

APPENDIX B: CARBON DIOXIDE CAPTURE TECHNOLOGY SHEETS

PRE-COMBUSTION SORBENTS



ADVANCED CARBON DIOXIDE CAPTURE TECHNOLOGY FOR LOW-RANK COAL INTEGRATED GASIFICATION COMBINED CYCLE (IGCC) SYSTEMS

primary project goals

TDA will investigate the technical and economic advantages of using an integrated carbon dioxide (CO₂) sorbent and water-gas shift (WGS) catalyst system in an integrated gasification combined cycle (IGCC) power plant, fueled with low-rank coal, and designed to capture more than 90 percent of the CO₂ emissions.

technical goals

- TDA will evaluate the physical mix of the sorbent and catalyst pellets within the same reactor housing and at synthesizing WGS catalyst onto the pores of the adsorbents.
- The performance of the integrated system, first in the bench-scale tests and then in a field demonstration using actual coal-derived synthesis (syngas) gas, will be optimized, and bench-scale experiments will demonstrate that the sorbent/catalyst combination works in the presence of the key contaminants.

technical content

Through systems analysis and physical tests, TDA will show the technical and economic advantages of using an integrated CO₂ sorbent and WGS catalyst system in an IGCC power plant, fueled with low-rank coal, and designed to capture more than 90 percent of the CO₂ emissions.

The proposed system uses a high-temperature physical adsorbent capable of removing CO₂ above the dew point of the syngas and a contaminant tolerant WGS catalyst that can effectively convert carbon monoxide (CO) to hydrogen and CO₂ in the presence of a wide range of contaminants, particularly the alkali, sulfur, and phosphorous compounds resulting from the gasification of low-rank coals. The integrated operation of the WGS catalyst and CO₂ removal processes in a single step drives the equilibrium-limited WGS reaction toward hydrogen without the need to add large amounts of water (H₂O) to the syngas, greatly reducing the cost of CO₂ capture. Preliminary system analysis suggests that maintaining the H₂O:C ratio of reactants entering the shift reactor close to that required by the reaction stoichiometry (1:1) rather than using an excess of close to 2:1 will improve IGCC plant efficiency by more than two percentage points by reducing the consumption of shift steam. The process intensification provided by carrying out two unit operations (WGS and CO₂ removal) in the same reactor will reduce the capital cost and improve the process economics of new IGCC plants.

In a prior U.S. Department of Energy (DOE)/National Energy Technology Laboratory (NETL) project, TDA developed the sorbent for pre-combustion CO₂ capture (Contract No. DE-FE0000469). TDA successfully completed a field demonstration at the National Carbon

technology maturity:

Bench-Scale Testing and Slipstream Field Testing with Actual Syngas

project focus:

CO₂ Capture for Low-Rank Coal IGCC Systems

participant:

TDA Research

project number:

FE0007966

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partners:

Southern Company
University of California Irvine
ConocoPhillips

performance period:

9/30/11 – 9/30/13

Capture Center (NCCC; Southern – Wilsonville, Alabama) in 2011 and demonstrated the sorbent's ability to remove CO₂ from a gasifier syngas stream. TDA also developed a contaminant tolerant WGS catalyst in another DOE project (DE-SC0004379). In bench-scale tests, TDA demonstrated the catalyst while maintaining stable performance in the presence of contaminants originating from coal-biomass co-gasification, including Na, K, P, Cl, S, all of which will also be present in the syngas generated by the gasification of low-rank coals.

In this project, TDA will work with UCI, Southern Company, and Conoco Phillips to demonstrate the viability of the new technology. Sorbent/catalyst and process design will be optimized and the efficacy of the integrated WGC/CO₂ capture system will be assessed, first in bench-scale experiments, and then slipstream field demonstrations. The slipstream testing will be conducted at Southern Company's Wilsonville, Alabama, air-blown gasifier.



Figure 1: TDA's CO₂ Removal Skid



Figure 2: TDA's Gas Conditioning Skid

technology advantages

- Capturing CO₂ above the dew point of the syngas significantly improves the net plant efficiency.
- Carbon dioxide recovered at pressure reduces compression costs for sequestration.
- The integration of the WGS catalyst and CO₂ removal processes in a single step drives the equilibrium-limited WGS reaction toward hydrogen, reducing the need for water, and greatly reducing the cost of CO₂ capture.
- The process intensification provided by carrying out two unit operations (WGS and CO₂ removal) in the same reactor will reduce the capital cost and improve the process economics of new IGCC plants.

R&D challenges

Achieving acceptable CO conversion and CO₂ capture rates in a mixed CO catalyst/CO₂ sorbent fixed-bed reactor design while maintaining a low-steam:CO ratio.

results to date/accomplishments

- Performed field demonstrations for a period of four weeks.
- Demonstrated that CO conversion in combination with the CO₂ yields high conversion rates even at steam:CO ratios less than 1.2.
- Demonstrated that the CO₂ capacity of the sorbent was unaffected by the catalyst.
- Completion of more than 1,140 cycles in the multiple cycle tests.
- Completed testing of sorbents/catalysts to determine working capacity and plant efficiency.

next steps

- Complete testing with prototype unit.
- Complete techno-economic analysis.
- Finalize design of the combined WGS and CO₂ removal unit.

available reports/technical papers/presentations

N/A.

B-17

PRE-COMBUSTION SORBENTS

EVALUATION OF DRY SORBENT TECHNOLOGY FOR PRE-COMBUSTION CO₂ CAPTURE

B-18

primary project goals

URS Group and the University of Illinois at Urbana-Champaign (UIUC) are developing dry carbon dioxide (CO₂) sorbent materials, through the coupling of thermodynamic, molecular simulation, as well as process simulation modeling with novel synthesis methods, that possess superior adsorption and regeneration properties at conditions applicable to water-gas shift (WGS) systems. If successful, this project will demonstrate that one or more sorbent materials are able to remove greater than 90 percent of the CO₂ from a simulated synthesis gas (syngas) at conditions applicable to a WGS reactor, thus meeting a key U.S. Department of Energy (DOE) program objective.

technical goals

Specific technical objectives of this project include:

- Determination of optimal CO₂ sorbent properties and operating conditions for CO₂ removal and regeneration and carbon monoxide (CO) conversion in a simulated syngas using a combination of computational and experimental methods.
- Development of one or more sorbents that recover high-quality heat during CO₂ adsorption, regenerate at elevated pressure, have minimal deactivation over multiple cycles, have high selectivity at high temperatures, have high adsorption capacity, and have acceptable thermal stability and mechanical integrity. This will result in sorbents capable of 90 percent CO₂ removal with high loading capacities and able to operate at the high temperatures and pressures typically encountered upstream of a WGS reactor. If successful, the sorbents developed in this program will augment or replace the CO conversion catalysts currently used in WGS reactors and improve overall WGS thermal efficiency.
- Determine the techno-economic feasibility of the sorption-enhanced WGS (SEWGS) process for removing CO₂.

technical content

URS Group, Inc. is leading an investigative effort for the development of a dry sorbent process configured to combine the WGS reaction with CO₂ removal for coal gasification systems. The result will be an SEWGS technology.

A novel approach is being taken that integrates the use of multiple computational models with sorbent synthesis and characterization activities to develop sorbents with optimal CO₂ removal properties at high temperatures and pressures applicable to WGS applications. Tests are being performed where sorbent performance is evaluated in simulated WGS gas mixtures at commercially relevant conditions. Appropriate data reduction and analysis is being conducted in order to provide suitable data that will provide the basis for a techno-economic analysis to evaluate the feasibility and scale-up potential of the SEWGS technology.

technology maturity:

Bench-Scale Using Simulated Syngas

project focus:

Sorbent Development for WGS

participant:

URS Group

project number:

FE-0000465

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partners:

Illinois Clean Coal Institute
University of Illinois at Urbana-Champaign (UIUC)

performance period:

1/1/10 – 9/30/13

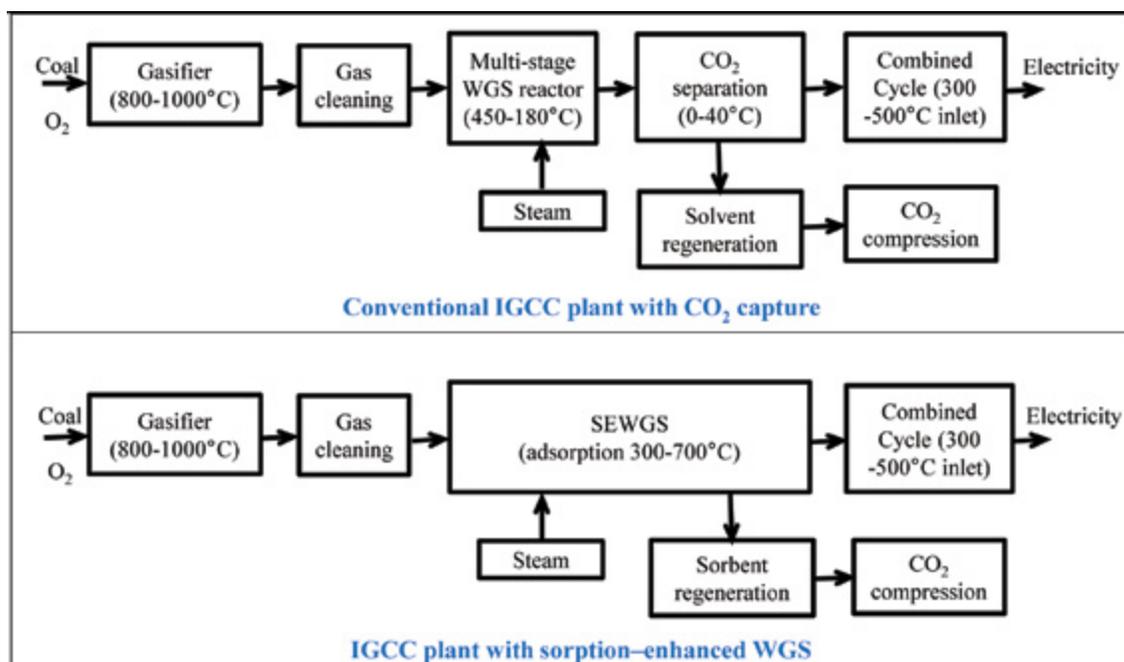


Figure 1: IGCC with SEWGS vs. Conventional IGCC

UIUC will perform process simulation modeling and sorbent molecular and thermodynamic analyses. These analyses will allow prediction of optimal sorbent properties and identification of optimal operating temperature and pressure windows to maximize the energy efficiency of the combined WGS and CO₂ capture processes. The thermodynamic study will include developing phase equilibrium diagrams for potential sorbents, identifying optimum operating conditions for CO₂ capture, understanding impacts of syngas impurities, and identifying promising sorbents. Molecular simulation will predict isotherms and properties, predict kinetics and dynamics, and identify sorbents with desired properties using quantum chemistry/mechanics, force field-based Molecular Dynamics (MD), and reactive dynamics (RD) simulations. Process simulation analysis will analyze various process scenarios for heat integration between SEWGS and integrated gasification combined cycle (IGCC) and process energy performance for individual sorbents.

Concurrently, UIUC will perform sorbent development. Sorbents will be synthesized with desired pore structure and composition guided by the first phase testing and modeling effort. Sorbents will be synthesized using various precursors, including calcium, magnesium, and other metal oxides, as well as zirconates, titanates, silicates, aluminates, and adsorbent-shift catalyst hybrid. Sorbent down-selection will proceed according to the decision tree shown in Figure 2.

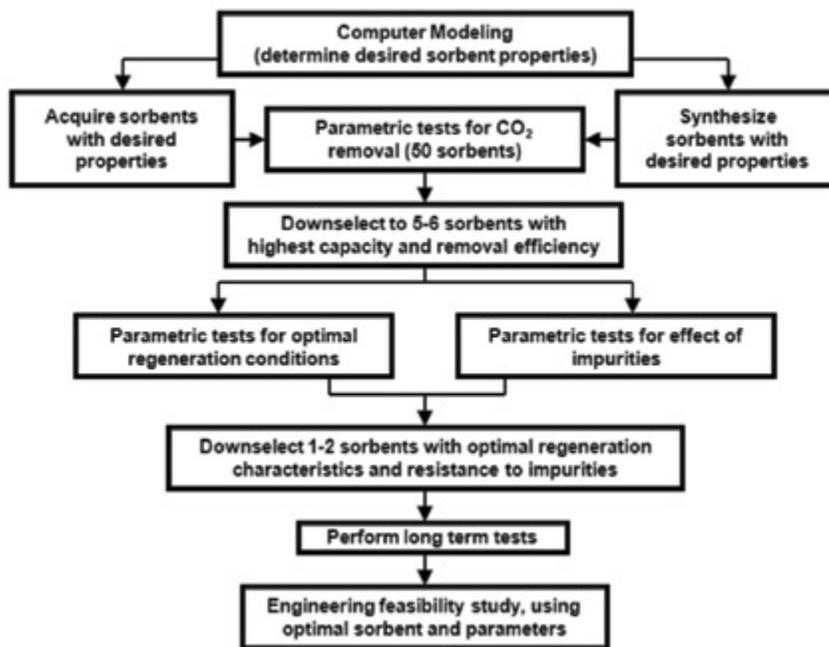


Figure 2: Sorbet Development and Analysis Decision Tree

UIUC will use an atmospheric-pressure thermogravimetric analyzer (TGA) and a high temperature and pressure reactor (HTPR) system capable of 300 pounds per square inch gauge (psig) and 950°C for screening sorbents for CO₂ removal. Also, URS will construct an HTPR to evaluate sorbet adsorption performance in presence of syngas impurities and regeneration performance. Five to seven down-selected sorbents will also be tested for sorbet resistance to syngas impurities and determine optimal regeneration parameters. One to two sorbents will be further down-selected and will be tested on a longer-term basis.

