Water Treatment and Water-Vapor Recovery Using Advanced Thermally Robust Membranes for Power Production

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Elevated Temperature Membrane Separations

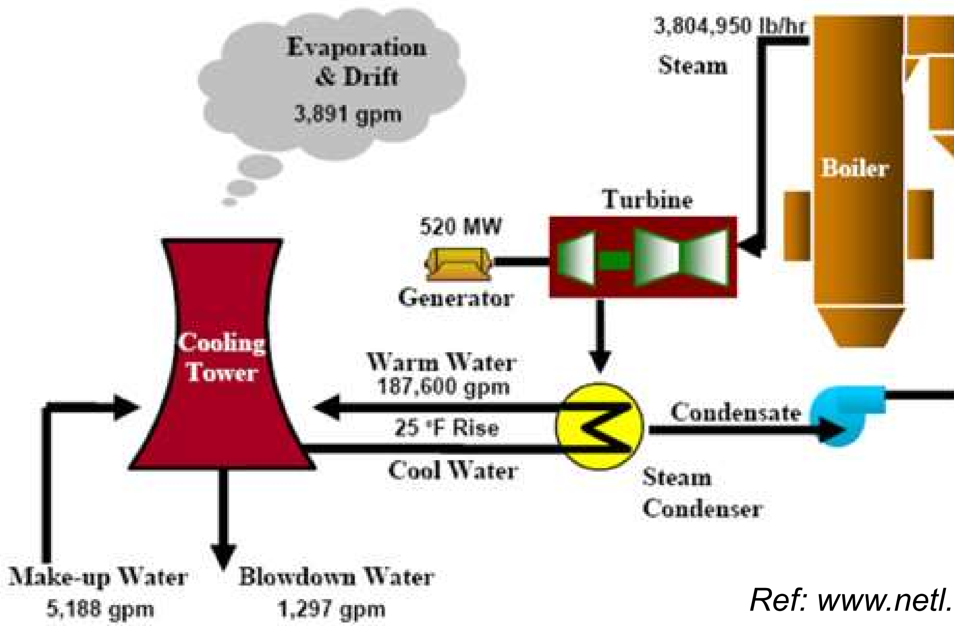
Applications of Interest:

Flue Gas Dehydration

Water Treatment

Energy-Water Nexus

- **Energy production from fossil fuels relies heavily on clean water**
  - Clean water for boiler steam, FGD unit & cooling – Water usage is dominated by cooling needs.



Ref: www.netl.gov

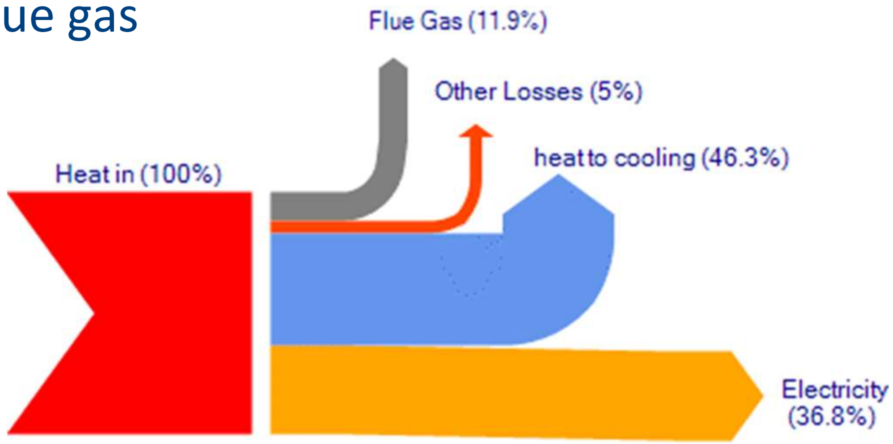
  - An estimated ½ gallon of water is consumed per kWh of electric power produced
  - Water needs will increase significantly due to carbon capture (CC)
    - 30% increase in water consumption due to CC in pulverized coal power plant

Ref: A. Delgado, M.S. Thesis, MIT, 2012

Water Management

Growing water and energy needs, and fresh water scarcity mandate water conservation, treatment & re-use

- **Lost water vapor recovery**
  - Evaporation from cooling towers and flue gas
    - 6 to 13 % water vapor depending on the coal feedstock and FGD
    - 20% water vapor capture enough to make power plant self-sufficient.
    - Water vapor recovery will improve efficiency by latent and sensible heat recovery
    - Difficult to capture: Low partial/total pressure



