SRI International

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

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Summary: The main goal of the proposed research is to introduce SRI-based polybenzimidazole (PBI) hollow-fiber membranes (HFMs) for flue gas desulfurization (FGD) wastewater (WW) treatment and Selenium (Se) release control. The PBI membranes are resistant to fouling and can be operated under substantially harsher conditions than those tolerated by commercial membranes. Success of this project will result in an effluent control system that reduces freshwater withdrawal by removing hazardous compounds and reusing the recovered water.

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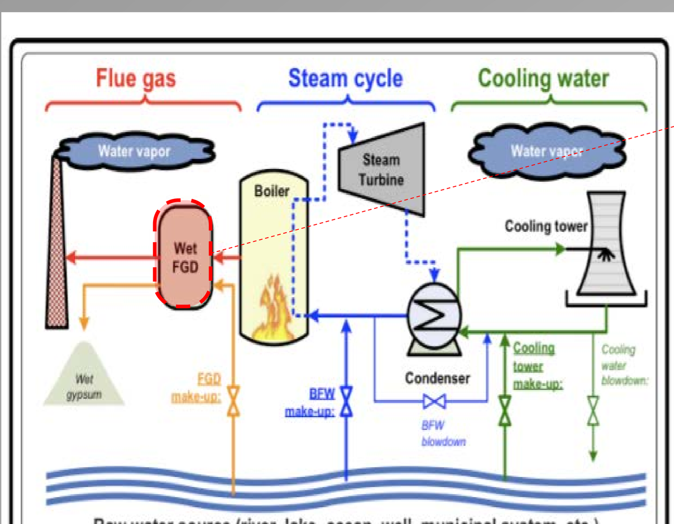
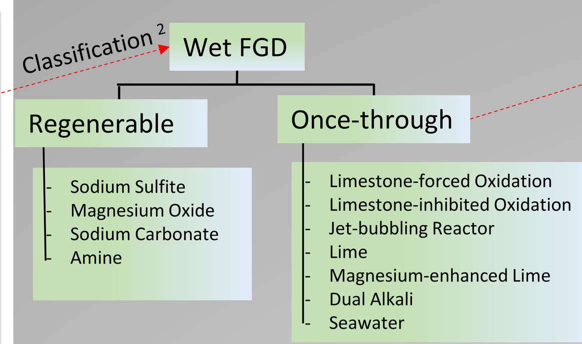
Background of Flue Gas Desulfurization Wastewater (FGD WW) Treatment and Selenium (Se) Pollution Control

FGD and Advantages of Minimum Liquid Discharge (MLD)



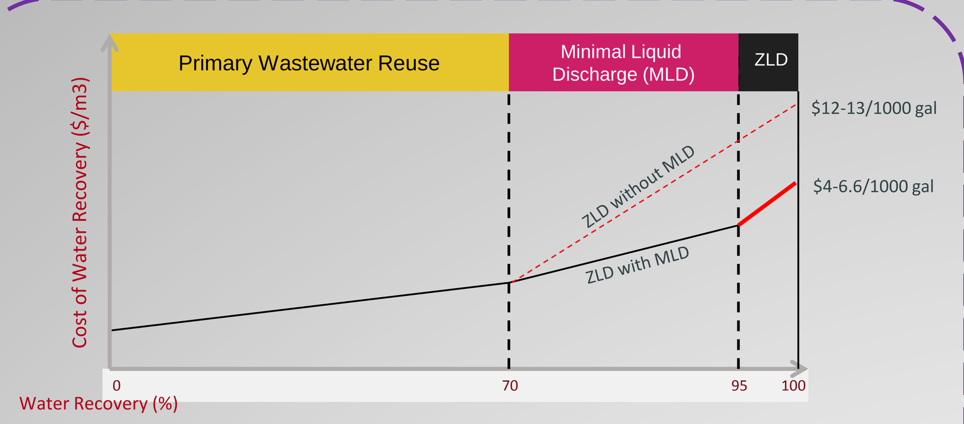
PC power plant with cooling and wet FGD [1]



Element/Ions in Untreated FGD Wastewater	Concentration (ppm)
Boron (B)	100 - 600
Calcium (Ca)	300 - 1000
Magnesium (Mg)	1000 - 4000
Potassium (K)	45
Sodium (Na)	500
Chloride (Cl^-)	10000 - 25000
Nitrate (NO_3^-)	1-400
Selenium (Se)	1-10
Sulfate (SO_4^{2-})	3000 - 20000

Minimum Liquid Discharge (MLD)[3]

- Membrane-based MLD is a more economical process than zero-liquid discharge (ZLD).
- The last 5% of ZLD is costly.