Lab results will be used in a preliminary engineering study of process feasibility for adsorbing and removing CO₂ as part of the WGS process with the comparison made to base WGS operation and other CO₂ removal strategies. Parameters to be evaluated include costs of >90 percent removal (cost of electricity [COE], operation and maintenance [O&M]), sorbet costs, anticipated lifetime (i.e., replacement rate), estimated future market costs of precursor materials, handling equipment, sorbet regeneration costs, heat/energy integration, compression costs with SEWGS, unit footprint, and capital costs and scalability.

TABLE 1: SOLID SORBENT PARAMETERS

	Units	Current R&D Value	Target R&D Value
Sorbent			
True Density @ STP	kg/m ³		TBD
Bulk Density	kg/m ³		TBD
Average Particle Diameter	mm	Nano (20-70 nm) or micro meter (0.5-10 μm) level; particles can be pelletized if needed	TBD based on the reactor design analysis
Particle Void Fraction	m ³ /m ³		
Packing Density	m ² /m ³		
Solid Heat Capacity @ STP	kJ/kg-K	<1	<1
Crush Strength	kg _f		
Manufacturing Cost for Sorbet	\$/kg		

TABLE 1: SOLID SORBENT PARAMETERS

	Units	Current R&D Value	Target R&D Value
Adsorption			
Pressure	bar	30 – 40	40
Temperature	°C	300 – 700	550 – 650
Equilibrium Loading	g mol CO ₂ /kg		
Heat of Adsorption	kJ/mol CO ₂	100 – 200	TBD
Desorption			
Pressure	bar	Up to 30	Highest possible up to 30
Temperature	°C	Depends on individual sorbent and highest regeneration pressure achievable	TBD; optimization based on minimal energy limit
Equilibrium Loading	g mol CO ₂ /kg		
Heat of Desorption	kJ/mol CO ₂		
Proposed Module Design		<i>(for equipment developers)</i>	
Flow Arrangement/Operation	-	Temperature swing	Temperature swing
Flue Gas Flowrate	kg/hr		
CO ₂ Recovery, Purity, and Pressure	percent / percent / bar	90 percent, 99 percent,	
Adsorber Pressure Drop	bar	Depending on sorbent properties, to be determined during project	TBD
Estimated Absorber/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., CO₂-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 CO₂ 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 CO₂ in equilibrium with the sorbent. If the vapor phase is pure CO₂, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO₂. Note that for a typical PC power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO₂ is about 13.2 percent. Therefore, the partial pressure of CO₂ 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 CO₂ 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 CO₂ in CO₂-rich product gas; assuming targets are met

This is a research and development (R&D) program involving fairly immature technology. As such, many target R&D values will be determined during execution of the test program and will be impacted by a number of key process parameters, including sorbent type and cost, sorbent performance and loading capacity, sorbent lifetime, regeneration conditions and cycling parameters, and complexity of integration of optimal adsorption and regeneration processing steps.

Sorbent Heating/Cooling Method – For sorbent regeneration, the sorbent is heated in a fluidized-bed or moving-bed configuration with heat supplied by either hydrogen (H₂) (or syngas) oxy-combustion or steam extracted from the gasification plant steam cycle. Before entering the adsorption bed, the regenerated sorbent is cooled by exchanging heat with inlet regeneration H₂/oxygen (O₂) or syngas. In the adsorption bed, a heat exchanger (such as a boiler tube bundle used in the fluidized-bed boiler) is used for recovering heat generated from CO₂ adsorption.

Heat of Adsorption Handling – Adsorption heat is recovered during CO₂ adsorption by using a heat exchanger to generate steam, which is combined into the gasification plant's steam cycle for electricity generation.

Heat Supply Method for Regeneration – Two methods will be considered. One is to burn a small amount of the H₂ or syngas using O₂ to supply heat directly. Another approach is to use the steam from the gasification plant's steam cycle if the regeneration temperature is below 1,000°F.

Contamination Resistance – This program will evaluate the impact of various syngas impurities on the adsorption and regeneration performance of promising CO₂ sorbents. Sorbents may not be resistant to sulfur species (hydrogen sulfide [H₂S], carbon disulfide [CS₂], etc).

Flue Gas Pretreatment Requirements – The pretreatment of H₂S/CS₂ is needed for sorbents with no sulfur resistance. If it is determined that the performance of identified sorbents is inhibited by sulfur species present in the syngas, additional work will focus on the development of sorbents materials that are resistant to sulfur; the objective will be to avoid the need for syngas pretreatment associated with this technology.

Waste Streams Generated – Desulfurization byproducts.

technology advantages

- High CO conversion with reduced steam addition.
- No or limited WGS catalyst use.
- High-quality adsorption heat usable for generation of high-quality steam.
- Limited gas cooling/reheating requirement downstream.
- No separate CO₂ capture unit required.
- Reduced energy requirement for CO₂ compression.

R&D challenges

- Sorbent pores may be plugged during adsorption, causing capacity and activity loss.
- Long-term capacity and activity stability after multiple cycles.
- Selectivity at high temperature.
- System/reactor issues, such as material transport and handling at high temperature and pressure.

results to date/accomplishments

- More than 40 sorbents were modeled and subsequently down-selected to seven candidates (magnesium oxide [MgO], calcium oxide [CaO], lithium zirconate [Li₂ZrO₃], calcium zirconium oxide [CaZrO₃], barium zirconate [BaZrO₃], barium titanate [BaTiO₃], and barium silicate [BaSiO₃]) for further development.
- Process simulations were performed for a baseline IGCC plant with WGS and a Selexol process and compared to an IGCC

with SEWGS. These showed a 0.5 to 2.4 percentage points increase in net thermal efficiency for the simulated plant with SEWGS.

- Molecular simulation studies included quantum chemical (QC) calculations and MD simulations with reactive field force (ReaxFF). Molecular simulation was successfully applied to assess carbonation and calcination reactions (CaO).
- The impacts of sorbent structure and the sintering of calcium oxide particles with and without CO₂ chemisorption, and the role of a dopant in reducing the sintering of CaO particles, were also determined.
- More than 60 SEWGS sorbents were synthesized using Mechanical alloying (MA), Ultrasonic Spray Pyrolysis (USP), and Flame Spray Pyrolysis (FSP) techniques.
- CaO sorbents prepared by dry and wet ball-milled MA methods exhibited improved CO₂ adsorption capacities and stabilities over commercial CaCO₃ materials. The performance of CaCO₃ sorbents was improved by doping with inert MgO.
- Hollow, porous CaCO₃ sorbents synthesized using the USP method were spheres of $\approx 1\mu\text{m}$ with a shell thickness of 50-100 nm. The CaO generated upon calcination of the CaCO₃ exhibited a high surface area (up to 75m²/g).
- A 75:25 w/w CaO:Ca₁₂Al₁₄O₃₃ (mayenite) sorbent retained 91 percent of its initial CO₂ capacity after 15 cycles and 79 percent after 50 cycles, while a USP CaO only retained 43 percent after 15 cycles.
- The surface area of nano-sized (<70 nm) CaO, ZrO₂-doped CaO, MgO, MgO-doped CaO, and ZrO₂-doped MgO sorbents synthesized using the FSP method ranged between 21 and 54 m²/g. ZrO₂ was found to be an effective dopant to improve the stability of CaO-based sorbents. A ZrO₂-CaO (Zr:Ca=0.2:1) sorbent maintained its capacity at 0.5g CO₂/g sorbent over 15 adsorption-desorption cycles.
- An HTPR tube reactor with quarter-inch ID and one-foot length was also used to test sorbents at UIUC. These tests were performed at 650°C and CO₂ partial pressures up to 4 bar adsorption conditions.

next steps

- CO₂ adsorption and combined CO₂ adsorption + WGS of selected sorbents using HTPR setup.
- Continue impurity testing and parametric regeneration optimization.
- Long-term tests on select sorbents.

available reports/technical papers/presentations

Steen, W.; Richardson, C.; Machalek, T.; Paradis, J.; Rostam-Abadi, M.; Lu, Y.; Lu, H.; Napoli, M.; and Everitt, E., "Solid Sorbent enhanced Water-Gas Shift Process for Pre-Combustion CO₂ Capture," Proceedings of the Power Plant Air Pollutant Control "Mega" Symposium, Paper #16, Baltimore, MD, August 2012.

Evaluation of Dry Sorbent Technology for Pre-combustion CO₂ Capture; Presentation at the 2012 NETL CO₂ Capture Technology Meeting, Pittsburgh, Pennsylvania, July 2012. <http://www.netl.doe.gov/publications/proceedings/12/co2capture/presentations/4-Thursday/B%20Steen-URS-Pre-combustion%20Sorbent.pdf>.

Lu, Y.; Lu, H.; Rostam-Abadi, M.; Sayyah, M.; Suslick, K.; Steen, W.; Richardson, C.; Hirschi, J.; and Napoli, M., "Evaluation of Dry Sorbent Technology for Pre-Combustion CO₂ Capture", Proceedings of the Clearwater Clean Coal Conference – 37th International Technical Conference on Clean Coal & Fuel Systems, Clearwater, FL, June 2012.

Steen, W.; Richardson, C.; Lu, Y.; Lu, H.; and Rostam-Abadi, M., "Evaluation of Dry Sorbent Technology for Pre-Combustion CO₂ Capture," Proceedings of the 2011 DOE-NETL CO₂ Capture Technology Meeting, Pittsburgh, PA, August 2011. <http://www.netl.doe.gov/publications/proceedings/11/co2capture/presentations/4-Thursday/25Aug11-Steen-URS-Dry%20Sorbent%20Pre-CombustionCapture.pdf>.

Richardson, C., and Lu, Y., "Evaluation of Dry Sorbent Technology," Presentation at the 2010 NETL CO₂ Capture Technology Meeting, Pittsburgh, Pennsylvania, September 2010. <http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/thursday/Carl%20Richardson%20-%20FE0000465.pdf>.

"Evaluation of Dry Sorbent Technology for Pre-Combustion CO₂ Capture," Pre-combustion CO₂ Capture Kick-off Meetings, Pittsburgh, Pennsylvania, November 2009. <http://www.netl.doe.gov/publications/proceedings/09/CO2capture/7-URS%20Dry%20Sorbent%20Kickoff%20Presentatin-111309.pdf>

ADVANCED ACID GAS SEPARATION TECHNOLOGY FOR THE UTILIZATION OF LOW-RANK COALS

B-24

PRE-COMBUSTION SORBENTS

primary project goals

Air Products and Chemicals will conduct extensive testing using a mobile, two-bed Sour Pressure Swing Adsorption (PSA) unit fed with North Dakota lignite coal-based synthesis gas (syngas) streams. The results of this testing will be used to generate a high-level pilot process design and to prepare a techno-economic assessment. Air Products' existing Sour PSA test unit will be modified to improve operability and reliability and operate under exposure to impurities from the gasification of low-rank coal. The test unit will then be attached to the Energy and Environmental Research Center's (EERC) fluidized bed gasifier and operated utilizing North Dakota lignite coal in both PSA and thermal swing adsorption (TSA) modes to determine the suitability of the unit to operate with such coal, and provide information necessary for the design of a high-level pilot unit and a techno-economic assessment, ultimately resulting in a reduction in cost of electricity (COE).

technical goals

- Modify PSA/TSA unit for tar gas operations.
- Run PSA/TSA unit with shifted sour syngas derived from EERC fluidized bed gasifier with a Montana Rosebud Powder River Basin (PRB) coal in oxy-blown mode.

technical content

Air Products and Chemicals has developed a proprietary alternative that consists of three process steps: (1) Sour PSA that separates the desired products from carbon dioxide (CO₂) and hydrogen sulfide (H₂S); (2) sulfur disposition that can be accomplished in several different modes; and (3) a CO₂ polishing and compression step that produces sequestration-ready CO₂.

