

Membrane Technology & Research – Spiral-Wound, Polymeric Membrane

<p><b>Project Title:</b>  <b>Membrane Process to Capture Carbon Dioxide from Coal-Fired Power Plant Flue Gas</b></p>	
<p><b>Technology Area:</b>                  Post-Combustion Membranes</p>	<p><b>Technology Maturity:</b>                  Pilot-scale slipstream on actual flue gas, one tonne of CO<sub>2</sub>/day</p>
<p><b>Primary Project Goal:</b>                  Membrane Technology &amp; Research, Inc. (MTR) is developing a spiral-wound, polymeric membrane and associated process for carbon dioxide (CO<sub>2</sub>) capture. The project includes conducting a slipstream field test using full-scale commercial membrane modules to treat combustion flue gas at a coal-fired power plant.</p>	
<p><b>Technical Goals:</b></p> <ul style="list-style-type: none"> <li>• Develop a thin film, composite, polymer-based membrane to increase CO<sub>2</sub> permeance while maintaining CO<sub>2</sub>/nitrogen (N<sub>2</sub>) selectivity.</li> <li>• Utilize incoming combustion air in a countercurrent sweep membrane module design to generate separation driving force and reduce the need for vacuum pumps and the associated parasitic energy cost.</li> <li>• Fabricate commercial-scale membrane modules that meet low pressure drop and high packing density performance targets.</li> <li>• Conduct a six-month field test of a membrane system at Arizona Public Services' (APS) Cholla Power Plant; the system will process 7,000 standard m<sup>3</sup>/day (0.25 MMscfd) of flue gas, separating about one tonne of CO<sub>2</sub>/day.</li> <li>• Analyze the performance of the membrane system, determine how it would be best integrated with a coal-fired power plant, and prepare a comparative study of the membrane-based CO<sub>2</sub> capture process versus other capture technologies.</li> </ul>	
<p><b>Technical Content:</b></p> <p>MTR is developing composite membranes with high CO<sub>2</sub> permeance and high CO<sub>2</sub>/N<sub>2</sub> selectivity for post-combustion flue gas applications. Tests indicate the membrane has 10 times the CO<sub>2</sub> 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<sub>2</sub> 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 rubbery polymers and is known by the trade name "Polaris™."</p> <p>Spiral-wound membrane modules are the most commonly used 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 desalination industry and 30 percent of the industrial gas separation market. Figure 1 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<sub>2</sub> to flow through the device.</p>	