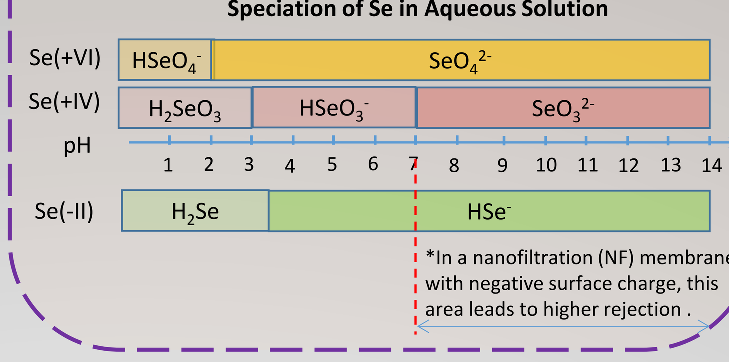
Comparison of the costs of MLD and ZLD.[3]

1. Water Requirements for Existing and Emerging Thermoelectric Plant Technologies. DOE/NETL, 2008.
2. Journal of the Air & Waste Management Association, 51 (2011) 1676-1688.
3. Journal AWWA, 100 (2008) 76-89.

Selenium Chemistry [4-6]

- For adults, the recommended daily Se intake is 55 mg, and the upper limit is 400 mg.
- Se toxicity: Se(+IV) < Se(+VI) < Se(-II).
- Environmental Protection Agency (EPA) criterion: acute concentration (20 ppb) and chronic concentration (5 ppb).
- In FGD WW, Se is present as Se(+VI) and Se(+IV).

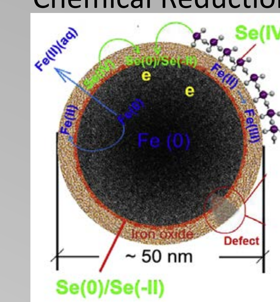
Speciation of Se in Aqueous Solution



4. Talanta, 154 (2016) 474-480.
5. Aquatic Life Ambient Water Quality Criterion for Selenium – Freshwater, EPA, 2016.
6. Applied Geochemistry, 11 (1996) 797-802.
7. Science of the Total Environment 521–522 (2015) 246–260.
8. Water Research, 71(2015) 274-281.
9. Geochimica et Cosmochimica Acta, 206 (2017) 236–253.
10. Environmental Science and Pollution Research 22 (2015) 3137-3137.
11. Biotechnology Advances 34 (2016) 886–907.
12. Membrane Separation Technology in Carbon Capture, Chapter 3, 60.
13. Nature Communication, 4:2344 (2013).

Comparison of Technologies for Se Removal[7]

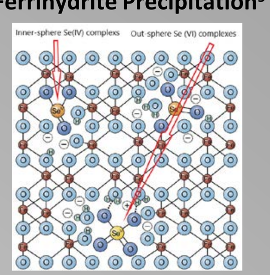
Chemical Reduction[8]



- Efficiency: ~100% removal, <10 ppb
- Long resident time
- pH and temperature dependent
- High cost of chemicals and waste disposal

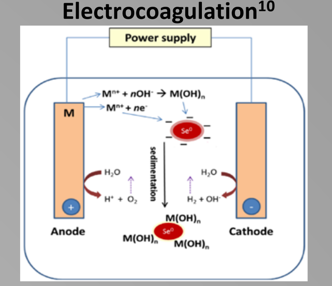
Coagulation

Ferrihydrite Precipitation[9]



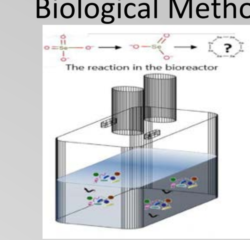
- Efficiency: <5 ppb
- Ineffective for SeO_4^{2-}
- Influenced by other anions
- pH dependent (4-6)
- Extra cost for solid waste disposal

Electrocoagulation[10]



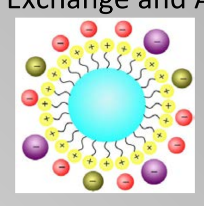
- Efficiency: ~ 98% removal
- High energy consumption
- Extra cost for electrolyzer construction and electrode replacement

Biological Method[11]