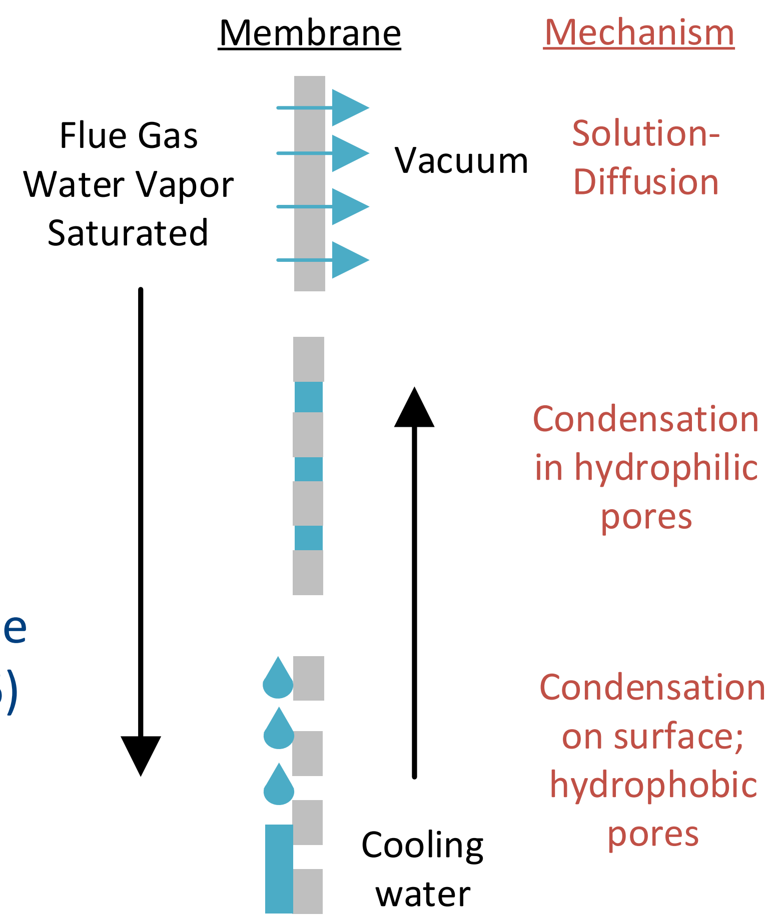
  - FGD & cooling tower blowdown water treatment & re-use
- **Alternate water resources: Extracted brines and RO reject stream**
  - Require extensive processing to produce power plant quality water
    - High salinity brine; salinity ranging from > 40,000 mg/L to >300,000 mg/L & elevated temperatures

Flue Gas Dehydration

- **No industry standard process to capture water from flue gas**
  - Condensing heat exchangers, membranes and desiccant based dehumidification techniques proposed for flue gas dehydration
- **Chemically challenging stream due to the presence of SOx & NOx**
  - Condensing heat exchangers (CHX) are effective but expensive (Levy, 2011)
    - Cost & benefit of CHX dependent on the flue gas temperature (135 °F downstream of FGD scrubber & 300 °F power plant without FGD scrubber)
    - Acid formation during condensation mandates the use of expensive alloys to minimize corrosion
    - Produced water can be used as cooling water or flue gas desulfurization make-up
  - Dessicant drying system are energy intensive
    - Parasitic energy loss in dessicant regeneration
    - Low quality of water produced
  - Membrane technology emerging as an energy efficient alternative for molecular separations including water vapor removal
    - Continuous operation, no moving parts and no regeneration required
    - Polymers are typically more chemically robust under corrosive conditions

Flue Gas Dehydration: Membranes

- **Selective transport of water vapor in dense hydrophilic polymer membrane under water vapor pressure gradient**
  - Sulfonated PEEK (Sijbesma, 2008) evaluated in pervaporation mode
    - High ideal H_2O/N_2 selectivity
    - Water quality was not high enough for boiler make-up; significant transport of SO_2 and NO_2
- **Membrane condensers**
  - Inorganic transport membrane condensers (Wang, 2012) enabled 40% water vapor capture
    - Presence of minor amount of sulfate and inorganic carbon in permeate water reported
  - Hydrophobic porous membrane to condense water vapor on feed side (Macedonio, 2016)
    - Processes using cold sweep gas (air) or cooling water proposed



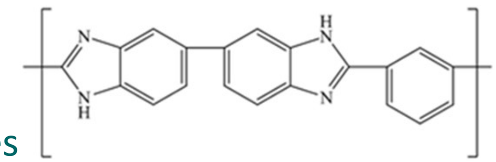
PBI Membranes for Flue Gas Dehydration

Goal

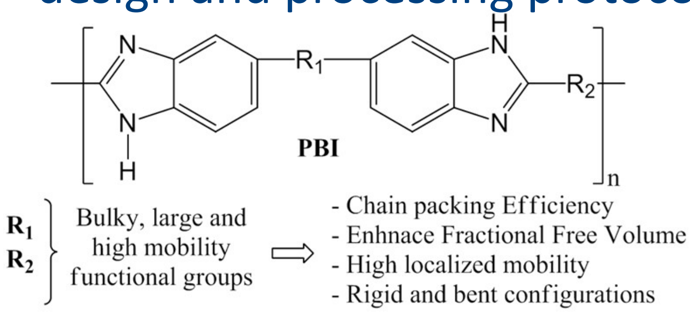
Thermo-chemically robust membrane material demonstration and fundamental performance data gathering for water vapor capture from power plant flue gas