The Sour PSA technology is based on adsorption processes that utilize pressure swing or temperature swing regeneration methods. The technology is being developed to meet the stringent demands of the desired hydrogen (H₂)-enriched product for power production, while simultaneously yielding a waste gas stream that can provide amenable recovery of sulfur and a high-purity CO₂ byproduct stream.

One option for a Sour PSA process configuration is the Sour PSA unit followed by a sour oxy-combustion unit and finally the CO₂ purification/compression unit (CPU). The Sour PSA is fed sour syngas and produces high-pressure, H₂-enriched product and low-pressure, CO₂/H₂S-rich tail gas. The oxy-combustion process is used to effectively combust flammable species in the tail gas (H₂, carbon monoxide [CO], methane [CH₄]) to CO₂ and H₂O, and H₂S to sulfur oxide (SO_x) and H₂O. This creates an effluent stream that contains highly enriched CO₂ with minor impurities. The heat generated from the combustion system can be used for preheating streams to a turbine in a power system, steam generation, additional reforming in a hydrogen system, or any other ancillary use of high-quality heat. The oxy-fuel

technology maturity:

Laboratory-Scale

project focus:

Advanced Acid Gas Separation

participant:

Air Products and Chemicals

project number:

FE0007759

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partners:

UNDEERC

performance period:

9/30/11 – 12/31/12

combustion may take place either in a once-through manner or with cooled flue gas recycle to moderate the combustion temperature.

The sour oxy-fuel combustion is accomplished by combusting the waste gas with an excess of pure oxygen (O_2), in which case the combustion products will be H_2O , CO_2 , sulfur dioxide (SO_2), sulfur trioxide (SO_3), and excess O_2 . The SO_2 and excess O_2 may be removed from the CO_2 by reactive processes applied during the compression sequence. Specifically, this requires careful design of the compression system coupled with acid production reactors of appropriate size.

A second option is to treat the tail gas from the PSA to remove the H_2S prior to purification of the CO_2 product stream. An acid gas enrichment (AGE) unit can be used for removing the H_2S from the tail gas stream and is generally configured in an absorber/stripper arrangement with a solvent that is selective to H_2S . The H_2S -enriched stream is then sent to a Claus plant that produces elemental sulfur. A partial condensation process may be used on the resulting sulfur-free CO_2 stream to produce the required CO_2 purity. In this project, Air Products conducted extensive testing using a mobile, two-bed, Sour PSA unit fed with North Dakota lignite coal-based syngas streams. This testing was conducted in collaboration with the University of North Dakota's EERC, utilizing their location and fluidized bed gasifier. Measurements of adsorbent and PSA unit performance over time were taken and analyzed. The adsorbent system was operated in TSA mode, as well as PSA mode, to determine the capability for TSA to operate when exposed to syngas derived from lower-rank coal. The two-bed PSA system processed syngas produced from the gasification of PRB low-rank coal for more than 1,000 cycles and reached cyclic steady state operation. Air Products used a proprietary simulation tool to estimate process performance for a commercial, multi-bed system using data derived from the two-bed system operation.

technology advantages

- Air Products' Sour PSA technology is an acid gas removal system capable of reducing the H_2S content in the treated stream down to parts-per-billion (ppb) level while also rejecting more than 99 percent of the CO_2 .
- Air Products' Sour PSA technology provides a more cost-effective solution for purifying raw syngas, mainly from the reduction in the capital cost of the equipment.
- In contrast to most incumbent technologies, the Sour PSA system does not require refrigeration and a complex network of exchangers for heat integration.
- The Sour PSA system is reliable and simple to operate since it does not have any moving parts (except valves) and does not require handling of any acid gas solvent.

R&D challenges

- The long-term stability of the Sour PSA process performance has not been evaluated. Extended two-bed PSA operation with a gasifier syngas slipstream over a period of at least two months is needed.
- All testing to date has been with a two-bed PSA unit, so only simple PSA cycles have been addressed. Sour or sweet syngas tests with a multi-bed PSA unit are needed to evaluate the impact of pressure equalization steps on performance.
- Previous work has focused on producing pure H_2 or enriched H_2 for power production. For syngas applications, both H_2 and CO must be recovered from the process. Development of the correct PSA adsorbent layering scheme and process cycle, as well as downstream sulfur disposition technologies, are required.

[results to date/accomplishments](#)

B-26

- Completed high-level pilot plant design work of a Sour PSA system for acid gas separation treatment of PRB-derived syngas, including a complete engineering design with associated cost estimate.
- Operated a laboratory-scale, two-bed PSA system to process syngas produced from the gasification of PRB low-rank coal for more than 1,000 cycles and reached cyclic steady state operation. Used Air Products' proprietary simulation tool to estimate process performance for a commercial, multi-bed system.
- Completed multiple techno-economic studies on the benefit of using Air Products' Sour PSA technology for acid gas removal in integrated gasification combined cycle (IGCC) applications. These studies show that using Sour PSA technology would result in at least a 15 percent reduction in the incremental cost of CO₂ capture compared to commercially available best technologies. The studies also demonstrated that the optimum sulfur disposition technology (acid production or elemental sulfur) is dependant of the sulfur content of the gasified fuel.

[next steps](#)

This project ended on December 31, 2012.

[available reports/technical papers/presentations](#)

Hufton, J.R.; Quinn, R.; Amy F.; Kloosterman, J.W.; O'Connell, E.M.; Dunham, G.; and Swanson, M., "Advanced Acid Gas Separation Technology for the Utilization of Low Rank Coals" presented at the 29th Annual International Pittsburgh Coal Conference, Pittsburgh, Pennsylvania, October 2012.

Kloosterman, J.W.; Hufton, J.R.; Golden, T.C.; Quinn, R.; Schaffer, C.L.; Hendershot, R.J.; Fogash, K.B.; Wright, A.; and White, V. "Advanced Hydrogen and CO₂ Capture Technology for Sour Syngas," Proceedings of the 2010 Gasification Technology Conference, Washington, D.C., October 2010.

EVALUATION OF DRY SORBENT TECHNOLOGY FOR PRE-COMBUSTION CO₂ CAPTURE

B-27

primary project goals

TDA Research set out to further develop a low-cost, high-capacity regenerable carbon dioxide (CO₂) sorbent technology, demonstrating its technical and economic viability for pre-combustion CO₂ capture from coal-derived synthesis gas (syngas) fueling integrated gasification combined cycle (IGCC) power plants.

technical goals

- Optimize chemical and physical properties of an existing sorbent.
- Modify the sorbent to improve capacity and stability.
- Scale-up sorbent production using commercially adoptable equipment.
- Demonstrate long-term sorbent performance at bench-scale in the presence of contaminants.
- Design and build a prototype unit to support slipstream demonstration tests using actual syngas.
- Detailed process design and cost analysis to evaluate sorbent's ability to remove CO₂ at a lower cost than current technologies.

technical content

TDA set out to develop a novel pre-combustion CO₂ capture technology that uses a TDA proprietary sorbent modified to remove CO₂ from shifted syngas. The CO₂ capture system uses two (or more) beds that switch positions between adsorption and regeneration. In addition to the conventional pressure and temperature swing operation, the sorbent can be regenerated under near isothermal and isobaric conditions, while the driving force for separation is provided by a swing in CO₂ concentration. The sorbent consists of a carbon support modified with surface functional groups that remove CO₂ via strong physical adsorption. The CO₂ surface interaction is strong enough to allow operation at elevated temperatures. Because the CO₂ is not bonded via a covalent bond, the energy input to the regeneration is low – only 4.9 kcal/mole of CO₂ removed (comparable to Selexol™). This energy requirement is much lower than that of the chemical absorbents (e.g., sodium carbonate [Na₂CO₃] requires 29.9 kcal/mol) and amine solvents (≈14 kcal/mol). The energy output loss of the IGCC plant is expected to be similar to that of Selexol's; however, a higher overall IGCC efficiency can be achieved due to higher temperature CO₂ capture.

Initially, the researchers optimized the chemical, mechanical, and physical properties of the sorbent to optimize the active material content; assess the impact of key synthesis parameters on surface area, pore volume, and pore size distribution; and determine crush strength and attrition resistance. Costs were kept to a minimum by evaluating low-cost raw materials and optimizing the production process. Sorbents were evaluated under simulated syngas, water-gas shift (WGS), and simulated contaminant conditions using two thermogravimetric analyzers (TGAs) and one-, three-, and six-inch bench-scale flow reactors. TDA and the

technology maturity:

Pilot-Scale Slipstream Using Actual Syngas

project focus:

High-Capacity Regenerable Sorbent

participant:

TDA Research

project number:

FE00004695

NETL project manager:

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partners:

ConocoPhillips
MeadWestvaco
Southern Company
University of California Irvine

performance period:

10/1/09 – 12/31/12

University of California Irvine (UCI) completed process design and modeling. Based on that information, UCI created multiple design options and the best option was selected for detailed simulation.

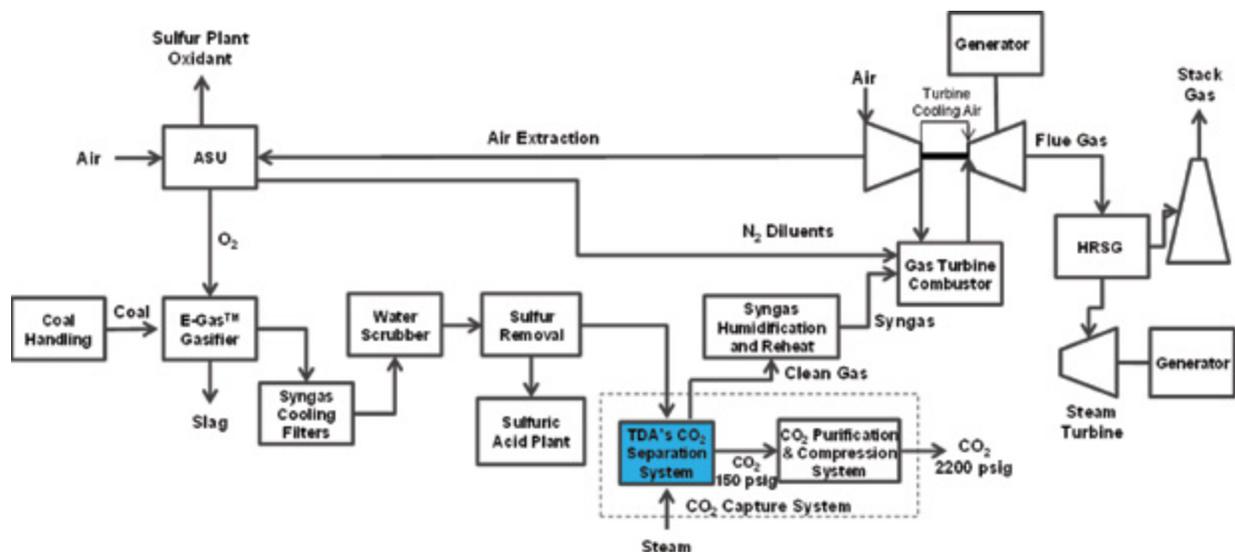


Figure 1: TDA's CO₂ Capture System Integrated with Phillips 66's E-Gas Gasifier

The next objective was to scale-up sorbent production by a factor of 10 at the end of Year 1 using commercially adoptable equipment. Scale-up explored the use of continuous or semi-continuous preparation approaches, and will reduce or optimize the number of processing steps via intensification (co-synthesis, co-firing, etc.). A preparation recipe was developed in cooperation with MeadWestvaco, who completed a detailed analysis to estimate the cost of the sorbent. Long-term tests were performed to ensure that the sorbent does maintain its CO₂ capacity over many cycles.

Year 2 of the project focused on designing, building, and testing a prototype unit using slipstream syngas and analyzing the results. TDA designed and sized sorbent reactors for two gasifier types: Phillips 66's E-Gas™ gasifier and the GE gasifier.

TDA and UCI optimized the process design and modeling. The focus of system analysis in Year 2 was on the integration of the CO₂ capture system with the IGCC plant. TDA fabricated the test module, which had a control rack using LabView programming to control, monitor, and log key process parameters. The test module also had an analyzer rack for continuous analysis of syngas on the adsorption and regeneration sides. TDA conducted all shakedown and troubleshooting before shipping the test system. Field tests were performed at ConocoPhillips' Wabash River IGCC Plant with the oxygen (O₂)-blown E-Gas gasifier in Terre Haute, Indiana, and in collaboration with the Southern Company at the National Carbon Capture Center (NCCC) using the syngas generated by an air-blown gasifier at Wilsonville, Alabama. Prototype unit field tests and system analysis studies were completed.

