APPENDIX B: CARBON DIOXIDE CAPTURE TECHNOLOGY SHEETS

POST-COMBUSTION MEMBRANES

CO_2 CAPTURE BY SUB-AMBIENT MEMBRANE OPERATION

Primary Project Goals

American Air Liquide, Inc. (AL) is developing a post-combustion carbon dioxide (CO_2) capture process based on sub-ambient temperature operation (<-10 °C) of a hollow fiber membrane.

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 will be conducted mainly at AL's Delaware Research and 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 (SO_2), nitrogen oxides (NO_x)] on membrane performance.
- Refine process simulation for integrated process with flue gas conditioning and CO_2 liquefier.
- Design slip-stream-scale unit for possible field test.

Technical Content

AL is developing a CO_2 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 CO_2/nitrogen (N_2) selectivity with minimal loss of CO_2 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 CO_2 prior to CO_2 partial condensation in a liquefaction unit. The cryogenic heat exchanger system provides energy integration between the membrane and CO_2 liquefaction system.

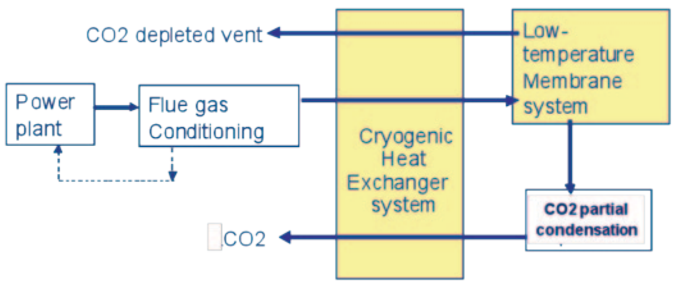

Figure 1: Block Diagram of Cold Membrane Process

Technology Maturity:
Laboratory/bench-scale

Project Focus:
Sub-Ambient Temperature, Hollow-Fiber Membrane

Participant:
American Air Liquide

Project Number:
FE0004278

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Partners:
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Air Liquide Process and Construction

Performance Period:
10/1/10 – 9/30/12

Figure 2 shows a schematic diagram of the membrane-based CO_2 compression and purification unit (CPU) process. The process lines in Figure 2 are color coded: black for ambient temperature, dark blue for ~-30 °C, and light blue for ~-50 °C. The pre-treated flue gas is compressed to ~230 pounds per square inch (psi) (16 bar). The heat of compression is captured in boiler feed water raising its temperature to ~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 -30 °C. The cooled, dried, compressed flue gas is then fed to the membrane to produce a residue stream with ~1.6% CO_2 at ~215 psi (15 bar) and a permeate stream with ~60 to 70% CO_2 at ~17 psi (1–2 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 CO_2 is pumped from the separator to provide a sequestration-ready product CO_2 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% CO_2. The higher CO_2 content improves the membrane separation.

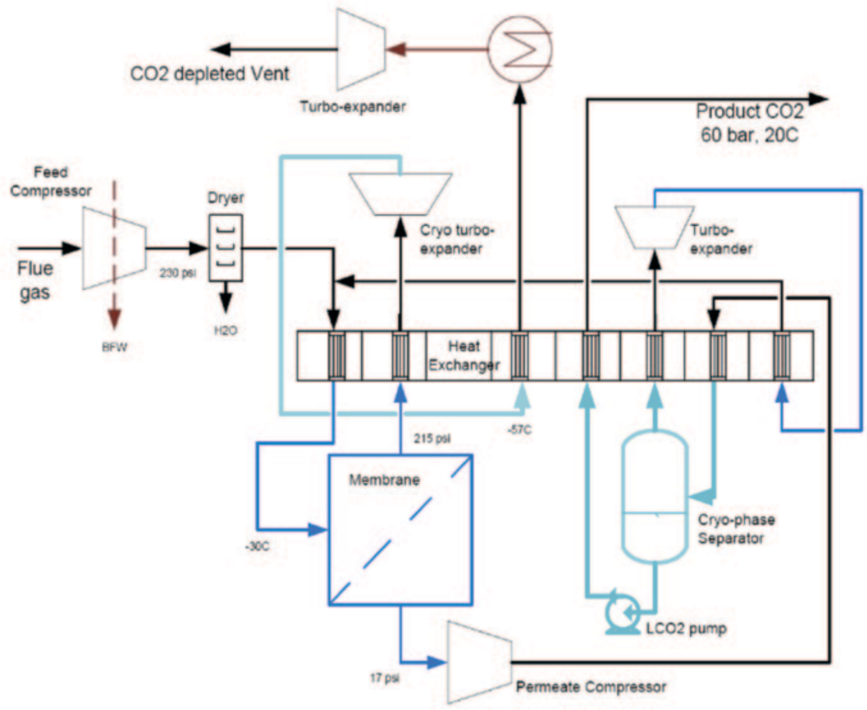

Figure 2: Schematic Diagram of Cold Membrane Process

Table 1: Membrane Process Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	—	—
	Materials of fabrication for support layer (if applicable)	—	—
	Selectivity of key gas components: CO_2/N_2 for post-combustion technology	>90 at proposed conditions	—
	Type of selectivity measurement (ideal or mixed gas)	Mixed gas	—
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	>90	—
	Temperature, °C	-30 to -40	—
	Laboratory-scale testing, hours without significant performance degradation	2,000	—
	Pilot-scale testing (if applicable), hours without significant performance degradation	—	—
	Maximum pressure differential achieved without significant performance degradation or failure, bar	24	—
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Hollow fiber	—
	Packing density, m^2/m^3	>1,000	—
	Pressure drop, bar (feed to residue)	~0.1 bar	—
	Estimated cost of manufacturing and installation, $\$/m^2$-GPU or equivalent	TBD	—
Product Quality	CO_2 purity, %	97+%	—
	N_2 concentration, %	—	—
	Other contaminants, %	—	—
Process Performance	Electricity requirement, kJ/kg CO_2	~800	—
	Heat requirement, kJ/kg CO_2	—	—
	Total energy (electricity equivalent), kJ/kg CO_2	~800	—

Other Membrane Parameters

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.