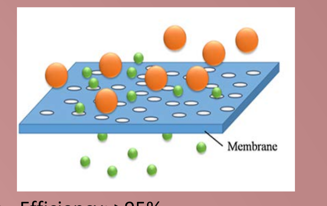
- Efficiency: <10 ppb
- Cheap and adaptable to various wastewaters
- More energy to remove oxygen in wastewater
- Remobilization of bio-reduced selenium
- Interference of other oxyanions (e.g., nitrate, sulfate)

Ion Exchange and Absorption[12]



- Efficiency: varies widely
- Low cost
- Not suitable for high levels of contaminants
- pH and temperature dependent
- Ion-competitive effects
- Extra cost for regeneration and disposal of exhausted absorbents

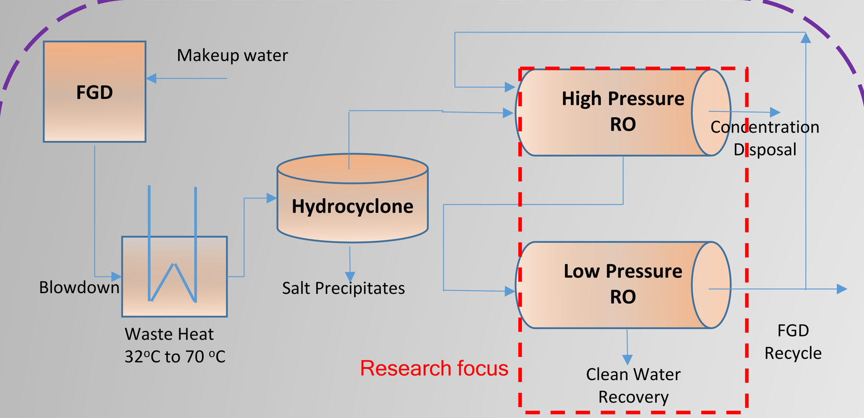
Membrane Separation [13]



- Efficiency: >95%
- pH independent
- Removes other pollutants simultaneously
- Operational cost is comparatively high

Our Approach

MLD Strategy Proposed by SRI



The main goal is to develop innovative efficient water management practices at coal-fired energy plants; we will also:

- Test the SRI seawater desalination PBI hollow-fiber membranes (HFMs) for separating sulfates and selenium from an FGD WW simulant and then from real-world FGD WW.
- 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 at an industrial site.

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:

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Principal Investigator:

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NETL

- Funding and technology oversight

SRI

- PBI membrane development
- Membrane testing

Enerfex, Inc.

- Membrane system modeling

PBI Performance Products, Inc.

- PBI dope source

Generon, IGS

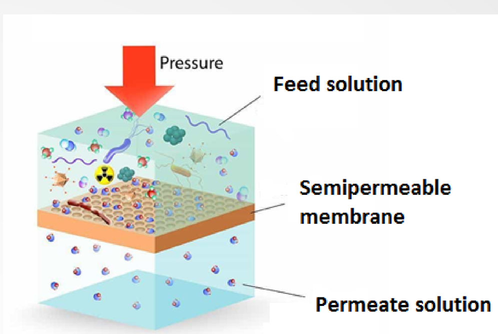
- Membrane fabrication site

OLI Systems

- Optional partner

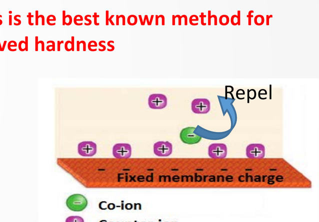
Membrane Separation Based on Polybenzimidazole Hollow-fiber Membranes (PBI HFMs)

Reverse Osmosis (RO) Technology

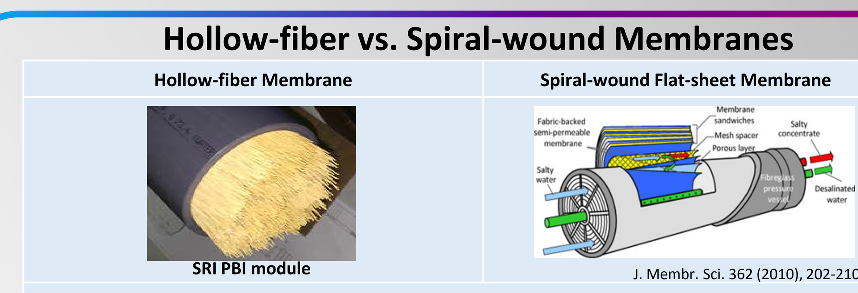


http://diagram.premamaz.com/reverse-osmosis-diagram/

- Pressure driven process (200-1000 psi) to overcome osmosis pressure
- Solution diffusion mechanism: RO membrane is assumed to be nonporous, and transport is by diffusion between the interstitial space of polymer chains or polymer nodules
- Donnan effect: works in charged membranes
- Reverse osmosis is the best known method for removing dissolved hardness