TABLE 1: SOLID SORBENT PARAMETERS

	Units	Current R&D Value	Target R&D Value
Sorbent			
True Density @ STP	kg/m ³	1,362	
Bulk Density	kg/m ³	589	
Average Particle Diameter	mm	3.2-6.4	
Particle Void Fraction	m ³ /m ³	0.567	
Packing Density	m ² /m ³	241.5	
Solid Heat Capacity @ STP	kJ/kg-K	0.93	
Crush Strength	kg _f	5.0-9.0	

TABLE 1: SOLID SORBENT PARAMETERS

	Units	Current R&D Value	Target R&D Value
Manufacturing Cost for Sorbent	\$/kg	5.30	
Adsorption			
Pressure	bar	33.8	
Temperature	°C	198	
Equilibrium Loading	g mol CO ₂ /kg	1.74	
Heat of Adsorption	kJ/mol CO ₂	20.5±1.7	
Desorption			
Pressure	bar	10	
Temperature	°C	195.5	
Equilibrium Loading	g mol CO ₂ /kg	0.16	
Heat of Desorption	kJ/mol CO ₂	18.0±3.3	
Proposed Module Design		<i>(for equipment developers)</i>	
Flow Arrangement/Operation	-	3-trains of 8 cycling fixed beds	
Flue Gas Flowrate	kg/hr	750,172	
CO ₂ Recovery, Purity, and Pressure	percent / percent / bar	95.9 percent, 99.9 percent, 17.8 bar	
Adsorber Pressure Drop	bar	0.93	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	139.3*	
* Cost of the CO ₂ separation unit, including purification stages (three trains of eight fixed beds with auxiliaries and purification unit).			

Definitions:

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

Sorbent – Adsorbate-free (i.e., CO₂-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 CO₂ 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 CO₂ in equilibrium with the sorbent. If the vapor phase is pure CO₂, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO₂. Note that for a typical PC power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO₂ is about 13.2 percent. Therefore, the partial pressure of CO₂ 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 CO₂ 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 CO₂ in CO₂-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – The sorbent consists of a carbon support modified with surface functional groups that remove CO₂ via strong physical adsorption. The CO₂ surface interaction is strong enough to allow operation at elevated temperatures. Because the CO₂ is not bonded via a covalent bond, the energy input to the regeneration is low – only 4.9 kcal/mole of CO₂ removed (comparable to Selexol).

Sorbent Contaminant Resistance – The sorbent will be resistant to syngas contaminants.

Sorbent Attrition and Thermal/Hydrothermal Stability – Very stable, similar to carbon molecular sieves.

Syngas Pretreatment Requirements – Particulate removal, bulk desulfurization, and WGS.

Sorbent Make-Up Requirements – Sorbent bed life is two years.

Waste Streams Generated – The spent sorbent will have to be replaced periodically (two years).

Process Design Concept – Flow sheet/block flow diagram is provided above.

Proposed Module Design – TDA's warm gas CO₂ capture system consists of three trains of eight-bed pressure swing adsorption (PSA) systems, containing a total of 24 beds that go through various PSA cycle steps. A 3-D layout of TDA's warm gas CO₂ capture system is shown below:

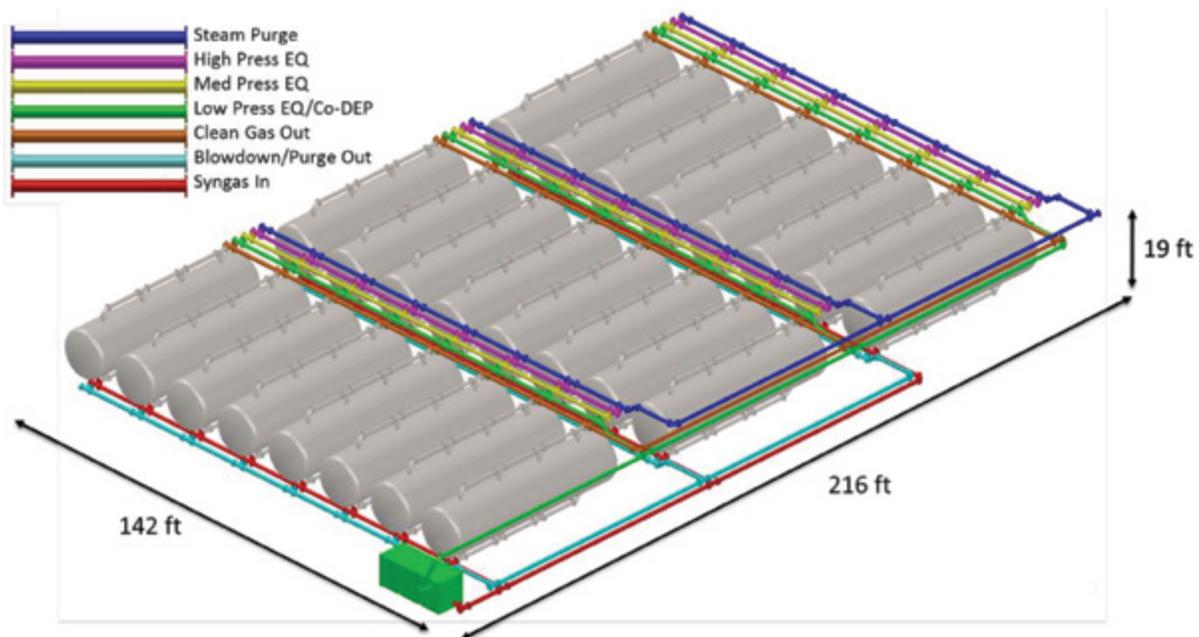


Figure 2: 3-D Layout of TDA's Warm Gas Capture System

technology advantages

- Capturing CO₂ above the dew point of the syngas significantly improves the net plant efficiency.
- Carbon dioxide recovered at pressure reduces compression costs for sequestration.
- A weak CO₂ surface interaction allows fast regenerations at low temperature with the minimal or no heat input.
- Short adsorption/regeneration cycles reduce bed size and weight.

R&D challenges

- Demonstration to the resistance of syngas contaminants.
- Reducing the use of purge gas during regeneration.

results to date/accomplishments

- Completed sorbent optimization.
 - Identified an optimum chemical composition.
 - Production scale-up.
- Demonstrated high CO₂ capacity in bench-scale experiments.
 - Saturation capacity approaching 20 percent wt. CO₂.
 - 6 to 8 percent wt. working capacity.
- Long-term durability was demonstrated through 11,650 cycles.
- For a nominal 600-megawatt (MW) IGCC plant, the CO₂ removal system consists of three trains of eight-bed high-temperature PSA units; total of 24 beds housing the sorbent.
- Fabricated a skid-mounted, four-bed, high-temperature PSA system and successfully carried out demonstrations with syngas from an air-blown gasifier at NCCC (Wilsonville, Alabama) and an O₂-blown gasifier at Wabash River IGCC power plant (Terra Haute, Indiana).
 - Sorbent maintained its performance over 1,030 adsorption/regeneration cycles at NCCC and over 715 cycles at Wabash River IGCC power plant (the same sorbent was used in the two demonstrations).
 - Similar CO₂ capacity was observed before, during, and after testing of the sorbent (altogether, 26,750 standard cubic feet [scf] of syngas has been treated), suggesting minimal impact of syngas impurities due to high-temperature operation.
- System simulation studies carried out in collaboration with UCI, indicates that TDA's CO₂ technology (warm gas CO₂ capture) will provide higher net plant efficiency and lower levelized cost of electricity (COE) than an IGCC plant equipped with Selexol (cold gas capture).
 - TDA's warm gas capture technology achieves a net plant efficiency of 34 percent compared to 31.6 percent for Selexol scrubbing technology
 - Water consumption is also lower, providing a water savings of 8.5 kmol per MWh.
 - Levelized COE, including transportation, storage, and monitoring (TS&M) costs for CO₂, is calculated as \$92.9/MWh for TDA's warm gas capture technology compared to \$105.2/MWh for Selexol scrubbing technology.

next steps

This project ended on December 31, 2012

available reports/technical papers/presentations

Alptekin, G.; Jayaraman, A.; and Copeland, R., "Low Cost, High Capacity Regenerable Sorbent for Precombustion CO₂ Capture," presented at the 2012 NETL CO₂ Capture Technology Meeting, Pittsburgh, Pennsylvania, July 2012.

Alptekin, G., "A Low Cost, High Capacity Regenerable Sorbent for CO₂ Capture," presented at the International Colloquium on Environmentally Preferred Advanced Power Generation (ICEPAG), Costa Mesa, California, February 2012. <http://www.netl.doe.gov/File%20Library/Events/2012/CO2%20Capture%20Meeting/G-Alptekin-TDA-Research-Pre-combustion-Sorbent.pdf>.

Alptekin, G.; Jayaraman, A.; Dietz, S.; and Schaefer, M., "High Capacity Regenerable Sorbent for Pre-Combustion CO₂ Capture," presented at the 28th Annual International Pittsburgh Coal Conference (IPCC), Pittsburgh, Pennsylvania, September 2011.

Alptekin, G.; Jayaraman, A.; and Copeland, R., "Low Cost, High Capacity Regenerable Sorbent for Precombustion CO₂ Capture," presented at the 2011 NETL CO₂ Capture Technology Meeting, Pittsburgh, Pennsylvania, August 22-26, 2011.

Alptekin, G., “A Low Cost, High Capacity Regenerable Sorbent for CO₂ Capture,” presented at the International Colloquium on Environmentally Preferred Advanced Power Generation (ICEPAG), Costa Mesa, California, February 2011.

B-32

Alptekin, G.; Jayaraman, A.; Dietz, S.; Brickner, L.; and Tracy, R., “High Capacity Regenerable Sorbent for Pre-Combustion CO₂ Capture,” presented at the 27th Annual International Pittsburgh Coal Conference (IPCC), Pittsburgh, Pennsylvania, October 2010.

Alptekin, G.; Jayaraman, A.; and Copeland, R., “Low Cost, High Capacity Regenerable Sorbent,” presented at the 2010 NETL CO₂ Capture Technology Meeting, Pittsburgh, Pennsylvania, September 2010. <http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/friday/Gokhan%20Alptekin%20-%20FE0000469.pdf>.

Alptekin, G., “A Low Cost, High Capacity Regenerable Sorbent for CO₂ Capture,” presented at the Power Plant Air Pollutant Control “MEGA” Symposium, Baltimore, Maryland, August 30 – September 2, 2010.

Alptekin, G., “High Capacity Regenerable Sorbent for Pre-Combustion CO₂ Capture,” presented at the American Institute of Chemical Engineer (AIChE) Spring National Meeting, San Antonio, Texas, March 2010.

Alptekin, G., “A Low Cost, High Capacity Regenerable Sorbent for CO₂ Capture,” presented at the International Colloquium on Environmentally Preferred Advanced Power Generation (ICEPAG), Costa Mesa, California, February 2010.

Alptekin, G., “A Low Cost, High Capacity Regenerable Sorbent for CO₂ Capture,” presented at the Air & Waste Management Association’s (A&WMA’s) 102nd Annual Conference & Exhibition, Detroit, MI, June 2009.

HIGH-PURITY HYDROGEN PRODUCTION WITH IN-SITU CARBON DIOXIDE AND SULFUR CAPTURE IN A SINGLE-STAGE REACTOR

primary project goals

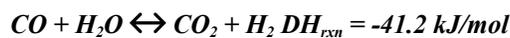
Ohio State University (OSU) set out to develop a Calcium Looping Process (CLP) to enhance hydrogen (H₂) production by integrating the water-gas shift (WGS) reaction with high-temperature carbon dioxide (CO₂), sulfur, and halide removal from synthesis gas (syngas) in a single-stage reactor for applications in large-scale H₂/electricity production from coal in a carbon-constrained scenario.

technical goals

- Reduce steam requirement and operate at near-stoichiometric steam consumption.
- Evaluate the regenerability of the calcium oxide (CaO) sorbent by repeated in-situ carbonation and regeneration for 10 to 100 cycles.
- Demonstrate simultaneous removal of CO₂, sulfur, and halides using a CaO sorbent in the bench-scale, fixed-bed unit.
- Produce either a 90 to 95 percent H₂ stream without WGS catalyst, or a 99+ percent high-purity H₂ stream with WGS catalyst at high temperatures and pressures.
- Demonstrate H₂ production with the sub-pilot-scale testing unit.
- Perform a techno-economic feasibility study for different integrated process scenarios using Aspen modeling.

technical content

The WGS reaction, which converts most of the syngas carbon monoxide (CO) to H₂ and CO₂ by reacting the CO with steam over a bed of catalyst, can be utilized to enhance H₂ production. The excess steam serves to drive the WGS equilibrium toward the products. The reaction is exothermic and, due to equilibrium constraints, typically consists of two stages: (1) high-temperature shift that benefits from high-reaction rates at elevated temperatures; and (2) low-temperature shift that yields more favorable reaction equilibrium.



