SRI International

Project Review (DE-FE0031552)

# Development of a Highly-Efficient Membrane-Based Wastewater Management System for Thermal Power Plants


Presented by:
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NATIONAL ENERGY TECHNOLOGY LABORATORY

SRI International
Membrane Fabrication & Testing

Enerfex, Inc.
Modeling & Cost-share

IGS GENERON INNOVATIVE GAS SYSTEMS
Module Fabrication & Cost-share

Pbi PERFORMANCE PRODUCTS, INC.
PBI Polymer & Cost-share

## 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 Manger: Anthony Zinn

# Disclaimer

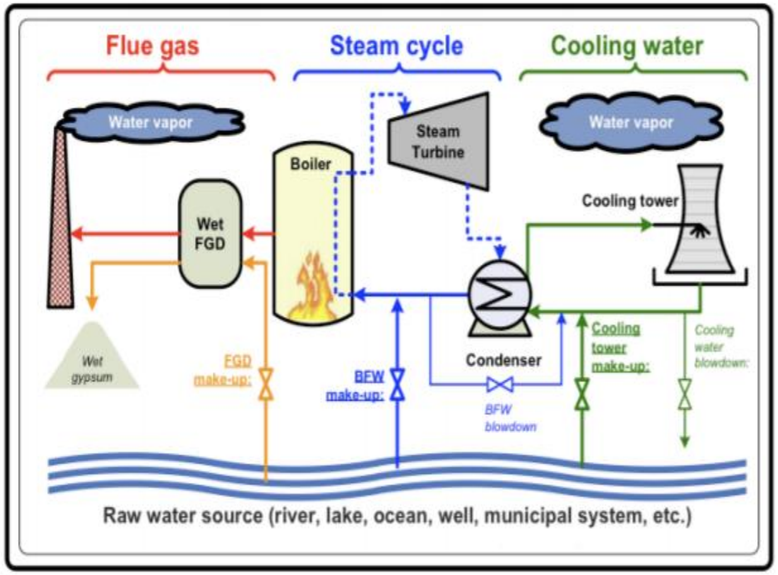


*"MODELED WATER SAVINGS IN YEAR 2043:*
*COMBINED TECHNOLOGIES COULD REDUCE*
*THERMOELECTRIC WATER WITHDRAWALS BY 603 BGY"*

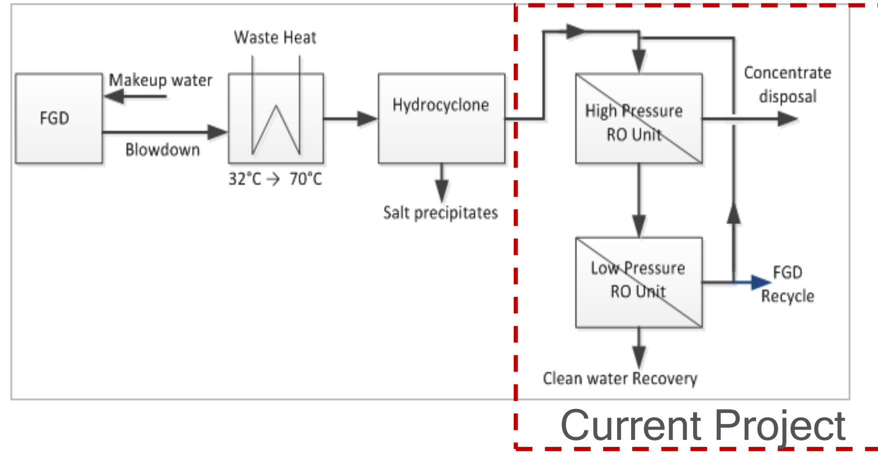
Source: NETL Water Management Program Update, Annual Project Review meeting- 3 September 2020

# Flue Gas Desulfurization Wastewater (FGD WW):

*Treatment for water recovery and reuse*




**Schematic for pulverized coal (PC) power plant with cooling and wet FGD**
Source: NETL Report, Dipietro, 2009



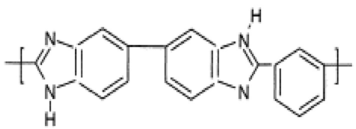

**Block diagram showing advanced mode of operation for recovering make-up water and quality water**

- To maintain optimum operating conditions in a wet scrubber, a purge stream is discharged from the system (primarily for efficient $SO_2$ 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.

