MEMBRANE PROCESS TO SEQUESTER CO_2 FROM POWER PLANT FLUE GAS

Final Technical Report
Report Period: October 1, 2007 – March 31, 2009
Tim Merkel (PI)

July 2009

Award Number DE-FC26-07NT43085

Submitted by
Membrane Technology and Research, Inc.
1360 Willow Road, Suite 103
Menlo Park, CA 94025

Prepared for
The U.S. Department of Energy, NETL
Attn: Jose Figueroa
626 Cochrans Mill Road, P.O. Box 10940
Pittsburgh, PA 15236-0940

Contributors:
Tim Merkel (PI)
Karl Amo
Richard Baker
Ramin Daniels
Bilgen Firat
Zhenjie He
Haiqing Lin
Adrian Serbanescu
Xiaotong Wei
Hans Wijmans

Disclaimer

ABSTRACT

The objective of this project was to assess the feasibility of using a membrane process to capture CO_2 from coal-fired power plant flue gas. During this program, MTR developed a novel membrane (Polaris™) with a CO_2 permeance tenfold higher than commercial CO_2-selective membranes used in natural gas treatment. The Polaris™ membrane, combined with a process design that uses a portion of combustion air as a sweep stream to generate driving force for CO_2 permeation, meets DOE post-combustion CO_2 capture targets. Initial studies indicate a CO_2 separation and liquefaction cost of $20 - $30/ton CO_2 using about 15% of the plant energy at 90% CO_2 capture from a coal-fired power plant.

Production of the Polaris™ CO_2 capture membrane was scaled up with MTR's commercial casting and coating equipment. Parametric tests of cross-flow and countercurrent/sweep modules prepared from this membrane confirm their near-ideal performance under expected flue gas operating conditions. Commercial-scale, 8-inch diameter modules also show stable performance in field tests treating raw natural gas. These findings suggest that membranes are a viable option for flue gas CO_2 capture. The next step will be to conduct a field demonstration treating a real-world power plant flue gas stream. The first such MTR field test will capture 1 ton CO_2/day at Arizona Public Service's Cholla coal-fired power plant, as part of a new DOE NETL funded program.

TABLE OF CONTENTS

EXECUTIVE SUMMARY

This final report describes development of a membrane process to capture carbon dioxide (CO_2) from power plant flue gas. The work was conducted at Membrane Technology and Research, Inc. (MTR) from 1 April 2007 through 31 March 2009. The goal of this research program was to assess the feasibility of using a membrane process to capture CO_2, and to determine the factors governing the competitiveness of this approach. Project work focused on membrane development and scale-up, module fabrication and parametric testing, and process design studies. Technical targets were met on or ahead of schedule. Initial design findings indicate a promising CO_2 separation and liquefaction cost of \$20 - \$30/ton CO_2 using about 15% of the plant energy at 90% CO_2 capture from a coal-fired power plant.

Direct CO_2 capture from power plant flue gas has been the subject of many studies, and while amine absorption seems to be the leading candidate technology, membrane processes have also been suggested. The Achilles heel of previous membrane processes has been the enormous membrane area required for separation because of the low partial pressure of carbon dioxide in flue gas. MTR has used a two-fold approach to address this issue:

(1) the development of high-permeance membranes to reduce the required membrane area and capital cost, and
(2) the use of incoming combustion air in a countercurrent/sweep module design to generate separation driving force and reduce the need for vacuum pumps and the associated parasitic energy cost.

During this program, MTR developed a novel membrane (Polaris™) with a CO_2 permeance tenfold higher than commercial CO_2-selective membranes used in natural gas treatment. The Polaris™ membrane has the highest CO_2/N_2 selectivity for any non-facilitated transport polymeric material. This combination of permeance and selectivity is sufficient to yield a very competitive membrane CO_2 capture process. High-performance Polaris™ membrane formulations were successfully scaled up using commercial casting and coating equipment. Over 200 m^2 of membrane were produced during this project.

Several conventional cross-flow and novel countercurrent/sweep modules were successfully fabricated from Polaris™ membranes. These modules were evaluated on a mixed-gas test system designed and built for this project. Parametric tests on cross-flow modules confirm their near-ideal performance under vacuum operation. This finding validates design calculations for cross-flow modules used in the first step of the proposed membrane CO_2 capture process. The second and critical step of this process relies on newly-developed countercurrent/sweep modules. Tests on such modules clearly demonstrate the effectiveness of air sweep operation. Under typical flue gas operating conditions, air sweep can enhance the CO_2 flux through a module by 10 to 20-fold. These results confirm that sweep modules can reduce the use of compression equipment and the associated energy losses.

In addition to laboratory module testing, several commercial-scale (8-inch diameter) Polaris™ modules were built and tested in the field with real process gases. For example, a three-month field test of Polaris™ modules treating raw natural gas containing acid gases (including CO_2)

and heavy hydrocarbons performed as expected throughout the duration of the test. Also during this project, a Polaris™ membrane skid to capture CO_2 from the flue gas of Arizona Public Service's Red Hawk natural gas-fired power plant was built and installed at the plant. This membrane system will provide CO_2 to algae reactors for biofuel production and is scheduled for startup in July 2009.

Based on the membrane and module performance obtained during this project, flow schemes for CO_2 capture in a coal-fired 600 MW_e power plant were developed; 90% of the CO_2 in flue gas is captured as high-pressure supercritical CO_2 ready for sequestration. The total power consumption of the process is 90 MW, or about 15% of the power plant's output. The expected cost of the CO_2 capture process to produce sequestration-ready supercritical CO_2 is $20 - $30/ton CO_2. Design calculations show that increasing membrane permeance or reducing the installed membrane cost can further improve the economics of CO_2 capture. However, increasing membrane CO_2/N_2 selectivity above about 30 produces little additional improvement in system performance due to pressure ratio limitations.

The findings summarized above meet the requirements for all of the four critical path milestones defined at the outset of this project. Based on these promising initial results, MTR and its partners, Arizona Public Service (APS) and Electric Power Research Institute (EPRI), have been awarded a new project funded by DOE NETL (Project number DE-NT0005312) to conduct a field site demonstration of our membrane process at the APS Cholla coal-fired power plant. The membranes, modules and process design developed in this project will be tested under real-world conditions. Critical issues such as the impact of residual particulate matter, or other contaminants in flue gas, on the membrane system can best be addressed by working with real flue gas. Insights from such a test will also be useful for scale-up of low-cost module skid designs that will improve the economics of CO_2 capture with membranes.

The results presented in this report suggest that membranes are a viable option for capturing CO_2 from coal-fired power plants. If developed to a mature state, membrane-based CO_2 capture technology appears to offer significant cost and energy savings over the best-case amine absorption processes. To clarify the true potential of membranes, we recommend that studies move to field demonstrations (such as the upcoming Cholla project) as soon as possible. Field tests provide critical operating experience and understanding of component lifetimes, and facilitate process integration optimization and cost reduction. They also generate confidence in a technology that is key to user acceptance and commercial application of the technology.

BACKGROUND AND RESEARCH APPROACH

Carbon dioxide (CO_2) emissions from coal-fired power plants are believed to contribute significantly to global warming climate change.[1] The direct approach to address this problem is to capture the carbon dioxide in flue gas and sequester it underground.[2-4] However, the high cost of separating and capturing CO_2 with conventional technologies has prevented the adoption of this approach. This project investigates the technical and economic feasibility of a new membrane process to capture CO_2 from power plant flue gas.

Direct CO_2 capture from power plant flue gas (referred to as simply "flue gas" for the rest of this report) has been the subject of many studies. Currently, CO_2 capture with amine absorption seems to be the leading candidate technology – although membrane processes have been suggested.[5,6] The Achilles heel of previous membrane processes has been the enormous membrane area required for separation, because of the low partial pressure of carbon dioxide in flue gas. To address this problem, MTR has proposed a two-pronged strategy:

1. develop extremely permeable membranes to reduce the membrane area required for CO_2 capture, and
2. design novel countercurrent/sweep modules and use combustion air to generate a driving force for CO_2 transport through these modules.

Membrane permeance directly impacts the capital cost and footprint of a membrane CO_2 capture system. Current commercial membranes have insufficient CO_2 permeances, resulting in membrane areas and capital costs that are not economically competitive with other technologies or the DOE's carbon capture goals. During this program, MTR developed new membranes with ten times the CO_2 permeance of conventional gas separation membranes. These membranes are part of the solution to achieving an economical carbon capture process.

The second aspect of our membrane solution is to use a countercurrent/sweep module design that utilizes a portion of the incoming combustion air as the sweep gas to generate separation driving force, thereby reducing the need for energy intensive compressors or vacuum pumps.[7] Figure 1 shows a simplified flow scheme illustrating our approach.

- In this design, after electrostatic precipitation and desulfurization treatment (not shown), the flue gas from the boiler (stream ①) is directed to a conventional cross-flow membrane module. Driving force for separation in this module is generated by a permeate-side vacuum pump.
- The CO_2-and-water-enriched permeate (stream ②) undergoes a series of compression-condensation steps that recover greater than 99% of the water in flue gas.
- The dried CO_2 (stream ⑦) is then sent to a final compression-condensation-membrane loop that generates a 99+% liquid CO_2 stream ready for sequestration.
- The CO_2-depleted flue gas that leaves as the residue from the first membrane step (stream ③) is sent to a second membrane step that employs a countercurrent/sweep module. This module uses incoming combustion air (stream ④) as a sweep to generate driving force for CO_2 transport. The air sweep strips the remaining CO_2 from the flue gas and then is sent to the boiler for combustion (stream ⑤).

- The treated flue gas leaves as the residue of the sweep module (stream ⑥) and is directed to the power plant stack. Because water has been removed by the membrane process, no reheating of the flue gas is required to prevent condensation in the stack.

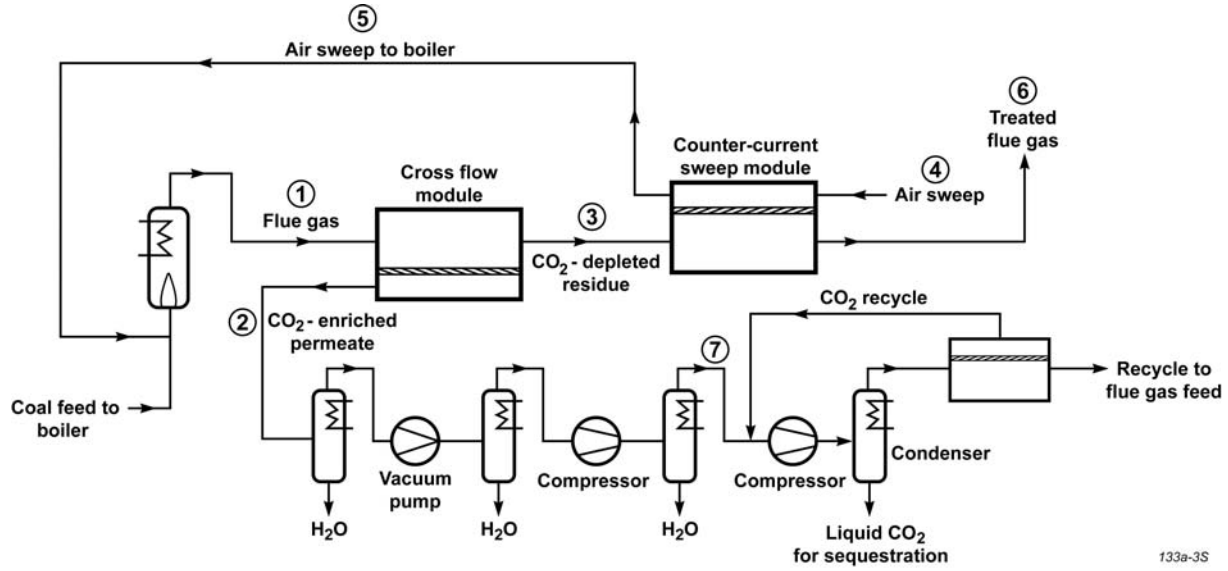

Figure 1. Simplified flow diagram of the proposed membrane process to capture and sequester CO_2 in flue gas from a coal-fired power plant.