OSU researchers set out to develop the CLP that combines the WGS reaction and high-temperature, sorbent-based acid gas removal in a single-stage reactor, as shown in Figure 1. By implementing the CLP near the high-temperature reaction zone, syngas cooling and re-heating is no longer required, and the process eliminates the need for the WGS catalyst. A CaO sorbent is used as the circulating material for in-situ removal of CO₂, sulfur, and halides. By incorporating sorbent-based CO₂ removal, not only is a near sequestration-ready stream of CO₂ produced, but plant efficiency and H₂ production are increased by driving the WGS reaction further to completion.

technology maturity:

Laboratory-Scale

project focus:

Calcium Looping for Hydrogen Production

participant:

Ohio State University-Department of Chemical Engineering

project number:

FC26-07NT43059

NETL project manager:

Jason Hissam

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principal investigator:

Liang Shih Fan

Ohio State University-Department of Chemical Engineering

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partners:

Clear Skies Consulting
Consol Energy Inc.

performance period:

7/5/07 – 7/31/11

As shown in Figure 2, the CLP is comprised of three reactors: (1) the carbonator, where high-purity H_2 is produced and contaminant removal takes place; (2) the calciner, where the CaO sorbent is regenerated and a sequestration-ready CO_2 stream is produced; and (3) the hydrator, which reactivates the CaO sorbent. The carbonator (either a fixed, fluidized-bed, or an entrained flow reactor) operates at high pressures ranging from 20 to 30 atm and temperatures of 550 to 650°C. The thermodynamic constraint of the WGS reaction is overcome in the carbonation reactor by the incessant removal of the CO_2 product from the reaction mixture, which enhances H_2 production. This is achieved by concurrent WGS reaction and carbonation reaction of CaO to form calcium carbonate ($CaCO_3$), thereby removing the CO_2 product from the reaction mixture and obviating the need for a WGS catalyst and excess steam addition. The CLP does not require syngas pretreatment, because the CaO sorbent also controls hydrogen sulfide (H_2S), hydrogen chloride (HCl), and carbonyl sulfide (COS) to parts-per-billion (ppb) levels. Key parameters for the CaO sorbent are provided in Table 1.

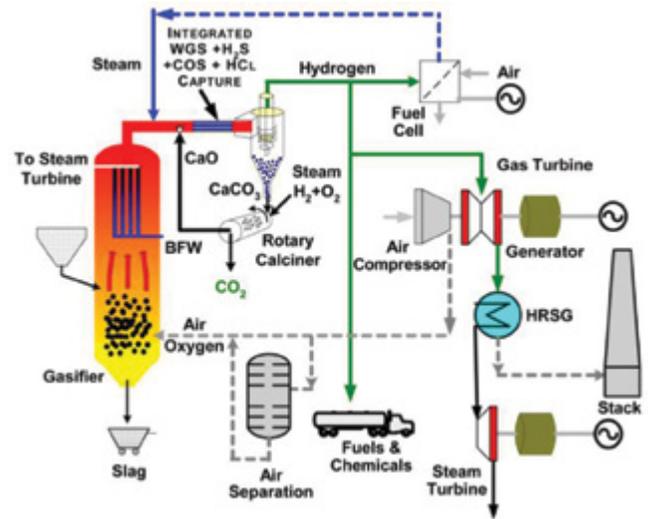


Figure 1: Calcium Looping Process for Enhanced Hydrogen Production with In-Site CO_2 and Sulfur Capture in a Single-Stage Reactor

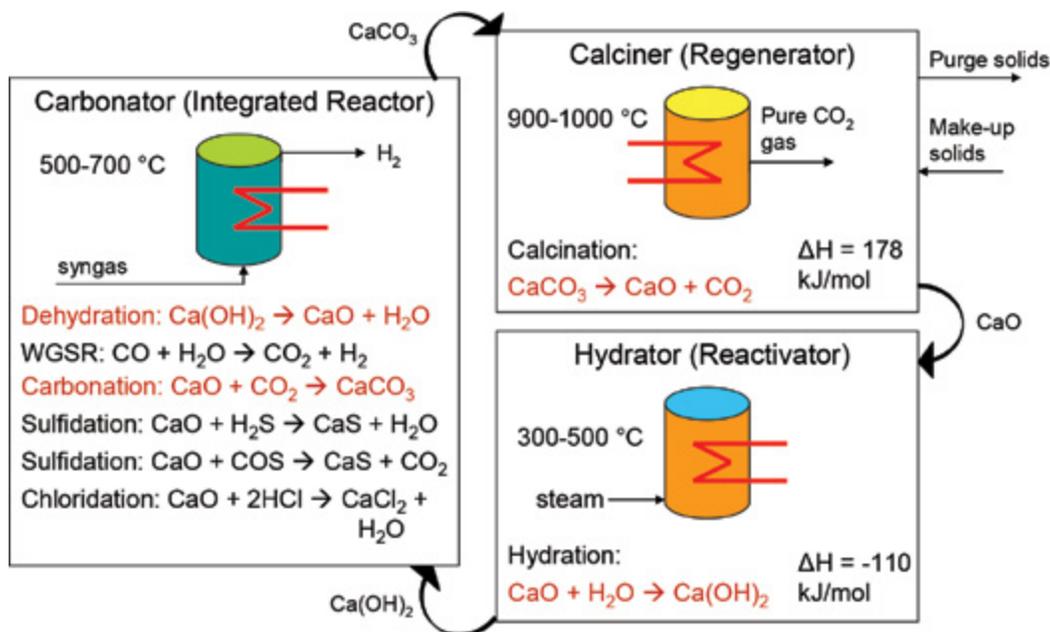


Figure 2: Illustration of the Reaction Schemes in the Calcium Looping Process

The spent sorbent, consisting mainly of $CaCO_3$, is regenerated back to CaO in the calciner, which operates at atmospheric pressure in a rotary, or a fluidized-bed system. Calcination occurs at temperatures above 900°C in the presence of 1 atm CO_2 , but CO_2 dilution via steam addition or syngas combustion in a direct-fired calciner permits calcination at lower temperatures. The regenerated CaO sorbent is then conveyed to the hydrator.

The hot solids from the calciner are then hydrated via contact with low-temperature steam in the hydrator. The calcination process causes sorbent sintering, which reduces the sorbent's reactivity; the hydration process reverses this effect by increasing the pore volume and surface area available for reaction with the gas mixture. The calcium hydroxide [$Ca(OH)_2$] decomposes in the carbonator to produce CaO and steam. The steam obtained from the dehydration reaction is used for the WGS reaction. Hence, no excess steam is required in the CLP, as the WGS steam is supplied to the hydrator.

TABLE 1: SOLID SORBENT PARAMETERS

	Units	Current R&D Value	Target R&D Value
Sorbent			
True Density @ STP	kg/m ³		
Bulk Density	kg/m ³		
Average Particle Diameter	mm	.01-.05	.01-.05
Particle Void Fraction	m ³ /m ³		
Packing Density	m ² /m ³	1.289g/cm ³	1.289g/cm ³
Solid Heat Capacity @ STP	kJ/kg-K	0.96(CaO)-1.23(CaCO ₃)	0.96(CaO)-1.23(CaCO ₃)
Crush Strength	kg _r		
Manufacturing Cost for Sorbent	\$/kg		
Adsorption			
Pressure	bar	1-30	1-30
Temperature	°C	600	600
Equilibrium Loading	g mol CO ₂ /kg		
Heat of Adsorption	kJ/mol CO ₂		
Desorption			
Pressure	bar	1	1
Temperature	°C	700-950	700-950
Equilibrium Loading	g mol CO ₂ /kg		
Heat of Desorption	kJ/mol CO ₂		
Proposed Module Design		<i>(for equipment developers)</i>	
Flow Arrangement/Operation	-		
Flue Gas Flowrate	kg/hr		
CO ₂ Recovery, Purity, and Pressure	percent / percent / bar		
Adsorber 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).

Sorbent – Adsorbate-free (i.e., CO₂-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 CO₂ 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 CO₂ in equilibrium with the sorbent. If the vapor phase is pure CO₂, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO₂. Note that for a typical PC power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO₂ is about 13.2 percent. Therefore, the partial pressure of CO₂ 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 CO₂ 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 CO₂ in CO₂-rich product gas; assuming targets are met.

technology advantages

- The removal of CO₂ in the same reactor drives the WGS reaction further to completion, which, due to operation at feed conditions (high temperature and pressure), will increase plant efficiency.
- The process also eliminates the need for a WGS catalyst.
- No separate steps necessary for removal of sulfur and halide impurities.
- High-quality exothermic heat available from all three reactors can be used to generate electricity.

R&D challenges

- Waste disposal.
- Solids handling and transport.
- Design of a high-temperature steam hydrator.

results to date/accomplishments

- Combined WGS, carbonation, and sulfidation reactions conducted in the absence of a catalyst in a bench-scale, fixed reactor.
- Performed detailed parametric investigation in the fixed-bed reactor. Parameters investigated include steam to carbon ratio (S:C), temperature, and pressure. The optimum operating temperature for the carbonator was found to be 600°C. The operating pressure was dependent on desired H₂ purity – 70 percent at 1 atm and greater than 99 percent at 21 atm.
- Developed a novel sorbent reactivation process (high-temperature steam hydration), and achieved sustained reactivity for multiple cycles.
- Based on fixed-bed results, the sub-pilot scale carbonator was designed, constructed, and successfully operated; 70 percent H₂ was achieved in the product with 100 percent CO₂ capture at S:C=3 and Ca:C=1.5, starting with a syngas-like gas mixture in the feed.
- Completed comprehensive techno-economic analyses for CLP integration in different scenarios (coal-to-H₂, integrated gasification combined cycle [IGCC], etc.), and found that CLP can reduce the cost of producing H₂/electricity by 9 to 12 percent when compared to traditional WGS and CO₂ capture technologies in a carbon-constrained scenario.

next steps

This project ended on July 31, 2011.

[available reports/technical papers/presentations](#)

Connell, D.P.; Lewandowski, D.; Ramkumar, S.; Phalak, N.; Statnick, R.M.; and Fan, L.-S. "Process simulation and economic analysis of the Calcium Looping Process (CLP) for hydrogen and electricity production from coal and natural gas," *Fuel* 2013, 103, 383-396.

Phalak, N.; Ramkumar, S.; Deshpande, N.; Wang, A.; Wang, W.; Statnick, R.M.; and Fan, L.-S. "Calcium Looping Process for Clean Coal Conversion: Design and Operation of the Subpilot-Scale Carbonator," *Ind. Eng. Chem. Res.* 2012, 51, 9938-9944.

Ramkumar, S.; and Fan, L.-S. "Calcium Looping Process (CLP) for Enhanced Noncatalytic Hydrogen Production with Integrated Carbon Dioxide Capture," *Energy Fuels* 2010, 24, 4408-4418.

Ramkumar, S.; Iyer, M.V.; and Fan, L.-S. "Calcium Looping Process for Enhanced Catalytic Hydrogen Production with Integrated Carbon Dioxide and Sulfur Capture," *Ind. Eng. Chem. Res.* 2011, 50, 1716-1729.

Sun, Z.; Yu, F.-C.; Li, F.; Li, S.; and Fan, L.-S. "Experimental Study of HCl Capture Using CaO Sorbents: Activation, Deactivation, Reactivation, and Ionic Transfer Mechanism," *Ind. Eng. Chem. Res.* 2011, 50, 6034-6043.

Ramkumar, S.; and Fan, L.-S. "Thermodynamic and Experimental Analyses of the Three-Stage Calcium Looping Process," *Ind. Eng. Chem. Res.* 2010, 49, 7563-7573.

HYDROGEN PRODUCTION AND PURIFICATION FROM COAL AND OTHER HEAVY FEEDSTOCKS

B-38

primary project goals

The University of North Dakota Energy and Environmental Research Center (UNDEERC) set out to evaluate the ability of various conventional and high-temperature carbon dioxide (CO₂) sorbents to resist the deleterious effects of hydrogen sulfide (H₂S)-containing (sour) synthesis gas (syngas).

technical goals

- Assess the performance of high-temperature and conventional CO₂ sorbents in simulated and real syngas.
- Evaluate the effect of H₂S on solid sorbents when operating in a fixed bed under simulated and real syngas conditions.
- Analyze CO₂ sorbents after exposure to real and simulated syngas.

technical content

Gasification of coal and other heavy feedstocks is becoming an attractive approach for power and chemical production. The solid fuels are transformed into a sour syngas which must be further processed to yield the desired final products (e.g., high-purity hydrogen [H₂] or H₂-rich fuel and a CO₂-rich byproduct). Two types of syngas treatment processes require information on the impact of sour gas species on the solid adsorbents and the ability of these adsorbents to reversibly adsorb H₂S and CO₂: a high-temperature process (400°C) and an ambient-temperature process.