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 (SO_2, 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, and 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, SO_2) separation, compressor materials of construction, particulate removal, Hg removal, and water management.

Results To Date/Accomplishments

- Initiated design and fabrication of a closed loop sub-ambient bench-scale test system for testing the membrane bundles at the proposed sub-ambient temperature conditions using synthetic flue gas (CO_2 and N_2).
- Modified an existing AL cold test facility in order to conduct laboratory testing of the membrane with feeds containing acidic components.

Next Steps

- Complete construction of the closed loop sub-ambient bench-scale test system.
- Initiate laboratory testing of the membrane using synthetic flue gas (CO_2 and N_2) that contains low concentrations of SO_2.

Final test results will not be available until after the September 2012 project completion date.

Available Reports/Technical Papers/Presentations

General project information is available on DOE/NETL website at: http://www.netl.doe.gov/technologies/coalpower/ewr/co2/post-combustion/sub-ambient-membrane.html

"CO_2 Capture By Sub-Ambient Membrane Operation," Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, PA, September 2010. http://www.netl.doe.gov/publications/proceedings/10/co2capture/index.html

HYBRID MEMBRANE/ABSORPTION PROCESS FOR POST-COMBUSTION CO_2 CAPTURE

Primary Project Goals

Gas Technology Institute (GTI) is developing a hybrid membrane/absorption process (known as Carbo-Lock™) for post-combustion carbon dioxide (CO_2) capture. The project includes bench-scale testing 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 CO_2 separation.
- Determine optimum solvent for use in process.
- Develop an energy efficient regeneration process that enables CO_2 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 CO_2 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 or 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 CO_2/nitrogen (N_2) selectivity is controlled by the chemical affinity of CO_2 with the selected solvent. The process could lower steam regeneration energy requirement as compared to conventional amine-based solvent processes, and the CO_2 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 CO_2 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.

Technology Maturity:

Laboratory/bench-scale testing using actual flue gas

Project Focus:

Hybrid with Solvent and Hollow-Fiber Membrane

Participant:

Gas Technology Institute

Project Number:

FE0004787

NETL Project Manager:

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Partners:

Aker Process Systems
Midwest Generation EME, LLC
PoroGen Corporation

Contract Performance Period

10/1/10 – 9/30/13

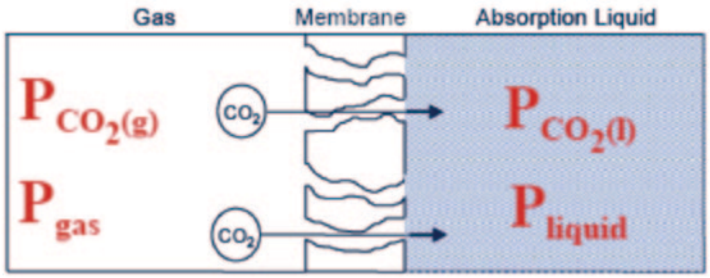

Figure 1: Mass Transfer Principle for Hybrid Membrane/Solvent Contactor

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 CO_2 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.

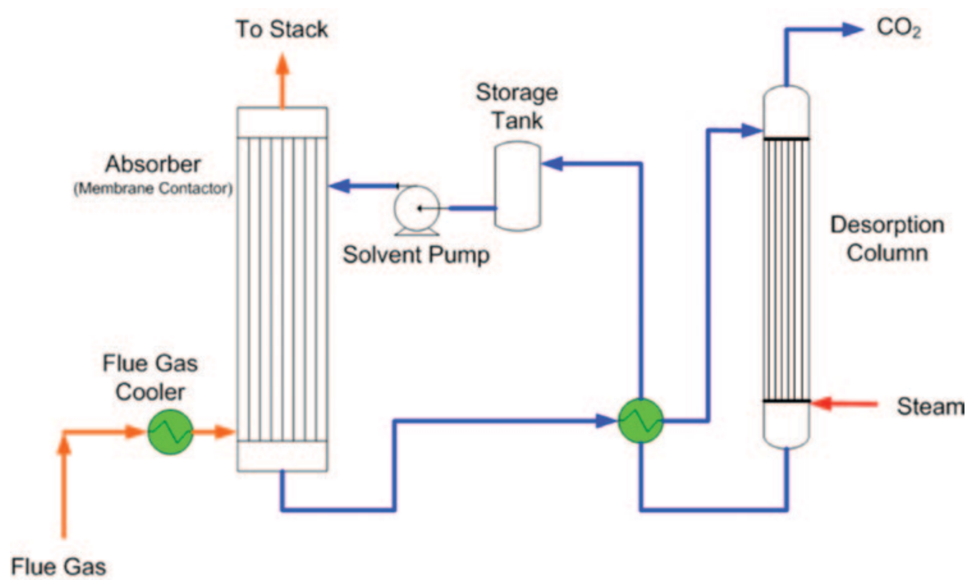

Figure 2: Process Schematic for Hybrid Membrane/Solvent Technology

The main process features of the hybrid membrane/solvent technology include: a higher CO_2 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

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Perfluoro-oligomer	Perfluoro-oligomer
	Materials of fabrication for support layer (if applicable)	PEEK	PEEK
	Selectivity of key gas components: CO_2/N_2 for post-combustion technology	Determined by solvent used	Determined by solvent used
	Type of selectivity measurement (ideal or mixed gas)	Mixed	Mixed
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	1,000–5,000	1,000–5,000
	Temperature, °C	20–50	20–50
	Bench-scale testing, hours without significant performance degradation	TBD	TBD
	Pilot-scale testing (if applicable), hours without significant performance degradation	N/A	N/A
	Maximum pressure differential achieved without significant performance degradation or failure, bar	N/A	N/A
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Hollow-fiber	Hollow-fiber
	Packing density, m^2/m^3	500–1,000	500–1,000
	Pressure drop, bar	0.2	0.1
	Estimated cost of manufacturing and installation, $\$/m^2$-GPU or equivalent	100	40
Product Quality	CO_2 purity, %	99%	99%
	N_2 concentration, %	TBD	TBD
	Other contaminants, %	TBD	TBD
Process Performance	Electricity requirement, kJ/kg CO_2	TBD	TBD
	Heat requirement, kJ/kg CO_2	TBD	TBD
	Total energy (electricity equivalent), kJ/kg CO_2	TBD	TBD

Other Membrane Parameters

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.

