Composite Hollow Fiber Membranes for Post Combustion CO₂ Capture

DOE Award: DE-FE0007514

Project Close Meeting

Paul Glaser
Fred Stewart
Bill Koros
Acknowledgment

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Project Goal & Team

Develop bench-scale coated composite hollow fiber membrane materials and processes for CO$_2$/N$_2$ separation in coal flue-gas at least 90% CO$_2$ capture with less than 35% increase in levelized cost of electricity.

- Hollow fiber fabrication & coating
- Module design
- Technical and economic feasibility analysis

- Membrane scale-up
- Polymer synthesis
- Fundamental studies
- Performance validation

- Polymer development
- Polymer property optimization
- Coating solution development

- Fiber coating process development
- Effect of fly ash on membranes

- Membrane performance validation in coal flue-gas
Project Team Members

- Teresa Grocela-Rocha
- Joe Suriano
- Paul Glaser
- David Moore
- Hongyi Zhou
- Pat McCloskey
- Surinder Singh
- Kristi Narang *
- Balajee Ananthasayanam
- Chris Orme
- John Klaehn
- Joshua McNally
- Lauraine Denault
- Jeff Manke *
- Paul Wilson
- Paul Howson *
- Dhaval Bhandari (PI) *
- Ali Rownaghi
- William Koros (PL)
- Jerrod Doss Isaak
- Fred Stewart (PL)
- Tom Barton
- Lucy Liu
- Vijay Sethi (PL)
Summary

The team fabricated small-scale hollow fiber modules for the separation of CO$_2$ from flue-gas streams.

Poly(phosphazene) materials were used in a selective layer in combination with a Torlon (polyamide-imide) porous support.

Significant difficulties involving performance degradation, both in permeance and in selectivity over time were identified and partially addressed using a variety of techniques, but significant barriers to implementing candidate materials in a robust system remain at the end of the award period.

Alternate routes towards increasingly robust systems and lines of further inquiry were identified for subsequent work. Technoeconomic and mechanical models were built to demonstrate the potential benefits of the overall approach if material challenges can be overcome.
## Project BP-1 Scorecard (2012-2013)

<table>
<thead>
<tr>
<th>BP-1 Deliverable</th>
<th>BP-1 Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ selective polymer material with P(_{\text{CO}<em>2}) = 200 Barrer, S(</em>{\text{CO}_2/N_2}) ≥ 30</td>
<td>Polyphosphazene materials synthesized with P(_{\text{CO}<em>2}) = 100-500 Barrer, S(</em>{\text{CO}_2/N_2}) = 20-40</td>
</tr>
<tr>
<td>Fabricate high porosity hollow fiber (HF) supports</td>
<td>1 m strands of HF support fabricated with P/(\ell)(_{\text{CO}_2}) &gt; 20,000 GPU, surface pores ≈ 20-50 nm</td>
</tr>
<tr>
<td>Develop processes to fabricate defect-free composite HF membranes</td>
<td>Batch, dip coating (lab-scale); roll-to-roll coating (bench-scale) processes developed. Defect-free 10” membrane modules fabricated.</td>
</tr>
<tr>
<td>Demonstrate stable performance under realistic flue-gas conditions</td>
<td>Composite HF membrane module tested under realistic flue-gas mixture. S(_{\text{CO}<em>2/N_2}) = 25-30, stability &gt; 100 h, P/(\ell)(</em>{\text{CO}_2}) &lt; 50 GPU.</td>
</tr>
<tr>
<td>Preliminary techno-economic analysis study</td>
<td>Membrane systems model developed using Aspen Plus® &amp; Aspen Custom Modeler®</td>
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</table>
## Project BP-2 Scorecard (2013-2014)

<table>
<thead>
<tr>
<th>BP-2 Deliverable</th>
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<th>Status</th>
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<tr>
<td>Scale-up polymer synthesis process</td>
<td>Polyphosphazene raw materials synthesized at 100 g scale with $P_{CO_2} = 100-500$ Barrer, $S_{CO_2/N_2} = 20-40$</td>
<td><img src="https://example.com/green.png" alt="Green" /></td>
</tr>
<tr>
<td>Scale-up HF support fabrication</td>
<td>50 m continuous spools of HF support fabricated with surface pore size $\approx 20-50$ nm, $P/l_{CO_2} &lt; 1,000$ GPU</td>
<td><img src="https://example.com/green-red.png" alt="Green/Red" /></td>
</tr>
<tr>
<td>Scale-up composite HF membrane fabrication</td>
<td>Defect-free 10” membrane modules with initial $S_{CO_2/N_2} \geq 30$ and $P/l_{CO_2}$ up to 1000 GPU fabricated.</td>
<td><img src="https://example.com/green.png" alt="Green" /></td>
</tr>
<tr>
<td>Demonstrate stable performance under realistic flue-gas</td>
<td>Membrane mini-modules with initial $S_{CO_2/N_2} \geq 30$ and $P/l_{CO_2}$ up to 1000 GPU → not stable $&gt;100$ h testing</td>
<td><img src="https://example.com/red.png" alt="Red" /></td>
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<tr>
<td>conditions</td>
<td>Membrane mini-modules with $S_{CO_2/N_2} \geq 30$ and 100 h stability → low $P/l_{CO_2} &lt; 50$ GPU</td>
<td></td>
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</tbody>
</table>
Project Overview

