

APPENDIX B: CARBON DIOXIDE CAPTURE TECHNOLOGY SHEETS
POST-COMBUSTION MEMBRANES



ELECTROCHEMICAL MEMBRANE FOR CARBON DIOXIDE CAPTURE & POWER GENERATION

B-371

primary project goals

FuelCell Energy, Inc. (FCE) is developing an electrochemical membrane (ECM)-based Combined Electric Power and Carbon Dioxide Separation (CEPACS) system for carbon dioxide (CO₂) capture that also provides additional electrical power generation. The project includes bench-scale testing of an 11.7 m²-area ECM (molten carbonate fuel cell) system for CO₂ capture, purification, and compression.

technical goals

- Perform contaminant effect testing to establish maximum permissible concentrations of impurities in flue gas without causing unacceptable degradation of the ECM.
- Perform bench-scale membrane tests using clean, simulated flue gas.
- Complete design of balance-of-plant (BOP) components, including flue gas pretreatment subsystem.

technical content

FCE, in collaboration with Pacific Northwest National Laboratory (PNNL) and URS Corporation, is developing a novel CEPACS system. The CEPACS system is based on FCE's ECM technology derived from their internal reforming carbonate fuel cell products carrying the trade name of Direct FuelCell® (DFC®). The prominent feature of the ECM is its capability to produce electric power while capturing CO₂ from the flue gas of a pulverized coal (PC) power plant, resulting in a net efficiency gain. The ECM does not require flue gas compression as it operates on the principle of electrochemistry. The membrane utilizes a supplemental fuel (such as coal-derived synthesis gas [syngas], natural gas, or a renewable resource) as the driver for the combined CO₂ capture and electric power generation. The ECM consists of ceramic-based layers filled with carbonate salts that separate CO₂ from the flue gas. Because of the electrode's fast reaction rates, the membrane does not require a high CO₂ concentration in its feed gas. Advancement of the ECM technology will be achieved by a combination of small-scale component fabrication and testing, contaminant pretreatment evaluation, and bench-scale testing of an 11.7-m² ECM separation unit with CO₂ compression and chilling.

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Electrochemical Membrane

participant:

FuelCell Energy

project number:

FE0007634

NETL project manager:

Jose Figueroa

jose.figueroa@netl.doe.gov

principal investigator:

Hossein Ghezal-Ayagh
FuelCell Energy, Inc.

hghezal@fce.com

partners:

URS Corporation
Pacific Northwest National
Laboratory

performance period:

10/1/11 – 3/31/2015

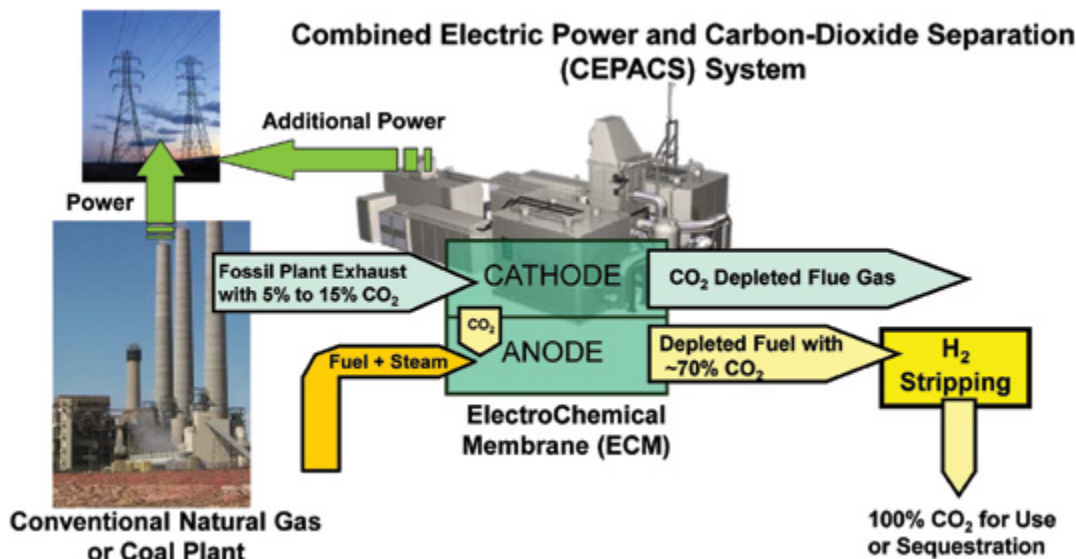


Figure 1: CEPACS System

TABLE 1: PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer	-	Alkali Carbonate/LiAlO ₂	
Materials of Fabrication for Support Layer	-	Stainless Steel	
Nominal Thickness of Selective Layer	μm	600	600
Membrane Geometry	-	Planar	Planar
Max Trans-Membrane Pressure	bar	<0.1	<0.1
Hours Tested Without Significant Degradation	-	1,000	6,000
Manufacturing Cost for Membrane Material	\$/m ²	100	100
Membrane Performance			
Temperature	°C	650	650
Volumetric Flux*	GPU or equivalent	0.009 cc/s/cm ² @ STP (1 atm, 0°C)	0.010 cc/s/cm ² @ STP (1 atm, 0°C)
CO ₂ /H ₂ O Selectivity	-	Infinity	Infinity
CO ₂ /N ₂ Selectivity	-	Infinity	Infinity
CO ₂ /SO ₂ Selectivity	-	Not Available	Not Available
Type of Measurement	-	Mixed	Mixed
Proposed Module Design			
Flow Arrangement	-	Cross Flow	
Packing Density	m ² /m ³	16	
Shell-Side Fluid	-	Retentate	
Flue Gas Flowrate	kg/hr	4640	
CO ₂ Recovery, Purity, and Pressure	% / % / bar	90%, 99.7%, 1 bar	
Pressure Drops Shell/Tube Side	bar	0.025/0.1	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	\$/kg/hr	550	

Definitions:

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

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

**GPU* – Gas Permeation Unit, which is equivalent to $10^{-6} \text{ cm}^3 (1 \text{ atm}, 0^\circ\text{C})/\text{cm}^2/\text{s}/\text{cm Hg}$. For non-linear materials, the dimensional units reported should be based on flux measured in $\text{cm}^3 (1 \text{ atm}, 0^\circ\text{C})/\text{cm}^2/\text{s}$ with pressures measured in cmHg. Note: $1 \text{ GPU} = 3.3464 \times 10^{-6} \text{ kg mol}/\text{m}^2\text{-s-kPa}$ [SI units]. Volumetric flux, rather than permeance, is considered a major performance parameter for the ECM. Permeance generally applies to membranes that use pressure or partial pressure as the driving force. In the case of ECM, the driving force is the electrochemical potential.

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

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

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

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

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

Other Parameter Descriptions:

Membrane Permeation Mechanism – The operating principle of ECM is shown in Figure 2, along with the electrochemical reactions involved. The ECM is composed of a thin matrix layer of ceramic material (Lithium Aluminate), with two electrodes (anode and cathode) on each side. The membrane is impregnated with a mixture of alkali metal (Li/Na/K) carbonate electrolyte, which constitutes a molten phase immobilized in the ECM pores at the operating temperature of 550 to 650°C. The anode and cathode are porous to allow gas diffusion. The inner matrix layer is completely filled with electrolyte and is impervious to gas transport while providing a path for ionic transfer across the membrane. Carbon dioxide and oxygen present in the flue gas of a coal power plant are used as reactants at the cathode. The ECM utilizes hydrogen (H_2) at the anode. The hydrogen is made available to the anode by a mixture of a fuel (such as natural gas, syngas, or biogas) and steam. The hydrocarbon content of the fuel is internally steam reformed to produce hydrogen in the anode chamber.

The electrochemical reactions (Figure 2) involve the formation of carbonate ions (CO_3^{2-}) at the cathode by the combination of O_2 , CO_2 , and two electrons; transport of the carbonate ions to the anode through electrolyte; and finally, reaction of the carbonate ion with H_2 at the anode, producing H_2O , CO_2 , and two electrons. The internal transport of carbonate ions in an ECM assembly (or cell) and the flow of electrons in the external circuit results in electric power generation as a consequence of the electrochemical CO_2 separation process. DC power produced is converted to AC power using an inverter. Overall, the operating mechanism of the ECM cell results in the separation (from flue gas) and transfer of CO_2 into the anode exhaust stream, which has a much reduced volumetric flow rate (resulting in a CO_2 -rich stream) compared to the original flue gas stream.

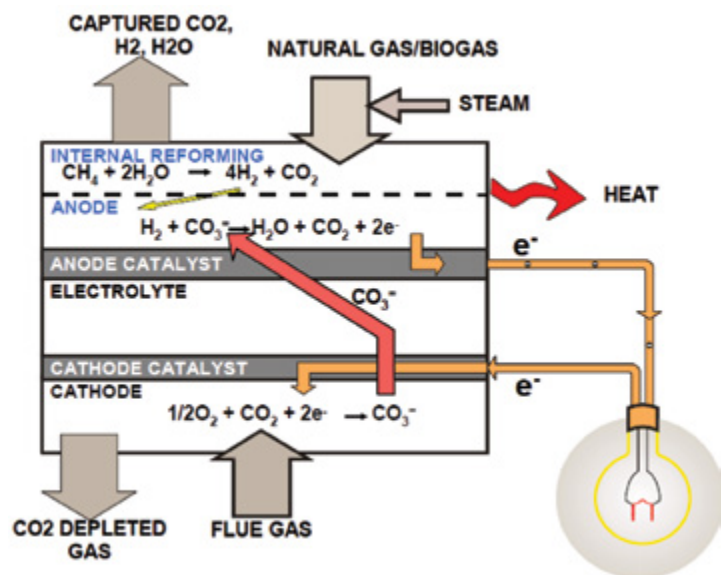


Figure 2: Separation of CO_2 in the Electrochemical Membrane Cell

Contaminant Resistance – The ECMs may be susceptible to certain levels of flue gas contaminants, especially sulfur oxide (SO_x). It is anticipated that other flue gas contaminants, such as nitrogen oxide (NO_x) and mercury, have no or minimal impact on the membrane performance. Laboratory tests have indicated that ECM has the potential for control of 60 to 70 percent of the NO_x species present in the flue gas of a coal power plant. Further testing of membranes is planned to characterize the ECM tolerance limits to various flue gas contaminants and to quantify its NO_x control capabilities.

Flue Gas Pretreatment Requirements – Flue gas entering the CEPACS plant is first routed through a polishing wet limestone flue gas desulfurization (FGD) system to further remove SO_x contaminants. The cleaned flue gas is then mixed with supplemental air. This serves to raise the oxygen partial pressure in the stream for proper operation of ECM modules. The mixed stream is preheated to the ECM operating temperature of ≈650°C using waste heat available in the system.

Membrane Replacement Requirements – The CEPACS is designed with the ECM modules replacement after 10 years of operation. Therefore, ECM modules are required to be replaced twice during the 30-year lifetime of the CEPACS plant.

Waste Streams Generated – The CEPACS plant produces minimal waste streams. Since water is generated by the electrochemical reactions within the ECM module, the system generates excess clean process water. This excess process water can be utilized in the existing PC plant to reduce raw water consumption. The polishing FGD generates a waste stream that is treated in the existing PC plant dewatering and water treatment equipment.

technology advantages

- Unlike other scrubber and membrane-based CO₂ capture technologies, the ECM-based CEPACS system produces additional electric power, rather than consuming power, using a supplemental fuel.
- The net efficiency of a CEPACS-equipped PC plant with >90 percent CO₂ capture is estimated to be ≈8 percent higher than the net efficiency of a baseline PC plant without CO₂ capture.
- The ECM technology is anticipated to reduce flue gas NO_x emissions by 60 to 70 percent.
- The ECM is a modular technology, allowing for phased addition of CO₂ capture capacity over time.
- The ECM-based CEPACS system has the potential to significantly reduce the cost of CO₂ capture.
- The CEPACS system generates excess clean water as part of the electrochemical separation process.

R&D challenges

- Contaminant tolerance of ECM technology must be characterized via testing.
- The membrane capability to separate 90 percent of CO₂ from PC plant flue gas at low-partial pressures needs to be verified in a bench-scale ECM module.
- The CEPACS process design needs to be demonstrated at large-scale.
- Membrane operational characteristics need to be investigated with consideration for minimization of the system cost.

results to date/accomplishments

- A preliminary technical and economic feasibility study (PT&EFS) was completed for a CEPACS system to separate 90 percent of CO₂ from the flue gas of a reference plant (550-MW PC).
 - The reference plant equipped with CEPACS has the potential for achieving the U.S. Department of Energy incremental cost of electricity target of 35 percent. It has the lowest total overnight cost (TOC of \$2,200/kW) and the highest overall efficiency (39.8 percent HHV) among the alternative systems studied.
 - The reference plant equipped with CEPACS has low cooling water consumption per unit of electricity produced. It reduces the process water consumption of the reference plant due to water-producing capabilities of the ECM operating inherently as a fuel cell.
 - The reference plant equipped with CEPACS has a cost of CO₂ captured of approximately \$14/ton of CO₂, which is the lowest among the alternatives studied.

[next steps](#)

- Perform laboratory and sub-scale ECM testing to characterize effects of flue gas contaminants on membrane performance.
- Quantify the NO_x control efficiency of the ECM.
- Perform membrane testing to optimize CEPACS system performance.
- Develop the design of a flue-gas pretreatment system required to reduce the contaminants down to tolerable levels prior to introduction of flue gas into the ECM module.
- Complete the technology gap analysis for identifying the equipment, material, or other components that would hinder advancement of the technology to a commercial product for CO₂ capture at a competitive cost.
- Update the PT&EFS as a result of the flue gas cleanup evaluation and sub-scale membrane-testing results.
- Construct a 11.7-m² membrane module bench-scale test facility and evaluate ECM performance using simulated flue gas.

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

H. Ghezel-Ayagh, "Electrochemical Membrane for CO₂ Capture and Power Generation No. DE-FE0007634 FuelCell Energy, Inc.," presented at the 2012 NETL CO₂ Capture Technology Meeting, Pittsburgh, Pennsylvania, July 2012.

H. Ghezel-Ayagh, S. Jolly, D. Patel, W. A. Steen, C. F. Richardson, and O. A. Marina, "Electrochemical Membrane for Carbon Dioxide Capture and Power Generation," presented at the 11th Annual Conference on Carbon Capture Utilization & Sequestration, Pittsburgh, Pennsylvania, April 30 – May 3, 2012.

J. Hunt, C. Willman, H. Ghezel-Ayagh, P. Singh, "Carbon Capture from the Industrial Sites Using a High Temperature Ionic Membrane," presented at the 11th Annual Conference on Carbon Capture Utilization & Sequestration, Pittsburgh, Pennsylvania, April 30 - May 3, 2012.

H. Ghezel-Ayagh, J. Hunt, S. Jolly, D. Patel, and R. Sanderson, "Energy Sustainability through Combined Electric Power Production and Carbon-Dioxide Separation (CEPACS) Systems," ECS Transactions, Editor(s): M. Williams, Volume 42, Issue No. 1, pp. 23-29, 2011.

H. Ghezel-Ayagh, "Electrochemical Membrane for Carbon Dioxide Capture and Power Generation," International Colloquium on Environmentally Preferred Advanced Power Generation (ICEPAG) Costa Mesa, CA, February 7-9, 2012.

NOVEL INORGANIC/POLYMER COMPOSITE MEMBRANES FOR CO₂ CAPTURE

B-376

primary project goals

Ohio State University is developing an inorganic/polymer composite membrane consisting of a thin, selective inorganic layer embedded in a polymer structure. The project includes development of a new membrane design to improve system performance through laboratory- and bench-scale testing and decrease costs through development of a continuous manufacturing process.

technical goals

- Develop membrane synthesis process that incorporates a thin, selective inorganic layer embedded in a polymer structure into spiral-wound modules.
 - Membranes will be developed and down-selected for a carbon dioxide (CO₂)/nitrogen (N₂) and H₂O/N₂ selectivity of >100 and a CO₂ permeance of >2,500 gas permeation units (GPU).
 - Continuous fabrication of the proposed hybrid membrane morphology will be performed with the use of a continuous membrane fabrication machine.
- Conduct membrane characterization via bench-scale testing.
 - Functional hybrid membranes will be synthesized for incorporation into three prototype membrane modules for parametric and continuous testing with simulated or actual flue gas.
- Complete system and cost analysis of the membrane system.

technical content

Ohio State University is developing a cost-effective design and manufacturing process for new membrane modules that capture CO₂ from flue gas. The membranes consist of a thin, selective inorganic layer embedded in a polymer structure so that it can be made in a continuous manufacturing process. The membrane will be incorporated in spiral-wound modules for bench-scale tests using coal-fired flue gas. Preliminary cost calculations show that a single-stage membrane process is economically unfavorable, primarily because of the low concentration of CO₂ (≈14%) in the flue gas stream. A two-stage process is more economical, but requires plant operation with a CO₂-enriched recycle stream.

technology maturity:

Bench-Scale, Using Simulated and Actual Flue Gas

project focus:

Inorganic/Polymer Composite Membrane

participant:

Ohio State University

project number:

FE0007632

NETL project manager:

Jose Figueroa

jose.figueroa@netl.doe.gov

principal investigator:

Dr. Winston Ho
Ohio State University

ho@chbmeng.ohio-state.edu

partners:

Gradient Technologies
Trisep Corporation
AEP

performance period:

10/1/11 – 3/31/2015

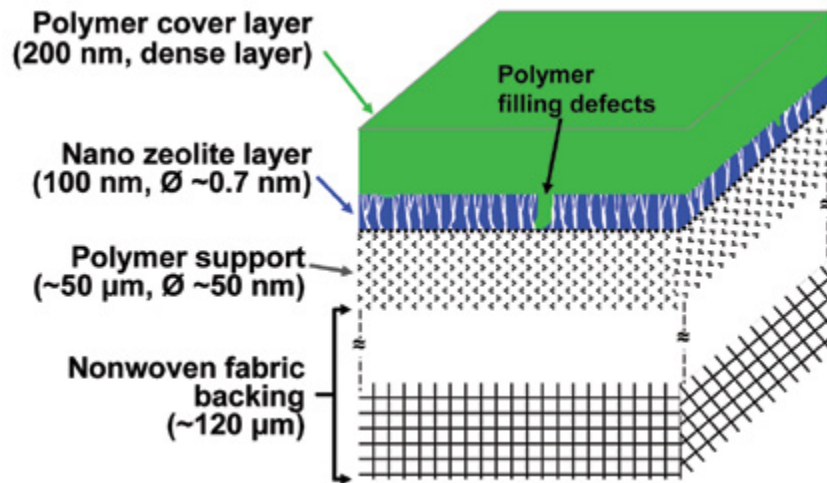


Figure 1: Supported Hybrid Membrane Concept

An important cost driver in current carbon capture membrane technologies is the energy requirement for maintaining the driving force for the membrane separation. The flue gas must be kept at atmospheric pressure and the concentrated CO₂ stream kept under vacuum (approximately three pounds per square inch [psi]) conditions. Preliminary calculations show that the carbon capture energy requirement can be sufficiently reduced in a two-stage process. In the first stage, CO₂ is removed from flue gas by evacuation; in the second stage, remaining CO₂ is removed using an air sweep such that the 90 percent capture target is met.