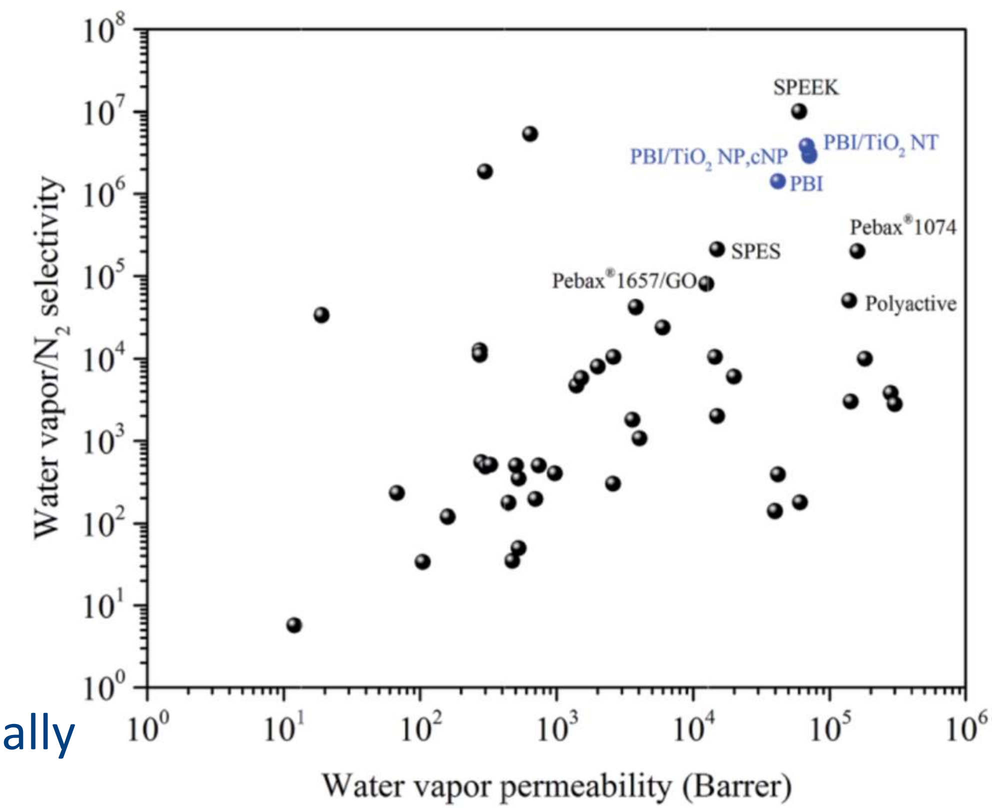
Background: PBI Based Materials/Membranes

- Polybenzimidazole-based materials/membranes exhibit exceptional thermo-chemical stability
  - Tg > 400 °C, board operating temperature opportunities
  - Tolerance to “bad actors” such as steam and H_2S at elevated temperatures



- High water uptake and water vapor perm-selectivity
  - 15 wt% water sorption
- Demonstrated ability to tailor transport properties via materials design and processing protocols





- Processability demonstrated, industrially attractive hollow fiber platform

Ref: Akhtar et.al., J. of Mater. Chem. A, 2017, 5, 21807

PBI Membrane Flue Gas Dehydration

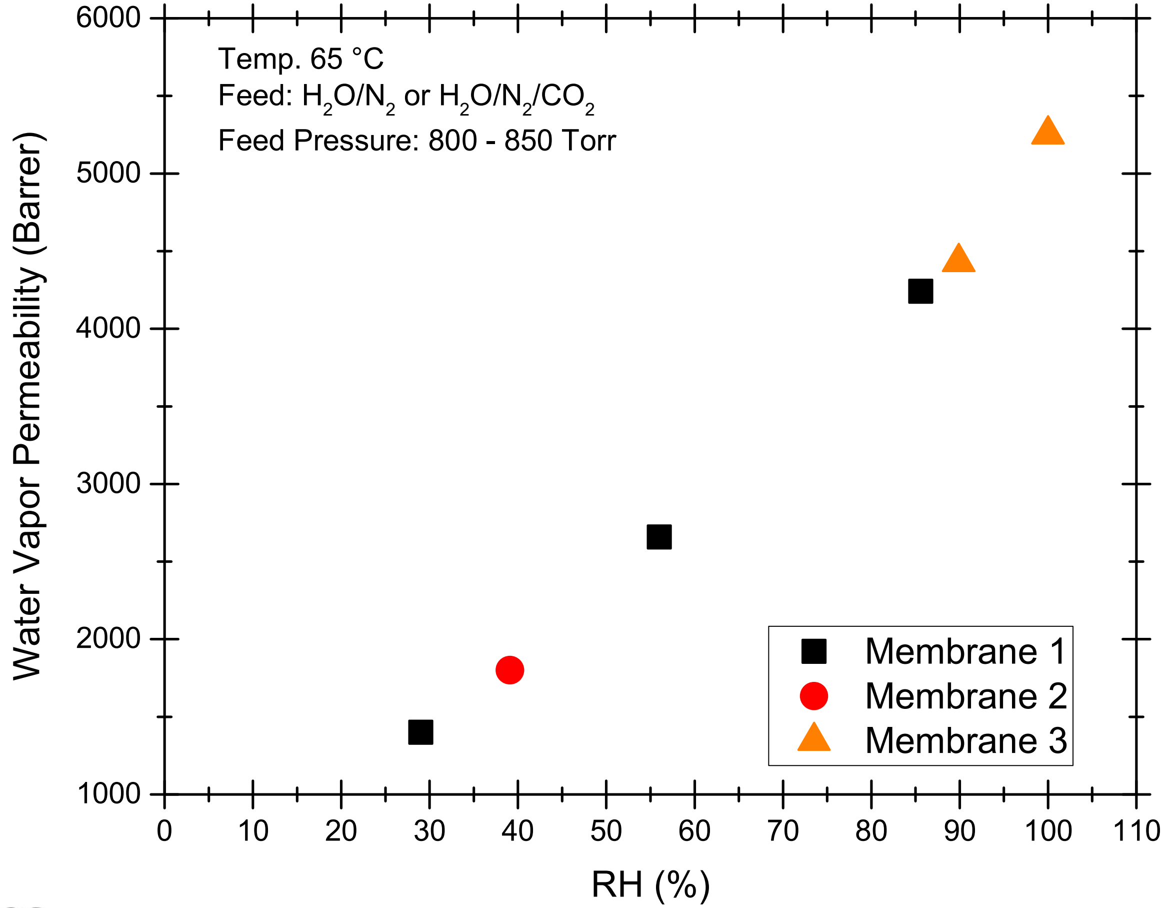
Measure PBI membrane performance at flue gas process conditions

