Engineering-Scale Design and Testing of Transformational Membrane Technology for CO₂ Capture

primary project goal

Gas Technology Institute (GTI) is advancing the Ohio State University's (OSU) transformational membrane-based carbon dioxide (CO₂) capture technology through engineering-scale testing on actual coal-derived flue gas at the Wyoming Integrated Test Center (ITC). The amine-containing CO₂-selective membranes developed under U.S. Department of Energy (DOE)-funded projects (FE0031731; FE0026919; FE0007632) consist of a thin selective layer coated on a polymer support and exhibit high CO₂ permeance and very high selectivity of CO₂ over nitrogen (N₂). The superior performance is based on a facilitated transport mechanism, in which a reversible CO₂ reaction with fixed-site and mobile amine carriers enhances the CO₂/N₂ separation. The objectives of this project are to fabricate commercial-size membrane modules; design and install a 1-megawatt-electric (MWe) CO₂ capture system at ITC; conduct parametric testing with one-and two-stage membrane processes at varying CO₂ capture rates (60–90%); perform continuous testing at steady-state operation for a minimum of two months; and gather the data necessary for further process scale-up.

technical goals

- Design and build an engineering-scale CO₂ capture system using OSU's transformational membrane in commercial-size membrane modules.
- Conduct tests on coal flue gas at ITC and demonstrate a continuous, steadystate operation for a minimum of two months. Gather the data necessary for process scale-up.
- Complete initial detailed techno-economic analysis (TEA) and detailed design of the engineering-scale system.
- Complete construction of the engineering-scale system and install it at ITC.
- Complete engineering-scale testing and analysis, achieve 95% CO₂ purity, and validate a capture cost of \$30/tonne of CO₂ captured and cost of electricity (COE) at least 30% less than DOE baseline approach.

technical content

OSU has developed a transformational membrane in commercial-size—a spiral-wound membrane module shown in Figure 1. The novel CO₂-selective membranes are synthesized by formulating amine-containing polymer into a thin-film composite membrane configuration (Figure 2). The polymer selective layer, typically 100–200-nm thick, carries out the CO₂/N₂ separation. The highly gas-permeable nanoporous support layer provides the mechanical strength necessary for use in a separation module.

program area:

Point Source Carbon Capture

ending scale:

Small Pilot

application:

Post-Combustion Power Generation PSC

key technology:

Membranes

project focus:

Membrane Technology for Coal-Fired Power Plants

participant:

Gas Technology Institute

project number:

FE0031946

predecessor projects:

FE0007632; FE0026919; FE0031731

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partners:

Ohio State University; Trimeric Corporation; Wyoming Integrated Test Center

start date:

10.01.2020

percent complete:

15%

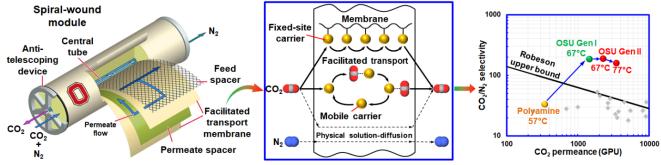


Figure 1: Diagrams of the membrane module (left), transport mechanism (middle), and performance (right).

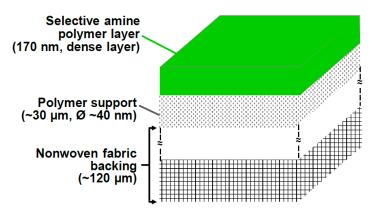


Figure 2: Schematic of the thin-film composite membrane.

In the presence of a transmembrane partial pressure difference, as illustrated in Figure 1 (middle), CO_2 molecules from the feed side dissolve in the selective layer via the reaction with the amine carriers ($CO_2 + R-NH_2 + H_2O \rightleftharpoons R-NH^+ + HCO_3^-$). The reaction product (HCO_3^-) diffuses across the membrane and eventually is converted back to the CO_2 molecules via the reverse reaction and released on the low-pressure side.

The fixed-site carrier is covalently bound to the polymer, and the mobile carrier exists as nonvolatile amino acid salt. Thus, the carriers stay in the membrane. The permeation of N_2 is extremely slow due to the lack of reactive diffusion. The disparate permeation rates result in a high CO_2 permeability and a high CO_2/N_2 selectivity, which are usually more than three-fold of those shown by membranes relying on size or condensability discrimination through the solution-diffusion mechanism.