Polymer composite hollow fiber membranes and processes for economical post-combustion CO₂ capture from coal flue-gas
Membrane System Considerations

Schematic representation of a membrane process for CO2 removal from coal flue gas

- Various membrane process designs considered
- Two stage membrane process shortlisted for further investigation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
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<tbody>
<tr>
<td>Membrane-I/Membrane-II</td>
<td>Vacuum/air sweep</td>
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<tr>
<td>Flue gas composition</td>
<td>DOE baseline case 11* CO₂/N₂/H₂O/O₂(vol.%)</td>
</tr>
<tr>
<td></td>
<td>13.53/68.08/15.17/2.40</td>
</tr>
<tr>
<td>Flue gas flow rate</td>
<td>540 m³/s</td>
</tr>
<tr>
<td>Flue gas pressure</td>
<td>1.2-3 Bar</td>
</tr>
<tr>
<td>Flue gas temperature</td>
<td>45 °C</td>
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<tr>
<td>Membrane Selectivity (CO₂/N₂)</td>
<td>30-80</td>
</tr>
<tr>
<td>Membrane Permeance</td>
<td>100-2500 GPU</td>
</tr>
</tbody>
</table>

*Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity, Revision 2, November 2010, DOE/NETL-2010/1397
Membranes Model Analysis

- Overall membrane area highly dependent on permeance and mildly on selectivity in the selected range

Sensitivity analysis of overall membrane area to permeance & selectivity*

*Assumptions – Counter/counter-current membranes, membrane-I pressure ratio = 10
Membranes Model Analysis

Sensitivity analysis of membrane process CO$_2$ purity to selectivity

- Overall membrane process CO$_2$ purity strongly dependent on selectivity
  *Assumptions - Counter/counter-current membranes, membrane-I pressure ratio = 10
## Module Development Risk Analysis - Mechanical

<table>
<thead>
<tr>
<th>Failure Mode</th>
<th>Risks</th>
<th>During Operation</th>
<th>During Manufacturing</th>
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<tr>
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<td>Gas Pressure</td>
<td>CTE</td>
<td>High Temperature Degradation</td>
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<tr>
<td>Coating/Intermediate Layer</td>
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<td>Green</td>
<td>Green</td>
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<td>Yellow</td>
<td>Green</td>
<td>Green</td>
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<tr>
<td>Substrate</td>
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<td>Green</td>
<td>Green</td>
</tr>
<tr>
<td>Pressure Vessel Housing / Flanges</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Module Joints</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

### Risk Probability
- **High**
- **Medium**
- **Low**

- Burst tests/tensile testing to estimate hollow fiber strength
- Analytical (FEA analysis) to estimate effect of thermal & pressure stresses
- 200-hr flue gas ($w/\text{SO}_2, \text{NO}_x$) performance tests followed by post testing evaluation
Poly(phosphazene) Materials for CO₂ separation

General structure of stabilized (methoxyethoxy) ethanol phosphazene (MEEP)

Crosslinking 2-allylphenol

Strong CO₂ interaction

Film forming 4-methoxyphenol

Permeability-selectivity plot for CO₂/N₂ gas pair

MEEP Polyphosphazene polymers provide CO₂ affinity, permeability, and tunability for coating

Poly(phosphazene) Synthesis

Sealed-tube reaction; generally produces around 30 g of \((\text{PCl}_2\text{N})_n\)

Step 1.

\[\text{O}^-\text{Na}^+ + \text{Cl}_n \rightarrow \text{Cl}_n\]

Step 2.

\[\text{OCH}_3 + \text{P} \rightarrow \text{P} \rightarrow \text{Cl}_n\]

Step 3.

\[\text{CH}_3 + \text{P} \rightarrow \text{P} \rightarrow \text{Cl}_n\]

Synthesis employs dissolution steps to isolate soluble materials for subsequent coating.

Scaled up to about 90 grams.

Characterization using NMR, DSC, TGA, viscometry, flat disc permeation testing.