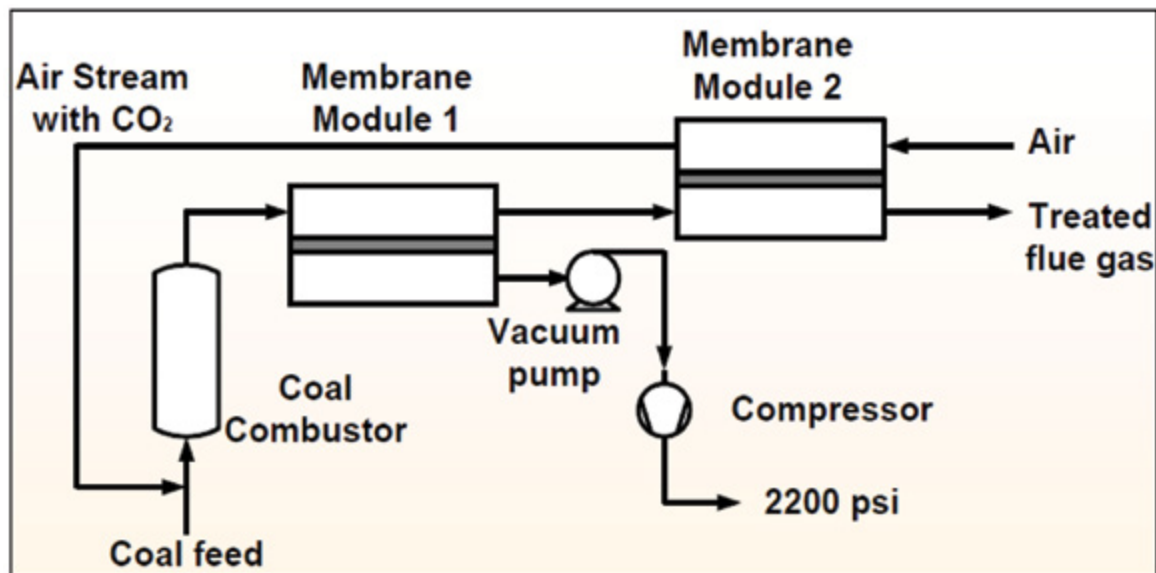


Figure 2: Process Concept for Two-Stage Membrane System

The entrance air sweep flow is the same as the air used in the current plant; the CO₂-enriched stream is used for combustion. The 95 percent pure CO₂, captured in the first stage, is then compressed to 15 MPa (≈2,200 psi). The U.S. Department of Energy cost targets can be met with a membrane that has a selectivity ≈150, a permeance of 3,000 GPU, and full stability against flue gas contaminants. This combination cannot be achieved with fully polymeric membranes. Fully inorganic, micro-porous membranes are sufficiently selective and stable, but generally too expensive due to high manufacturing costs. A design that combines favorable inorganic membrane selectivity with the cost-effectiveness of polymer processing in continuous mode will be the focus. The micro-porous membranes are aluminosilicates. Fully inorganic structures have CO₂/N₂ selectivities of >200, and permeances of <300 GPU. The latter can be improved by reducing membrane thickness, in combination with defect abatement with a thin polydimethylsiloxane (PDMS) layer. In the membrane compositions, zeolite Y layers can be grown from solutions at 95°C. Zeolite Y exhibits better properties but requires long growth time, which needs to be reduced to minutes. Indications are good that the growth time can be shortened significantly and that the membrane system can be deposited on available polyethersulfone or polysulfone supports.

TABLE 1: PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer	-	Zeolites	
Materials of Fabrication for Support Layer	-	Polyethersulfone or polysulfone on non-woven fabric	
Nominal Thickness of Selective Layer	nm	200 – 500	50 – 150
Membrane Geometry	-	Flat sheet	Spiral-wound sheet
Max Trans-Membrane Pressure	bar	Can be 50	0.2 – 1.5
Hours Tested Without Significant Degradation	-	30 hrs	200 hrs
Manufacturing Cost for Membrane Material	\$/m ²	50	15
Membrane Performance			
Temperature	°C	100°C	57°C
CO ₂ Pressure Normalized Flux	GPU or equivalent	1,100 GPU	>2,500 GPU
CO ₂ /H ₂ O Selectivity	-	Not yet determined	Not yet determined
CO ₂ /N ₂ Selectivity	-	$\alpha = 800$ for 20 CO ₂ /80 N ₂ with $p_{tot} = 101$ kPa	$\alpha > 100$ for flue gas conditions
CO ₂ /SO ₂ Selectivity	-	Not yet determined	Not yet determined
Type of Measurement	-	Mixed gas	Mixed gas
Proposed Module Design			
Flow Arrangement	-	Countercurrent	
Packing Density	m ² /m ³	About 2000	
Shell-Side Fluid	-	Air sweep	
Flue Gas Flowrate	kg/hr	About 200	
CO ₂ Recovery, Purity, and Pressure	% / % / bar	>90%, >95%, 0.2 – 1.2 bar	
Pressure Drops Shell/Tube Side	bar	About 0.05/0.05	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	About 90	

Definitions:

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

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

GPU – Gas Permeation Unit, which is equivalent to 10⁻⁶ cm³ (1 atm, 0°C)/cm²/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm³ (1 atm, 0°C)/cm²/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10⁻⁶ kg mol/m²-s-kPa [SI units].

Type of Measurement – Mixed gas measurements; target permeance and selectivities should be for mixture of gases found in desulfurized flue gas.

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

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

Shell-Side Fluid – Either the permeate (CO₂-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO₂ in CO₂-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Surface adsorption and diffusion and molecular sieving for the zeolite selective layer; solution-diffusion for the polymer cover layer.

Contaminant Resistance – Fully resistant polymer and inorganic materials.

Flue Gas Pretreatment Requirements – Removal of particulates, possibly dehydration.

Membrane Replacement Requirements – Estimated approximately four years.

Waste Streams Generated – N₂ with H₂O, <1 percent CO₂ and minor impurities.

technology advantages

Cost-effective separation principle.

R&D challenges

Synthesis and scale-up of sufficiently selective and permeable membranes.

results to date/accomplishments

- Membrane synthesis:
 - Zeolite/polymer composite membranes showed a CO₂ permeance of 1,100 GPU and a CO₂/N₂ selectivity of >200.
 - Achieved deposition of zeolite Y on polyethersulfone support.
 - Significant membrane synthesis improvements were made, including: (1) discovery of rapid zeolite synthesis (< one hour) for continuous membrane fabrication; (2) inorganic/organic spiral-wound membrane element; and (3) ceramic membrane processing also improved (20 minutes in lieu of 43 hours), but membrane performance poor.
 - The membrane process without cryogenic distillation was selected for development.
- Membrane characterization analyses:
 - Conducted electron microscopy of 2-D focused ion beam (FIB) cross-sections.
 - Tested membrane transport using the mixed gas simulating flue gas CO₂, N₂, and H₂O concentrations.
 - Obtained X-ray diffraction (XRD) patterns indicative of zeolite formation.
 - Characterized zeolite nanoparticles by dynamic light scattering (DLS) and transmission electron microscopy (TEM) for particle size.
 - Characterized zeolites by nuclear magnetic resonance spectroscopy (NMR) for silicon (Si)/aluminum (Al) ratio.
- System and cost analysis:
 - Completed the preliminary system model in Aspen.
 - Used the model to conduct preliminary techno-economic calculations.
 - Preliminary techno-economic calculations (1,026 GPU and >150 selectivity) showed ≈46.1% cost of electricity increase and ≈\$31.2/tonne CO₂.

- Membrane synthesis:
 - Growth of thin, selective zeolite Y layers.
 - Optimization/improvement of zeolite and polymer layer depositions.
 - Membrane scale-up using continuous membrane fabrication machine.
- Membrane characterization analyses:
 - Characterization of transport properties of lab and scale-up membranes using the mixed gas simulating flue gas CO₂, N₂, and H₂O concentrations.
 - Competitive H₂O/CO₂ transport studies.
 - Complete TEM FIB films.
 - Characterization of zeolites synthesized by XRD, DLS, NMR, and TEM.
- System and cost analysis:
 - Continuation of system studies.
 - Update of preliminary techno-economic calculations using improved membrane transport data.
 - Environmental health and safety evaluation.

available reports/technical papers/presentations

Verweij, H., "Novel Inorganic/Polymer Composite Membranes for CO₂ Capture," presented at the 2012 NETL CO₂ Capture Technology Meeting, Pittsburgh, Pennsylvania, July 2012. <http://www.netl.doe.gov/File%20Library/events/2012/co2%20capture%20meeting/H-Verweij-OSU-Composite-Membranes.pdf>.

MEMBRANE PROCESS TO CAPTURE CARBON DIOXIDE FROM COAL-FIRED POWER PLANT FLUE GAS

B-381

primary project goals

Membrane Technology & Research, Inc. (MTR) is developing a polymeric membrane and associated process for carbon dioxide (CO₂) capture. The project includes conducting slipstream (0.05 MWe) and small pilot-scale (1 MWe) field tests using full-scale commercial membrane modules to treat combustion flue gas at the National Carbon Capture Center (NCCC).

technical goals

- Develop a thin film, composite, polymer-based membrane to increase CO₂ permeance while maintaining CO₂/nitrogen (N₂) selectivity.
- Develop a countercurrent sweep membrane module design using incoming combustion air to generate separation driving force and reduce the need for vacuum pumps and the associated parasitic energy cost.
- Fabricate commercial-scale membrane modules that meet low pressure-drop and high packing-density performance targets.
- Conduct slipstream field testing of a membrane system at NCCC; the system will process 7,000 standard m³/day (0.25 MMscfd) of flue gas (equivalent to approximately 0.05 MWe), separating about one tonne of CO₂/day.
- Further scale-up the process in order to conduct a six-month small pilot-scale field test of a membrane system at a coal-fired power plant (equivalent to approximately 1 MWe, or about 20 tonne of CO₂/day).
- Analyze the performance of the membrane system, determine how it would be best integrated with a coal-fired power plant, and prepare a comparative economic analysis of the membrane-based CO₂ capture process versus other capture technologies.

technical content

MTR is developing composite membranes with high CO₂ permeance and high CO₂/N₂ selectivity for post-combustion flue gas applications. Tests indicate the membrane has 10 times the CO₂ permeance of conventional gas separation membranes. The combination of these membranes with a novel countercurrent module design that utilizes incoming combustion air to generate separation driving force greatly reduces the projected cost of CO₂ capture. MTR is developing a commercial-scale membrane module that can meet low pressure-drop and high packing-density performance targets. This thin-film membrane utilizes hydrophilic polymers and is known by the trade name “Polaris™.”

Polaris™ membranes will be used in a novel two-step membrane process design, as shown in Figure 1. The process includes two types of membrane arrangements: a conventional cross-flow module and a novel countercurrent sweep module. First, the combustion flue gas enters a cross-flow module, which removes most of the CO₂. The retentate from the cross-flow module is then fed into a countercurrent sweep module, from which the permeate is

technology maturity:

Pilot-Scale, Actual Flue Gas
(equivalent to 1 MW)

project focus:

Polymeric Membranes

participant:

Membrane Technology &
Research Inc.

project number:

FE0005795, DE-NT0005312,
and FC26-07NT43085

NETL project manager:

José Figueroa
jose.figueroa@netl.doe.gov

principal investigator:

Tim Merkel
Membrane Technology
& Research, Inc.
tmerkel@mtrinc.com

partners:

Arizona Public Service
Babcock & Wilcox
EPRI
Helios-NRG
Southern Company/NCCC
Worley Parsons

performance period:

4/1/07 – 9/30/15

recycled back to the boiler via an air sweep, which increases the CO₂ concentration of the flue gas entering the initial cross-flow module. The CO₂-rich permeate from the cross-flow module is then dehydrated and compressed. A second-stage cross-flow module is used after compression to further enrich the CO₂ stream by recycle of the permeate back to the inlet of the compressor.

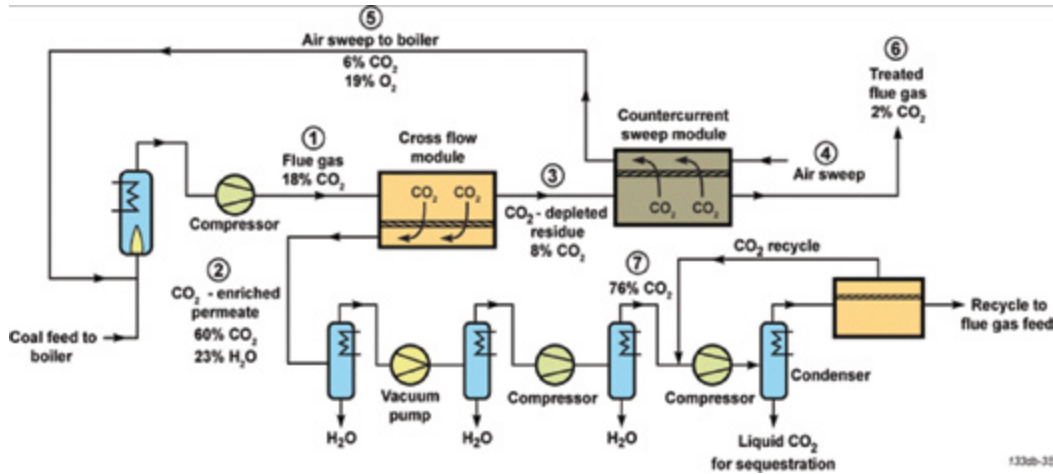


Figure 1: Process Design for the Membrane System

Polaris™ membranes will be packed into spiral-wound membrane modules, the most commonly used module design for commercial membrane installations today. Spiral-wound modules are robust, resistant to fouling, and economical; they are used in 95 percent of the reverse osmosis (RO) desalination industry and more than 60 percent of the membrane market for CO₂ removal from natural gas. Figure 2 shows the general design features of a spiral-wound membrane module. The module consists of a permeate collection tube with a spiral formation of permeate spacers and feed spacers, which allow the flue gas and separated CO₂ to flow through the device.

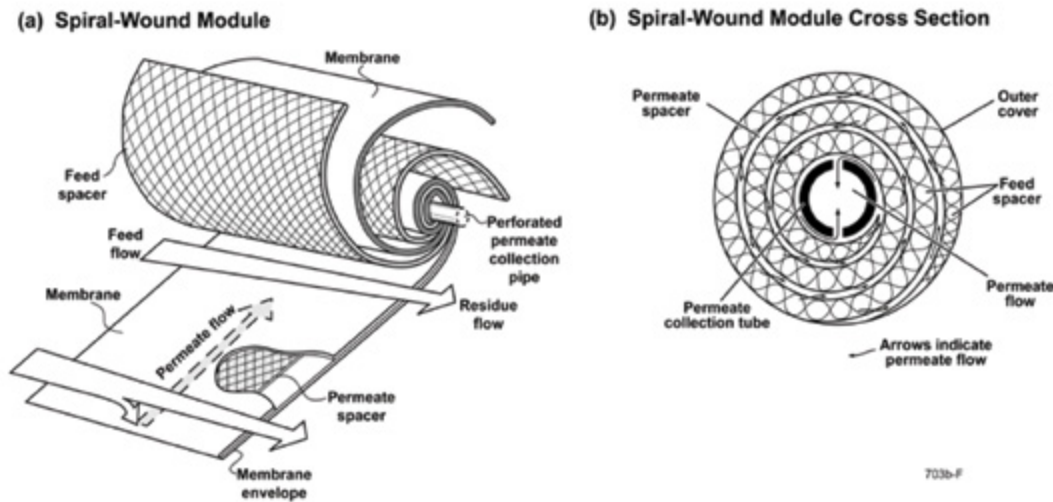


Figure 2: Schematic Diagram of a Spiral-Wound Membrane Module

MTR estimates that a total membrane area of about 0.5 million m² is required to achieve 90 percent CO₂ capture for a 550-MWe plant using this process design and would consume approximately 20 to 25 percent of the plant’s gross power output. Figure 3 shows a proposed design for a full-scale membrane system. Each set of modules would be stacked on a skid and connected together to form a single “mega-module.” About 130 mega-module skids would be required for a 550-MWe power plant (current RO plants already use similar numbers of modules and module skids).

