to 44% with a selectivity of 20 after five stages in the crossflow pattern.

technology advantages

- Material formulations featuring ultra-thin and chemically stable membranes for CO_2 separation.
- T-FLO technique enables controllable pore size fabrication and thickness, enabling improved performance of the active membrane layer.
- Efficient and scalable CO_2 separation system.
- High-permeance membrane that is scalable for commercial applications.
- Mechanically, chemically, and thermally stable membranes reduce costs since the feed streams would not require pretreatment.
- Development of spiral-wound modules and parallel membranes allows for maximum packing density with lower pressure tolerances, enabling maximum CO_2 separation and minimum energy use.

R&D challenges

- Optimizing permeance, permeability, and CO_2 selectivity performance.

status

This project was completed on May 31, 2023. InnoSense Corporation developed hybrid polymer formulations and fabricated HypoMem samples with different compositions. The hybrid polymer HypoMem samples were reasonably large size (~8x12 cm) and have verified consistent thicknesses and morphologies of both active polymer layer and epoxy support layers. Researchers constructed an onsite gas permeation testing apparatus and observed high permeance values: 6.83x10^5 gas permeation unit (GPU) for CO_2 and 2.15x10^5 GPU for N_2 at a pressure drop across the membrane of ~95 kPa. The CO_2 selectivity was observed to be 3.17 at permeance of 6,830 GPU. The researchers observed a trend of an increase in CO_2 permeance and selectivity with doping stage. Computer simulation and modeling suggested that a multi-stage process is required to achieve the desired CO_2 permeate concentration for successful DAC CO_2 separation.

available reports/technical papers/presentations

Palash Panja, Chamila Manankandayalage, Maksudul M. Alam, Milind Deo, "Understanding the Performance of Membrane for Direct Air Capture of CO_2," *Journal of Applied Polymer Science*, 2024, *141(3)*, e54802(1–13). *https://doi.org/10.1002/app.54802*.

Maksudul M. Alam, "Doping and Redoping Effects on Hybrid Polymer Membranes for Direct Air Capture of CO_2," Final Technical Report, Pittsburgh, PA, March 2023. *https://netl.doe.gov/projects/files/Final%20Technical%20Report.pdf*.

Maksudul M. Alam, "Doping and Redoping Effects on Hybrid Polymer Membranes for Direct Air Capture of CO_2," 2022 Carbon Management Project Review Meeting, Pittsburgh, PA, August 2022. *https://netl.doe.gov/projects/plp-download.aspx?id=13804&filename=Doping+and+Redoping+Effects+on+Hybrid+Polymer+Membranes+for+Direct+Air+Capture+of+CO2.pdf*.

Maksudul M. Alam, Adrien Hosking, Milind Deo, "Development of Hybrid Polymer Membranes for Direct Air Capture of Carbon Dioxide," 2021 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Alam.pdf*.

Maksudul M. Alam, "High-Performance, Hybrid Polymer Membrane for Carbon Dioxide Separation from Ambient Air," Direct Air Capture Kickoff Meeting Presentation, Pittsburgh, PA, February 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11095&filename=High-Performance%2c+Hybrid+Polymer+Membrane+for+Carbon+Dioxide+Separation+from+Ambient+Air.pdf*.

Membrane Adsorbents Comprising Self-Assembled Inorganic Nanocages (SINCs) for Super-Fast Direct Air Capture Enabled by Passive Cooling

primary project goal

The State University of New York (SUNY)–Buffalo, in collaboration with Trimeric Corporation, developed highly porous membrane adsorbents comprising CO_2-philic polymers and self-assembled inorganic nanocages (SINCs) for rapid temperature swing adsorption using electricity-free solar heating and radiative cooling, enabling an economically viable approach for direct air capture (DAC).

technical goals

- Design and prepare membrane adsorbent based on CO_2-philic polymers and SINCs and design operation cycles with solar heating and radiative cooling for CO_2 capture from air.
- Construct and characterize a DAC prototype with the advanced sorbent and electricity-free desorption; demonstrate 100-hour continuous operation for DAC.
- Complete the TEA using performance data from the sorbent experiments.
- Develop an understanding of breakdown pathways and confirm the revolutionary stability of the new solvent using various laboratory techniques.

technical content

The project team developed highly porous membrane adsorbents comprising CO_2-philic polymers and SINCs with a low resistance to airflow and heat transfer for rapid temperature swing adsorption of CO_2 from the air, enabled by electricity-free solar heating and radiative cooling. The core technical activities combined three key innovations:

1. Highly porous flat-sheet membrane adsorbents contain CO_2-philic amines that can be easily produced using a phase inversion method.
2. CO_2-philic SINCs can be easily dispersed in the polymers with great stability (compared with the metal-organic frameworks [MOFs]).
3. The adsorption and desorption are integrated with solar heating and radiative cooling for rapid continuous operation, in contrast to traditional long-cycle separate operation.

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Membranes

project focus:
Membrane Sorbents with Self-Assembled Inorganic Nanocages for DAC

participant:
State University of New York–Buffalo

project number:
FE0031960

predecessor projects:
N/A

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partners:
Trimeric Corporation

start date:
10.01.2020

percent complete:
100%

The membrane adsorbents containing amines, polymers, and SINCs can be produced using a one-step industrial process. The porous membranes coupled with porous SINCs offer low resistance for airflow and fast CO_2 sorption/desorption cycles, while the incorporation of the additional amine groups provides high CO_2 sorption capacity.

Figure 1 shows the integrated membrane adsorbents and cooling technology into a single portable system to realize continuous and rapid CO_2 production. A thin sorbent membrane (e.g., 20–100 µm thick) is continuously rotated by a cylinder. The thin film at the bottom of the cylinder can reach saturation within five minutes (i.e., adsorption [A]) due to the rapid CO_2 and thermal transport within this thin film into the pores. The use of SINCs instead of MOFs enables the active sorbent sites to be highly dispersed and eliminates the need for the pore-to-pore diffusion that limits cycling time in MOFs. The CO_2 will be released at the top side of the cylinder (i.e., the desorption process [D] in the temperature range of 65–100°C), also within five minutes by the heater illuminated by a concentrated solar beam or battery-driven heater during nighttime. The obtained CO_2 may be used for algae culturing or greenhouse or further purification. Afterward, the adsorbents will be cooled by topology-optimized convection and radiative cooling structure to accelerate the cycle and improve the sorption capacity.

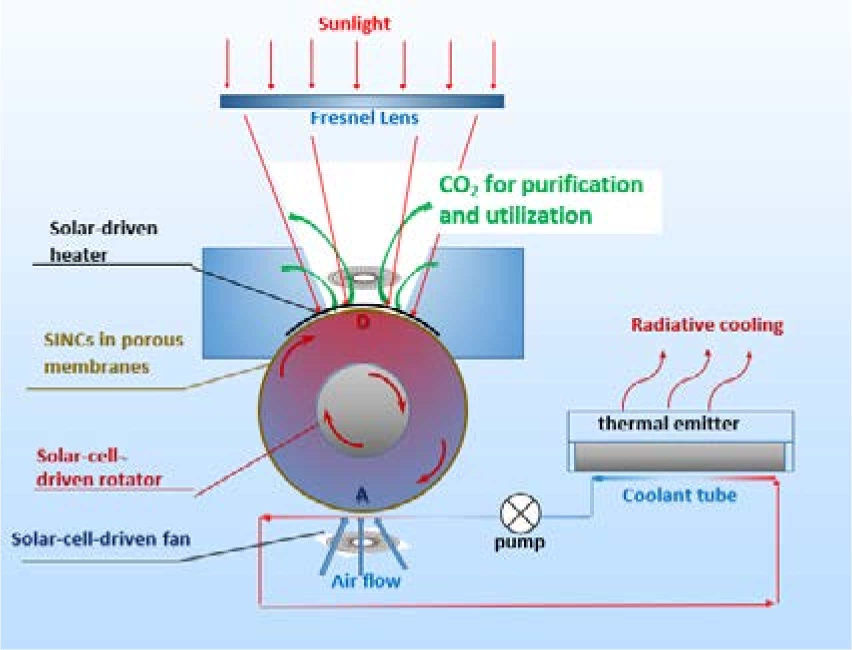

Figure 1: Integrated electricity-free radiative cooling, membrane adsorption, solar heating and desorption, and CO_2 product for further purification and utilization.

One of the key challenges for adsorption, heating, desorption, and cooling of the adsorbents is the time needed for the mass transfer and heat transfer. Ideally, the adsorbents should be embedded in a macroscopic scaffold that effectively exposes them to the air and can be easily heated for desorption. This project proposes a novel sorbent-containing, highly porous, flat-sheet membrane platform (20–100 µm) to decrease the cycle time and thus increase the capacity of CO_2 adsorption. As shown in Figure 2, the porous membranes, with a porosity of 60%–95%, can contain CO_2-philic polymers such as polyethylenimine (PEI). Similar to the hollow fiber membranes (HFM)-based adsorbents, these membrane sorbents can be fabricated using existing membrane fabrication equipment and allow for similar CO_2 capture as packed bed systems while significantly reducing pressure drop and accelerating the adsorption and desorption. On the other hand, the flat-sheet platform allows easy packaging into systems with low pressure drop, and the SINCs can be well- dispersed in these highly porous polymers to further reduce mass and heat transfer resistance compared with the MOFs used in the HFM adsorbents

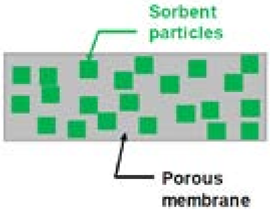

Figure 2: Flat-sheet membrane adsorbents with porosity 60%–95% comprising CO_2-philic SINCs and polymers.

Figure 3 shows an example of a sorbent-containing polyvinylidene fluoride (PVDF) membrane developed by SUNY-Buffalo. PVDF membranes can be prepared using phase-inversion processes with pore sizes of 100–1,000 nm and porosity of greater than 90%, as shown in Figure 3a. More importantly, PVDF has high polarity and interactions with SINCs. Figure 3b shows that example SINCs (copper-MOF) are dispersed in the PVDF, and these nanoparticles even decrease the crystallinity of the PVDF, indicating the strong molecular interactions. Physically mixing SINCs with monomer lead to pore filling and blocking, whereas mixing SINCs with solubilized polymer and then casting films, it is possible to maintain porosity. The SINC/polymer integration can also be tailored by functionalizing the SINC ligands with short-chain oligomers to assist with solubilization into the polymer ink and increasing integration without relying on host/guest interactions into the pores.

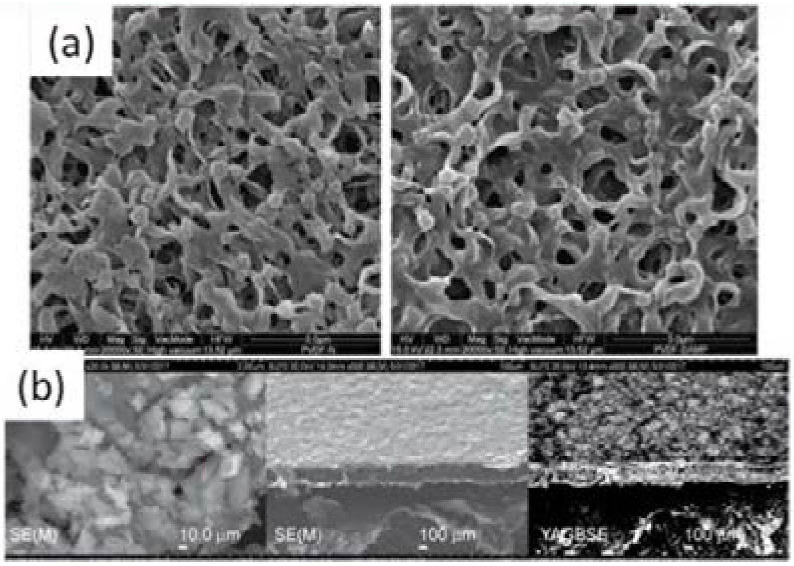

Figure 3: (a) Typical scanning electron microscopy (SEM) photo of the surface of a porous PVDF membrane, (b) SEM of the hybrid PVDF and example SINCs (copper-MOF).