UNDEERC conducted two major sets of experiments in this program. In Phase I, a 10-bed exposure unit was built and operated, and the impact of a synthetic sour syngas on various high- and low-temperature CO₂ adsorbents was determined. Most of the adsorbents showed an increase in sulfur content and subsequent decrease in surface area and CO₂ adsorption capacity with exposure. Two materials were able to maintain their CO₂ capacity at ambient temperature.

In the next phase of work, these two materials were tested in a fixed-bed skid (Figure 1). The unit consisted of two packed beds, with the necessary valves and heating equipment to permit regeneration by pressure swing adsorption (PSA) or temperature swing adsorption (TSA) cycles.

Breakthrough experiments were conducted with 2 percent H₂S in H₂ feed gas to determine the H₂S adsorption capacity and mass transfer coefficients for the two materials. Hydrogen sulfide adsorption was shown to be reversible and rapid.



Figure 1: Fixed-Bed Reactor Skid

technology maturity:

Laboratory- and Pilot-Scale

project focus:

Hydrogen Production and Purification

participant:

University of North Dakota Energy and Environmental Research Center

project number:

FC26-05NT42465-1.4

NETL project manager:

Arun C. Bose
arun.bose@netl.doe.gov

principal investigator:

Grant Dunham
UNDEERC
gdunham@undeerc.org

partners:

none

performance period:

6/23/05 – 5/31/11

The fixed-bed unit was then connected to UNDEERC's existing lab-scale circulating fluidized-bed gasifier. The gasifier processed Powder River Basin (PRB) sub-bituminous coal spiked with elemental sulfur (S) to generate a syngas with an elevated H₂S concentration. The syngas was continuously fed to the fixed-bed unit (operating in PSA mode) for more than 1,000 cycles. The adsorbent beds were capable of reducing H₂S in the product stream to less than 50 parts per million (ppm). The H₂S capacity of the adsorbent decreased with initial syngas exposure (first couple of hundred cycles), but then remained stable. Post-mortem analysis of the adsorbent showed some deposition of S and chlorine (Cl) species at the front of the bed and capture of organic tar species.

UNDEERC operated the entrained-flow gasifier under oxygen-blown conditions with petcoke feed to generate a second sour syngas feed to the fixed-bed unit. The system was operated under various conditions (temperature and process flow rates) to determine the impact on separation performance. At the end of the testing, the adsorbent was systematically removed and analyzed to monitor changes in capacity/integrity. UNDEERC also modified the exposure unit to allow injection of low levels of iron carbonyl, carbonyl sulfide, and hydrogen fluoride. Impact of exposure was determined for the most promising adsorbent to date.

technology advantages

High-temperature acid gas (H₂S and CO₂) removal from integrated gasification combined cycle (IGCC) syngas streams has the potential to increase the net power system efficiency by maintaining a high-temperature, high-moisture feed stream to the combustion turbine power cycle. These advantages also hold for applications that utilize the syngas for coproducing hydrogen, fuels, or chemicals. Energy losses through syngas cooling and re-heating resulting from cool acid gas removal (such as Rectisol[®] or Selexol[™]) are prevented with high-temperature separation.

An ambient-temperature acid gas separation process based on adsorption would also be attractive relative to typical liquid absorption-based processes because of reductions in steam consumption and capital cost.

R&D challenges

The physical/chemical stability of the adsorbents in a sour syngas environment remains a concern, as does the ultimate fate of trace components (mercury, Cl, particulate matter) and the reversibility of heavy component (tars) adsorption.

results to date/accomplishments

- Identified two promising ambient-temperature adsorbents that exhibited little CO₂ capacity loss after sour syngas exposure.
- Conducted H₂S breakthrough experiments, both with and without CO₂, which showed that the most promising adsorbent is selective for H₂S over CO₂, the mass transfer rate of H₂S is described by macropore diffusion, and H₂S adsorption is reversible.
- Operated the fixed-bed test unit in PSA mode with coal-based syngas produced in a circulating fluidized-bed gasifier. Demonstrated that H₂S and CO₂ can be effectively rejected from the sour syngas. Completed roughly 1,500 adsorption/regeneration cycles. Showed that the H₂S capacity initially dropped, but then leveled off at approximately 80 percent of the fresh capacity.
- Conducted postmortem analysis of adsorbent to determine progression of Cl, S, and organics into bed. Chlorine and sulfur were limited to the first few inches of the bed. Organics were found to penetrate deeper, and are thought to be responsible for the initial drop in H₂S capacity.
- Operated a second batch of adsorbent in the fixed-bed unit with syngas generated from petroleum coke in an entrained-flow gasifier. Observed negligible levels of organics in the syngas. Completed more than 1,000 adsorption/regeneration cycles with no indication of H₂S capacity loss.

next steps

This project ended on May 31, 2011.

available reports/technical papers/presentations

“Hydrogen Production and Purification from Coal and Other Heavy Feedstocks - Final Topical Report” May 2011.

INTEGRATED WARM GAS MULTI-CONTAMINANT CLEANUP TECHNOLOGIES FOR COAL-DERIVED SYNGAS

primary project goals

Research Triangle Institute (RTI) set out to develop a modular warm, multi-contaminant synthesis gas (syngas) cleaning system that can be adapted to meet the specifications for both power and chemical/fuels production.

technical goals

- Develop a modular high-temperature (150 to 370°C or 300 to 700°F) and high-pressure (up to 83 atm or 1,200 pounds per square inch gauge [psig]) cleanup process that produces an effluent syngas suitable for chemical/fuels production by controlling trace contaminants to the levels shown in Table 1.

TABLE 1: TARGETED CONTROL LEVELS FOR SYNGAS CONTAMINANTS

Contaminant	Control Level	Contaminant	Control Level
Sulfur (S)	< 50 ppbw	Selenium (Se)	0.2 ppm
Ammonia (NH ₃)	10 ppm	Arsenic (As)	5 ppb
Chlorine (Cl)	10 ppb	Phosphorus (P)	< 20 ppbw
Mercury (Hg)	5 ppbw		

- Utilize a transport reactor and regenerable sorbents to control bulk syngas contaminants, such as hydrogen sulfide (H₂S), carbonyl sulfide (COS), ammonia (NH₃), and hydrogen chloride (HCl).
- Evaluate the performance of high-temperature carbon dioxide (CO₂) sorbents and promoters.

technical content

In this project, RTI worked on developing a sequential process where high-temperature syngas is cleaned using a transport reactor and a multi-functional fixed-bed system. The system is designed to operate at syngas feed conditions (150 to 370°C [300 to 700°F]) and 28 to 83 atm (400 to 1,200 psig), which will improve plant efficiency by eliminating the need for syngas cooling and re-heating. RTI's novel warm syngas cleaning technology could represent a significant improvement for chemical/fuels production applications due to reduced capital and operating costs; however, development and optimization for trace contaminant removal and warm CO₂ capture is needed to achieve the target syngas specifications for both power (integrated gasification combined cycle [IGCC] applications) and chemical/fuels production.

The bulk contaminant removal system consists of a transport reactor containing regenerable sorbents that target H₂S, COS, NH₃, and HCl. RTI investigated three sorbents: (1) RTI-3 for sulfur; (2) CBV-712 for NH₃; and (3) a sodium carbonate-based sorbent for chlorine.

technology maturity:

Bench-Scale

project focus:

Warm Gas Cleanup

participant:

Research Triangle Institute

project number:

FC26-05NT42459

NETL project manager:

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Brian S. Turk

Research Triangle Institute

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partners:

Nexant

performance period:

05/12/05 – 09/30/10

Syngas leaving the transport reactor is routed to a multi-functional, fixed sorbent bed that reduces contaminants to parts per billion by volume (ppbv) levels.

RTI employed the modified, high-pressure thermal gravimetric analyzer (TGA), shown in Figure 1, and a microreactor system to evaluate the performance of high-temperature CO₂ sorbents. The bench-scale CO₂ sorbent testing campaign included experiments with lithium orthosilicate (Li₄SiO₄) and magnesium oxide (MgO) sorbents, as well as several promoters and support structures. RTI's Li₄SiO₄ sorbent exhibited a CO₂ adsorption capacity of about 35 wt percent at high temperatures, but a technical-economic analysis concluded that the regeneration stage is prohibitively expensive.



Figure 1: Modified TGA for CO₂ Sorbent Testing

Meanwhile, a promoted MgO sorbent demonstrated a CO₂ capacity of nearly 60 wt percent and the ability to be regenerated at a CO₂ partial pressure of about 150 psig. RTI developed a knowledge base for the promoted MgO sorbent and focused research on fundamental issues, including sorbent preparation procedures, sorbent support structures and binders, and syngas pretreatment requirements.

TABLE 1: CO₂ SOLID SORBENT PARAMETERS

	Units	Current R&D Value	Target R&D Value
Sorbent			
True Density @ STP	kg/m ³		
Bulk Density	kg/m ³		
Average Particle Diameter	mm		
Particle Void Fraction	m ³ /m ³		
Packing Density	m ² /m ³		
Solid Heat Capacity @ STP	kJ/kg-K		
Crush Strength	kg _f		
Manufacturing Cost for Sorbent	\$/kg		
Adsorption			
Pressure	bar	≈24	40
Temperature	°C	350-450	350-450
Equilibrium Loading	g mol CO ₂ /kg		
Heat of Adsorption	kJ/mol CO ₂		
Desorption			
Pressure	bar		
Temperature	°C		
Equilibrium Loading	g mol CO ₂ /kg		
Heat of Desorption	kJ/mol CO ₂		
Proposed Module Design		<i>(for equipment developers)</i>	
Flow Arrangement/Operation	-		
Flue Gas Flowrate	kg/hr		
CO ₂ Recovery, Purity, and Pressure	percent / percent / bar		
Adsorber 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).

Sorbent – Adsorbate-free (i.e., CO₂-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 CO₂ 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 CO₂ in equilibrium with the sorbent. If the vapor phase is pure CO₂, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO₂. Note that for a typical pulverized coal (PC) power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO₂ is about 13.2 percent. Therefore, the partial pressure of CO₂ 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 CO₂ 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 CO₂ in CO₂-rich product gas; assuming targets are met.

In parallel with this experimental program, RTI investigated potential process configurations and operating conditions to exploit the attributes of the promoted MgO sorbent. Research was geared toward developing a suitable fluidized version of the sorbent to facilitate sorbent transport between the adsorption and stripping columns, while also improving the heat transfer coefficient of the sorbent bed. RTI also worked to identify the temperature window between adsorption and regeneration that maximizes the sorbent’s CO₂ working capacity, while minimizing the sensible heating requirement. In addition, RTI explored techniques to reuse the high-quality heat generated during the high-temperature CO₂ adsorption process, (e.g., transferring the high-quality heat to the steam cycle to generate additional power, or replacing a portion of the steam generated in the radiant syngas cooler).

technology advantages

Warm syngas cleanup will increase IGCC net power plant efficiency by eliminating the need for syngas cooling and re-heating, while also producing an effluent syngas suitable for chemical/fuels production and high-purity CO₂ for storage.

R&D challenges

Integration and scale-up of the bench-scale transport reactor and multi-functional fixed-bed system, as well as startup and standby options for the warm syngas cleanup technologies.

results to date/accomplishments

- Technical support provided to U.S. Department of Energy (DOE)/National Energy Technology Laboratory (NETL) researchers has resulted in a computational fluid dynamics (CFD) model that predicts temperature and differential pressure profiles similar to actual pilot plant results.

- Demonstrated that combustion products (CO₂, steam, and carbon monoxide [CO]) do not adversely affect the desulfurization performance of RTI-3.
- Adapted existing bench-scale testing system to support phosphine (in addition to arsine and hydrogen selenide) testing.
- Developed a coconut-based charcoal as a quality control cartridge for supporting mass balance determination during phosphine testing.
- Identified a family of promoters that increased the CO₂ capacity of the MgO sorbent from <2 wt percent to 40 to 60 wt percent.
- Completed a technical-economic analysis of warm CO₂ capture using RTI's Li₄SiO₄ sorbent, which concluded that the regeneration stage is prohibitively expensive.
- Independent system analysis by both Nexant and Noblis indicate that RTI's warm syngas cleaning system can yield a three-to-four-point increase in the net higher heating value (HHV) thermal efficiency and a 10 to 15 percent reduction in capital costs, compared to an IGCC plant equipped with Selexol™ for acid gas removal.
- Identified a new process configuration/operating cycle that demonstrates technical and economic promise and achieves 82 to 87 percent CO₂ capture with warm Mgo-based sorbent CO₂ capture.
- Demonstrated that the operational cycle (higher adsorption temperature than regeneration temperature) is valid.
- Demonstrated the potential to achieve low effluent CO₂ concentrations (≈100 parts per million by volume [ppmv]) with Mgo-based sorbents at pressures from 150 to 325 psig.
- Completion of preliminary techno-economic evaluations by RTI and Noblis for multiple warm CO₂ capture processes with RTI's promoted MgO sorbents demonstrating a slight thermal efficiency advantage.