Ring Opening Polymerization

250°C, 24-48 hours

Sealed-tube reaction; generally produces around 30 g of \((\text{PCl}_2\text{N})_n\)

Synthesis employs dissolution steps to isolate soluble materials for subsequent coating.

Scaled up to about 90 grams.

Characterization using NMR, DSC, TGA, viscometry, flat disc permeation testing.
Poly(phosphazene) Coating Development

Compatibility
• Solubility in solvents benign to HF supports

Properties
• Improve physical handling
• High MW to reduce support infiltration

Performance
• Achieve target permeability and selectivity
• Long term stability

Cross-linking
• Maintain dimensional integrity

Permeability-selectivity plot for CO₂/N₂ at 30 °C (Pure gas-Flat sheet)
Poly(phosphazene) Coating Development

PZ materials like MEEP show great promise for the CO₂ - N₂ separation system.

How do we engineer them onto hollow-fiber supports while achieving the desired level of performance?

Permeability-selectivity plot for CO₂/N₂ gas pair
Torlon® HF Supports – Flexible & Tough

- Porous 1m HF support strands with controlled surface porosity fabricated and spinning parameters developed
- CO₂ permeance > 20,000 GPU; surface pore size ≈ 20-50 nm achieved
Coating PZ on Hollow Fibers

Defect Free Hollow fiber support

Porous support maintains high flux
Thin, crosslinked layer provides selectivity and flux.
Must be stable over time.

PZ solution

PZ coating infiltrates porous support
Solvent system degrades support
Flux attenuated

Layer is not defect-free.
PZ coating does not provide selectivity.
Using PDMS as a “caulking” layer

- Porous polymer “primed” with PDMS coating
- Crosslinked PZ coating provides affords three-layer composite membrane

Steps are intended to maintain, but not recover lost permeance / flux

- Hollow fiber
- PDMS solution
- PZ solution + crosslinking

High permeance, no real selectivity
Composite hollow fiber membrane prepared on 10cm scale
The allylphenol group is responsible for crosslinking the polymer. Thermal free-radical initiators such as AIBN and benzoyl peroxide were used in the course of the project. The initiators are mixed with the polymer solution, coated on to hollow fibers, and heated.
Poly(phosphazene) Cross-Linking

Effect of cross-linking time on polyphosphazene flat sheet permeability and selectivity

Poly(phosphazene) separation performance was found to be related to crosslinking phenomena.
Composite HF Membrane Module Testing

- Composite HF membrane modules with high cross-link density showed Selectivity$_{CO_2/N_2} \geq 30$ and $>100$ h stability, but with low permeance$_{CO_2} \approx 1$-$2$ GPU

HF membrane module performance testing at WRI under realistic flue gas conditions
Composite HF Membrane Module Testing

HF membrane module performance testing at GE under simulated flue gas conditions

- Composite HF membrane modules with lower cross-link density showed initial Selectivity$_{CO_2/N_2} \geq 30$ with permeance$_{CO_2}$ up to 1000 GPU, but poor stability over 100 h testing
Factors affecting performance

### Effect of crosslinking time:
in this study, CO₂ permeance increased, but selectivity dropped precipitously.

<table>
<thead>
<tr>
<th>Module ID</th>
<th>$q_{CO2/N2}$</th>
<th>CO₂ (P/I) (GPU)</th>
<th>Processing Time (h)</th>
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<tbody>
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<td>ARS8-724-St.7</td>
<td>21.00</td>
<td>159.0</td>
<td>24</td>
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<td>ARS3-691-St.1</td>
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<td>248.1</td>
<td>96</td>
</tr>
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</table>

### Different PZ coating techniques:
(pre-crosslinking, in this case) were not effective.
Challenges encountered in producing robust modules

A series of experiments including
- different initiators,
- cure conditions,
- pre-crosslinking of PZ
- post-treatments
- solvents
- different polymer batches
- fiber repair methods
was conducted.

Conditions were **not** identified which provided robust permeance & selectivity values in HF modules approaching target values.

Degradation over time was observed in many cases.

Ethanol, a preferred solvent for casting PZ films had a deleterious effect on porous Torlon. Demonstrated by depressing the onset of a sub-$T_g$ transition.

Even though Torlon is remarkably solvent-resistant and tough, the porous *structure* is susceptible to degradation.

The PDMS coating may delay, but may not prevent PZ migration over time into a porous polymeric support, driving unpredictable performance.
Performance loss over time – a hypothesis

Porous polymer “primed” with PDMS

PDMS solution

PZ solution + crosslinking

Hollow fiber

High permeance, no selectivity

PZ coating provides affords three-layer composite membrane

Time
Hollow Fiber Support Fabrication
Composite Hollow Fiber Fabrication

Batch coater

Coating solutions

HF modules
Linear Dip Coating Process

- Fiber
- Linear Drive
- Coating Solution
Continuous ‘Roll-to-Roll’ Coating Process
Scale up of hollow fibers at GRC

After spinning, hollow fibers are solvent-exchanged with a series of increasingly non-polar solvents to remove bore fluids and generate porosity.