This membrane design has several advantages over previously proposed membrane processes:

- Using an existing air stream to generate a CO_2 partial pressure gradient in the second membrane step reduces the need for compressors or vacuum pumps and the associated energy costs. In this way, the sweep module avoids the energy penalty of compression or vacuum treatment and provides an essentially "free" separation.
- By recycling CO_2 to the boiler via the air sweep loop, the CO_2 concentration in the flue gas exiting the boiler increases from about 13% to approximately 18%. This increases the CO_2 partial pressure driving force for transport in the first membrane step. Consequently, the membrane area and system cost is reduced.

Simulations suggest that the Figure 1 process design can separate 90% of the CO_2 in coal-fired flue gas and produce supercritical CO_2 ready for sequestration using less than 20% of the plant energy. The cost of such a membrane capture system is estimated to be in the \$20-\$30/ton CO_2 captured range.

In addition to potential cost and energy benefits, membrane processes, such as that shown in Figure 1, offer a number of other advantages over conventional amine CO_2 capture processes. For example:

- Membrane permeation is a simple, passive operation with no chemical reaction between the membrane and CO_2; therefore, no heat is required to recover CO_2.
- The membranes are not affected by oxygen, water, SO_2, or other acid gases.

- The membrane process does not use hazardous chemicals, and does not require large quantities of liquid absorbent to be pumped around.
- The membrane process does not use extra power plant water; in fact, the Figure 1 design will recover most of the combustion water present in flue gas.
- Membrane systems are compact and modular, and often have $1/10^{th}$ the footprint of equal capacity amine systems in offshore natural gas treatment.

Because of these inherent advantages and recent membrane progress, membrane systems warrant further examination for flue gas CO_2 capture. This project was aimed at clarifying the potential of membranes for this important application and determining priorities for future work.

RESULTS AND DISCUSSION

A number of important accomplishments were achieved during this project; highlights include:

- Membranes with transport properties better than the original project targets were successfully developed, scaled up and produced on our commercial casting and coating equipment. These membranes, called Polaris™ by MTR (and referred to as Polaris™ in the rest of this report), have CO_2 permeances approximately tenfold higher than commercial CO_2 membranes, and two- to three-fold higher than our baseline membrane properties used for the original proposal design calculations. Over 200 m^2 of membrane were prepared during this project.
- A new mixed-gas test system was designed and built to allow parametric module testing with simulated flue gas mixtures under different sweep and non-sweep conditions.
- Conventional cross-flow and novel countercurrent/sweep modules were successfully fabricated from high-CO_2-permeance Polaris™ membrane. Mixed-gas module test data collected under simulated flue gas conditions confirm near-ideal performance of cross-flow vacuum operation and demonstrate the effectiveness of sweep operation.
- Optimized process designs using the properties of the new Polaris™ membranes were developed. These designs suggest a membrane process can capture 90% of flue gas CO_2 as a supercritical stream ready for sequestration using about 15% of the power plant energy. This energy use is about 20% better than that predicted in our proposal design.
- Process design studies also show that improving membrane CO_2 permeance or reducing installed membrane cost are the best ways to further improve the economics of CO_2 capture with membranes. Increasing membrane CO_2/N_2 selectivity above 30 has no benefit because a real-world membrane process to capture CO_2 from flue gas is pressure ratio limited.
- Commercial-scale Polaris™ modules were tested in the field with raw natural gas streams for up to three months of continuous operation. The membrane modules exhibited excellent stability.
- MTR delivered a Polaris™ membrane system to Arizona Public Services (APS) to process 0.15 MMscfd of natural gas-fired flue gas; the system – scheduled for startup in July 2009 – will separate CO_2 from flue gas so that the concentrated CO_2 can be delivered to an algae farm for biofuels production.

Specific details of these results are reported below, organized by task number as described in the project statement of work. All tasks for this project were completed on time and within budget.

Tasks 1 and 2. Membrane Development

Previous membranes could not capture CO_2 from flue gas in an economically viable manner because the membrane CO_2 permeance was too low. This fact, combined with the low partial pressure of CO_2 in flue gas and the enormous flue gas flow rates, resulted in prohibitively large membrane areas. Our design calculations indicate that membranes need to have a minimum CO_2 permeance of about 1,000 gpu (where 1 gpu = 10^{-6} cm^3 (STP)/ $cm^2 \cdot s \cdot cmHg$) and CO_2/N_2 selectivity of greater than 20 to make CO_2 capture with membranes economically feasible.

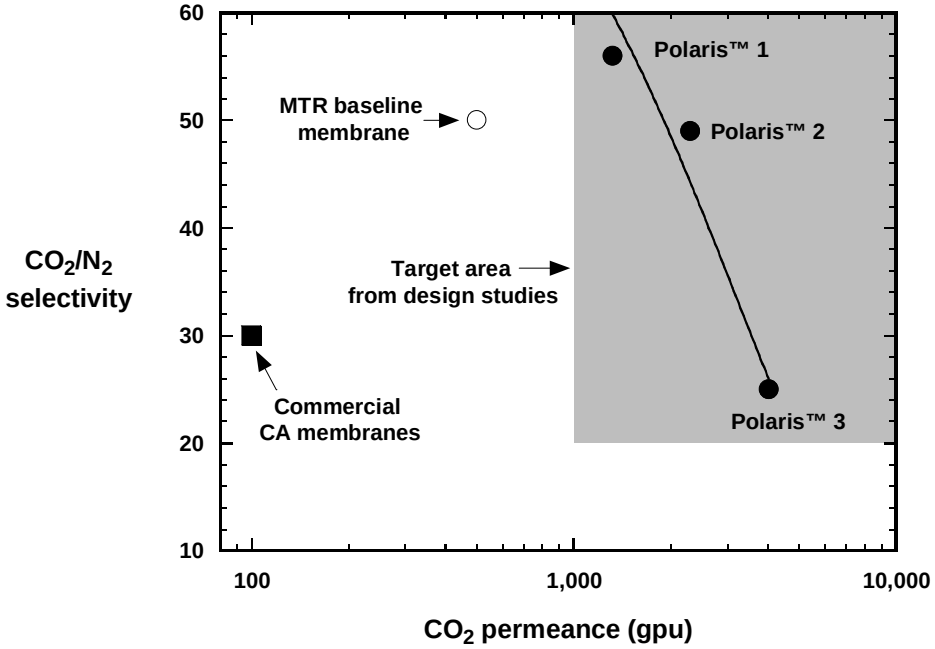

Figure 2. A CO_2/N_2 trade-off plot showing data for MTR membranes developed during this project (Polaris™ 1-3) compared with the baseline MTR membrane and the properties of a commercial cellulose acetate (CA) membrane. The shaded region in the upper-right-hand corner of the plot is the membrane performance target area that is necessary for an economic CO_2 capture process. Data are pure-gas values at room temperature.

Figure 2 shows a trade-off plot of CO_2/N_2 selectivity versus CO_2 permeance for the Polaris™ membranes developed in this project, the original baseline target membrane, and the target window for membrane performance. Polymeric membranes typically exhibit a trade-off relationship between selectivity and permeance; highly selective membranes have low permeances and vice versa. The Polaris™ membranes developed in this project generally follow this trend. However, note that compared to conventional cellulose acetate (CA) membranes used for CO_2 removal from natural gas, the Polaris™ membranes are generally more selective and much more permeable to CO_2. Several Polaris™ membrane formulations exceed the original

baseline membrane properties and extend into the desirable performance window identified from design calculations.

The fabrication of Polaris™ membranes was scaled up from small hand samples, to a laboratory 12-inch-wide coating machine, and finally to our 40-inch-wide commercial coating machine. These membranes can now be prepared reproducibly in the large rolls necessary for commercial use. Table 1 shows sample results for a production run of Polaris™ membrane conducted during this project. This run produced a roll of membrane 300 ft long by 40 inches wide. The membrane made in this run exhibits very uniform properties as illustrated in Figure 3; the average CO_2 permeance is 990 gpu (with a range from 860 to 1,070 gpu) and CO_2/N_2 selectivity averages 55 (ranging from 50 to 61).

Table 1. Pure-Gas Permeances and Selectivities of Polaris™ Membrane Made on MTR's Commercial Casting and Coating Equipment.

Sample Location Along the Membrane Roll		Permeance (gpu)				Selectivity		
		N_2	CH_4	H_2	CO_2	CO_2/H_2	CO_2/N_2	CO_2/CH_4
7 ft	Left	19	65	83	1,070	13	56	17
	Middle	21	65	84	1,070	13	51	17
	Right	20	66	86	1,010	12	51	15
140 ft	Left	18	59	74	960	13	52	16
	Middle	17	57	74	945	13	55	17
	Right	17	54	73	860	12	50	16
205 ft	Left	17	55	76	970	13	57	18
	Middle	18	61	81	1,020	13	55	17
	Right	16	53	72	915	13	57	17
300 ft	Left	18	58	78	1,030	13	59	18
	Middle	17	56	77	1,030	13	61	18
	Right	17	55	73	970	13	59	18

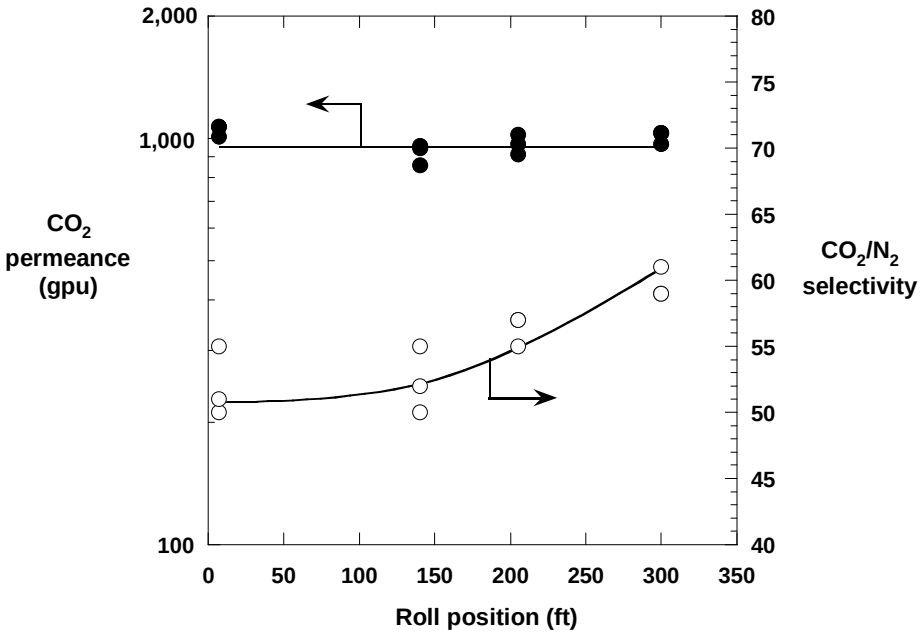

Figure 3. Pure-gas CO_2 permeance and CO_2/N_2 selectivity as a function of sample position along the length of a 300-foot membrane roll.

These results demonstrate the successful commercial development of a high-performance CO_2 capture membrane. A detailed discussion of the performance of this membrane under expected flue gas operating conditions is given in the Task 5 discussion.

