Novel Inorganic/Polymer Composite Membranes for CO_2 Capture

primary project goals

Ohio State University developed an inorganic/polymer composite membrane consisting of a thin, selective inorganic-containing layer embedded in a polymer structure. The project developed the new membrane design to improve system performance through laboratory, bench-scale, and pilot-scale testing, and developed a continuous manufacturing process to decrease costs.

technical goals

- Develop membrane synthesis process that incorporates a thin, selective inorganic-containing layer embedded in a polymer structure.
  - Membranes were developed and down-selected to achieve the Department of Energy (DOE) target of <$40/tonne carbon dioxide (CO_2) captured for 2025 (for a CO_2/nitrogen [N_2] selectivity of >100 and a CO_2 permeance of >800 gas permeation units [GPU]).
  - Continuous fabrication of the proposed hybrid membrane morphology was performed with the use of a continuous membrane fabrication machine.
- Conduct membrane characterization via bench-scale testing.
  - Functional hybrid membranes were synthesized for incorporation into three prototype membrane modules for parametric and continuous testing with simulated or actual flue gas.
- Complete system and cost analysis of the membrane system.

technical content

Ohio State University developed a cost-effective design and manufacturing process for new membrane modules that capture CO_2 from flue gas. In one approach, the membranes are comprised of a thin, selective inorganic particle-containing layer embedded in a polymer structure so that it can be made in a continuous manufacturing process. In another approach, a continuous zeolite membrane is rapidly synthesized on a polymer support. Figures 1 and 2 show the two hybrid membrane concepts studied in this project. The membrane of the first approach was incorporated in spiral-wound modules for testing with simulated and actual coal-fired flue gas. Preliminary cost calculations showed that a single-stage membrane process is economically unfavorable, primarily because of the low concentration of CO_2 (≈14 percent) in the flue gas stream. A two-stage process is more economical, but requires plant operation with a CO_2-enriched recycle stream. An important cost driver in current carbon capture membrane technologies is the energy requirement for maintaining the driving force for the membrane separation. The flue gas must be kept at atmospheric pressure and the concentrated CO_2 stream kept under vacuum (approximately 3 pounds per square inch [psi]) conditions. Preliminary calculations showed that the carbon capture energy requirement can be sufficiently reduced in a two-stage process. In the first stage, CO_2 is removed from flue gas by evacuation; in the second stage, remaining CO_2 is removed using an air-sweep such that the 90 percent capture target is met.

technology maturity:
Pilot-Scale, Actual Flue Gas

project focus:
Inorganic/Polymer Composite Membranes

participant:
Ohio State University

project number:
FE0007632

predecessor projects:
N/A

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100%

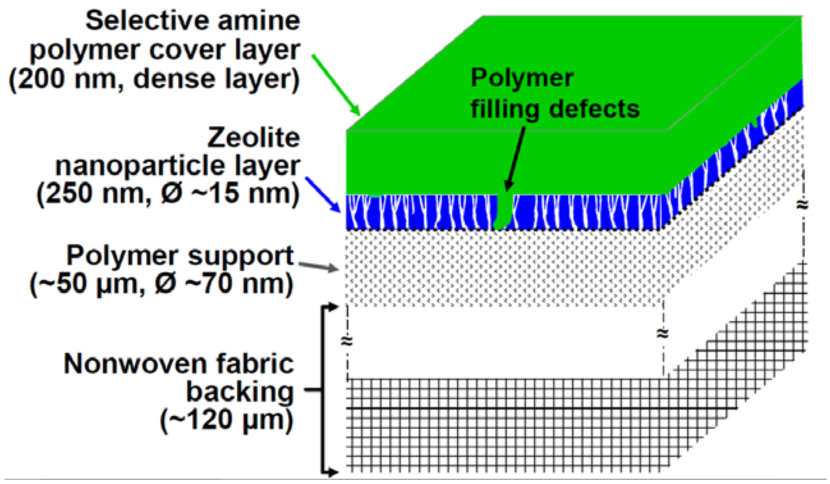

Figure 1: Membrane concept with selective amine polymer layer on zeolite nanoparticles embedded in polymer support