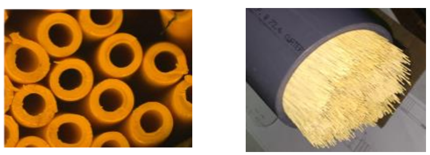
# Membrane Material for Hollow Fiber Production

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.

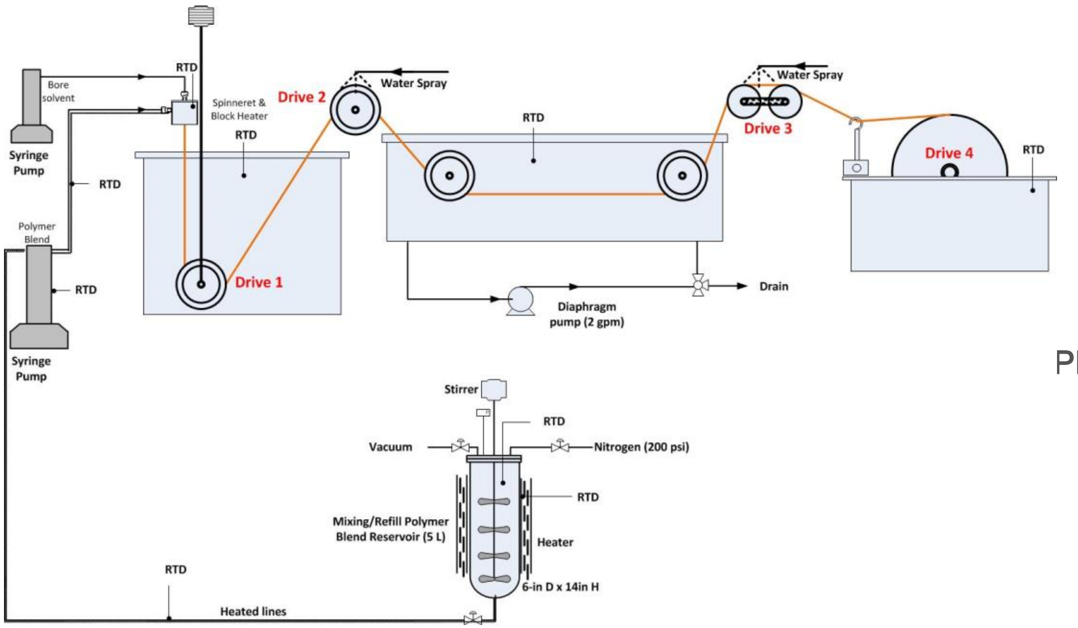
- Superb thermal stability: Tg = 450°C, degradation at 450°C in air, continuous operating temperature to 250°C.
- Excellent resistance to chemicals, acid, and base hydrolysis.
- Commercially available from the US entity, PBI Performance Products. The polymer is available in powder form or various formulations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



