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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Advanced Technology and Systems Division
SRI International

Project Team

NATIONAL ENERGY TECHNOLOGY LABORATORY

Pbi PERFORMANCE PRODUCTS, INC.

Enerfex, Inc.

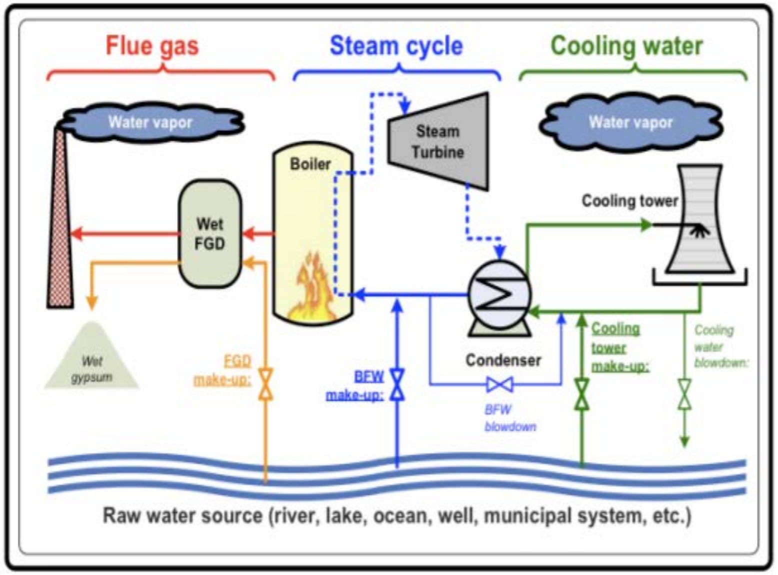
IGS GENERON INNOVATIVE GAS SYSTEMS

January 29, 2019 • NETL• Pittsburgh, Pennsylvania

CONTENT

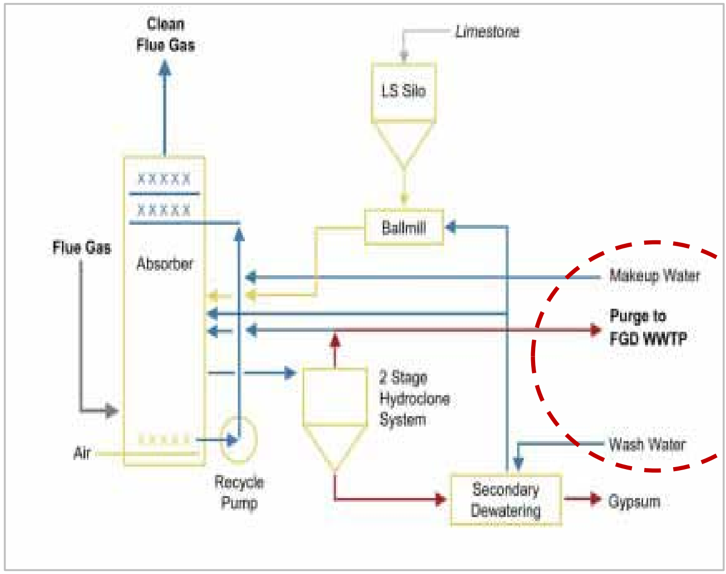
- ❖ Project Background
  - Goals and Our Approach
  - Work Plan and Schedule
  - Budget and Team
- ❖ Project Progress and Future Work
  - Membrane Development and Testing
    - Simulated solutions and field samples tests
  - Membrane System Modeling
    - Module arrangement

Power Plant Water Management:
Flue Gas Desulfurization Wastewater (FGD WW)



Schematic for pulverized coal (PC) power plant with cooling and wet FGD

Source: NETL Report, Dipietro, 2009



Simplified FGD effluent flow

Source: Michael R. Riffe et al. "Wastewater Treatment for FGD Purge Streams", 2008

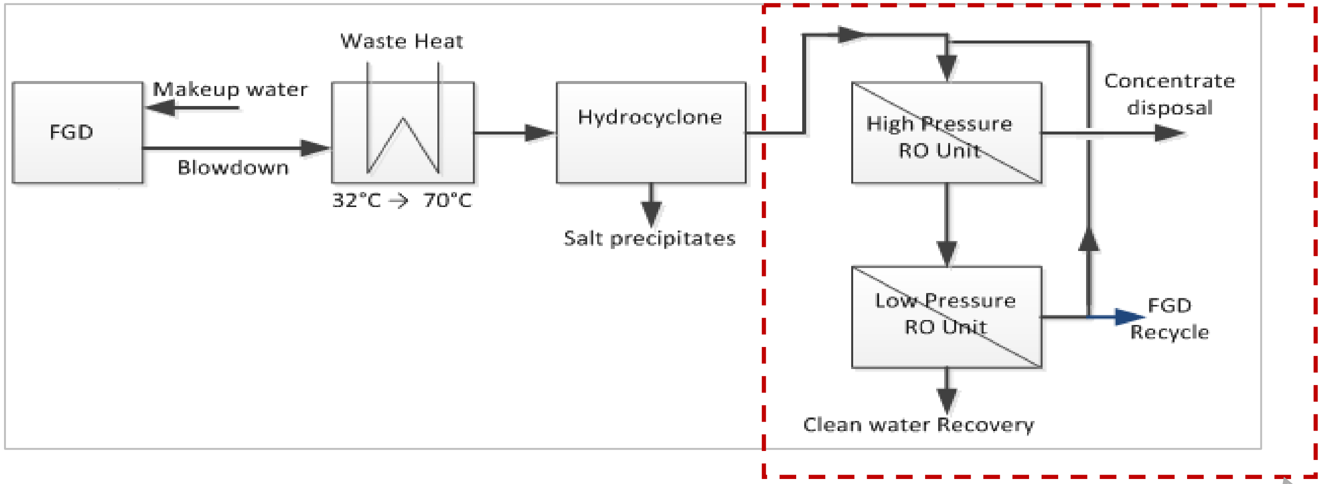
To maintain optimum operating conditions in a wet scrubber, a purge stream is discharged from the system (primarily for efficient SO_2 removal and chloride and corrosion control). This aqueous purge stream (FGD blowdown) is acidic (pH ~ 4-6), supersaturated with gypsum, and contains high levels of total dissolved solids (TDS) and total suspended solids (TSS).

The TDS is composed of heavy metals, chlorides, sulfates, calcium, magnesium, and dissolved organic compounds.

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

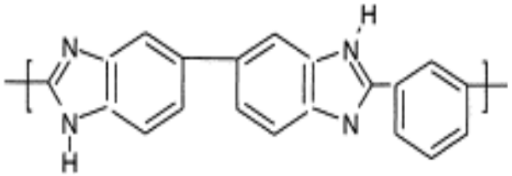


Block diagram showing advanced mode of operation for recovering make-up water and quality water

Research Focus

Membrane Material

- We use polybenzimidazole (PBI) hollow-fiber membrane (HFM)-based separation technology for removing salts from FGD wastewater.



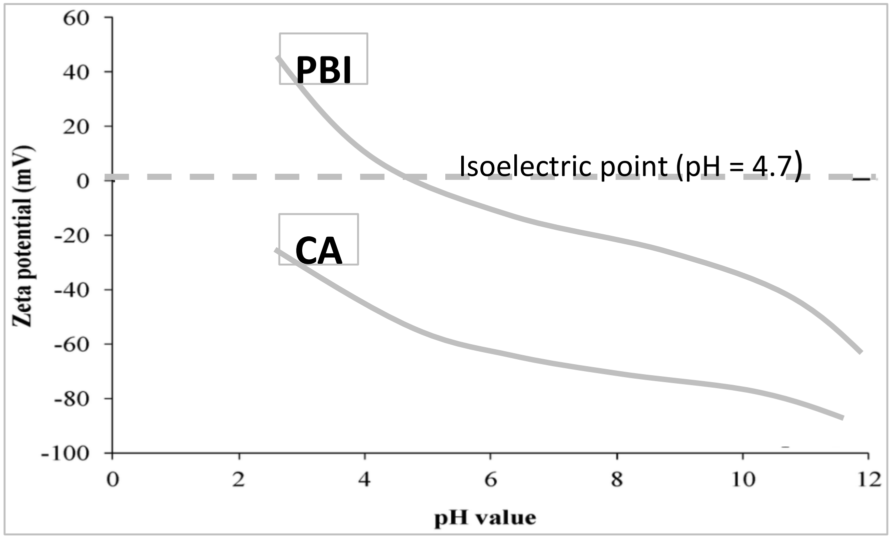
Polybenzimidazole

PBI HFM cross-section

- The PBI membranes are resistant to fouling and can be operated under substantially harsher environments than conditions tolerated by commercially available membranes.