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 CO_2 is generated at pressure, reducing compression costs.
- Up to 70% 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

- Optimization of the super-hydrophobic PEEK membranes morphology for the preferred 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 CO_2 separation and capture test results.
- Contactor module design was initiated, the prototype laboratory-scale module design was completed, and the laboratory test module was constructed and is ready for testing.

Next Steps

- PEEK membrane morphology will be further optimized for MDEA solvent system and tested for non-wetting characteristics in longer term tests and at elevated temperatures (50 and 120–130 °C).
- PEEK membrane morphology will be optimized for the carbonate solvent system. PEEK hollow fiber dimensions will be optimized for flue gas application to minimize pressure drop.
- PEEK membrane test modules (2-inch diameter and 10 ft^2 area) will be constructed for laboratory-scale tests. Manufacturing procedures and module design will be further optimized based on test results.
- Conduct CO_2 capture laboratory tests utilizing simulated flue gas.
- Liquid break through tests will be extended to elevated temperatures.

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

Available Reports/Technical Papers/Presentations

General project information is available on DOE/NETL website at: http://www.netl.doe.gov/technologies/coalpower/ewr/co2/post-combustion/hybrid-membrane.html

"Hybrid Membrane/Absorption Process for Post-Combustion CO_2 Capture (Membrane Contactor)," Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, PA, September 2010. http://www.netl.doe.gov/publications/proceedings/10/co2capture/index.html

CO_2 CAPTURE MEMBRANE PROCESS FOR POWER PLANT FLUE GAS

Primary Project Goals

Research Triangle Institute (RTI) is developing 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% of the carbon dioxide (CO_2) from the plant's flue gas.

Technical Goals

- Develop new fluorinated polymers as membrane materials that have superior CO_2 separation properties compared to conventional and competitive membrane platforms. A minimum selectivity of 30 for CO_2 over nitrogen (N_2) and CO_2 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 (SO_2), and nitrogen oxide (NO_x) contaminants present in flue gas.
- Develop next-generation polycarbonate hollow-fiber membranes and membrane modules with higher CO_2 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 CO_2 permeate flow rates with minimal pressure drop.
- Identify and develop CO_2 capture membrane process design and integration strategies suitable for retrofit installation.
- Demonstrate CO_2 capture performance and durability of membrane modules using actual coal-fired flue gas.

Technical Content

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

RTI is pursuing the development of two membrane material platforms. As a near-term membrane platform solution, RTI is working with Generon to develop next-generation, high-flux polycarbonate hollow-fiber membranes and membrane modules with higher CO_2 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. Two large prototype membrane modules of the high-flux polycarbonate membrane fibers have been produced and will be evaluated for field performance and durability with a real combustion flue gas slipstream at a coal-fired power plant in Chapel Hill, NC.

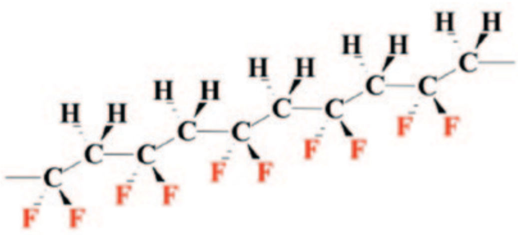

Figure 1: Chemical Structure of PVDF

For a longer-term membrane platform solution, RTI is working with Arkema to develop improved CO_2 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 $[CH_2\text{-}CF_2]_n$ repeat unit. PVDF is well suited for contact with flue gas, possessing high chemical resistance to

Technology Maturity:

Bench-scale using actual flue gas (120 scfm)

Project Focus:

Hollow-Fiber, Polymeric Membranes

Participant:

RTI International

Project Number:

NT0005313

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Partners:

Arkema
Generon IGS

Performance Period:

10/1/08 –3/31/11

acids and oxidants, specific affinity for CO_2 for high CO_2 solubility, and high thermal stability (T_d ~340 °C). PVDF also features excellent physical and mechanical properties, durability, and longevity suited to the fiber 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 is thus synthesizing and developing advanced PVDF based copolymers possessing improved CO_2 permeance and selectivity.

In this project, the membrane is being developed in the form of hollow fibers that are packaged into compact, high surface area-to-volume module devices. Multiple modules will be 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.

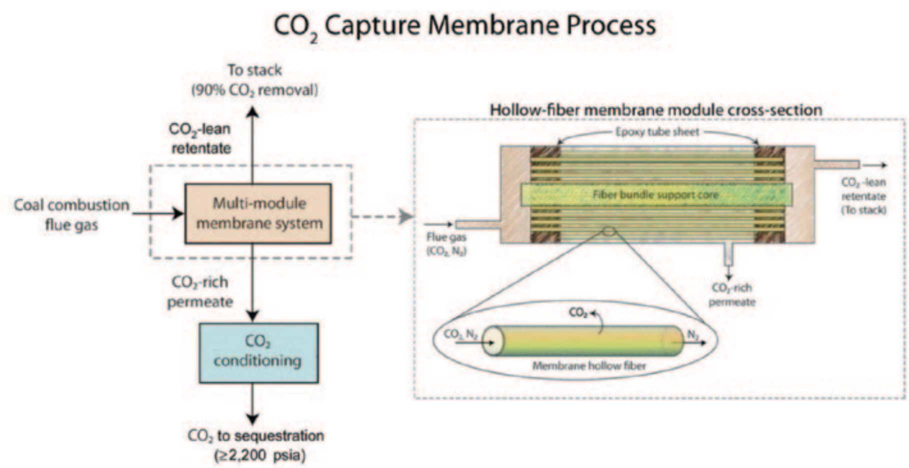

Figure 2: Cross-Section of a Hollow-Fiber Membrane Module

Individual Membrane Hollow Fibers | **Small Bundle Loop of Hollow Fibers** | **Various Membrane Module Sizes**

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% 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 CO_2-rich M2 permeate is then compressed and dehydrated to produce the final, sequestration-ready CO_2 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% CO_2 capture and 95% CO_2 purity in the capture stream using the high-flux polycarbonate membrane (400 GPU; CO_2/N_2 = 35).