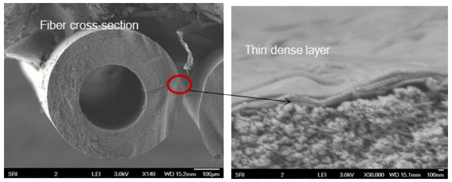
Polybenzimidazole



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




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




PBI hollow-fiber membrane asymmetric structure

# Project Tasks Timeline and Milestones

| Task | Start Date | End Date |
|---|---|---|
| **PBI HFM BP1 and BP2** | **12/1/17** | **5/31/20** |
| **Task 1.0 - Project Management and Planning** | **12/1/17** | **5/31/20** |
| **Task 2-0: Membrane Development and Testing** | **2/1/18** | **7/31/19** |
| Subtask 2.1 - Development of a Test Plan | 12/1/18 | 1/31/19 |
| Subtask 2.2 - Membrane Selection and Testing | 2/1/18 | 7/31/19 |
| Subtask 2.3 - Development of Small Diameter Fibers | 10/1/18 | 3/31/19 |
| Subtask 2.4 - Preliminary Membrane Modeling | 1/5/18 | 2/28/19 |
| **Task 3.0 - Testing With Filed Samples** | **4/1/19** | **12/31/20** |
| Subtask 3.1 - Performance Evaluation | 4/1/19 | 6/30/19 |
| Subtask 3.2 - Long Term Testing and Fouling Testing | 7/1/19 | 4/30/20 |
| Subtask 3.3 - Fabrication and Testing of Small Diameter Fibers | 10/1/19 | 3/31/20 |
| **Task 4.0 - Modeling** | **4/1/19** | **5/31/20** |
| Subtask 4.1 - Modeling of Module Arrangement | 4/1/19 | 8/31/19 |
| Subtask 4.2-Modeling of System Integration | 8/1/19 | 4/30/20 |
| | | |
| **Final Report** | | |

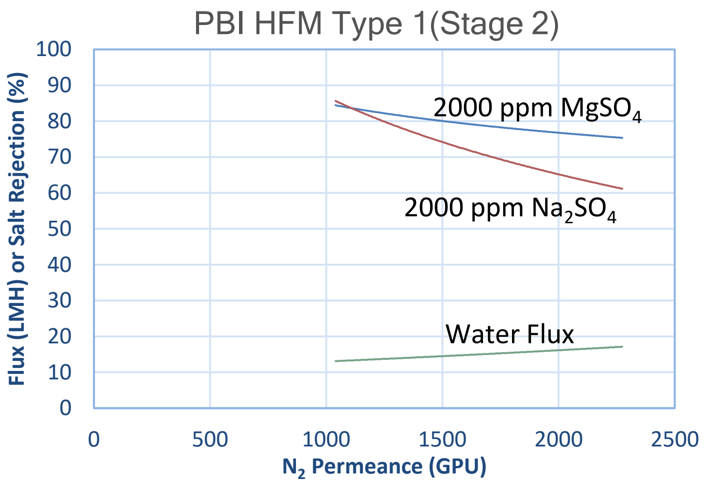
| Q0 | | Q1 | | | Q2 | | | Q3 | | | Q4 | | | Q5 | | | Q6 | | | Q7 | | | Q8 | | | Q9 | | | Q10 | | | Q11 | | | Q12 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Dec | Jan | Feb | March | April | May | June | July | Aug. | Sep. | Oct. | Nov. | Dec. | Jan. | Feb. | March | April | May | June | July | Aug. | Sep. | Oct. | Nov. | Dec. | Jan. | Feb. | March | April | May | June | July | Aug. | Sep. | Oct. | Nov. | Dec. |

| Task/Sub task No. | Milestone Description | Status |
|---|---|---|
| 1 | Updated PMP | COMPLETED |
| 1 | Kickoff Meeting | |
| 2.3 | Completion of small-diameter RO membrane fabrication protocol development | |
| 2.4 | Completion of preliminary membrane system modeling | |
| 2.2 | Completion of membrane testing with synthestic water and data analysis | |
| 3.1 | Completion of PBI membrane performance testing with real field wastewater samples | |
| 3.2 | Completion of longer-term membrane fouling testing | |
| 3.3 | Completion of fabrication and pressure testing of small-diameter RO membranes | 90% Complete |
| 4.1 | Completion of membrane module assembly array | Completed |
| 4.2 | Completion of identification of system components for effluent management system | |
| 1 | Final report | Net Yet Started |