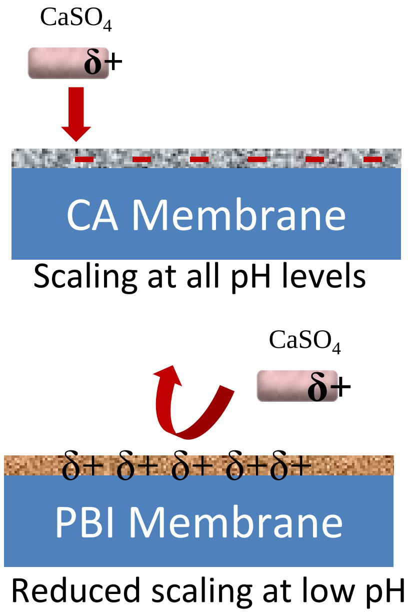
PBI Characteristics and Commercial Availability

- 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



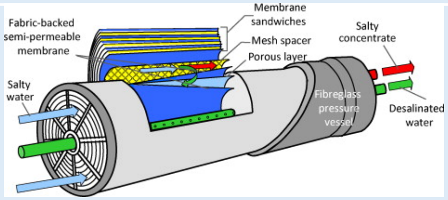
Zeta potential data for PBI and CA (cellulose acetate)

Source: Membranes, 2013, 3(4), 354-374

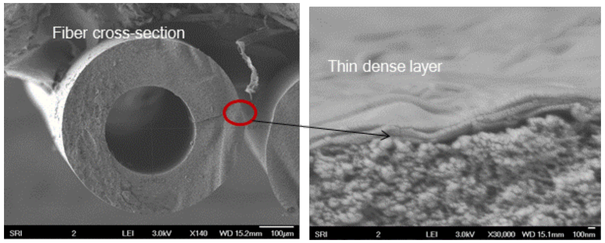


Advantages of Hollow-Fiber Membrane Architecture

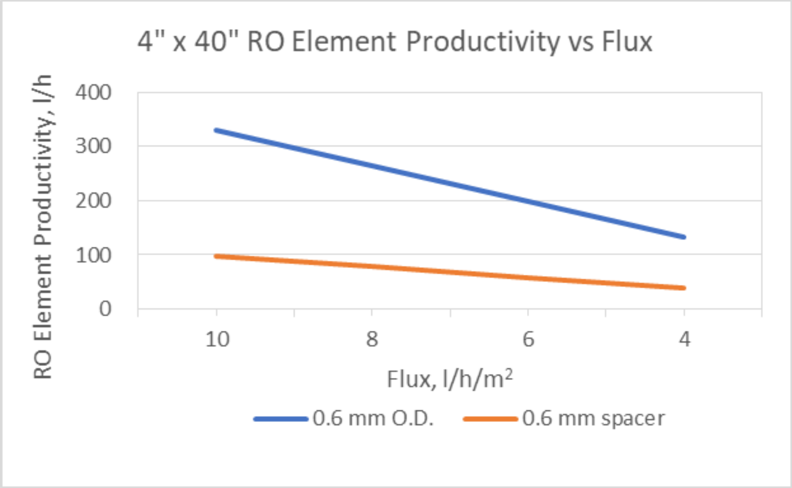
Hollow-Fiber vs. Spiral-Wound Membrane

Hollow Fiber	**Spiral-Wound Flat Sheet Membrane**
 **SRI PBI module**	 J. Membr. Sci. 362 (2010), 202-210

- No need for spacers
- Self-supporting structure
- High surface area per unit of membrane module volume: spiral-wound packing density is 800 m^2/m^3 and hollow fiber is 6000 m^2/m^3 (Source: Lux Research, Inc.)



PBI Hollow-Fiber Membrane Asymmetric Structure



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

NETL

- Funding and technology oversight

SRI

- PBI membrane development
- Membrane testing

Enerfex, Inc.

- Membrane system modeling

PBI Performance Products, Inc.

- Provide PBI dope

Generon, IGS

- Module and optional membrane fabrication site

Key Team Members

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

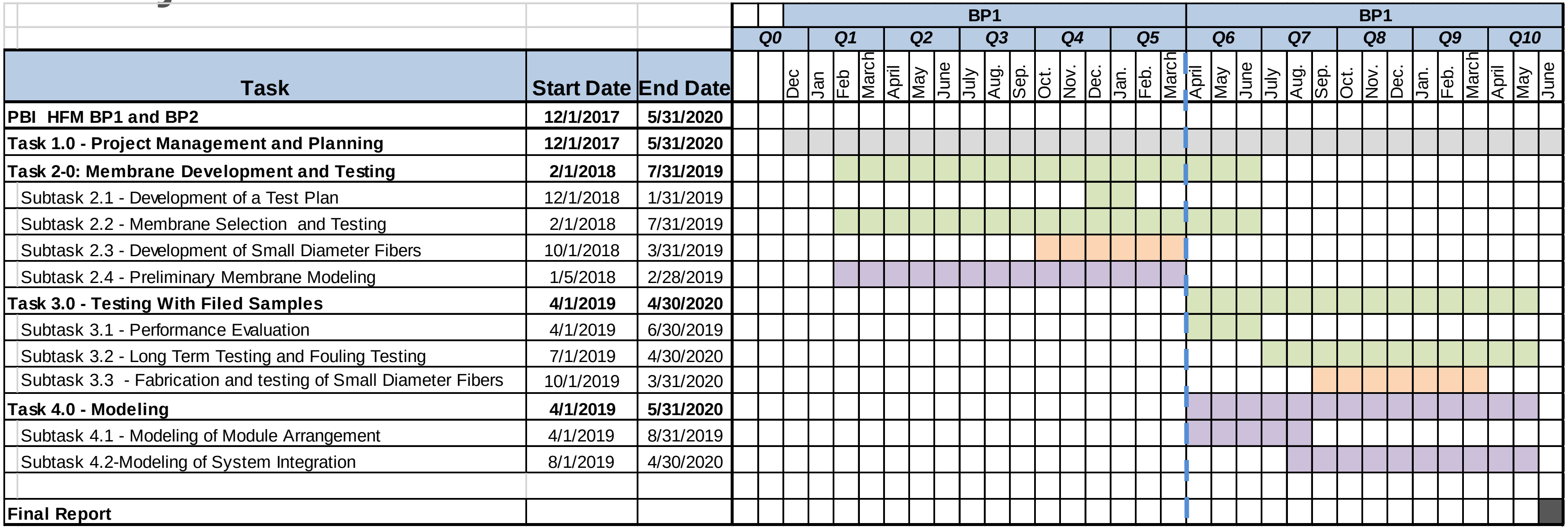
Enerfex: Richard Callahan

PBI: Greg Copeland and Michael Gruender

Our Work Plan

- Test the SRI seawater desalinization 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



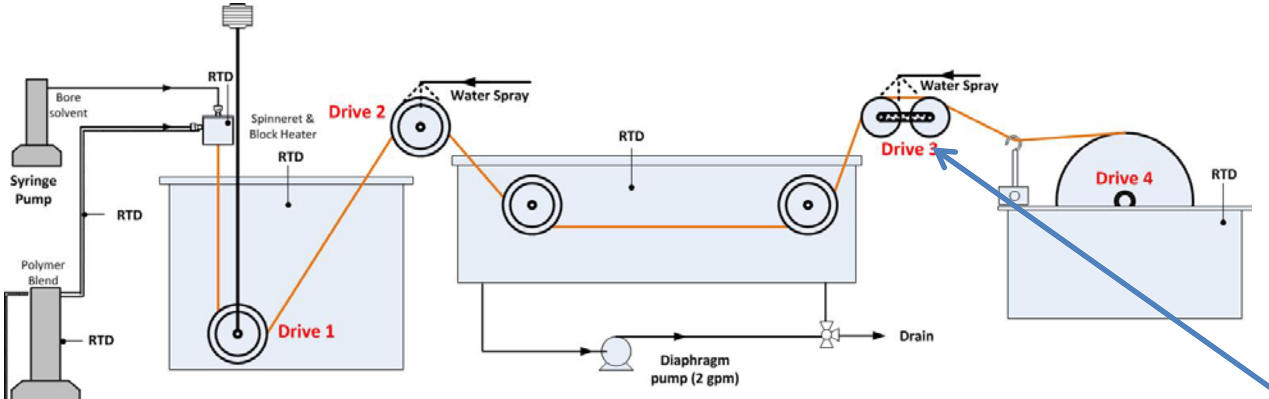
Task	Start Date	End Date
PBI HFM BP1 and BP2	**12/1/2017**	**5/31/2020**
Task 1.0 - Project Management and Planning	**12/1/2017**	**5/31/2020**
Task 2-0: Membrane Development and Testing	**2/1/2018**	**7/31/2019**
Subtask 2.1 - Development of a Test Plan	12/1/2018	1/31/2019
Subtask 2.2 - Membrane Selection and Testing	2/1/2018	7/31/2019
Subtask 2.3 - Development of Small Diameter Fibers	10/1/2018	3/31/2019
Subtask 2.4 - Preliminary Membrane Modeling	1/5/2018	2/28/2019
Task 3.0 - Testing With Filed Samples	**4/1/2019**	**4/30/2020**
Subtask 3.1 - Performance Evaluation	4/1/2019	6/30/2019
Subtask 3.2 - Long Term Testing and Fouling Testing	7/1/2019	4/30/2020
Subtask 3.3 - Fabrication and testing of Small Diameter Fibers	10/1/2019	3/31/2020
Task 4.0 - Modeling	**4/1/2019**	**5/31/2020**
Subtask 4.1 - Modeling of Module Arrangement	4/1/2019	8/31/2019
Subtask 4.2-Modeling of System Integration	8/1/2019	4/30/2020
Final Report		