Based on the process design studies discussed later in this report (Task 6), future optimization work on the Polaris™ membrane will focus on improving membrane CO_2 permeance while maintaining CO_2/N_2 selectivity. There is a compelling reason to strive for higher CO_2 permeance: doubling the CO_2 permeance will roughly halve the required membrane area, and thus, significantly reduce the capital cost of the membrane system. We believe there is potential to further increase CO_2 permeance by a factor of up to 4.

Task 3. Module Fabrication and Design Optimization

Another innovation that significantly improves the economics of flue gas CO_2 capture with membranes is the use of combustion air as a sweep gas to generate driving force for separation. An air sweep reduces the partial pressure of CO_2 on the permeate side of the membrane, allowing more CO_2 to permeate the membrane. This sweep design replaces a vacuum pump and reduces energy consumption. To utilize air for this purpose requires the development of countercurrent/sweep modules.

Figure 4 shows a diagram of a conventional gas separation spiral-wound module. This device consists of alternating sheets of membrane and spacers wound around a central collection pipe. The spacers create flow channels for the feed and permeated gases as well as providing mechanical support for the membrane sheets. Feed passes axially down the module across the

membrane envelope. A portion of the feed permeates the membrane, flows toward the center of the module, and exits through the permeate collection pipe.

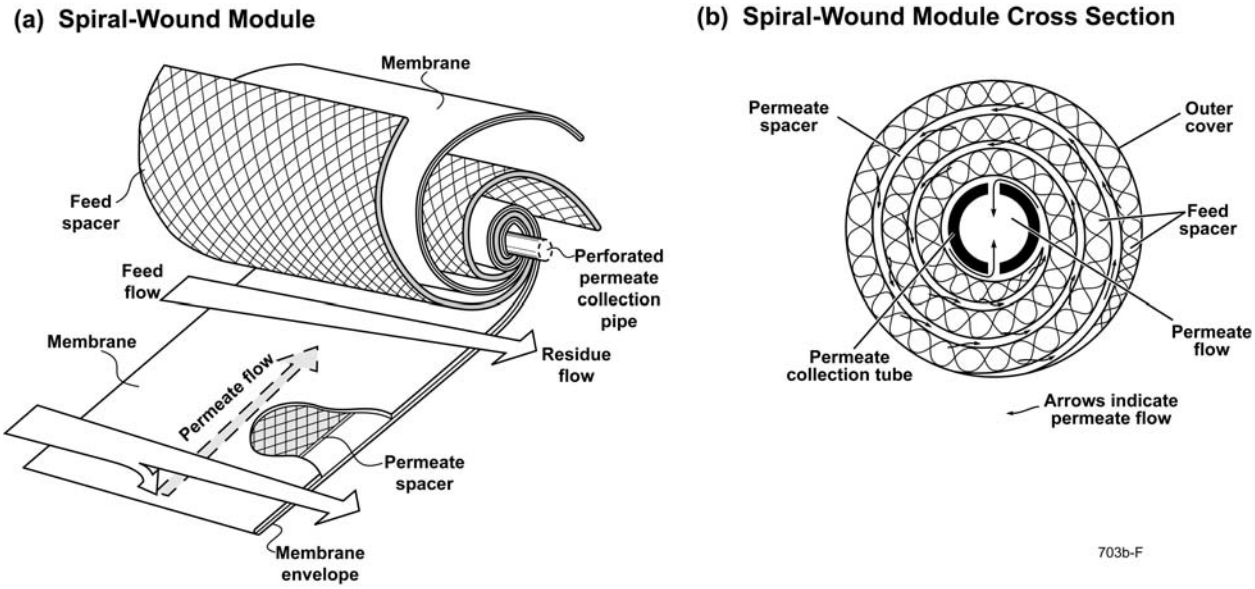

Figure 4. (a) Exploded view of a conventional spiral-wound gas separation module and (b) a cross-section of this module.

The membrane industry standard spiral-wound module is an 8-inch-diameter module containing 15 to 30 membrane envelopes with a total membrane area of 20 to 40 m^2 per module. Spiral-wound modules have captured more than 90% of the reverse osmosis market, more than 70% of the ultrafiltration market, and perhaps 30% of the gas separation market.[8] This module design is robust, fouling resistant, and – most importantly – very economical.

Modification of a conventional spiral-wound module for use as the simplest possible counter-flow membrane contactor is illustrated in Figure 5. This figure shows an exploded view of a single membrane envelope. Two simple changes are required to achieve a countercurrent effect. First, the permeate collection pipe is closed in the middle, forming two separate compartments. Second, during module fabrication, additional glue lines can be applied to direct gas flow in the permeate channel. As shown in Figure 5(b), these modifications allow the permeate channel to be swept with a sweep gas and the module to operate in a partial countercurrent mode. The permeate gas, together with the sweep gas, flows countercurrent to the feed gas flow.

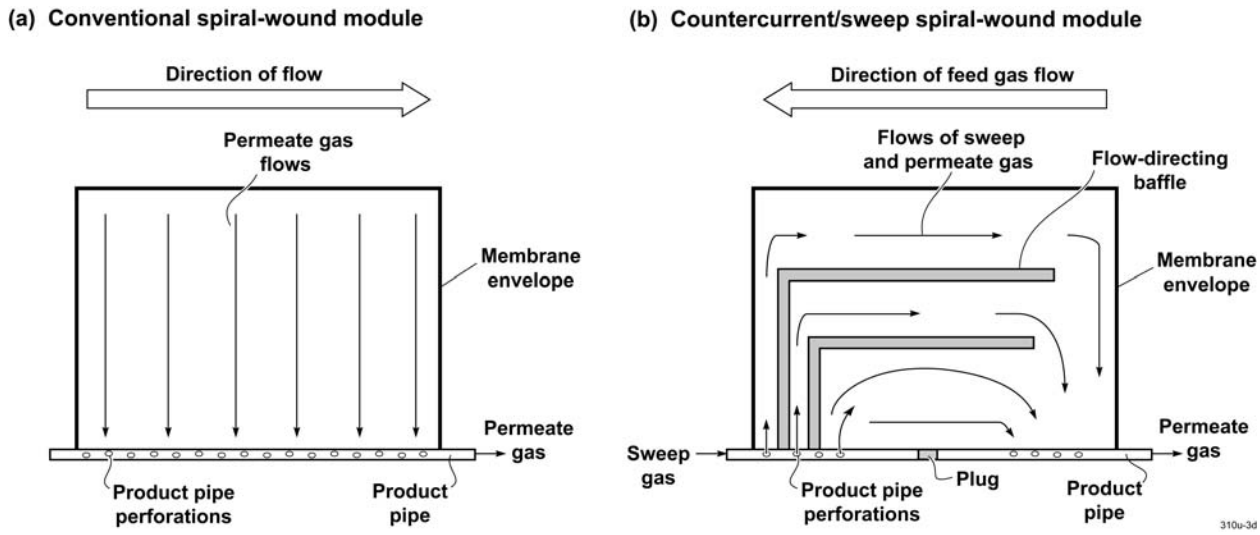

Figure 5. Unwound view of the membrane envelope for two types of spiral-wound modules. The flow pattern in the conventional module (a) is cross-flow, whereas the modified module (b) accepts a sweep gas on the permeate side and operates in a partial countercurrent pattern.

MTR has used the simple, countercurrent/sweep module design – shown in Figure 5(b) - in research projects for several years, and it has been effective for certain separations and process conditions. However, in flue gas CO_2 capture, where the pressure differential across the membrane is low, it was necessary to revisit the module design to optimize separation. Previous results for similar process conditions have shown that there are several potential inefficiencies that limit the effectiveness of countercurrent/sweep operation. These potential inefficiencies include

- sweep-side pressure drop,
- concentration polarization (especially on the sweep side in the porous support layer of the membrane),
- poor utilization of membrane area due to module geometry, and
- non-countercurrent flow patterns.

The goal of module design work is to minimize these inefficiencies. Sweep module test results, which are discussed later in this report (see the Task 5 discussion), show that our current design yields effective sweep operation. Of the issues listed above, sweep-side pressure drop appears to be the most critical challenge.

Sweep-Side Pressure Drop

One module characteristic that can reduce the effectiveness of sweep operation is sweep-side pressure drop. If there is significant resistance to gas flow through the sweep side of a module, additional energy will be required to push gas through the module elements. In addition, higher pressure at the module sweep-side entrance is detrimental to system performance because it will increase the driving force for undesirable oxygen transport through the membrane. Because of

the low operating pressure of the flue gas treatment system, even small pressure drops within a module should be avoided to maximize efficiency. This situation is different from conventional high-pressure membrane separations where 5 to 20 psi pressure drops through a module are typical and easily tolerated.

Flow channels in spiral-wound modules are created by spacer elements. Alternating sheets of membrane and spacers are wound around a central collection pipe, as shown in Figure 4(a). In addition to forming flow channels for the feed and permeated gases, spacers provide mechanical support for the membrane sheets. Most spacers are made from relatively low-cost plastics (polyethylene, polypropylene, polyesters) extruded into nettings or meshes formed by woven/nonwoven textile methods. An example of a spacer material is shown in Figure 6. Such spacers are used in gas separation and reverse osmosis modules because of their low cost, ability to resist channel collapse in high-pressure-differential operation, and inherently tortuous flow path that promotes good mixing and limits boundary layer effects.

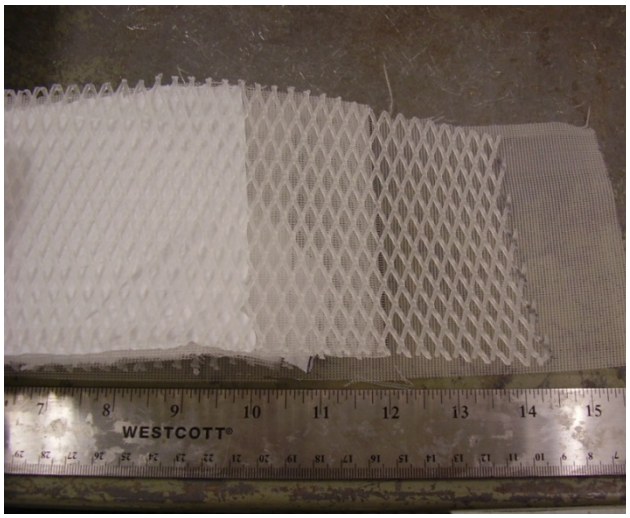

Figure 6. An example of a netting spacer used in gas separation membrane modules.

Pressure drop of a gas in a spacer channel is caused by flow resistance. Different spacer materials impart different flow resistances depending on the porosity and geometry of the spacer. The pressure drop through a porous spacer channel can be described by the Dusty-Gas model, which has the following form for a single gas:[9]

$$J = K\Delta P / L \tag{1}$$

where J is the gas molar flux, K is the permeability coefficient of the channel, ΔP is the pressure drop in the channel, and L is the channel length. The channel permeability coefficient consists of diffusive (Knudsen diffusion) and convective contributions:

$$K = D + B\bar{P} \tag{2}$$

where D is the Knudsen diffusion coefficient, B is a convective flow parameter, and $\bar{P}$ is the average pressure in the channel. According to equation (2), a plot of the permeability coefficient versus the average channel pressure will yield a straight line with a slope equal to B and an intercept equal to D. For spacer materials such as those shown in Figure 6, the Knudsen contribution is negligible ($D = 0$), and simple flow tests can be used to determine B. Data from such tests can be used to compare different materials and estimate the anticipated pressure drop in a full-scale module.