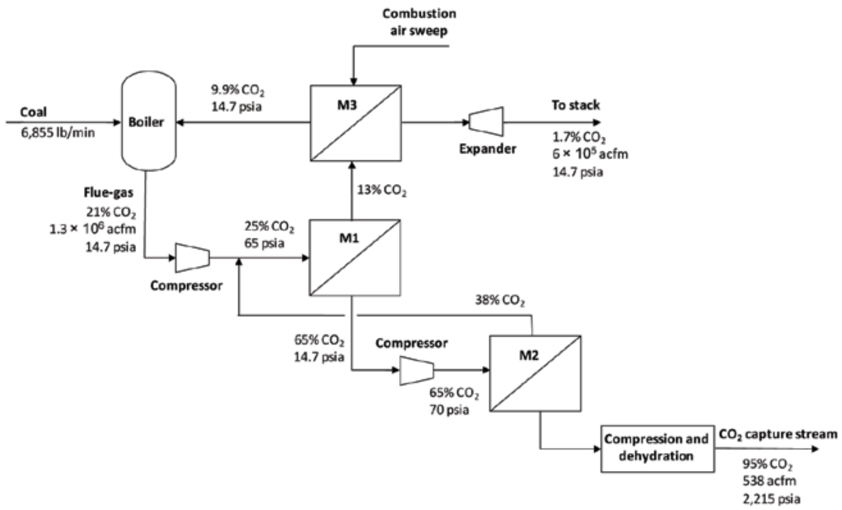

Figure 4: RTI's Three-Stage CO_2 Capture Membrane Process Design

Table 1: Membrane Process Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Polycarbonate-based	Vinylidene fluoride-based
	Materials of fabrication for support layer (if applicable)	N/A	N/A
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	35	50
	Type of selectivity measurement (ideal or mixed gas)	Ideal and mixed	Ideal and mixed
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	400	1,000
	Temperature, °C	25–30	50
	Bench-scale testing, hours without significant performance degradation	165	300 (coal)
	Pilot-scale testing (if applicable), hours without significant performance degradation	N/A	N/A
	Maximum pressure differential achieved without significant performance degradation or failure, bar	15 (not tested higher)	15
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Hollow-fiber	Hollow-fiber
	Packing density, m^2/m^3	9,000	9,000
	Pressure drop, bar	0.5	<0.1
	Estimated cost of manufacturing and installation, $/m²-GPU or equivalent	0.08	0.02
Product Quality	CO_2 purity, %	95	95+
	N_2 concentration, %	4%	<1%
	Other contaminants, %	1%	<0.5%
Process Performance	Electricity requirement, kJ/kg CO_2	1,250	900
	Heat requirement, kJ/kg CO_2	0	0
	Total energy (electricity equivalent), kJ/kg CO_2	1,250	900

Other Membrane Parameters

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).

Waste Streams Generated: Because the membrane permeates and concentrates water into the CO_2 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 CO_2 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 CO_2 concentration of 13–15%, 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 CO_2 separation properties and chemical resistance, improved membrane module design and engineering, and novel process design and integration strategies.

Results To Date/Accomplishments

- Development and fabrication of next-generation, high-flux polycarbonate membrane hollow fibers with CO_2 permeance of 410 GPU, which is four times greater than the CO_2 flux of current commercial standard polycarbonate fibers, and CO_2/N_2 selectivity (25–35) comparable to that of the standard fibers. Eight laboratory-scale modules made from these fibers were investigated with pure N_2, oxygen (O_2), and CO_2 at feed pressures up to 200 pounds per square inch gauge (psig) and with CO_2/N_2 mixtures with and without flue gas contaminants, including 290 parts per million (ppm) SO_2, 255 ppm nitric oxide (NO), and 30 ppm nitrogen dioxide (NO_2), at 75 psig feed pressure.
- Development and fabrication of high-flux polycarbonate membrane hollow fibers with a 25% increase in fiber diameter to reduce the axial pressure drop by 50%.
- Successful fabrication scale-up of high-flux polycarbonate hollow fibers into 10 large prototype membrane modules (6 by 36 inches) with 6,000–12,000 times more membrane area than that of laboratory-scale modules. In quality control checks, the prototype modules showed CO_2 permeation properties consistent with those of the laboratory-scale modules.
- Development and synthesis of novel fluorinated VDF-based copolymers having excellent resistance to flue gas contaminants (SO_2, NO_x, moisture) and improved CO_2 separation properties.

- Flue gas contaminants had no plasticization or detrimental effect on VDF-based copolymer platform as shown by stable (constant) CO_2 permeance and selectivity in continuous seven-day tests with CO_2/N_2 mixtures containing 30 ppm NO_2, 250 ppm NO, 290 ppm SO_2, or ~1% water vapor.
- VDF-co-A copolymer series achieved up to 17–18 times higher CO_2 permeability (permeance) than the base PVDF homopolymer with no adverse impact on base CO_2/N_2 selectivity.
- VDF-co-B copolymer series achieved up to 1.7–3.0 times higher CO_2/N_2 selectivity and up to six to eight times higher CO_2 permeability (permeance) than the base PVDF polymer.
- Process temperature may be used to further enhance CO_2 permeance in the VDF-based material platform as a substantial 10-fold increase in permeance was measured over only a small 35 °C temperature rise.

• Successful preparation of fine hollow fibers from selected VDF-co-A copolymer candidate in trial fiber spin runs, thus demonstrating the feasibility of making fibers from the new VDF-based material platform.

• Development of three-stage CO_2 capture membrane process design to achieve 90% CO_2 capture and 95% CO_2 purity.

Next Steps

• Continued development of VDF-based membrane polymer platform by exploring other synthetic strategies to further increase CO_2 permeability (permeance) and selectivity.

• Design and construction of a field CO_2 capture membrane test skid.

