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

Presented by:

Indira Jayaweera, Sr. Program Manager
Advanced Technology and Systems Division
SRI International

Project Team

Enerfex, Inc.
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❖ Project Progress and Future Work
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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.
Project Description
Project Goals

- The main goal of the current research project is to develop innovative effluent water management practices at coal-fired power plants.
  - Use a membrane separation technology for (1) removing selenium from FGD WW below the effluent discharge limits and (2) recovering FGD makeup water and quality water.

Block diagram showing advanced mode of operation for recovering make-up water and quality water.
Membrane Material

- 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.
PBI Characteristics and Commercial Availability

- Superb thermal stability: Tg=450°C, degradation at 450°C in air, continuous operating temperature to 250°C
- Excellent resistance to chemicals, acid, and base hydrolysis.
- Commercially available from the US entity, PBI Performance Products, Inc. The polymer is available in powder form or various formulations solubilized in N,N-dimethyl acetamide (DMAc)
- PBI membranes are expected to perform better than conventional membranes for treating FGD WW

Zeta potential data for PBI and CA (cellulose acetate)
Source: Membranes, 2013, 3(4), 354-374
Advantages of Hollow-Fiber Membrane Architecture

Hollow-Fiber vs. Spiral-Wound Membrane

<table>
<thead>
<tr>
<th>Hollow Fiber</th>
<th>Spiral-Wound Flat Sheet Membrane</th>
</tr>
</thead>
</table>

- No need for spacers
- Self-supporting structure
- High surface area per unit of membrane module volume: spiral-wound packing density is 800 m²/m³ and hollow fiber is 6000 m²/m³ (Source: Lux Research, Inc.)

Comparison of RO element productivity and flux for HFM and spiral-wound modules (Enerfex modeling)
Project Budget and Team

Cooperative Agreement Grant with U.S. DOE:
- Contract No.: DE-FE0031552

Period of Performance:
- 12/19/2017 – 06/18/2020

Funding:
- U.S. Department of Energy: $639,949
- Cost share: $160,000
- Total: $799,949

NETL Project Manager:
- Anthony Zinn: anthony.zinn@netl.doe.gov

Principal Investigator:
- Indira Jayaweera: indira.jayaweera@sri.com

Key Team Members

SRI: Indira Jayaweera, Xiao Wang, Palitha Jayaweera, Elisabeth Perea, Regina Elmore and William Olsen

Enerfex: Richard Callahan

PBI: Greg Copeland and Michael Gruender
Our Work Plan

- Test the SRI seawater desalination PBI HFMs for separating sulfates and selenium from an FGD WW simulant and then from real-world FGD WW samples
- Use the data to design and model the optimized membrane unit arrangement for reduced energy operation
- Fabricate high-strength PBI HFMs suitable for processing high-salinity (high-osmotic pressure) brines
# Project Timeline and Milestones

## Task/Sub task No.

<table>
<thead>
<tr>
<th>Task/Sub task No.</th>
<th>Milestone Description</th>
<th>Planned Completion</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Updated PMP</td>
<td>1/18/2018</td>
<td>COMPLETED</td>
</tr>
<tr>
<td>1</td>
<td>Kickoff Meeting</td>
<td>3/18/2018</td>
<td>COMPLETED</td>
</tr>
<tr>
<td>2.3</td>
<td>Completion of small-diameter RO membrane fabrication protocol development</td>
<td>3/18/2019</td>
<td>COMPLETED</td>
</tr>
<tr>
<td>2.4</td>
<td>Completion of preliminary membrane system modeling</td>
<td>3/18/2019</td>
<td>COMPLETED</td>
</tr>
<tr>
<td>2.2</td>
<td>Completion of membrane testing with synthestic water and data analysis</td>
<td>7/30/2019</td>
<td>50% COMPLETE</td>
</tr>
<tr>
<td>3.1</td>
<td>Completion of PBI membrane performance testing with real field wastewater samples</td>
<td>10/30/2019</td>
<td>STARTED</td>
</tr>
<tr>
<td>3.2</td>
<td>Completion of longer-term membrane fouling testing</td>
<td>5/18/2020</td>
<td>NOT YET STARTED</td>
</tr>
<tr>
<td>3.3</td>
<td>Completion of fabrication and pressure testing of small-diameter RO membranes</td>
<td>4/18/2020</td>
<td>STARTED</td>
</tr>
<tr>
<td>4.1</td>
<td>Completion of membrane module assembly array</td>
<td>9/18/2019</td>
<td>STARTED</td>
</tr>
<tr>
<td>4.2</td>
<td>Completion of identification of system components for effluent management system</td>
<td>5/18/2020</td>
<td>NOT YET STARTED</td>
</tr>
<tr>
<td>1</td>
<td>Final report</td>
<td>6/18/2020</td>
<td></td>
</tr>
</tbody>
</table>
Task 2. Membrane Development and Testing
Task 3. Testing with Field Samples
The new spinning line was crucial for developing an improved and robust spinning process that can be transferred to industry. The new line enabled:

- Use of multiple coagulation solvents
- Optimization of fiber diameter by controlled stretching
- Optimization of the fiber dense-layer thickness
Small Diameter Fiber Development

Achievement:
More than 40% HFM diameter reduction from SRI base HFMs
Established the protocol to fabricate less than 350 µm OD HFMs
Completed the Protocol Development for small diameter fibers

336 micron OD and 186 micron ID
Preparation of PBI HFM for High-Flux Applications

*(HFM choice for the second stage)*

Starting PBI HFM is shown here.
PBI HFM Lumen Surface Before and After the Interfacial Polymerization (previous work)

Left: High-magnification picture of the lumen surface of the PBI HFM
Right: High-magnification picture of the PBI HFM lumen surface after interfacial polymerization to generate a very thin polyamide dense layer

Note: The uneven lumen surface is a good support structure and a high surface area. The ridges on the composite layer also provide a very high surface area → high flux.
HFM Performance

Performance with seawater and 2000 ppm NaCl

Rejection >95%

2000 ppm NaCl

Seawater

Flux (LMH)

Pressure (psi)

63J Series - seawater
63J-H - 2000 ppm NaCl
63J-G - 2000 ppm NaCl

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Fiber Optimization and Testing

- Vary the HFM dense layer thickness by adjusting the spinning parameters
- Use N$_2$ permeation (GPU) measurement for fiber screening
- Evaluate the performance using 2000 ppm NaCl, MgSO$_4$ or NaSO$_4$

<table>
<thead>
<tr>
<th>HFM ID</th>
<th>63C-1</th>
<th>63C-2</th>
<th>63J-1</th>
<th>63J-2</th>
<th>63F-1</th>
<th>63F-2</th>
<th>63E-1</th>
<th>63E-2</th>
<th>63H-1</th>
<th>63I-1</th>
<th>63I-2</th>
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</thead>
<tbody>
<tr>
<td>Pressure (psi)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2000 ppm MgSO$_4$</td>
<td>514</td>
<td>515</td>
<td>503.5</td>
<td>504</td>
<td>512</td>
<td>512.5</td>
<td>509</td>
<td>509</td>
<td>514</td>
<td>516</td>
<td>518</td>
</tr>
<tr>
<td>Flux (LMH)</td>
<td>17.4</td>
<td>20.9</td>
<td>8.97</td>
<td>12.3</td>
<td>14.7</td>
<td>12.0</td>
<td>12.2</td>
<td>16.5</td>
<td>10.2</td>
<td>17.9</td>
<td>16.5</td>
</tr>
<tr>
<td>Rejection (%)</td>
<td>71.2</td>
<td>74.6</td>
<td>82.6</td>
<td>81.3</td>
<td>85.3</td>
<td>86.1</td>
<td>78.8</td>
<td>79.9</td>
<td>84.3</td>
<td>75.9</td>
<td>75</td>
</tr>
<tr>
<td>Flux (LMH)</td>
<td>16</td>
<td>19.6</td>
<td>11.3</td>
<td>12.5</td>
<td>13.2</td>
<td>11.6</td>
<td>13.8</td>
<td>16.0</td>
<td>9.12</td>
<td>18.9</td>
<td>17.2</td>
</tr>
<tr>
<td>Rejection (%)</td>
<td>82</td>
<td>83</td>
<td>77.5</td>
<td>76.5</td>
<td>83.5</td>
<td>84.3</td>
<td>85.2</td>
<td>85.6</td>
<td>81.3</td>
<td>58.9</td>
<td>59.4</td>
</tr>
</tbody>
</table>