MOFs are a class of porous materials that have attracted much attention due to their permanent porosity and ability to be tuned at the molecular level through straightforward modular synthetic methods. MOFs are formed by the assembly of metal-containing nodes (metal ions or metal-based clusters) that function as structural building units and organic ligands. Carbon dioxide capture is one of the most active and attractive research areas in MOF applications. The primary challenge of MOF sorbents is their slow adsorption/desorption rate and affinity for CO_2, such that they can capture at the relatively low concentrations found in air. To overcome these challenges, SINCs are proposed as an alternative sorbent, guided by recent successes in the MOF literature. There is a growing library of MOFs that are capable of DAC, and the proposed SINC sorbent materials exploit all of their promising features (high selectivity, high uptake, long-term stability) while reducing adsorption and desorption times to a fraction of those required by frameworks. This reduction is made possible because (i) SINCs obviate the need for air/CO_2 to diffuse throughout large crystallites, and (ii) SINCs are less than 10 nm in diameter and can therefore be incorporated into ultra-thin films that enable innovations to air-capture design, as shown in Figure 4. Even when synthesized as a microcrystalline powders, MOFs range from 150–200 nm, orders of magnitude larger than SINCs. Furthermore, SINCs may be readily functionalized to either enhance mixing into polymers or for covalent incorporation into polySINCs, analogous to recently emerging polyMOFs. The use of ultra-thin porous membranes (i.e., 20–100 µm thick) increases the mass transfer of air to the sorbent sites and decreases the pressure drop, leading to super-fast sorption and desorption and lower energy.

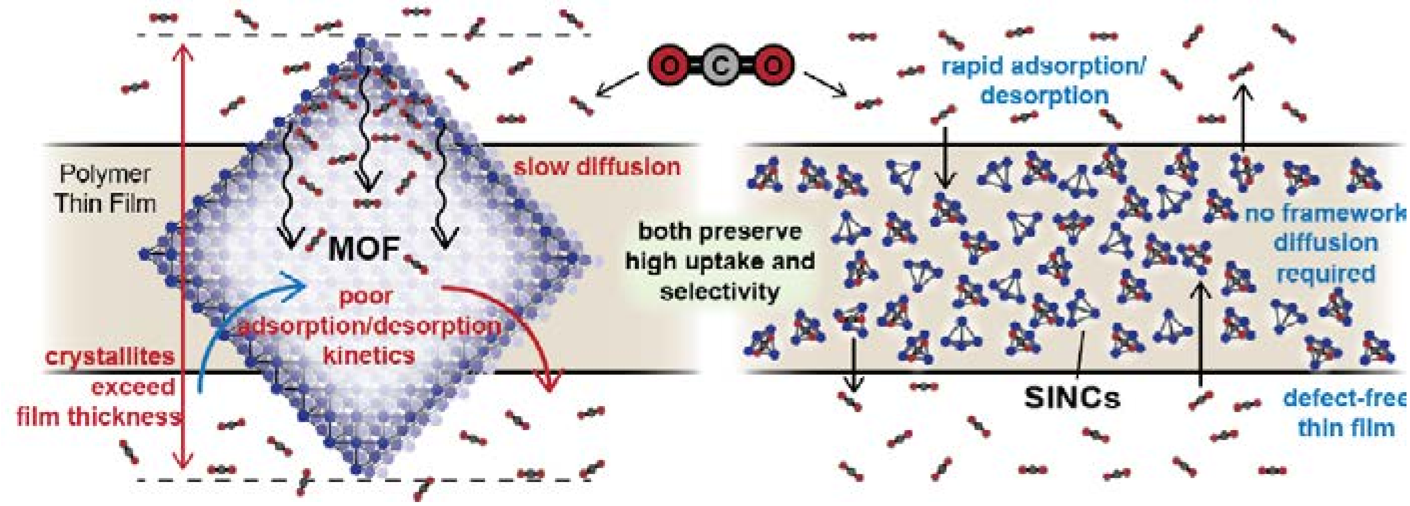

Figure 4: SINC sorbents preserve the high uptake and selectivity of MOFs for DAC while improving upon processability and the kinetics of capture and release of CO_2.

While the solar heating has been widely practiced, daytime radiative cooling has recently emerged as a promising technology to passively cool, even under direct sunlight, by combining a solar reflector with a thermal emitter. The reflector functions in the visible to the near-infrared (IR) spectral region where solar energy is concentrated. It functions as a good thermal emitter in the mid-IR spectral region where room-temperature objects emit most of their radiation energy. Such spectral mismatch is achieved by using nanoscale optical engineering. Recently, SUNY-Buffalo demonstrated electricity-free radiative cooling that operates under direct sunlight. It does not use any energy and yet can provide a cooling power of ~100 Watt/meter^2 (W/m^2) through passive radiative cooling that reaches sub-ambient temperature. It consists of layers of polydimethylsiloxane (PDMS) on an aluminum (Al) substrate with a thickness of 100 µm and 1 mm, respectively. The thermal radiation is primarily emitted by the PDMS layer, which has a near-unity emissivity for wavelengths longer than 4.5 µm due to Si–O and Si–C bond vibrations (Figure 5a), given sufficient film thickness (i.e., larger than 100 µm, as modeled in Figure 5b). Simultaneously, PDMS is transparent to sunlight, which is efficiently reflected by the Al substrate. The resulting emissivity is shown as the red line in Figure 5a.

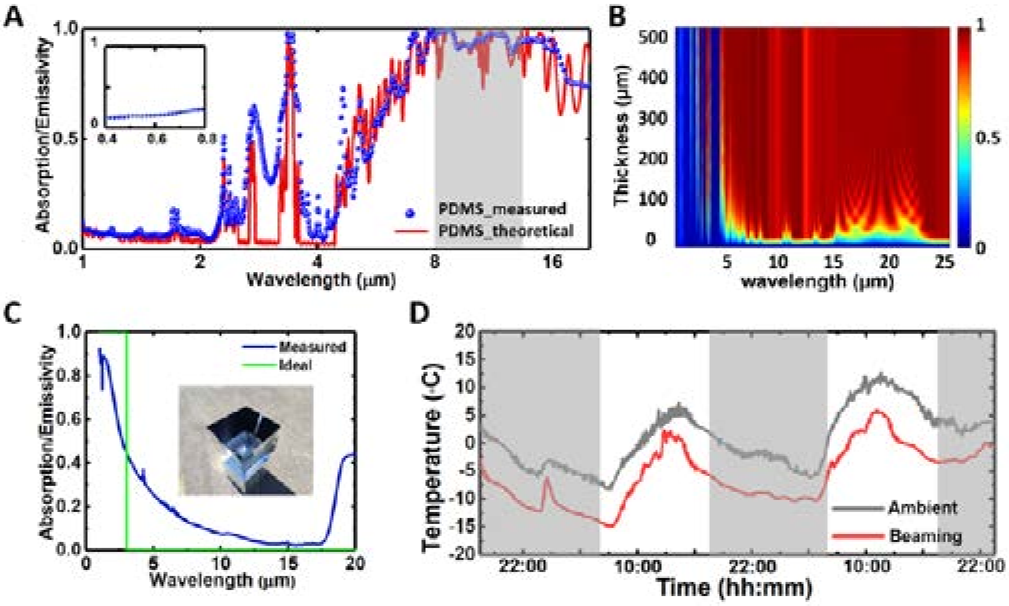

Figure 5: (a) Absorption/emissivity spectra of a planar PDMS/aluminum film with a thickness of 150 µm (solid curve shows numerical modeling and spheres represent measured data); the inset shows that the PDMS film also absorbs part of the solar irradiation in the visible

and near-IR regime, (b) the modeled absorption spectra of the planar PDMS/aluminum film as the function of the PDMS film thickness, (c) absorption spectra of an ideal selective absorber (green line) and a commercial spectral selective absorber (blue line), (d) continuous 48-hour cooling test: the grey line indicates the ambient temperature and the red line is the beaming system temperature.

The emissivity of the structure is characterized using Fourier transform infrared (FTIR) spectroscopy. The daytime radiative cooler system reflects almost 96% of the solar radiation (0.3–4 µm) and emits efficiently in the mid-IR region (greater than 4 µm). The radiator was placed inside an insulating box made from polystyrene. A polyethylene film covers the opening of the box to reduce convective heat losses. In addition, a selective solar absorber was used to develop a V-shaped beam-shaping structure to guide the thermal radiation (see the photo in the inset of Figure 5c). Figure 5d compares the temperature of the system (red curve) and the ambient air (grey curve) in 48 hours. This cooler achieves a temperature reduction of about 7°C throughout the day, validating the electricity-free cooling using sunlight.

technology advantages

- Regeneration cycle achieved by solar heating.
- Electricity-free radiative cooling.
- SINCs have been found to increase CO_2 capacity of membrane sorbents.
- SINCs provide permanent pores to increase gas diffusivity and open metal sites to interact with CO_2.

R&D challenges

- Achieving sufficient radiative cooling for this application.
- Carry out radiative cooling and heating outside.

status

The project was completed on December 31, 2022. A working prototype of the solar thermal porous membrane DAC sorption system has been designed, assembled, and tested. The membrane adsorbents exhibit CO_2 capacity of ~0.5 mmol CO_2/g at 400 parts per million (ppm) CO_2 in air at 22°C. Increasing the sorption temperature from 22 to 50°C resulted in 50%–100% higher CO_2 capacity and amine efficiency. The project concluded that low loading of SINCs increases amine efficiency by 57% and the CO_2 capture cost decreases with increasing sorbent lifetime before leveling off at one year.

available reports/technical papers/presentations

Haiqing Lin, Timothy Cook, Qiaoqiang Gan, and Andrew Sexton, Membrane Adsorbents Comprising Self-Assembled Inorganic Nanocages (SINCs) for Super-fast Direct Air Capture Enabled by Passive Cooling," Final Technical Report, April 2023. *https://www.osti.gov/servlets/purl/1967498/*.

Haiqing Lin, Timothy Cook, Qiaoqiang Gan, and Andrew Sexton, Membrane Adsorbents Comprising Self-Assembled Inorganic Nanocages (SINCs) for Super-fast Direct Air Capture Enabled by Passive Cooling," 2022 Project Review Meeting, Pittsburgh, PA, December 2022. *https://netl.doe.gov/projects/plp-download.aspx?id=14305&filename=Membrane+Adsorbents+Comprising+Self-Assembled+Inorganic+Nanocages+(SINCs)+for+Super-fast+Direct+Air+Capture+Enabled+by+Passive+Cooling.pptx*.

Thien (James) Tran, "Membrane Adsorbents Comprising Self-Assembled Inorganic Nanocages (SINCs) for Super-fast Direct Air Capture Enabled by Passive Cooling," NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Lin.pdf.*

Haiqing Lin, "Membrane Adsorbents Comprising Self-Assembled Inorganic Nanocages (SINCs) for Super-fast Direct Air Capture Enabled by Passive Cooling," Direct Air Capture Kickoff Meeting Presentation, PA, February 2021.

https://www.netl.doe.gov/projects/plp-download.aspx?id=11074&filename=Membrane+Adsorbents+Comprising+Self-Assembled+Inorganic+Nanocages+(SINCs)+for+Super-fast+Direct+Air+Capture+Enabled+by+Passive+Cooling.pdf.

Haiqing Lin, Timothy Cook, Qiaoqiang Gan, Andrew Sexton, "Membrane Adsorbents Comprising Self-Assembled Inorganic Nanocages (SINCs) for Super-fast Direct Air Capture Enabled by Passive Cooling," Project kickoff meeting presentation, Pittsburgh, PA, November 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11076&filename=Membrane+Adsorbents+Comprising+Self-Assembled+Inorganic+Nanocages+(SINCs)+for+Super-fast+Direct+Air+Capture+Enabled+by+Passive+Cooling.pdf*.