We conducted a series of flow rate versus pressure drop experiments in a specially designed test cell to quantify the flow characteristics of different spacer materials. This cell allows for rapid screening and evaluation of the intrinsic flow properties of different spacers. Table 2 shows the convective flow parameter, B, for several different spacers used by MTR. The convective flow parameter characterizes the relative ease of flow through a spacer, with higher B values indicating less resistance to transport. The data in Table 2 show that the ease of transport through the spacers examined varies by nearly two orders of magnitude. Consequently, for the same flow rate and cross-sectional area, a spacer channel formed by Type RP will incur substantially lower pressure drop than one formed by Type H1. At the same time, the Type H1 spacer, because it is denser, provides better mechanical support for the membrane. These factors must be balanced when choosing the appropriate material for an application. Because of the low operating pressures and minimal pressure drop requirements for sequestration, open spacers such as Type RP are preferred.

Table 2. Convective Flow Coefficient, B, for Various Module Spacers.

Spacer Type Tested[a,b]	Spacer Height (mm)	Viscous Flow Coefficient (B), (cm^3 (STP) cm / (cm^2·s·$cmHg^2$))
Two Type H1	0.370	2.04
Two Type S MD	0.312	4.57
Two Type 10PR MD[c]	0.384	12.4
Two Type H2 MD	0.480	12.8
One Type LP MD	0.508	25.6
One Type LN CD	0.520	27.3
One Type LN MD	0.520	61.6
One Type RP MD	0.846	138

a. Each type designation for a spacer (for example, Type H, Type S) represents a different chemical/polymer composition; specific compositions are confidential.
b. MD = machine direction; CD = cross direction.
c. The 10 PR spacers were nested; actual thickness of a single spacer is 0.254 mm.

The spacer flow parameters summarized in Table 2 have been utilized to select the appropriate materials for use in the membrane modules that are tested and described in Task 5. These data also allow the pressure drop in full-scale module skids that will be used to treat flue gas to be estimated.

Task 4. Bench-Scale System Construction

Due to the frequency and nature of module tests required in this project, we designed and built a dedicated bench-scale system for evaluating module performance. A picture of this test system

is shown in Figure 7. The system is designed to test 4-inch diameter bench-scale modules with an active membrane area of about 1 m^2. Both cross-flow and countercurrent/sweep modules can be tested with simulated flue gas mixtures. Various operating parameters, such as flow rates, temperature, and pressures, can be varied over the anticipated flue gas process conditions. This system was used to collect the bench-scale module performance data described in Task 5.

Figure 7. Mixed-gas bench-scale module test system.

Figure 8 shows a flow diagram for the module test system. The cross-flow and countercurrent/sweep pressure vessels are situated in parallel, allowing for easy switching between module types during testing. Both vessels take the same stream as feed, which is split downstream of the compressor. The residues of both vessels are recycled to the compressor. However, while the permeate stream of the cross-flow vessel is recycled, the permeate and sweep stream of the countercurrent module is vented to the atmosphere. The sweep stream is pure air, and venting the permeate and sweep stream prevents the recycle loop from being diluted with this gas. Because of the partial pressure difference between permeate and feed sides, some oxygen will permeate to the feed side of the sweep module and build up in the recycle loop. Thus, for safety reasons, an oxygen sensor is in place on the feed side of the module.

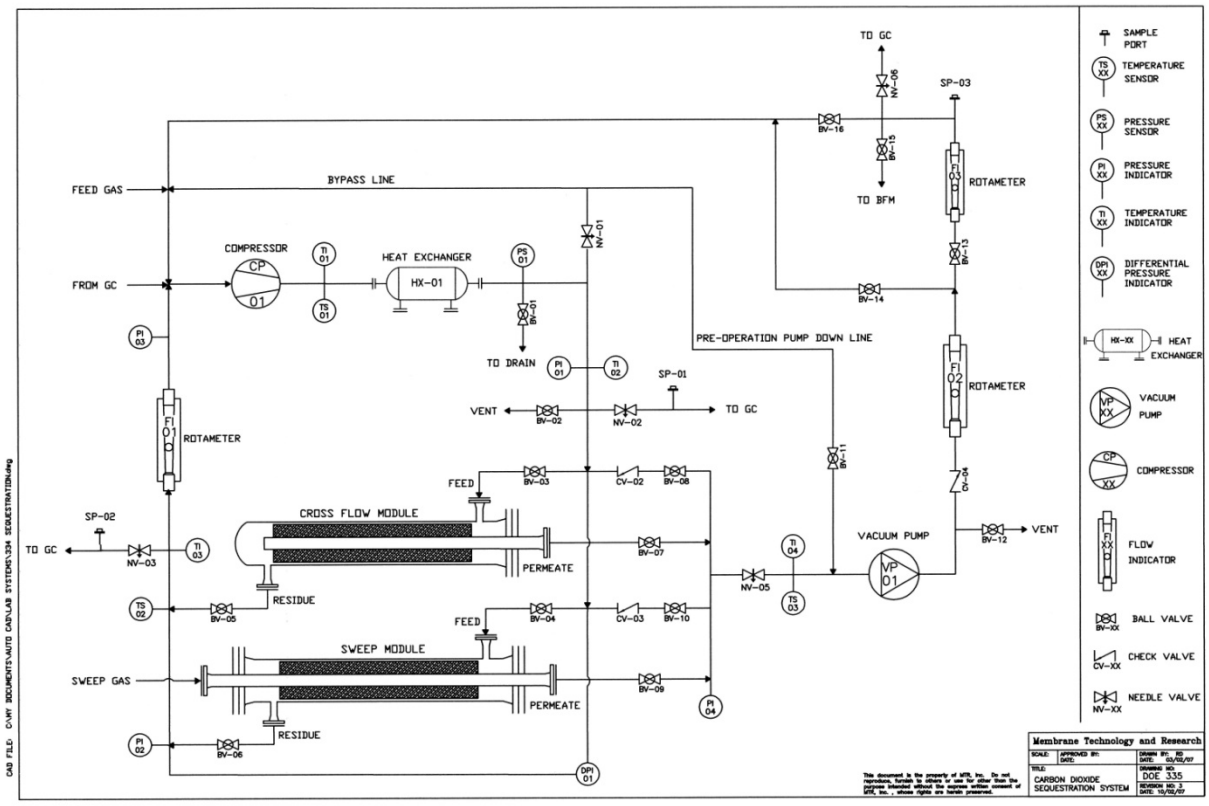

Figure 8. Flow diagram for the module test system built to test cross-flow and countercurrent/sweep modules in parallel.

Task 5. Parametric Module Tests

Using the new system built in Task 4, parametric testing was conducted on a number of Polaris™ membrane modules. The purpose of these tests was to evaluate how well actual module performance matches the intrinsic membrane properties, to identify areas where module improvement efforts should be focused, and to obtain module performance data for use in design calculations.

As shown in our proposed process design (see Figure 1), to effectively recover CO_2 from flue gas, two different types of modules are required – conventional cross-flow modules to provide a first-cut bulk CO_2 removal, and countercurrent/sweep modules to recover the remainder of the CO_2 in a cost- and energy-efficient manner. During this project, several modules of each type were tested. Representative results for each type of module are discussed separately in the following sections of the report.

Cross-Flow Module Test Results

Table 3 shows pure-gas permeances and selectivities as a function of temperature for one of the first Polaris™ cross-flow modules (4389) made during this project. The Polaris™ membrane used to prepare this module had a pure-gas CO_2 permeance of about 600 gpu coupled with a pure-gas CO_2/N_2 selectivity of 55. Optimized Polaris™ membrane produced later in the project

would show better CO_2 permeance (see Table 1); nevertheless, the temperature and mixture effects described below for module 4389 are still relevant for improved, higher permeance modules.

Table 3. Pure-Gas Permeances and Selectivities in Module 4389 as a Function of Temperature. The feed pressure is 20 psia and permeate pressure is 5 psia.

Temperature (°C)	Gas Permeance (gpu)			Selectivity	
	N_2	O_2	CO_2	CO_2/N_2	CO_2/O_2
21	12	28	530	44	19
35	22	50	908	41	18
50	43	93	1,160	27	12

Based on the data in Table 3, the pure-gas CO_2/N_2 selectivity of module 4389 at room temperature is lower than that of stamps taken from the membrane used to prepare the module. The primary reason for this difference appears to be related to CO_2 feed pressure in the permeation tests. For the module, pure-gas CO_2 permeance was measured at 5 psig, while the membrane stamps were measured with a feed pressure of 50 psig. CO_2 permeance increases with increasing feed pressure in Polaris™ membranes, so the lower module CO_2/N_2 selectivity is likely related to the test conditions.

Also shown in Table 3 is the effect of temperature on the performance of module 4389. As temperature increases, pure gas permeances increase, while CO_2/N_2 and CO_2/O_2 selectivities decrease. This behavior is typical for polymer membranes, largely because of solubility effects. As temperature increases, the solubility of condensable CO_2 decreases much more than that of light gases, such as N_2 or O_2. On the other hand, the diffusivity of all of the gases increases with increasing temperature. As a result, permeability – equal to the product of solubility and diffusivity – increases faster with increasing temperature for the light gases. Consequently, membrane CO_2/N_2 selectivity decreases with temperature. If flue gas CO_2 capture occurs at 50°C, the membrane selectivity (27 in these tests) will be lower than at room temperature, but the CO_2 permeance will be higher. As described later in this report, higher permeance is preferred as long as a target CO_2/N_2 selectivity of 20 or so is maintained at real operating conditions.

Figure 9 shows test results for module 4389 with a feed gas containing between 16% and 20% CO_2 in N_2 at different temperatures and feed or permeate pressures. As feed pressure increases or permeate pressure decreases, the CO_2 partial pressure difference across the membrane increases, leading to an increase in CO_2 flux. These results are consistent with theoretical expectations. As feed temperature increases from 35 to 50°C, the module mixed-gas CO_2 flux also increases, consistent with the pure-gas results shown in Table 3.

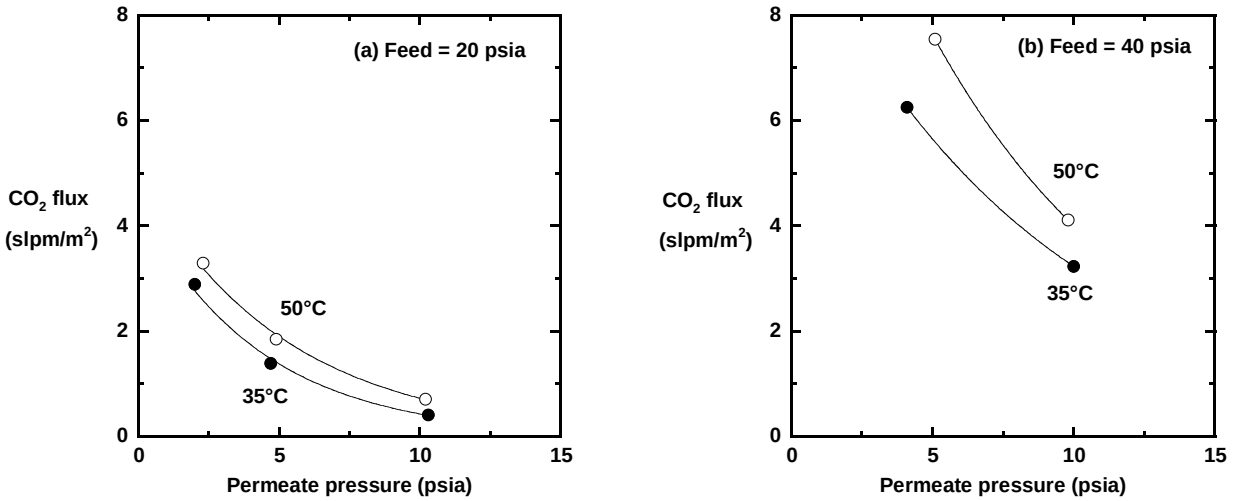

Figure 9. CO_2 flux (slpm/m^2: standard liters per minute/m^2 membrane area) as a function of temperature and permeate pressure in cross-flow module 4389 at (a) 20 psia feed pressure and (b) 40 psia feed pressure. The feed contains 16% to 20% CO_2 in N_2. The lines on the graph are provided to guide the eye.