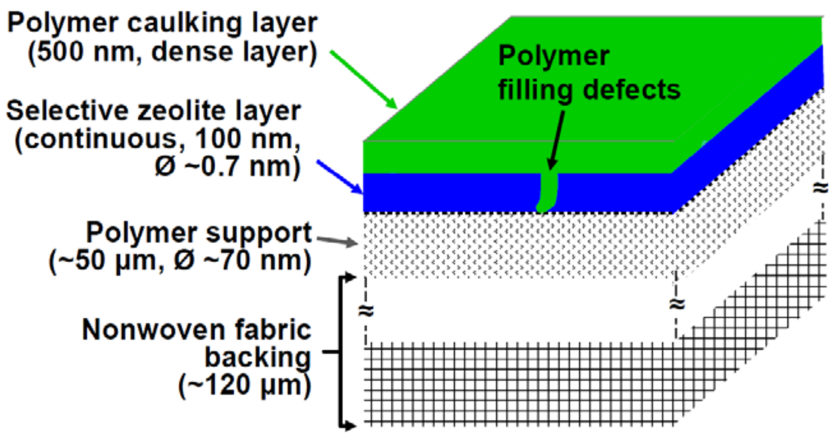

Figure 2: Membrane concept with polymer caulking layer on selective zeolite membrane grown on polymer support

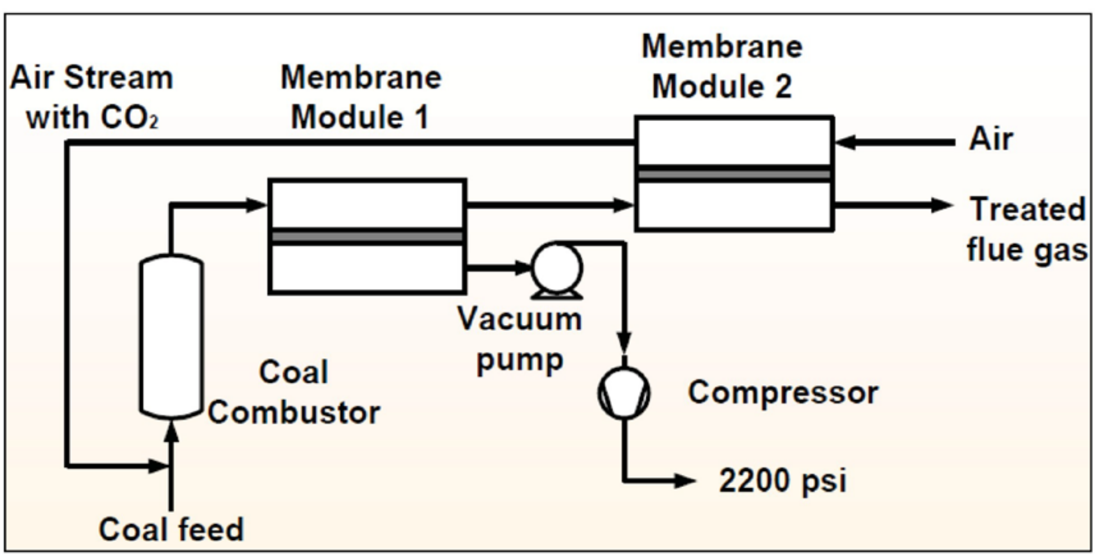

Figure 3: Process concept for two-stage membrane system

The entrance sweep flow is the same as the combustion air used in the current plant; the now CO_2-enriched stream is subsequently used for combustion. The 95 percent pure CO_2, captured in the first stage, is then compressed to 15 MPa (≈2,200 psi). DOE's cost targets can be met with a membrane that has a selectivity ≈170, a permeance of 1,100 GPU, and full stability against flue gas contaminants. This combination cannot be achieved with fully polymeric membranes. Fully inorganic, micro-porous membranes are sufficiently selective and stable, but generally too expensive due to high manufacturing costs. The focus of this project was a design that combines favorable inorganic membrane selectivity with the cost-effectiveness resulting from the manufacture of a composite membrane in continuous mode. The micro-porous membranes are aluminosilicates. Fully inorganic structures have CO_2/N_2 selectivities of >200, and permeances of <3,000 gas GPU. The latter can be improved by reducing membrane thickness, in combination with defect abatement with a thin polydimethylsiloxane (PDMS) layer. Two types of inorganic selective layers including alumina and zeolite Y (zeolite Y has a silica-to-alumina ratio of their framework of three or greater) were investigated. Membrane fabrication with growth of zeolite Y (ZY) into a continuous layer offers better selectivity, lower processing cost, and is easier to scale-up than membrane fabrication with rapid modification of the top aluminum oxide layer to form a microporous layer. A zeolite Y/polymer composite membrane was down-selected for further studies. Zeolite Y layers can be grown from solutions at 95 °C; however, the zeolite Y layer requires long growth time, which was reduced to 1 hour via application of a novel zeolite synthesis approach. The membrane system can be deposited on available polyethersulfone supports, which are fabricated into 14-inch supports with a continuous fabrication machine.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	zeolites and/or amine-containing polymer	
Materials of Fabrication for Support Layer	—	polyethersulfone or polysulfone on non-woven fabric	
Nominal Thickness of Selective Layer	nm	150–250	150–250
Membrane Geometry	—	flat sheet	spiral-wound sheet
Max Trans-Membrane Pressure	bar	can be 0.2–50	0.2–1.5
Hours Tested without Significant Degradation	—	200 hours	200 hours
Manufacturing Cost for Membrane Material	$/m^2	20	20
Membrane Performance			
Temperature	°C	57 °C and 102 °C	57 °C
CO_2 Pressure Normalized Flux	GPU or equivalent	800 GPU	>800 GPU
CO_2/H_2O Selectivity	—	not determined	not determined
CO_2/N_2 Selectivity	—	α = 140–800 for 20 CO_2/80 N_2 with p_{tot} = 101 kPa	α >100 for flue gas conditions
CO_2/SO_2 Selectivity	—	not determined	not determined
Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	countercurrent	
Packing Density	m^2/m^3	about 1800	
Shell-Side Fluid	—	air sweep	
Flue Gas Flowrate	kg/hr	about 0.2	
CO_2 Recovery, Purity, and Pressure	%/%/bar	>90%, >95%, 0.2–1.2 bar	
Pressure Drops Shell/Tube Side	bar	about 0.05/0.05	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in desulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Membrane Permeation Mechanism – Surface adsorption and diffusion and molecular sieving for the zeolite selective layer; solution-diffusion for the polymer cover layer; facilitated transport for amine-containing selective layer.