Enhanced Depolarized Electro-Membrane System (EDEMS) for Direct Capture of Carbon Dioxide from Ambient Air

primary project goal

The University of Kentucky Center for Applied Energy Research (UK CAER) developed a lab-scale enhanced depolarized electro-membrane system (EDEMS) for direct air capture (DAC). The EDEMS consists of a low-pressure ceramic membrane contactor/absorber in a tailored electrochemical process that leverages depolarization to regenerate and concentrate both a capture solvent and carbon dioxide (CO_2) extracted by the membrane.

technical goals

Develop a capture technology to extract CO_2 from atmosphere that reduces the cost of capture through:

- Developing and screening membrane-based contact absorbers to capture ambient CO_2.
- Developing an electrochemical process to regenerate the capture solvent and up-concentrate captured CO_2 at low power requirement.
- Demonstrating stability and performance of absorber for greater than 24 hours with less than 5% reduction in CO_2 flux by leveraging the regeneration capability of ceramic membrane contactor.

technical content

The EDEMS DAC technology streamlines the energy input and reduces the number of unit operations necessary for removing low-concentration CO_2. This process intensifies CO_2 capture using surface patterned ceramic membranes and solvent regeneration via depolarization in electrochemical cells that leverage previously developed UK CAER electrode stabilization techniques.

The separation of CO_2 from other gasses is an important component of many industrial processes, including ammonia production, steel manufacturing, and power generation. Unlike these industrial processes with point source CO_2, a key challenge with DAC is the low concentration of open-source CO_2, approximately 400 parts per million (ppm), requiring large volumes of air to be treated per mole of CO_2 extracted. Consequently, materials with strong CO_2 binding are required for its extraction, limiting sorbent options to mostly alkalines and amines. Figure 1 shows a benchmark DAC process where potassium hydroxide (KOH) removes CO_2 as carbonate via an exothermic reaction (ΔH = -63.5 kJ/mol). Using a membrane contactor, instead of a packed-bed or spray tower absorber, allows for

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Novel Concepts

project focus:
Enhanced Depolarized Electro-Membrane System for DAC

participant:
University of Kentucky Center for Applied Energy Research

project number:
FE0031962

predecessor projects:
N/A

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partners:
University of Kentucky; ALL4 Inc

start date:
10.01.2020

percent complete:
100%

low-pressure operation and provides better process control while avoiding column flooding issues. However, the regeneration of CO_2 and the capture solvent requires several intensive unit operations, including (1) causticization to convert soluble K_2CO_3 to less soluble $CaCO_3$ and regenerate KOH, (2) clarification to dewater $CaCO_3$ and air separation to provide an oxygenated environment to a calcination step, (3) calcination at high temperatures to extract and release concentrated CO_2, and (4) finally slaking by recombining CaO with water to form $Ca(OH)_2$ to restart the causticization process. The calcination process is the most energy-intensive of the regeneration steps ($\Delta H = 179.2$ kJ/mol), and it also leads to significant water loss via evaporation from the process. A DAC system based on this methodology can cost as much as $2,200/tonne CO_2 per year, which is more than 10 times the cost for post-combustion CO_2 capture. To address the challenges associated with the benchmark DAC process, UK CAER proposed an EDEMS (Figure 2) for the removal of CO_2 from ambient air with an intensified process that significantly reduces the number of unit operations and results in greater than 30% reduction in energy cost to capture and concentrate CO_2 and regenerate the capture solvent by leveraging chemical energy from depolarization.

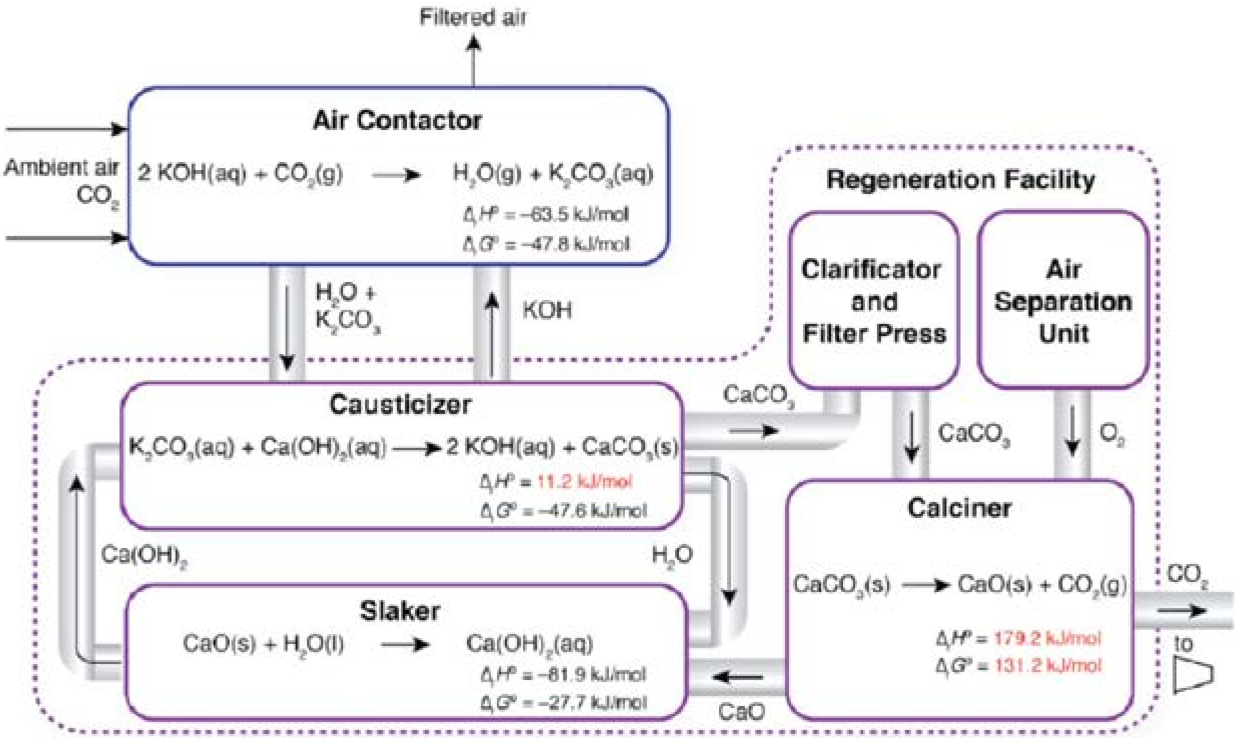

Figure 1: Solvent-based direct air capture system.

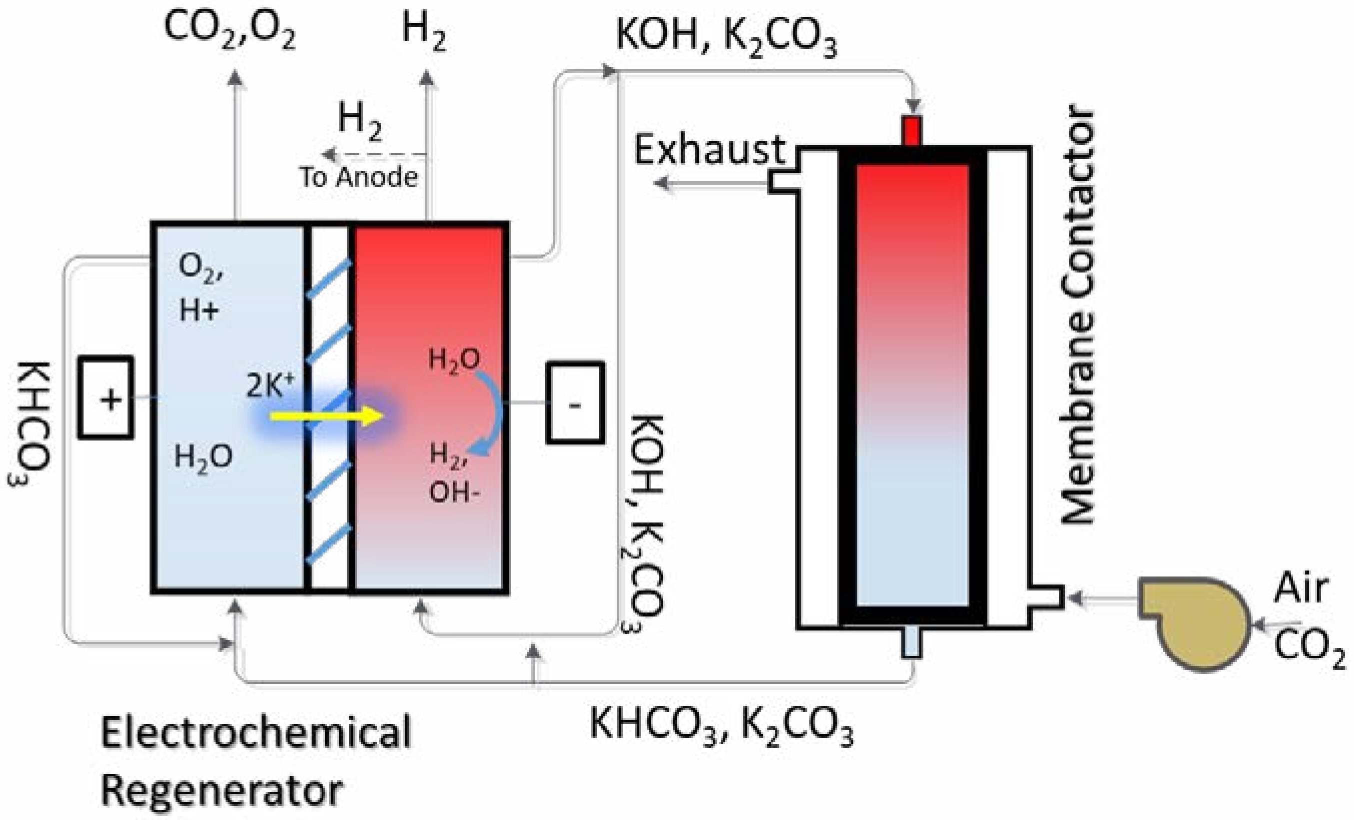

Figure 2: University of Kentucky enhanced depolarized electro-membrane system.

The UK CAER process is composed of (1) a surface-structured enhanced and entirely solvent-compatible ceramic membrane contactor with regenerative wetted surface characteristics, and (2) an advanced depolarized electrochemical cell (DEC) unit with in situ production of hydroxides (KOH, NaOH, etc.) for CO_2 scrubbing in the contactor.

The UK CAER contactor/absorber features α-alumina-type ceramic membranes with superhydrophobic layer and greater than two times expanded surface (compared to a pristine membrane) where influent ambient CO_2 is absorbed into KOH through the membrane. The UK CAER contactor, which can increase packing density by more than 50% compared to typical ceramic contactors due to the larger area density provided by its patterned interface, is also chemically stable. Polymeric hollow fiber membranes are also difficult to regenerate following surface wetting and loss of hydrophobicity, while the performance of the UK CAER contactor membranes may be preserved by regenerating the wetted surface at greater than 50°C. Following DAC, K_2CO_3/$KHCO_3$ from the membrane is fed to the DEC to liberate concentrated CO_2. Under normal operation, water splitting with the hydrogen evolution reaction (HER; $2H_2O + \text{electrons} = H_2 + 2OH^-$) and oxygen evolution reaction (OER; $2H_2O = O_2 + 4H^+ + \text{electrons}$), are the dominant cathode and anode reactions. The hydrogen produced can be sold to offset some of the capture cost, facilitate energy storage, or depolarize the DEC, leading to lower energy requirement. The DEC leverages depolarization by using H_2 (from HER) for the hydrogen oxidation reaction (HOR, $H_2 = 2H^+ + \text{electrons}$) in place of the OER at the anode. The depolarization reduces the overpotential (i.e., potential difference required to drive current) by more than 50%, primarily due to its chemical potential contributions. The K_2CO_3/$KHCO_3$ from the contactor is fed to the anode side (some to the cathode as electrolyte), K^+ ions are transported via a cation exchange membrane (e.g., Neosepta CMX or Nafion) to the cathode to combine with OH^-, while CO_3^{2-} or HCO_3^- is converted to CO_2 by reacting with protons produced at the anode.

The UK CAER EDEMS process (Figure 2) can improve on the benchmark processes by:

1. Minimizing the footprint of the treatment process by intensifying the capture and regeneration into two unit operations, avoiding the need for seven units to facilitate cyclical operation.
2. Reducing the need for make-up water, as no thermal evaporation occurs.