Figure 10 compares the measured performance of module 4389 to the maximum separation performance of the module as calculated in simulations. Figure 10(a) shows the ideality of CO_2 flux, which is defined as the percentage of measured CO_2 flux through the module relative to the theoretical or ideal CO_2 flux. The values of ideal CO_2 flux were obtained with computer simulation software (ChemCad 5.6) modified by MTR with proprietary membrane process code. For these calculations, the measured feed composition, pressure and flow rate; membrane area; and pure-gas permeances (as shown in Table 3) were used. For all experimental data points, the measured CO_2 flux is at least 80% of the theoretical value obtained from simulations. These results confirm that under mixture conditions similar to those expected in real-world flue gas, the module performs as expected with regard to CO_2 permeation.

For the same set of experiments as described above, Figure 10(b) shows CO_2/N_2 separation performance (or CO_2 enrichment) in module 4389 by providing a plot of the permeate CO_2 concentration as a function of permeate pressure at 50°C. The membrane module can effectively enrich CO_2 in the permeate. For example, one pass through module 4389 can enrich CO_2 from 16% in the feed to 58% in the permeate at a permeate pressure of 2.3 psia. Figure 10(b) also compares the experimental and simulated separation performance. Experimental CO_2 concentrations in the permeate are slightly below the simulation results, suggesting that membrane selectivity in the mixture is lower than the ideal pure-gas values used in the calculations. Nevertheless, these results generally confirm that this cross-flow Polaris™ module performs as expected and will be effective for CO_2 capture from flue gas.

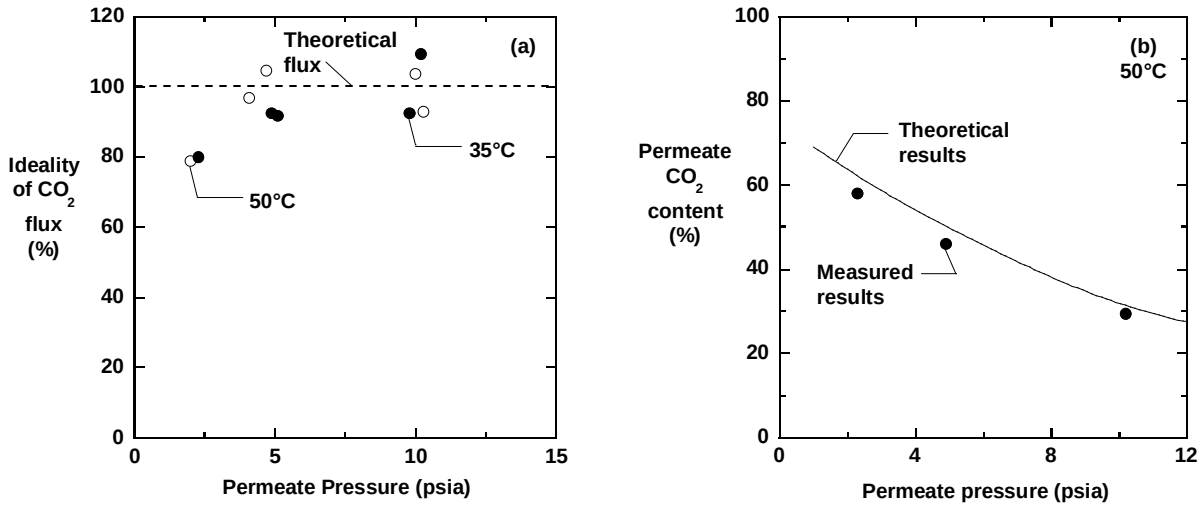

Figure 10. CO_2/N_2 separation performance in crossflow module 4389 as a function of permeate pressure with a feed containing 16% to 20% CO_2 in N_2. The stage cut in these experiments varies from 6 to 15%. (a) Ideality of CO_2 flux, which is defined as the percentage of measured CO_2 flux relative to the ideal (or theoretical) CO_2 enhanced with membrane process code. The simulation uses pure-gas permeance values as shown in Table 3. (b) Comparison of simulated and measured CO_2 concentration in the permeate at 50°C.

For additional modules prepared in this project, our focus was on increasing membrane permeance and improving pressure drop characteristics. For example, Table 4 compares data for three 4-inch diameter, 40-inch long (commercial length) test modules fabricated later in this project. As shown in Table 4, the newest module (5549) has the highest pure-gas permeances produced to date, due to the use of improved membranes.

Table 4. Comparison of Pure-Gas Permeances and CO_2/N_2 Selectivity and Feed-to-Residue Pressure Drop in Modules 4488, 5414 and 5549.

Module	Membrane Formulation	Module Design	Feed-to-Residue Pressure Drop (psi)	Pure-Gas Permeance* (gpu)		Pure-Gas CO_2/N_2 Selectivity
				N_2	CO_2	
4388	Regular	Generation 1	2.0	12	530	44
5414	Regular	Generation 2	<0.1	9	450	50
5549	New	Generation 2	0.1	17	890	54

* In permeance measurements, the feed pressure was 25 psia and permeate pressure was 15 psia.

During this project, we also changed the module design to achieve a lower feed-to-residue pressure drop. Comparing the feed-to-residue pressure drops of modules 4488 and 5414 in Table 4, the new generation module (5414) shows lower pressure drops compared to Module 4488.

This improvement is important to minimize the energy penalty associated with pumping flue gas through the CO_2 capture membrane system. More details of the performance of later generation modules, such as 5549 and 5414, are described in quarterly reports for project DE-NT0005312, which overlapped with the end of this project.

In summary, cross-flow Polaris™ modules were successfully fabricated from high-performance membrane to be used in the first step of our flue gas process design (see Figure 1). The modules exhibit near-ideal performance when tested with a simulated flue gas (CO_2 and N_2) under a range of conditions that might be expected in the actual application. These experimental findings validate the process design calculations discussed in Task 6.

Countercurrent/Sweep Module Results

Several countercurrent/sweep modules based on the MTR Polaris™ membranes were made during this project. Figure 11 compares the measured CO_2 flux of module 4429 at various sweep/feed flow ratios to the theoretical results for these experimental conditions and for the case of no sweep (ChemCad 5.6). Without the use of sweep, the CO_2 flux through the module is relatively low because of a small CO_2 partial pressure difference across the membrane. As the sweep flow rate increases, the CO_2 flux through the module increases dramatically in agreement with theoretical predictions. For example, in going from 0 to 60% sweep/feed ratio, the CO_2 flux through the module increases nearly tenfold. Further increases in sweep flow rate have little effect on CO_2 flux, again in agreement with the asymptotic theoretical behavior. In the Figure 1 design, the sweep/feed flow ratio is likely to be 70 – 100%.

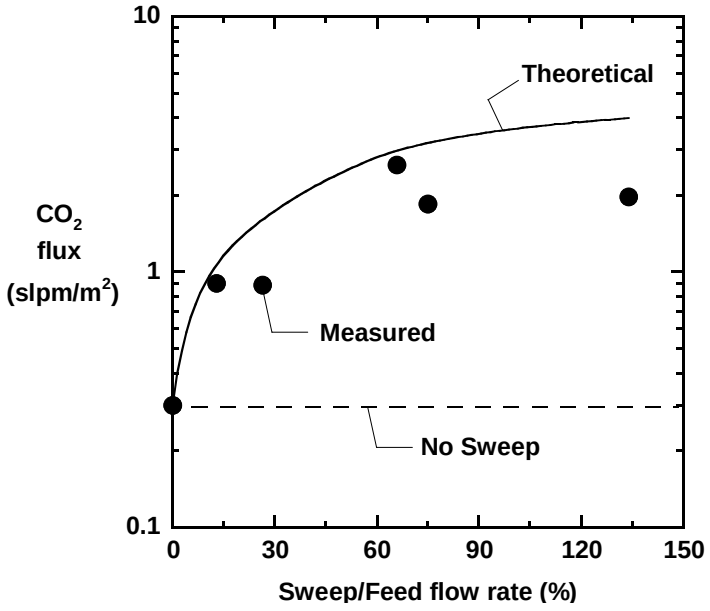

Figure 11. Comparison of experimental and theoretical CO_2 flux as a function of sweep/feed flow ratio for module 4429. The feed gas in these experiments was 10% CO_2 in nitrogen at 20 psig and the sweep gas was pure nitrogen at 0 psig. The dashed line shows the theoretical CO_2 flux if no sweep is used.

Overall, the performance of sweep module 4429 is very good. The experimental CO_2 fluxes are slightly below the theoretical line perhaps due to resistance in the support membrane substructure that hinders mixing of the sweep gas and permeated CO_2. While some further optimization is possible, the Figure 11 results show that current Polaris™ sweep modules can be effectively used in the second step of our design to capture CO_2 from flue gas.

Different spacer materials and configurations were tested to improve the pressure drop performance of sweep modules. Figures 12(a-d) compare pressure drop values in the feed and permeate streams of two modules, 4299 and 4429. By optimizing the spacer materials and module design, module 4429 exhibits much less pressure drop on both feed and permeate sides compared to module 4299. Low feed-to-residue and sweep-to-permeate module pressure drops are critical to minimize the energy burden on the feed side blower/compressor and the permeate side vacuum pump. The dotted lines in the figures represent the anticipated operational superficial velocities (375 cm/s for the feed side and 40 cm/s for the sweep side) in the actual flue gas application.

Module 4429 clearly shows improved pressure drop performance. For example, at the expected feed superficial velocity, the feed-to-residue pressure drop of module 4429 is 0.5 psi compared to 2.6 psi in module 4299. Similarly, on the permeate side, the pressure drops at the expected sweep superficial velocity are 2.0 psi and 7.0 psi, respectively, in modules 4429 and 4299. Although the pressure drops through module 4429 are quite low and consistent with estimates used in design calculations, further optimization, particularly, on the permeate or sweep side of the module, has the potential to noticeably improve the energy requirements for a membrane CO_2 capture process. For example, for the air stream going to a 600 MW power plant, every additional 1 psi of pressure drop through the modules requires roughly 2-3 MW of blower capacity.