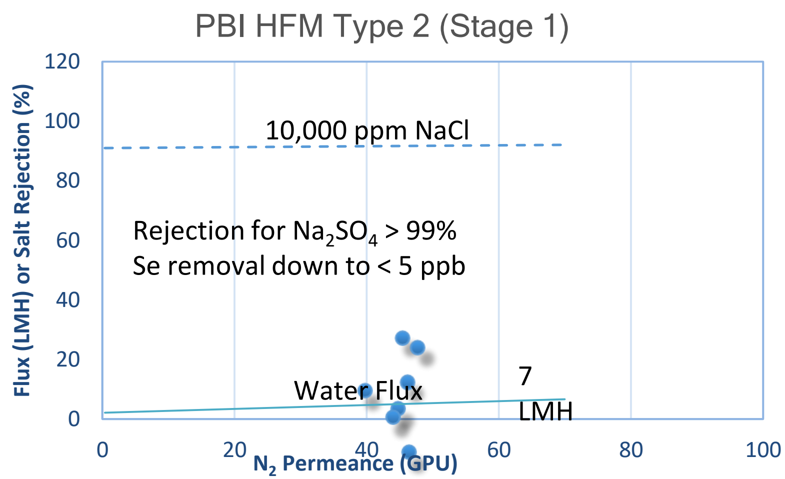
# PBI HFM Selection for Testing

HFM Screening

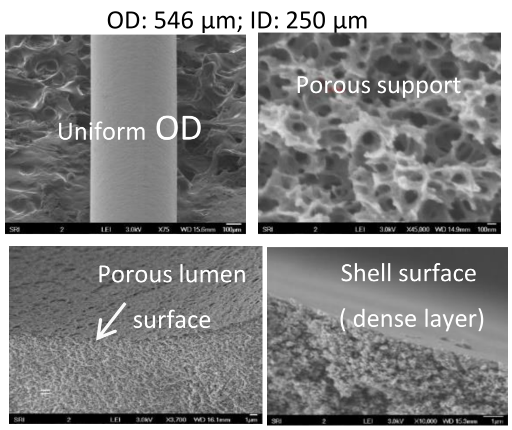
- Use $N_2$ permeation (GPU) measurement for fiber screening
- Evaluate the performance using 2000 ppm NaCl, $MgSO_4$ or $NaSO_4$




Water flux or salt rejection as a function of $N_2$ permeance though the membrane in PBI HFMs with dense layer thickness < 0.3-micron.

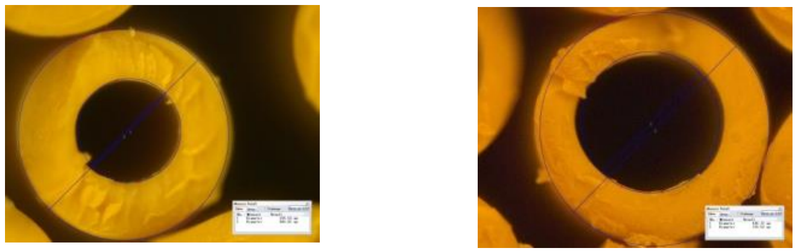



Water flux or salt rejection as a function of $N_2$ permeance though the membrane in PBI HFMs with dense layer thickness > 0.3-micron.




High magnification photographs of PBI HFM.





PBI HFM ID: 53A PBI HFM ID: 51A

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

| Parameters Varied | Value |
|---|---|
| pH | 4 to 10 |
| Temperature | RT and 50 °C |
| Duration | Short and long |
| Concentration | 2000 to 22,000 ppm |
| Se doping | 250 ppb |
| Pressure | 200 to 500 psi |

**Typical Synthetic FGD Test Solution Composition**

| Salt | Concentration (ppm) | Ions | Concentration (ppm) |
|---|---|---|---|
| $CaSO_4$ | 2511 | $Ca^{2+}$ | 3272 |
| $CaCl_2$ | 7029 | $Mg^{2+}$ | 1908 |
| $MgCl_2$ | 7553 | $Na^{+}$ | 681 |
| NaCl | 1731 | $Cl^{-}$ | 11191 |
| Total | 18824 | $SO_4^{2-}$ | 1773 |