3. Avoiding the need for large thermal input and providing a cost-effective process.
4. Generating hydrogen for sale.
5. Seamless compatibility with renewable direct-current electrical power sources, such as solar cells, for stand-alone remote operation.

In addition, by combining the anode and cathode depolarization using a staging approach, voltage requirements may be further reduced.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Material Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Hydrophobic Layer	—	Fluoroalkylsilane	
Materials of Fabrication for Support Layer	—	Alumina	
Nominal Thickness of Hydrophobic Layer	µm	N/A	N/A
Membrane Geometry	—	Tubular	Tubular
Hours Tested without Significant Degradation	hrs	100	100
Membrane Performance			
Temperature	°C	21	21
CO_2 Pressure Normalized Flux	GPU or equivalent	64	90
CO_2/H_2O Selectivity	—	N/A	N/A
CO_2/N_2 Selectivity	—	N/A	N/A
Type of Measurement (ideal or mixed gas)	—	Real Air	Real Air
Capture Fluid		2 wt% KOH, countercurrent	
Regeneration Voltage	V	3.5	<1.8

Definitions:

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464 × 10^{-6} kg mol/m^2-s-kPa [SI units].

Shell-Side Fluid – Capture solvent.

Atmospheric Air Feed-Gas Assumptions – Update values below to describe the air feed-gas pressure, temperature, and composition entering the capture system:

		Composition						
		vol%					ppmv	
Pressure	Temperature	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	68-72°F	0.04	variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

Membrane Permeation Mechanism – The driving force for permeation is partial pressure difference between the gas and liquid sides of the membrane. The electrochemical cell regenerates the solvent after CO_2 is absorbed into the liquid.

Gas Pretreatment Requirements – No treatment of influent air is required.

Product Streams Generated – Hydrogen is generated from the process for sale, energy storage, or depolarization to reduce the energy requirement for capture solvent regeneration.

technology advantages

- Provides stable performance facilitated by the DEC and hydrophobic contact absorber.
- Reduces the energy requirement by up to 30% through intensifying the electrochemical and CO_2 release reactions.
- Provides easy integration with renewable power sources for remote operation and reducing carbon emissions.

R&D challenges for state-of-the-art

- Low CO_2 concentration requires facile capture solvent due to low driving force.
- Regeneration step is energy-intensive.
- Water make-up requirement is high.
- Air separation unit introduces additional cost.

status

This project was completed on March 31, 2022. Contactor preparation, stability, and performance testing were conducted. Tubular membranes treated with fluoroalkylsilane achieved greater than 90% CO_2 capture using laser-patterned ceramic membrane contactor bundle and a performance similar to polymeric membranes. UK CAER's integrated membrane absorber and electrochemical solvent regenerator were capable of simultaneous carbon capture and hydrogen production, which can provide flexibility for the process operation. The membrane absorber provided a stable and effective contactor for DAC with capture facilitated at high pH and the depolarized operation is a promising technique for reducing the energy requirement for DAC while simultaneously mitigating the complexities of downstream O_2 removal. The electrochemical-aided solvent regeneration approach for DAC is continued in DE-FE0032125.

available reports/technical papers/presentations

Ayokunle Omosebi, et al., "Enhanced Depolarized Electro-Membrane System (EDEMS) for Direct Capture of Carbon Dioxide from Ambient Air," Final Technical Report, Pittsburgh, PA, June 2022. *https://www.osti.gov/biblio/1874498*.

Ayokunle Omosebi, "Enhanced Depolarized Electro-Membrane System (EDEMS) for Direct Capture of Carbon Dioxide from Ambient Air," 2022 Final Briefing Meeting, Pittsburgh, PA, April 2022.

Ayo Omosebi, "Enhanced Depolarized Electro-Membrane System (EDEMS) for Direct Capture of Carbon Dioxide from Ambient Air," NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Omosebi.pdf*.

Ayo Omosebi, "Enhanced Depolarized Electro-Membrane System (EDEMS) for Direct Capture of Carbon Dioxide from Ambient Air," Direct Air Capture Kickoff meeting, Pittsburgh, PA, February 2021. *https://netl.doe.gov/sites/default/files/netl-file/21DAC_Omosebi.pdf*.

Ayo Omosebi, "Enhanced Depolarized Electro-Membrane System (EDEMS) for Direct Capture of Carbon Dioxide from Ambient Air," Project Kickoff meeting, Pittsburgh, PA, November 2020. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11082&filename=Enhanced+Depolarized+Electro-Membrane+System+(EDEMS)+for+Direct+Capture+of+Carbon+Dioxide+from+Ambient+Air.pdf*.

Filer City BiCRS Net-Negative Study

primary project goal

Northstar Clean Energy Company is performing an initial engineering design study for installing a solvent-based carbon dioxide (CO_2) capture facility at Filer City Generating Station in Manistee County, Michigan. The design study includes an AACE Class 4 cost estimate based on the capture of at least 500,000 net tonnes of CO_2 per year.

technical goals

- Complete an initial engineering design study for the capture system and produce a capital cost estimate covering both engineering design and costing for the bioenergy conversion, carbon capture process and balance of plant systems requiring modification.
- Confirm availability of sustainably sourced biomass (20-year supply).
- Complete study to confirm the boilers are capable of operating on 100% biomass as a feedstock.

technical content

Northstar Clean Energy Company is executing an initial design engineering study to retrofit the Filer City Station with a post-combustion CO_2 capture technology and to retrofit the existing boilers to fire 100% sustainably sourced woody biomass. Babcock & Wilcox's (B&W) solvent-based system—SolveBright™ CO_2 Capture System, which uses an amine-based solvent scrubbing process with an absorber/regenerator—is being studied for implementation. The station is a 70-megawatt (MW) gross output rated facility with twin stoker boilers placed in service in 1990, each with the ability to burn coal, waste wood, natural gas, and tire-derived fuel. It is the objective of the project team to convert the station to primarily a waste wood-fueled facility, eliminating the dependence on coal, with the addition of post-combustion capture technology that can remove greater than 95% of the CO_2 from the flue gas to capture approximately 500,000 tonnes of CO_2 per year. The captured CO_2 will be compressed and transported via an existing high-pressure pipeline rated for CO_2 delivery to geologic storage formations located approximately 10 miles away.

program area:
Carbon Dioxide Removal

ending scale:
pre-FEED

application:
Biomass with carbon removal and storage (BiCRS)

key technology:
Solvents

project focus:
Pre-FEED Study for Bioenergy with Carbon Capture and Storage at Filer City Station

participant:
Northstar Clean Energy Company

project number:
FE0032262

predecessor projects:
N/A

NETL project manager:
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Timothy.Gehring@cmsenergy.com

partners:
Babcock & Wilcox; Sargent & Lundy

start date:
08.01.2023

percent complete:
75%

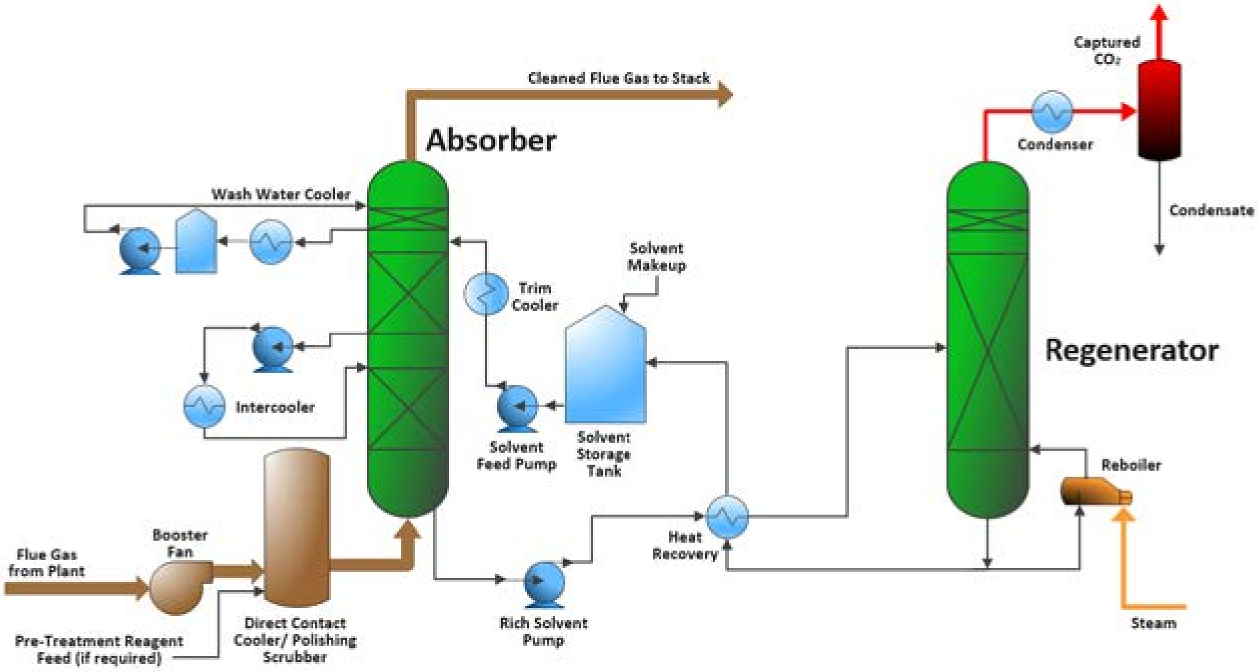

Figure 1: Amine-based solvent scrubbing process.

Due to location, the station has the unique ability to achieve the objective of obtaining sufficient sustainably sourced biomass to operate for 20 years. Filer City Station is located in the lower peninsula of Michigan at the edge of the northern Michigan forest region. It is estimated that northern Michigan has more than 3 million tonnes per year of excess growth of waste biomass available for harvesting and, within 100 miles of the station, there is more than 1.25 million tonnes of annual waste wood growth available for harvesting. In addition, the station has access to barge and rail deliveries along with truck supply, providing many options for low-carbon import of biomass from other Great Lakes port locations.

Another unique locational aspect for Filer City is its proximity to existing subsurface storage of CO_2. The Filer City Station is located on top of the Northern Niagaran Reef Trend, which has been approved by the U.S. Environmental Protection Agency (EPA) for storing CO_2 in enhanced oil recovery (EOR) operations and for injection into deep geologic formations for permanent storage. Core Energy is the preeminent oil and gas company in northern Michigan with extensive experience in EOR, having injected more than 2.3 million tonnes of CO_2 in oil fields for permanent storage. The Filer City Station site is only 3,000 feet from existing high-pressure pipeline infrastructure that can be utilized for CO_2 transportation to Core Energy's fields where CO_2 is currently used for EOR. Based on fluctuations in oil pricing, it is the intent of this project to review the opportunity to convert the existing oil fields and Class II wells to Class VI permitted wells to ensure permanent storage is possible in the previously used fields. Since the fields currently inject and permanently store CO_2 as part of the EOR process, upgrading to Class VI permitted wells is not expected to be a technical limitation.

Filer City Station consists of two 300,000 lb/hour stoker-fed traveling grate boilers with air quality control (AQCS) consisting of a dry spray lime gas (SDA) scrubbers and high-efficiency baghouses. Steam produced is fed to a single high-pressure 70-MW gross output rated steam turbine generator. While these AQCS pollution control systems are required for use with coal, they are expected to be operated in a more limited capacity once boilers are converted to biomass. Stoker boilers are well-designed to use biomass and blends of other unique fuels, due to the method in which fuel is fed to the boiler as compared to using pulverizers, pneumatic conveying and injection burners. As such, the station was selected as a viable asset to convert to 100% biomass and produce "negative carbon" electricity. Once converted to 100% biomass, the flue gas is expected to pass through the existing AQCS path, including the baghouse and flue gas desulfurization system, to limit the contaminants entering the carbon capture process and atmosphere. Steam required for capture will be derived from the existing steam cycle, so as not to add additional onsite combustion needs.

Figure 2: TES Filer City Station coal-fired power plant, Lake Manistee, Michigan.