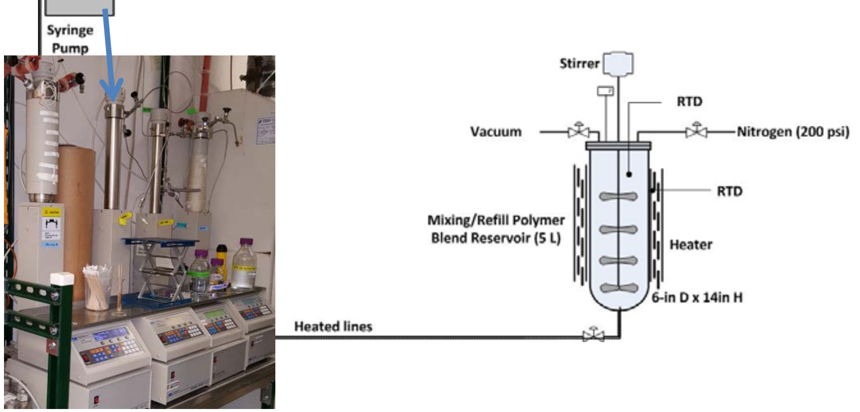
Task/Sub task No.	Milestone Description	Planned Completion	Status
1	Updated PMP	1/18/2018	COMPLETED
1	Kickoff Meeting	3/18/2018	
2.3	Completion of small-diameter RO membrane fabrication protocol development	3/18/2019	
2.4	Completion of preliminary membrane system modeling	3/18/2019	
2.2	Completion of membrane testing with synthetic water and data analysis	7/30/2019	50% COMPLETE
3.1	Completion of PBI membrane performance testing with real field wastewater samples	10/30/2019	STARTED
3.2	Completion of longer-term membrane fouling testing	5/18/2020	NOT YET STARTED
3.3	Completion of fabrication and pressure testing of small-diameter RO membranes	4/18/2020	STARTED
4.1	Completion of membrane module assembly array	9/18/2019	STARTED
4.2	Completion of identification of system components for effluent management system	5/18/2020	NOT YET STARTED
1	Final report	6/18/2020	

Task 2. Membrane Development and Testing
Task 3. Testing with Field Samples

Spinning Line Installed at SRI in 2015

DE-FE0012965





Photograph of Drive 3

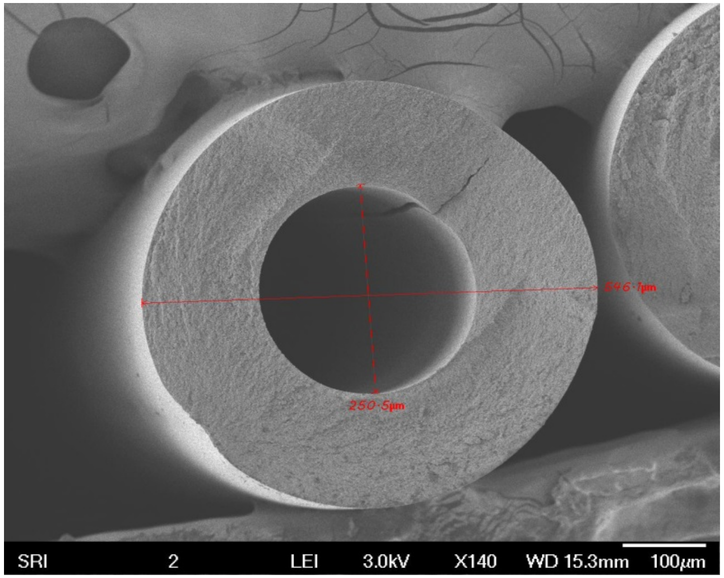
Dope from PBI Performance Products

The new spinning line was crucial for developing an improved and robust spinning process that can be transferred to industry.

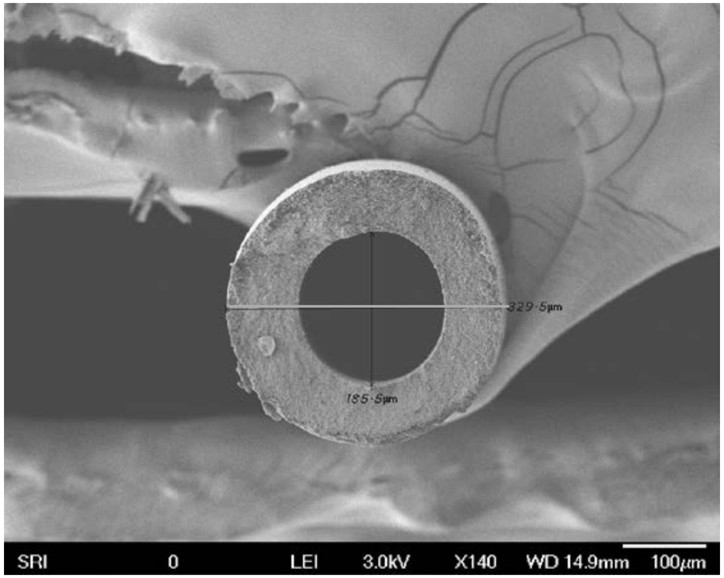
The new line enabled:

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

Small Diameter Fiber Development



OD: 546 µm; ID: 250 µm

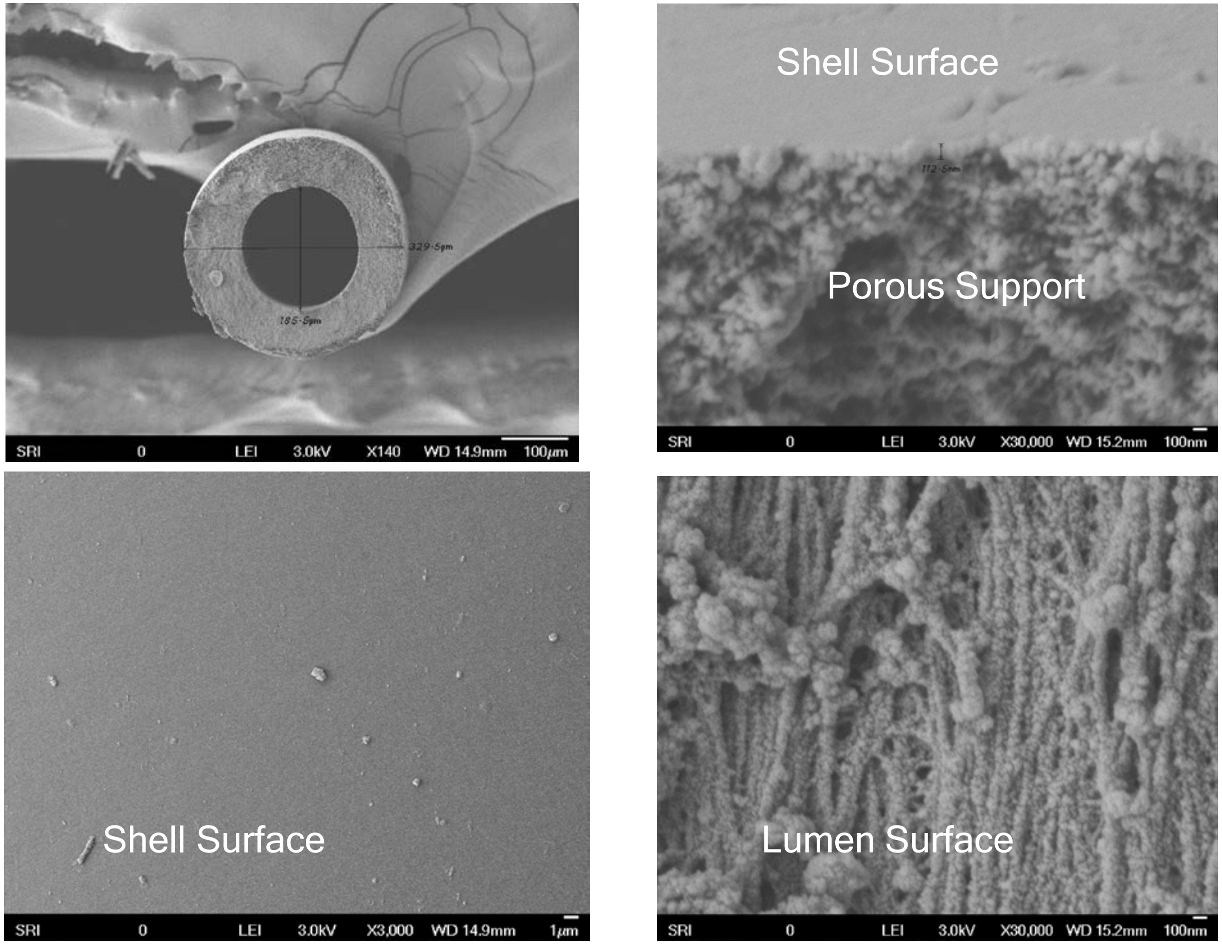


OD: 329 µm; ID: 185 µm

Achievement:

More than 40% HFM diameter reduction from SRI base HFMs
Established the protocol to fabricate less than 350 µm OD HFMs

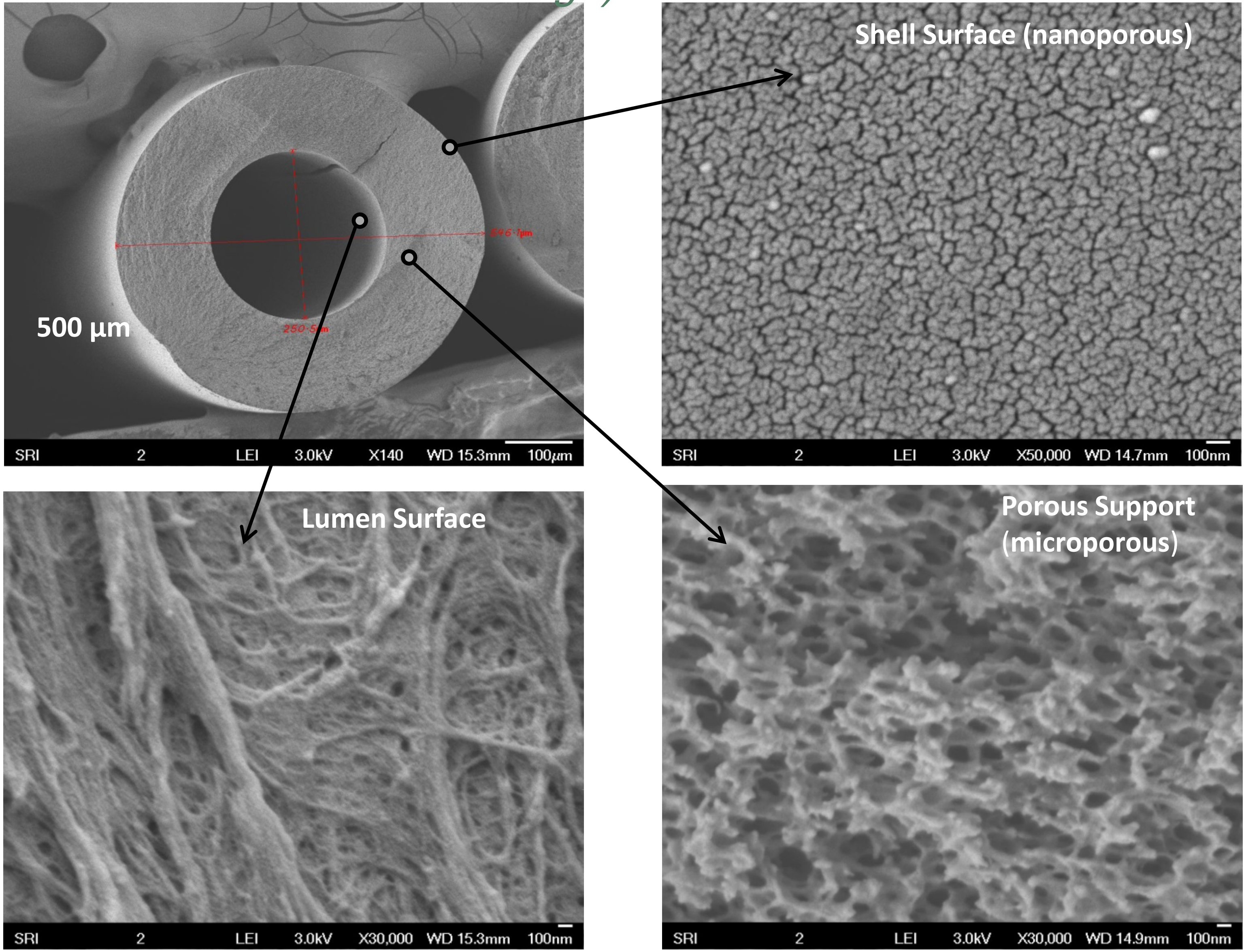
Completed the Protocol Development for small diameter fibers



336 micron OD and 186 micron ID

Preparation of PBI HFMs for High-Flux Applications

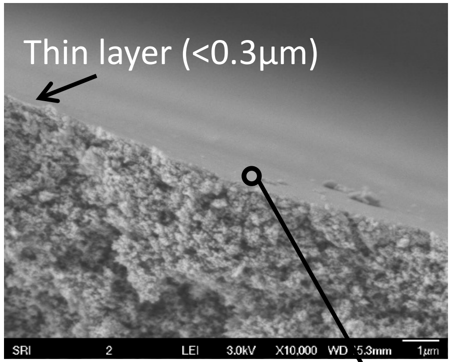
(HFM choice for the second stage)



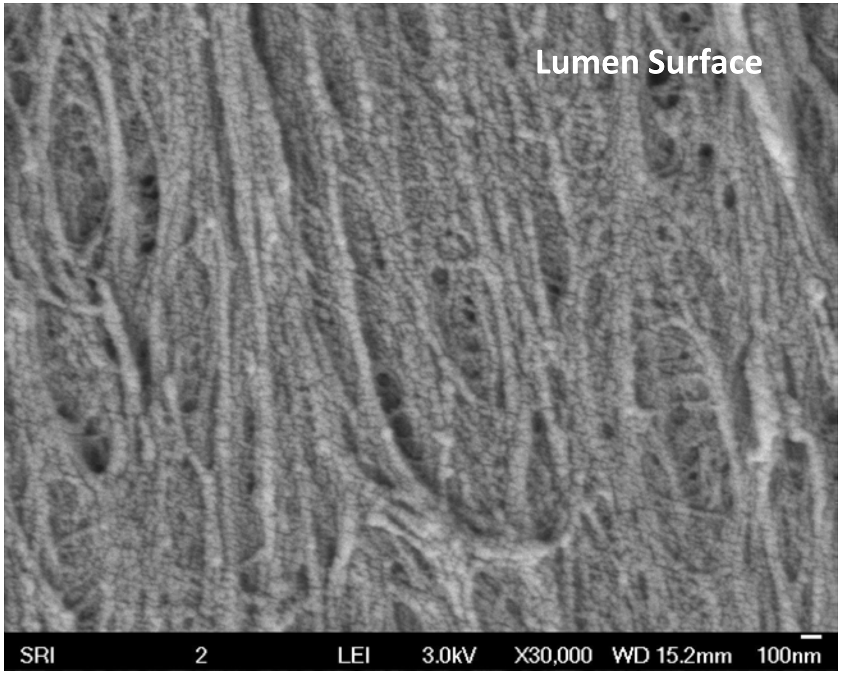
Starting PBI HFM is Shown here

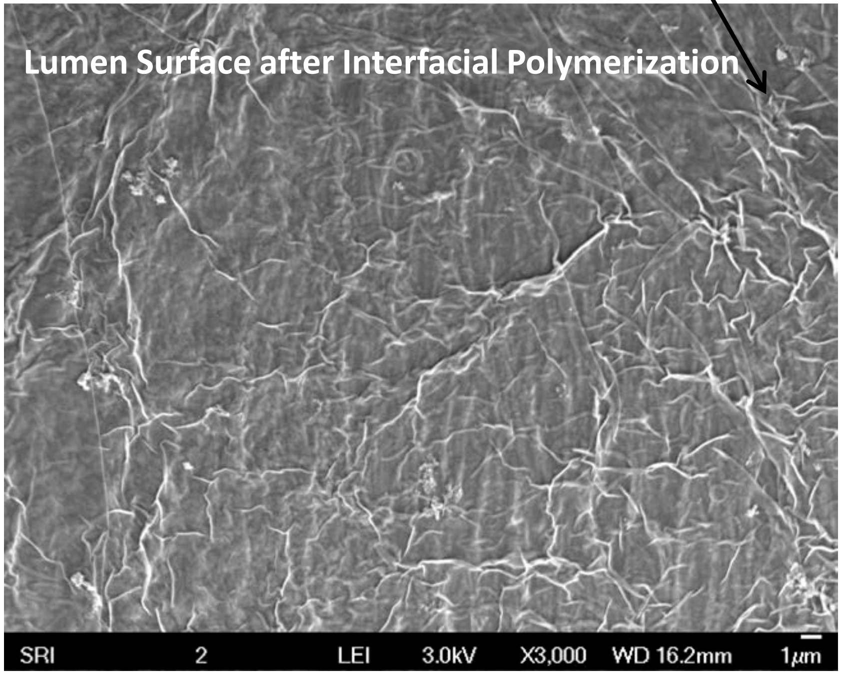
Fiber Series 63J

PBI HFM Lumen Surface Before and After the Interfacial Polymerization (previous work)