Typical Flue Gas Composition	
N_2	70-72% (vol.)
CO_2	13-14%
O_2	3-4%
H_2O	6 to 20%
SOx	~200 ppm
NOx	~200 ppm
HF/HCL	<10 ppm
Temp.	50 to 180 °C

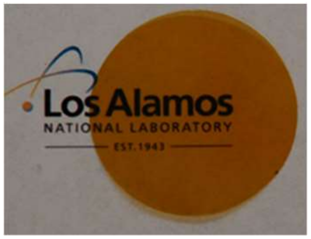
- Permeability & selectivity at varied operating conditions
- H_2O, SO_2 and NO detection using FTIR multi-gas detector
- N_2 and CO_2 analysis using GC

Attractive Water Vapor Permeation

- **Ideal water vapor transport characteristics of PBI measured at flue gas representative conditions**
  - Consistent water vapor permeability measured for 3 samples

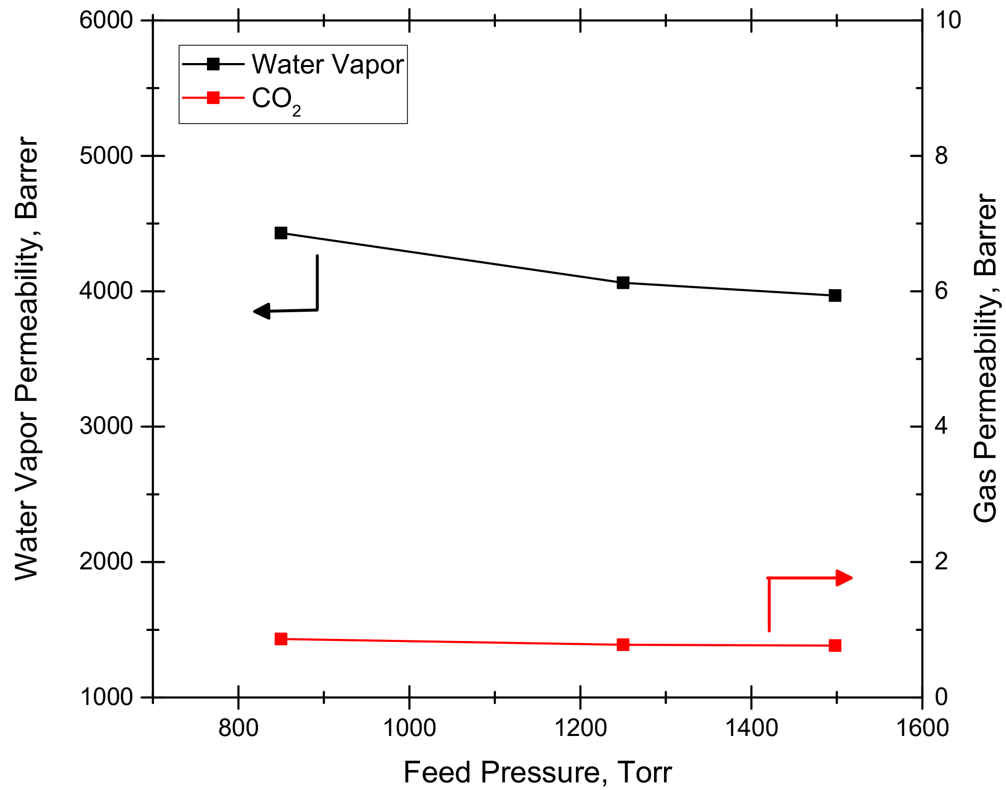


- Film Thickness ≅ 55 µm
- Sweep gas: He



High Water Vapor Perm-Selectivity

- **PBI has high vapor perm-selectivity over CO_2 and N_2 at flue gas representative conditions**
  - Water vapor permeability decreased with feed pressure
  - H_2O/CO_2 selectivity = 5000
  - H_2O/N_2 selectivity estimated at > 20,000 based on GC N_2 detection limit



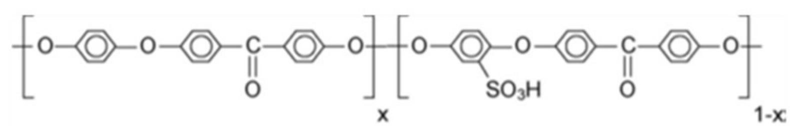
Test Conditions
- Feed RH: 89.9%, CO_2 =10 to 11%, Bal: N_2
- Temp: 65 °C
- Thin film ≅ 55 µm
- Sweep gas: He

Comparison to Other Membranes

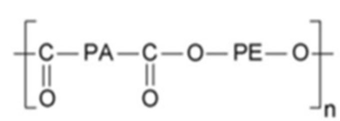
PBI membrane performance compared to literature data available for sPEEK and PEBAX membranes

- sPEEK and PEBAX has much higher water vapor permeability than PBI
- Gas permeability of PBI is lower than sPEEK and PEBAX in wet feed conditions
- SOx & NOx rejection: PBI membranes will be tested
  - sPEEK test in actual flue gas: 50-100 and 150-300 ppm SO_2 & NO_2, respectively present in the condensed water

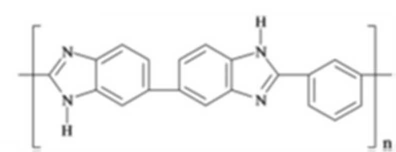
Component	Permeability (Barrer)		
	PBI	sPEEK	PEBAX 1074
Single Gas[b]:			
Temp, °C	30	30	30
N_2	0.0231	0.003	2.45
CO_2	0.342	0.11	122
Mixed Gas:			
Temp, °C	65	30 to 65 °C	30 to 65 °C
H_2O	4000[a]	$1x10^4$ to $1x10^6$	200,000[b]
N_2	0.05 (est.)[1]	0.14 to 0.2	1.9 to 13
CO_2	0.8	5 (est.)[2]	90 (est.)[2]