The solvent and process parameters are provided in Table 1. This station is being designed to be capable of operation with either 30% monoethanolamine (MEA) or 55% diglycolamine (DGA) solution. Solvent inputs are provided for the 55% DGA solution.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value
Molecular Weight	mol^{-1}	105.136
Normal Boiling Point	°C	223
Normal Freezing Point	°C	-12.5
Vapor Pressure @ 15°C	bar	1.6E-4
Working Solution		
Concentration	kg/kg	0.55
Specific Gravity (15°C/15°C)	-	1.05
Specific Heat Capacity @ STP	kJ/kg-K	1.05
Viscosity @ STP	cP	10
Absorption		
Pressure	Bar-g	0.05
Temperature	°C	50
Solution Viscosity	cP	4.75
Desorption		
Pressure	Bar-g	0.9
Temperature	°C	118

Proposed Module Design			(for equipment	
Flue Gas Flowrate	kg/hr	395.622		
CO_2 Recovery, Purity, and Pressure	% / % / bar-g	95	>95	93

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine DGA in an aqueous solution).

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of DGA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
1 in wc	194°F	11.6	26.6	57.8	4.0	-	1	97

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – CO_2 from the flue gas is chemically absorbed by an amine based solvent in the absorber vessel. This facility is being designed specifically for MEA and DGA, which are both primary amines which react with CO_2 to form the respective carbamate species. However, the process design can also accommodate other amines (i.e. secondary, tertiary, and hindered amines) which may have different reaction mechanisms and which will lead to different performance which must be evaluated before a solvent change.

Solvent Contaminant Resistance – No chemicals are initially being considered that may improve the solvents contaminant resistance, although trials with various additives may be possible as part of the post-operation testing. This is possible as space is reserved in the carbon capture building allowing the easy addition of various chemicals to the solvent. The primary strategy to address contaminants is through the proper upstream treatment of the flue gas, which will pass through a spray dryer absorber, a fabric filter and a direct contact cooler (with acid gas polishing capabilities) prior to contacting the solvent in the absorber.

Solvent Foaming Tendency – The long-term foaming potential of this solvent on a biomass flue gas will be determined during operation. Equipment such as carbon beds and thermal reclaiming are included to reduce the foaming potential of the solvent. In addition, space is reserved in the carbon capture building allowing the easy addition of various anti-foam chemicals to the solvent.

Flue Gas Pretreatment Requirements – The carbon capture system is being designed based on the existing spray dryer and fabric filter and pollutant concentrations exiting that equipment. The direct contact cooler is also being designed with the capability of additional acid gas removal if necessary. Lastly, boiler modifications planned during the conversion to biomass firing include urea injection to limit nitrogen oxide (NO_X).

Solvent Make-Up Requirements – Solvent make-up requirements have been estimated based on available data but will be determined more accurately during operation. The system has been designed with adequate storage of fresh solvent from a chemical supplier that can be added to the process as needed.

Waste Streams Generated – The largest waste stream from the carbon capture system is condensate collected in the direct contact cooler. This wastewater stream is expected to have low total dissolved solids and will be sent to the cooling tower as make-up water. In addition, the thermal reclaimer will produce a waste product containing degradation products of the solvent. This stream will be disposed of accordingly based on its determined composition. Periodic change outs of the carbon beds are also expected. This material will be disposed of as required.

Process Design Concept – Basic Indicative Process Flow Diagram included above (Figure 1).

Proposed Module Design – The absorber and regenerator towers are both large vessels that will be shipped in large truck-shippable sections modularized for simplified field erection. These towers include various sections of structured packing to meet performance requirements.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS*

Economic Values	Units	Current R&D Value
Cost of Carbon Captured	\$/tonne CO_2	60.73
Cost of Carbon Avoided	\$/tonne CO_2	131.03
Capital Expenditures	\$/ MWhr	1,682
Operating Expenditures	\$/ MWhr	249
Levelized Cost of Electricity with Carbon Capture	\$/MWhr	380

*The Filer City BiCRS Pre-FEED Study is not yet complete and estimated economic data is subject to change.

technology advantages

- The project will provide the necessary data to pursue conversion of the Filer City facility to 100% biomass and implementation of a commercial-scale CO_2 capture technology, thus extending its economic service life sustainably.
- More than 61 million tons of unutilized sustainable biomass is located within trucking distance of the Filer City Station.
- A high-pressure pipeline exists 2,600 feet from the Filer Plant that can deliver the captured CO_2 to secure geologic storage sites.

R&D challenges

- Achieving 95%+ capture given the many variables involved, including lower carbon content of the fuel source and its variable heat content.

- Continuing to validate use of lower-cost MEA/DGA solvents to accomplish elevated capture.

status

A preliminary life cycle analysis (LCA) and an initial engineering design have been completed. A hazard identification (HAZID) study has also been performed for the CO_2 capture system and integration into the steam cycle to identify and evaluate any process or equipment risks. The project team is developing an overall project capital cost estimate that is consistent with an AACE Class 4 cost estimate (approximate accuracy of -30% to +50%).

available reports/technical papers/presentations

Gehring, T. “Filer City Biomass Carbon Removal and Storage (BiCRS) Net-Negative Study,” Project Closeout Meeting, Pittsburgh, PA, October 2024. *https://netl.doe.gov/projects/files/Filer%20City%20Biomass%20Carbon%20Removal%20and%20Storage%20(BiCRS)%20Net-Negative%20Study.pptx*.

Gehring, T. “Filer City Biomass Carbon Removal and Storage (BiCRS) Net-Negative Study,” Presented at the 2024 FECM/NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2024. *https://netl.doe.gov/sites/default/files/netl-file/24CM/24CM_CDR_9_Gehring.pdf*.

Gehring, T. “Filer City Biomass Carbon Removal and Storage (BiCRS) Net-Negative Study,” Presented at the 2023 FECM/NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2023. *https://netl.doe.gov/sites/default/files/netl-file/23CM_CDR31_Gehring.pdf*.

Assessment of the Potential for the Decarbonization of Natural Gas with RNG and Bioenergy with Carbon Capture and Storage

primary project goal

Oak Ridge National Laboratory (ORNL), in collaboration with the National Energy Technology Laboratory (NETL) and the Advanced Research Projects Agency–Energy (ARPA-E), conducted an economics survey for the decarbonization of natural gas. For this process, renewable natural gas (RNG) is created from biomass by means of anaerobic digestion ("bio-gasification") followed by methanation. The objective of this study was to determine the economics of such a process, the point at which the life cycle emissions of such a strategy become zero, and whether or not the costs can compete with traditional natural gas production processes.

technical goals

- Identify a variety of potential sites for an RNG-CCS plant.
- Determine the availability of local biomass at each potential site.
- Perform a life cycle analysis (LCA) to determine carbon avoidance levels and perform a techno-economic analysis (TEA) to determine cost of avoidance.
- Develop marginal carbon avoidance cost (MCAC) curves for each location.
- Perform a sensitivity analysis for each case with respect to multiple process parameters.

technical content

The project began with a comprehensive geologic and preliminary economics survey of more than 200 locations throughout the United States. Key fundamentals for a successful plant site have been identified as large demand for natural gas, access to existing natural gas infrastructure, and existing carbon dioxide (CO_2) transport and storage (saline reservoirs) infrastructure. Other factors considered include available biomass tonnage and diversity, local materials costs, and local competition from other resources. An example of a potential site in Houston, Texas is shown in Figure 1. Sites with at least five terrestrial biomass sources were selected from this survey. A similar approach was undertaken by ARPA-E for macroalgae biomass. The sites were identified using the Oak Ridge Siting Analysis for Power Generation Expansion (OR-SAGE) software tool. OR-SAGE is a spatially explicit biorefinery siting model that utilizes raster analysis, excluding areas that do not meet specified criteria.

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Biomass Carbon Removal and Storage

key technology:
Novel Concepts

project focus:
Economics Survey of Biomass-to-Natural Gas Processes with CCS

participant:
Oak Ridge National Laboratory

project number:
FWP-FEAA422

NETL project manager:
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principal investigator:
Matthew Langholtz
Oak Ridge National Laboratory
langholtzmh@ornl.gov

partners:
NETL; ARPA-E

start date:
10/01/2021

percent complete:
100%

According to the 2016 Billion-Ton Report, biomass availability across the continental United States is high, and a diverse array of bioenergy resources is available, as shown in Figure 2, including municipal solid wastes (MSWs), agricultural waste/residues, woody/forest biomass, and crops. This particular study also included "wet" biomass, such as macroalgae. In total, the survey included the following types of specific biomass species for the LCA and TEA: logging residue, whole trees, herbaceous energy crops (switchgrass), crop residues (corn stover), wastes (MSW, construction and demolition [C&D] wastes, and manure), fossil natural gas, macroalgae, and sorghum.

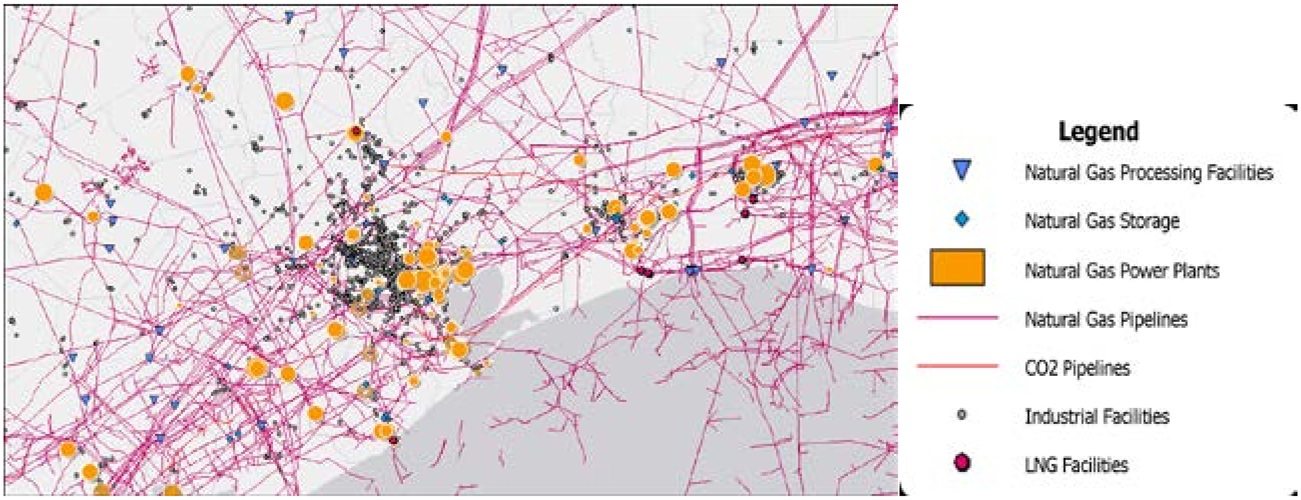

Figure 1: Sample survey location—Houston, Texas.

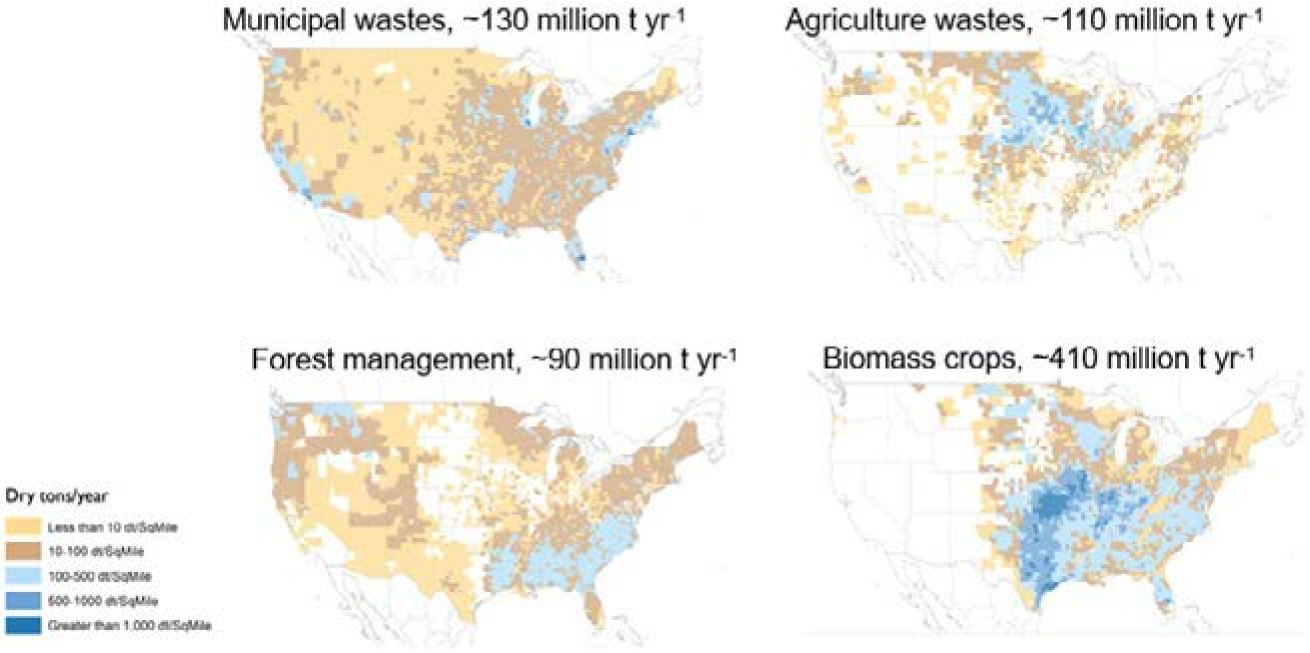

Figure 2: Biomass availabilities at $60/short ton.