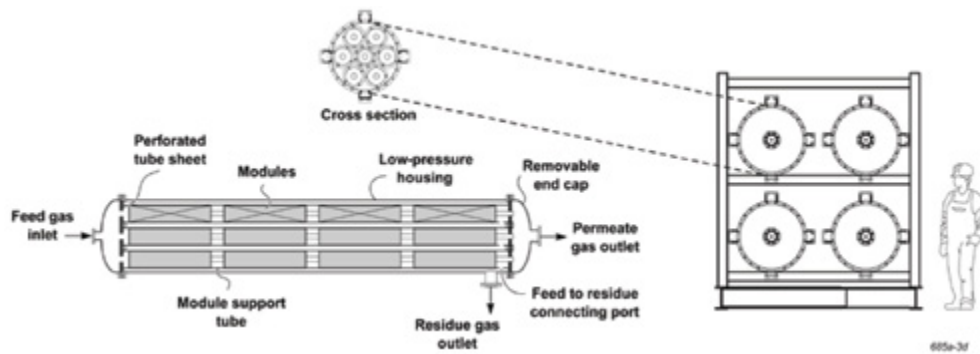


Figure 3: Proposed Design for Full-Scale Membrane System

Figure 4 shows the membrane skid used for the pilot-scale slipstream test at the coal-fired Cholla Power Plant operated by APS. The skid can hold up to eight (four cross-flow and four countercurrent sweep), 8-inch diameter Polaris™ membrane modules. The membrane skid is designed to capture one tonne of CO₂ per day from a 7,000 standard m³/day (250,000 scfd) flue gas slipstream. The test is demonstrating membrane operation in commercial-scale modules and will determine typical membrane lifetimes under coal combustion flue gas operating conditions.



Figure 4: Membrane Skid Used for 1-TPD Pilot-Scale Slipstream Testing of NCC

TABLE 1: MEMBRANE PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer		Proprietary polymer	
Materials of Fabrication for Support Layer		Proprietary polymer	
Nominal Thickness of Selective Layer	μm	<1	<1
Membrane Geometry		spiral	spiral
Maximum Trans-Membrane Pressure	bar	70	70
Hours Tested Without Significant Degradation		1,000 (coal)	5,000 (coal)
Manufacturing Cost for Membrane Material	\$/m ²		
Membrane Performance			
Temperature	°C	30	30
CO ₂ Pressure Normalized Flux	GPU or equivalent	1,500	>2,500
CO ₂ /H ₂ O Selectivity	-		
CO ₂ /N ₂ Selectivity	-	25	25
CO ₂ /SO ₂ Selectivity	-		
Type of Measurement	ppm	mixed	mixed
Proposed Module Design			
Flow Arrangement	-	Crossflow and countercurrent	
Packing Density	m ² /m ³	1,000	
Shell-Side Fluid	-	N/A	
Flue Gas Flowrate	kg/hr	500	
CO ₂ Recovery, Purity, and Pressure	% / % / bar	90%, >96%, 140 bar	
Pressure Drops Shell/Tube Side	% / % / bar	Feed: <0.05 / Sweep: 0.2	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	250	50

Definitions:

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

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

GPU – Gas Permeation Unit, which is equivalent to 10⁻⁶ cm³ (1 atm, 0°C)/cm²/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm³ (1 atm, 0°C)/cm²/s with pressures measured in cmHg. Note: 1 GPU = 3.3464×10⁻⁶ kg mol/m²-s-kPa [SI units].

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

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

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

Shell-Side Fluid – Either the permeate (CO₂-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO₂ in CO₂-rich product gas; assuming targets are met.

Other Parameter Descriptions:

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

Contaminant Resistance – The membranes are known to be unaffected by water (H₂O), oxygen (O₂), and sulfur dioxide (SO₂). The effect of trace contaminants, such as mercury, arsenic, etc., is unknown and is being examined in the ongoing field demonstration at NCCC.

Flue Gas Pretreatment Requirements – Currently, pretreatment requirements are unknown. The current demonstration tests at NCCC treat post-flue gas desulfurization (FGD) flue gas and will help determine the need for gas treatment prior to entering the membrane system. The greatest concern of species present in flue gas is that particulate matter will foul the membranes, reducing module lifetimes. Particulate filters that can achieve an order of magnitude better ash removal than a standard bag house, and are used today to treat refinery and gasification streams, may be needed.

Membrane Replacement Requirements – Membrane lifetime is being studied in ongoing demonstration tests at NCCC. The target membrane module lifetime is three years, which is at the conservative end of the typical industrial gas separation module lifetime of three to five years.

Waste Streams Generated – The membrane process will recover >95 percent of the H₂O in flue gas as liquid. The quality of this H₂O and its potential to be re-used in the plant will be studied in future work.

technology advantages

- The membranes developed are 10 times more permeable to CO₂ than conventional membranes, which reduce the required membrane area and capital costs.
- A membrane system does not contain any chemical reactions or moving parts, making it simple to operate and maintain.
- The membrane material has a high tolerance of wet acid gases and is inert to O₂.
- The membrane system has a compact footprint and low energy cost.
- The membrane capture system can recover water from flue gas.
- The use of an existing air stream to generate a CO₂ partial-pressure gradient in the countercurrent sweep membrane stage reduces the need for compressors or vacuum pumps, thus reducing the overall energy cost.
- The recycled CO₂ from the air sweep to the boiler increases the CO₂ partial-pressure driving force for separation in the initial cross-flow membrane stage, reducing the required membrane area and total system cost.

R&D challenges

- The membrane process requires a large membrane surface area to achieve separation due to the low partial pressure of CO₂ in flue gas.
- The countercurrent sweep module design could result in several potential inefficiencies, including: sweep-side pressure drop, concentration polarization, poor utilization of the membrane area due to module geometry, and non-countercurrent flow patterns.
- Particulate matter needs to be controlled to reduce its potential impact on the membrane lifetime.
- Feed and permeate side pressure drops may lead to excessive energy losses.
- Cost reductions for the membrane module materials will be needed if the technology is to become economically viable.
- The membrane process depends on large rotating equipment (vacuum pumps, booster fans). The availability of cost-effective equipment that can operate on full-scale flue gas streams has yet to be demonstrated.
- Scale-up and integration issues are a possibility given the large number of membranes needed to service a 550-MWe plant.

- Scaled-up and produced high permeance membrane formulations on commercial casting and coating equipment. Produced more than 1,000 m² of Polaris™ membrane material used to construct 203-mm (8-inch) diameter, commercial-sized, conventional cross-flow and novel countercurrent sweep modules.
- Field tested pilot- and commercial-scale membrane modules with various industrial gas streams (raw coal-fired flue gas, raw natural gas-fired flue gas, and synthesis gas [syngas] containing sulfur species) for up to three months of continuous operation. The modules showed stable performance throughout these tests.
- Field tests revealed the membrane permeance is 10 times higher than existing materials and the membranes possess good stability in acid gases.
- Provided a membrane system to APS to process 4,250 m³/day (0.15 MMscfd) of natural-gas fired flue gas to provide concentrated CO₂ for testing at an experimental algae farm.
- In mid-2010, MTR conducted a three-month field test of a small slipstream membrane system at the Cholla Unit 3 power plant. The membrane test skid can process 7,000 m³/day (0.25 MMscfd) of coal-fired flue gas and capture one tonne CO₂/day. The test skid is composed of four, 8-inch diameter Polaris™ membrane modules that demonstrate the cross-flow and sweep configurations. The membrane modules showed stable performance for 45 days during the field testing, consistent with laboratory test results. There was minimal membrane fouling by particulates in the gas stream, which was originally anticipated to be a concern. Most of the system downtime was related to mechanical and electrical problems with the rotating equipment (feed compressor and permeate vacuum pump) caused by the corrosive operating environment. Use of equipment with more appropriate materials of construction in future testing should solve these problems.
- MTR developed new, sweep-side flow channel configurations for the membrane sweep modules. Bench-scale testing indicated the new designs lower the sweep-side pressure drop, while maintaining the sweep performance efficiency.
- MTR estimates the membrane-based CO₂ separation and liquefaction process can capture 90 percent CO₂ using 20 to 25 percent of the plant's energy and cost \$30 per tonne of CO₂ captured.
- B&W conducted computational fluid dynamic (CFD) computer modeling to examine the effect of CO₂ recycle to the boiler, which demonstrated that secondary air laden with CO₂ appears feasible as a retrofit.
- MTR's 1-TPD slipstream system was installed at NCCC in November 2011 and continuous operation was initiated in spring 2012 using first-generation Polaris™ modules. Overall, membrane module performance was stable. During the initial 1,000 hours of operation, the membrane enriched CO₂ by about six times in the permeate (approximately 60 percent capture). After 1,000 hours operation, additional modules were loaded to increase the capture rate to 85 percent.

next steps

- Continue to operate the 1-TPD slipstream membrane system at NCCC. Use this system to evaluate new second-generation Polaris™ membrane.
- Conduct field testing on the 1-TPD slipstream membrane system with new flow channel configurations with a goal of minimizing pressure drop through the membrane system.
- Complete construction and operate the 20-TPD small pilot-scale (approximately 1 MWe equivalent gas flow) membrane system for a six-month field test at NCCC beginning in spring 2014.
- Analyze the performance of the membrane system, determine how it would be best integrated with a coal-fired power plant, and prepare a comparative economic analysis of the membrane-based CO₂ capture process versus other capture technologies.
- Lower the membrane module cost by incorporating low-cost components with a target of \$50/m².
- Integrate a CO₂ liquefaction section into the overall CO₂ capture system.
- Test options for recycling the air sweep from the countercurrent sweep module to the boiler.

Amo, K., et.al, "Slipstream Testing of a Membrane CO₂ Capture Process," presented at the 2012 NETL CO₂ Capture Technology Meeting, Pittsburgh, Pennsylvania, July 2012. <http://www.netl.doe.gov/publications/proceedings/12/co2capture/presentations/1-Monday/T%20Merkel-MTR-Membrane%20Process.pdf>.

Merkel, T., et.al, "Pilot Test of an Efficient Membrane Process for Post-Combustion CO₂ Capture Process," presented at the 2011 NETL CO₂ Capture Technology Meeting, Pittsburgh, Pennsylvania, August 2011. <http://www.netl.doe.gov/publications/proceedings/11/co2capture/presentations/1-Monday/22Aug11-Merkel-MTR-Efficient%20Membrane%20Pilot%20Test.pdf>.

Amo, K. et.al, "Membrane Process to Capture CO₂ from Coal-Fired Power Plant Flue Gas," presented at the 2010 NETL CO₂ Capture Technology Meeting, Pittsburgh, Pennsylvania, September 2010. <http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/tuesday/Xiaotong%20Wei%20-%20NT0005312%20and%20NT43085.pdf>.

Merkel, T., et.al, "Power plant post-combustion carbon dioxide capture: An opportunity for membranes," Journal of Membrane Science, Volume 359, Issues 1-2, 1 September 2010, pages 126-139.

Merkel, T., et.al, "Opportunities for Membranes in Power Generation Processes," Gordon Research Conference Presentation, July 27, 2010.

Merkel, T., et.al, "A Membrane Process to Capture CO₂ from Coal-Fired Power Plant Flue Gas," presented at the Annual NETL CO₂ Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009. <http://www.netl.doe.gov/publications/proceedings/09/CO2/pdfs/5312%20MTR%20membrane%20%28Merkel%29%20mar09.pdf>.

"The Membrane Solution to Global Warming," 6th Annual Conference on Carbon Capture and Sequestration, Pittsburgh, Pennsylvania, May 2007.

BENCH-SCALE, HIGH-PERFORMANCE, THIN FILM COMPOSITE HOLLOW FIBER MEMBRANE FOR POST-COMBUSTION CARBON DIOXIDE CAPTURE

primary project goals

General Electric Global Research (GE) is developing high-performance, thin film polymer composite hollow fiber membranes and advanced processes for economical post-combustion carbon dioxide (CO₂) capture. The project includes bench-scale testing to tune the properties of a novel phosphazene polymer membrane and decrease costs through development of innovative fabrication techniques.

technical goals

- Optimize phosphazene polymer and coating solution: Synthesize phosphazene polymer, optimize separation performance, and develop processable coating solutions.
- Fabricate hollow fiber support layer: Produce highly porous, robust hollow fiber supports with controlled surface porosity from commercially available materials.
- Fabricate composite coated hollow fiber membranes: Develop processes to apply thin layer coatings on hollow fiber supports and elucidate fundamental polymer properties.
- Test membranes at bench-scale under flue gas conditions: Exposure and performance test materials and membranes under flue-gas conditions.
- Conduct process evaluation and module design: Conduct technical and economical process evaluation and module design and fabrication.

technical content

GE and partners are developing a high-performance, thin film polymer composite hollow fiber membrane and advanced process for economical post-combustion CO₂ capture. The project utilizes novel phosphazene polymeric materials to produce an economical and scalable composite hollow fiber membrane module. The membrane will be optimized at bench-scale, including tuning the properties of the phosphazene polymer in a coating solution and fabricating highly engineered porous hollow fiber supports. The project will also define the processes for coating the fiber support to manufacture thin, defect-free composite hollow fiber membranes.



Figure 1: GE Test Rig – Flat Sheet and Hollow Fiber Membranes

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Composite Hollow Fiber Membranes

participant:

General Electric Global Research Center

project number:

FE0007514

NETL project manager:

Isaac Aurelio
isaac.aurelio@netl.doe.gov

principal investigator:

Dhaval Bhandari
General Electric
bhandari@ge.com

partners:

Idaho National Laboratory
Western Research Institute
Georgia Institute of Technology

performance period:

10/1/11 – 9/30/14

The physical, chemical, and mechanical stability of the materials (individual and composite) to flue gas components will be evaluated using exposure and performance tests. Membrane fouling and cleanability studies will define long-term performance.

GE and the Georgia Institute of Technology (Georgia Tech) will work together on developing processes to apply the thin layer coating formulations onto the hollow fiber supports. GE will leverage the knowledge gained from using its flat sheet film coating apparatus to enable development of the continuous dip process for coating of hollow fiber membrane supports. Georgia Tech will use the in situ process developed to coat porous cellulose acetate hollow fibers with defect-free layers as a benchmark, which will be further adapted to obtain thin, defect-free coated layers. Both the continuous dip coating and batch in situ processes will be optimized to provide economical and scalable coated composite hollow fiber membranes.

Working with Idaho National Laboratory, Georgia Tech will characterize phosphazene material properties in films cast on porous polymer supports to elucidate polymer properties including aging, membrane fouling, and cleanability. The characterization techniques will enable a better understanding of polymer and composite membrane performance. Membrane performance validation testing under flue-gas conditions will be performed at Western Research Institute’s coal combustion test facility. Module design and technical and economic feasibility analyses will be conducted to evaluate the overall performance and impact of the process on the cost of electricity.



Figure 2: Georgia Tech Hollow Fiber Fabrication Line

TABLE 1: PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer		Phosphazene	
Materials of Fabrication for Support Layer		Polymer	
Nominal Thickness of Selective Layer	µm	1 – 10	<1
Membrane Geometry		Flat sheet/Hollow fiber	Hollow fiber
Maximum Trans-Membrane Pressure	bar	2 – 5	Up to 10
Hours Tested Without Significant Degradation		200 (flat sheet) 100 (hollow fiber)	100 – 1,000
Manufacturing Cost for Membrane Material	\$/m ²	-	-
Membrane Performance			
Temperature	°C	30 and 65	30 and 60
CO ₂ Pressure Normalized Flux	GPU or equivalent	50-275 Barrer (flat sheet 30 °C) 100-425 Barrer (flat sheet 65 °C) Up to 70 GPU (Hollow fibers 35 °C)	1,000 – 2,500 GPU (Hollow fibers)
CO ₂ /H ₂ O Selectivity	-	8-10	8 – 10
CO ₂ /N ₂ Selectivity	-	15 – 20 (65 °C) flat sheet 30 – 40 (30 °C) flat sheet 10 – 35 (35 °C) hollow fibers	30 – 40
CO ₂ /SO ₂ Selectivity	-	Not tested	Non tested
Type of Measurement	-	mixed gas	mixed gas
Proposed Module Design			
Flow Arrangement	-	Counter current	

TABLE 1: PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Packing Density	m ² /m ³		>1,000
Shell-Side Fluid	-		Retentate
Flue Gas Flowrate	kg/hr		<1
CO ₂ Recovery, Purity, and Pressure	% / % / bar		>90%, 60–80%, 0.2–1 bar
Pressure Drops Shell/Tube Side	bar		1–4
Estimated Module Cost of Manufacturing and Installation	—		<\$100/m ²

Definitions:

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

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

GPU – Gas Permeation Unit, which is equivalent to 10⁻⁶ cm³ (1 atm, 0°C)/cm²/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm³ (1 atm, 0°C)/cm²/s with pressures measured in cmHg. Note: 1 GPU = 3.3464×10⁻⁶ kg mol/m²-s-kPa [SI units].

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

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

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

Shell-Side Fluid – Either the permeate (CO₂-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO₂ in CO₂-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Solution-diffusion mechanism.