Fiber Series 63J

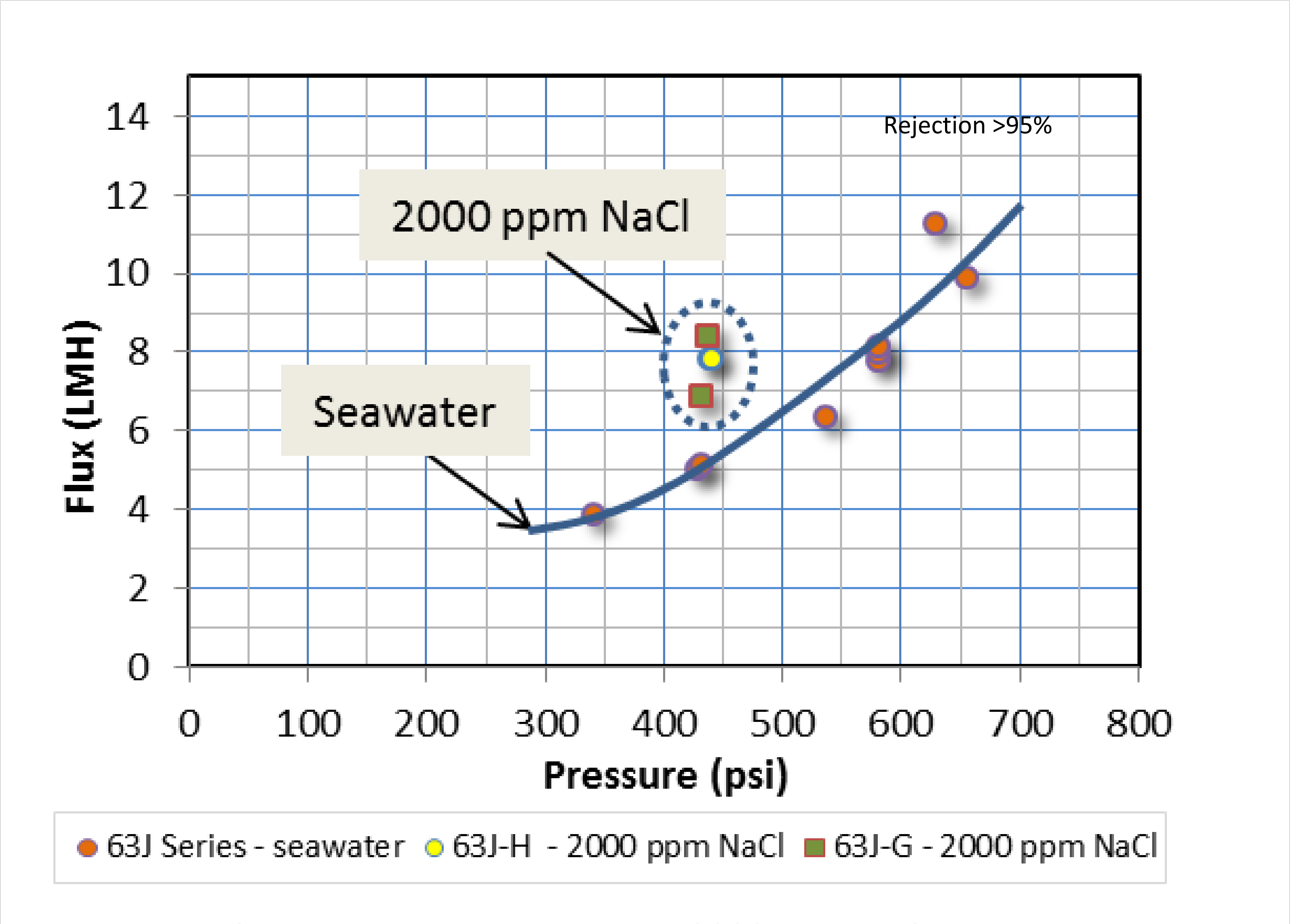




Left: High-magnification picture of the lumen surface of the PBI HFM
Right: High-magnification picture of the PBI HFM lumen surface after interfacial polymerization to generate a very thin polyamide dense layer

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

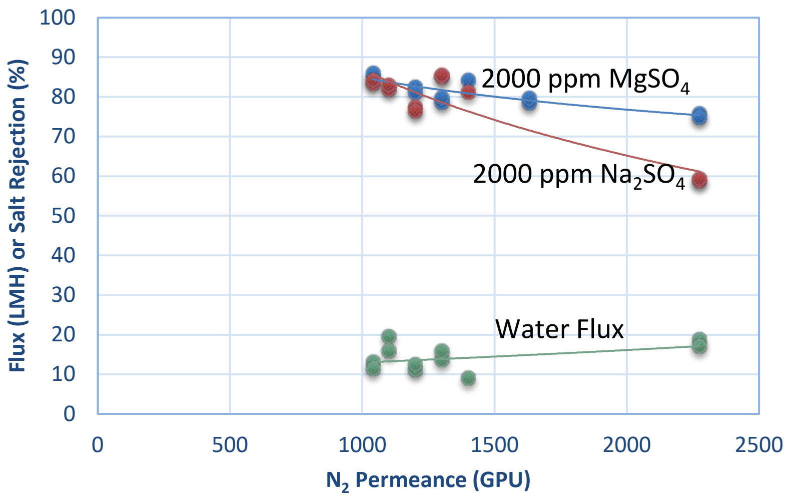


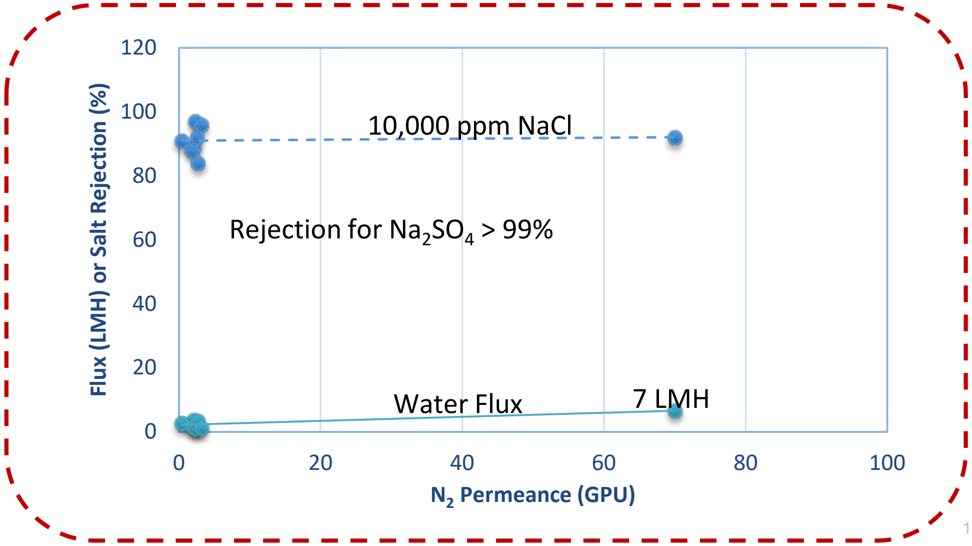
Performance with seawater and 2000 ppm NaCl