N$_2$ Permeance (GPU)

- 2000 ppm MgSO$_4$
- 2000 ppm Na$_2$SO$_4$
- Water Flux
- 10,000 ppm NaCl
- Rejection for Na$_2$SO$_4$ > 99%
- Water Flux 7 LMH
Test Results for Synthetic Solutions (<15,000 ppm)

### Flux and Rejection

**Feed TDS : ~ 15,000**

<table>
<thead>
<tr>
<th>Module O</th>
<th>Time</th>
<th>Flux (LMH)</th>
<th>Permeate solution conductivity/TDS</th>
<th>Rejection (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 hr</td>
<td>5.70</td>
<td>0.805 ms/535 ppm</td>
<td>96.3</td>
<td></td>
</tr>
<tr>
<td>4 hr</td>
<td>5.69</td>
<td>0.803 ms/532 ppm</td>
<td>96.3</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Module P</th>
<th>Time</th>
<th>Flux (LMH)</th>
<th>Permeate solution conductivity/TDS</th>
<th>Rejection (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 hr</td>
<td>5.87</td>
<td>0.213 ms/141 ppm</td>
<td>99.0</td>
<td></td>
</tr>
<tr>
<td>4 hr</td>
<td>5.75</td>
<td>0.237 ms/159 ppm</td>
<td>98.9</td>
<td></td>
</tr>
</tbody>
</table>

* PBI-IFP is a surface modified PBI HFM

### Test Solution Composition

<table>
<thead>
<tr>
<th>Salt</th>
<th>Concentration (ppm)</th>
<th>Composition</th>
<th>Ions</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaSO₄</td>
<td>2511</td>
<td></td>
<td>Ca²⁺</td>
<td>3272</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>7029</td>
<td></td>
<td>Mg²⁺</td>
<td>1908</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>7553</td>
<td></td>
<td>Na⁺</td>
<td>681</td>
</tr>
<tr>
<td>NaCl</td>
<td>1731</td>
<td></td>
<td>Cl⁻</td>
<td>11191</td>
</tr>
<tr>
<td>Total</td>
<td>18824</td>
<td></td>
<td>SO₄²⁻</td>
<td>1773</td>
</tr>
</tbody>
</table>

### Pressure vs. Time Profile of the Membrane Module O

- Feed TDS : ~ 15,000
- Feed TDS : ~ 1,500

**PBI HFM performance is as Predicted**
Concentrated Synthetic Solution Testing

*Feed TDS: >20,000 ppm*

**Synthetic Solutions**
- Prepared solution with solids was stirred overnight to saturate the dissolved salt concentration
- Particle settling tendency was tested and a decanted solution was used in HFM performance evaluation
- Initial PBI HFM performance evaluation was done at 580 psi and the testing is ongoing (>95% salt removal with water flux of 3 to 5 LMH)

**FGD Raw Water**
- Currently evaluating the best method to process the raw FGD water
Bench-Scale UF Systems at SRI

Modified applied membrane UF system for testing 2.5-in PBI hollow-fiber membranes.

Small-scale performance testing station (1-in modules) for UF applications

Both these systems are recent installments.
Bench-Scale RO Systems at SRI

Small-scale performance testing station (1-in modules) for RO applications

Modified Applied Membrane’s RO system (1-5 gpm) for testing 2 to 4-in PBI hollow-fiber membranes.