ORNL managed the feedstock and site selection and analysis, as well as surveyed the available conversion processes up to the point the natural gas is transported to its end-use. NETL handled the RNG logistics for upgrading, CCS, natural gas end-use, and pipeline access, and was chiefly responsible for the final TEA and LCA. Finally, ARPA-E was responsible for all data for macroalgae and anaerobic digestion. The end-use for the produced RNG was chosen to be an optimized natural gas combined cycle (NGCC) plant. The baseline plant with no installed CCS served as the baseline for all cases, which was compared to two CCS schemes—those being 90% and 97% capture. The complete scenario matrix for each of the parameters is given in Table 1.

TABLE 1: MATRIX OF PARAMETERS SELECTED FOR ALL SCENARIOS

Feedstocks (ORNL/ARPA-E)	Conversion Processes (ORNL/ARPA-E)	Pipeline Transport (NETL/ORNL)	Power Production (NETL/ORNL)	CCS (NETL)
Wastes	Gasification	Natural Gas	NGCC	LCA
Ag. Residues	Pyrolysis	CO_2 (+storage)	NGCC w/ 90% CCS	TEA
Forestland Resources	Anaerobic Digestion		NGCC w/ 97% CCS	Systems/Markets
Energy Crops	CO_2 Storage Basins			
Macroalgae				

technology advantages

- Modeling of biomass resources for decarbonization.
- Quantification of carbon avoidance cost across multiple feedstock-conversion-end-use pathways.

R&D challenges

- Determining optimal site for each type of facility and facility size.
- Completing the LCA and TEA in a timely manner.
- Acquiring the necessary cost and carbon-efficiency data.

status

The project was completed on April 30, 2022. The project team determined that near-term biomass resources could be used to produce more than 2 trillion cubic feet of RNG at a cost of $17–29 per million British Thermal Units (MMBtu), which would result in up to 112 million tonnes of avoided CO_2 emissions. The cost of capture for RNG+CCS reaches cost parity with ordinary natural gas with CCS when the price of said natural gas is greater than $10/MMBtu.

available reports/technical papers/presentations

Langholtz, M., 2021, "RNG+NG+CCS: Assessment of the Potential for Decarbonization of NG with RNG and Bioenergy with Carbon Capture and Storage." Project Kickoff Meeting. DOE/NETL. Pittsburgh, PA. *https://netl.doe.gov/projects/plp-download.aspx?id=11789&filename=Assessment+of+the+Potential+for+Decarbonization+of+NG+with+RNG+and+Bioenergy+with+Carbon+Capture+and+Storage.pptx*.

Bioenergy Knowledge Discovery Framework (KDF), 2016, "Billion-Ton Report - Advancing Domestic Resources for a Thriving Bioeconomy." U.S. Department of Energy, Oak Ridge National Laboratory. Oak Ridge, TN. *https://bioenergykdf.net/2016-billion-ton-report*.

King City Asbestos Corporation (KCAC) Mine Carbon Mineralization Field Test

primary project goal

Lawrence Livermore National Laboratory (LLNL) is evaluating various approaches to carbon dioxide (CO_2) mineralization of asbestos-bearing serpentinite rocks/mine tailings to determine the most successful approach and to enable the U.S. Department of Energy (DOE) and project developers to make informed choices about this pathway of carbon removal. Testing is being carried out at a former asbestos mine site containing a high concentration of brucite in order to measure uptake under applied conditions and evaluate the validity of model assumptions.

technical goals

- Develop safety protocols to protect human health and the environment.
- Develop monitoring protocols to reliably and cost-effectively measure CO_2 uptake.
- Demonstrate enhanced weathering methodologies via material sampling at an abandoned mine site to demonstrate an increase in the uptake of CO_2 by two to five times compared to the background rate.
- Achieve greater than 90% carbonation of brucite and labile magnesium (Mg).
- Show that the proportion of atmospheric carbon incorporated into newly formed carbonate minerals is significantly higher than the proportion of incorporated recycled bedrock carbon and/or biogenic carbon.
- Establish that the full life cycle CO_2 budget is net-negative.
- Develop and accelerate processes that result in carbon dioxide removal (CDR) costs of less than $100/tonne CO_2.
- Demonstrate site restoration to the original condition or better.

technical content

Carbon mineralization is a technique that accelerates the natural process of chemical weathering in order to absorb atmospheric CO_2 more quickly than would occur naturally. The natural process of chemical weathering is shown in Figure 1, where silicate minerals chemically react with CO_2 to form new carbonate minerals that lock CO_2 away. However, this natural process captures CO_2 at about the same rate that it is released into the atmosphere by volcanic activity. The process of accelerated carbon mineralization aims to remove CO_2 from the atmosphere more quickly than is possible through natural chemical weathering. The process of accelerated carbon mineralization has three primary rate-limiting factors: the CO_2 supply, mineral dissolution, and carbonate precipitation. However, techniques,

program area:
Carbon Dioxide Removal

ending scale:
Small Pilot

application:
Enhanced Mineralization

key technology:
Novel Concepts

project focus:
Field Testing of Accelerated Carbon Mineralization Approaches

participant:
Lawrence Livermore National Laboratory

project number:
FWP-FEW0278

predecessor projects:
N/A

NETL project manager:
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principal investigator:
Briana Schmidt
Lawrence Livermore National Laboratory
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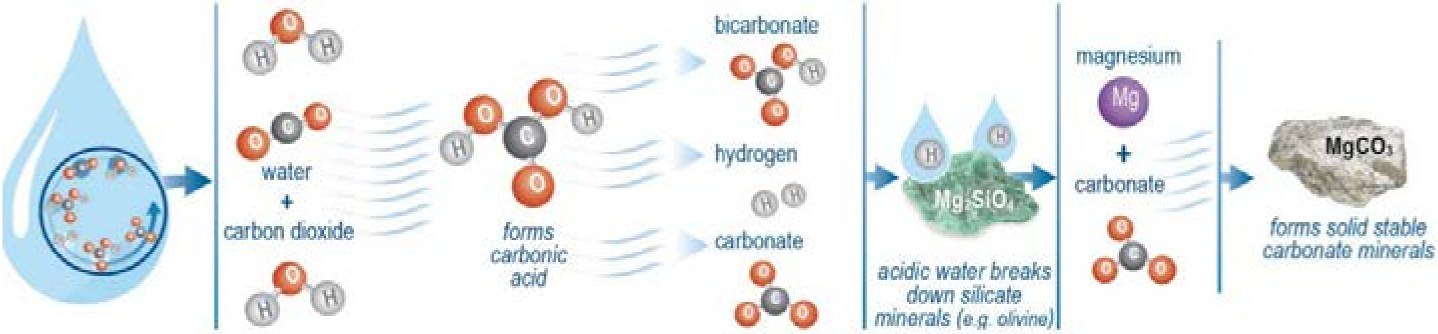
partners:
Bureau of Land Management; University of British Columbia

start date:
09.01.2021

percent complete:
50%

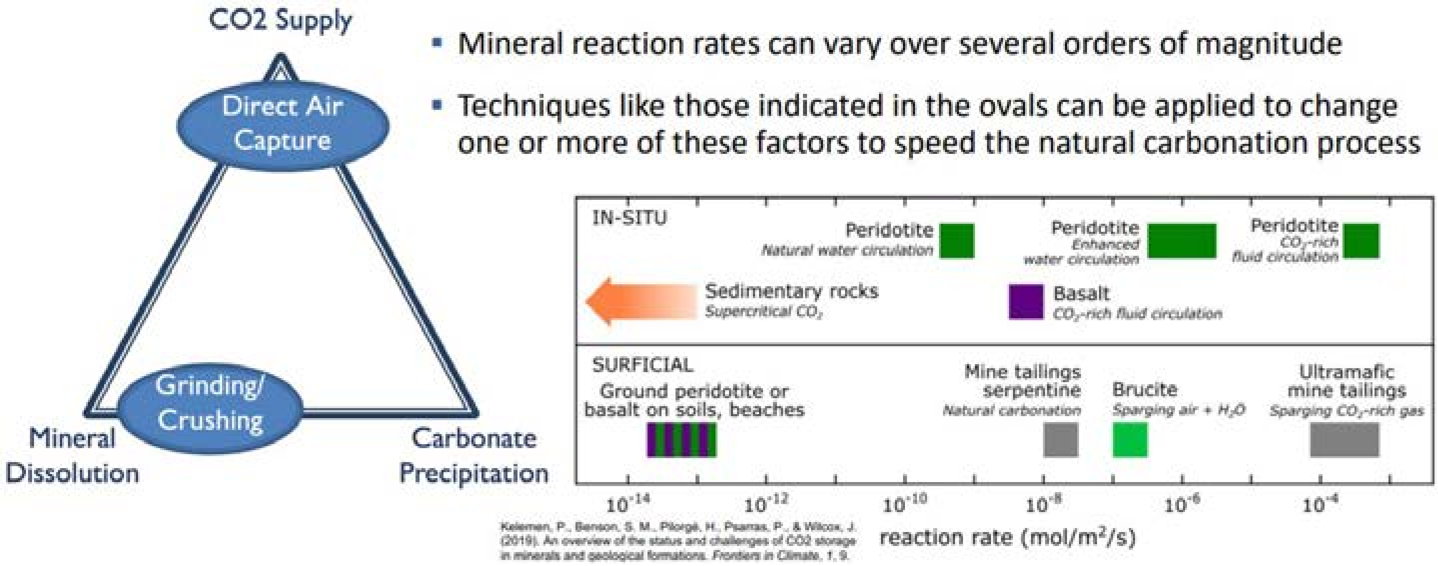
such as those in the ovals of Figure 2, can be used to speed up the natural carbonation process and thus remove CO_2 directly from the atmosphere to halt and reverse climate change.

The concept of accelerating carbon mineralization has been recognized as a promising approach to remove CO_2 from the atmosphere; however, the concept has largely been explored on the bench scale or in small field trails. Assessing the potential viability of this technology and advancing the field requires larger-scale field trials, as is the focus of this work.



Chemical weathering draws down ~0.3 Gt CO_2/y, which over geologic timescales is approximately balanced by the amount of CO_2 released from volcanoes.

Figure 1: Natural chemical weathering and CO_2 capture.