• Field performance and durability testing (300 hours cumulative) of two prototype high-flux polycarbonate membrane modules with 120 scfm slipstream of real coal-derived flue gas at a coal-fired power plant (32 MWe) in Chapel Hill, NC. Field-test plans also include testing of the VDF-based membrane platform.

• Techno-economic evaluation, using the field-test data collected, of the "best" integrated CO_2 capture membrane process design package.

Final test results will not be available until after the September 2011 project completion date.

Available Reports/Technical Papers/Presentations

General project information is available on the DOE/NETL website at: http://www.netl.doe.gov/technologies/coalpower/ewr/co2/post-combustion/membrane-process.html

"CO_2 Capture Membrane Process for Power Plant Flue Gas," 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, September 2010. http://www.netl.doe.gov/publications/proceedings/10/co2capture/index.html

"CO_2 Capture Membrane Process for Power Plant Flue Gas," Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, PA, March 2009.

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

Primary Project Goals

Membrane Technology and Research, Inc. (MTR) is developing a polymeric membrane and associated process for carbon dioxide (CO_2) 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 a coal-fired power plant.

Technical Goals

- Develop a thin film, composite, polymer-based membrane to increase CO_2 permeance while maintaining CO_2/nitrogen (N_2) 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.
- Continue slipstream field testing of a membrane system at a coal-fired power plant; the system will process 7,000 standard m^3/day (0.25 MMscfd) of flue gas (equivalent to approximately 0.05 MWe), separating about one tonne of CO_2/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 CO_2/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 CO_2 capture process versus other capture technologies.

Technical Content

MTR is developing composite membranes with high CO_2 permeance and high CO_2/N_2 selectivity for post-combustion flue gas applications. Tests indicate the membrane has 10 times the CO_2 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 CO_2 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 CO_2. The retentate from the cross-flow module is then fed into a countercurrent sweep module, from which the permeate is recycled back to the boiler

Technology Maturity:

Small pilot-scale on actual flue gas (equivalent to 1 MW)

Project Focus:

Spiral-Wound, Polymeric Membranes

Participant:

Membrane Technology and Research, Inc.

Project Number:

FE0005795
NT0005312
NT43085

NETL Project Manager:

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

Performance Period:

4/1/07 – 9/30/15

via an air sweep, which increases the CO_2 concentration of the flue gas entering the initial cross-flow module. The CO_2-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 CO_2 stream by recycle of the permeate back to the inlet of the compressor.

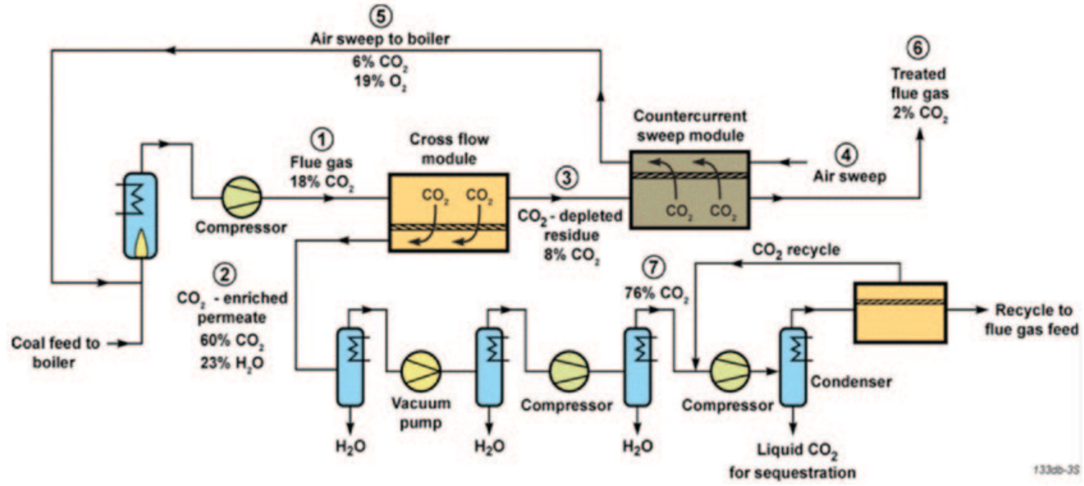

Figure 1: Process Design for the Membrane System

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% of the reverse osmosis (RO) desalination industry and more than 60% of the membrane market for CO_2 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 CO_2 to flow through the device.

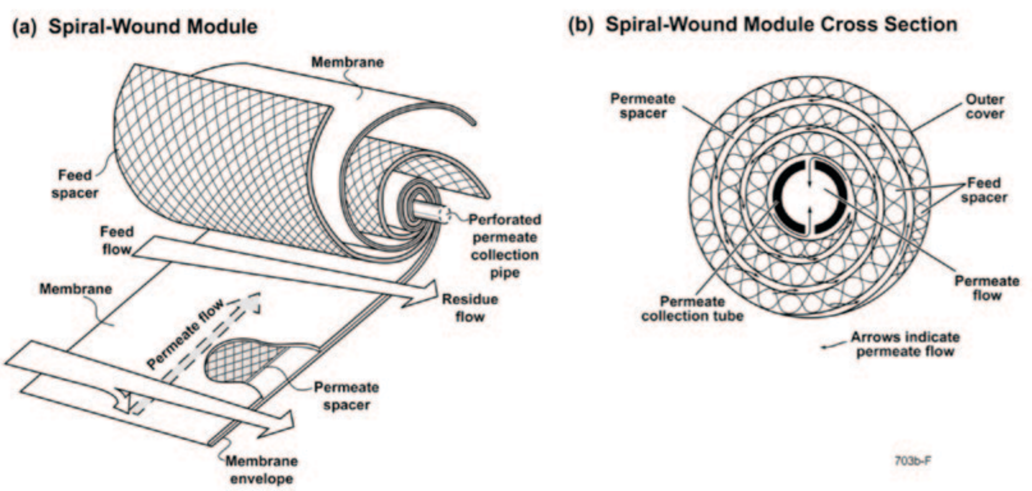

Figure 2: Schematic Diagram of a Spiral-Wound Membrane Module

MTR estimates that a total membrane area of about 0.5 million m^2 is required to achieve 90% CO_2 capture for a 550-MWe plant using this process design and would consume approximately 20–25% 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).