Contaminant Resistance – Phosphazene-based membranes have been tested to be resistant to contaminant species such as oxygen (O₂), nitrogen oxide (NO_x), sulfur dioxide (SO₂), and moisture present in coal flue gas.

Flue Gas Pretreatment Requirements – Fly ash particulate removal.

Membrane Replacement Requirements – Membranes found to be stable with up to 200 hours of testing. Long-term stability tests are currently in progress.

Waste Streams Generated – Acidic water condensate stream.

technology advantages

- Surface property optimization to reduce fly ash adhesion.
- Highly scalable, low-cost hollow fiber support platform.
- Ease of cleaning should provide longer membrane life.
- Phosphazene polymer with high permeability and selectivity.

R&D challenges

- Fouling potential from fly ash/particulates.
- Permeability and selectivity at 60°C lower than anticipated.
- Large membrane area requirements and process integration.

results to date/accomplishments

- Synthesized phosphazene polymer, characterized separations performance under realistic flue gas conditions, and developed hollow fiber support coating solutions.
- Developed engineered, high-porosity, hollow fiber supports.
- Built/upgraded bench-scale membrane coating and testing facilities.
- Completed initial process technical and economic feasibility study.
- Fabricated phosphazene coated defect-free hollow fiber membranes.

next steps

- Optimize phosphazene polymer coatability on hollow fiber supports.
- Optimize the continuous dip and batch coating processes to provide economical and scalable coated composite hollow fiber membranes.
- Conduct preliminary membrane fouling and aging studies.
- Test coated composite hollow fiber membranes at bench-scale under flue gas conditions.
- Conduct final technical and economic feasibility analyses and an environmental, health, and safety assessment.

available reports/technical papers/presentations

Bhandari, D., et al., “Composite Hollow Fiber Membranes for Post Combustion CO₂ Capture,” presented at the 2012 NETL CO₂ Capture Technology Meeting, Pittsburgh, Pennsylvania, July 2012. <http://www.netl.doe.gov/File%20Library/events/2012/co2%20capture%20meeting/D-Bhandari-GEGR-Hollow-Fiber-Membranes.pdf>.

LOW-PRESSURE MEMBRANE CONTACTORS FOR CO₂ CAPTURE

B-392

primary project goals

Membrane Technology & Research (MTR) is developing a new type of membrane contactor (or mega-module) to decrease capture costs, energy use, and system footprint through bench-scale testing of a module with a membrane area that is 500 m², 20 to 25 times larger than that of current modules used for carbon dioxide (CO₂) capture.

technical goals

- Develop a module design to reduce energy cost by lowering module pressure drop.
- Develop a module design with a large membrane area.
- Develop a module design to reduce manifold complexity, footprint, and cost.

technical content

MTR is developing a new type of membrane contactor (or mega-module) to separate CO₂ from power plant flue gas. This module's membrane area is 500 m², which is 20 to 25 times larger than that of current modules used for CO₂ capture. The countercurrent sweep module is crucial to the MTR-developed CO₂ removal from flue gas process, as this membrane module permits the use of air as a sweep gas, which increases the CO₂ flux through the membrane without requiring additional compression energy. This means the CO₂ concentration in the flue gas is increased at a minimal energy cost.

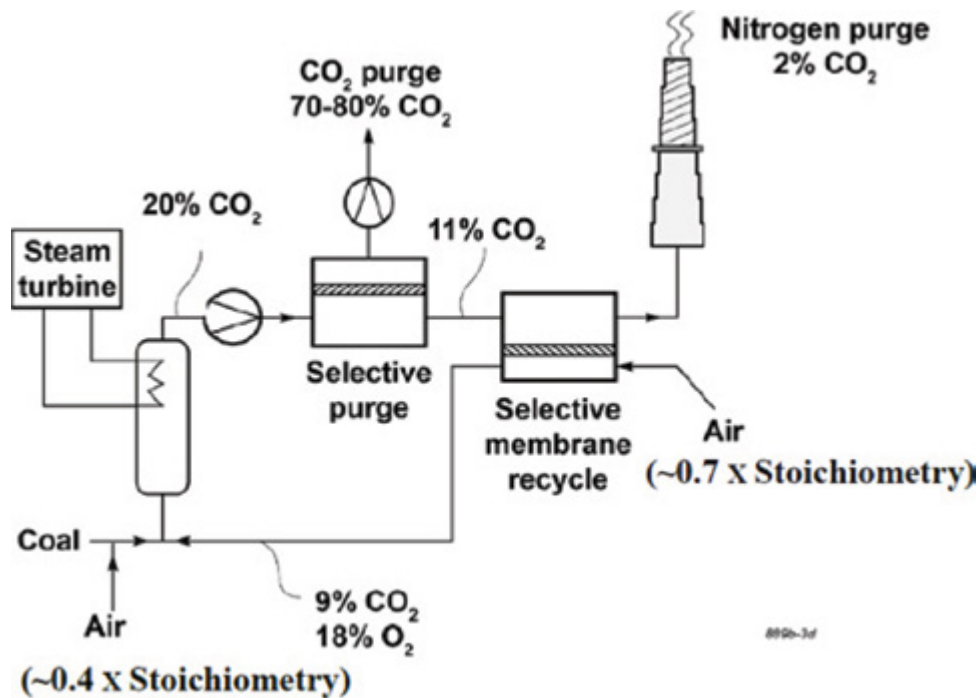


Figure 1: Two-Stage Membrane CO₂ Capture Process

technology maturity:

Bench-Scale, Simulated and Actual Flue Gas

project focus:

Low-Pressure Membrane Contactors (Mega-Module)

participant:

Membrane Technology & Research, Inc.

project number:

FE0007553

NETL project manager:

Morgan Mosser
morgan.mosser@netl.doe.gov

principal investigator:

Richard Baker
Membrane Technology & Research, Inc.
richard.baker@mtrinc.com

partners:

University of Toledo

performance period:

10/1/11 – 9/30/14

TABLE 1: PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer		Proprietary polymer	
Materials of Fabrication for Support Layer		Proprietary polymer	
Nominal Thickness of Selective Layer	μm	<1	<1
Membrane Geometry		Plate-and-Frame	Plate-and-Frame
Maximum Trans-Membrane Pressure	bar	70	70
Hours Tested Without Significant Degradation		500	500
Manufacturing Cost for Membrane Material	\$/m ²	100	20
Membrane Performance			
Temperature	°C	30	30
CO ₂ Pressure Normalized Flux	GPU or equivalent	1,500	>2,500
CO ₂ /H ₂ O Selectivity	-	0.5	0.5
CO ₂ /N ₂ Selectivity	-	50	50
CO ₂ /SO ₂ Selectivity	-	0.5	0.5
Type of Measurement	-	Pure gas	Pure gas
Proposed Module Design			
Flow Arrangement	-	Countercurrent	
Packing Density	m ² /m ³	1,000	
Shell-Side Fluid	-	N/A	
Flue Gas Flowrate	kg/hr	5000	
CO ₂ Recovery, Purity, and Pressure	% / % / bar	90%, >96%, 140 bar	
Pressure Drops Shell/Tube Side	bar	Feed: 0.1; Sweep: 0.2	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	250	50

Definitions:

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

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

GPU – Gas Permeation Unit, which is equivalent to 10⁻⁶ cm³ (1 atm, 0°C)/cm²/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm³ (1 atm, 0°C)/cm²/s with pressures measured in cmHg. Note: 1 GPU = 3.3464×10⁻⁶ kg mol/m²-s-kPa [SI units].

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

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

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

Shell-Side Fluid – Either the permeate (CO₂-rich) or retentate (flue gas) stream.

Other Parameter Descriptions:

Contaminant Resistance – The membranes are known to be unaffected by water (H₂O), oxygen (O₂), and sulfur dioxide (SO₂). The effect of trace contaminants, such as mercury, arsenic, etc., is unknown and is being examined in the ongoing field demonstration at the National Carbon Capture Center (NCCC) in Wilsonville, Alabama, under a different U.S. Department of Energy National Energy Technology Laboratory (DOE/NETL)-sponsored project (DE-FE0005795).

Flue Gas Pretreatment Requirements – Currently, pretreatment requirements are unknown. The current demonstration tests at NCCC treat post-flue gas desulfurization (FGD) flue gas and will help determine the need for gas treatment prior to entering the membrane system. The greatest concern of species present in flue gas is that particulate matter will foul the membranes, reducing module lifetimes. Particulate filters that can achieve an order of magnitude better ash removal than a standard bag house, and are used today to treat refinery and gasification streams, may be needed.

Waste Streams Generated – The membrane process will recover >95 percent of the H₂O in flue gas as liquid. The quality of this H₂O and its potential to be reused in the plant will be studied in future work.

technology advantages

- In flue gas applications, the novel countercurrent sweep module recycles CO₂ to the boiler with an air sweep, which increases the CO₂ concentration in the flue gas with minimal energy input.
- The recycle of CO₂ to the boiler increases the concentration of CO₂ in the flue gas, which could make the CO₂ capture process easier for technologies other than membranes.
- The novel countercurrent sweep module design has low-pressured drop, which reduces the energy costs.
- Mega-modules (500 m² or larger) reduce the manifolding complexity, footprint, and cost of the membrane system.

R&D challenges

- The novel sweep plate and framed design will need to overcome several issues, including: sweep-side pressure drop, poor utilization of the membrane area due to module geometry, and non-countercurrent flow patterns.
- Spacer design and selection needs to maximize packing density and mechanical support while minimizing pressure drop.
- Scale-up issues associated with building membrane modules 10 to 20 times larger than conventional modules.

results to date/accomplishments

- Completed design and fabrication of various 20-m² prototype membrane modules.
- Completed pressure drop and CO₂ separation performance testing of various 20-m² prototype membrane modules with bench-scale lab test system
- Completed design and construction of larger lab test system, sized for parametric studies of 100-m² membrane modules.
- Conducted CFD simulations of various sweep module designs that incorporate pressure drop, velocity profiles, and mass transfer.

next steps

- Conduct parametric testing of 100-m² membrane modules on large lab test unit at MTR.
- Scale up to full-scale module (> 500-m²) for testing at NCCC on MTR's 20-TPD small pilot-scale test system.
- Refinement of CFD and process simulation calculations to rationalize module performance.
- Evaluation of hybrid process designs for CO₂ capture from flue gas.

available reports/technical papers/presentations

Baker, R., et.al, “Low-Pressure Membrane Contactors for CO₂ Capture,” presented at the 2012 NETL CO₂ Capture Technology Meeting, Pittsburgh, Pennsylvania, July 2012. <http://www.netl.doe.gov/publications/proceedings/12/co2capture/presentations/1-Monday/R%20Baker-MTR-LP%20Membrane%20Contactors.pdf>.

B-395

POST-COMBUSTION MEMBRANES

HYBRID MEMBRANE/ABSORPTION PROCESS FOR POST-COMBUSTION CO₂ CAPTURE

B-396

primary project goals

Gas Technology Institute (GTI) is developing a hybrid membrane/absorption process (known as Carbo-Lock™) for post-combustion carbon dioxide (CO₂) capture. The Carbo-Lock™ process combines solvent absorption and a hollow-fiber membrane to leverage capture cost and performance advantages of two different capture technologies through bench-scale testing on synthetic and actual flue gas to evaluate mass transfer and regeneration. The bench-scale testing using actual flue gas is to be conducted on a 25 kWe-equivalent slipstream at Midwest Generation's Joliet Power Station.

technical goals

- Develop hollow-fiber membranes suitable for the membrane absorption application with improved mass transfer. Porous and composite membrane configurations are being evaluated.
- Demonstrate feasibility of the membrane contactor technology for flue gas CO₂ separation.
- Determine optimum solvent for use in process.
- Develop an energy-efficient regeneration process that enables CO₂ separation at elevated pressures.
- Conduct bench-scale testing of the process using actual flue gas.
- Conduct process design and preliminary economic analysis.

technical content

GTI is partnering with PoroGen Corporation and Aker Process Systems in a three-year effort to develop a hybrid technology for CO₂ capture based on a combination of solvent absorption and hollow fiber membrane technologies. The membrane contactor is a novel gas separation technology based on a gas/liquid membrane concept. It operates with a solvent on one side of the membrane and gas on the other. The membrane contactor process combines the advantageous features of membrane and absorption technologies and enables economical utilization of advanced absorption solvents. The PoroGen hollow-fiber membrane is based on a chemically and thermally resistant commercial engineered polymer (poly ether ether ketone [PEEK]). The hybrid technology increases gas/liquid contact area by a factor of 10 over conventional packed or tray absorption columns, thus increasing mass transfer. The membrane CO₂/nitrogen (N₂) selectivity is controlled by the chemical affinity of CO₂ with the selected solvent. The process could lower steam regeneration energy requirement as compared to conventional amine-based solvent processes by reducing the amount of water loss, and the CO₂ could be generated at pressure, reducing compression costs.

Figure 1 shows the basic mass transfer principle using the porous, hollow-fiber PEEK membrane contactor. The membrane matrix is filled with gas and mass transfer occurs via a diffusion reaction mechanism. The driving force is the difference in chemical potential of the

technology maturity:

Bench-Scale, Using Actual Flue Gas

project focus:

Hybrid Membrane/Absorption Process

participant:

Gas Technology Institute

project number:

FE0004787

NETL project manager:

José Figueroa
jose.figueroa@netl.doe.gov

principal investigator:

Shaojun Zhou
Gas Technology Institute
shaojun.zhou@gastechnology.org

partners:

Aker Process Systems
Midwest Generation EME, LLC
PoroGen Corporation

performance period:

10/1/10 – 12/31/13

CO₂ in the gas side versus the liquid side of the membrane. The mass transfer is not pressure-driven and, therefore, the absolute pressure difference between the membrane shell and tube side is either low or close to zero.

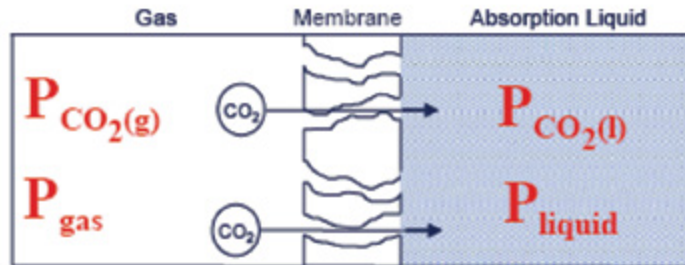


Figure 1: Mass Transfer Principle for Hybrid Membrane/Solvent Contactor

An advanced hindered amine and promoted carbonate solvents are being tested in combination with the membrane contactor system. The use of these solvents will decrease regeneration energy requirements as well as absorbent degradation. For the hindered amine solvent, the regeneration will be carried out in a membrane contactor at high temperature to generate CO₂ at elevated pressure. For the carbonate solvent, the regeneration will be carried out in a membrane contactor with low-pressure steam sweep to decrease regeneration energy. Both solvent systems are being evaluated initially and the most optimal system will be selected for the bench-scale field tests. Figure 2 shows a schematic diagram for the hybrid membrane/solvent process showing the absorber (membrane contactor) and regeneration columns.

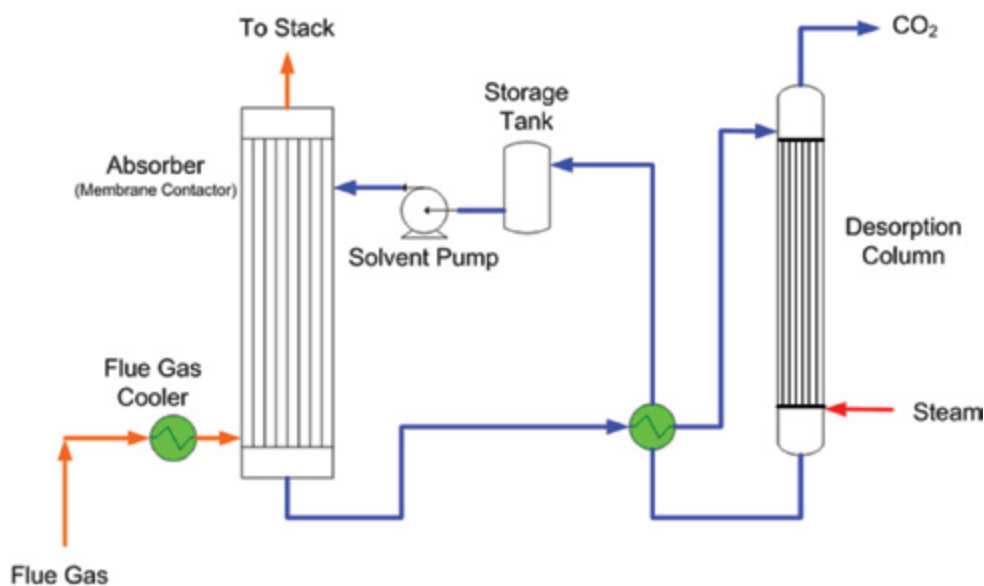


Figure 2: Process Schematic for Hybrid Membrane/Solvent Technology

The main process features of the hybrid membrane/solvent technology include: a higher CO₂ loading differential between rich and lean solvent is possible; increased mass transfer reduces system size; high specific surface area available for mass transfer; independent gas and liquid flow; linear scale up; and concentrated solvents or specialty absorbents can be used. Table 1 provides a summary of the membrane process parameters.