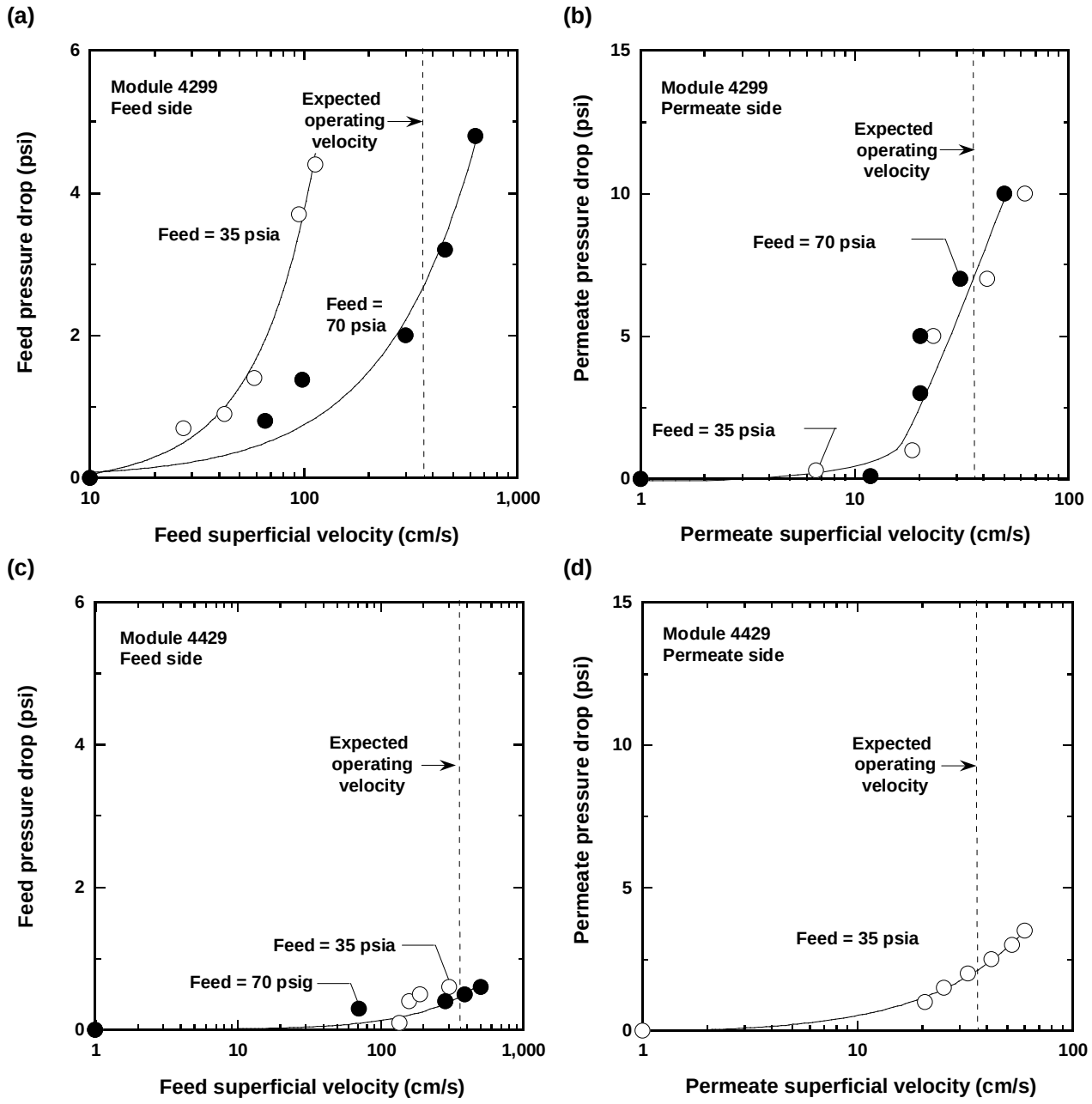

Figure 12. Comparison of pressure drop characteristics in modules 4299 and 4429. (a) Feed side pressure drop in module 4299; (b) permeate side pressure drop in module 4299; (c) feed side pressure drop in module 4429; and (d) permeate side pressure drop in module 4429. Superficial velocity is defined as gas flow (cm^2(STP)/s) per cm^2 of cross-sectional area. The dotted lines represent the anticipated superficial velocity of the process design.

Field Tests

Field tests of our CO_2 capture membrane were not included in the work plan of this project. However, because of rapid progress on membrane and module development, we felt that

Polaris™ modules were ready for testing with real-world gas mixtures. Our previous experience with commercial membrane systems has shown that there is no substitute for actual real-world operating experience. While we did not have access to industrial flue gas sites during this project, we had the opportunity to include our membranes in a field test involving the removal of CO_2 and heavy hydrocarbons from raw natural gas.

Figure 13 shows a picture of MTR's test system at BP's Pascagoula, Louisiana natural gas processing plant. This system was installed and run as part of an earlier DOE NETL funded program (DE-FC26-99FT40723). On the left, module housings containing 8-inch diameter (20 m^2) membrane modules are visible. Three 8-inch Polaris™ modules were built, installed at the site, and processed feed gas at 950 psia on this system for three months.

Figure 13. A picture of an MTR membrane test skid for treating natural gas. This unit was installed at BP's Pascagoula, Louisiana gas processing plant.

The initial pure-gas properties of the modules tested at Pascagoula are summarized in Table 5. During the field test, the modules were exposed to a feed mixture containing CH_4, CO_2, N_2, and various hydrocarbon (C_2 to C_{6+}) vapors. The modules selectively removed CO_2 and the hydrocarbon vapors from natural gas and maintained expected performance throughout the test period. After 3 months of operation, the modules were returned to MTR and found to be in excellent condition. Pure-gas tests showed module performance consistent with initial properties. This test demonstrated the robustness of the membrane modules in a challenging industrial environment (high pressure and high C_{3+} content).

Table 5. Pure-Gas Permeances of Three 8-inch Polaris™ Modules Field Tested With Raw Natural Gas. Data were measured at room temperature and a feed pressure of 5 psig prior to installation and testing at Pascagoula.

Module	Gas Permeance (gpu)				CO_2/N_2 Selectivity
	N_2	CH_4	H_2	CO_2*	
4522	18	56	78	630	35
4523	19	57	76	630	33
4205	13	36	57	520	40

* Feed pressure reading for the CO_2 permeance tests was 0.8 psig. Because of this low pressure reading, the CO_2 permeance data are somewhat uncertain. CO_2 permeances for the membranes used to make the modules ranged from 700 to 1,000 gpu.

After the Pascagoula test, Arizona Public Services (APS) ordered a membrane system to concentrate CO_2 from their Red Hawk natural gas power plant (Phoenix, AZ) for delivery to an algae farm. By concentrating CO_2 with a membrane system, the volume of gas that must be piped from the power plant stack to the algae farm can be greatly reduced. MTR built and delivered a Polaris™ membrane system to APS in 2008. As shown in Figure 14, the system can accommodate two 8-inch diameter (20 m^2) Polaris™ modules. There is a liquid ring vacuum pump on the permeate side of the membrane, which can provide a permeate pressure as low as 2 psia. This demonstration system will treat 0.15 MMscfd of flue gas and capture about 250 lb CO_2/day. The system has been installed and will be started up in the summer of 2009.

Figure 14. Photograph of an MTR membrane test skid for enriching CO_2 from natural gas-fired flue gas. This unit has been delivered to APS' Red Hawk natural gas-fired power plant, just west of Phoenix, AZ.

While the flue from a natural gas power plant lacks the contaminants that are generated by a coal-fired plant, the Red Hawk membrane system will provide valuable operational experience working in a power plant environment. In addition to providing technical data, a successful test run will help generate user confidence in membrane CO_2 capture technology. Such a reference will be useful when selecting coal-fired power plant test sites. Results from this system will be reported in progress reports for our new DOE NETL program.

Task 6. Process Designs and Technical/Economic Analysis

An important, often overlooked, aspect of research on using membranes to capture CO_2 from flue gas is process design. Frequently, literature sources focus on the simplest possible membrane designs, such as those illustrated in Figure 15. In these single-stage membrane processes, flue gas is fed to a membrane module and a pressure driving force is generated by either (a) compression on the feed side or (b) a vacuum on the permeate side of the membrane. Calculations show that the required energy is considerably lower for the vacuum process because the vacuum only has to pump roughly 10% of flue gas that permeates the membrane (largely CO_2), whereas a feed compressor pressurizes all of the flue gas (CO_2 plus the bulk N_2). While the vacuum process uses less energy than feed compression, it requires a much larger membrane area because the pressure difference across the membrane is small.

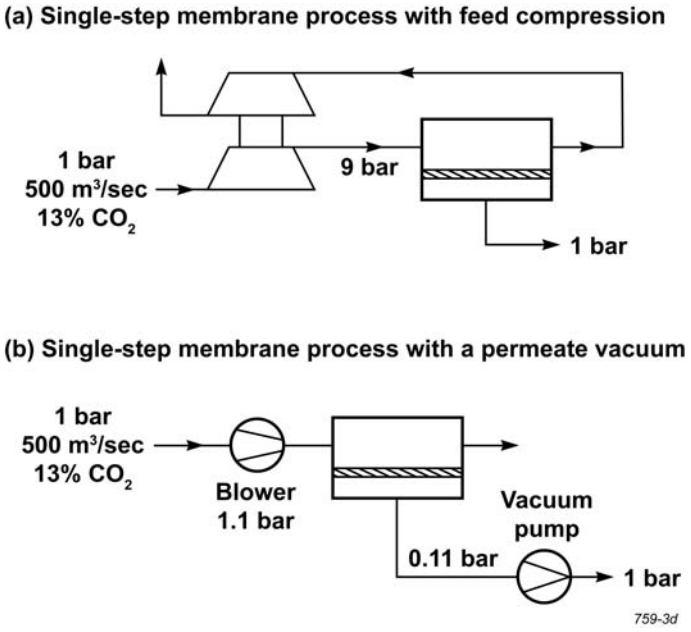

Figure 15. Single-step membrane processes to capture CO_2 in flue gas using (a) feed compression and (b) permeate vacuum at a 600 MW power plant. For (a) the membrane area is 590,000 m^2 and the power is 104 MW; for (b) the area is 4.8 million m^2 and the power is 68 MW.

In addition to large membrane area or power requirements, single-stage membrane designs are unable to produce high-purity CO_2 *combined* with high CO_2 recovery. In fact, a single-stage membrane process alone cannot produce high-purity CO_2 in the permeate with 90% CO_2 recovery, regardless of the membrane selectivity. This is because the system performance is limited by the pressure ratio across the membrane.

The importance of pressure ratio in the separation of gas mixtures can be illustrated by considering the separation of a gas mixture with component concentrations c_{i_o} and c_{j_o} at a feed pressure of p_o. A flow of component *i* across the membrane can only occur if the partial pressure of component *i* on the feed side of the membrane, $c_{i_o} p_o$, is greater than the partial pressure of

component i on the permeate side of the membrane, $c_{i_l} p_l$. That is, permeation occurs if $c_{i_o} p_o > c_{i_l} p_l$. It follows that the maximum separation achieved by the membrane can be expressed as

$$\frac{c_{i_l}}{c_{i_o}} \leq \frac{p_o}{p_l} \tag{3}$$

This means that the separation achieved can never exceed the pressure ratio of p_o / p_l , no matter how selective the membrane. In practical separation applications, the pressure ratio across the membrane is usually between 5 and 15. Higher pressure ratios can be achieved by using larger compressors on the feed gas or larger vacuum pumps on the permeate, but the capital and energy cost of this equipment limits the practical range.

An example of the impact of pressure ratio on membrane separations is the membrane vacuum process shown in Figure 15(b). In this case, the feed-to-permeate pressure ratio is 10 (1.1 bar/0.11 bar). Under these conditions, the difference in performance for a membrane with a selectivity of 50 or one with selectivity of 500 is small. This point is illustrated in Figure 16 which shows the permeate CO_2 concentration as a function of permeate pressure for membranes with these selectivities. In these calculations, the CO_2 recovery is fixed at 90%.

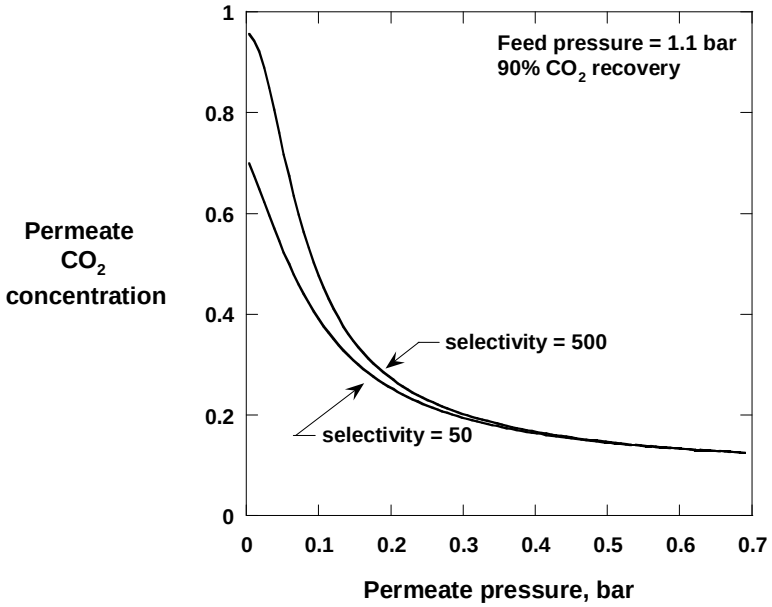

Figure 16. Calculated permeate CO_2 concentration as a function of permeate pressure for membranes with a CO_2/N_2 selectivity of 50 and 500. CO_2 recovery was fixed at 90%.

