Project Review (DE-FE0031552)

**DEVELOPMENT OF A HIGHLY-EFFICIENT MEMBRANE-BASED WASTEWATER MANAGEMENT SYSTEM FOR THERMAL POWER PLANTS**

Presented by:
Indira Jayaweera (PI), Sr. Program Manager
Integrated Systems Division
SRI International

**Project Partnerships**
(to enable domestic fossil fuel utilization for power production with a reduced freshwater withdrawal)

Department of Energy (DOE): $639,949; Cost share: $160,000; DOE Project Manager: Anthony Zinn

Enerfex, Inc.
Modeling & Cost-share

Membrane Fabrication & Testing

PBI Polymer & Cost-share

GENERON
Module Fabrication & Cost-share
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“MODELED WATER SAVINGS IN YEAR 2043: COMBINED TECHNOLOGIES COULD REDUCE THERMOELECTRIC WATER WITHDRAWALS BY 603 BGY”

Source: NETL Water Management Program Update, Annual Project Review meeting- 3 September 2020
Flue Gas Desulfurization Wastewater (FGD WW): 
*Treatment for water recovery and reuse*

To maintain optimum operating conditions in a wet scrubber, a purge stream is discharged from the system (primarily for efficient SO₂ removal and chloride and corrosion control). This aqueous purge stream (FGD blowdown) is acidic (pH ~ 4-6), supersaturated with gypsum, and contains high levels of total dissolved solids (TDS) and total suspended solids (TSS). The TDS is composed of heavy metals, chlorides, sulfates, calcium, magnesium, and dissolved organic compounds.

Our approach is to use a membrane separation technology for (1) recovering FGD makeup water and clean water (2) removing selenium from FGD WW until it is below the effluent discharge limits.
Membrane Material for Hollow Fiber Production

We use polybenzimidazole (PBI) hollow-fiber membrane (HFM) based separation technology for removing salts from FGD wastewater. The PBI membranes are resistant to fouling and can be operated under substantially harsher environments than conditions tolerated by commercially available membranes.

- Superb thermal stability: $T_g = 450^\circ\text{C}$, degradation at $450^\circ\text{C}$ in air, continuous operating temperature to $250^\circ\text{C}$.
- Excellent resistance to chemicals, acid, and base hydrolysis.
- Commercially available from the US entity, PBI Performance Products. The polymer is available in powder form or various formulations solubilized in $N,N$-dimethyl acetamide (DMAc).

![Diagram of PBI HFM spinning line](image)

**PBI HFM spinning line**  
(SRI has two spinning lines with 10 m/min capacity)

![Diagram of PBI HFM cross-section and bundle](image)

**PBI HFM cross-section (left) and a bundle (right)**

![Diagram of PBI hollow-fiber membrane asymmetric structure](image)

**PBI hollow-fiber membrane asymmetric structure**

![Diagram of PBI HFM cross-section and bundle](image)

**Polybenzimidazole**
## Project Tasks Timeline and Milestones

<table>
<thead>
<tr>
<th>Task/Sub task No.</th>
<th>Milestone Description</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Updated PMP</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Kickoff Meeting</td>
<td></td>
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<tr>
<td>2.1</td>
<td>Completion of small-diameter RO membrane fabrication protocol</td>
<td></td>
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<tr>
<td>2.2</td>
<td>Completion of preliminary membrane system modeling</td>
<td></td>
</tr>
<tr>
<td>2.3</td>
<td>Completion of membrane testing with synthetistic water and data analysis</td>
<td></td>
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<tr>
<td>2.4</td>
<td>Completion of PBI membrane performance testing with real field wastewater samples</td>
<td></td>
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<tr>
<td>3.1</td>
<td>Completion of longer-term membrane fouling testing</td>
<td></td>
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<tr>
<td>3.2</td>
<td>Completion of fabrication and pressure testing of small-diameter RO membranes</td>
<td>90% Complete</td>
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<tr>
<td>4.1</td>
<td>Completion of membrane module assembly array</td>
<td>Completed</td>
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<tr>
<td>4.2</td>
<td>Completion of identification of system components for effluent management system</td>
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<tr>
<td>1</td>
<td>Final report</td>
<td>Net Yet Started</td>
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PBI HFM Selection for Testing

HFM Screening
- Use N₂ permeation (GPU) measurement for fiber screening
- Evaluate the performance using 2000 ppm NaCl, MgSO₄ or NaSO₄

Water flux or salt rejection as a function of N₂ permeance though the membrane in PBI HFMs with dense layer thickness < 0.3-micron.

Water flux or salt rejection as a function of N₂ permeance though the membrane in PBI HFMs with dense layer thickness > 0.3-micron.