- Mineral reaction rates can vary over several orders of magnitude
- Techniques like those indicated in the ovals can be applied to change one or more of these factors to speed the natural carbonation process

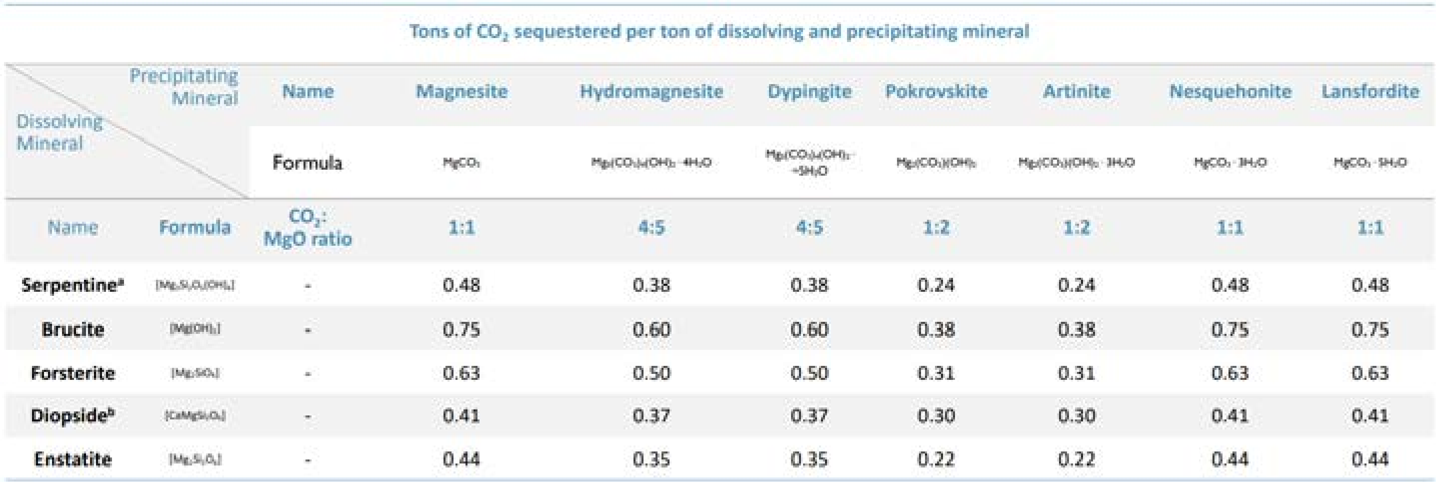
Kelemen, P., Benson, S. M., Pilorgé, H., Psarras, P., & Wilcox, J. (2019). An overview of the status and challenges of CO2 storage in minerals and geological formations. *Frontiers in Climate*, 1, 9.

Figure 2: CO_2 mineralization influences and rates.

The King City Asbestos Corporation (KCAC) Joe Pit Mine, a former asbestos mine in San Benito County, California, was selected specifically for its unique attributes and ideal conditions for this scientific research. As shown in Figure 3, this site is located in the New Idria Serpentinite Body. The KCAC site has highly reactive rock with up to 25% of a key mineral called brucite and a uniquely high proportion of the serpentine mineral chrysotile, one of the very few locations in the world with this particular mineralogical makeup. Figure 4 highlights the tons of CO_2 that can be stored per ton of dissolving and precipitating mineral.

California's ultramafic rocks, mostly serpentinite, cover surprising amounts of the state's land. Arrow points to the New Idria Serpentinite Body.

Figure 3: Location of California's ultramafic rocks (mostly serpentinite).



Tons of CO_2 sequestered per ton of dissolving and precipitating mineral

Dissolving Mineral \ Precipitating Mineral		Name	Magnesite	Hydromagnesite	Dypingite	Pokrovskite	Artinite	Nesquehonite	Lansfordite
		Formula	$MgCO_3$	$Mg_5(CO_3)_4(OH)_2\cdot 4H_2O$	$Mg_5(CO_3)_4(OH)_2\cdot 5H_2O$	$Mg_2(CO_3)(OH)_2$	$Mg_2(CO_3)(OH)_2\cdot 3H_2O$	$MgCO_3\cdot 3H_2O$	$MgCO_3\cdot 5H_2O$
Name	Formula	CO_2: MgO ratio	1:1	4:5	4:5	1:2	1:2	1:1	1:1
Serpentine[a]	$[Mg_3Si_2O_5(OH)_4]$	-	0.48	0.38	0.38	0.24	0.24	0.48	0.48
Brucite	$[Mg(OH)_2]$	-	0.75	0.60	0.60	0.38	0.38	0.75	0.75
Forsterite	$[Mg_2SiO_4]$	-	0.63	0.50	0.50	0.31	0.31	0.63	0.63
Diopside[b]	$[CaMgSi_2O_6]$	-	0.41	0.37	0.37	0.30	0.30	0.41	0.41
Enstatite	$[Mg_2Si_2O_6]$	-	0.44	0.35	0.35	0.22	0.22	0.44	0.44

Modified from I. M. Power, A. L. Harrison, G. M. Dipple, S. A. Wilson, P. B. Kelemen, M. Hitch, G. Southam, Carbon Mineralization: From Natural Analogues to Engineered Systems. Reviews in Mineralogy and Geochemistry, 77, 305–360 (2013).

Figure 4: Amount of CO_2 stored per ton of dissolving and precipitating mineral.

Project Concept and Overview

The project is being conducted in two phases. During Phase I, LLNL and its partners characterized the site, including mineralogical and geochemical variability in site materials, as well as baseline conditions, including CO_2 flux and local climate. Designs were then established for the second, experimental phase of the project. The results from Phase I demonstrate that despite prolonged exposure to the atmosphere, reactive material is still present and accessible and is naturally taking up atmospheric CO_2. However, these natural rates are still well below rates that can be achieved by applying practices that can accelerate the CO_2 mineralization reaction.

Figure 5: Location of test site at the KCAC Joe Pit Mine.

This work also entailed the development of an environmental, health, and safety (EH&S) plan for working at the KCAC test site. The handling of asbestos-containing material required training and monitoring for all site users, and the methodologies established in this work will be informative to potential future developments.

During Phase II, LLNL and its partners will test two methods to accelerate the rate of CO_2 mineralization, which are the Greenhouse Method and the Tilling Method. The team estimated that these methods can increase the CO_2 mineralization rate by up to five times greater than the natural background rate. An initial life cycle analysis (LCA) concluded that the baseline version of the Greenhouse and Tilling methods at commercial scale are expected to achieve a CDR efficiency of 97% and 71%, respectively (cumulative, more than 30 years of operation). An Initial techno-economic analysis (TEA) found the levelized, 30-year costs of the baseline Greenhouse and Tilling methods to be \$95/t-CO_2 and \$119/t-CO_2, respectively, and that costs could be brought to well below \$100/t-CO_2 for either method by scaling up the volume of rock utilized. An initial EH&S risk assessment, evaluating the potential EH&S risks of the proposed carbon mineralization methods at commercial scale, was completed by LLNL EH&S professionals for these two methods.

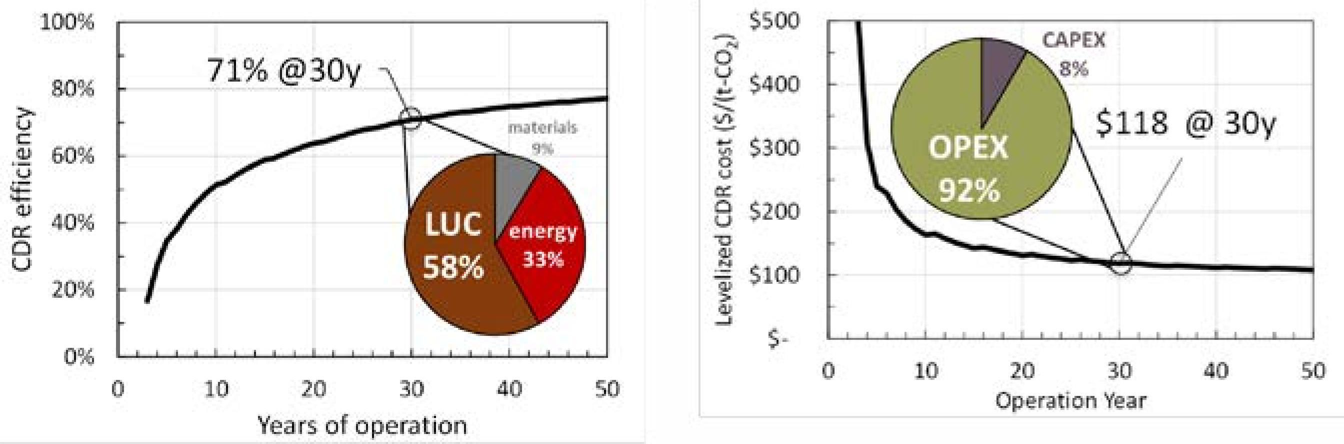


Figure 6: CDR efficiency and cost estimates using the Tilling Method.

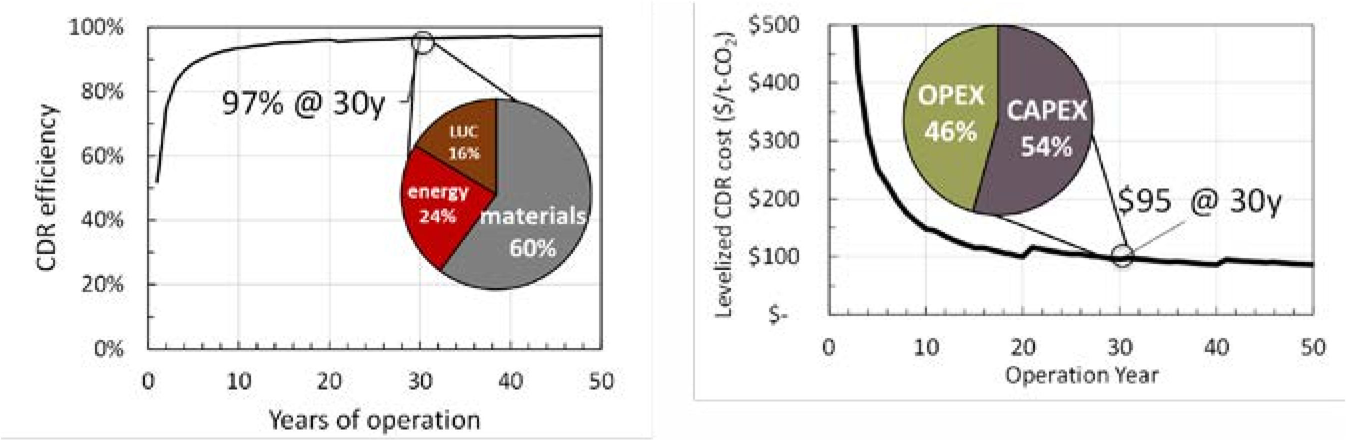


Figure 7: CDR efficiency and cost estimates using the Greenhouse Method.

technology advantages

- Accelerates the natural mineralization process to capture CO_2.
- Potential for a net-negative CO_2 budget.
- Potential for large-scale CO_2 storage.

R&D challenges

- Human health hazards due to exposure to asbestos-bearing serpentinite rocks/mine tailings.
- Environmental hazards due to disturbance of asbestos-bearing serpentinite rocks/mine tailings.
- Effective monitoring of CO_2 flux and uptake.
- Developing successful accelerated carbon mineralization experiments at low cost.

status

The project team has completed mineralogy studies and conducted initial site characterizations. The results from these experiments have established baseline performance measurements, which have informed initial TEA and LCA. An initial TEA shows costs down to \$95/t-CO_2 with the Greenhouse Method and \$119/t-CO_2 with the Tilling Method. An initial EH&S plan was also completed by LLNL EH&S professionals. In the second phase of the project, two methods to accelerate the carbonation reaction will be tested, informed by data gathered in the first phase.

available reports/technical papers/presentations

"King City Asbestos Corporation (KCAC) Mine Carbon Mineralization Field Test," Budget Period 1 Review Meeting, November 8, 2022. *https://netl.doe.gov/projects/plp-download.aspx?id=14313&filename=King+City+Asbestos+Corporation+(KCAC)+Mine+Carbon+Mineralization+Field+Test.pdf*.

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CARBON CAPTURE TECHNOLOGY SHEETS

R&D Collaboration

National Carbon Capture Center

primary project goal

The U.S. Department of Energy (DOE)/National Energy Technology Laboratory (NETL) and Southern Company operate the National Carbon Capture Center (NCCC), a neutral research facility working to advance technologies to reduce greenhouse gas emissions from fossil-based power plants and industrial processes, and to promote carbon conversion and carbon removal innovations such as direct air capture (DAC). Located in Wilsonville, Alabama, the center offers a unique test bed for third-party evaluations of cost-effective carbon dioxide (CO_2) capture, CO_2 conversion and DAC technologies—bridging the gap between laboratory research and large-scale demonstrations and deployment.

technical content

The NCCC offers exceptional benefits to technology developers by providing them with testing opportunities in the real-world operating conditions of an industrial site, thereby accelerating the commercialization of low-cost carbon capture and conversion processes, as well as emerging DAC technologies. The center has surpassed 150,000 hours of testing for innovators from the United States and six other countries. Through the testing of more than 75 technologies, the center has directly participated in the reduction of the projected cost of CO_2 capture from fossil generation by more than 40%.