TABLE 1: MEMBRANE PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer	-	Perfluoro-oligomer	
Materials of Fabrication for Support Layer	-	PEEK	
Nominal Thickness of Selective Layer	μm		
Membrane Geometry	-	Hollow Fiber	Hollow Fiber
Max Trans-Membrane Pressure	bar		
Hours Tested Without Significant Degradation	-	100 hours	140 hours
Manufacturing Cost for Membrane Material	\$/m ²		
Membrane Performance			
Temperature	°C	20 – 50	20 – 120
CO ₂ Pressure Normalized Flux	GPU or equivalent	1,000 – 5,000	1,000 – 2,000
CO ₂ /H ₂ O Selectivity	-		
CO ₂ /N ₂ Selectivity	-	Determined by solvent used	Determined by solvent used
CO ₂ /SO ₂ Selectivity	-		
Type of Measurement	-	Mixed	Mixed
Proposed Module Design			
Flow Arrangement	-	Countercurrent	
Packing Density	m ² /m ³	500 – 2,500	
Shell-Side Fluid	-	Chemical Solvent+CO ₂	
Flue Gas Flowrate	kg/hr		
CO ₂ Recovery, Purity, and Pressure	% / % / bar	95%, 99%, 97%	
Pressure Drops Shell/Tube Side	bar	1/0.1	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$		

Definitions:

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

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

GPU – Gas Permeation Unit, which is equivalent to 10⁻⁶ cm³ (1 atm, 0°C)/cm²/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm³ (1 atm, 0°C)/cm²/s with pressures measured in cmHg. Note: 1 GPU = 3.3464×10⁻⁶ kg mol/m²-s-kPa [SI units].

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

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

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

Shell-Side Fluid – Either the permeate (CO₂-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO₂ in CO₂-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – The hybrid membrane/absorption process is driven by the chemical potential difference of CO₂ between the gas phase and the solvent phase and high purity of CO₂ product can be generated in a single stage. The process selectivity for the hybrid membrane/absorption process approaches thousands and is determined by the chemical affinity of the absorption solvent to CO₂. As compared with the conventional membrane process, the permeate side partial pressure of CO₂ can be considered to be close to zero due to the chemical interaction of CO₂ with the absorption solvent. Therefore, the pressure ratio in the hybrid membrane/absorption process approaches infinity. Note that membrane selectivity is not required in a hybrid membrane/absorption process, although the porous super-hydrophobic membranes used in this project showed some selectivity for CO₂ over N₂.

Contaminant Resistance – Membrane is resistant to all contaminants. Absorbents will be affected by contaminants to a lesser extent than a conventional packed or tray column. Membrane will provide a measure of protection for the solvents from degradation by contaminants (a barrier).

Flue Gas Pretreatment Requirements – Particle removal.

Membrane Replacement Requirements – To be determined.

Waste Streams Generated – None.

technology advantages

- The membrane contactor process combines the advantageous features of membrane and absorption technologies and enables economical utilization of advanced absorption solvents.
- The hybrid technology increases interfacial gas/liquid area by a factor of 10 over conventional packed or tray absorption columns, thus increasing mass transfer.
- The process requires lower steam regeneration energy compared to conventional amine-based solvent processes.
- The CO₂ is generated at pressure, reducing compression costs.
- Up to 70 percent reduction in system size and footprint compared to a conventional solvent-based process.

R&D challenges

- Membrane hydrophobic properties may change with contact time in solvent causing solvent leakage. Long-term testing required.
- Mass transfer coefficient not sufficiently high for gas absorption and solvent regeneration in the membrane contactor.
- Develop solvent regeneration process in membrane module.
- Reduce process capital and operating costs.

results to date/accomplishments

- Develop hollow-fiber membranes suitable for the membrane absorption application:
 - Optimization of the super-hydrophobic PEEK membranes morphology for the preferred methyl-diethanolamine (MDEA) solvent system is close to completion. A membrane with “non-wetting” characteristics towards the MDEA solvent system was developed. The membrane morphology will be further optimized based on CO₂ separation and capture test results.
 - Membrane CO₂ permeance of approximately 2,000 GPU has been achieved.
 - Design of commercial-size module completed and design validated through computational fluid dynamic (CFD) modeling. Scaled-up module from 1 m² (lab-scale) to 100 m² (8-inch diameter x 60-inch long, commercial-scale).
 - Established production capability of eight-inch diameter module on commercial-scale equipment.

- Demonstrate feasibility of the membrane contactor technology:
 - Conducted laboratory-scale testing (2-inch diameter x 15-inch long, 1 m²) for membrane absorber using synthetic flue gas and achieved technical goal: ≥ 90 percent CO₂ removal in one stage; gas side pressure drop: 1.6 pounds per square inch (psi); mass transfer coefficient: 1.7 1/s.
 - Conducted laboratory-scale testing (2-inch diameter x 15-inch long, 1 m²) for membrane desorber using synthetic flue gas and achieved technical goal: CO₂ purity (97%) and CO₂ stripping rate (4.1 kg/m²/h) achieved. Operation optimization is ongoing to ensure “lean” solvent is lean enough for membrane absorber.
- Determine optimum solvent for use in process:
 - Commercial aMDEA (40 wt%), activated K₂CO₃ (20 wt%), and Hitachi’s H₃-1 solvent have been evaluated.
- Develop an energy efficient regeneration process:
 - Conducting regeneration tests with and without steam sweep.
- Conduct bench-scale testing using actual flue gas:
 - Completed construction of 25-kW (0.5 ton CO₂ per day) bench-scale membrane skid.
- Conduct process design and preliminary economic analysis:
 - Preliminary economic evaluation based on membrane absorber only results in a 56 percent increase in COE.
 - Preliminary evaluation based on membrane absorber and desorber testing results in a 54 percent increase in COE.

next steps

- Continue membrane development based on regeneration testing results.
- Continue evaluation of regeneration mode and down select optimal mode for slip-stream, bench-scale testing.
- After regeneration mode is down selected, use reflux in membrane desorber to improve regeneration efficiency (target: “lean” solvent lean enough for membrane absorber).
- Refine the process economics based on the laboratory test data.
- Finalize testing plan for slip-stream, bench-scale testing.
- Conduct slip-stream field test of the bench-scale skid at Midwest Generation power plant beginning summer 2013.

Final test results will not be available until after the September 2013 project completion date.

available reports/technical papers/presentations

Zhou, J., et al., “Hybrid Membrane/Absorption Process for Post-Combustion CO₂ Capture (Membrane Contactor),” presented at the 2012 NETL CO₂ Capture Technology Meeting, Pittsburgh, Pennsylvania, July 2012. <http://www.netl.doe.gov/File%20Library/events/2012/co2%20capture%20meeting/J-Zhou-GTI-Hybrid-Membrane-Process.pdf>.

Li, S., et al., “Hybrid Membrane/Absorption Process for Post-Combustion CO₂ Capture (Membrane Contactor),” presented at the 2011 NETL CO₂ Capture Technology Meeting, Pittsburgh, Pennsylvania, August 2011. <http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/22Aug11-Li-GTI-Hybrid-Membrane-Absorption-Process.pdf>.

Zhou, J., et al., “Hybrid Membrane/Absorption Process for Post-Combustion CO₂ Capture (Membrane Contactor),” presented at the 2010 NETL CO₂ Capture Technology Meeting, Pittsburgh, Pennsylvania, September 2010. <http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/Shaojun-Zhou---Gas-Technology-Institute.pdf>.

CO₂ CAPTURE BY SUB-AMBIENT MEMBRANE OPERATION

B-401

primary project goals

American Air Liquide, Inc. (AL) set out to develop a post-combustion carbon dioxide (CO₂) capture process based on sub-ambient temperature operation (< -10°C) of a hollow-fiber membrane. The project included bench-scale testing to demonstrate the membrane's high selectivity/permeance, mechanical integrity, and long-term operability at low temperatures.

technical goals

- Demonstrate membrane performance (high selectivity and permeance) operating at sub-ambient temperature with a commercial-scale membrane module in a bench-scale test skid. The bench-scale test work was to be mainly conducted at AL's Delaware Research & Technology Center.
- Verify mechanical integrity of commercial-scale membrane module structural components at sub-ambient temperatures.
- Demonstrate the long-term operability of the sub-ambient temperature membrane skid.
- Evaluate the effect of possible contaminants (e.g., sulfur dioxide [SO₂], nitrogen oxides [NO_x]) on membrane performance through laboratory testing.
- Refine process simulation for integrated process with flue gas conditioning and CO₂ liquefier.
- Design process flow diagram of slip-stream-scale unit for possible field test.

technical content

AL set out to develop a CO₂ capture process based on sub-ambient temperature operation of a hollow-fiber membrane. For most membrane materials, permeability decreases and selectivity increases with a decrease in operating temperature. However, laboratory measurements of the AL membranes operated at temperatures below -20°C show two to four times higher CO₂/nitrogen (N₂) selectivity with minimal loss of CO₂ permeance compared to ambient temperature values.

Figure 1 presents a simplified block diagram of the cold membrane process. A highly selective cold membrane provides pre-concentration of CO₂ prior to CO₂ partial condensation in a liquefaction unit. The cryogenic heat exchanger system provides energy integration between the membrane and CO₂ liquefaction system.

technology maturity:

Laboratory/Bench-Scale

project focus:

Low-Temperature Membrane

participant:

American Air Liquide

project number:

FE0004278

NETL project manager:

Andrew O'Palko

andrew.opalko@netl.doe.gov

principal investigator:

Sudhir Kulkarni

American Air Liquide Inc.

sudhir.kulkarni@airliquide.com

partners:

Air Liquide Advanced

Technologies US – MEDAL

Air Liquide Engineering S.A.

performance period:

10/1/10 – 11/30/12

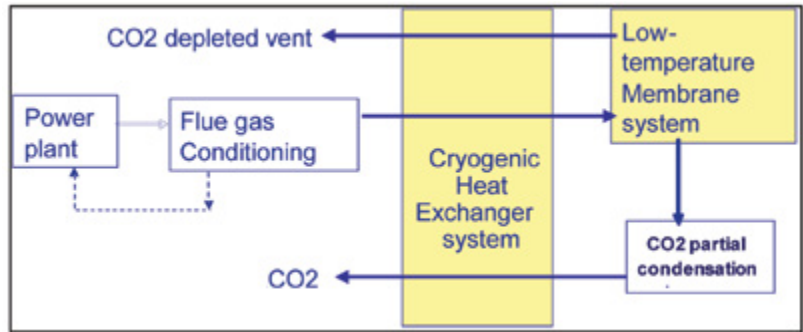


Figure 1: Block Diagram of Cold Membrane Process

Figure 2 shows a schematic diagram of the membrane-based CO₂ compression and purification unit (CPU) process. The process lines in Figure 2 are color-coded (black for ambient temperature; dark blue for approximately -30°C; and light blue for approximately -50°C). The pre-treated flue gas is compressed to approximately 230 pounds per square inch (psi) (16 bar). The heat of compression is captured in boiler feed water, raising its temperature to approximately 147°C. The compressed flue gas is then dried in a dehydration unit to prevent water condensation when the stream is cooled in the economizing heat exchanger to approximately -40°C. The cooled, dried, compressed flue gas is then fed to the membrane to produce a residue stream with approximately 1.6 percent CO₂ at approximately 215 psi (15 bar) and a permeate stream with approximately 60 to 70 percent CO₂ at approximately 17 psi (1 to 2 bar). After the residue is sent through one pass of the heat exchanger, further cooling and energy recovery is done via a series of turbo-expanders with the resulting cold residue stream at -57°C sent through the heat exchanger. Finally, the excess pressure energy remaining in the warmed residue is partly recovered in a warm turbo-expander before venting. A fraction of the vent gas is used to regenerate the drier. The permeate stream is re-compressed, cooled in the heat exchanger, and undergoes phase separation in the cryo-phase separator. Liquid CO₂ is pumped from the separator to provide a sequestration-ready product CO₂ at approximately 870 psi (60 bar), or greater, and 20°C. The overhead from the cryo-phase separator is warmed through the heat exchanger and then undergoes energy recovery in a turbo-expander. This stream is mixed with the incoming dried flue gas, which raises the mixed feed concentration entering the membrane to 18 percent CO₂. The higher CO₂ content improves the membrane separation.

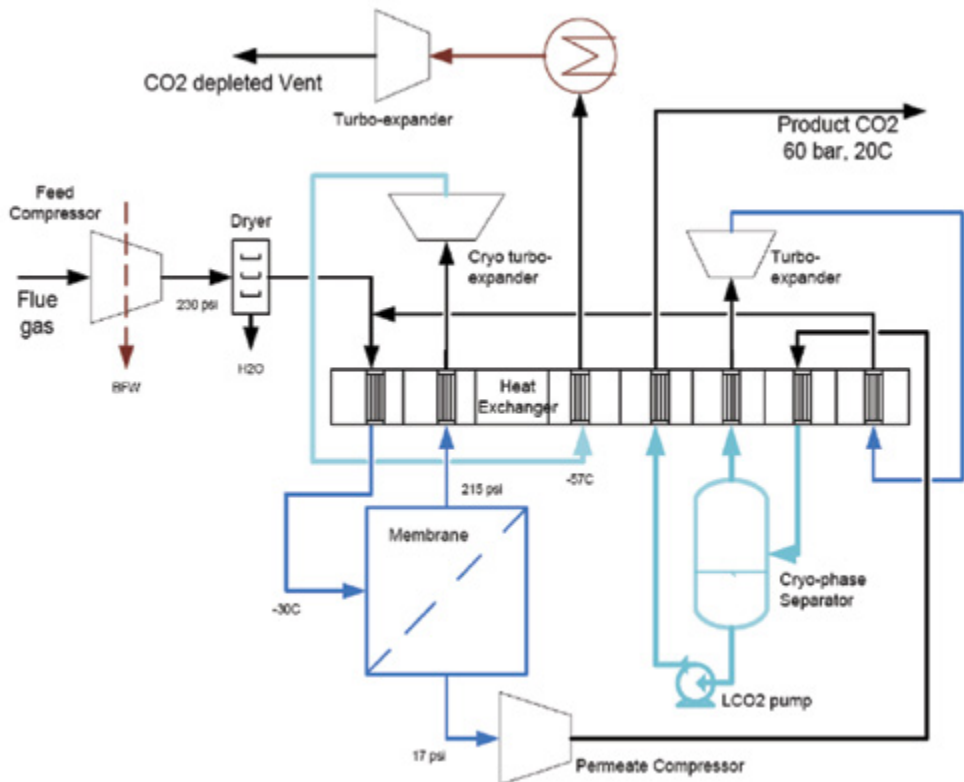


Figure 2: Schematic Diagram of Cold Membrane Process

TABLE 1: MEMBRANE PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer	-		
Materials of Fabrication for Support Layer	-	(if applicable)	
Nominal Thickness of Selective Layer	μm		
Membrane Geometry	-	Hollow fiber	
Max Trans-Membrane Pressure	bar	24	
Hours Tested Without Significant Degradation	-	8,000	
Manufacturing Cost for Membrane Material	\$/m ²		
Membrane Performance			
Temperature	°C	-30 to -45	
CO ₂ Pressure Normalized Flux	GPU or equivalent	>90	> 90
CO ₂ /H ₂ O Selectivity	-		
CO ₂ /N ₂ Selectivity	-	80 at proposed conditions	90
CO ₂ /SO ₂ Selectivity	-		
Type of Measurement	-	Mixed gas	
Proposed Module Design			
Flow Arrangement	-	Counter-current hollow fiber	
Packing Density	m ² /m ³	>1,000	
Shell-Side Fluid	-	Permeate	
Flue Gas Flowrate	kg/hr	150 - 550	
CO ₂ Recovery, Purity, and Pressure	% / % / bar	97+%	
Pressure Drops Shell/Tube Side	bar	≈ 0.1 bar (feed to residue)	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$		

Definitions:

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

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

GPU – Gas Permeation Unit, which is equivalent to 10⁻⁶ cm³ (1 atm, 0°C)/cm²/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm³ (1 atm, 0°C)/cm²/s with pressures measured in cmHg. Note: 1 GPU = 3.3464×10⁻⁶ kg mol/m²-s-kPa [SI units].

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

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

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

Shell-Side Fluid – Either the permeate (CO₂-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO₂ in CO₂-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Nominally based on solution-diffusion.

Contaminant Resistance – Expected to be resistant to acidic components based on experience to date.

Flue Gas Pretreatment Requirements – Particulate removal and acid component removal to meet compressor specifications, dehydration to meet cold box specifications, mercury (Hg) removal to meet heat exchanger specification.

Membrane Replacement Requirements – Membrane productivity decline was too small to be quantified in bench-scale test with synthetic gases.

Waste Streams Generated – Acidic water.

technology advantages

- Sub-ambient operation improves membrane performance.
- Process design provides partial recovery of the flue gas compression energy.
- Process design provides an economic method of cooling the flue gas feed to the required sub-ambient temperature for optimal membrane operation without external refrigeration.
- The process design can be combined with a novel scheme for contaminant (SO₂, NO_x) removal.