On <1 m scale, this is easily handled with a batch operation.

Solvent exchanging full “lassos” proved to be more difficult.
Spin 17 Water exchange

- Fibers spun
- Several 2 m strands cut from the beginning of each state from winder spool
- Remaining fiber removed from spool as continuous lasso (20-50 m)
- Lasso laid in bttm of water tank
- Tank filled with ~ 10 gallons DI water
- Water recirculated in tank, heated to 40 °C
- Water held in tank for 1 day at these conditions
- After 1 day, water drained from the bottom of the tank (~ 15 min)
- Tank refilled and process repeated for 7 additional days (total 8 days)
Continuous water circulation & heating solvent exchange setup

Water Solvent exchange – Day 1

Water Solvent exchange – Day 2

Water Solvent exchange – Day 3

• Poor solvent exchange of NMP residual solvent in stationery water presumed

• Solvent exchange protocol modified to improve the mass transfer rate. Continuous circulation of water and keep the water warm (40 °C) during day time, heat and circulation during night

• Better leaching of solvent and additives observed during modified solvent exchange. After day 3, water quality remained visibly unchanged
Solvent exchange at scale – H₂O to CH₃OH to Hexane

- Water drained from tank, lasso remains in bottom of tank
- Tank filled with ~ 4 gallons methanol
- Soak for ~ ½ day (3-4 hours)
- Drain methanol from tank
- Tank filled with ~ 4 gallons hexane
- Soak for ~ ½ day (3-4 hours)
- Drain hexane from tank
- Lasso removed from tank
- Laid out to air dry overnight
- Fibers transferred to convection oven to dry at 180 °C for 3 days, air atm
GaTech Spin 8 – Fibers Comparison (Increasing Permeance Order)

ARS8-2 (10,189 GPU)  
ARS8-8 (13,781 GPU)  
ARS8-7 (17,250 GPU)  
ARS8-3 (19,782 GPU)  
ARS8-1 (21,000 GPU)  
ARS8-4 (24,294 GPU)
GE Spin 15 scaleup– Fibers Comparison

State-1 (38 GPU)

State-2 (0.4 GPU)

State-3 (3 GPU)

State-4 (33 GPU)

State-5 (48 GPU)
Large scale preparation of Torlon hollow fibers: Path Forward

Hollow Fiber porosity was limited by solvent exchange and post-spinning procedures, not spinning parameters, polymer purity, etc.

A re-evaluation of large batch solvent exchange to better understand transport and pore development phenomena is recommended.

These scaleup challenges would likely yield to straightforward process development studies.

<table>
<thead>
<tr>
<th>Strand</th>
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<th>2S</th>
<th>3S</th>
<th>4S</th>
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<td>O2</td>
<td>Total</td>
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<td>N2</td>
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Path forward – Beyond MEEP

To address some of the challenges identified with implementing MEEP polymers in an engineered solution, an Interpenetrating network (IPN) scheme was identified.

By blending and crosslinking a more rigid PZ polymer into MEEP, improved properties could be attained.

This interpenetrating network (IPN) scheme offers improvement in dimensional stability & creep behavior for advantaged separation materials, while allowing for solution coating of various substrates.
Polymer 1: 80% MEEP

Crosslinkable (2-AP) groups

X: Y: Z = 5:15:80

Polymer 2: PPOP

X or Y

X: Y = 1:99

Mix & Crosslink

Path forward: MEEP/PPOP IPN
Path forward – Initial proof of IPN concept

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Temperature (°C)</th>
<th>CO₂ Permeability (Barrers)</th>
<th>CO₂/N₂ Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPN 3 70 % (80 % MEEP) / 30 % PPOP</td>
<td>30</td>
<td>458.6</td>
<td>35.8</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>661.6</td>
<td>20.4</td>
</tr>
</tbody>
</table>

Initial results show good performance with 100h stability on disc substrates

Smooth, hard surfaces with little tack

Implementation on HF systems would require solvent optimization, processing studies etc.
Final Thoughts

Important interactions between materials & processes needed to construct an advantaged composite HF system for CO$_2$ separation were uncovered through this work. The importance of testing systems long enough to measure slow changes was made clear.

These interactions would not be readily predictable from examining the components *a priori* (polymer, support, process)

The team and its members can offer informed guidance for future work in this area to address these risks as part of large or focused programs.