Sulfonated - PEEK



PEBAX - 1074



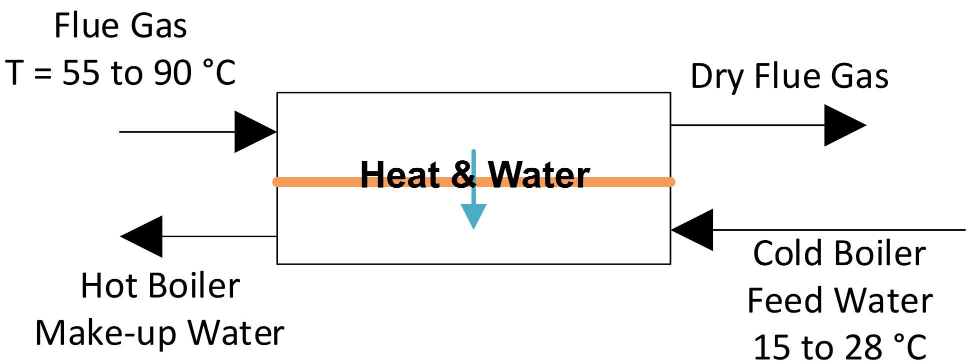
PBI

[a] Measured using $N_2/CO_2/H_2O$ feed at 86% RH. [b] Pure gas measured using constant volume/variable pressure. [1] CO_2 permeability (0.8 barrer) divided by CO_2/N_2 selectivity (14.8) at 40 °C. [2] N_2 permeability (0.14 barrer) multiplied by CO_2/N_2 selectivity (37). sPEEK and PEBAX data from J. Membr. Sci. 2008, 313 (1-2), 263-276

Flue Gas Dehydration Process Design

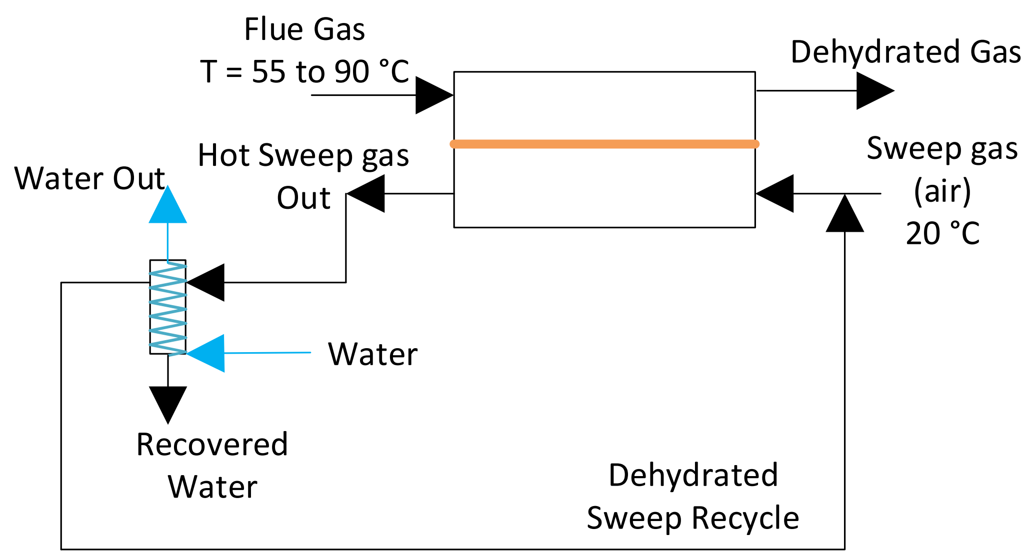
Four preliminary process configurations possible

- Permeate sweep (water or gas) process configuration



<u>Membrane Contactor (Gas-Liquid)</u>
Based on the saturation water vapor pressure difference between hot flue gas and cold boiler water.

<u>Sweeping Gas Configuration</u>
Sweep gas to create partial pressure driving force followed by condensation of water from sweep gas to get clean water