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 $NaSO_4$

HFM ID		63C-1	63C-2	63J-1	63J-2	63F-1	63F-2	63E -1	63E -2	63H-1	63I-1	63I-2
2000 ppm $MgSO_4$	Pressure (psi)	514	515	503.5	504	512	512.5	509	509	514	516	518
	Flux (LMH)	17.4	20.9	8.97	12.3	14.7	12.0	12.2	16.5	10.2	17.9	16.5
	Rejection (%)	71.2	74.6	82.6	81.3	85.3	86.1	78.8	79.9	84.3	75.9	75
2000 ppm Na_2SO_4	Pressure (psi)	522.5	526	522.5	523.5	504.5	508.5	502	504	514	512	509
	Flux (LMH)	16	19.6	11.3	12.5	13.2	11.6	13.8	16.0	9.12	18.9	17.2
	Rejection (%)	82	83	77.5	76.5	83.5	84.3	85.2	85.6	81.3	58.9	59.4
N_2 Permeance (GPU)		1100	1100	1200	1200	1040	1040	1300	1300	1400	2274	2274





Test Results for Synthetic Solutions (<15,000 ppm)

Flux and Rejection

Feed TDS : ~ 15,000

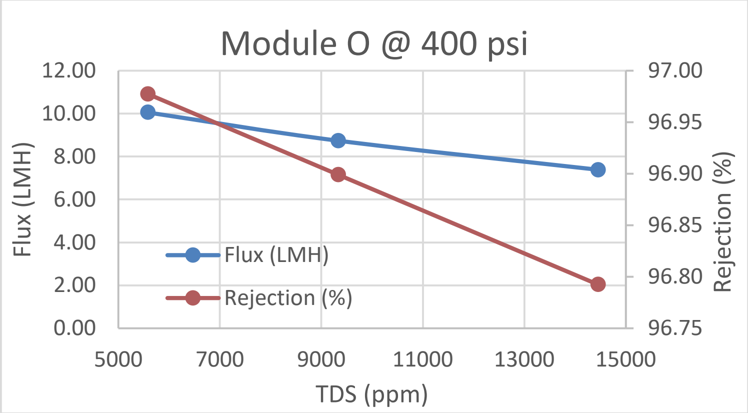
Module O	Time	Flux (LMH)	Permeate solution conductivity/TDS	Rejection (%)
	2 hr	5.70	0.805 ms/535 ppm	96.3
	4 hr	5.69	0.803 ms/532 ppm	96.3

Module P	Time	Flux (LMH)	Permeate solution conductivity/TDS	Rejection (%)
	2 hr	5.87	0.213 ms/141 ppm	99.0
	4 hr	5.75	0.237 ms/159 ppm	98.9

*. PBI-IFP is a surface modified PBI HFM

Flux and Rejection as a Function of Concentration

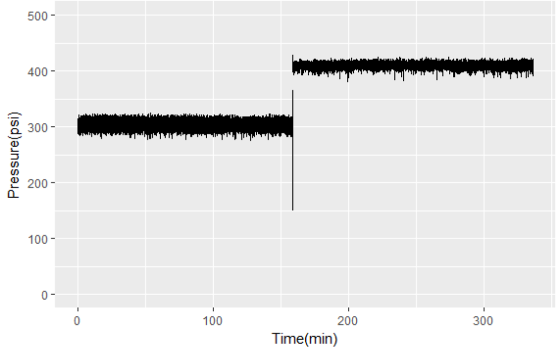
Feed TDS : ~ 1,500



Test Solution Composition

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

Pressure vs. Time Profile of the Membrane Module O



PBI HFM performance is as Predicted

Concentrated Synthetic Solution Testing

Feed TDS : >20,000 ppm

Fully Mixed

After 30 sec settling

As received

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)

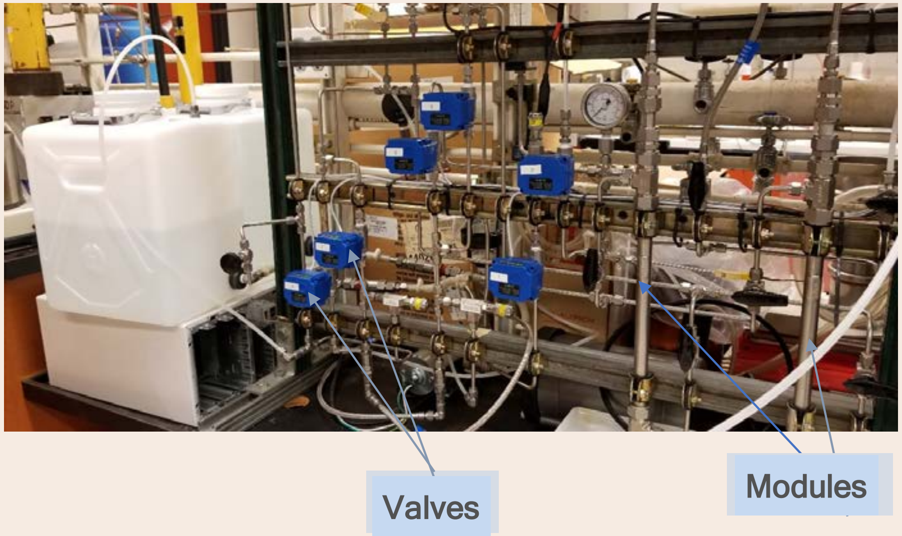
FGD Raw Water

- 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.

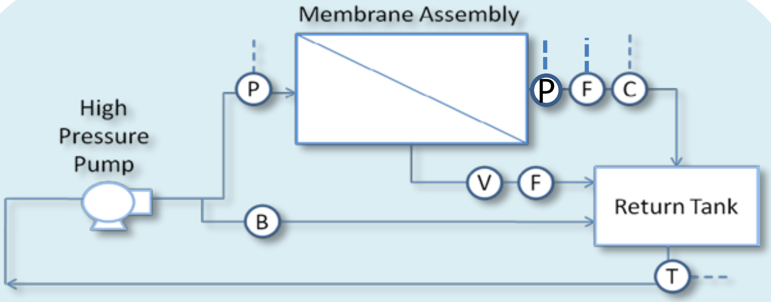
Small-scale performance testing station (1-in modules) for UF applications



Both these systems are recent installments

Bench-Scale RO Systems at SRI

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


Membrane Assembly

High Pressure Pump

P

P

F

C

V

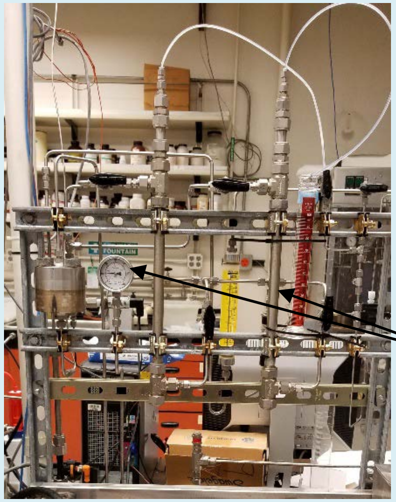
F

B

Return Tank

T

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



Pumps, storage tanks and data acquisition systems are not shown

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


A photograph of the front


A photograph of the back showing two vessels for testing commercial module in parallel with SRI PBI HFMs

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

	1st Stage, m^2 = 49.0				2nd Stage, m^2 = 6.1		
	1st stg. net press. diff, selectivity = 8.3				2nd stg. net press.diff. selectivity = 38.2		
	FGD WW	FGD WW Plus R2 Recycle = F1	retentate R1 concentrate	permeate P1 interstage	Feed F2 Interstage	Retentate R2 Mbr. Recycle	Permeate P2 Clean Wateer
psia	314.7	314.7	311.7	150.0	317.7	314.7	15.0
LMH	n/a	2.17	0.95	1.22	9.76	0.97	8.79
L/H	100.08	106.15	46.41	59.74	59.74	5.95	53.78
LB/H	220.58	233.95	102.19	131.66	131.66	13.10	118.54
SeO_4^{-2} ppb	250	258.0	535.7	42.6	42.6	396.1	3.6
Mass Bal.	100.0%	n/a	46.3%	n/a	n/a	n/a	53.7%