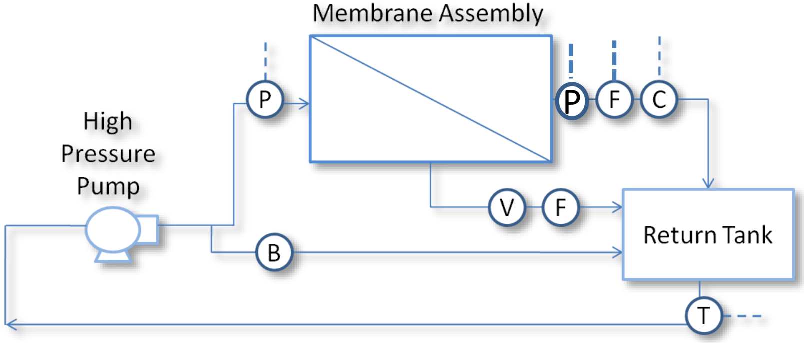
**FGD WW* from an operating Coal Power Plant in Illinois**

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

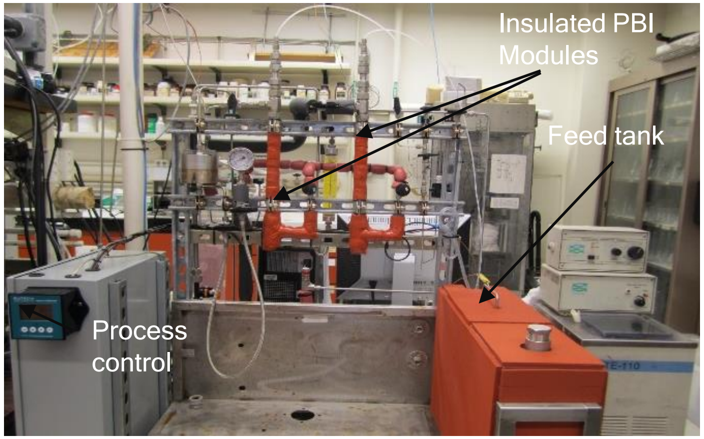
FGD WW as received (10 gal)

FGD WW after long standing

Microfiltration to remove suspended solids



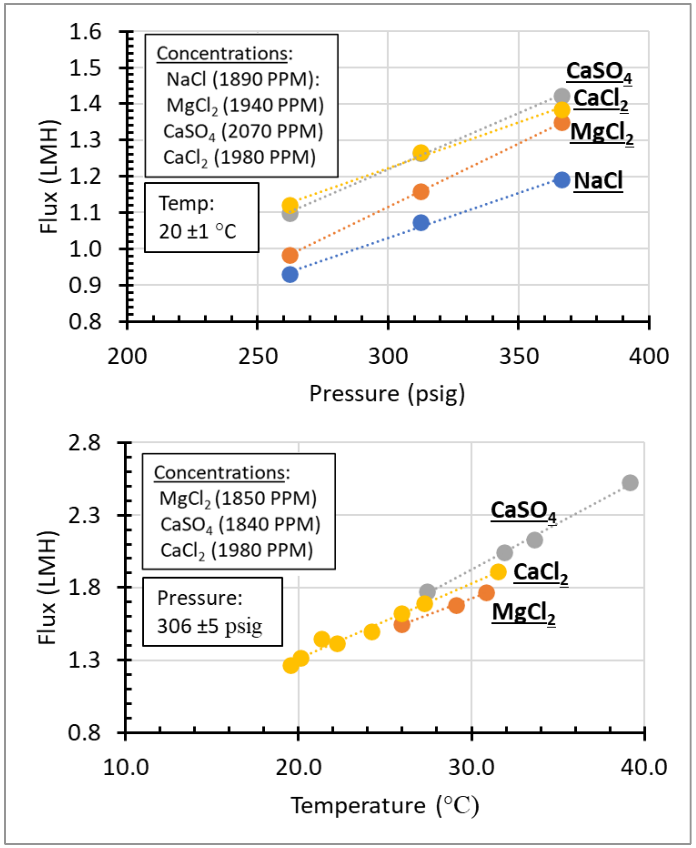

C: Conductivity meter; P: Pressure transducer; T: Thermocouple;
F: Flow meter; B: Backpressure regulator; V: Valve
- - - : Computer interface