Hollow-fiber vs. Spiral-wound Membranes



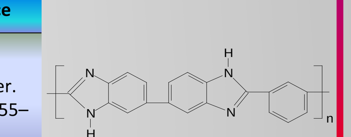
Advantages of Hollow-fiber Membranes

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

PBI HFM

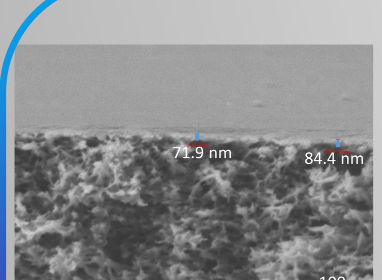
PBI vs. Other Membrane Materials

RO Membrane Materials	Property	Reference
PBI	Superior thermal stability: Tg=450°C, degradation at 450°C in air, continuous operating temperature up to 250°C; High mechanical strength; Outstanding chemical resistance; Excellent chlorine resistance.	Fire Mater. 26(2002),155–168
Cellulose Triacetate	Low thermal resistance (<30°C); Low chemical resistance (working pH=2-8) Poor chlorine resistance	Desalination 326(2013), 79-95
Polyamide	Poor chlorine resistance	

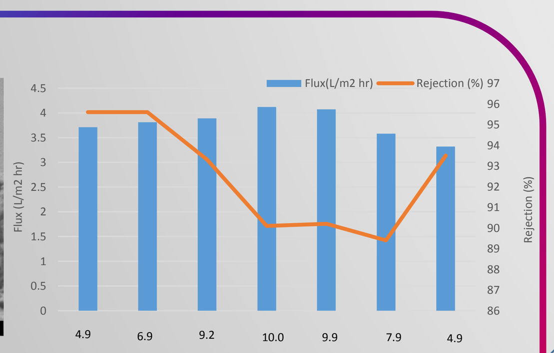


PBI molecular structure

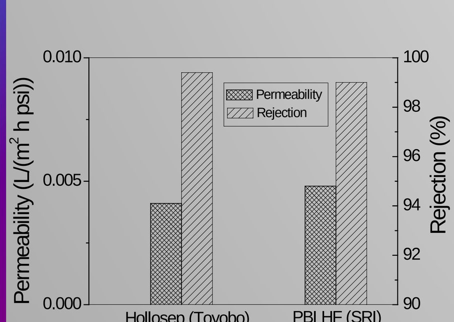
Two Different Types of Hollow-fiber Membranes (HFMs) and Their Performance



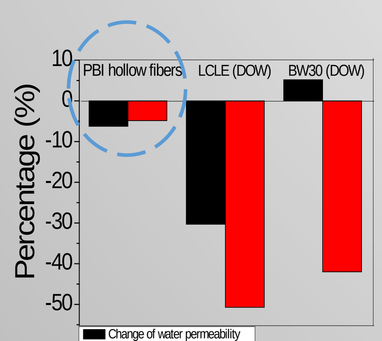
❖ Ultra-thin PBI barrier layer



❖ Higher selectivity at low pH value



❖ Performance is comparable to the commercial HF [14]

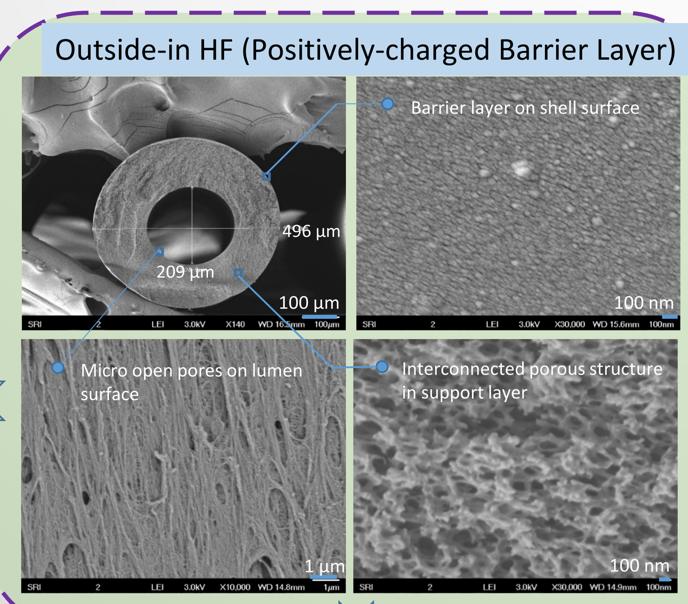


❖ Superior chlorine resistance [15] (Chlorine exposure: 4,000 ppm· h, pH=11, Feed solution: 2,000 ppm NaCl)