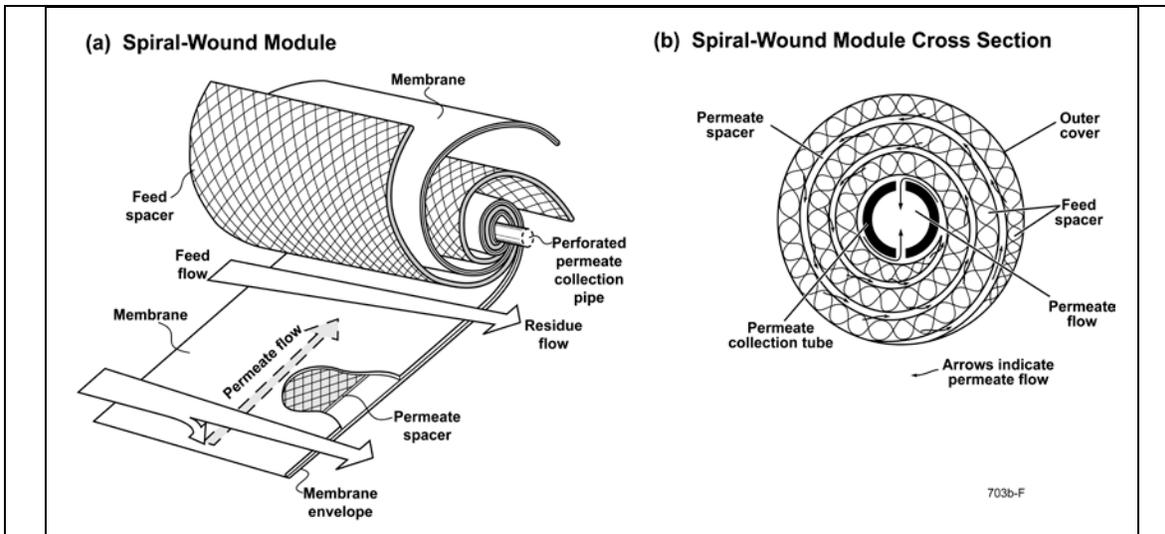


Figure 1: General Design Features of a Spiral-Wound Membrane Module

A schematic comparison of gas flow characteristics for a conventional spiral-wound membrane and the countercurrent sweep module is shown in Figure 2. The countercurrent sweep module is a modified version of the spiral-wound module that utilizes sweep gas on the permeate side and operates in a partial countercurrent pattern. This countercurrent sweep module permits the use of air as a sweep gas, which increases CO<sub>2</sub> flux through the membrane without requiring additional compression energy.

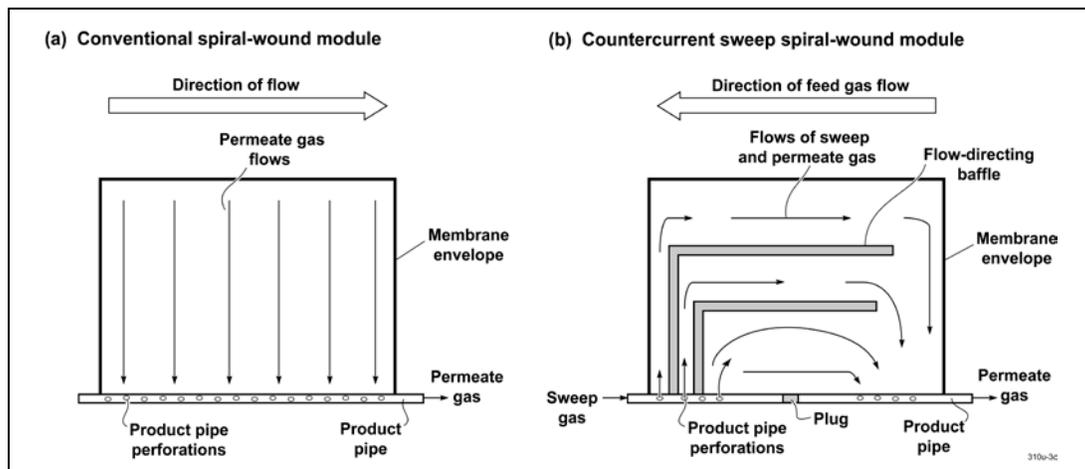


Figure 2: Schematic Comparison of Gas Flow Characteristics for a Conventional Spiral-Wound Membrane and the Countercurrent Sweep Module

Figure 3 shows the process design for the membrane system. 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<sub>2</sub>. 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 via an air sweep, which increases the CO<sub>2</sub> concentration of the flue gas entering the initial cross-flow module. The CO<sub>2</sub>-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<sub>2</sub> stream by recycle of the permeate back to the inlet of the compressor.

