Project Title:

CO_2 Capture Membrane Process for Power Plant Flue Gas

Technology Area:	**Technology Maturity:**
Post-Combustion Membranes	Pilot-Scale Using Actual Flue Gas

Primary Project Goal:

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.

Technical Goals:

- Develop new fluorinated polymer membrane materials that have excellent chemical stability to moisture, sulfur dioxide (SO_2), and nitrogen oxide (NO_X) contaminants present in flue gas; 30 to 50 selectivity for carbon dioxide (CO_2) over nitrogen (N_2); and a 300 to 3,000 gas permeance unit (GPU) permeance for CO_2.
- Identify and develop CO_2 capture membrane process integration strategies.
- Develop and fabricate improved membrane hollow fibers and module designs to handle large flue gas flow rates and a high CO_2 permeance.
- Demonstrate CO_2 capture performance and reliability of membrane modules using actual coal-fired process flue gas.

Technical Content:

RTI's research effort includes membrane materials development, module design, and process design.

RTI is pursuing the development of two hollow-fiber membrane materials. First, RTI is working with Generon to develop a membrane material constructed of polycarbonate-based polymers. Standard polycarbonate is being used as a baseline for comparison to next generation polycarbonates. Lab-scale membrane modules are being studied with simulated flue-gas mixtures with and without flue gas emission contaminants. Two larger-scale polycarbonate membrane module prototypes are being tested with a slipstream of actual flue gas from the U.S. Environmental Protection Agency's (EPA) Multipollutant Combustion Research Facility (MPCRF).

RTI is also working with Arkema to develop the second membrane material constructed of polyvinylidene fluoride (PVDF)-based polymers. A PVDF molecule is comprised of a $[CH_2\text{-}CF_2]_n$ repeat unit, as shown in Figure 1. PVDF is well suited to contact with flue gas, possessing a high resistance to acids and oxidants, a specific affinity to CO_2 and a high CO_2 solubility, and a high thermal stability (T_d ~ 340°C). PVDF also features excellent physical and mechanical properties, durability, and longevity suited to the weaving process used for the hollow fiber tube fabrication. Conventional PVDF comes as a homopolymer with semicrystalline properties, a CO_2 permeance of ~5 GPU, and a CO_2/N_2 selectivity of ~23. Arkema is developing advanced PVDF materials to improve its permeance and selectivity parameters.

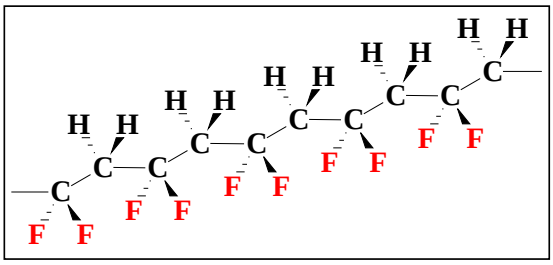

Figure 1: PVDF Molecule

Figure 2 shows a cross-section of a hollow-fiber membrane module. Multiple modules will be utilized in a given CO_2 capture system for power plant applications due to the large quantity of flue gas to be processed. A module consists of numerous small diameter hollow fibers. As the flue gas flows through the fibers, CO_2 preferentially flows across the fiber walls (permeate). The remaining flue gas (retentate) flows out of the membrane module and to the plant stack for discharge to the atmosphere.