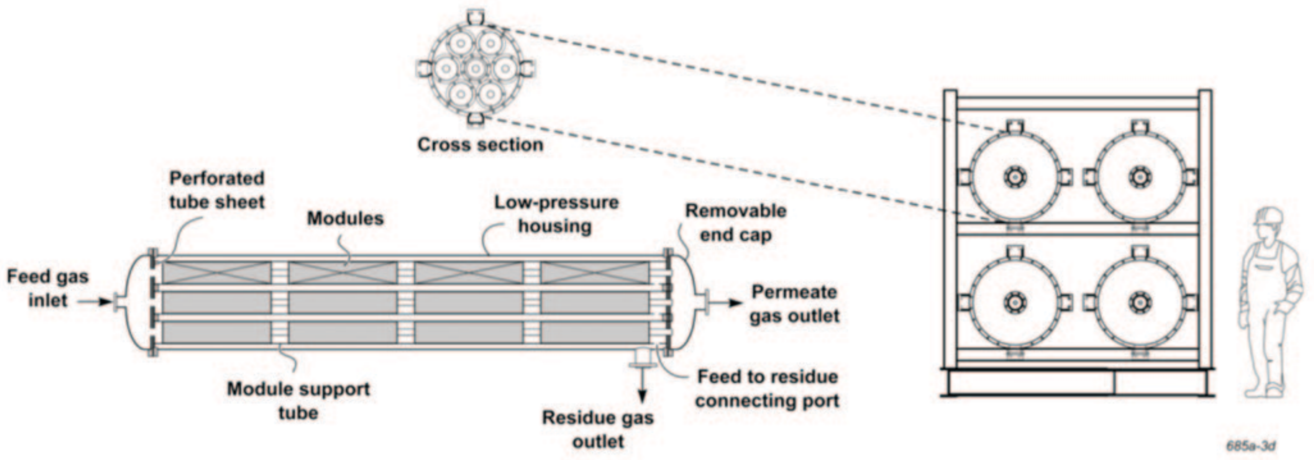

Figure 3: Proposed Design for Full-Scale Membrane System

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 CO_2 per day from a 7,000 standard m^3/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 Pilot-Scale Slipstream Testing at the APS Cholla Power Plant

Table 1: Membrane Process Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Polymer	Polymer
	Materials of fabrication for support layer (if applicable)	Polymer	Polymer
	Selectivity of key gas components: CO_2/N_2 for post-combustion technology	25	25
	Type of selectivity measurement (ideal or mixed gas)	Mixed	Mixed
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	1,500	2,500+
	Temperature, °C	50	50
	Bench-scale testing, hours without significant performance degradation	1,500	1,500
	Pilot-scale testing (if applicable), hours without significant performance degradation	1,000 (coal)	5,000 (coal)
	Maximum pressure differential achieved without significant performance degradation or failure, bar	70	70
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Spiral	Spiral
	Packing density, m^2/m^3	700	1,000
	Pressure drop, bar	0.1	<0.05
	Estimated cost of manufacturing and installation, $\$/m^2$-GPU or equivalent	0.3	0.05
Product Quality	CO_2 purity, %	No data	98+
	N_2 concentration, %	No data	1
	Other contaminants, %	No data	<0.1
Process Performance	Electricity requirement, kJ/kg CO_2	No data	750
	Cooling requirement, kJ/kg CO_2	No data	150
	Total energy (electricity equivalent), kJ/kg CO_2	No data	900

Other Membrane Parameters

Contaminant Resistance: The membranes are known to be unaffected by water (H_2O), oxygen (O_2), and sulfur dioxide (SO_2). The effect of trace contaminants (e.g., mercury, arsenic, etc.) is unknown and is being examined in the Cholla slipstream field testing.

Flue Gas Pretreatment Requirements: Currently, pretreatment requirements are unknown. The Cholla slipstream test is treating post-flue gas desulfurization (FGD) flue gas and will clarify the need for gas treatment prior to entering the membrane system. Of the species present in flue gas, the greatest concern is that particulate matter will foul the membranes, reducing module lifetimes. Particulate filters—which 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% of the H_2O in flue gas as liquid. The quality of this H_2O, 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 CO_2 than conventional membranes, which reduce the required membrane area and capital costs.
- A membrane system does not contain any chemical reactions or moving parts, making it simple to operate and maintain.

- The membrane material has a high tolerance of wet acid gases and is inert to O_2.
- 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 CO_2 partial pressure gradient in the countercurrent sweep membrane stage reduces the need for compressors or vacuum pumps, thus reducing the overall energy cost.
- The recycled CO_2 from the air sweep to the boiler increases the CO_2 partial pressure driving force for separation in the initial 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 CO_2 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.

Results To Date/Accomplishments

- Scaled up and produced high permeance membrane formulations on commercial casting and coating equipment. Produced more than 1,000 m^2 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 m^3/day (0.15 MMscfd) of natural-gas fired flue gas to provide concentrated CO_2 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 m^3/day (0.25 MMscfd) of coal-fired flue gas and capture one tonne CO_2/day. The test skid is composed of four, 8-inch diameter Polaris™ membrane modules which 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 CO_2 separation and liquefaction process can capture 90% CO_2 using 20–25% of the plant's energy and cost $30 per tonne of CO_2 captured.

Next Steps

- Continue to operate the slipstream (0.05 MWe equivalent gas flow) membrane system at a coal-fired power plant. Use this system to evaluate new membrane formulations with a goal of doubling CO_2 permeance from that of the baseline Polaris™ membrane.
- Conduct field testing on the small slipstream membrane system of modules with new flow channel configurations with a goal of minimizing pressure drop through the membrane system.
- Understand sweep flow distribution and pressure drop in membrane modules by computational fluid dynamics (CFD) simulations.
- Design, construct, and operate a small pilot-scale (approximately 1 MWe equivalent gas flow) membrane system for a six-month field test at a coal-fired power plant beginning in 2013.
- 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 CO_2 capture process versus other capture technologies.
- With Babcock & Wilcox, analyze the impact of CO_2 recycle in sweep air on boiler performance.
- Lower the membrane module cost by incorporating low-cost components with a target of $\$50/m^2$.
- Integrate a CO_2 liquefaction section into the overall CO_2 capture system.
- Test options for recycling the air sweep from the countercurrent sweep module to the boiler.