The NCCC, shown above, supports the evaluation of advanced technologies from domestic and international developers. These evaluations are critical in identifying and resolving environmental, health and safety, operational, component, and system development issues, as well as achieving scale-ups and process enhancements in collaboration with technology developers. DOE-sponsored projects, as well as projects from industry, universities and other collaborative institutions, provide a full spectrum of technologies for testing at the center.

The DOE Office of Fossil Energy and Carbon Management's NETL, in cooperation with Southern Company, established the NCCC in 2009 to provide an independent, centralized, flexible, cost-efficient carbon capture testing facility with industrial operating conditions. Since its inception, researchers at the NCCC have conducted numerous tests for the advancement of post-combustion carbon capture for natural gas and coal power plants, as well as industrial sources.

project focus:

Carbon Capture, Conversion and DAC Testing Center

participant:

Southern Company

project number:

FE0022596

predecessor project:

NT0000749

NETL Project Manager:

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Southern Company
jnorthin@southernco.com

partners:

American Electric Power; BP; ClearPath Foundation; Electric Power Research Institute; ExxonMobil; NRECA; Tennessee Valley Authority; TotalEnergies; Wyoming Integrated Test Center

start date:

06.06.2014

percent complete:

85%

Early testing also included more than 30 projects in the gasification and pre-combustion carbon capture areas, a scope of work that has since concluded. In 2020, the NCCC added infrastructure to broaden its post-combustion test capabilities under actual natural gas-fired conditions. Additionally, the center now hosts CO_2 conversion and DAC technologies, as well as carbon capture process intensification projects. The testing infrastructure supports the capability to test hybrid concepts that include both DAC and CO_2 capture from concentrated sources. Since its creation, the NCCC has more than tripled its plant capacity (from 12,000 to 40,000 pounds per hour [lb/hr] of flue gas) and has added systems (lab-scale test unit [LSTU], advanced flash stripper, natural gas flue gas infrastructure, etc.), along with enhanced instrumentation, sampling methods and analysis tools. Performance data generated in testing at the NCCC has validated laboratory data allowing for engineering scale-up and, in turn, driving new breakthroughs in carbon management solutions.

The NCCC's post-combustion test facilities include a natural gas boiler system that produces flue gas representative of an actual, commercial natural gas combined-cycle power plant. The NCCC also operates utilizing flue gas from Alabama Power's Plant Gaston Unit 5, a commercial, base-loaded, 880-megawatt (MW) supercritical pulverized coal-fueled unit. Developers have the ability to switch between natural gas and coal flue gas during test campaigns. The NCCC provides test bays for simultaneous lab-, bench- and pilot-scale operation of advanced technologies at commercially relevant process conditions. These include two fully integrated processes for solvent evaluations—a pilot-scale test unit (PSTU) and a bench-scale slipstream solvent test unit (SSTU)—as well as seven pilot- and bench-scale test bays and an indoor lab-scale test area. The center also provides support for design, procurement, construction, installation, operation, data collection and analysis, and reporting in compliance with environmental and government requirements. Figure 1 shows the test facilities and the natural gas and coal flue gas configurations.

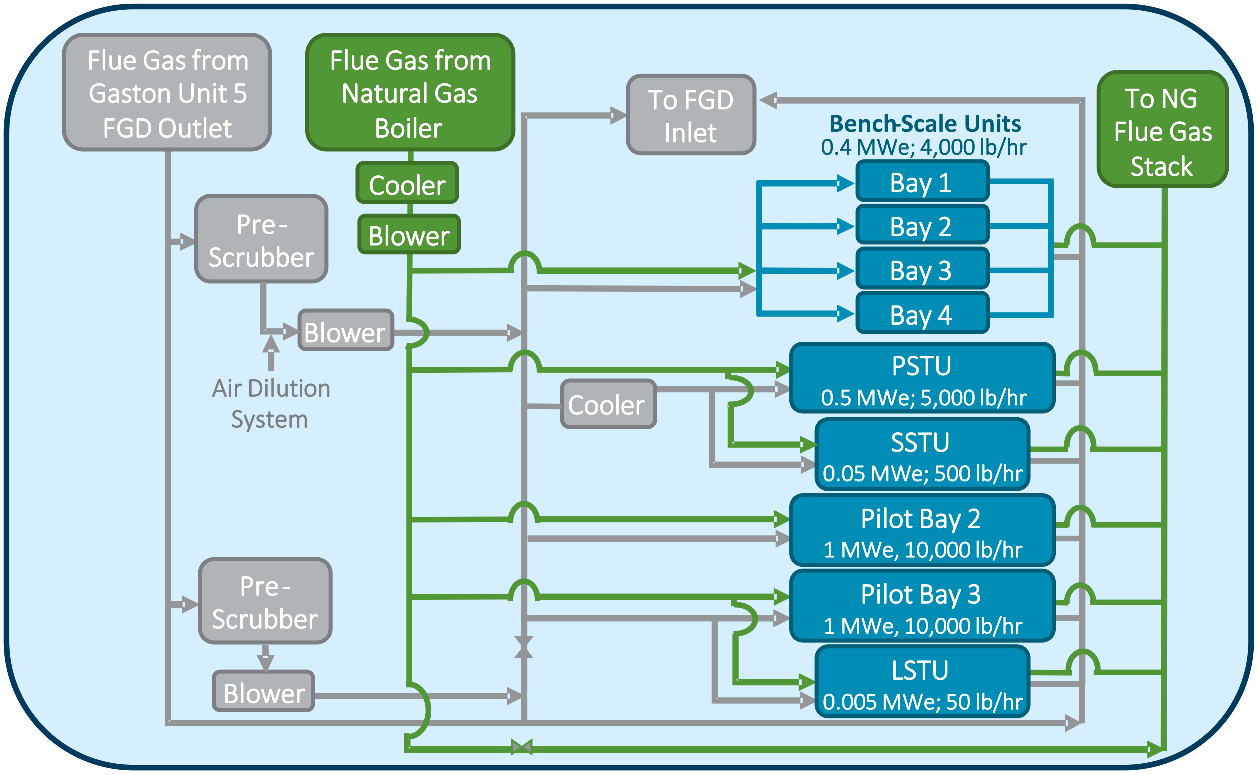

Figure 1: Diagram of post-combustion test facilities at the National Carbon Capture Center.

The PSTU is a nominal 0.5-megawatt-electric (MWe) solvent-based CO_2 capture absorber/stripper system designed to process a flow rate of 5,000 lb/hr of coal-derived flue gas or up to 8,000 lb/hr of natural gas-derived flue gas. The major components of the system are a pre-scrubber, cooler/condenser, absorber, wash tower and regenerator. The PSTU has three options available for solvent regeneration to release the CO_2 from the solvent:

1. A packed-bed column regenerator that provides heat via steam in a sump-located, pump-around loop with a shell and tube heat exchanger to release CO_2 in a conventional simple stripper configuration.

2. A continuous stirred tank reactor, designed by GE Global Research for their testing, which is a one-stage separation unit with reduced space requirements and potentially lower capital requirements compared to conventional regenerator columns.
3. An advanced flash stripper, developed by the University of Texas at Austin and AECOM for their testing, which recovers the stripping steam heat by employing cold and warm rich bypasses.

The SSTU is a 0.05-MWe solvent-based CO_2 absorber/regenerator system with the ability to test innovative CO_2 capture solvents under a variety of conditions using up to 500 lb/hr of flue gas. The SSTU is optimized for validating lab-based results under industrial conditions to yield scalable data for further pilot-scale testing.

technology advantages

The NCCC's ability to support multiple developers and tests simultaneously at various scales, and to offer flexibility in capacity and process conditions, offers a wide range of data and information to accelerate the commercialization of CO_2 capture and utilization technologies. The NCCC also offers advantages to DAC developers, including a proficient staff, the capability to test both DAC and CO_2 capture/conversion from concentrated sources (or hybrid concepts), and assistance in finding domestic and international partners for scale-up.

R&D challenges

The NCCC's state-of-the-art facility, which delivers necessary infrastructure, flue gases, utilities, and other support, enables the effects of system interactions to be understood to ensure a smooth transition of technologies from a laboratory setting to an industrial setting. By executing field testing under realistic power plant conditions, technologies can be scaled up with confidence for larger-scale demonstrations and commercial deployment. For technologies that are not ready for scale-up, improvements are identified and further engineering-scale testing needs are defined.

status

NCCC operation has provided more than 150,000 hours of testing enzymes, membranes, sorbents, solvents, hybrids and associated systems for post-combustion carbon capture, as well as CO_2 conversion technologies and DAC technologies. More than 75 technologies from more than 50 developers (including eight international developers) have been tested, with nine technologies scaled up (or ready) to be demonstrated at 10+ MW. The PSTU has operated for more than 32,000 hours in support of commercial developers and DOE's Carbon Capture Simulation Initiative, with several technologies progressing to larger-scale testing at other facilities and commercial demonstration. More than 8,500 hours of testing have been conducted under simulated natural gas conditions.

The NCCC has completed three carbon conversion tests to date, including demonstration of a Southern Research thermochemical process to produce ethylene by using CO_2 from coal-fired flue gas and ethane, and a demonstration of the CarbonBuilt Reversa™ CO_2 mineralization process, which uses CO_2 in flue gas and coal combustion residuals to produce low-carbon concrete. In addition, the NCCC completed tests in April 2023 with Helios-NRG LLC on the first algae conversion technology—a novel, multi-stage continuous algae-based system to capture CO_2 from power plant flue gas. The NCCC also completed its first DAC onsite test, in collaboration with Southern States Energy Board (SSEB) and Aircapture, in December 2023 and is performing additional testing with the addition of a liquefaction skid.

available reports/technical papers/presentations

"National Carbon Capture Center (FE0022596)," presented by Tony Wu, Southern Company, 2023 NETL Carbon Management Research Project Review Meeting, August 2023. *https:/netl.doe.gov/sites/default/files/netl-file/23CM_PSCC29_Wu.pdf.*

"National Carbon Capture Center (FE0022596)," presented by Tony Wu, Southern Company, 2022 NETL Carbon Management Project Review Meeting, August 2022. *https://netl.doe.gov/sites/default/files/netl-file/22CM_PSC16_Wu.pdf.*

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"Carbon Utilization and the National Carbon Capture Center," presented by John Northington, Southern Company, 2020 NETL Integrated Project Review Meeting – Carbon Utilization, October 2020. *https://netl.doe.gov/sites/default/files/netl-file/20VPRCU_Northington.pdf*.

"Advanced Carbon Capture Testing at the National Carbon Capture Center (FE0022596)", presented by Michele Corser, Southern Company, 2019 NETL Carbon Capture, Utilization and Storage, and Oil and Gas Technologies Integrated Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/M-Corser-Southern-Co-NCCC-Testing.pdf*.

"Status of Technology Development at the National Carbon Capture Center," presented by Justin Anthony, John Carroll, Michele Corser, Frank Morton, Tony Wu, and Ruth Ann Yongue, Southern Company, International Conference on Greenhouse Gas Control Technologies, GHGT-14, October 2018. *https://papers.ssrn.com/sol3/papers.cfm?abstract_id=3366390*.

"Update on National Carbon Capture Center (FE0022596)," presented by Tony Wu, Southern Company, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/sites/default/files/netl-file/T-Wu-Southern-National-Carbon-Capture-Center.pdf*.

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"Advanced Technology Testing at the National Carbon Capture Center," presented by Justin Anthony and John Carroll, Southern Company, 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File Library/Events/2016/c02 cap review/1-Monday/J-Anthony-SouthernCo-Testing-at-National-Carbon-Capture-Center.pdf*.

National Carbon Capture Center website: *https://www.nationalcarboncapturecenter.com/*.

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