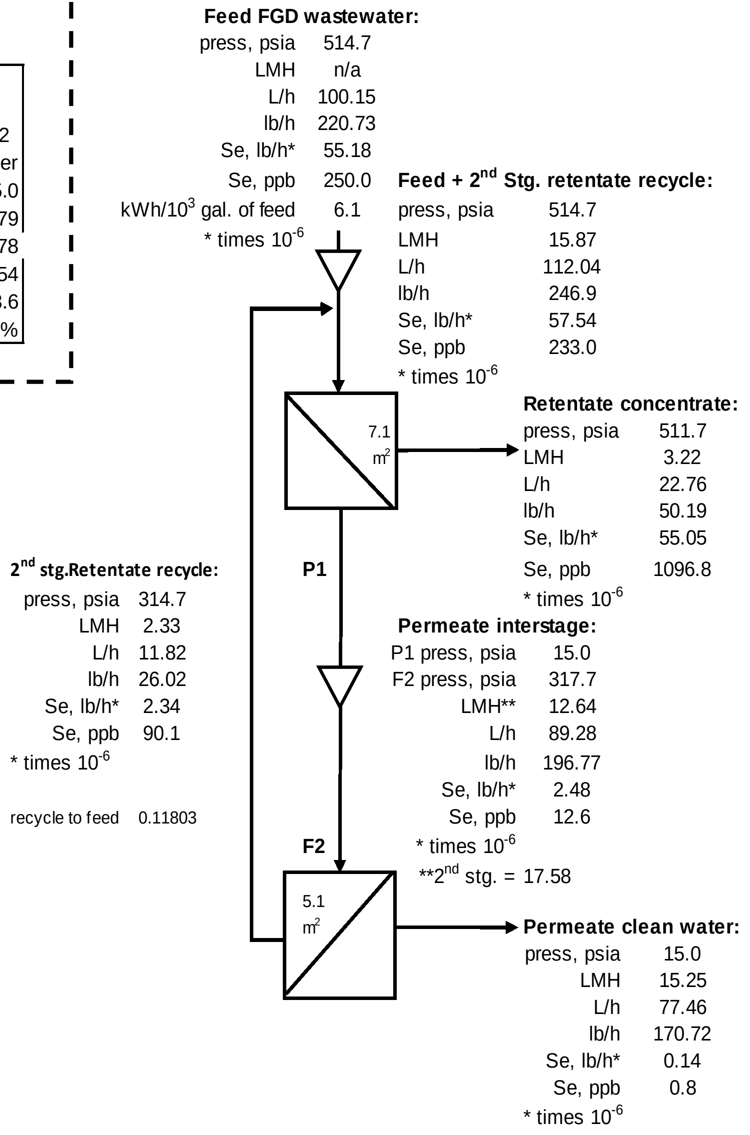
solute rejection = 98.6%

Water Productivity

	Stage one		Stage two		System		Stage one
	retentate		permeate				permeate
	Se reject	psi	Se reject	psi	H_2O rec.	Se, ppb	LMH
SRI PBI	99.8%	515	0.25%	318	77%	0.8	12.64
VSEP - 1	100 %	515	0.009%	318	78%	0.2	50.91

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.



Feed FGD wastewater:

press, psia	514.7
LMH	n/a
L/h	100.15
lb/h	220.73
Se, lb/h*	55.18
Se, ppb	250.0
kWh/10^3 gal. of feed	6.1

* times 10^{-6}

Feed + 2nd Stg. retentate recycle:

press, psia	514.7
LMH	15.87
L/h	112.04
lb/h	246.9
Se, lb/h*	57.54
Se, ppb	233.0

* times 10^{-6}

Retentate concentrate:

press, psia	511.7
LMH	3.22
L/h	22.76
lb/h	50.19
Se, lb/h*	55.05
Se, ppb	1096.8

* times 10^{-6}

2nd stg.Retentate recycle:

press, psia	314.7
LMH	2.33
L/h	11.82
lb/h	26.02
Se, lb/h*	2.34
Se, ppb	90.1

* times 10^{-6}

recycle to feed 0.11803

Permeate interstage:

P1 press, psia	15.0
F2 press, psia	317.7
LMH**	12.64
L/h	89.28
lb/h	196.77
Se, lb/h*	2.48
Se, ppb	12.6

* times 10^{-6}

**2nd stg. = 17.58

Permeate clean water:

press, psia	15.0
LMH	15.25
L/h	77.46
lb/h	170.72
Se, lb/h*	0.14
Se, ppb	0.8

* times 10^{-6}

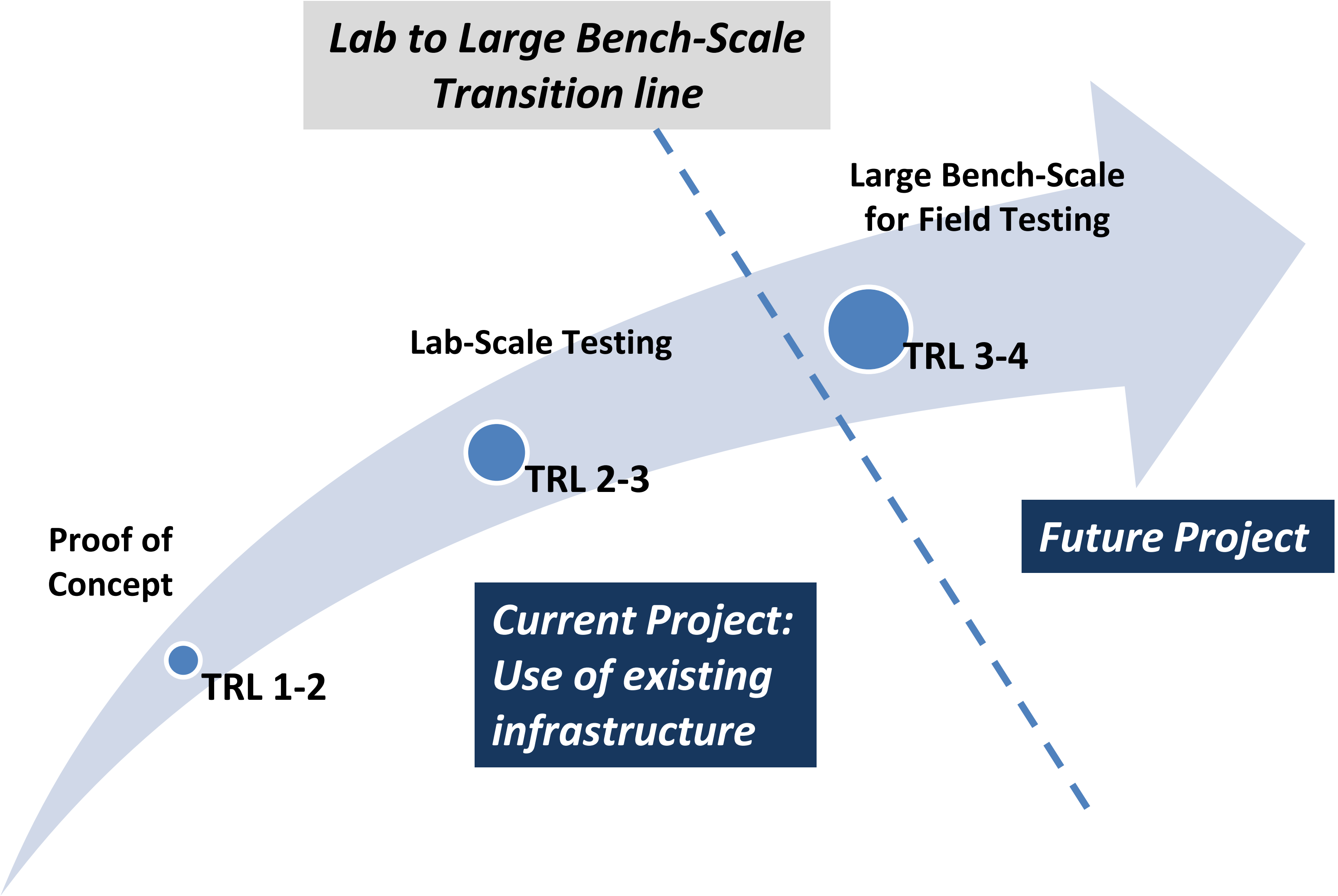
Modeling of 2-stage system

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

The Road to Large Bench-Scale and Field Testing



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)**

Disclaimer

SRI International

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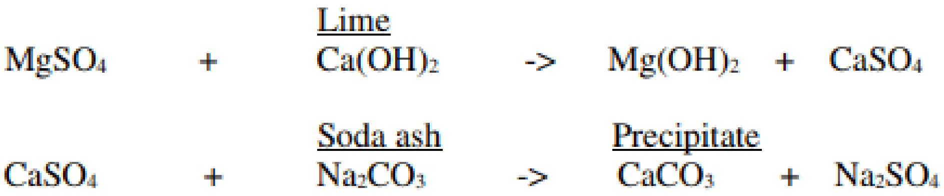
Thank You

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)



$$MgSO_4 \quad + \quad \overset{\underline{\text{Lime}}}{Ca(OH)_2} \quad \text{->} \quad Mg(OH)_2 \quad + \quad CaSO_4$$