[next steps](#)

This project ended on September 30, 2010.

[available reports/technical papers/presentations](#)

Turk, B.; Gupta, R.; Sharma, P.; Albritton, J.; and Jamal, A., "Integrated Warm Gas Multicontaminant Cleanup Technologies for Coal-Derived Syngas," Final Technical Report, March 2012.

Gupta, R.; Jamal, A.; Turk, B.; and Leseman, M., "Scaleup and Commercialization of Warm Syngas Cleanup Technology with Carbon Capture and Storage," presented at the 2010 Gasification Technologies Conference, Washington, DC, October 2010.

Gupta, R.; Turk, B.; and Leseman, M., "RTI/Eastman Warm Syngas Clean-up Technology: Integration with Carbon Capture," presented at the 2009 Gasification Technologies Conference, Colorado Springs, Colorado, October 2009.

Turk, B., et.al, "Warm Syngas Cleanup for Chemical Applications using Regenerable CO₂ Sorbents," presented at the 26th International Pittsburgh Coal Conference, Pittsburgh, Pennsylvania, September 2009.

"High Temperature CO₂ Capture from Syngas for Gasification Applications," presented at the Eighth Annual Carbon Capture & Sequestration Conference, Pittsburgh, PA, May 2009.

Turk, B., et.al, "Development of a Warm Gas Cleanup Technology Platform for Power and Chemicals Production," presented at the Pittsburgh Coal Conference, Pittsburgh, PA, September 2008.

NOVEL SORPTION ENHANCED REACTION PROCESS FOR SIMULTANEOUS PRODUCTION OF CO₂ & H₂ FROM SYNTHESIS GAS PRODUCED BY COAL GASIFICATION

primary project goals

Lehigh University has evaluated the feasibility of the novel thermal swing sorption enhanced reaction (TSSER) process to simultaneously separate carbon dioxide (CO₂) and carry out the water-gas shift (WGS) reaction as a single-unit operation in a fixed-bed reactor.

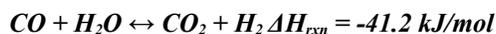
technical goals

While evaluating the feasibility of the TSSER process through experiments and process modeling, develop a sorbent that exhibits:

- High selectivity of CO₂ in the presence of steam at 200 to 500°C.
- Adequate CO₂ working capacity at the reaction temperature.
- Low heat of adsorption for reversible CO₂ sorption and desorption.
- Adequately fast kinetics of CO₂ sorption and desorption.
- Thermal stability.

technical content

The WGS reaction, which converts most of the synthesis gas (syngas) carbon monoxide (CO) to hydrogen (H₂) and CO₂ by reacting the CO with water over a bed of catalyst, can be utilized to enhance H₂ production at an integrated gasification combined cycle (IGCC) plant. The excess steam serves to drive the shift equilibrium toward the products. The reaction is exothermic and, due to equilibrium constraints, typically consists of two stages: (1) high-temperature shift that benefits from high-reaction rates at elevated temperatures; and (2) low-temperature shift that yields more favorable reaction equilibrium.



The TSSER process (Figure 1), under development by Lehigh University, simultaneously carries out the WGS reaction and the separation of CO₂ as a single-unit operation in a sorber-reactor (Step A). According to this process, the syngas from the coal gasifier (after removal of sulfur impurities) is introduced to a sorber-reactor, which is packed with an admixture of a WGS catalyst and a CO₂ sorbent that can selectively sorb CO₂ in the presence of excess steam. Removal of CO₂ (for geological storage) from the reaction zone drives the reversible reaction to the product side (circumventing equilibrium limits) and enhances the forward reaction rate.

technology maturity:

Laboratory-Scale

project focus:

Sorption Enhance Reaction Process

participant:

Lehigh University

project number:

FC26-05NT42455

NETL project manager:

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partners:

N/A

performance period:

5/25/05 – 6/4/10

An essentially pure (fuel cell grade) stream of H₂ (dry basis) is produced at feed gas pressure. The sorbed CO₂ is periodically removed (regeneration) by counter-currently purging the reactor with superheated steam at feed gas and near-ambient pressures, as well as at a temperature higher than that of the feed step. An intermediate step of co-current CO₂ rinse at feed gas pressure prior to the regeneration step produces an essentially pure CO₂ stream at high pressure. This significantly reduces CO₂ compression costs.

Two novel CO₂ sorbents have been identified as candidates for the TSSER concept, and key parameters for the optimal CO₂ sorbent are provided in Table 1.

- Potassium carbonate (K₂CO₃)-promoted hydrotalcite (400 to 550°C).
- Sodium oxide (Na₂O)-promoted alumina (200 to 550°C).

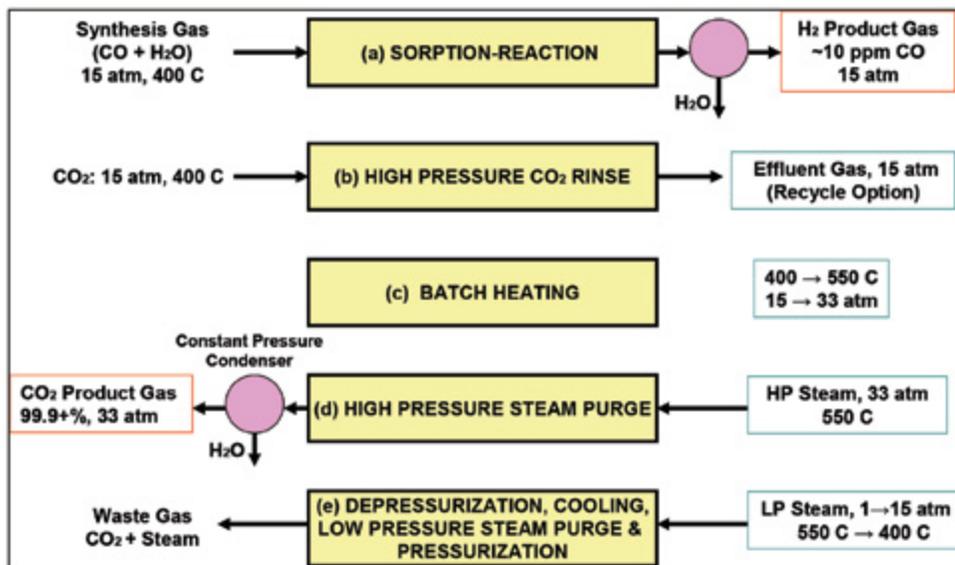


Figure 1: Components of the TSSER Process

This research project includes retrofitting an existing single-column sorption apparatus for measurement of high-pressure CO₂ adsorption characteristics; measurement of high-pressure CO₂ adsorption equilibria, kinetics, and sorption/desorption column dynamic characteristics under the conditions of thermal swing operation of the TSSER process; experimental evaluation of the individual steps of the TSSER process; development of a detailed mathematical model for simulating the performance of the individual steps of the TSSER process for optimization, process scale-up, and for guiding future work; simulation and testing of the TSSER concept using a realistic syngas composition; demonstration of the thermal stability of sorbents using a thermogravimetric analysis (TGA) apparatus; and evaluating the effects of sulfur compounds (hydrogen sulfide [H₂S]) present in coal-derived syngas on the CO₂ sorbents.

TABLE 1: PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Sorbent			
True Density @ STP	kg/m ³		
Bulk Density	kg/m ³		
Average Particle Diameter	mm	1.5	1.5
Particle Void Fraction	m ³ /m ³		
Packing Density	m ³ /m ³	0.694	0.694
Solid Heat Capacity @ STP	m ² /m ³	1.05	1.05
Crush Strength	kJ/kg-K		
Manufacturing Cost for Sorbent	kg _f		

TABLE 1: PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Adsorption			
Pressure	bar	Up to ≈25	Up to ≈25
Temperature	°C	200-400	200-400
Equilibrium Loading	g mol CO ₂ /kg-sorbent		
Heat of Adsorption	kJ/mol CO ₂	64.9	64.9
Desorption			
Pressure	bar	Up to 40	
Temperature	°C	550	550
Equilibrium Loading	g mol CO ₂ /kg-sorbent		
Heat of Desorption	kJ/mol CO ₂		
Proposed Module Design		<i>(for equipment developers)</i>	
Flow Arrangement/Operation	-		
Flue Gas Flowrate	kg/hr		
CO ₂ Recovery, Purity, and Pressure	percent / percent / bar		
Adsorber 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).

Sorbent – Adsorbate-free (i.e., CO₂-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 CO₂ 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 CO₂ in equilibrium with the sorbent. If the vapor phase is pure CO₂, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO₂. Note that for a typical pulverized coal (PC) power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO₂ is about 13.2 percent. Therefore, the partial pressure of CO₂ 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 CO₂ 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 CO₂ in CO₂-rich product gas; assuming targets are met.

technology advantages

The simultaneous removal of CO₂ drives the WGS reaction to completion, which, along with operation at feed conditions (high temperature and pressure), will increase plant efficiency. Regeneration via thermal swing with steam maximizes the CO₂ working capacity of the sorbent, while eliminating H₂ losses that occur during system purging with pressure swing adsorption processes. The TSSER process also produces high-purity H₂ and CO₂ streams.

R&D challenges

- Qualitative results suggest that the chemisorbents cannot be exposed to trace sulfur dioxide (SO₂) or H₂S impurities in the TSSER feed gas, and they must be removed by a conventional method such as selective sorption on zinc oxide (ZnO) employing a pretreatment system.
- A considerable amount of time is required to regenerate the sorbents via thermal swing cycling.

results to date/accomplishments

- Retrofitted and debugged an existing test apparatus for high-pressure operation.
- Characterized the CO₂ sorbents at high pressures, including measurement of isotherms, kinetics, and sorption/desorption column dynamics for CO₂ adsorption from nitrogen (N₂).
- Ascertained the thermal stability of the sorbents.
- Evaluated isothermal and isobaric high-pressure desorption of CO₂ by N₂ purge.
- Developed a CO₂ adsorption isotherm model for use in data analysis and process simulation.
- Developed a process model for data correlation and process simulation.
- Evaluated the performance of each step of the TSSER process.
- Identified Na₂O-promoted alumina as the best available CO₂ sorbent for the TSSER process.

next steps

This project ended on June 4, 2010.

available reports/technical papers/presentations

Sircar, S., et.al, "Novel Sorption Enhanced Reaction Process for Simultaneous Production of CO₂ and H₂ from Synthesis Gas Produced by Coal Gasification," June 2010, Final Report. <http://www.osti.gov/bridge/servlets/purl/1035862/1035862.pdf>.

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Lee, K. B, et.al, "Novel Thermal Swing Sorption Enhanced Reaction Process Concept for H₂ Production by Low Temperature Steam-Methane Reforming," Ind. Eng. Chem. Res., 46, 5003 (2007).

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Beaver, M.G., Caram, H.S., Sircar, S., "Selection of CO₂ chemisorbent for fuel-cell grade H₂ production by sorption-enhanced water gas shift reaction," *Int. J. Hydrogen Energy*, 34, 2972 (2009).

Beaver, M. G., Caram, H. S., Sircar, S., "Sorption Enhanced Reaction Process for Direct Production of Fuel Cell Grade Hydrogen by Low Temperature Catalytic Steam- Methane Reforming," *J. Power Sources*, 195, 1998-2002, (2009).

Beaver, M. G., et.al, "Effect of Reaction Temperature on Performance of Thermal Swing Sorption Enhanced Reaction Process for Simultaneous Production of Fuel-Cell Grade H₂ and Compressed CO₂ from Synthesis Gas," Presented at 25th International Pittsburgh Coal Conference, Pittsburgh, Pennsylvania, September 2008 and at AIChE Annual Meeting, Philadelphia, November 2008.

Beaver, M. G., et.al, "Utilization of High Temperature CO₂ Chemisorbents in Sorption Enhanced Reaction Concepts for Production of Fuel Cell Grade H₂ from Fossil Fuel Feedstocks," Presented at 26th International Pittsburgh Coal Conference on September 2009.

"Selection of CO₂ Chemisorbent for Fuel-Cell Grade H₂ Production by Sorption Enhanced Water-Gas-Shift & Steam- Methane-Reforming Reaction," Presented at American Institute of Chemical Engineering Annual Meeting, Nashville, Tennessee, November 2009.