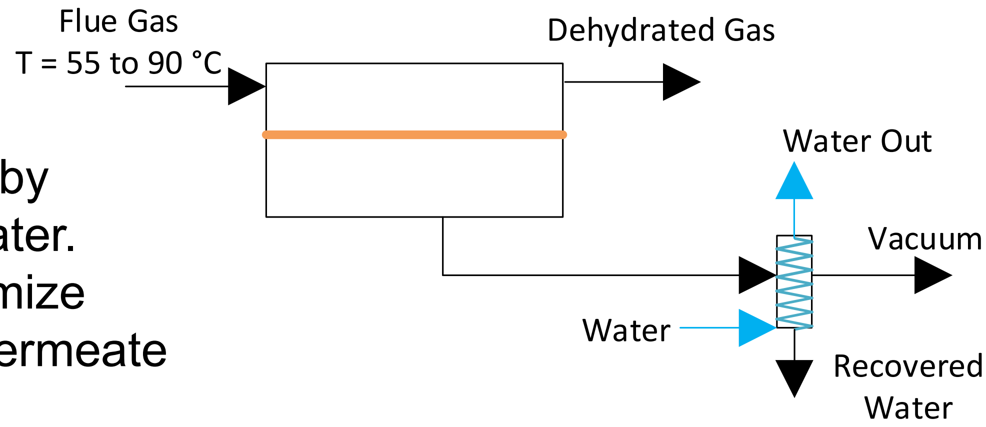


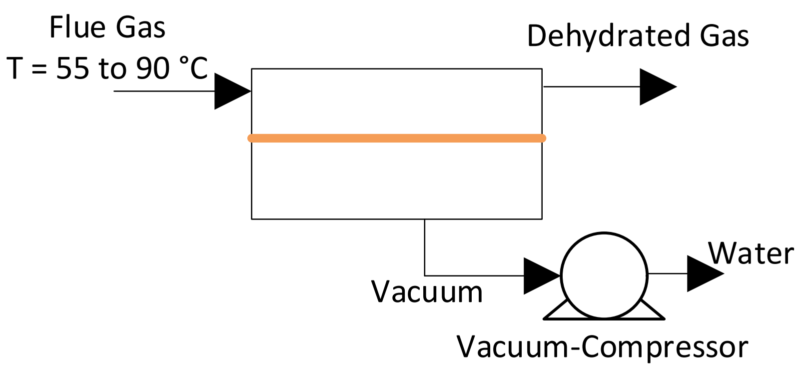
Flue Gas Dehydration Process Design (cont.)

- Permeate vacuum process configurations

<u>Pervaporation</u>

Vacuum on permeate side to create partial pressure driving force followed by use of condenser to recovery clean water. Low gas permeability required to minimize vacuum duty. Cooling water use for permeate side water vapor condensation





<u>Vapor-Compression</u>

A variation of pervaporation configuration using vapor compression to condense water vapor. Very low gas (N_2 & CO_2) permeability required to minimize compression duty

Summary: Flue Gas Dehydration

- **Water vapor transport characteristics of PBI materials attractive for flue gas dehydration**
  - Water vapor permeability 4000 – 5000 Barrer at flue gas representative conditions (65 °C)
  - Extremely low N_2 and CO_2 permeability beneficial for high process efficiency enabled by low parasitic (energy) loss resulting from their permeation
  - Four preliminary process designs proposed for deployment of PBI membranes for water vapor capture from flue gas
- **Future work**
  - Evaluate PBI membranes for water vapor perm-selectivity at flue gas representative conditions in the presence of SO_2 and NO.
    - Multi-gas FTIR flue gas test system enables direct H_2O, CO_2, SO_2 and NO analysis
  - Perform preliminary energy calculations to estimate energy needs for the envisioned PBI membrane flue gas processes.

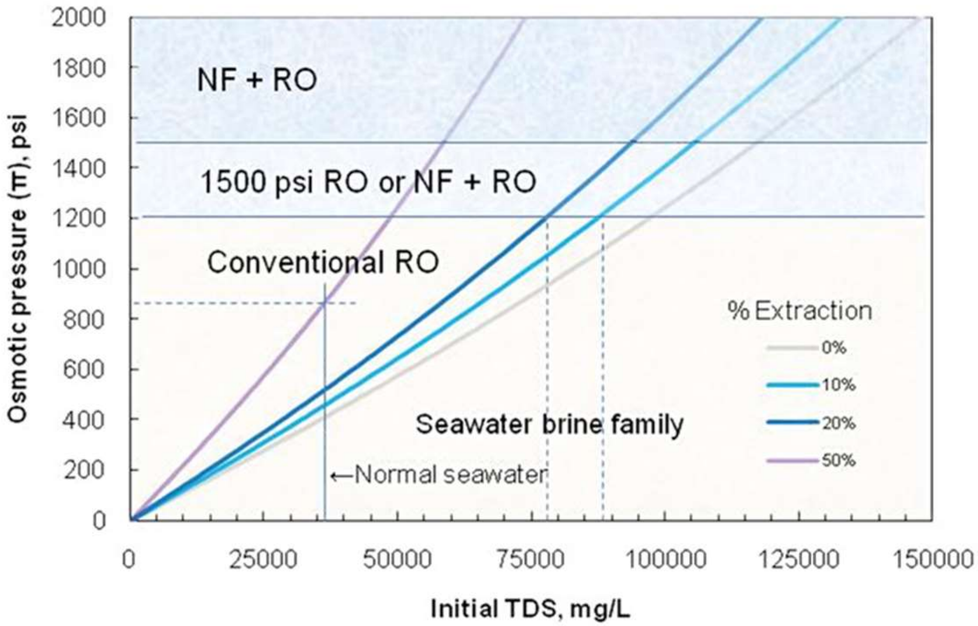
Water Treatment

Goal

Membrane distillation/pervaporation approach to waste water and high salinity brine treatment

High Salinity Brine Treatment

- **Reverse osmosis – Most energy efficient for desalination**
  - Widely used for seawater (TDS < 40,000) desalination on large industrial scale
  - Inherently limited to low salinity brine