R&D challenges

- Sub-ambient membrane operation requires development of suitable membrane module materials with adequate permeance and selectivity in a commercial membrane module.
- Long-term membrane module performance stability.
- Integration of sub-ambient membrane process, including energy integration with the CPU, as well as energy integration with the power plant, such as compression and turbo-expansion schemes, heat economizers, and energy conservation.
- Flue gas contaminant-specific challenges, including acid gas (NO_x, SO₂) separation, compressor materials of construction, particulate removal, Hg removal, and water management.

results to date/accomplishments

- Conducted closed-loop, bench-scale testing of 6- and 12-inch diameter membrane bundles (equivalent to 2 to 2.5 ton CO₂ per day, or 0.1 MW) at the proposed sub-ambient temperature conditions using synthetic flue gas (CO₂ and N₂).
 - The majority of the testing was run at 200 psi, -45°C, and 18 percent CO₂ feed. Parametric testing was conducted over a broad range of feed conditions: temperature (-25 to -45°C), pressure (160 to 200 pounds per square inch gauge [psig]), and CO₂ feed concentration (18 to 12%).
 - Stability of membrane performance at sub-ambient temperature was successfully demonstrated over eight months; there were no signs of mechanical degradation.
 - The membrane performance was approximately 10 percent lower CO₂/N₂ selectivity and 15 percent higher CO₂ permeance than the estimate based on previous laboratory testing. However, this results in a favorable trade-off between capital and operating cost: a 7 percent increase in specific energy of capture and 40 percent decrease in membrane surface area.
 - Parametric tests indicated that the membrane performance would be best at the coldest temperature and highest feed pressure that can be achieved.
- Conducted laboratory testing of the membrane using synthetic flue gas (CO₂ and N₂) that contains low concentrations (100 parts per million [ppm]) of SO₂, NO₂, and NO using an existing AL cold-test facility.
 - Both SO₂ and NO₂ are more permeable than CO₂. This implies that these contaminants will be efficiently removed with CO₂ into the membrane permeate. NO permeance is intermediate between CO₂ and N₂; hence, NO concentration is expected to be unchanged by the membrane.

- Completed a techno-economic study of the proposed sub-ambient temperature membrane process.
 - The specific energy estimates for CO₂ capture by this process ranges from 216 to 242 kWh per ton CO₂ captured.
 - The conceptual membrane design basis for a 500-MW net coal power plant would include 140 duplex bundle housings containing 36-inch diameter x 40-inch long membrane bundles.
 - The energy capture estimate was coupled with capital cost estimates to calculate the levelized cost of electricity (LCOE) for 90 percent CO₂ capture from an air-fired, 550-MW net coal power plant. This analysis indicates increases in LCOE between 48 and 53 percent.
- Completed a study to determine requirements for conducting future bench-scale testing of the process using actual flue gas.

[next steps](#)

The project ended on November 30, 2012.

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

“CO₂ Capture By Sub-Ambient Membrane Operation,” Final Report, January 2013.

Kulkarni, S., et al., “CO₂ Capture By Sub-Ambient Membrane Operation,” presented at the 2012 NETL CO₂ Capture Technology Meeting, Pittsburgh, Pennsylvania, July 2012. <http://www.netl.doe.gov/publications/proceedings/12/co2capture/presentations/1-Monday/S%20Kulkarni-AAL-Sub-ambient%20Membrane.pdf>.

Sanders, E., et al., “CO₂ Capture By Sub-Ambient Membrane Operation,” presented at the 2011 NETL CO₂ Capture Technology Meeting, Pittsburgh, Pennsylvania, August 2011. <http://www.netl.doe.gov/publications/proceedings/11/co2capture/presentations/1-Monday/22Aug11-Sanders-AirLiquide-SubAmbient%20Membrane%20Operation.pdf>.

Kulkarni, S., et al., “CO₂ Capture By Sub-Ambient Membrane Operation,” presented at the 2010 NETL CO₂ Capture Technology Meeting, Pittsburgh, Pennsylvania, September 2010. <http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/Sudhir-Kulkarni---American-Air-Liquide--DRTC-.pdf>.

DEVELOPMENT OF DENSE CERAMIC MEMBRANES FOR HYDROGEN SEPARATION

B-406

primary project goals

Argonne National Laboratory is developing a dense ceramic or cermet (ceramic/metallic composite) membrane for separating hydrogen (H_2) from synthesis gas (syngas) generated during coal gasification, resulting in a high concentration carbon dioxide (CO_2) stream.

technical goals

Develop a membrane that is:

- Chemically stable in the presence of steam, carbon monoxide (CO), CO_2 , methane (CH_4), hydrogen sulfide (H_2S), ammonia (NH_3), mercury (Hg), and halides.
- Mechanically stable under high pressures, high temperatures, and temperature cycles.
- Capable of providing industrially significant fluxes at desired levels of H_2 selectivity.

technical content

During coal gasification, large volumes of H_2 and CO_2 are produced. Dense ceramic and cermet membranes are being developed for use with coal gasification process to separate H_2 from CO_2 . These membranes must be capable of achieving a high flux and selectivity in order to reduce the surface area required to process the high volumes of gas produced. Reducing a membrane thickness can increase H_2 flux; however, to maintain selectivity, the membrane must remain defect free. Dense ceramic and cermet membranes are capable of providing reduced thickness while avoiding the formation of defects.

High density membranes are achieved by sintering the cermet at high temperatures. Sintering aids have been developed that prevent delamination of the cermet from the porous ceramic substrate. Figure 1 shows a cermet membrane with cobalt nitrate as the sintering aid on a TZ-3Y (zirconium dioxide [ZrO_2] partially stabilized with yttrium oxide [Y_2O_3]) substrate.

The chemical stability of the membranes is also important for their use in the corrosive syngas stream produced from coal gasification. Hydrogen sulfide is a particularly corrosive contaminant to membranes containing palladium (Pd). When H_2S reacts with Pd, palladium sulfide (Pd_4S) forms on the surface of the membrane, which greatly reduces H_2 permeation through the membrane. Therefore, it is important to identify the temperatures and pressures at

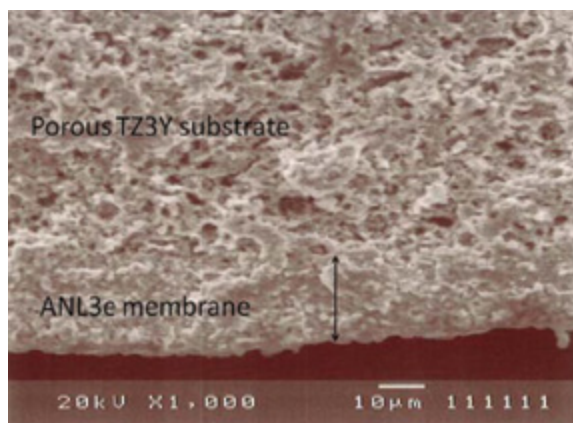


Figure 1: Cross-Sectional View of ANL-3e Thin Film Membrane Sintered at 1,160°C on Porous TZ-3Y Substrate

technology maturity:

Laboratory and Bench-Scale,
Using Simulated Flue Gas

project focus:

Dense High Temperature
Ceramic Membranes

participant:

Argonne National Laboratory

project number:

FWP-49601

NETL project manager:

Richard Dunst
richard.dunst@netl.doe.gov

principal investigator:

U. (Balu) Balachandran,
Argonne National Laboratory
balu@anl.gov

partners:

N/A

performance period:

3/31/98 – 9/30/11

which the membrane is stable. The Pd-containing cermet being developed are stable between about 430 and 680°C (700 K and 950 K) in stable a gas containing 73 percent H₂ with between approximately 60 to 400 parts per million (ppm) H₂S. When the gas contains only 10 percent H₂, the membrane is stable for H₂S concentrations between approximately 8 to 50 ppm. Thin cermet membranes have been tested at 440°C with syngas stream at ≈184 psig.

TABLE 1: ANL MEMBRANE PARAMETER

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer		Pd/TZ-3Y cermet	
Materials of Fabrication for Support Layer		Alumina/Zirconia	
Nominal Thickness of Selective Layer	μm	15	5
Membrane Geometry		Disk/short tube	Long tubes
Maximum Trans-Membrane Pressure	bar	12.2	20.4
Hours Tested Without Significant Degradation		1200	1200
Manufacturing Cost for Membrane Material	\$/m ²		
Membrane Performance			
Temperature	°C	400-600	250-500
H ₂ Pressure Normalized Flux	GPU or equivalent	160 scfh/ft ²	300 schf/ft ²
H ₂ /H ₂ O Selectivity	-		
H ₂ /CO ₂ Selectivity	-	150	10,000
H ₂ /H ₂ S Selectivity	-		
Sulfur Tolerance	ppm	50	50
Type of Measurement	-	Mixed gas	Mixed gas
Proposed Module Design			
Flow Arrangement	-		
Packing Density	m ² /m ³		
Shell-Side Fluid	-	Retentate	
Syngas Gas Flowrate	kg/hr		
CO ₂ Recovery, Purity, and Pressure	% / % / bar	>99%, 98%, 12	
H ₂ Recovery, Purity, and Pressure	% / % / bar	96%, 98%, 1	
Pressure Drops Shell/Tube Side	bar	11	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$		

Definitions:

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

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

GPU – Gas Permeation Unit, which is equivalent to 10⁻⁶ cm³ (1 atm, 0°C)/cm²/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm³ (1 atm, 0°C)/cm²/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10⁻⁶ kg mol/m²-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

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

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

Shell-Side Fluid – Either the permeate (H_2 -rich) or retentate (syngas) stream.

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

Other Parameter Descriptions:

Description of Membrane Permeation Mechanism – In cermet hydrogen transport is in the form of atomic hydrogen (follows Sievert's Law). In mixed-conductor membranes, the transport is in the form of protons.

Contaminant Resistance – The membrane is tolerant to H_2S between 430 and 680°C in gas containing 73 percent H_2 and approximately 60 to 400 ppm H_2S .

Syngas Pretreatment Requirements – Remove H_2S below 50 ppm level.

Membrane Replacement Requirements – Our membranes are modular in nature which allows individual membranes to be replaced without shutting down the entire operation.

Waste Streams Generated – Our membrane generates high purity H_2 and sequestration-ready CO_2 . Our membrane doesn't generate waste streams.

Proposed Module Design – Module design not proposed in this project.

technology advantages

- Ceramic phase of the cermet membrane provides 3-D mechanical support that can blunt or deflect crack propagation through the metallic phase.
- Dense ceramic membranes operate at high pressures and temperatures.
- Dense ceramic membranes have no interconnected porosity; therefore, selectivity for H_2 is high.
- Dense ceramic membranes remove H_2 from H_2 and CO_2 mixtures, resulting in a concentrated stream of CO_2 that is near sequestration-ready.

R&D challenges

- Reducing membrane thickness increases flux, but can lead to pin-holes in the membrane, which reduces H_2 selectivity. Therefore, reducing defects in thinner membrane is desired.
- Developing low-temperature sintering methods to avoid loss of Pd to evaporation during sintering at high temperatures.
- Determining stability restrictions in order to limit the reaction of Pd with H_2S , which forms Pd_4S and reduces H_2 flux.
- Understanding chemical stability in the presence of NH_3 , Hg, and halides.
- Increasing the resistance to the effects of particulates impacting the membrane surface.
- Developing leak-proof metal/ceramic seals at high pressures under thermal cycling.
- Reducing the cost of the membrane by employing non-precious metals/alloys to form the cermet membrane.

results to date/accomplishments

- Developed dense, cermet membranes that non-galvanically separate H₂ from mixed-gas streams.
- Measured an H₂ flux of 52 cm³/min-cm² at 900°C on an 18-μm thick membrane composed of Pd and TZ-3Y using a feed of 1 atm H₂.
- Achieved H₂ permeation exceeding 150 cm³/min (0.32 scfh) measured in short, 8-cm long tubular membranes at 600°C and ambient pressures.
- Demonstrated durability of membrane during cycling in temperature and H₂ concentration.
- Maintained flux stability for 1,200 hours in feed stream with 400 ppm H₂S at 900°C.
- Achieved regeneration of sulfur-poisoned, cermet membrane.
- Long-term (≈four months) flux measurements showed that cermet membranes are stable in NETL Test Protocol test 1 gas mixtures.
- Sintering technique developed to densify membranes and improve selectivity.
- Measured a highest hydrogen recovery of ≈96 percent at 625°C using 90 percent H₂/bal. He mixture as feed at 186 psig and argon as sweep gas at 18 psig.
- Measured hydrogen flux of ≈80 cm³/min-cm² (≈160 scfh/ft²) at 440°C with simulated syngas at 186 psig as feed gas.

next steps

Project completed September 30, 2011.

available reports/technical papers/presentations

Balachandran, U., et al., “Development of Dense Membranes for Hydrogen Purification from Coal Gasification Stream,” presented at the Hydrogen + Fuel Cell 2011 Conference (HFC 2011), Vancouver, Canada, May 15-18, 2011

Balachandran, U., et al., “Hydrogen Separation Membranes Annual Report for FY₂₀₁₀,” publication date January 30, 2011, <http://www.ipd.anl.gov/anlpubs/2011/03/69523.pdf>

Zuo, C., et al., “Composite Ni-Ba(Zr_{0.1}Ce_{0.7}Y_{0.2})O₃ Membrane for Hydrogen Separation,” J. Power Sources, 159(2), 1291 (2006)

Balachandran, U., et al., “Development of Cermet Membranes for Hydrogen Separation from Coal Gasification Stream,” presented at 26th Annual Pittsburgh Coal Conference, Pittsburgh, Pennsylvania, September 2009.

CO₂ CAPTURE MEMBRANE PROCESS FOR POWER PLANT FLUE GAS

B-410

primary project goals

Research Triangle Institute (RTI) set out to develop an advanced hollow-fiber, polymeric membrane-based process that can be cost-effectively retrofitted into current pulverized coal (PC)-fired power plants to capture at least 90 percent of the carbon dioxide (CO₂) from the plant's flue gas.

technical goals

- Develop new fluorinated polymers as membrane materials that have superior CO₂ separation properties compared to conventional and competitive membrane platforms. A minimum selectivity of 30 for CO₂ over nitrogen (N₂) and CO₂ permeance in excess of 300 gas permeance unit (GPU) are targeted. Fluorinated polymers are a promising material platform because they exhibit excellent chemical stability to moisture, sulfur dioxide (SO₂), and nitrogen oxide (NO_x) contaminants present in flue gas.
- Develop next-generation polycarbonate hollow-fiber membranes and membrane modules with higher CO₂ permeance than current commercial polycarbonate membranes.
- Develop and fabricate improved membrane hollow fibers and module designs to handle large flue gas flow rates and high CO₂ permeate flow rates with minimal pressure drop.
- Identify and develop CO₂ capture membrane process design and integration strategies suitable for retrofit installation.

technical content

Project research efforts include development of membrane materials and membrane hollow fibers, membrane module design and fabrication, and process design.

RTI pursued the development of two membrane material platforms. As a near-term membrane platform solution, RTI worked with Generon to develop next-generation, high-flux polycarbonate hollow-fiber membranes and membrane modules with higher CO₂ permeance than current-generation, commercial polycarbonate membranes. Hollow-fiber membranes made from the high-flux polycarbonate have been successfully developed, scaled up, and fabricated into module separation devices. Laboratory-scale membrane modules have been studied with simulated flue gas mixtures with and without flue gas contaminants.

For a longer-term membrane platform solution, RTI worked with Arkema to develop improved CO₂ capture membrane materials based on the polymer chemistry of polyvinylidene fluoride [PVDF], the chemical structure of which is shown in Figure 1 and comprises the [CH₂-CF₂]_n repeat unit. PVDF is well suited for contact with flue gas, possessing high chemical resistance to acids and oxidants, specific affinity for CO₂ for high CO₂ solubility, and high thermal stability (T_d ≈ 340°C). PVDF also features excellent physical and mechanical properties, durability, and longevity suited to the fiber

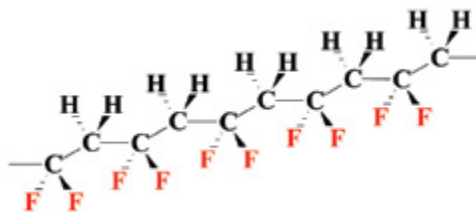


Figure 1: Chemical Structure of PVDF

technology maturity:

Bench-Scale, Using Simulated Flue Gas

project focus:

Hollow-Fiber, Polymeric Membrane

participant:

Research Triangle Institute

project number:

NT0005313

NETL project manager:

Andrew O'Palko
andrew.opalko@netl.doe.gov

principal investigator:

Lora Toy
Research Triangle Institute
ltoy@rti.org

partners:

Arkema
Generon IGS

performance period:

10/1/08 – 9/30/11

extrusion process used to fabricate membrane hollow fibers. However, conventional PVDF is a homopolymer that is semicrystalline and has CO_2/N_2 selectivity of ≈ 23 and low CO_2 permeance of ≈ 10 GPU. Arkema has pursued synthesizing and developing advanced, PVDF based copolymers possessing improved CO_2 permeance and selectivity.

In this project, the membrane under development was in the form of hollow fibers that are packaged into compact, high surface area-to-volume module devices. Multiple modules were utilized in a given CO_2 capture membrane system for power plant applications due to the large quantity of flue gas to be processed. The modularity of the membrane separation devices allows for easy adaptation to different levels of CO_2 removal desired by simply adding or subtracting the number of membrane modules used. Figure 2 shows a cross-section of a hollow-fiber membrane module. A single-membrane module consists of hundreds of thousands to more than a million micron-sized diameter hollow fibers bundled together. A couple of individual membrane hollow fibers, a small bundle loop of fibers, and modules of different sizes are shown in Figure 3. As flue gas flows through the membrane fibers, the feed is split into two streams. A permeate stream enriched in CO_2 is produced by the preferential transport of CO_2 across the fiber walls. The remaining flue gas (non-permeate) flows out of the membrane module as a CO_2 -depleted retentate stream that is sent to the plant stack for discharge to the atmosphere.

