BENCH-SCALE, HIGH-PERFORMANCE, THIN FILM COMPOSITE HOLLOW FIBER MEMBRANE FOR POST-COMBUSTION CARBON DIOXIDE CAPTURE

primary project goals

General Electric Global Research (GE) is developing high-performance, thin film polymer composite hollow fiber membranes and advanced processes for economical post-combustion carbon dioxide (CO_2) capture. The project includes bench-scale testing to tune the properties of a novel phosphazene polymer membrane and decrease costs through development of innovative fabrication techniques.

technical goals

- Optimize phosphazene polymer and coating solution: Synthesize phosphazene polymer, optimize separation performance, and develop processable coating solutions.
- Fabricate hollow fiber support layer: Produce highly porous, robust hollow fiber supports with controlled surface porosity from commercially available materials.
- Fabricate composite coated hollow fiber membranes: Develop processes to apply thin layer coatings on hollow fiber supports and elucidate fundamental polymer properties.
- Test membranes at bench-scale under flue gas conditions: Exposure and performance test materials and membranes under flue-gas conditions.
- Conduct process evaluation and module design: Conduct technical and economical process evaluation and module design and fabrication.

technical content

GE and partners are developing a high-performance, thin film polymer composite hollow fiber membrane and advanced process for economical post-combustion CO_2 capture. The project utilizes novel phosphazenepolymeric materials to produce an economical and scalable composite hollow fiber membrane module.

The membrane will be optimized at bench-scale, including tuning the properties of the phosphazene polymer in a coating solution and fabricating highly engineered porous hollow fiber supports. The project will also define the processes for coating the fiber support to manufacture thin, defect-free composite hollow fiber membranes.

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Composite Hollow Fiber Membranes

participant:

General Electric Global Research Center

project number: FE0007514

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partners:

Idaho National Laboratory, Western Research Institute, Georgia Institute of Technology

performance period: 10/1/11 - 12/31/14



Figure 1: GE Test Rig – Flat Sheet and Hollow Fiber Membranes

The physical, chemical, and mechanical stability of the materials (individual and composite) to flue gas components will be evaluated using exposure and performance tests. Membrane fouling and cleanability studies will define long-term performance.

GE and the Georgia Institute of Technology (Georgia Tech) will work together on developing processes to apply the thin layer coating formulations onto the hollow fiber supports. GE will leverage the knowledge gained from using its flat sheet film coating apparatus to enable development of the continuous dip process for coating of hollow fiber membrane supports. Georgia Tech will use the in situ process developed to coat porous cellulose acetate hollow fibers with defect-free layers as a benchmark, which will be further adapted to obtain thin, defect-free coated layers. Both the continuous dip coating and batch in situ processes will be optimized to provide economical and scalable coated composite hollow fiber membranes.



Figure 2: Georgia Tech Hollow Fiber Fabrication Line

Working with Idaho National Laboratory, Georgia Tech will characterize phosphazene material properties in films cast on porous polymer supports to elucidate polymer properties including aging, membrane fouling, and cleanability. The characterization techniques will enable a better understanding of polymer and composite membrane performance. Membrane performance validation testing under flue-gas conditions will be performed at Western Research Institute's coal combustion test facility. Module design and technical and economic feasibility analyses will be conducted to evaluate the overall performance and impact of the process on the cost of electricity.