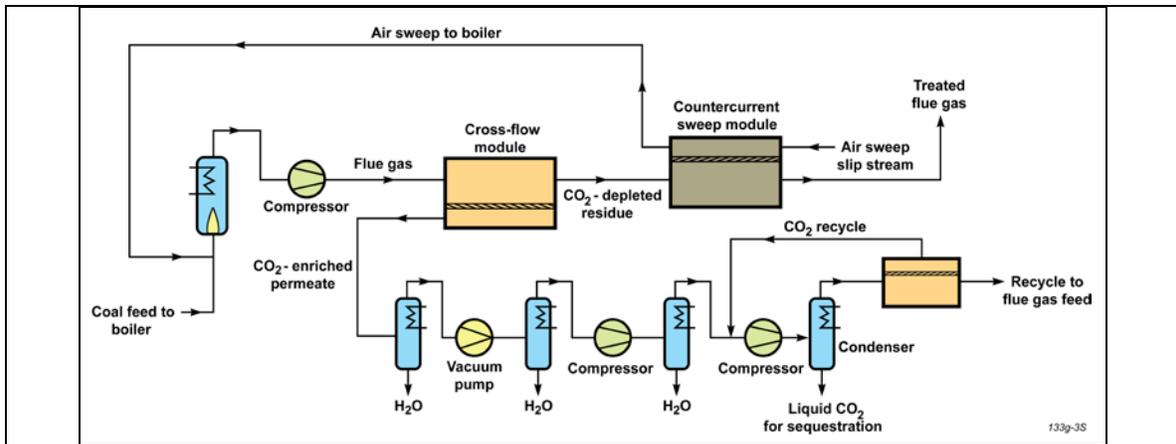


Figure 3: Process Design for the Membrane System

MTR estimates that a 0.5-1.0 million m<sup>2</sup> total membrane area is required to achieve 90% CO<sub>2</sub> capture for a 550-MW plant using this process design and would consume approximately 15- 18% of the plant's gross power output. Figure 4 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-MW power plant (current RO plants already use similar numbers of modules and module skids.).

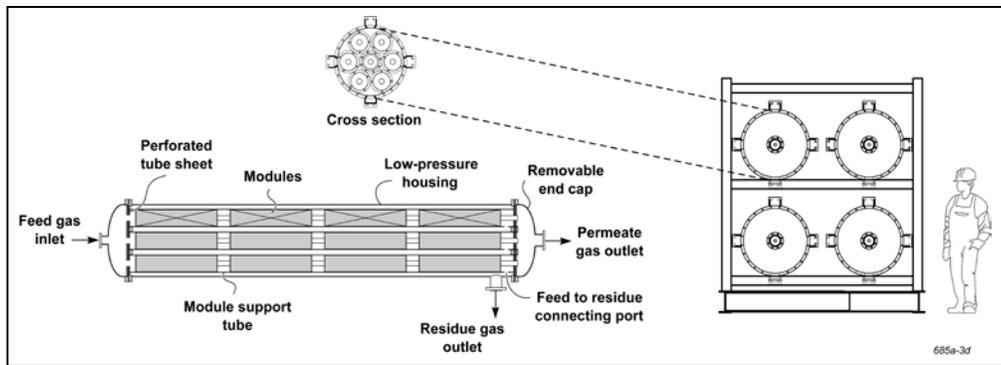


Figure 4: Proposed Design for Full-Scale Membrane System

Figure 5 shows the membrane skid that will be used for the six-month pilot-scale slipstream test being conducted at the coal-fired Cholla Power Plant operated by APS. The skid can hold up to eight (four cross-flow and four countercurrent sweep) eight-inch diameter Polaris™ membrane modules. The membrane skid is designed to capture one tonne of CO<sub>2</sub> per day from a 7,000 standard m<sup>3</sup>/day (250,000 scfd) flue gas slipstream. The test will demonstrate membrane operations in commercial-scale modules and determine typical membrane lifetimes under coal combustion flue gas operating conditions.



Figure 5: Membrane Skid Used for Six-Month Pilot-Scale Slipstream Test Conducted at APS's Cholla Power Plant

Table 1: Membrane Process Parameters

	Parameter	Current R&D Value	Target R&D Value
<b>Membrane Properties</b>	Materials of fabrication for selective layer	polymer	polymer
	Materials of fabrication for support layer (if applicable)	polymer	polymer
	Selectivity of key gas components: H <sub>2</sub> /CO <sub>2</sub> for pre-combustion technology CO <sub>2</sub> /N <sub>2</sub> 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	1,000	1,500+
	Temperature, °C	50	50
	Bench-scale testing, hours without significant performance degradation	500	500
	Pilot-scale testing (if applicable), hours without significant performance degradation	500+ (natural gas)	5,000 (coal)
	Maximum pressure differential achieved without significant performance degradation or failure, bar	70	70
<b>Module Properties</b>	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	spiral	spiral
	Packing density, m <sup>2</sup> /m <sup>3</sup>	700	1,000
	Pressure drop, bar	0.1	<0.05
	Estimated cost of manufacturing & installation, \$/m <sup>2</sup> -GPU or equivalent	0.5	0.1
<b>Product Quality</b>	CO <sub>2</sub> purity, %	No data	98+
	N <sub>2</sub> concentration, %	No data	1
	Other contaminants, %	No data	<0.1
<b>Process Performance</b>	Electricity requirement, kJ/kgCO <sub>2</sub>	No data	750
	Cooling requirement, kJ/kgCO <sub>2</sub>	No data	150
	Total energy (electricity equivalent), kJ/kgCO <sub>2</sub>	No data	900

**Other Membrane Parameters:**

Contaminant resistance: The membranes are known to be unaffected by water (H<sub>2</sub>O), oxygen (O<sub>2</sub>), and sulfur dioxide (SO<sub>2</sub>). The effect of trace contaminants such as mercury, arsenic, etc. is unknown and will be examined in the upcoming Cholla field demonstration.