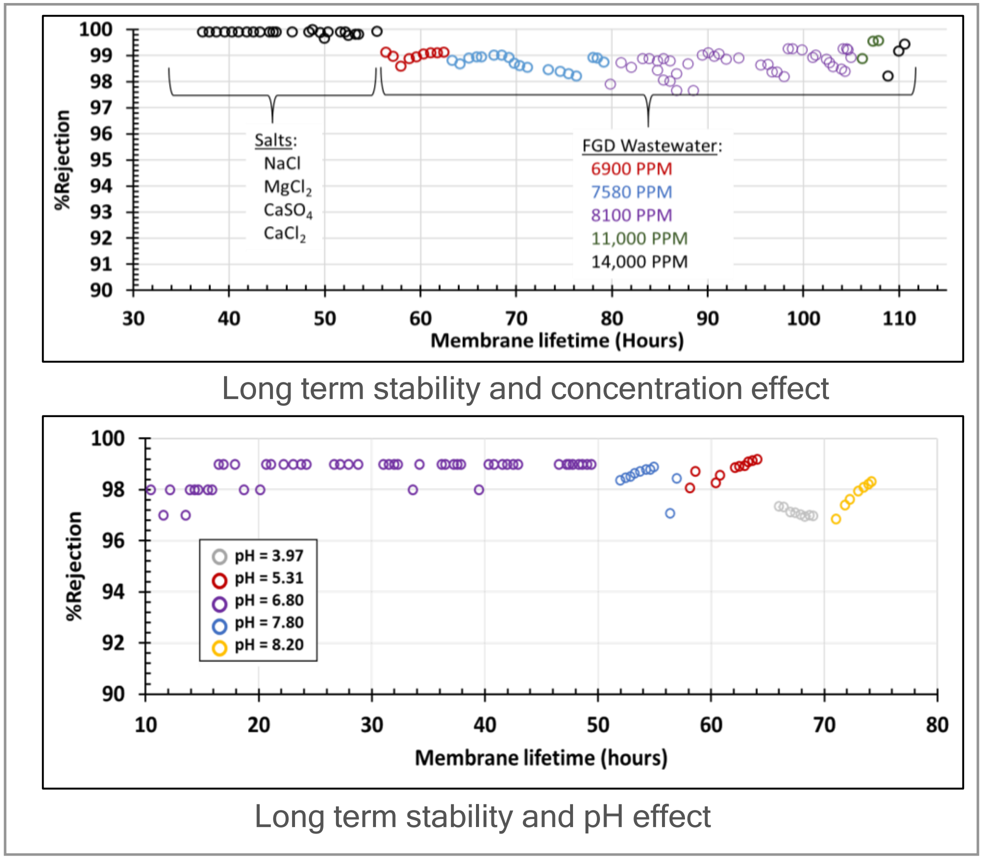

**Bench-scale desalination system: Simplified schematic (*left*) and photograph (*right*) of the system.**

# Results:

## *For synthetic solutions and long-term testing of FGD WW*




**Observed water flux for synthetic solutions at varying Temperatures and pressures.**

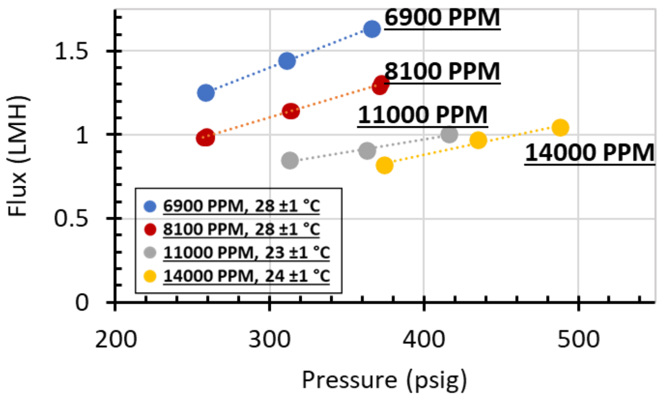



**Observed long term stability at varying concentrations and pH.**

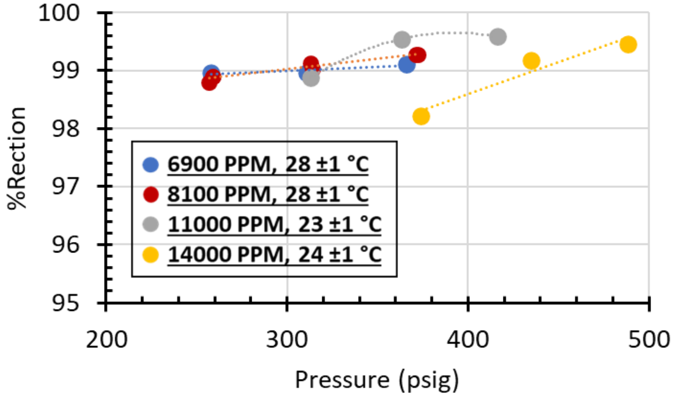
Synthetic Solutions: Water flux increased linearly with pressure and temperature. This is expected behavior for RO