The small bench-system is used for performance evaluation of the membranes under the current project.
Task 4. Modeling
Modeling of Module Arrangements

- Setting up the model to simulate array of HFM modules
- Selenium data [SRI test data] simulation and evaluation of the permeability coefficients
- Simulation of a 2 stage system without a recycle
- Simulation of a 2 stage system with a recycle
- Selenium removal technology comparison
- Estimation of the water productivity in a HFM based modules
Preliminary Results from Modeling

Modeling of Se Removal

<table>
<thead>
<tr>
<th></th>
<th>1st Stage, m² = 49.0</th>
<th>2nd Stage, m² = 6.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>FGD WW</td>
<td>314.7</td>
<td>317.1</td>
</tr>
<tr>
<td>FGD WW Plus</td>
<td>314.7</td>
<td>317.1</td>
</tr>
<tr>
<td>R2 Recycle F1</td>
<td>311.7</td>
<td>314.7</td>
</tr>
<tr>
<td>Retentate R1</td>
<td>150.0</td>
<td>150.0</td>
</tr>
<tr>
<td>Permeate P1</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

2nd stg. net press. diff, selectivity = 38.2

Feed F2
Interstage
Retentate R2
Mbr. Recycle
Permeate P2
Clean Water

<table>
<thead>
<tr>
<th></th>
<th>Feed</th>
<th>Retentate</th>
<th>Permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>press, psia</td>
<td>514.7</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>LMH</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>L/h</td>
<td>100.15</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>lb/h</td>
<td>220.73</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Se, lb/h*</td>
<td>55.18</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Se, ppb</td>
<td>250.0</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

kWh/10³ gal. of feed

* times 10⁻⁶

<table>
<thead>
<tr>
<th></th>
<th>1st Stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>net press. diff, selectivity = 8.3</td>
<td></td>
</tr>
</tbody>
</table>

FGD WW FGD WW Plus Recycle = F1

<table>
<thead>
<tr>
<th></th>
<th>1st Stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>press, psia</td>
<td>314.7</td>
</tr>
<tr>
<td>LMH</td>
<td>n/a</td>
</tr>
<tr>
<td>L/H</td>
<td>100.08</td>
</tr>
<tr>
<td>LB/H</td>
<td>220.58</td>
</tr>
<tr>
<td>SeO₄²⁻ ppb</td>
<td>250.0</td>
</tr>
<tr>
<td>Mass Bal.</td>
<td>100.0% n/a</td>
</tr>
</tbody>
</table>

Solute rejection = 98.6%

Water Productivity

<table>
<thead>
<tr>
<th></th>
<th>Stage one</th>
<th>Stage two</th>
<th>System</th>
<th>Stage one</th>
</tr>
</thead>
<tbody>
<tr>
<td>retentate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>permeate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O rec.</td>
<td>77%</td>
<td>78%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Se, ppb</td>
<td>0.8</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LMH</td>
<td>12.64</td>
<td>50.91</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ref: VSE-1 is commercial waste water treatment membrane system (Hydranautic’s ESPA2-LD modules) by New Logic Research, Inc.,

Due to the PBI hollow fiber membrane’s higher active membrane area per element, a hollow fiber element with a 12.6 LMH specific permeate flow will yield the same total clean water permeate product flow as a spiral membrane of the same element volume having a 50.9 LMH specific permeate flow.
Ongoing and Future Project Work
Current Ongoing Work

- **Task 1. Project Management**
  - Continuing project discussions with Enerfex and PBI Performance Products
  - Initiating discussions with Generon to establish a subcontract
- **Tasks 2 & 3. Membrane Development and Testing**
  - Continuation of testing according to the test plan
    - Testing with simulated solutions and field samples
- **Task 4. Membrane Development and Testing**
  - Modeling of the system Integration
Concurrent development of membrane technology for multiple applications would be advantageous in scale-up efforts. Currently SRI has two parallel membrane development projects.
Acknowledgements