14. Desalination 125(1999) 55-64
15. J. Membr. Sci., 451(2014), 205-215

Previous Test

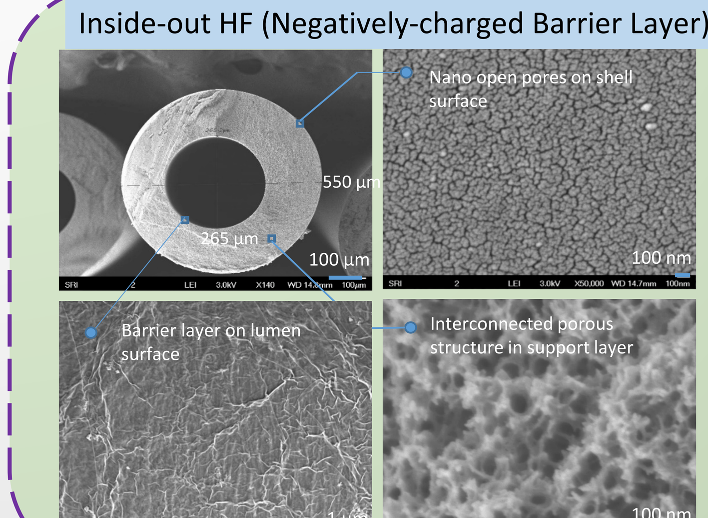
Outside-in HF (Positively-charged Barrier Layer)



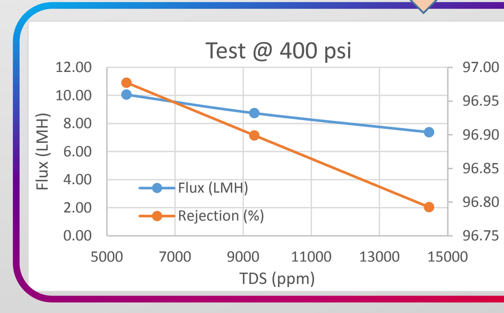
Preliminary Test

Pressure	Module #1 Flux	Module #1 Rejection	Module #2 Flux	Module #2 Rejection
Test @ room temp (TDS=~5000)				
300	1.52	98.4	1.26	98.8
400	1.81	99.0	1.59	99.1
Test @ 50 °C (TDS=~5000)				
300	1.95	98.7	1.73	98.9
400	2.66	99.0	2.21	99.0

Inside-out HF (Negatively-charged Barrier Layer)



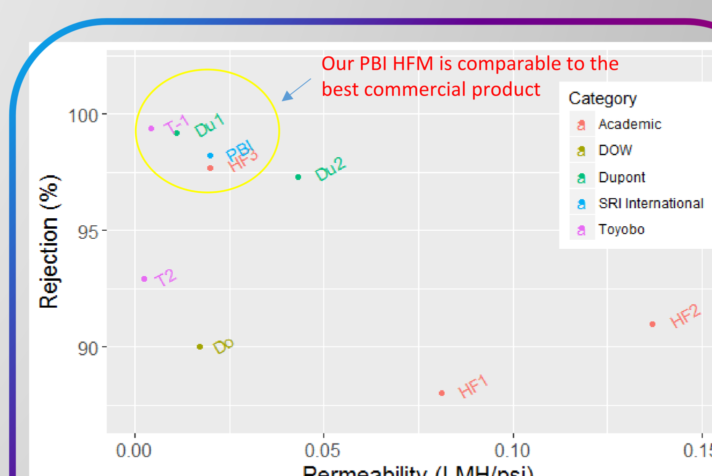
Preliminary Test



Composition of Feed Solution (TDS=~1500)