membranes. The order of water flux by salt solution was $CaSO_4$ > $CaCl_2$ > $MgCl_2$ > NaCl. Salt rejection was >99% in all cases.
FGD WW: Observed a stable water flux and >98% salt rejection.

# Results (continued):

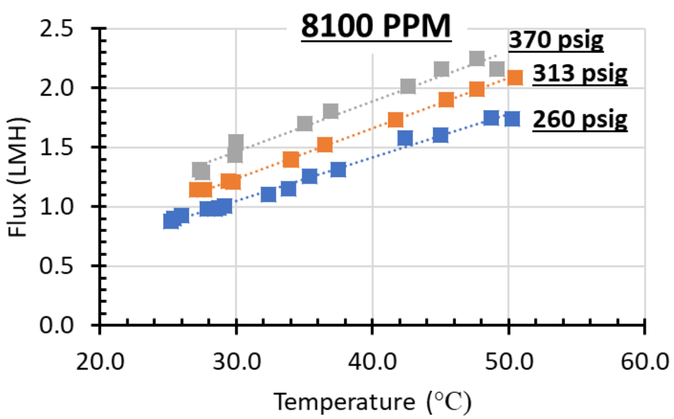
*For raw and diluted FGD WW ( 6,900 to 14,000 ppm range)*



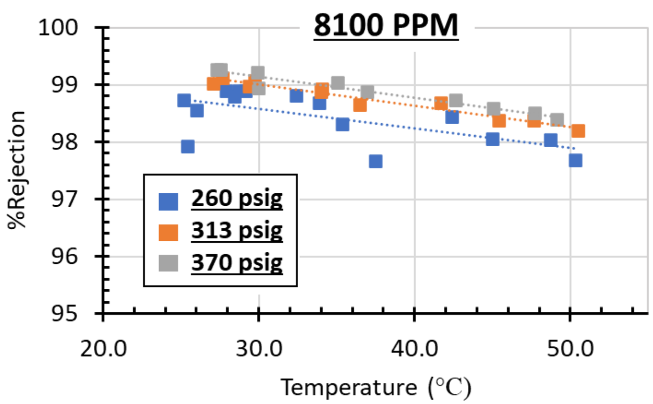

Observed water flux for FGD water as a function of temperature and pressure.




Observed salt rejection for FGD water as a function of pressure.




Observed water flux for 8100 ppm FGD water at varying temperatures and pressures.