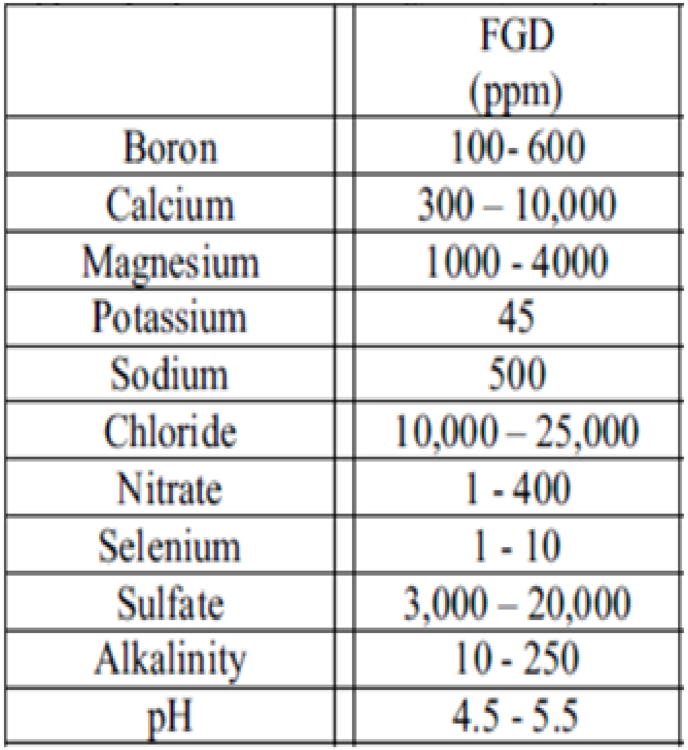
$$CaSO_4 \quad + \quad \overset{\underline{\text{Soda ash}}}{Na_2CO_3} \quad \text{->} \quad \overset{\underline{\text{Precipitate}}}{CaCO_3} \quad + \quad Na_2SO_4$$

- 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

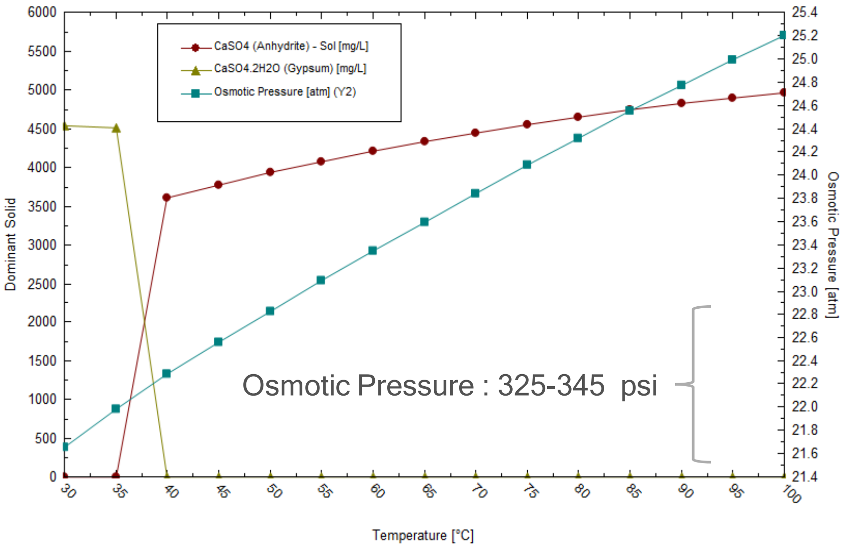
FGD WW Composition, Solubility, and Osmotic Pressure

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



	FGD (ppm)
Boron	100- 600
Calcium	300 – 10,000
Magnesium	1000 - 4000
Potassium	45
Sodium	500
Chloride	10,000 – 25,000
Nitrate	1 - 400
Selenium	1 - 10
Sulfate	3,000 – 20,000
Alkalinity	10 - 250
pH	4.5 - 5.5

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



Osmotic Pressure : 325-345 psi

Gypsum and anhydrite precipitation from a concentrated brine solution. Source: OLI Systems

Feed and retentate compositions for a RO membrane operating with >50% water recovery

Component (mg/l)	Raw FGD wastewater	Retentate
Calcium	3290	7000
Magnesium	1850	4000
Sodium	663	1300
Chloride	11,050	23000
Sulfate	1,945	4000

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

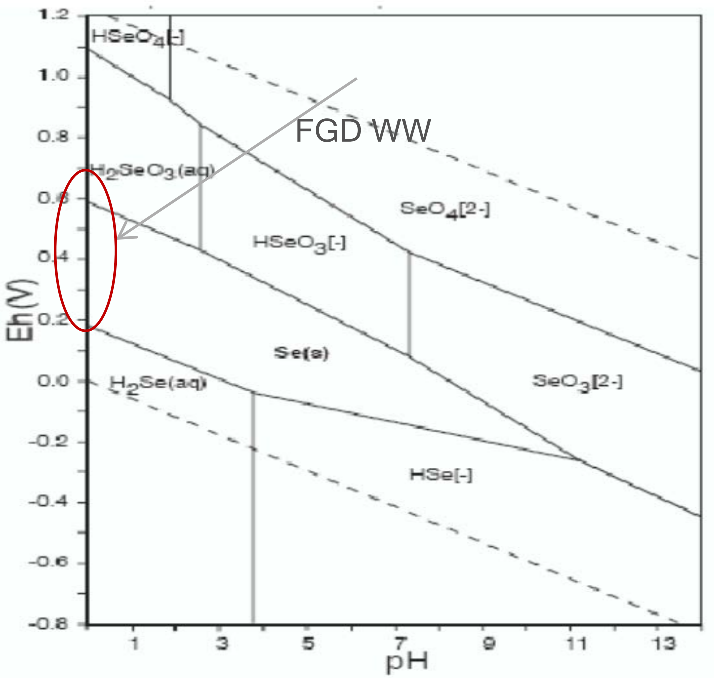
- The most common technologies to date for Se: media filtration, chemical treatment, and biomediated removal

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)

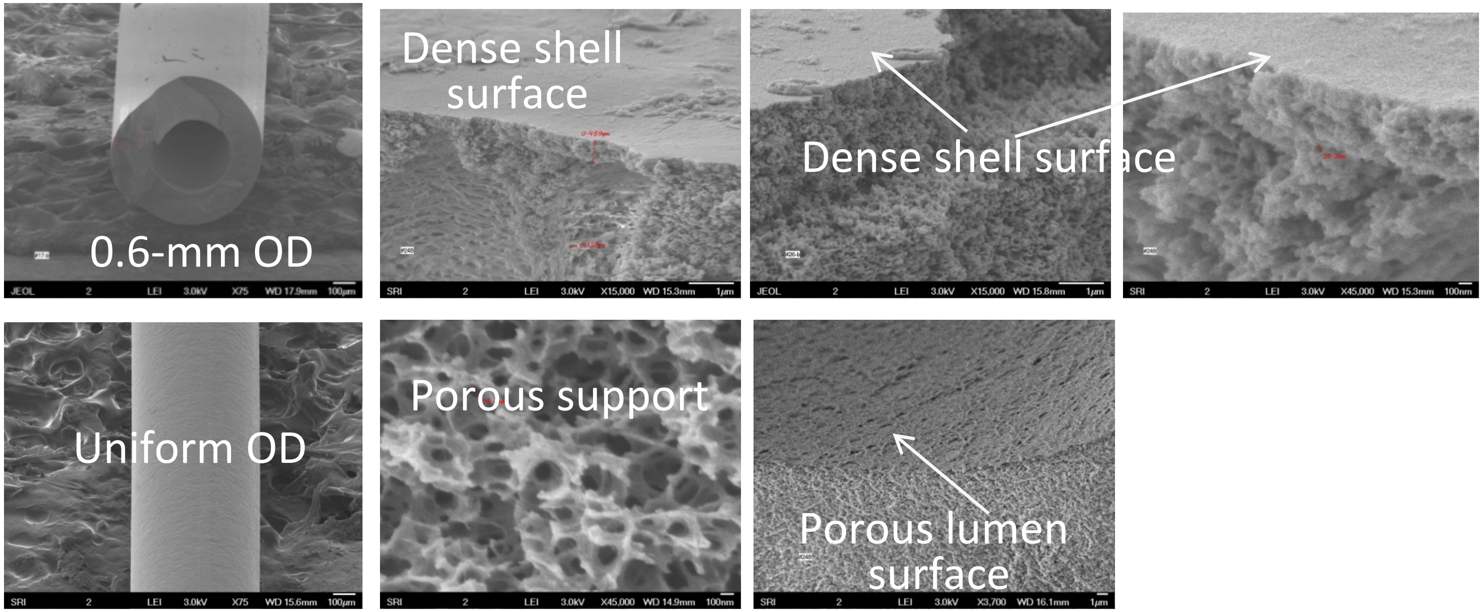
- The selenate, SeO_4^{2-} is present as doubly charged even below pH 4 (pKa ~ 1.7)

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

Source: New Logic Research

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**

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