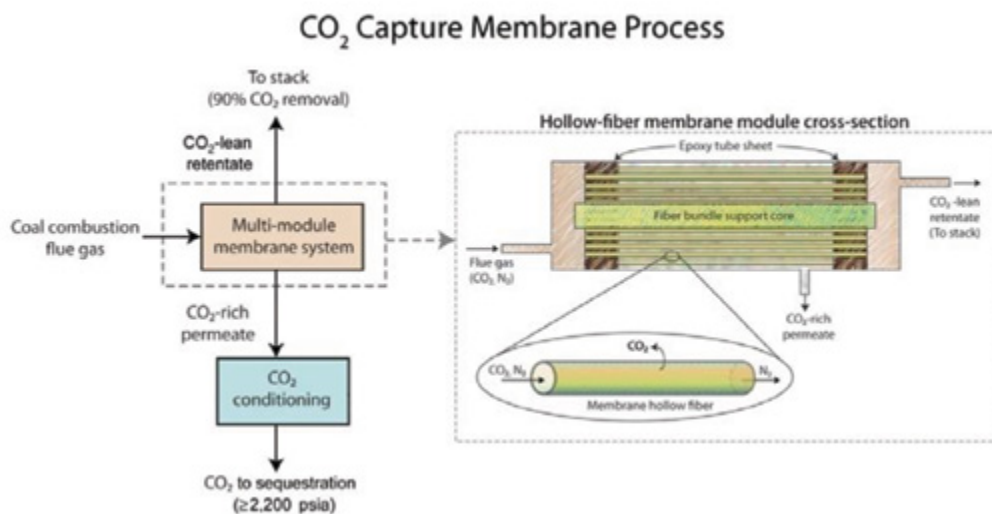


Figure 2: Cross-Section of a Hollow-Fiber Membrane Module

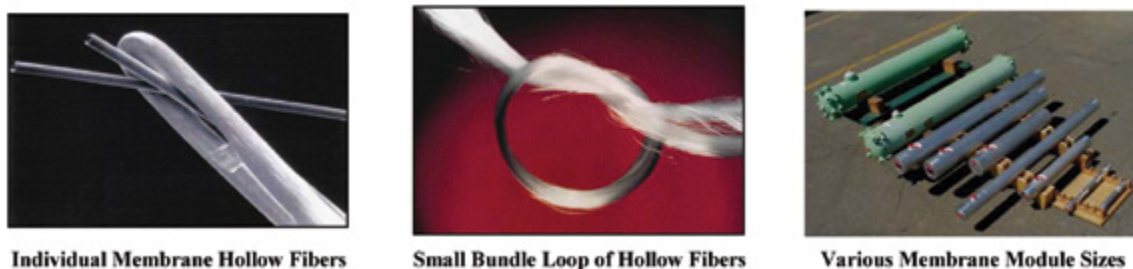


Figure 3: Membrane Hollow Fibers

Process simulations for a single-stage membrane process were conducted to determine the sensitivity of CO_2 removal performance and permeate CO_2 purity to different parameters, including membrane flux (permeance), membrane selectivity, membrane fiber dimensions, and membrane pressure driving force. An important outcome of this sensitivity analysis was the understanding that membrane property development should focus on improving both permeance and selectivity together rather than individually.

To achieve high levels of CO_2 capture and purity, RTI developed the three-stage membrane process shown in Figure 4, where the membrane stages are represented by M1, M2, and M3. The flue gas is compressed and fed to the first membrane stage M1. To obtain a net 90 percent removal of CO_2 from the stream ultimately sent to the stack, the CO_2 -depleted retentate exiting M1 is fed to M3, which is operated with a permeate-side air sweep to enhance removal of more CO_2 . Before being released into the stack, the pressurized M3 retentate is sent to an expander to recover the energy associated with high pressure. The resulting M3 permeate is a CO_2 enriched air stream that is sent back to the boiler. In the second membrane stage M2, the CO_2 captured in the M1

permeate is further concentrated. The resulting CO₂-rich M2 permeate is then compressed and dehydrated to produce the final, sequestration-ready CO₂ capture stream. The M2 retentate is recycled and fed back to M1. The numbers shown in Figure 4 are for a 550-MW coal-fired power plant to achieve 90 percent CO₂ capture and 95 percent CO₂ purity in the capture stream using the high-flux polycarbonate membrane (400 GPU; CO₂/N₂ = 35).

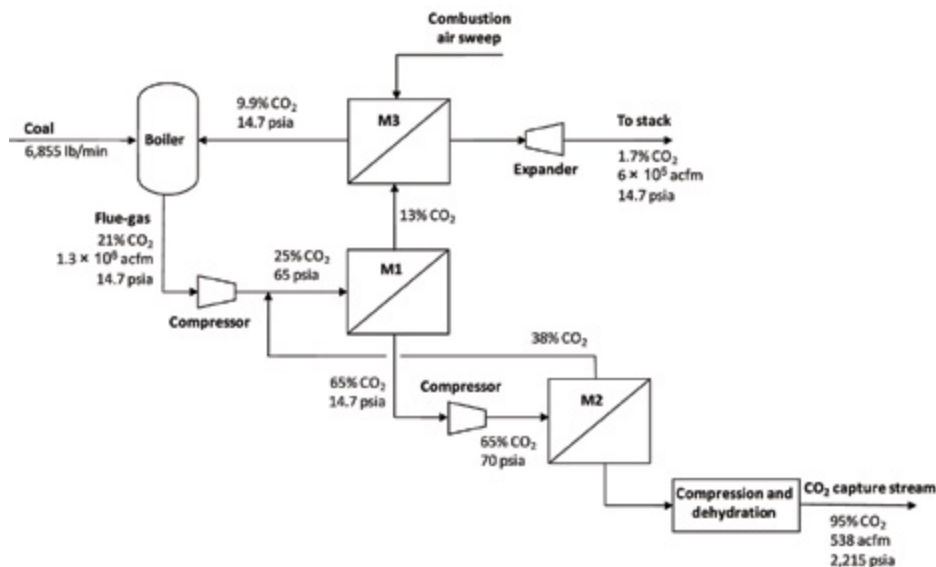


Figure 4: RTI's Three-Stage CO₂ Capture Membrane Process Design

TABLE 1: MEMBRANE PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer	-	Polycarbonate-based and Vinylidene fluoride-based	
Materials of Fabrication for Support Layer	-	N/A	
Nominal Thickness of Selective Layer	μm	0.05	0.05
Membrane Geometry	-	Hollow-fiber	Hollow-fiber
Max Trans-Membrane Pressure	bar	15 (Not tested higher)	15
Hours Tested Without Significant Degradation	-	165	300 (coal)
Manufacturing Cost for Membrane Material	\$/m ²	32	8
Membrane Performance			
Temperature	°C	25 – 30	50
CO ₂ Pressure Normalized Flux	GPU or equivalent	400	1,000
CO ₂ /H ₂ O Selectivity	-	0.04	0.01 – 0.02
CO ₂ /N ₂ Selectivity	-	35	50
CO ₂ /SO ₂ Selectivity	-	≈1	<0.5 or >2
Type of Measurement	-	Ideal and mixed	Ideal and mixed
Proposed Module Design			
Flow Arrangement	-	Countercurrent	
Packing Density	m ² /m ³	9,000	
Shell-Side Fluid	-	Permeate	
Flue Gas Flowrate	kg/hr	(Unknown at this stage)	
CO ₂ Recovery, Purity, and Pressure	% / % / bar	90%, 95+%, 1 bar	

TABLE 1: MEMBRANE PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Pressure Drops Shell/Tube Side	bar		<0.1
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$		(Unknown at this stage)

Definitions:

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

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

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

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

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

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

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

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

Other Parameter Descriptions:

Membrane Permeation Mechanism – Gas permeation in the high-flux polycarbonate and PVDF-based membrane platforms occurs due to a partial pressure driving force across the membrane. The specific permeation mechanism obeyed is the solution-diffusion model for gas transport in nonporous polymers. According to this model, preferential permeation of certain gas species occurs because they are more soluble in the polymer membrane, have a higher diffusion coefficient in the polymer membrane, or both. In this project, the preferentially permeated species CO_2 has both greater diffusivity and greater solubility than N_2 in the polycarbonate- and PVDF-based membranes.

Contaminant Resistance – Membrane resistance to contaminant species (NO_x , SO_2 , moisture) found in flue gas was investigated in continuous, seven-day, bench-scale separation performance stability tests with contaminant-containing CO_2/N_2 mixtures. The permeance of the high-flux polycarbonate membrane showed some sensitivity to contaminants such as NO_x , but its selectivity was stable. The new PVDF-based membrane material platform, because of its intrinsically high-chemical resistance, exhibited excellent permeability (permeance) and selectivity stability in the contaminant tests.

Flue Gas Pretreatment Requirements – Before being fed to the membrane system, the flue gas from the plant stack must be conditioned to remove solid particulates and any condensed/entrained liquids (essentially liquid water).

Membrane Replacement Requirements – Based on seven-day, bench-scale contaminant resistance testing results, replacement cycle for high-flux polycarbonate membranes is anticipated to be roughly every five years. In the presence of flue-gas contaminants, the high-flux polycarbonate membrane has shown gradual permeance loss without loss in selectivity in continuous, seven-day testing. For PVDF-based membranes, the replacement cycle is anticipated to be every 10 years because of the excellent chemical and separation performance stability exhibited by them in the presence of flue-gas contaminants in seven-day tests. Much longer-term contaminant exposure testing of these membranes to real coal-derived flue gas, however, is recommended to confirm/refine the above membrane replacement requirements.

Waste Streams Generated – Because the membrane permeates and concentrates water into the CO₂ capture stream, a liquid water stream is recovered by the membrane process during compression of the capture stream to sequestration pressure. A water condensate stream is also produced upstream of membrane stages M1 and M2 because of compression of their feed gas streams, followed by cooling of this compressed gas with cooling water to the optimum membrane operating temperature. The quality of these liquid water streams is not known and will need to be determined.

technology advantages

Membrane-based processes have the potential to provide PC-fired power plants with a cost-effective technology option for CO₂ capture. They are inherently energy-efficient because the membrane enables passive separation of gases. Their compact footprint and modular nature allows for easy installation into an existing PC-fired plant, and, with no moving parts, they are simple to operate and maintain. In addition, the hollow fiber membrane approach taken in this project is particularly well suited for high-volume applications such as the large flue gas volumes that must be handled in post-combustion carbon capture. Hollow-fiber modules have much higher membrane packing density and lower cost-per-membrane area than other module types. The hollow-fiber membrane tubes are economically produced on a commercial scale by using existing fiber manufacturing equipment technology.

R&D challenges

Flue gas properties, such as low CO₂ concentration of 13 to 15 percent, low flue gas pressure of 1 atm, large flue gas volumes, and the presence of moisture and contaminants (sulfur oxides [SO_x], NO_x, and particulate matter), can pose certain challenges for a conventional membrane separation process. These technology challenges are being addressed in this project through the development of new membrane materials with improved CO₂ separation properties and chemical resistance, improved membrane module design and engineering, and novel process design and integration strategies.

results to date/accomplishments

- Development and scale-up of Generon next-generation, high-flux polycarbonate membrane hollow fibers with up to four times higher CO₂ flux (410 GPU) than that of Generon standard polycarbonate membrane fibers.
 - CO₂/N₂ selectivity of high-flux polycarbonate hollow-fiber membrane was comparable to that of standard (current-generation) polycarbonate hollow-fiber membrane. However, it was only 60 to 70 percent of its intrinsic CO₂/N₂ selectivity (35 to 37), meaning that the high-flux polycarbonate membrane properties could still be improved.
 - Fibers of high-flux polycarbonate with 25 percent larger dimensions were successfully spun as an option for managing parasitic axial pressure drops in the module.
 - High-flux polycarbonate membrane would be best operated at temperatures below room temperature to benefit from substantial increase in CO₂/N₂ selectivity without much decrease in CO₂ permeance due to its weak temperature dependence.
 - High-flux polycarbonate membrane displayed some sensitivity to flue-gas contaminants (NO_x and SO₂), which led to a permeance decline but had minimal to no effect on CO₂/N₂ selectivity. This observed sensitivity did not seem to degrade the membrane as it recovered much of its original properties when the contaminants were removed. In practice, therefore, feed pretreatment should be considered for this membrane.
- Successful formation of Generon high-flux polycarbonate membrane fibers into lab-scale modules and larger prototype (2,200 ft²) modules.
- Development and synthesis of novel Arkema VDF-based copolymers with improved CO₂ permeance and improved CO₂/N₂ selectivity.
 - Copolymerization of a bulky, low-dipole Comonomer A into the VDF chain backbone can increase gas permeability by disrupting chain packing density and crystallinity in the polymer matrix.
 - VDF-co-A copolymer family was developed with up to 17 to 18 times higher CO₂ permeability than the base PVDF homopolymer, while maintaining the CO₂/N₂ selectivity of 24 of the base PVDF.
 - Copolymerization of a bulky, high-dipole Comonomer B into the VDF chain backbone can increase CO₂/N₂ selectivity by enhancing the CO₂ affinity of the polymer while also improving gas permeability relative to the base PVDF homopolymer.

- VDF-co-B copolymer family was developed with 2.5 to 3 times higher CO₂/N₂ selectivity and six times higher CO₂ permeability than base PVDF homopolymer.
- Strong temperature dependence of CO₂ permeance in VDF-based polymers could be exploited as a key process variable for increasing and optimizing CO₂ permeance to increase gas processing throughput in the capture process while maintaining reasonable CO₂ removal.
- VDF-based polymer platform demonstrated excellent stability of its gas separation properties to contaminants SO₂, NO_x, and water vapor.
- Fabrication of the first developmental hollow fibers from new Arkema VDF-based copolymer platform.
 - VDF-A.2 was down-selected for fiber development because it had among the best balance of CO₂ permeability and selectivity of the new copolymers in this fluorinated platform.
 - Synthesis of VDF-A.2 was successfully scaled up to pilot scale to prepare 200 pounds of this resin for fiber development.
 - Fiber tackiness, fiber shape stability, and solvent extraction kinetics were identified as key issues that must be addressed and managed for the VDF-based polymers.
 - Hollow-fiber cores of the VDF-based materials were successfully spun on commercial fiber-spinning equipment. Fibers had good gas flux but exhibited no gas selectivity. Development of a membrane structure with gas selectivity will require additional research and development (R&D) effort.
- Development of three-stage CO₂ capture membrane process design to achieve 90 percent CO₂ capture and 95 percent CO₂ purity.
- Completed techno-economic evaluation of three-stage CO₂ capture membrane process design based on Generon's high-flux polycarbonate hollow-fiber membrane assuming a CO₂ permeance of 400 GPU and CO₂/N₂ selectivity of 35.
 - Increase in levelized cost of electricity (LCOE) estimated for subcritical coal power plant with RTI membrane process was estimated to be ≈73 to 82 percent over that of a plant with no capture, with the LCOE increase depending strongly on compressor cost.
 - Compressor costs made up the majority of equipment costs for the process, with 64 percent of costs attributed to compressors needed for the CO₂ separation process and 10 percent to the compressor for compression/drying of the captured CO₂ product.
 - Cost of CO₂ capture was estimated to be ≈\$42/ton-CO₂.
 - The energy penalty was the biggest contributor to the LCOE.

next steps

This project ended on September 30, 2011.

available reports/technical papers/presentations

“CO₂ Capture Membrane Process for Power Plant Flue Gas,” Final Report, April 2012. <http://www.netl.doe.gov/publications/factsheets/program/05313%20Final%20Report%20April%202012.pdf>.

Toy, L., et al., “CO₂ Capture Membrane Process for Power Plant Flue Gas,” presented at the 2011 NETL CO₂ Capture Technology Meeting, Pittsburgh, Pennsylvania, August 2011. <http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/22Aug11-Toy-RTI-CO2-Capture-Membrane-Process.pdf>.

Toy, L., et al., “CO₂ Capture Membrane Process for Power Plant Flue Gas,” presented at the 2010 NETL CO₂ Capture Technology Meeting, Pittsburgh, Pennsylvania, September 2010. <http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/Lora-Toy--NT0005313.pdf>.

Toy, L., et al., “CO₂ Capture Membrane Process for Power Plant Flue Gas,” presented at the Annual NETL CO₂ Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009. <http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/5313-RTI-membrane--Toy--mar09.pdf>.