<u>TDS Limitations</u>

- Limited opportunities to treat high salinity brine having TDS > 50,000 mg/L

<u>Temperature Limitations</u>

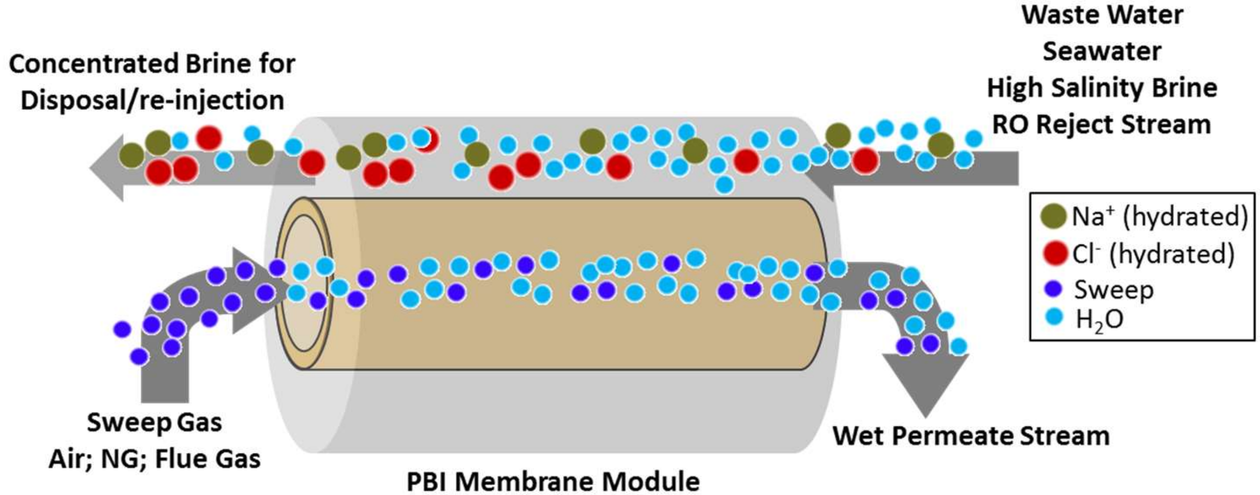
- The low operating temperatures of current RO membranes (typ. < 50 °C) limits energy efficient integration into high temperature high salinity streams (70 to > 150 °C) and power plant waste streams (120 to 140 °C).

- **Other Industrial technologies: Evaporative crystallization (EC) and mechanical vapor compression (MVC)**
  - High Cost, High Parasitic Load, Energy Inefficient

Aines, R.D., et al., Fresh water generation from aquifer-pressured carbon storage: feasibility of treating saline formation waters. Energy Procedia, 2011;Shaffer, D. L., et al., Desalination and Reuse of High-Salinity Shale Gas Produced Water: Drivers, Technologies, and Future Directions. Environ Sci Technol 2013, 47 (17).

Advanced Water Treatment Method

- **Membrane distillation/pervaporation is attractive technology for brine separations.**
  - Supplement clean water needs for power plants operation
  - Improve power generation opportunities/efficiencies (e.g. Brayton cycle)
  - Reduce extracted water disposal costs by reducing volumes



Hot Sweep Membrane Brine Separations (HGSMBS)

- HGSBSM can be thought of as MD in extreme operating environments

Technology Challenges & Opportunities

- **Advances in membrane materials and systems capable of withstanding thermo-chemically challenging operating conditions of the HGSMBS process are required.**
  - High hydrolytic and thermo-oxidative stability (process scheme dependent)
  - Stability in high TDS environments
  - Fouling resistance
  - Resistance to other extracted water components/contaminants
  - Appropriate water/water-vapor transport properties
- **Current commercial membrane limitations for HGSMBS**
  - Low thermo-chemical stability especially in presence of steam, superheated water, and oxidizing environments
    - Industry standard membrane materials cellulose acetate, polyamide, polyimide have low hydrolytic stability
  - Fouling and degradation in high salinity feed streams

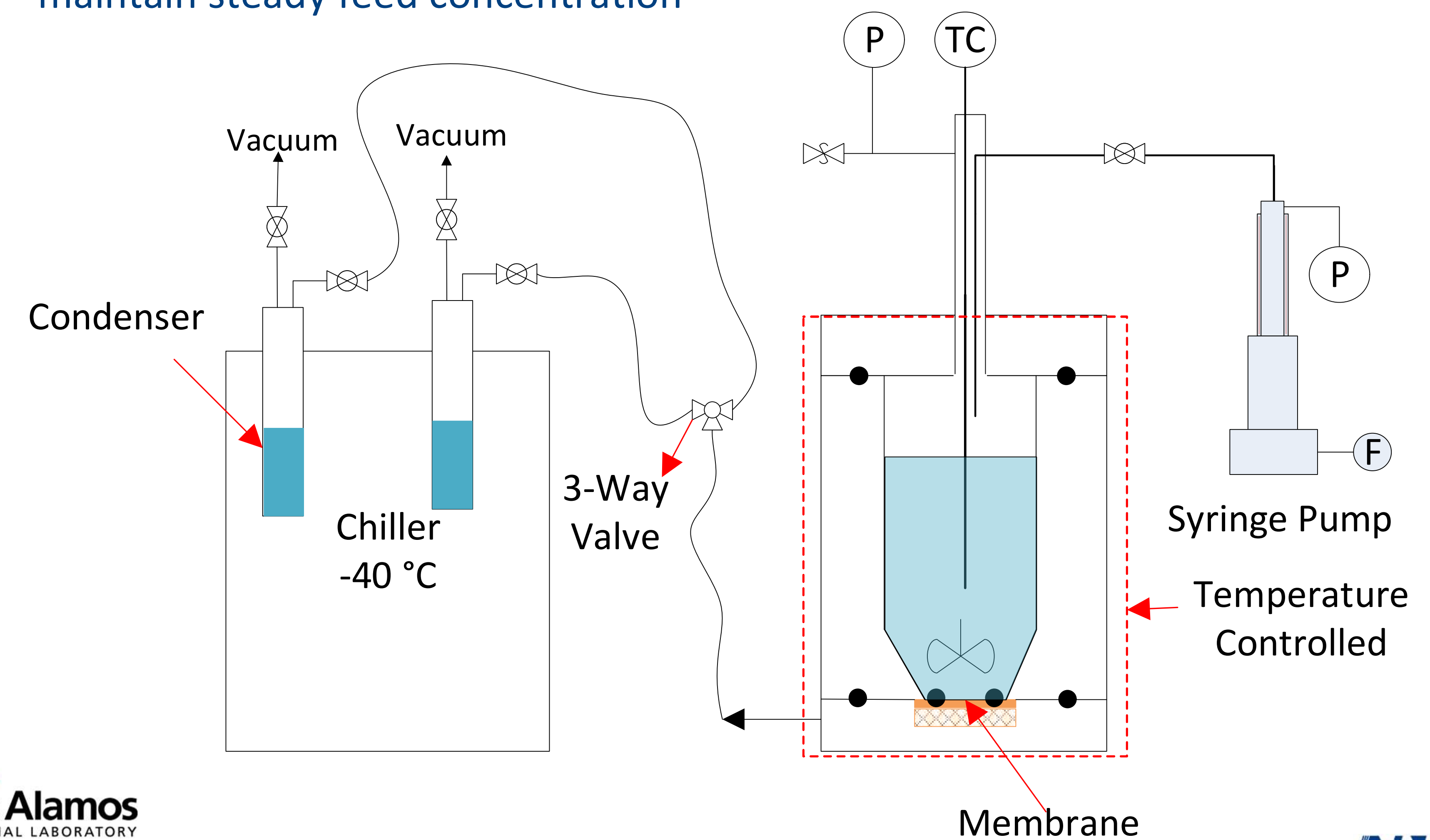
PBI Membranes for High Salinity Brine Treatment