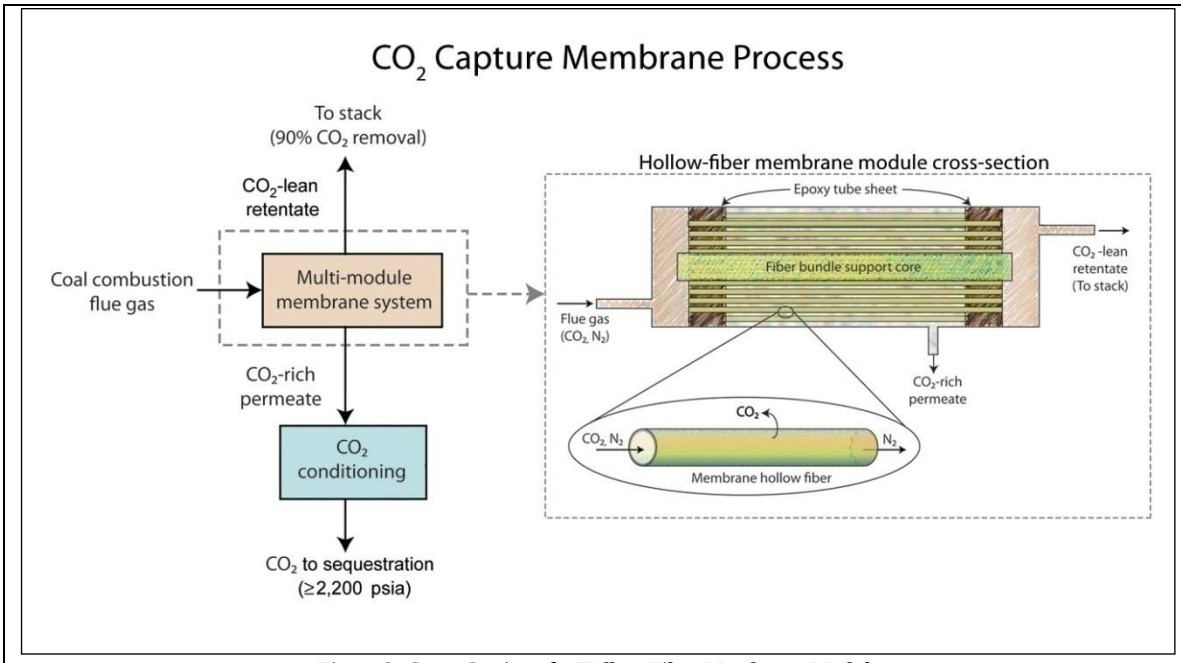

Figure 2: Cross-Section of a Hollow-Fiber Membrane Module

Process simulations for a single-stage membrane process are being conducted to determine the sensitivity of CO_2 removal performance and permeate CO_2 purity on different parameters, including membrane flux, membrane selectivity, membrane fiber dimensions, and membrane pressure driving force.

Technology Advantages:

Membranes could provide PC-fired power plants with a cost-effective method for CO_2 capture. The membrane module system is relatively easy to install within an existing PC-fired plant and does not require any major modifications to the existing equipment and infrastructure. The membrane utilizes passive separation of gases, making it energy efficient because it does not require regeneration energy, as do solvent and sorbent processes. The module's compact design and ability to link with hundreds of modules in tandem makes the hollow fiber membrane system easy to scale and retrofit. The membrane also lacks any moving parts, meaning there is no risk of a mechanical failure.

R&D Challenges:

The flue gas properties may pose certain challenges when using a membrane module. A low CO_2 concentration of 13% to 15%, a low gas pressure of 1 atm, large volumes of gas, and the presence of moisture and contaminants (sulfur oxide [SO_X], NO_X, and particulate matter) can all pose potential challenges to the membrane technology. The compression of the flue gas and CO_2 permeate tends to have a high parasitic energy cost. The fabrication process for the hollow fiber tubes is susceptible to defects and pressure drop issues. The fiber weaving process and module housing design will need to be optimized to achieve the desired flow distribution and other benchmarks.

Results To Date/Accomplishments:

- Four lab-scale modules made from Generon's standard polycarbonate hollow fibers were investigated at 23-25°C and feed pressures up to 200 psig with pure N_2, oxygen (O_2), and CO_2; a mixture of 15% CO_2 in N_2; and a mixture containing 290 ppm SO_2, 15% CO_2, and balance N_2. The two smaller modules (0.75 ft^2 area) showed CO_2 permeance in a range of 70 to 150 GPU, and their CO_2/N_2 selectivity ranged from 20 to 40. However, the two larger modules (100 ft^2 area) gave only a CO_2 permeance of 17 to 24 GPU and CO_2/N_2 selectivity of nine to 12. RTI suspects this result for the larger modules is associated with the significant decrease in pressure driving force for the CO_2 as its permeation occurs down the length of the fibers.

- Arkema's fluoropolymer membrane material has shown improved flux (approximately 700 to 800 GPU) and selectivity, but it has not yet been formed into a hollow fiber.

Next Steps:

- Synthesize novel polymers and membrane films and produce membrane hollow fibers.
- Fabricate lab-scale, hollow fiber membrane modules leading to the construction of a membrane test skid.
- Gather separation performance data on lab-scale membrane modules made from standard polycarbonate membrane hollow fibers to formulate a baseline for future tests.
- Identify the CO_2 capture membrane process system design options and their respective process flow schemes.
- Conduct 300 hours of field testing for the CO_2 capture membrane test skid with real coal-fired flue gas.
- Complete a techno-economic evaluation of the "best" integrated/retrofitted CO_2 capture membrane process package developed during the project.

Final test results will not be available until the December 2010 project completion date.

Available Reports/Technical Papers/Presentations:

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

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