DEVELOPMENT OF BIOMIMETIC MEMBRANES FOR NEAR-ZERO PC POWER PLANT EMISSIONS

B-416

primary project goals

Carbozyme set out to develop an enzyme-based, contained liquid membrane (CLM) to extract carbon dioxide (CO₂) from coal and natural gas combustion flue gas. Carbozyme also set out to evaluate a state-of-the-art electro-dialytic (EDI) method for CO₂ capture, comparing its performance with that of the CLM.

technical goals

- Scale-up the enzyme-catalyzed, CLM permeator design (4 to 400 m²) to include multiple units organized as a skid (3×40 m²) for testing with various coal ranks and natural gas.
- Implement a pretreatment conditioner to ensure that the flue gas constituents will not adversely impact the CLM permeator.
- Validate technology to cost-effectively produce carbonic anhydrase (CA) enzymes for the CLM.
- Test and analyze three different EDI test cells: a controlled pH resin wafer, a hollow fiber fed bipolar membrane (BPM), and an ion exchange membrane-resin wafer (IEM-RW).
- Conduct a commercialization study for both the CLM and EDI technologies.

technical content

The enzyme-based CA CLM membrane process mimics the natural process for removing CO₂ from an organism. An organism's blood stream is used to transport oxygen (O₂) and CO₂ to and from its cells, respectively. CA is an enzyme in the blood that captures the CO₂ from the cells and converts it to bicarbonate (HCO₃⁻). The enzyme reverses this reaction in the lungs, allowing the CO₂ to be exhaled. Figure 1 shows the configuration for the enzyme-based CA CLM membrane process Carbozyme set out to develop. The CA CLM membrane is able to incorporate the absorption and stripping processes into a single unit. A membrane module consists of two groups of hollow fibers – one group contains the incoming CO₂ lean flue gas, and the second group contains the CO₂ rich permeate stream. The CA enzyme is contained in a thin-film liquid between the two groups of fibers. The CA helps

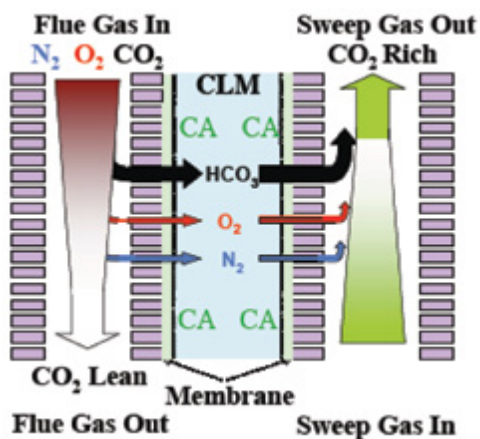


Figure 1: Configuration for Carbozyme-Developed, Enzyme-Based Carbonic Anhydrase Contained Liquid Membrane

technology maturity:

Laboratory/Bench-Scale,
Using Simulated Flue Gas

project focus:

Biomimetic Membrane

participant:

Carbozyme

project number:

FC26-07NT43084
FG26-06NT42824

NETL project manager:

José Figueroa
jose.figueroa@netl.doe.gov

principal investigator:

Michael Trachtenberg
Carbozyme, Inc.
mct@cz-na.com

partners:

Argonne National Laboratory
EERC
Electrostep
Kansas State University
Siemens
SRI
Visage Energy

performance period:

3/28/07 – 7/31/09

catalyze the CO_2 to HCO_3^- to promote permeation across the CO_2 lean membrane and reverses the process, promoting permeation across the CO_2 -rich membrane. CA is one of the fastest acting enzymes with a turnover rate of 600,000 katal (catalyzes the hydration of 600,000 molecules of CO_2 per second per molecule of CA).

Figure 2 shows a process schematic for the CA CLM. Pretreated combustion flue gas from the boiler enters the membrane. A vacuum system is used to provide the driving force across the membrane. After the CO_2 is separated from the flue gas, it goes through a knockback condenser for water removal prior to compression. The resulting product is a 95 percent pure CO_2 stream. The remaining flue gas is sent to the plant stack.

The concentrated ammoniated solution is used to capture CO_2 and hydrogen sulfide (H_2S) from synthesis gas (syngas) at high pressure. This technique reduces the size of the CO_2 stripper and operates at high pressure, reducing CO_2 compression needs; both reduce electric power consumption. AC has high net CO_2 loading, is a low-cost and readily available reagent, and requires little solvent makeup; the solubility of hydrogen (H_2), carbon monoxide (CO), and methane (CH_4) in absorber solution is extremely low.

The project, in its first phase, constructed a bench-scale batch reactor unit to test the technology at SRI's facility in California. Testing was performed to validate the concept and to determine the optimum operating conditions.

Absorber testing was conducted to first determine the solubility of shifted-gas components (H_2 , CO , nitrogen [N_2], argon [Ar]), then to determine the reactivity of CO_2 and H_2S ; mixed-gas testing was performed to determine the relative reaction kinetics.

Regenerator testing was conducted to determine CO_2 and H_2S release characteristics, as well as the relative kinetics of CO_2 and H_2S release. Optimal operating conditions derived in bench-scale testing will be used at the pilot-scale test.

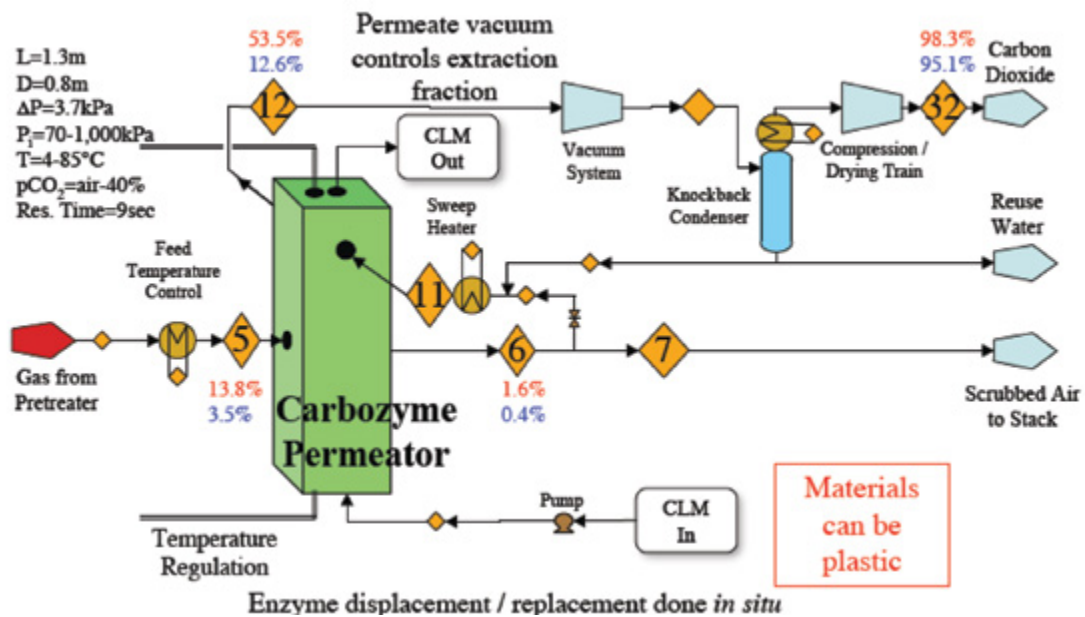


Figure 2: Process Schematic for the Carbonic Anhydrase Contained Liquid Membrane

technology advantages

B-418

- The CA enzyme catalyst does not contain any toxic chemicals or byproducts, making it more environmentally friendly than competing technologies.
- The CA enzyme catalyst has a fast CO₂ production rate with low energy requirements and boosts separation and purification due to its low nitrogen (N₂) and O₂ solubility.
- The enzyme catalyst is not vulnerable to oxidation or the formation of stable salts.
- The CA CLM system requires only minimal pumping and no heat exchangers, allowing it to consume 30 to 50 percent less energy compared to competing technologies.
- The CA CLM system recycles nearly all of its water and a portion of its waste heat.
- The modular design of the membrane makes it easy to manufacture, install, and scale up.

R&D challenges

- The cost of the purified CA enzyme remains high and production costs will need to be reduced in order to be considered economically viable.
- Early immobilization of the CA enzyme needs to be addressed.
- Sulfur dioxide (SO₂) acidification of the carbonate carrier fluid needs to be addressed via flue gas pretreatment.
- Ionized mercury in the flue gas could reduce enzyme activity.

results to date/accomplishments

Development progress for the CA CLM process was made in several categories, such as flue gas stream analysis and conditioning, enzyme selection, enzyme immobilization, membrane module construction, and economic analysis.

Specific accomplishments include:

- Developed an immobilized CA enzyme catalyst based on a thermophilic form of CA that can maintain a high activity at elevated temperature ($\approx 50^{\circ}\text{C}$). The enzyme was immobilized using a proprietary surface activation method using an ultrathin polyamino acid (PAA) layer that can be removed and replaced, as needed. Enzyme testing indicated up to 80 percent of initial activity was retained over a 60-day period.
- Developed a 0.5-m² bench-scale CLM permeator that combines absorption and desorption in a single house through use of dual hollow-fiber, spiral-wound, polymer membranes. In this configuration, CO₂ capture is driven by a combination of pressure, vacuum, and temperature. More than 90 percent CO₂ capture was achieved during testing.
- Developed an alternate process technology based on separate absorption/desorption modules using single hollow-fiber, spiral-wound, polymer membranes.
- Fabricated an 11-m² CLM module for scale-up testing.
- Developed and tested a flue gas pre-treatment system for the CLM process.
- Developed computer modeling for CLM process components and integrated systems.
- Developed and tested a second technology based on a resin-wafer EDI system that uses a pH shift to accomplish CO₂ absorption/desorption.

next steps

This project ended on July 31, 2009.

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

“Development of Biomimetic Membranes for Near Zero PC Power Plant Emissions,” Final Report for Project #43084, March 2011.

“Capture of CO₂ by the Carbozyme Permeator,” 8th Annual Conference on Carbon Capture and Sequestration, Pittsburgh, Pennsylvania, May 2009.

“Development of Biomimetic Membranes for Near-Zero Power Plant Emissions,” Annual NETL CO₂ Capture Technology for Existing Plants R&D meeting, Pittsburgh, Pennsylvania, March 2009.

“Membrane-based, Enzyme Facilitated, Efficient, Carbon Dioxide Capture,” 9th International Conference on Greenhouse Gas Control Technologies, Washington, DC, November 2008.

“Progress on Carbozyme’s HFCLM Permeator Technology Scale-up Project,” 7th Annual Conference on Carbon Capture and Sequestration, Pittsburgh, Pennsylvania, May 2008.

“Biomimetic Membrane for CO₂ Capture from Flue Gas,” Final Report for Project #42824, August 2007.

B-419

NOVEL DUAL FUNCTIONAL MEMBRANE FOR CONTROLLING CARBON DIOXIDE EMISSIONS FROM FOSSIL-FUELED POWER PLANTS

primary project goals

The University of New Mexico set out to develop a new, dual-functional, silica-based membrane for carbon dioxide (CO₂) emissions capture from coal-fired power plants.

technical goals

- Achieve a membrane CO₂/nitrogen (N₂) selectivity of 100 and a CO₂ permeance of 1,000 gas permeance units (GPU) or greater.
- Formulate a sol-gel composition to be used in the preparation of clear aminosilicate coatings for membrane deposition onto the siliceous support matrix.
- Setup multi-component gas separation tests for preliminary membrane performance analysis.
- Refine the sol-gel compositions for optimal membrane deposition.
- Study the influence of sulfur dioxide (SO₂), water vapor, and trace oxygen (O₂) on membrane performance.
- Optimize membrane deposition on alternative economical membrane supports.
- Conduct preliminary economic analysis of the membrane process for post-combustion CO₂ capture.
- Identify a processing window that allows reproducible preparation of an asymmetric microporous silica membrane.
- Stabilize membrane performance through a nickel (Ni)-doping approach.
- Prepare an ultra-thin silica membrane using a plasma-assisted, atomic layer deposition technique (PA-ALD).

technical content

The dual-functional, silica-based membrane is prepared by a unique sol-gel dip-coating process for depositing a microporous amino-silicate membrane on a porous tubular ceramic support. It consists of a microporous inorganic siliceous matrix,

with amine functional groups physically immobilized or covalently bonded on the membrane pore walls. Strong interactions between the permeating CO₂ molecules and the amine functional membrane

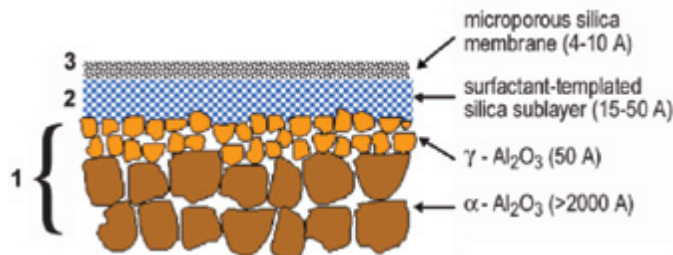


Figure 1: Cross-Section of Membrane

technology maturity:

Laboratory-Scale, with Simulated Flue Gas

project focus:

Dual Functional, Silica-Based Membrane

participant:

University of New Mexico

project number:

FG26-04NT42120

NETL project manager:

José Figueroa

jose.figueroa@netl.doe.gov

principal investigator:

C. Jeffrey Brinker

University of New Mexico

cjbrink@sandia.gov

partners:

T3 Scientific LLC

performance period:

8/23/04 – 4/30/09

pores enhance surface diffusion of CO₂ on the pore wall of the membrane, subsequently blocking other gases. The membrane is composed of three distinct layers as shown in Figure 1: (1) a commercially available tubular or hollow-fiber ceramic support; (2) a mesoporous surfactant-templated silica sub-layer with pore size 15-50 Å; and (3) a microporous aminosilicate gas separation membrane layer with pore size 4-10 Å.

TABLE 1: MEMBRANE PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer	-	Aminosilicate/doped-silicate	
Materials of Fabrication for Support Layer	-	Surfactant-templated silica on alumina	
Nominal Thickness of Selective Layer	µm		
Membrane Geometry	-	Plate-and-frame	Hollow-fiber
Max Trans-Membrane Pressure	bar	3 bar	N/A
Hours Tested Without Significant Degradation	-	168 hrs	100 hrs
Manufacturing Cost for Membrane Material	\$/m ²		
Membrane Performance			
Temperature	°C	25 – 250°C	25 – 80°C
CO ₂ Pressure Normalized Flux	GPU or equivalent	CO ₂ : 400 GPU	CO ₂ : 1,000 GPU
CO ₂ /H ₂ O Selectivity	-		
CO ₂ /N ₂ Selectivity	-	CO ₂ /N ₂ =80-100 (dry feed); CO ₂ /N ₂ = 50-60 (humidified feed)	CO ₂ /N ₂ = 100
CO ₂ /SO ₂ Selectivity	-		
Type of Measurement	-	Mixed gas	Mixed gas
Proposed Module Design			
Flow Arrangement	-		
Packing Density	m ² /m ³	980	
Shell-Side Fluid	-		
Flue Gas Flowrate	kg/hr		
CO ₂ Recovery, Purity, and Pressure	% / % / bar	>90%	
Pressure Drops Shell/Tube Side	bar	0.01 – 0.02	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$		

Definitions:

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

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

GPU – Gas Permeation Unit, which is equivalent to 10⁻⁶ cm³ (1 atm, 0°C)/cm²/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm³ (1 atm, 0°C)/cm²/s with pressures measured in cmHg. Note: 1 GPU = 3.3464×10⁻⁶ kg mol/m²-s-kPa [SI units].

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

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

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

Shell-Side Fluid – Either the permeate (CO₂-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO₂ in CO₂-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Contaminant Resistance – SO₂ > 10 parts per million (ppm).

Flue Gas Pretreatment Requirements – Particulate removal.

Waste Streams Generated – None.

technology advantages

The dual-functional, silica-based membrane will have a higher CO₂ selectivity and permeance compared to conventional membranes that separate gases based on differences in molecular size only.

R&D challenges

- The permeance of the new membrane will need to be increased by a factor of five to meet the research and development (R&D) target.
- The selectivity for the new membrane must remain constant under temperatures of 50 to 70°C and high humidity conditions.
- The presence of particulates in the flue gas could adversely affect membrane performance.
- Previous membrane designs suffered from a gradual reduction in permeance and selectivity under elevated temperature and humidity conditions due to pore shrinkage/blockage.

results to date/accomplishments

- Three classes of microporous, sol-gel derived, silica-based membranes were developed for CO₂ removal under simulated flue gas conditions.
- A novel class of amine-functional, microporous silica membranes was prepared using an amine-derivatized alkoxy silane precursor, exhibiting enhanced CO₂:N₂ selectivity (>70) in the presence of water vapor, but its CO₂ permeance (<1.25 cm³[STP]/cm²-min-atm [\approx 275 GPU]) was below the target.
- Pure siliceous membranes showed higher CO₂ permeance (1.5-2 cm³[STP]/cm²-min-atm [\approx 330-440 GPU]), but subsequent densification occurred under prolonged simulated flue gas conditions.
- Nickel oxide (NiO) was incorporated into the membrane's microporous network to retard densification and achieved CO₂ permeance of 0.5 cm³(STP)/cm²-min-atm (\approx 110 GPU) and CO₂:N₂ selectivity of \approx 50 after 163 hours exposed to simulated flue gas conditions.
- The implementation of a novel ALD processing scheme shows evidence that a vapor-processed membrane can exhibit higher thermal/structural stability combined with higher flux and selectivity compared to the traditional liquid phase processing approach (sol-gel).

next steps

This project ended on April 30, 2009.

available reports/technical papers/presentations

“Novel Dual-Functional Membrane for Controlling Carbon Dioxide Emissions from Fossil Fuel Power Plants,” Final Scientific/ Technical Report, August 2009. <http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/2009Novel-Dual-Functional-Membrane-for-Controlling-Carbon-Di.pdf>.

“Tubular Ceramic-Supported Sol-Gel Silica-Based Membranes for Flue Gas Carbon Dioxide Capture and Sequestration,” J. Memb. Sci., 341 (2009) 30-36.

“Novel Dual-Functional Membrane for CO₂ Capture,” Seventh Annual Carbon Capture and Sequestration Conference, Pittsburgh, Pennsylvania, May 2008.

“Anodic Alumina Supported Dual-Layer Microporous Silica Membranes,” J. Memb. Sci., 287, (2007) 157-161.

“Microporous Sol-Gel Derived Aminosilicate Membrane for Enhanced Carbon Dioxide Separation,” Separation and Purification Technology, 42(3) (2005) 249-257.

B-423

POST-COMBUSTION MEMBRANES