Because of pressure ratio limitations, the difference in CO_2 permeate concentration for the two membranes is small when the permeate pressure is 0.1 bar or greater. The higher selectivity membrane will only improve performance if the pressure ratio is increased by increasing the feed pressure or reducing the vacuum pressure. Both of these approaches

increase capital and energy costs in an unacceptable manner. We make this point because there is a widespread belief that higher selectivity membranes are required for a useful CO_2 separation membrane. In fact, the point of diminishing returns is reached at a CO_2/N_2 selectivity of 20 to 30, or about 3 times the normal maximum practical pressure ratio.

For the reasons given above, a multi-step or multi-stage membrane design is required to achieve the desired CO_2 recovery and purity.

Two-Step Membrane Design with Countercurrent Sweep

A number of different multi-stage and multi-step designs were considered to identify an efficient membrane process for carbon dioxide capture from flue gas. The objective of these calculations was to identify a membrane design that would minimize the energy and capital cost of a CO_2 capture process. Specifically, the targets were a process that would capture 90% of the CO_2 in flue gas and deliver high-purity liquid CO_2 ready for sequestration, while using less than 20% of the power plant energy and providing a CO_2 capture cost of less than $40/ton CO_2.

Our current best design is the process illustrated in Figure 1, and repeated for convenience in Figure 17. In this design, a vacuum pump is used on the permeate side of the first membrane step. As discussed above, because the volume of the permeate gas (stream ②) passing through the vacuum pump is only a fraction of the volume of the flue gas (stream ①), the power used by the vacuum pump is much smaller than the power consumed by compressing the feed gas. This first membrane unit only removes a portion of the CO_2 in flue gas, to reduce the membrane area and energy required in this step. The residue gas leaving the first membrane unit (stream ③) still contains 7.4% CO_2. This gas passes on one side of a second membrane unit that has countercurrent/sweep configuration. The feed air to the boiler (stream ④) passes on the other side of this membrane as a sweep stream. Because of the difference in concentration of CO_2, some CO_2 passes through the membrane and is recycled with the feed air to the boiler (stream ⑤). The treated flue gas (stream ⑥) leaving the countercurrent membrane unit contains only 1.8% CO_2 and is vented – 90% CO_2 removal is achieved.

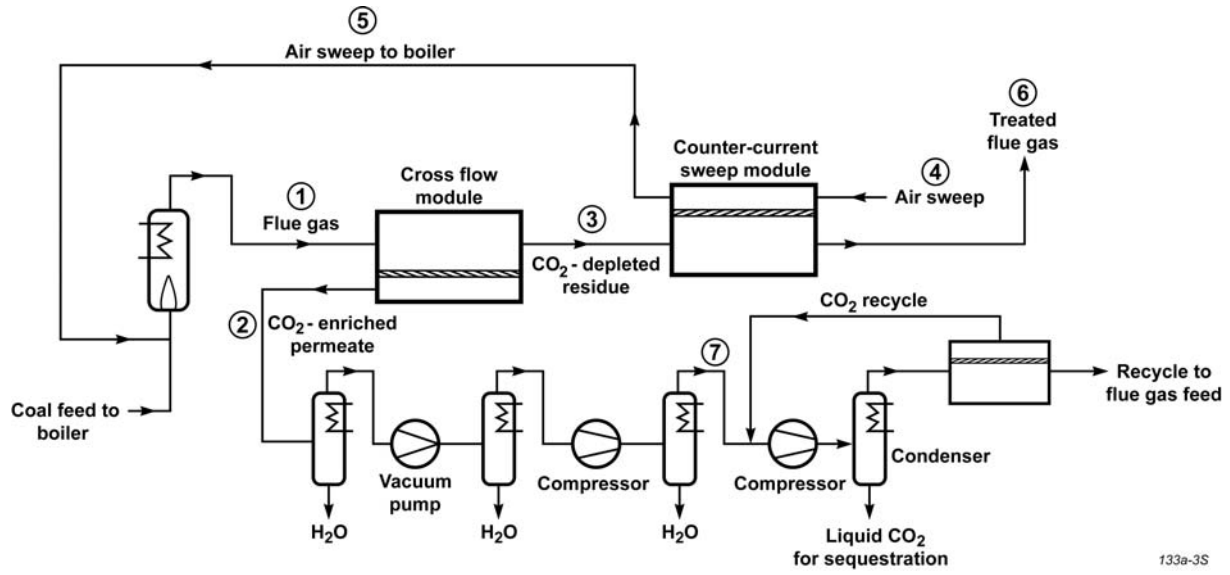

Figure 17. Flow diagram of the proposed membrane process to capture CO_2 in flue gas from a coal-fired power plant. Optimization and sensitivity studies conducted in Task 6 were based on this design.

Compared to the simple designs discussed above, the two-step design with countercurrent sweep offers a number of benefits:

- Lower energy use because the countercurrent module design uses incoming combustion air to generate driving force for CO_2 separation;
- Lower membrane area because the CO_2 recycled in the combustion air stream increases the CO_2 partial pressure gradient in the first membrane step;
- Greater than 99% recovery of water in the flue gas, with the consequence that no reheating of the flue gas is required to prevent condensation in the stack;
- A high efficiency compression-condensation-membrane loop that delivers >98% liquid CO_2 ready for sequestration.

Using the process shown in Figure 17, sensitivity studies were conducted to examine the effect of various design parameters on the efficiency of CO_2 capture. There are a number of metrics that can be used to evaluate the efficiency of a CO_2 capture design including the capital cost of the capture equipment, the parasitic energy requirement for capture, the increase in the cost of electricity due to capture, and the overall cost of capture per ton of CO_2 captured. These measures of capture efficiency are subject to a number of assumptions that are necessary to estimate their values. As a consequence, values quoted in literature sources can vary considerably. To establish a baseline, the assumptions used in our calculations are summarized in Table 6.

The compressor/pump efficiencies and cost factors are today's values for commercial gas separation systems. The base-case membrane cost of \$150/m^2 is lower than the range for today's commercial gas separation systems (\$500-\$750/m^2). However, industrial gas separation systems operate at high pressure with corrosive gases. Consequently, they use expensive steel housings

and tubing. Industrial gas separation systems also tend to be more than an order of magnitude smaller than the proposed flue gas CO_2 capture system. In contrast, commercial reverse osmosis systems can be very large, with more than 1 million m^2 of membrane area – as large as a membrane system needed to capture CO_2 from a 600 MW coal-fired power plant. These reverse osmosis systems benefit from economies of scale and low-cost plastic components (housing, valves, tubing, etc.), and accordingly, the average installed membrane cost is less than $\$50/m^2$. Because the flue gas membrane system will operate at low pressures and can use low-cost components, we believe low installed membrane costs, such as those found in the reverse osmosis industry, can be achieved. For the base case, we have used a conservative value of $\$150/m^2$.

Table 6. Assumptions Used in Base Case Design Calculations.

Category	Value	Units
Compressor efficiency	0.80	-
Turbo expander efficiency	0.85	-
Vacuum pump efficiency	0.75	-
Compressor and turbo expander cost	500	$/kW
Membrane CO_2 permeance	1,000	gpu
Membrane CO_2/N_2 selectivity	50	-
Membrane cost	150	$/m^2$
Membrane equipment installation factor	1.6	-
Capital depreciation/interest	20	%
Cost of power	0.04	$/kW
Capacity factor	85	%
Plant lifetime	25	years

The cost to capture CO_2, *CC* ($/ton CO_2), can be defined as the cost to operate capture equipment divided by the quantity of CO_2 captured:

$$CC = \frac{(P \times T \times E) + (0.2 \times C)}{F_{CO_2} \times T} \quad (4)$$

where *P* is the power required for capture (kW), *T* is the plant annual operating time (h/y), *E* is the cost of electricity to run the capture equipment ($/kWh), *C* is the capital cost of the capture equipment ($), and F_{CO_2} is the mass flow rate of sequestered captured CO_2 (ton/h). Typical *CC* values for conventional flue gas CO_2 capture technologies, such as amine scrubbing, are in the $40 to $80/ton CO_2 range. For the membrane process calculations described below, the *CC* values include compression to supercritical CO_2.

Figure 18 presents the cost of capture as a function of CO_2 recovery for the process design shown in Figure 17 where either feed pressure, the first step membrane area, or the second step membrane area have been varied. The cost of sequestration initially decreases with increasing CO_2 recovery, reaches a minimum between 70 and 85 % recovery, and then increases sharply at higher recoveries. The curves have a similar shape regardless of the method of varying CO_2 recovery.

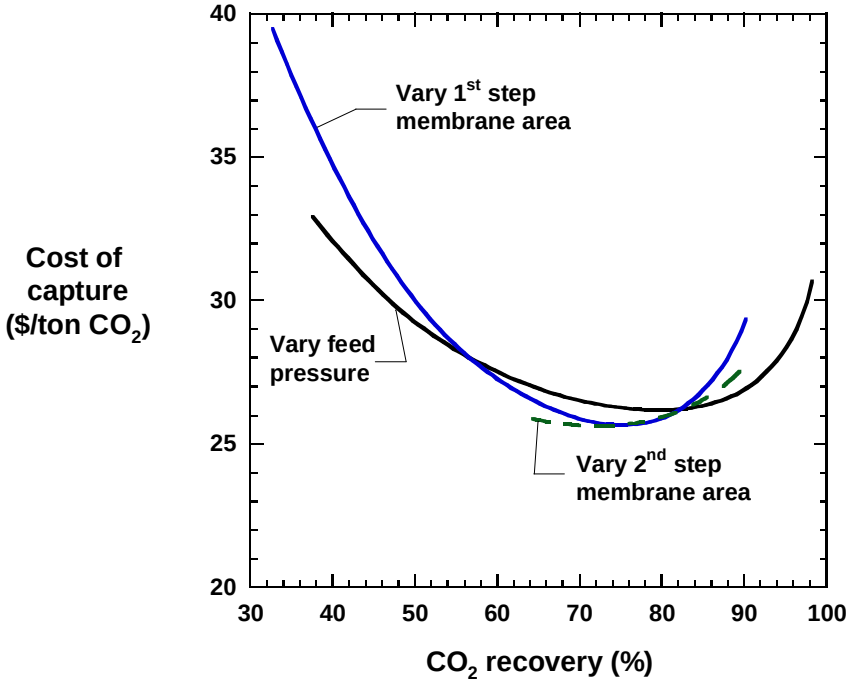

Figure 18. Cost of capture as a function of CO_2 recovery for the two-step countercurrent/ sweep membrane design. The CO_2 recovery was varied either by changing the feed pressure, the first step membrane area, or the second step membrane area as shown in the figure.

A minimum in the capture cost occurs because of the competing effects of the factors that go into the cost of capture calculation.