The project is to design and build a nominal 1-MWe engineering-scale unit (approximately 20 tonnes per day [TPD]) using this transformational membrane with commercial-size modules and test it with coal-fired flue gases at ITC, located at Basin Electric Power Cooperative's Dry Fork Station, seven miles north of Gillette, Wyoming. The testing goal is to capture 60–90% CO₂ of the feed CO₂ with approximately 95% CO₂ purity. The test system will proceed in two modes—a single-stage process that is anticipated to be preferred for the lower CO₂ capture rates and an innovative retentate recycle two-stage process for the higher CO₂ capture rates (Figure 3). The data will be used in the TEA to determine the optimum configuration to meet DOE's programmatic goals.

60-80% CO2 capture

80-90+% CO₂ capture

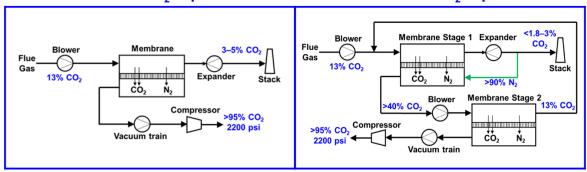


Figure 3: Flow diagrams of a one-stage membrane process to achieve 60–80% capture (left) and an innovative process to achieve >80% capture (right).

TABLE 1: MEMBRANE PROCESS PARAMETERS

| Materials Properties | Units | Current R&D Value | Target R&D Value | |
|---|-------------------|--------------------------------------|------------------|--|
| Materials of Fabrication for Selective Layer | _ | amine-containing polymer | | |
| Materials of Fabrication for Support Layer | _ | polyethersulfone on non-woven fabric | | |
| Nominal Thickness of Selective Layer | nm | 170 | 170 | |
| Membrane Geometry | _ | flat sheet | flat sheet | |
| Max Trans-Membrane Pressure | bar | 4 | 4 | |
| Hours Tested without Significant Degradation | _ | 2,500 | 2,500 | |
| Manufacturing Cost for Membrane Material | \$/m² | 20 | 20 | |
| Membrane Performance | | | | |
| Temperature | °C | 77 | 77 | |
| CO ₂ Pressure Normalized Flux | GPU or equivalent | 3,500 | 3,500 | |
| CO ₂ /H ₂ O Selectivity | _ | 1 | 1 | |
| CO ₂ /N ₂ Selectivity | _ | 160 | 160 | |
| Type of Measurement | _ | mixed gas | mixed gas | |
| Proposed Module Design | | (for equipment developers) | | |
| Flow Arrangement | _ | spiral-wound, countercurrent | | |
| Packing Density | m^2/m^3 | ca. 2,000 | | |
| Permeate-Side Fluid | _ | vacuum or retentate recycle | | |
| Flue Gas Flowrate | ft³/min | 30 | .9 | |
| CO ₂ Recovery, Purity, and Pressure | %/%/bar | 60–90 >9 | 5 1 | |
| Pressure Drops Shell/Tube Side | psi/m | 1.5/1.5 | | |
| Estimated Module Cost of Manufacturing and Installation | <u>\$</u> m² | 21.2 | | |

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 cm Hg. Note: $1 \text{ GPU} = 3.3464 \times 10^{-10} \text{ kg mol/m}^2\text{-s-kPa [SI units]}$.

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, 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 (CO₂-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO₂ in CO₂-rich product gas; assuming targets are met.

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

| | | Composition | | | | | | |
|------------|--------------------|-------------|--------|-------|-------|------|-----|--------|
| Pressure | Temperature | | | vol% | | | рр | mv |
| 14.79 psia | 135°F | CO_2 | H_2O | N_2 | O_2 | Ar | SOx | NO_X |
| | | 12.46 | 14.97 | 68.12 | 3.64 | 0.81 | 42 | 74 |

Other Parameter Descriptions:

Membrane Permeation Mechanism – Facilitated transport for amine-containing selective layer.

Contaminant Resistance - Resist up to 3 parts per million volume (ppmv) SO₂ and NO₂, respectively.