Contaminant Resistance – Fully resistant polymer and inorganic materials.

Flue Gas Pretreatment Requirements – Removal of particulates, possibly dehydration.

Membrane Replacement Requirements – Estimated approximately 4 years.

Waste Streams Generated – N_2 with water (H_2O), about 1 percent CO_2 and minor impurities.

Process Design Concept – See Figure 3.

technology advantages

High CO_2/N_2 selectivity and cost-effective separation principle.

R&D challenges

Synthesis and scale-up of sufficiently selective and permeable membranes.

status

The project was completed on December 31, 2015, resulting in the development of a pilot-scale continuous casting machine for the fabrication of 14-inch polymer substrates and the development of a pilot-scale continuous membrane fabrication machine for the deposition of zeolite particles on polymer substrates using a vacuum-assisted dip coating method, followed by coating of the amine-containing polymer cover layer on the zeolite/polymer substrates. The pilot-scale amine-containing composite membranes were rolled into spiral-wound modules and implemented in a two-stage CO_2 capture process. These membrane modules were tested with real flue gas at the National Carbon Capture Center (NCCC), achieving >800 GPU of CO_2 permeance and >150 CO_2/N_2 selectivity. A process for rapid (1 hour) zeolite membrane growth, involving a continuous zeolite layer grown within polymer support, was also developed.

available reports/technical papers/presentations

Ho, W., "Novel Inorganic/Polymer Composite Membranes for CO_2 Capture," Final project review meeting presentation, Pittsburgh, PA, February 2016. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0007632-Project-Meeting-Final-public-release-2-26-16.pdf.*

Ho, W. "Novel Inorganic/Polymer Composite Membranes for CO_2 Capture," presented at the 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/W-Ho-OSU-Inorganic-Polymer-Composite-Membranes.pdf.*

Ho, W., "Novel Inorganic/Polymer Composite Membranes for CO_2 Capture," presented at the Continuation Application Status Meeting, Pittsburgh, PA, August 2014. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0007632-Continuation-Application-Status-Mtg-public-release-8-11-14.pdf.*

Ho, W., "Novel Inorganic/Polymer Composite Membranes for CO_2 Capture," presented at the 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/W-Ho-OSU-Inorganic-Polymer-Composite-Membranes.pdf.*

Ho, W., "Novel Inorganic/Polymer Composite Membranes for CO_2 Capture," presented at the 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/Events/2013/CO2%20Capture/W-Ho-OSU-Inorganic-Polymer-Composite-Membranes.pdf.*

Verweij, H., "Novel Inorganic/Polymer Composite Membranes for CO_2 Capture," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012. *https://www.netl.doe.gov/File%20Library/events/2012/co2%20capture%20meeting/H-Verweij-OSU-Composite-Membranes.pdf.*

Verweij, H., "Novel Inorganic/Polymer Composite Membranes for CO_2 Capture," project kickoff meeting presentation, December 2011. *https://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/NETL-kick-off.pdf.*