Pilot Test of a Nanoporous, Super-hydrophobic Membrane Contactor Process for Post-combustion CO\textsubscript{2} Capture

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Yong Ding, Uttam Shanbhag, and Ed Sanders, \textit{Air Liquide Advanced Separations (ALaS)}

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National Energy Technology Laboratory
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Virtual Meetings, August 12, 2021
Project overview

- **Performance period**: October 1, 2013 – June 30, 2022
- **Total funding**: $15.6MM (DOE: $12.5MM, Cost share: $3.1MM)
- **Objectives**:
  - Build and operate a 0.5 MW_e pilot-scale CO₂ capture system and conduct tests on coal flue gas at the National Carbon Capture Center (NCCC)
  - Demonstrate a continuous, steady-state operation for ≥ 2 months
- **Goal**: Achieve DOE’s goal of ≥95% CO₂ purity at a cost of ≤$40/tonne of CO₂ captured by 2025

- **Team**:

<table>
<thead>
<tr>
<th>Member</th>
<th>Roles</th>
</tr>
</thead>
<tbody>
<tr>
<td>gti</td>
<td>• Project management and planning</td>
</tr>
<tr>
<td>Air Liquide</td>
<td>• Process design and testing</td>
</tr>
<tr>
<td>ALaS</td>
<td>• Membrane and module development</td>
</tr>
<tr>
<td>Porogen</td>
<td>• Techno-Economic Analyses (TEA)</td>
</tr>
<tr>
<td>Trimeric Corp.</td>
<td>• Site host</td>
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<tr>
<td>NCCC</td>
<td></td>
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</table>
Hollow Fiber Membrane Contactor (HFMC) technology

HFMC: high surface area device that facilitates mass transfer

Centerline of bore – not to scale

Bore Side | Pores | Shell Side
---|---|---
GAS | CO₂(g) | CO₂
MEMBRANE | | |
ABSORPTION LIQUID | P<sub>CO₂</sub>(l) | P<sub>CO₂</sub>
gas | | |
P<sub>gas</sub> | | |

Hydrophobic coating layer to prevent wetting

PEEK spun into high-packing density, hollow fibers

8-inch-diameter commercial cartridges with ~2,000 GPU intrinsic CO₂ permeance used in pilot scale testing

NCCC PSTU solvent system (0.5 MW<sub>e</sub>)

GTI HFMC system (0.5 MW<sub>e</sub>)

Pilot plant (10 ton/day) being tested at the National Carbon Capture Center (NCCC)

PEEK = Polyether Ether Ketone; HFMC = Hollow fiber membrane contactor
HFMC process at NCCC

NCCC’s PC4

PEEK HFMC 0.5 MW_e plant

Membrane absorber

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>P (psig)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40-60</td>
<td>1-20</td>
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</tbody>
</table>

Flash desorber

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>P (psig)</th>
</tr>
</thead>
<tbody>
<tr>
<td>~130</td>
<td>1-50</td>
</tr>
</tbody>
</table>

Plant Gaston

- 80 MW: 13,000 lb CO₂
- 80 MW: 60,000 lb CO₂

PC4

- Bench Scale Test Units
- 80 MW: 13,000 lb CO₂
- 80 MW: 60,000 lb CO₂
- 1 MW: 70 lb CO₂
- Pilot Scale Test Unit
- 0.5 MW: 18 lb CO₂
- Pilot Scale Test Unit

CO₂

(aMDEA solvent

Storage Tank

Solvent Pump

Steam

CO₂ (50 psig)

CO₂ (20 psig)

Membrane absorber

T (°C) | P (psig)
40-60  | 1-20

Filter

Blower
Integrated testing in the previous lab and bench (coal flue gas) project showed performance and stability

@A, started testing with simulated flue gas.
@B, a solvent level control failure caused the liquid side temperature to rise above the gas side temperature.
@C, N\textsubscript{2} flow rate to the bores of the absorber increased by a factor of 7.5 to dry out the bores for 6 hours.
@D, gas flow rate was reset to 80% of the initial flow rate while still maintaining a 13% CO\textsubscript{2} feed. The CO\textsubscript{2} removal rate remained higher than 90% in the next 46 hours.
2018’s testing with 28 membrane modules

- **Observation**: Performance declined with time
- **Analysis**: Quantitative analysis indicated three causes: 1) contaminants (powder and rust particles); 2) vapor condensation in fiber bores; and 3) capillary condensation of vapor in PEEK pores
- **Decision made at that point**: Resolve issue of contaminants (powder and rust particles) first

*Note: slope -0.0026 indicates a drop in 26% value per 100 hours
Additional flue gas filters and pre-membrane mesh pads installed to protect the membrane; orifice plates installed to monitor if there is a flow maldistribution issue.
2019’s testing with 8 modules (7 used and one new)

- **Observation**: stability improved, especially during the 2\textsuperscript{nd} 313 h
- **Analysis**: 2% drop/100h during the 2\textsuperscript{nd} 313h, might be because: 1) 7 used membranes (containing particles inside) were used, and 2) rusts from carbon steel piping; new membranes were expected to be stable
- **Decision made at that point**: move forward to fabricate 28 new membrane cartridges, replace carbon steel piping with stainless steel piping between filter and membrane header, and perform tests

*Note: slope -0.0002 indicates a drop in 2% value per 100 hours*
Modified skid with stainless steel piping (February 2020)
2021’s testing with 28 modules

- **January 17**: Started testing
- **January 21** (system operated for ~92h): Shutdown due to power plant’s shutdown
- **February 6**: Flue gas was back at NCCC, system brought back online
- **February 20** (system operated for ~347 total hours): Observed CO₂ capture rate dropped from 90% to ~39%. The decision was made to shut down system and look into approaches to recover performance and improve stability
- **February 20 – March 26**: Investigated: 1) approaches to recover performance, and 2) approaches to improve stability and performance
- **March 26**: System shutdown due to power plant’s shutdown
- **March 26 – April 12**: Data analysis and reporting
Inspection: Inlet mesh pads were clean after system improvements, no visible rust or particulates present on the mesh pads, indicating the issue of particles had been resolved.