Flue Gas Pretreatment Requirements – Removal of particulates; SO₂ and NO₂ polishing to 3 ppmv.

Membrane Replacement Requirements – Estimated approximately four years.

Waste Streams Generated - Nitrogen with water, about 1% CO₂, and minor impurities.

Process Design Concept – Flowsheet diagrams shown in Figure 3.

Proposed Module Design - See Figure 1 (left).

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS (90% CAPTURE)

| Economic Values | Units | Current R&D Value | Target R&D Value |
|-------------------------|--------------------------|-------------------|------------------|
| Cost of Carbon Captured | \$/tonne CO ₂ | 40.3 | 40.0 |
| | | | |
| Capital Expenditures | \$/MWhr | 19.8 | 20.0 |
| Operating Expenditures | \$/MWhr | 10.5 | 12.0 |
| Cost of Electricity | \$/MWhr | 100.5 | 100.4 |

TABLE 3: POWER PLANT CARBON CAPTURE ECONOMICS (70% CAPTURE)

| Economic Values | Units | Current R&D Value | Target R&D Value | |
|-------------------------|--------------------------|-------------------|------------------|--|
| Cost of Carbon Captured | \$/tonne CO ₂ | 33.6 | 30.0 | |
| Capital Expenditures | \$/MWhr | 10.6 | 10.5 | |
| Operating Expenditures | \$/MWhr | 6.8 | 7.0 | |
| Cost of Electricity | \$/MWhr | 85.9 | 86.0 | |

Definitions:

Cost of Carbon Captured - Projected cost of capture per mass of CO₂ captured under expected operating conditions.

Capital Expenditures - Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – "Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity, Rev. 4" report (https://www.netl.doe.gov/energy-analysis/details?id=3745).

Scale of Validation of Technology Used in TEA – Bench-scale testing.

Qualifying Information or Assumptions – A direct contact cooler is not needed to condition the flue gas since the membrane is operated at 77°C. The purchased equipment cost for the turbo expander is \$300/kWe based on literature data.

technology advantages

- Simplicity of membrane design leads to low-cost membranes.
- High CO₂ selectivity due to facilitated transport mechanism.
- Sensitivity study suggests that the COE at 70% CO₂ capture can be ca. 30% less than the DOE baseline approach.

R&D challenges

- Membrane stability in the presence of high-level contaminants, such as SO₂ and nitrogen oxide (NO_X).
- Corrosion or particulates fouling of membrane system equipment.

status

OSU has successfully developed their Gen II membrane, which has CO₂ permeance of 3,500 GPU and CO₂/N₂ selectivity of 160. Long-term stability was confirmed on simulated flue gas for the OSU Gen II membrane and on simulated and actual flue gas at the National Carbon Capture Center (NCCC) for the OSU Gen I membrane. The TEA based on bench-scale data suggests the membrane can achieve ca. 30% reduction in COE for a 70% CO₂ capture rate with a one-stage process compared with the DOE baseline approach and ca. \$40/tonne for a 90% CO₂ capture rate with an innovative two-stage process. Current efforts are focusing upon designing an engineering-scale CO₂ capture system using OSU's transformational membrane and process for field testing at ITC. Fabrication and testing of prototype membrane and commercial-sized membrane modules are currently underway.

available reports/technical papers/presentations

Shiguang Li, Yang Han, Winston Ho, Travis Pyrzynski, Weiwei Xu, Howard Meyer, and John Marion, "Engineering Scale Design and Testing of Transformational Membrane Technology for CO₂ Capture," Project kickoff meeting presentation, Pittsburgh, PA, July 2021. http://www.netl.doe.gov/projects/plp-download.aspx?id=11034&filename=Engineering+Scale+Design+and+Testing+of+Transformational+Membrane+Technology+for+CO2+Capture.pdf.

Shiguang Li, Yang Han, Winston Ho, Travis Pyrzynski, Weiwei Xu, and Howard Meyer, "Engineering Scale Design and Testing of Transformational Membrane Technology for CO₂ Capture," NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. https://netl.doe.gov/sites/default/files/netl-file/S-Li%2C-GTI-Transformational-Membrane-Testing.pdf