- Anthony Zinn and others at NETL
- SRI Team: Indira Jayaweera, Xiao Wang, Regina Elmore, Palitha Jayaweera, Elisabeth Perea, Srini Bhamidi and Bill Olson
- Richard Callahan (Enerfex, Inc.)
- Greg Copeland and Michael Gruender (PBI Performance Products)
- John Jensvold and his team (Generon IGS)
- Prodip Kundu (OLI Systems)
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Thank You
Current State of the Art (SOA) in FGD WW Treatment

The SOA is a combination of the following methods:

- Lime softening to remove magnesium hardness
- Soda ash softening to remove calcium hardness (20% of the total cost)

\[
\begin{align*}
\text{MgSO}_4 + \text{Ca(OH)}_2 & \rightarrow \text{Mg(OH)}_2 + \text{CaSO}_4 \\
\text{CaSO}_4 + \text{Na}_2\text{CO}_3 & \rightarrow \text{CaCO}_3 + \text{Na}_2\text{SO}_4
\end{align*}
\]

- Ion exchange to reduce calcium down to 50 ppm (acid regeneration is required for high-salinity FGD WW)
- Thermal process
- **Membrane separation**
  (microfiltration, MF; ultrafiltration, UF; reverse osmosis, RO; and/or forward osmosis, FO).

Main Challenge in Membrane Separation: **Membrane fouling** is attributed to high levels of sulfate present in FGD WW systems.
FGD WW Composition, Solubility, and Osmotic Pressure

Average pollutants in untreated FGD WW (Source: Smith, 2009)

<table>
<thead>
<tr>
<th>Component (mg/l)</th>
<th>Raw FGD wastewater</th>
<th>Retentate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>3290</td>
<td>7000</td>
</tr>
<tr>
<td>Magnesium</td>
<td>1850</td>
<td>4000</td>
</tr>
<tr>
<td>Sodium</td>
<td>663</td>
<td>1300</td>
</tr>
<tr>
<td>Chloride</td>
<td>11,050</td>
<td>23000</td>
</tr>
<tr>
<td>Sulfate</td>
<td>1,945</td>
<td>4000</td>
</tr>
</tbody>
</table>

Understanding sulfate solubility/precipitation with varying temperature and compositions is important in designing the overall effluent management system.
Selenium Separation

The speciation of Se with pH can play a key role in effectiveness of separation, especially at low levels

• The most common form of Se in the FGD wastewater is selenite

• The most common technologies to date for Se: media filtration, chemical treatment, and biomediated removal

Challenge

• The FGD WW has a high concentration of total dissolved solids (TDS) ranging from 15,000 to 45,000 mg/l, which makes selectively removing the Se very difficult and often requires systems to be large enough to treat a significant portion of the TDS before being able to reach an acceptable Se concentration

• The solubility of calcium selanate is much higher than that of calcium sulfate; therefore, Se is not effectively removed with gypsum

• The weak sorption on common adsorbents such as flocculating polymers, carbon, and ion exchange make it difficult to achieve the lower Se

Eh-pH diagram for selenium species in water

• The selenite is present as the single-charged anion, HSeO$_3^-$ (below pH 7) but as the double-charged anion, SeO$_3^{2-}$ (above pH 7)

• The selenate, SeO$_4^{2-}$ is present as doubly charged even below pH 4 (pKa ~ 1.7)

It has already been shown that RO can be used to remove selenium oxyanions from FGD WW

Source: New Logic Research

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Fabrication of Fibers with Good Reproducibility

Quality control is the KEY to success when scaling-up

- Developed protocols for spinning < 0.3-µm dense layer hollow-fiber membranes with membrane OD 450 to 650 µm. ABOVE: ~ 0.1-µm fibers with ~ 600-µm OD.
- Fabricated hollow-fiber membrane with a very thin, dense layer (< 0.3 µm) in kilometer lengths with very good reproducibility
- Tested more than 100 fiber bundles (1-in) for fiber-spinning optimization
- Spun > 100 km of fiber for modules fabrication (4-in)

Achievements (Gas Separation Membrane):
- Dense-layer thickness reduced from 1 µm to < 0.3 µm
- Fiber diameter reduced from 1 mm to less than 600 µm

DE-FE001296