Final test results will not be available until after the September 2015 project completion date.

Available Reports/Technical Papers/Presentations

General project information is available on DOE/NETL website at: http://www.netl.doe.gov/technologies/coalpower/ewr/co2/post-combustion/slipstream-membrane-process.html

"Membrane Process to Capture CO_2 from Coal-Fired Power Plant Flue Gas," Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, PA, September 2010.
http://www.netl.doe.gov/publications/proceedings/10/co2capture/index.html

Merkel 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. Available electronically at doi:10.1016/j.memsci.2009.10.041.

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

"A Membrane Process to Capture CO_2 from Coal-Fired Power Plant Flue Gas," Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, PA, March 2009.

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

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

Primary Project Goals

Carbozyme is developing an enzyme-based, contained liquid membrane (CLM) to extract carbon dioxide (CO_2) from coal and natural gas combustion flue gas. Carbozyme is also evaluating a state-of-the-art electrodialytic (EDI) method for CO_2 capture and comparing its performance with that of the CLM.

Technical Goals

- Scale up the enzyme-catalyzed, CLM permeator design (4–400 m^2) to include multiple units organized as a skid (3 × 40 m^2) 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 CO_2 from an organism. An organism's blood stream is used to transport oxygen (O_2) and CO_2 to and from its cells, respectively. CA is an enzyme in the blood that captures the CO_2 from the cells and converts it to bicarbonate (HCO_{3^-}). The enzyme reverses this reaction in the lungs, allowing the CO_2 to be exhaled. Figure 1 shows the configuration for the enzyme-based CA CLM membrane process being developed by Carbozyme. 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 CO_2 lean flue gas and the second group contains the CO_2 rich permeate stream. The CA enzyme is contained in a thin-film liquid between the two groups of fibers. The CA helps 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 katals (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% pure CO_2 stream. The remaining flue gas is sent to the plant stack.

Technology Maturity:
Laboratory/bench-scale

Project Focus:
Biomimetic Membrane

Participant:
Carbozyme, Inc.

Project Number:
NT43084
NT42824

NETL Project Manager:
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Principal Investigator:
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Partners:
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Electrostep
Kansas State University
Siemens
SRI
Visage Energy

Performance Period:
3/28/07 – 7/31/09

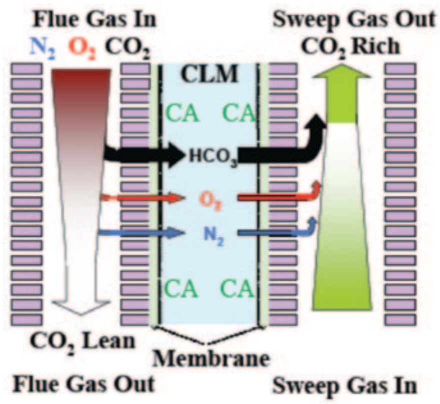

Figure 1: Configuration for Carbozyme-Developed, Enzyme-Based Carbonic Anhydrase Contained Liquid Membrane

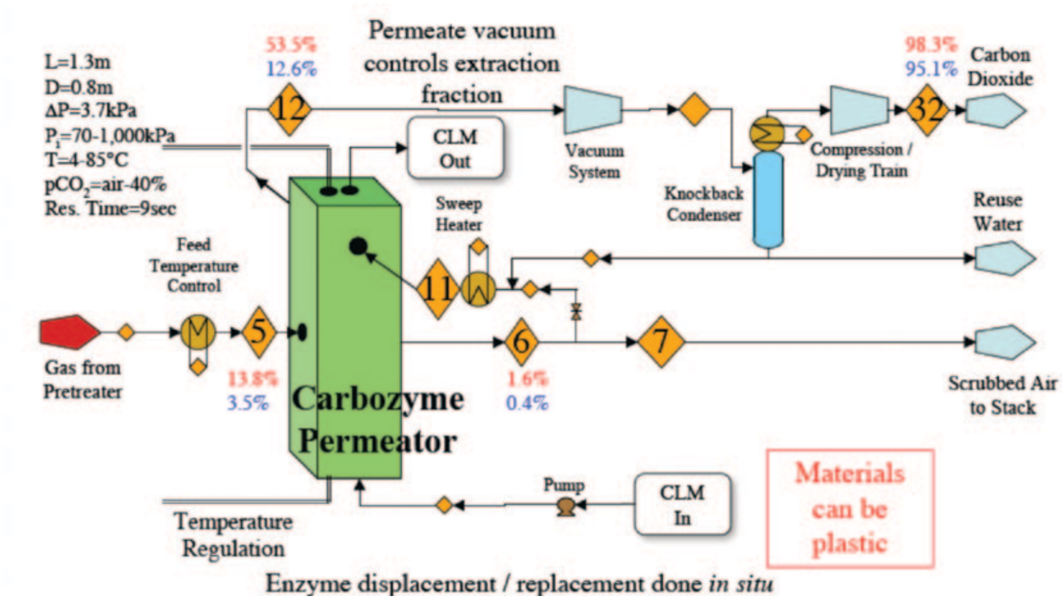

Figure 2: Process Schematic for the Carbonic Anhydrase Contained Liquid Membrane

Technology Advantages

- 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 CO_2 production rate with low energy requirements and boosts separation and purification due to its low nitrogen (N_2) and O_2 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 30–50% 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 (SO_2) 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 (~50 °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% of initial activity was retained over a 60-day period.
- Developed a 0.5 m^2 bench-scale CLM permeator that combines absorption and desorption in a single housing through use of dual hollow fiber, spiral wound, polymer membranes. In this configuration, CO_2 capture is driven by a combination of pressure, vacuum, and temperature. More than 90% CO_2 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 m^2 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 CO_2 absorption/desorption.

Next Steps

Project #43084 was completed July 2009. The draft final report is under review by NETL.

