Project Title:

Novel Dual Functional Membrane for Controlling Carbon Dioxide Emissions from Fossil-Fueled Power Plants

Technology Area:	**Technology Maturity:**
Post-Combustion Membranes	Laboratory-Scale, with Simulated Flue Gas

Primary Project Goal:

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

Technical Goals:

- Achieve a membrane CO_2/nitrogen (N_2) selectivity of 100 and a CO_2 permeance of 1,000 gas permeance units (GPU) or greater.
- Formulate a sol-gel composition to be used in the preparation of clear aminosilicate coatings for membrane deposition onto the siliceous support matrix.
- Setup multi-component gas separation tests for preliminary membrane performance analysis.
- Refine the sol-gel compositions for optimal membrane deposition.
- Study the influence of sulfur dioxide (SO_2), water vapor, and trace oxygen (O_2) on membrane performance.
- Optimize membrane deposition on alternative economical membrane supports.
- Conduct preliminary economic analysis of the membrane process for post-combustion CO_2 capture.
- Identify a processing window that allows reproducible preparation of an asymmetric microporous silica membrane.
- Stabilize membrane performance through a Ni-doping approach.
- Prepare an ultra-thin silica membrane using a plasma-assisted, atomic layer deposition technique (PA-ALD).

Technical Content:

The dual-functional, silica-based membrane is prepared by a unique sol-gel dip-coating process for depositing a microporous amino-silicate membrane on a porous tubular ceramic support. It consists of a microporous inorganic siliceous matrix, with amine functional groups physically immobilized or covalently bonded on the membrane pore walls. Strong interactions between the permeating CO_2 molecules and the amine functional membrane pores enhance surface diffusion of CO_2 on the pore wall of the membrane, subsequently blocking other gases. The membrane is composed of three distinct layers as shown in Figure 1: (1) a commercially available tubular or hollow fiber ceramic support; (2) a mesoporous surfactant-templated silica sub-layer

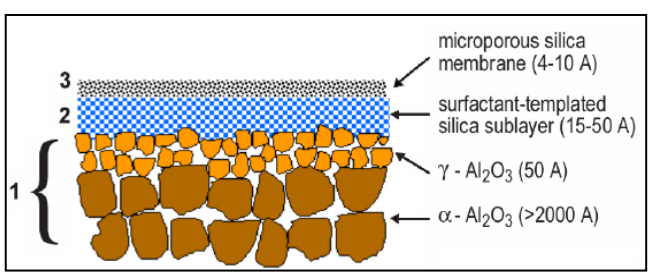

Figure 1: Cross-Section of Membrane

with pore size 15-50 Å; and (3) a microporous aminosilicate gas separation membrane layer with pore size 4-10 Å.

Table 1: Membrane Process Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Aminosilicate/doped-silicate	Aminosilicate/doped silicate
	Materials of fabrication for support layer (if applicable)	Surfactant-templated silica on alumina	Surfactant-templated silica on alumina
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology; CO_2/N_2 for post-combustion technology	CO_2/N_2=80-100 (dry feed); CO_2/N_2 = 50-60 (humidified feed)	CO_2/N_2 = 100
	Type of selectivity measurement (ideal or mixed gas)	Mixed gas	Mixed gas
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	CO_2: 400 GPU	CO_2: 1,000 GPU
	Temperature, ºC	25-250°C	25-80°C
	Bench-scale testing, hours without significant performance degradation	168 hrs	100 hrs
	Pilot-scale testing (if applicable), hours without significant performance degradation	N/A	N/A
	Maximum pressure differential achieved without significant performance degradation or failure, bar	3 bar	N/A
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Plate-and-frame	Hollow-fiber
	Packing density, m^2/m^3	500	980
	Pressure drop, bar	0.01-0.02	0.01-0.02
	Estimated cost of manufacturing and installation, $\$/m^2$-GPU or equivalent	$0.33-$0.39/m^2-GPU	N/A
Product Quality	CO_2 purity, %	>90%	90%
	N_2 concentration, %	<10%	10%
	Other contaminants, %	N/A	N/A
Process Performance	Electricity requirement, kJ/kgCO_2	1313 KJ/kgCO_2 or 0.365 kWh/kgCO_2	1333 KJ/kgCO_2 or 0.370 kWh/kgCO_2
	Heat requirement, kJ/kgCO_2	0	0
	Total energy (electricity equivalent), kJ/kgCO_2	1313 KJ/kgCO_2 or 0.365 kWh/kgCO_2	1333 KJ/kgCO_2 or 0.370 kWh/kgCO_2

Note: Values for membrane properties are experimental. Other values are calculated based on membrane properties.
Contaminant resistance: SO_2 > 10ppm
Flue gas pretreatment requirements: particulate removal
Waste streams generated: None

Technology Advantages:

The dual-functional, silica-based membrane will have a higher CO_2 selectivity and permeance compared to conventional membranes that separate gases based on differences in molecular size only.

R&D Challenges:

- The permeance of the new membrane will need to be increased by a factor of five to meet the research and development (R&D) target.
- The selectivity for the new membrane must remain constant under temperatures of 50°C to 70°C and high humidity conditions.
- The presence of particulates in the flue gas could adversely affect membrane

performance.

- Previous membrane designs suffered from a gradual reduction in permeance and selectivity under elevated temperature and humidity conditions due to pore shrinkage/blockage.

Results To Date/Accomplishments:

- Three classes of microporous, sol-gel derived, silica-based membranes were developed for CO_2 removal under simulated flue gas conditions.
- A novel class of amine-functional, microporous silica membranes was prepared using an amine-derivatized alkoxysilane precursor, exhibiting enhanced CO_2:N_2 selectivity (>70) in the presence of water vapor, but its CO_2 permeance (<1.25 cm^3[STP]/cm^2-min-atm [~275 gpu]) was below the target.
- Pure siliceous membranes showed higher CO_2 permeance (1.5-2 cm^3[STP]/cm^2-min-atm [~330-440 gpu]), but subsequent densification occurred under prolonged simulated flue gas conditions.
- Nickel oxide (NiO) was incorporated into the membrane's microporous network to retard densification and achieved CO_2 permeance of 0.5 cm^3(STP)/cm^2-min-atm (~110 gpu) and CO_2:N_2 selectivity of ~50 after 163 hours exposed to simulated flue gas conditions.
- The implementation of a novel ALD processing scheme shows evidence that a vapor-processed membrane can exhibit higher thermal/structural stability combined with higher flux and selectivity compared to the traditional liquid phase processing approach (sol-gel).

Next Steps:

Project completed April 2009. Final report not yet available.

Available Reports/Technical Papers/Presentations:

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

"Novel Dual-Functional Membrane for CO_2 Capture," Seventh Annual Carbon Capture and Sequestration Conference, Pittsburgh, Pennsylvania, May 2008.

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

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

Contract No.:	**NETL Project Manager:**
DE-FG26-04NT42120	José Figueroa Jose.Figueroa@netl.doe.gov
Principal Investigator:	**Partners:**
C. Jeffrey Brinker University of New Mexico cjbrink@sandia.gov	T3 Scientific LLC