- At low recoveries, the amount of CO_2 captured (the denominator in Equation 4) is small, while the capital investment (membrane area and/or compression equipment) is installed and not used efficiently.
- As CO_2 recovery increases, the membrane area or power increase, but more slowly than the increasing amount of CO_2 captured. As a result, the cost of capture decreases.
- At high CO_2 recoveries (>80%), relatively large increases in power or membrane area are required to obtain small increases in the amount of CO_2 captured. Consequently, the cost of capture increases sharply at these high CO_2 recoveries.

Figure 19 shows the effects of membrane and electricity costs on the cost of CO_2 capture. If the membrane cost can be reduced from the base case value of $\$150/m^2$ to the current price of reverse osmosis membranes – $\$50/m^2$ – the cost of sequestration drops significantly, especially at

lower CO_2 recoveries. For example, at 70% CO_2 recovery, the cost of capture with \$150/m^2 membranes is about \$27/ton CO_2 compared to \$19/ton CO_2 for \$50/m^2 membranes. The different shape of the curve for \$50/m^2 membranes in Figure 19(a) reflects the fact that the inefficient use of the membrane area at low recoveries is mitigated by the low cost of the membranes. In this case, power is the dominant factor in the cost calculation and as power requirements increase with increasing recovery, so does the cost of capture. For the low cost membranes, Figure 19(b) shows that if the cost of power is halved, the cost of sequestration decreases by slightly more than 20%.

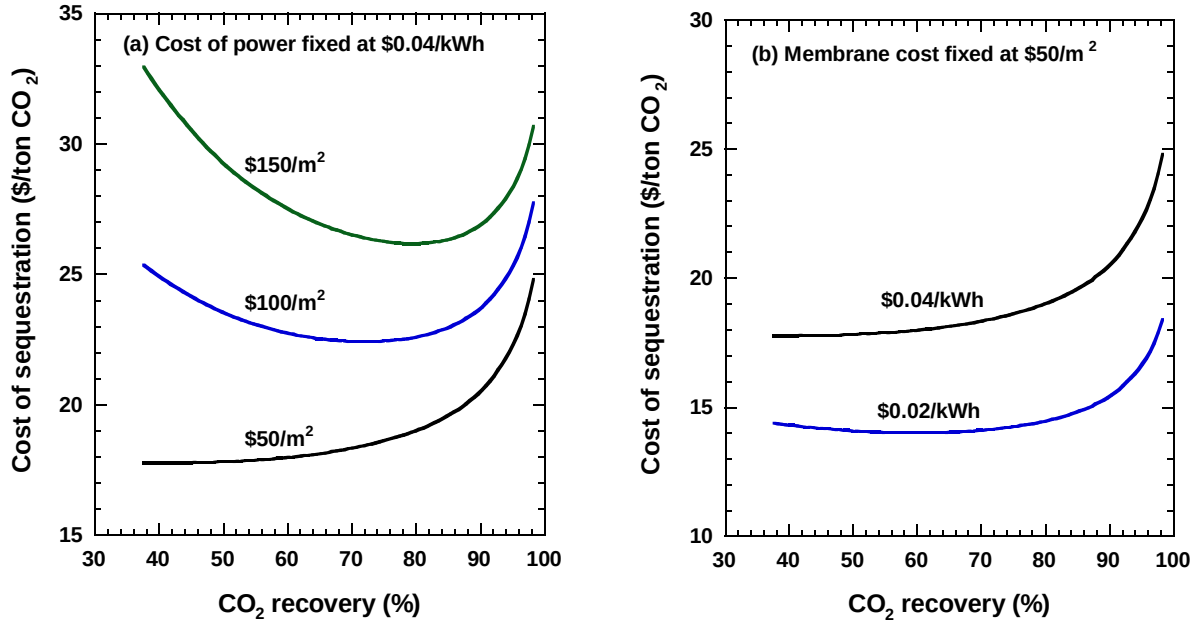

Figure 19. The cost of capture as a function of CO_2 recovery for (a) different membrane costs and (b) different electricity costs. Calculations are for the two-step countercurrent/sweep design shown in Figure 17.

Figure 20 shows the effects of membrane CO_2 permeance and CO_2/N_2 selectivity on the cost of capture for the two-step countercurrent/sweep process design. The calculations show that the cost of capture is a strong function of membrane selectivity at CO_2/N_2 selectivities of less than 30. For example, as the membrane CO_2/N_2 selectivity increases from 10 to 30, the cost of capture decreases from \$38 to \$28/ton CO_2 for a 1,000 gpu CO_2 membrane. However, at higher selectivities, the cost of capture is a weak function of selectivity. For instance, as the CO_2/N_2 selectivity increases from 30 to 100, the capture cost for the same membrane drops only from \$28 to \$26/ton CO_2.

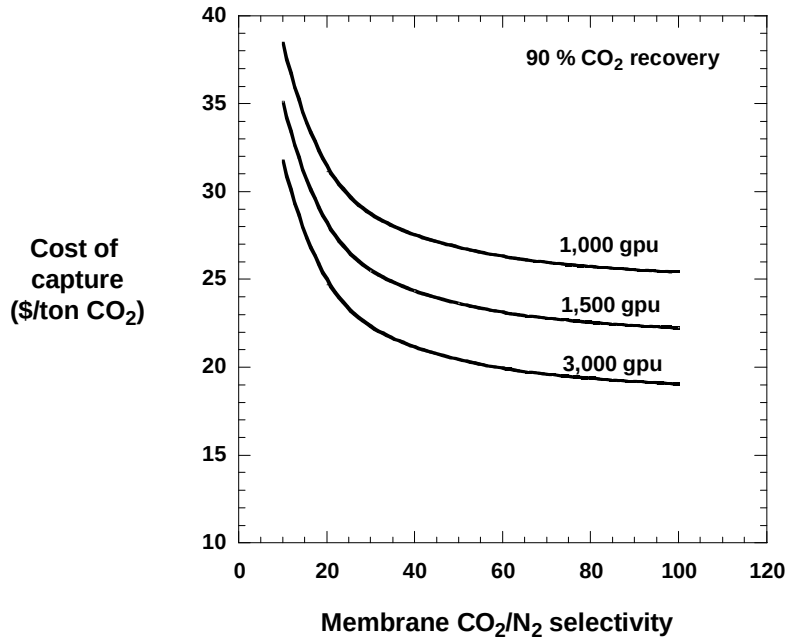

Figure 20. Effect of membrane CO_2 permeance and CO_2/N_2 selectivity on the cost of capture. Feed pressure was fixed at 2.6 bar and permeate pressure at 0.2 bar in these calculations.

From the Figure 20 data, it appears that at CO_2/N_2 selectivities above 30, increases in membrane CO_2 permeance are more important than further increases in selectivity. This reflects the fact that in a real-world membrane process designed to treat flue gas, such as that shown in Figure 17, the membrane operates in a pressure-ratio-limited regime. Under these conditions, increasing membrane permeance will help reduce the required membrane area (and capital cost), but increasing selectivity has only a small impact on product purity (which affects power requirements and operating costs).

To summarize, the sensitivity studies in Figures 18-20 show that

- The lowest CO_2 capture costs for membrane-based flue gas treatment are achieved at 70 to 85% capture. At lower CO_2 capture rates, the installed membrane equipment is not used efficiently;
- If membrane costs are reduced to $\$50/m^2$ or less, the cost of power for running compression equipment becomes the dominant contribution to the overall CO_2 capture cost. This result suggests that to minimize capture costs, large membrane areas of low-cost membrane with minimal feed compression should be used;
- Increasing membrane CO_2 permeance reduces CO_2 capture cost more than increasing membrane CO_2/N_2 selectivity once the selectivity is higher than 30. This is because a real-world membrane process to treat flue gas is pressure-ratio limited.

CONCLUSIONS

All the technical objectives defined at the outset of this project have been accomplished. The key findings include:

- Membranes with transport properties better than the original project targets were developed. These membranes have CO_2 permeances approximately tenfold higher than commercial CO_2 membranes, and two- to threefold higher than our baseline membrane properties used for the proposal design calculations.
- High permeance membrane formulations were successfully scaled up and produced on our commercial casting and coating equipment. Over 200 m^2 of membrane were prepared.
- A new mixed-gas test system was designed and built to allow parametric module testing under different sweep and non-sweep conditions
- Conventional cross-flow and novel countercurrent/sweep modules were successfully fabricated from high-CO_2-permeance membrane.
- Mixed-gas module test data were collected that (a) confirm near-ideal performance of cross-flow vacuum operation and (b) demonstrate the effectiveness of sweep operation.
- Membrane process design studies indicate that CO_2 capture and liquefaction can be accomplished at \$20-\$30/ton CO_2. Enhanced membrane permeance or lower installed membrane cost can further improve the economics of CO_2 capture, while CO_2/N_2 selectivities of more than 30 produce little additional improvement in system performance due to pressure ratio limitations.

Based on these promising initial findings, we received a new project funded by DOE NETL (DE-NT0005312) to conduct a field site demonstration at the APS Cholla coal-fired power plant. The new project started in October 2008 with the field test scheduled to begin at the end of 2009.

The results presented in this report suggest that membranes are a viable option for capturing CO_2 from coal-fired power plants. If developed to a mature state, membrane-based CO_2 capture technology appears to offer significant cost and energy savings over the best-case amine absorption processes. To clarify the true potential of membranes, we recommend that studies move to field demonstrations (such as the upcoming Cholla project) as soon as possible. Field tests provide critical operating experience and understanding of component lifetimes, and facilitate process integration optimization and cost reduction. They also generate confidence in a technology that is critical to user acceptance and commercial application of the technology.

PUBLICATIONS AND PRESENTATIONS

A paper titled "Power Plant Post-Combustion Carbon Dioxide Capture: An Opportunity for Membranes," was submitted to the *Journal of Membrane Science* in June 2009, for potential use in a special issue on membranes for CO_2 separations; it is currently being peer reviewed. Presentations related to this project have been given at several meetings, including the International Congress on Membranes and Membrane Processes (ICOM) meeting in July 2008, the NETL Project Review Meeting in late March 2009 and the Existing Plants, Emissions and Capture Peer Review in late April 2009. Documents for these presentations have already been provided to NETL.

REFERENCES

[1] J.T. Houghton, Y. Ding, D.J. Griggs, M. Noguer, P.J. van der Linden, X. Dai, K. Maskell, and C.A. Johnson, *Climate Change 2001: The Scientific Basis*, Cambridge University Press, New York (2001).

[2] M.I. Hoffert, *et al.*, "Advanced Technology Paths to Global Climate Stability: Energy for a Greenhouse Planet," *Science 298*(5595), 981-987 (2002).

[3] J. Johnson, "Getting to Clean Coal," *C&ENews 82*, 20 (February 23, 2004).

[4] "The Future of Coal – Options for a Carbon Constrained World," MIT Interdisciplinary Study (2007).

[5] A.B. Rao and E.S. Rubin, "Identifying Cost-effective CO_2 Control Levels for Amine-based CO_2 Captive Systems," *Ind. Eng. Chem. Res. 45*, 2421-2429 (2006).

[6] M.T. Ho, G. Leamon, G.W. Allinson, and D.E. Wiley, "Economics of CO_2 and Mixed Gas Geosequestration of Flue Gas Using Gas Separation Membranes," *Ind. Eng. Chem. Res. 45*, 2546-2552 (2006).

[7] H. Lin, T.C. Merkel, and R.W. Baker, "The Membrane Solution to Global Warming," *the Sixth Annual Conference on Carbon Capture & Sequestration*, Pittsburgh, PA (May 2007).

[8] R.W. Baker, *Membrane Technology and Applications*, 2nd ed., John Wiley & Sons Ltd., Chichester, England pp. 544 (2004).

[9] E.A. Mason and A.P. Malinauskas, *Gas Transport in Porous Media: The Dusty Gas Model*, Elsevier, Amsterdam (1983).