Used mesh pad top surface after March 2019 testing: rust particles observed because between filter and membrane header carbon steel piping was used at that time.

Used mesh pad top surface after 2021 testing: clean.
2021’s testing: Decline in performance observed for the 1st 347 hours with 28 modules

\[ Y = -0.0011x + 0.7748 \]

*Note: slope -0.0011 indicates a drop in 11% value per 100 hours*
Approaches to recover membrane performance

• **Approach 1**: Water wash followed by air dry
  1. Drain liquid from membrane shell side
  2. Remove inlet mesh pad
  3. Connect demineralized water to gas inlet, allow water to flow down to gas outlet
  4. Connect instrument air to the gas inlet, purge fibers with air
  5. Replace gas inlet mesh pad, bring membrane back online

• **Approach 2**: Air dry
  1. Drain liquid from membrane shell side
  2. Remove inlet mesh pad
  3. Connect instrument air to the gas inlet, purge fibers with air
  4. Replace gas inlet mesh pad, bring membrane back online
Performance can be recovered, but stability was not improved

- Air purge alone was not sufficient in recovering performance
- Water wash + air purge can recover the performance but doesn’t resolve continual decline issue

*Note: slope -0.0007 indicates a drop in 7% value per 100 hours
<table>
<thead>
<tr>
<th>Cause #</th>
<th>Explanation</th>
<th>Sub-cause #</th>
<th>Explanation</th>
<th>Mitigating Information/Action Required to Resolve</th>
<th>Resolved?</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><strong>Contaminants in the flue gas</strong></td>
<td>A</td>
<td>Solids observed on inlet tubesheets and in bores</td>
<td>Replaced piping with stainless steel, installed filter, mesh pads in 2020</td>
<td>Yes</td>
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<td></td>
<td></td>
<td>B</td>
<td>Within bore or pore, water vapor condenses, blocking CO$_2$ passage</td>
<td>Reduced flue gas dewpoint with no effect on degradation. Liquid found in bore is consistent with amine, NOT flue gas</td>
<td>Yes, verified not to be the cause</td>
</tr>
<tr>
<td>2</td>
<td><strong>Liquid was observed from the bore side drain with amine concentration close to solvent</strong></td>
<td>A</td>
<td>Poor membrane potting into epoxy tubesheet provides a path</td>
<td>ALaS developed an infusion technique to eliminate leak path in 2016</td>
<td>Yes, verified not to be the cause</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B</td>
<td>Broken fibers during operations provide a path for amine to get into the top tubesheet and into the bores</td>
<td>Solvent permeation test, single gas permeation tests, and cyclohexane permeation tests on used modules</td>
<td>Ongoing</td>
</tr>
<tr>
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<td>C</td>
<td>Defects of the membrane superhydrophobic layer coating during handling or operation</td>
<td>SEM and other characterizations, Solvent permeation test, single gas permeation tests, and cyclohexane permeation tests on used modules</td>
<td>Need action</td>
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<tr>
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<td>D</td>
<td>Membrane hydrophobicity change (especially surface contact angle) after long-term contact with liquid</td>
<td>ALaS: measure contact angle as a function of time in the presence of solvent</td>
<td>Need action</td>
</tr>
<tr>
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<td>E</td>
<td>Vapor phase permeation of the solvent through the membrane and then condensation in the pores and in the bore</td>
<td>GTI: V-L-E data for amine solution, amine and water permeances to calculate the amine concentration of the condensed liquid; ALaS: prepare PEEK with pores &gt; 50 nm (current pores have average size of 13-16 nm).</td>
<td>Need action</td>
</tr>
</tbody>
</table>
Testing underway to verify the causes of instability; solvent permeation tests suggest quality of the hydrophobic coating layer needs to be improved to be impermeable to solvent.

Testing conditions: 65°F; shell side (solvent) pressure: 4.1, 6.4 and 8.1 psig; bore side pressure: ~0 psig
Summary

▪ Made modifications to skid – filters, stainless steel piping, mesh pads, 28 new membrane cartridges fabricated and installed
▪ Performed testing early 2021, solid issue resolved, decline in performance observed
▪ Developed an approach to recover performance, but stability was not improved
▪ Data analysis indicates most probable cause to instability: liquids in the pores
▪ Additional tests are ongoing to verify the causes of instability and resolve the issue
Acknowledgements

- Financial and technical support

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JIP Partners

NETL: Andrew O’Palko, Steven Mascaro, Dan Hancu, José Figueroa, and Lynn Brickett
Appendix – Organization Chart

Department of Energy

Project Oversight

GTI
Ms. Kate Jauridez
Contract administrator

GTI
Mr. Howard Meyer-PM
Dr. Shiguang Li- PI
- Project management
- Coordinate project activities
- Partnership coordination
- Project QA/QC

GTI
Mr. Travis Pyrzynski
- Design of the skid
- Testing

ALaS, PoroGen
Dr. Yong Ding, Dr. Uttam Shanbhag, Dr. Ed Sanders
- Membrane module fabrication
- Membrane module economics

GTI
Mr. John Marion
Senior Program Director
- Internal consultant

Trimeric
Dr. Andrew Sexton
- TEA

GTI
Mr. Don Stevenson
VP, Energy Supply & Conversion
- Internal consultant

NCCC
Mr. Tony Wu
- Supporting testing at NCCC
Appendix – Gantt Chart
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