HYDROGEN PRODUCTION USING WATER-GAS SHIFT CATALYST WITH CO₂ SORBENTS

primary project goals

The University of North Dakota Energy & Environmental Research Center (UNDEERC) set out to develop a high-temperature carbon dioxide (CO₂) sorbent to enhance the water-gas shift (WGS) reaction and produce a synthesis gas (syngas) stream that is at least 90 percent hydrogen (H₂) on a nitrogen-free basis.

technical goals

- Develop hydrotalcite sorbent briquettes and determine the required chemical composition for optimal WGS and CO₂ capture conditions.
- Test a pressure swing absorber on a continuous fluidized-bed reactor (CFBR) gasification system.
- Test lithium silicate and hydrotalcite sorbents in a bench-scale, heated fixed-bed reactor using a slipstream from the CFBR gasification system.
- Determine the optimum high-temperature CO₂ sorbent.

technical content

The WGS reaction, which converts most of the syngas carbon monoxide (CO) to H₂ and CO₂ by reacting the CO with steam over a bed of catalyst, can be utilized to enhance H₂ production at an integrated gasification combined cycle (IGCC) plant. The excess steam serves to drive the shift equilibrium toward the products. The reaction is exothermic and, due to equilibrium constraints, typically consists of two stages: (1) high-temperature shift that benefits from high reaction rates at elevated temperatures; and (2) low-temperature shift that yields more favorable reaction equilibrium.



The sorption-enhanced WGS (SEWGS) process, which combines a high-temperature CO₂ sorbent and a WGS catalyst in a packed-bed reactor that can operate at high temperature and pressure, represents one approach to further promote H₂ production. The SEWGS reactor consists of an initial adsorbent bed to remove inherent CO₂ from the syngas, followed by a second bed wherein the WGS reaction occurs as the CO₂ produced during the reaction is simultaneously captured by the adsorbent bed. Regeneration of the saturated adsorbent bed is accomplished by pressure swing absorption. By incorporating sorbent-based CO₂ removal, not only is a near capture-ready stream of CO₂ produced, but the efficiency of the plant is increased by driving the WGS reaction further to completion.

By routing a slipstream from the CFBR gasification system to the bench-scale, heated fixed-bed reactors shown in Figure 1, UNDEERC evaluated the performance of high-temperature lithium orthosilicate (Li₄SiO₄) and hydrotalcite CO₂ sorbents in the SEWGS process. Hydrotalcites are anionic clays with positively charged brucitelike (Mg[OH]₂) layers and inter layers of anions such as carbonates. Although the hydrotalcite sorbent did exhibit some enhanced WGS properties during bench-scale testing, the sorbent is unlikely

technology maturity:

Bench-Scale,
Using Simulated Syngas

project focus:

Sorbent Enhanced
Water-Gas Shift

participant:

University of North Dakota
Energy and Environmental
Research Center (UNDEERC)

project number:

FC26-98FT40320-03.13

NETL project manager:

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partners:

N/A

performance period:

4/1/05 – 3/31/09

to be a cost-effective option for IGCC power plants due to the observed low CO₂ adsorption capacity and the long purge cycles required for regeneration.

UNDEERC also compared the performance of two Li₄SiO₄ sorbents provided by Toshiba and Research Triangle Institute (RTI). Lithium orthosilicate, which reacts with CO₂ via the following reversible reaction, has exhibited a CO₂ adsorption capacity of approximately 35 percent (based on sorbent weight) at high temperatures.



As shown in Table 1, the Toshiba sorbent demonstrated superior adsorption at elevated temperatures, whereas the sorbent supplied by RTI showed higher adsorption capacity at relatively lower temperatures. One notable pattern is the sorbent provided by Toshiba demonstrated a reduction in adsorption capacity with decreasing CO₂ concentrations, eventually leading to inferior adsorption at higher temperatures as compared to RTI's sorbent.

Additionally, it was found that RTI's sorbent had slightly better desorption properties with complete desorption taking place at 700°C, whereas Toshiba's sorbent required temperatures as high as 800°C to attain complete desorption in a 100 percent nitrogen atmosphere.



Figure 1: Heated Fixed-Bed Reactors

TABLE 1: COMPARISON OF ADSORPTION PROPERTIES OF SORBENTS PROVIDED BY TOSHIBA AND RTI

Temperature (°C)	100 percent CO ₂		40 percent CO ₂		20 percent CO ₂	
	Adsorption (wt percent)		Adsorption (wt percent)		Adsorption (wt percent)	
	Toshiba	RTI	Toshiba	RTI	Toshiba	RTI
400	1.32	4.33	0.89	2.48	0.69	1.43
500	19.32	14.10	18.04	12.48	15.89	14.10
600	23.26	15.22	19.87	14.04	18.61	14.39
700	33.32	15.88	31.68	-	2.41	8.97
800	3.46	-	1.45	-	1.31	-

technology advantages

The simultaneous removal of CO₂ drives the WGS reaction to completion, which, along with operation at feed conditions (high temperature and pressure), will increase IGCC power plant efficiency by maintaining a high-temperature, high-pressure feed gas to the combustion turbine. The Li₄SiO₄ sorbents exhibit high CO₂ adsorption capacity at elevated temperatures and effectiveness across a wide range of CO₂ concentrations.

R&D challenges

A considerable amount of time is required to regenerate a Li₄SiO₄ sorbent that, when coupled with the large quantity of sorbent required, imposes significant limitations for industrial use.

results to date/accomplishments

- Completed testing of a pressure swing absorber on a continuous fluid-bed gasification system.
- Produced 20 wt percent potassium carbonate/80 wt percent hydrotalcite briquettes.
- Completed testing of Li_4SiO_4 sorbents in heated fixed-bed reactors using a slipstream from the CFBR gasification system, and determined the physical strength in high-moisture atmospheres and the CO_2 adsorption capacity of the sorbents at various operating conditions.

next steps

This project ended on March 31, 2009.

available reports/technical papers/presentations

Base Research Program – Final Report, August 2009.

B-51

PRE-COMBUSTION SORBENTS

HIGH-DENSITY ACTIVATED CARBON FOR HIGH-PRESSURE HYDROGEN PURIFICATION

B-52

primary project goals

The University of North Dakota Energy and Environmental Research Center (UNDEERC) set out to develop high-density, electrically conductive monolithic-activated carbon for use in a high-pressure swing adsorber to produce hydrogen (H₂) and sequestration-ready carbon dioxide (CO₂) from gasification synthesis gas (syngas).

technical goals

- Prepare a high-density, electrically conductive monolithic-activated carbon sorbent for H₂/CO₂ separation.
- Measure adsorptivity, pressure drop, and electrical conductivity (for regeneration) of monolith.
- Determine the feasibility of using activated carbons as CO₂ sorbents in gasification syngas.

technical content

UNDEERC worked with SGL Carbon to produce a monolithic, high-density activated carbon sorbent for use in high-pressure swing adsorbers to separate H₂ and CO₂ in a high-pressure syngas stream, while maintaining the pressure of the H₂ near that of the incoming syngas. By producing and purifying the H₂ from liquid feedstocks at high pressure, the associated cost of compressing the H₂ is reduced. This process, if employed at an integrated gasification combined cycle (IGCC) power plant, could potentially be used to produce high-purity CO₂ for storage.

As syngas passes through the activated carbon adsorbers, CO₂ is adsorbed onto the surface of the material, leaving relatively pure H₂ to pass through. Once saturated, the adsorbers can possibly be regenerated by passing an electrical current through it at constant pressure. Oak Ridge National Laboratory (ORNL) has worked to develop such a process and has produced a continuous, low-density, porous, fiber-reinforced activated carbon. By being continuous, it can conduct electricity at low voltage and can be sealed in a horizontal container that will not allow gas bypass. However, when used at high pressures, the high pore volume requires significant H₂ for backflushing. UNDEERC attempted to significantly increase the density of the carbon monolith in order to reduce the amount of clean H₂ required for backflushing at high pressures and decrease the regeneration interval.

During this project, UNDEERC attempted to activate four different formulations of high-density carbon fiber/carbon matrix composites. Activation methods included heating to 450°C in static, high-pressure steam or oxygen and the use of chemical activation. However, only butane adsorptivities of 2 to 3 percent were able to be obtained for the activated carbon produced from the monolithic carbon fiber composite, whereas commercial granulated activated carbons have butane adsorptivities of up to 18 percent. In follow-on work, the focus was on pressing mixtures of granular and powdered activated carbon and binder. These results were successful in making conductive monoliths with twice the density of

technology maturity:

Laboratory-Scale

project focus:

High-Density Active Carbon

participant:

University of North Dakota Energy and Environmental Research Center (UNDEERC)

project number:

FC26-05NT42465-3.1

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SGL Carbon

performance period:

06/23/05 – 06/22/07

granular beds, or approximately 40 percent of the theoretical skeletal carbon density. In addition, a method of treatment of the activated carbon granules were developed to reduce the resistivity of the monoliths by a factor of 10 relative to those made from the commercially available granular activated carbon.

Figure 1 shows how well the monolith separates different components from a simulated reformer gas stream. The figure is a plot of gas breakthrough curves for a monolith tested at 200 pounds per square inch gauge (psig) with a simulated reformer gas stream. The horizontal dashed lines show the concentrations of the different gases in the incoming gas stream. The light blue curve on the lower left is oxygen coming out of the monolith that was originally saturated with air. The difference between the sums of the curves and 100 percent is due to nitrogen, which was not directly detected. The monoliths were tested at higher pressures in a follow-on U.S. Department of Defense (DoD) project and were tested for their ability to be regenerated by passing an electric current through the monolith, possibly to disrupt the Vander Waals forces holding the gas molecules to the activated carbon surface or to resistively heat the monolith in a thermal swing adsorption process.

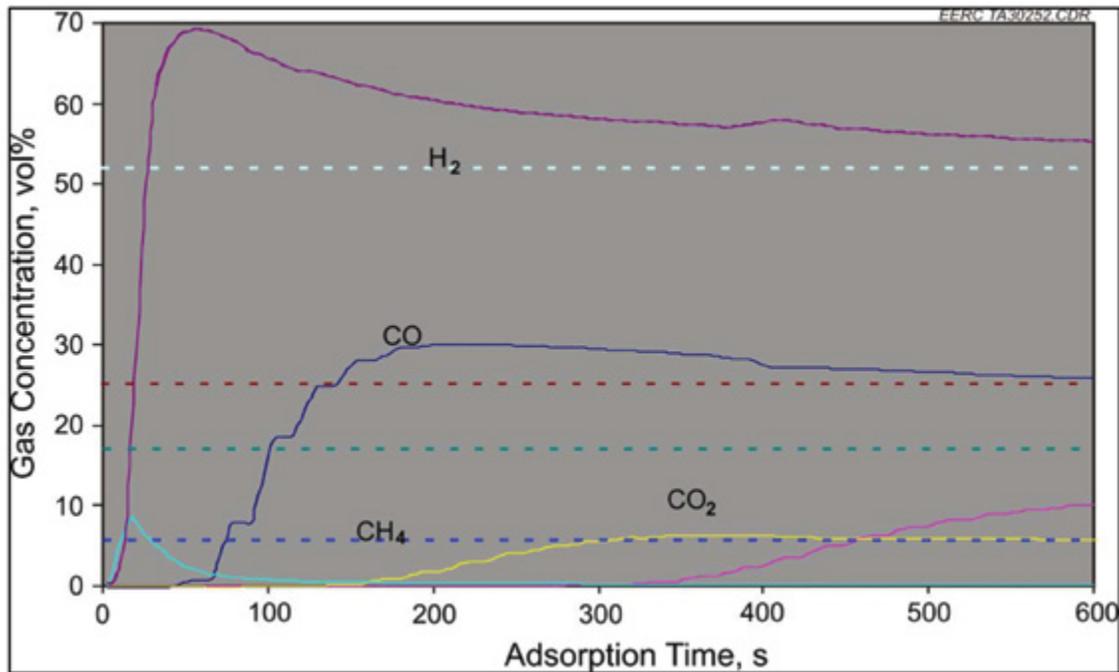


Figure 1: Gas Breakthrough Curves for a Monolith Tested at 200 psig

technology advantages

High-pressure H₂/CO₂ separation, coupled with isobaric sorbent regeneration using an electrical current, will increase plant efficiency by reducing the parasitic load associated with gas compression. Also, because of the high density of the monolith, the gas adsorption per unit volume is nearly doubled, and the amount of H₂ necessary to flush the intergranular spaces is cut by 25 percent.

R&D challenges

The project team discovered that the carbon sorbents require a long adsorption/desorption cycle time and no activation occurred during exposure to steam for 24 hours, while attempts to activate the material by reaction with an oxidizing gas showed limited results. Further, the introduction of reactive metals had a nominal effect on surface area creation.

results to date/accomplishments

B-54

- Prepared high-density, monolithic-activated carbons for high-pressure H₂/CO₂ separation.
- Measured the surface area, pressure drop, and electrical conductivity of the activated carbon sorbents.

next steps

This project ended on June 22, 2007.

available reports/technical papers/presentations

Hurley, J.P. High-Density Activated Carbon for High-Pressure Hydrogen Purification; Final Report; U.S. DOE, April 2008.