Available Reports/Technical Papers/Presentations

General project information is available on DOE/NETL website at: http://www.netl.doe.gov/technologies/coalpower/ewr/co2/post-combustion/biomimetric.html

"Capture of CO_2 by the Carbozyme Permeator," 8th Annual Conference on Carbon Capture and Sequestration, Pittsburgh, PA, May 2009.

"Development of Biomimetic Membranes for Near-Zero Power Plant Emissions," Annual NETL CO_2 Capture Technology for Existing Plants R&D meeting, Pittsburgh, PA, 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, PA, May 2008.

"Biomimetic Membrane for CO_2 Capture from Flue Gas," Final Report for Project #42824, August 2007.

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

Technology Maturity:

Laboratory-scale, with simulated flue gas

Project Focus:

Dual-Functional, Silica-Based Membrane

Participant:

University of New Mexico

Project Number:

NT42120

NETL Project Manager:

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Partners:

T3 Scientific, LLC

Performance Period:

8/23/04 – 4/30/09

Primary Project Goals

The University of New Mexico is developing a new, dual-functional, silica-based membrane for carbon dioxide (CO_2) emissions capture from coal-fired power plants.

Technical Goals

- Achieve a membrane CO_2/nitrogen (N_2) selectivity of 100 and a CO_2 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 (SO_2), water vapor, and trace oxygen (O_2) on membrane performance.
- Optimize membrane deposition on alternative economical membrane supports.
- Conduct preliminary economic analysis of the membrane process for post-combustion CO_2 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 CO_2 molecules and the amine functional membrane pores enhance surface diffusion of CO_2 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.

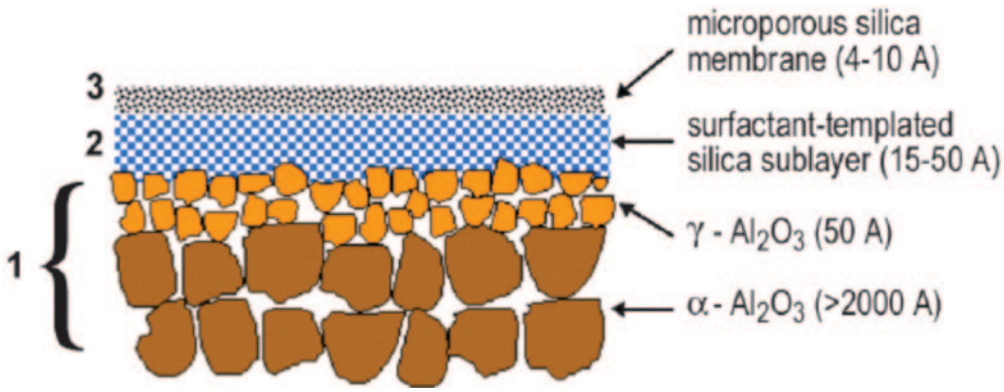

Figure 1: Cross-Section of Membrane

Table 1: Membrane Process Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Aminosilicate/doped-silicate	Aminosilicate/doped silicate
	Materials of fabrication for support layer (if applicable)	Surfactant-templated silica on alumina	Surfactant-templated silica on alumina
	Selectivity of key gas components: CO_2/N_2 for post-combustion technology	CO_2/N_2 = 80–100 (dry feed); CO_2/N_2 = 50–60 (humidified feed)	CO_2/N_2 = 100
	Type of selectivity measurement (ideal or mixed gas)	Mixed gas	Mixed gas
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	CO_2: 400 GPU	CO_2: 1,000 GPU
	Temperature, °C	25–250 °C	25–80 °C
	Bench-scale testing, hours without significant performance degradation	168 hrs	100 hrs
	Pilot-scale testing (if applicable), hours without significant performance degradation	N/A	N/A
	Maximum pressure differential achieved without significant performance degradation or failure, bar	3 bar	N/A
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Plate-and-frame	Hollow-fiber
	Packing density, m^2/m^3	500	980
	Pressure drop, bar	0.01–0.02	0.01–0.02
	Estimated cost of manufacturing and installation, $/m^2$-GPU or equivalent	$0.33–$0.39/m^2-GPU	N/A
Product Quality	CO_2 purity, %	>90%	90%
	N_2 concentration, %	<10%	10%
	Other contaminants, %	N/A	N/A
Process Performance	Electricity requirement, kJ/kg CO_2	1,313 KJ/kg CO_2 or 0.365 kWh/kg CO_2	1,333 KJ/kg CO_2 or 0.370 kWh/kg CO_2
	Heat requirement, kJ/kg CO_2	0	0
	Total energy (electricity equivalent), kJ/kg CO_2	1,313 KJ/kg CO_2 or 0.365 kWh/kg CO_2	1,333 KJ/kg CO_2 or 0.370 kWh/kg CO_2

Note: Values for membrane properties are experimental. Other values are calculated based on membrane properties.

Other Membrane Parameters

Contaminant Resistance: SO_2 >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 CO_2 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 50–70 °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 CO_2 removal under simulated flue gas conditions.
- A novel class of amine-functional, microporous silica membranes was prepared using an amine-derivatized alkoxysilane precursor, exhibiting enhanced CO_2:N_2 selectivity (>70) in the presence of water vapor, but its CO_2 permeance [<1.25 cm^3 (STP)/cm^2-min-atm (~275 GPU)] was below the target.
- Pure siliceous membranes showed higher CO_2 permeance [1.5–2.0 cm^3 (STP)/cm^2-min-atm (~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 CO_2 permeance of 0.5 cm^3 (STP)/cm^2-min-atm (~110 GPU) and CO_2:N_2 selectivity of ~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

Project completed April 2009.

Available Reports/Technical Papers/Presentations

General project information is available on DOE/NETL website at: http://www.netl.doe.gov/technologies/coalpower/ewr/co2/post-combustion/dual-function.html

"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/technologies/coalpower/ewr/co2/pubs/2009Novel%20Dual-Functional%20Membrane%20for%20Controlling%20Carbon%20Di.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 CO_2 Capture," Seventh Annual Carbon Capture and Sequestration Conference, Pittsburgh, PA, 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.

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