Flue gas pretreatment requirements: Currently, pretreatment requirements are unknown. The upcoming

Cholla test will treat post-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 – that can achieve an order-of-magnitude better ash removal than a standard bag house, and are used today to treat refinery and gasification streams – may be needed.

Waste streams generated: The membrane process will recover >95% of the H<sub>2</sub>O in flue gas as liquid. The quality of this H<sub>2</sub>O, 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<sub>2</sub> than conventional membranes, which reduces 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<sub>2</sub>.
- 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<sub>2</sub> 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<sub>2</sub> from the air sweep to the boiler increases the CO<sub>2</sub> 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<sub>2</sub> 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 materials will be needed if the technology is to become economically viable.
- Scale up and integration issues are a possibility given the large number of membranes needed to service a 550-MW plant.

**Results To Date/Accomplishments:**

- Scaled up and produced high permeance membrane formulations on commercial casting and coating equipment. Produced more than 500 m<sup>2</sup> of Polaris™ membrane material used to construct 203 mm (eight-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 natural gas, and synthesis gas [syngas] containing sulfur species) for up to three months of

<p>continuous operation. The modules showed stable performance throughout these tests.</p> <ul style="list-style-type: none"> <li>• Field tests revealed the membrane permeance is 10 times higher than existing materials and the membranes possess good stability in acid gases.</li> <li>• Provided a membrane system to APS to process 4,250 m<sup>3</sup>/day (0.15 MMscfd) of natural-gas fired flue gas to provide concentrated CO<sub>2</sub> for testing at an experimental algae farm.</li> <li>• Designed and built a membrane system that will process 7,000 m<sup>3</sup>/day (0.25 MMscfd) of coal-fired flue gas and capture one tonne CO<sub>2</sub>/day from the Cholla power plant operated by APS. The system will begin operation in early 2010.</li> <li>• MTR estimates the membrane-based CO<sub>2</sub> separation and liquefaction process can capture 90% CO<sub>2</sub> using 15-18% of the plant's energy and cost \$20-\$30 per tonne of CO<sub>2</sub> captured.</li> </ul>	
<p><b>Next Steps:</b></p> <ul style="list-style-type: none"> <li>• Conduct a six-month field test at the coal-fired Cholla Power Plant.</li> <li>• Develop plans for a larger, pilot-scale 20 tonne CO<sub>2</sub> per day membrane capture system.</li> <li>• Lower the membrane module cost by incorporating low-cost components with a target of \$150/m<sup>2</sup>.</li> <li>• Integrate a CO<sub>2</sub> liquefaction section into the overall CO<sub>2</sub> capture system.</li> <li>• Test options for recycling the air sweep from the countercurrent sweep module to the boiler.</li> </ul> <p>Final test results will be available at the December 2010 project completion date.</p>	
<p><b>Available Reports/Technical Papers/Presentations:</b></p> <p>"Power plant post-combustion carbon dioxide capture: An opportunity for membranes," Journal of Membrane Science (2009), doi:10.1016/j.memsci.2009.10.041.</p> <p>"A Membrane Process to Capture CO<sub>2</sub> from Coal-Fired Power Plant Flue Gas," Annual NETL CO<sub>2</sub> Capture Technology for Existing Plants R&amp;D Meeting, Pittsburgh, Pennsylvania, March 2009.</p> <p>"The Membrane Solution to Global Warming," 6th Annual Conference on Carbon Capture and Sequestration, Pittsburgh, Pennsylvania, May 2007.</p>	
<p><b>Contract No.:</b></p> <p>DE-NT0005312 and FC26-07NT43085</p>	<p><b>NETL Project Manager:</b></p> <p>José Figueroa  <a href="mailto:Jose.Figueroa@NETL.DOE.GOV">Jose.Figueroa@NETL.DOE.GOV</a></p>
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