TABLE 1: PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer		phosphazene	
Materials of Fabrication for Support Layer		polymer	
Nominal Thickness of Selective Layer	μm	1–10	<1
Membrane Geometry		flat sheet/hollow fiber	hollow fiber
Max Trans-Membrane Pressure	bar	2–5	up to 10
Hours Tested Without Significant Degradation		200 (flat sheet) 100 (hollow fiber)	100-1,000
Manufacturing Cost for Membrane Material	\$/m ²	_	—
Membrane Performance			
Temperature	°C	30 and 65	30 and 60
CO ₂ Pressure Normalized Flux	GPU or equivalent	50–275 Barrer (flat sheet 30 °C) 100–425 Barrer (flat sheet 65 °C) up to 70 GPU (hollow fibers 35 °C)	1,000–2,500 GPU (hollow fibers)
CO ₂ /H ₂ O Selectivity	—	8–10	8–10
CO ₂ /N ₂ Selectivity	_	15–20 (65 °C) flat sheet 30–40 (30 °C) flat sheet 10–35 (35 °C) hollow fibers	30–40
CO ₂ /SO ₂ Selectivity		not tested	non tested
Type of Measurement		mixed gas	mixed gas
Proposed Module Design		(for equipment developers)	
Flow Arrangement	_	countercurrent	
Packing Density	m²/m³	>1,000	
Shell-Side Fluid		retentate	
Flue Gas Flowrate	kg/hr	<1	
CO ₂ Recovery, Purity, and Pressure	%/%/bar	>90%, 60–80%, 0.2–1 bar	
Pressure Drops Shell/Tube Side	bar	1–4	

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 cm³ (1 atm, 0 °C)/cm²/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm³ (1 atm, 0 °C)/cm²/s with pressures measured in cmHg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m²-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 de-sulfurized 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, construction 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 (CO₂-rich) or retentate (flue gas) stream.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Solution-diffusion mechanism.

Contaminant Resistance – Phosphazene-based membranes have been tested to be resistant to contaminant species such as oxygen (O_2) , nitrogen oxide (NO_x) , sulfur dioxide (SO_2) , and moisture present in coal flue gas.

Flue Gas Pretreatment Requirements - Fly ash particulate removal.

Membrane Replacement Requirements – Membranes found to be stable with up to 200 hours of testing. Long-term stability tests are currently in progress.

Waste Streams Generated - Acidic water condensate stream.

technology advantages

- Surface property optimization to reduce fly ash adhesion.
- Highly scalable, low-cost hollow fiber support platform.
- Ease of cleaning should provide longer membrane life.
- Phosphazene polymer with high permeability and selectivity.

R&D challenges

- Fouling potential from fly ash/particulates.
- Permeability and selectivity at 60 °C lower than anticipated.
- Large membrane area requirements and process integration.

results to date/accomplishments

- Synthesized phosphazene polymer, characterized separations performance under realistic flue gas conditions, and developed hollow fiber support coating solutions.
- Developed engineered, high-porosity, hollow fiber supports.
- Built/upgraded bench-scale membrane coating and testing facilities.
- Completed initial process technical and economic feasibility study.
- · Fabricated phosphazene coated defect-free hollow fiber membranes.
- Membrane performance studies conducted showed stability over >100 hours of testing.

next steps

- Optimize phosphazene polymer coatability on hollow fiber supports.
- Optimize the continuous dip and batch coating processes to provide economical and scalable coated composite hollow fiber membranes.
- Continue testing of coated composite hollow fiber membranes at bench scale under flue gas conditions.
- Conduct final technical and economic feasibility analyses and an environmental, health, and safety assessment.

available reports/technical papers/presentations

Bhandari, D., et al., "Composite Hollow Fiber Membranes for Post Combustion CO₂ Capture," presented at the 2014 NETL CO₂ Capture Technology Meeting, Pittsburgh, PA, July 2014.

http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO₂%20Capture/D-Ajit-Bhandari-GE-Composite-Hollow-Fiber-Membranes.pdf.

Bhandari, D., et al., "Composite Hollow Fiber Membranes for Post Combustion CO₂ Capture," presented at the 2013 NETL CO₂ Capture Technology Meeting, Pittsburgh, PA, July 2013. http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/CO₂/DBhandari-GEGR-2013-CO₂-NETL-Conference.pdf.

Bhandari, D., et al., "Composite Hollow Fiber Membranes for Post Combustion CO₂ Capture," presented at the 2013 North American Membrane Society Meeting, Boise, ID, June 2013. http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/CO₂/GEGR-2013-CO₂-NAMS-Conference.pdf.

Bhandari, D., et al., "Composite Hollow Fiber Membranes for Post Combustion CO₂ Capture," presented at the 2012 NETL CO₂ Capture Technology Meeting, Pittsburgh, PA, July 2012.