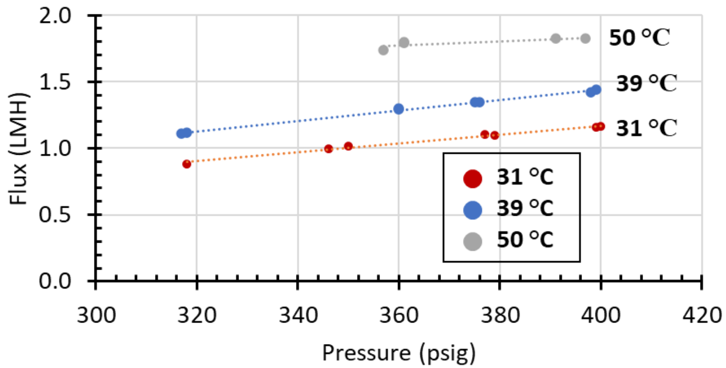


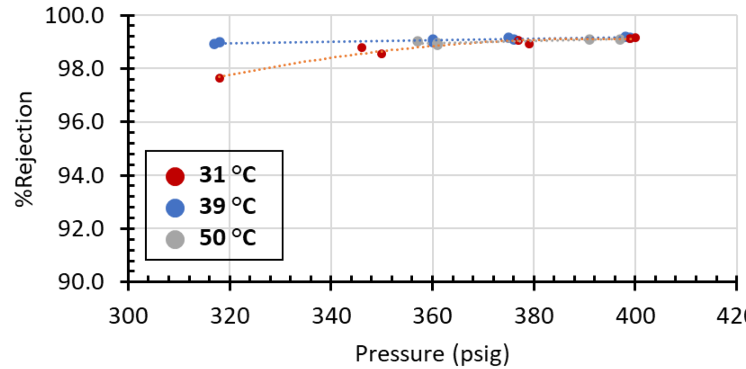

Observed salt rejection 8100 ppm FGD water at varying temperatures and pressures.

As expected, water flux increased linearly with pressure and temperature
>98% salt rejection observed

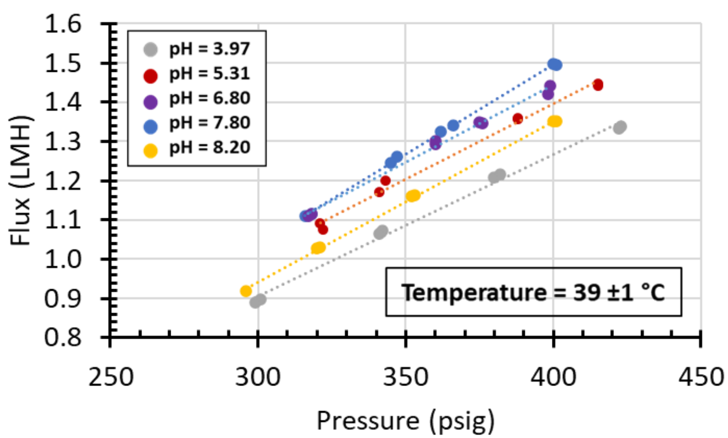
# Results (continued):

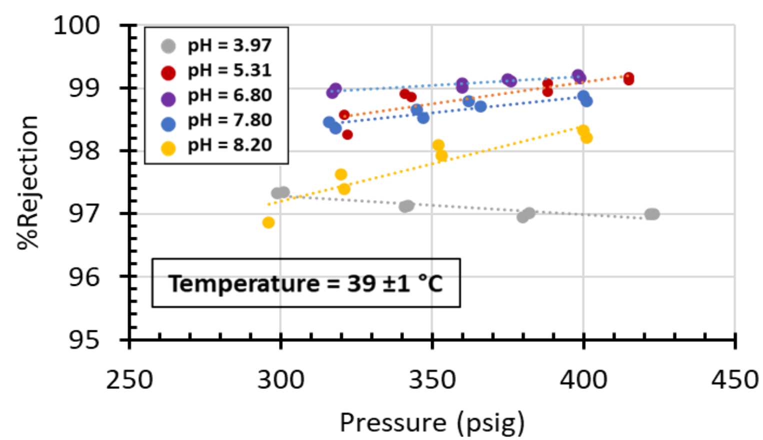
*For 14,400 ppm FGD WW*




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 rage 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.

4-in element (*left*) currently being fabricated at Generon facility to fit into commercial standard 1000 psi 4-in vessel (*right*).

Generon made 2.5-in modules-SRI fibers inside (500 psi).

# 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)
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