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	$SO4^{2-}$	1773

Previous Test

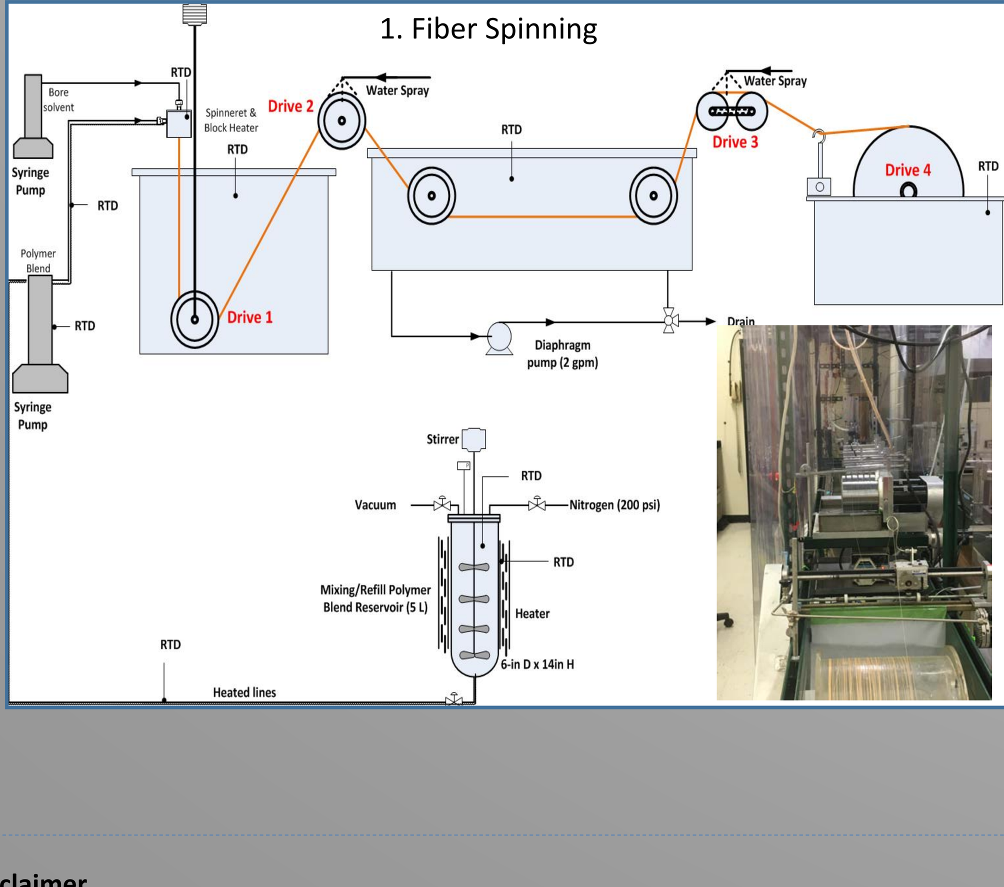


Test with ~2000 ppm NaCl solution@400 psi at room temperature

Point	Material	Reference
Do	DowEX (cellulose triacetate)	Desalination 102 (1995) 225-234
Du1	Permasep B-10 (polyamide)	Desalination 126 (1999) 33-39
Du2	Permasep B-9 (polyamide)	Desalination 48 (1983) 1-16
T-1	Hollosep MH10255 (Cellulose triacetate)	Desalination 125(1999) 55-64
T2	Hollosep HA8130 (Cellulose triacetate)	Journal of Membrane Science 236 (2004) 1—16
HF1	Dual layer (Polyethersulfone/polyamide)	Environ. Sci. Technol. 46(2012), 7358–7365
HF2	Dual layer (Polyester/polyamide)	Environ. Sci. Technol. 47(2013), 7430–7436
HF3	Electrospun fibers (polyacrylonitrile)	Journal of Membrane Science 363 (2010) 195–203

Fabrication of Polybenzimidazole Hollow-fiber Modules

1. Fiber Spinning



2. Crosslinking

3. Post treatment

4. Potting

5. Large fiber module

4" diameter module containing 10,000 fibers
(Gas-separation PBI membrane elements are pictured)

Conclusions

- ❖ **Both operational cost and energy consumption will be significantly decreased by the use of reverse osmosis (RO) technology in flue gas desulfurization wastewater (FGD WW) management approaches.**
- ❖ **Among the existing technologies, membrane separation, especially using RO, is the most promising way to remove Se and other heavy metals in FGD WW.**
- ❖ **The hollow-fiber (HF) format reduces membrane module size and operational cost relative to spiral-wound membranes.**
- ❖ **Inside-out HF can provide both high flux and rejection comparable to that of commercial flat-sheet membranes.**
- ❖ **Outside-in HF can tolerate harsh operating conditions, and its separation performance is comparable to that of commercial membranes.**

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