Type 2 membranes with two different wall thicknesses were used in the current project; cross sections are shown. Majority of the testes were conducted using 51A.
Test Solutions and the Test System

<table>
<thead>
<tr>
<th>Parameters Varied</th>
<th>Value</th>
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<tbody>
<tr>
<td>pH</td>
<td>4 to 10</td>
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<tr>
<td>Temperature</td>
<td>RT and 50 °C</td>
</tr>
<tr>
<td>Duration</td>
<td>Short and long</td>
</tr>
<tr>
<td>Concentration</td>
<td>2000 to 22,000 ppm</td>
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<tr>
<td>Se doping</td>
<td>250 ppb</td>
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<tr>
<td>Pressure</td>
<td>200 to 500 psi</td>
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</table>

<table>
<thead>
<tr>
<th>Salt</th>
<th>Concentration (ppm)</th>
<th>Ions</th>
<th>Concentration (ppm)</th>
</tr>
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<tbody>
<tr>
<td>CaSO₄</td>
<td>2511</td>
<td>Ca²⁺</td>
<td>3272</td>
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<tr>
<td>CaCl₂</td>
<td>7029</td>
<td>Mg²⁺</td>
<td>1908</td>
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<tr>
<td>MgCl₂</td>
<td>7553</td>
<td>Na⁺</td>
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<tr>
<td>NaCl</td>
<td>1731</td>
<td>Cl⁻</td>
<td>11191</td>
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<tr>
<td>Total</td>
<td>18824</td>
<td>SO₄²⁻</td>
<td>1773</td>
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</table>

Typical Synthetic FGD Test Solution Composition

FGD WW* from an operating Coal Power Plant in Illinois

FGD type: Wet FGD
Coal type: Subbituminous
Total TDS: ~ 15,000 ppm
Total Organic C: 81 ppm
Chloride/Sulfate Ratio (ppm/ppm) = >5
FGD WW provided by Water Team at University of Illinois Urbana-Champaign

FGD WW as received (10 gal)
FGD WW after long standing
Microfiltration to remove suspended solids

Bench-scale desalination system: Simplified schematic (left) and photograph (right) of the system.
Results:
For synthetic solutions and long-term testing of FGD WW

Synthetic Solutions: Water flux increased linearly with pressure and temperature. This is expected behavior for RO membranes. The order of water flux by salt solution was CaSO\(_4\) > CaCl\(_2\) > MgCl\(_2\) > NaCl. Salt rejection was >99% in all cases.

FGD WW: Observed a stable water flux and >98% salt rejection.
Results (continued):

For raw and diluted FGD WW (6,900 to 14,000 ppm range)

- Observed water flux for 8100 ppm FGD water at varying temperatures and pressures.
- Observed salt rejection for FGD water as a function of pressure.

As expected, water flux increased linearly with pressure and temperature >98% salt rejection observed.
Results (continued):

For 14,400 ppm FGD WW

Effects of temperature and pressure on water flux and % rejection for FGD WW.

Effects of pressure and pH on water flux and % rejection for FGD WW.

Flux increases with increasing temperature and pressure; >98% salt rejection. Maximum salt rejection observed at pH range 5.3 to 7.8 at about 40°C and 400 psi.
Results Summary

• The testing of PBI HFM synthetic solutions (single & mixed salts) with real FGD WW were successful.
  - Synthetic solutions consisting of CaSO$_4$, CaCl$_2$, MgCl$_2$, and NaCl (up to 22,000 showed >99% rejection.
  - Synthetic solutions doped with 250 ppb Se showed <1 ppb Se can be achieved using a two-stage membrane system.
  - FGD WW solutions showed >98% rejection during 100 hr. testing. No flux reduction observed with PBI HFM with fiber OD/ID ratio <1.7. pH and temperature effects as expected. The water flux increased by a factor of 2 at 50 °C compared to RT.
  - Enerfex modeled a membrane system for treating 200GPM FGD WW stream based on the measured PBI HFM performance at 500 psi. Validated performance for reusing 50% of the FGD WW as make-up.
  - Manuscript has been prepared for peer-review publication.
• Industry involvement at early development phase.
  - Generon successfully fabricated PBI HFM cartridges for 2.5 and 4-in standard commercial modules.

Future Developments

• Longer term testing (500 hr) with preconditioning (e.g., UF) of FGD WW.
• Design, build, and test a 2-stage prototype system.
Acknowledgements

- Anthony Zinn and others at NETL
- Eminet Gebremichael, Michael Wales, Xiao Wang, Palitha Jayaweera, Elisabeth Perea, and Bill Olson (SRI)
- Richard Callahan (Enerfex, Inc.)
- Greg Copeland and Michael Gruender (PBI Performance Products)
- John Jensvold and his team (Generon IGS)
- Nandakishore Rajagopalan and Sriraam Chandrasekaran, (University of Illinois at Urbana-Champaign)
Contact:

Dr. Indira Jayaweera  
Sr. Staff Scientist and Sr. Program Manager  
indira.jayaweera@sri.com  
1-650-859-4042

Thank You