Goal

Leveraging high water vapor perm-selectivity & exceptional thermo-chemical tolerance of PBI membranes for high salinity brine treatment at elevated temperatures

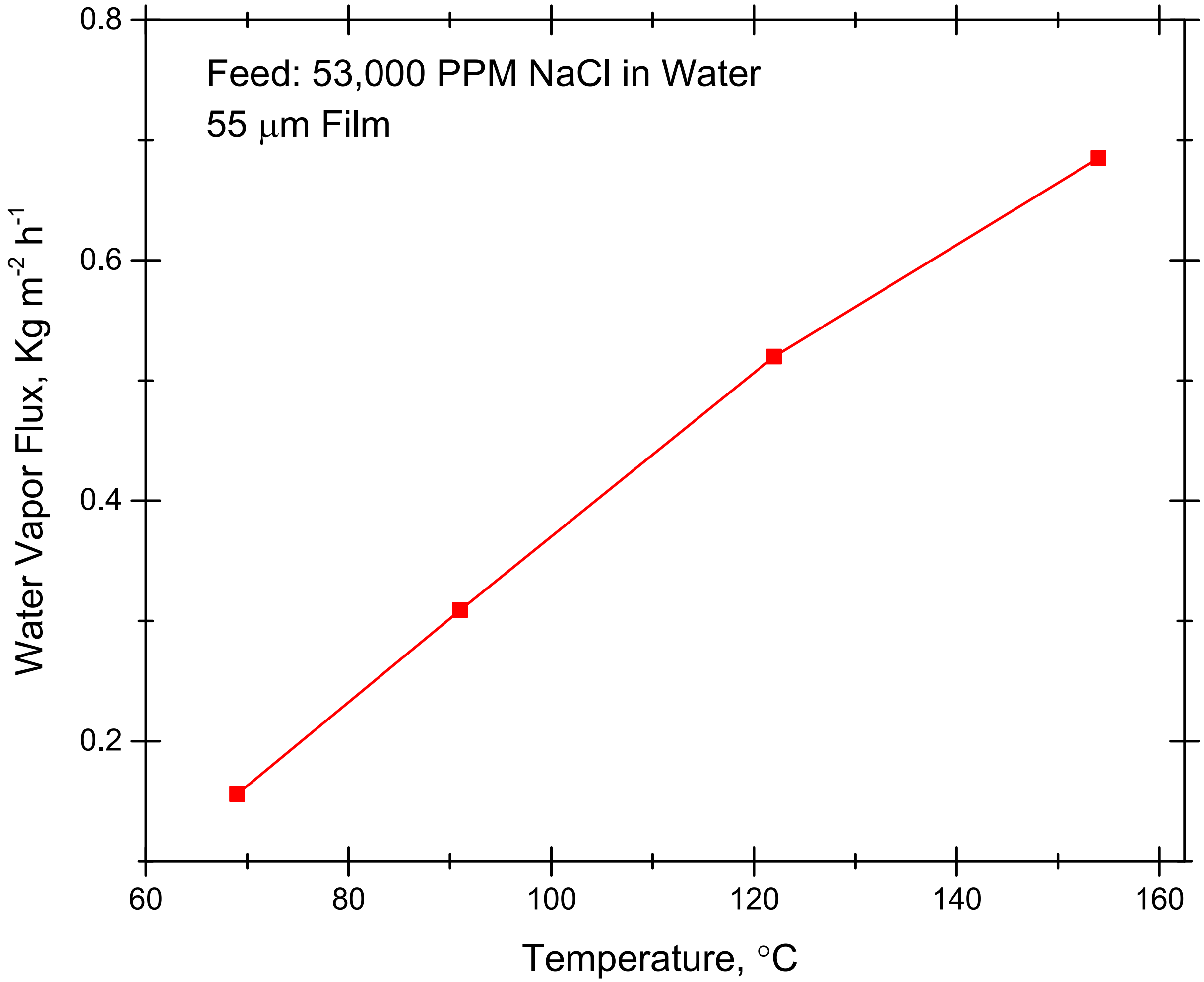
High Salinity Brine: Vapor Permeation Evaluation

- **PBI membranes evaluated in semi-continuous pervaporation mode**
  - High temperature and pressure membrane stir cell with feed injection to maintain steady feed concentration



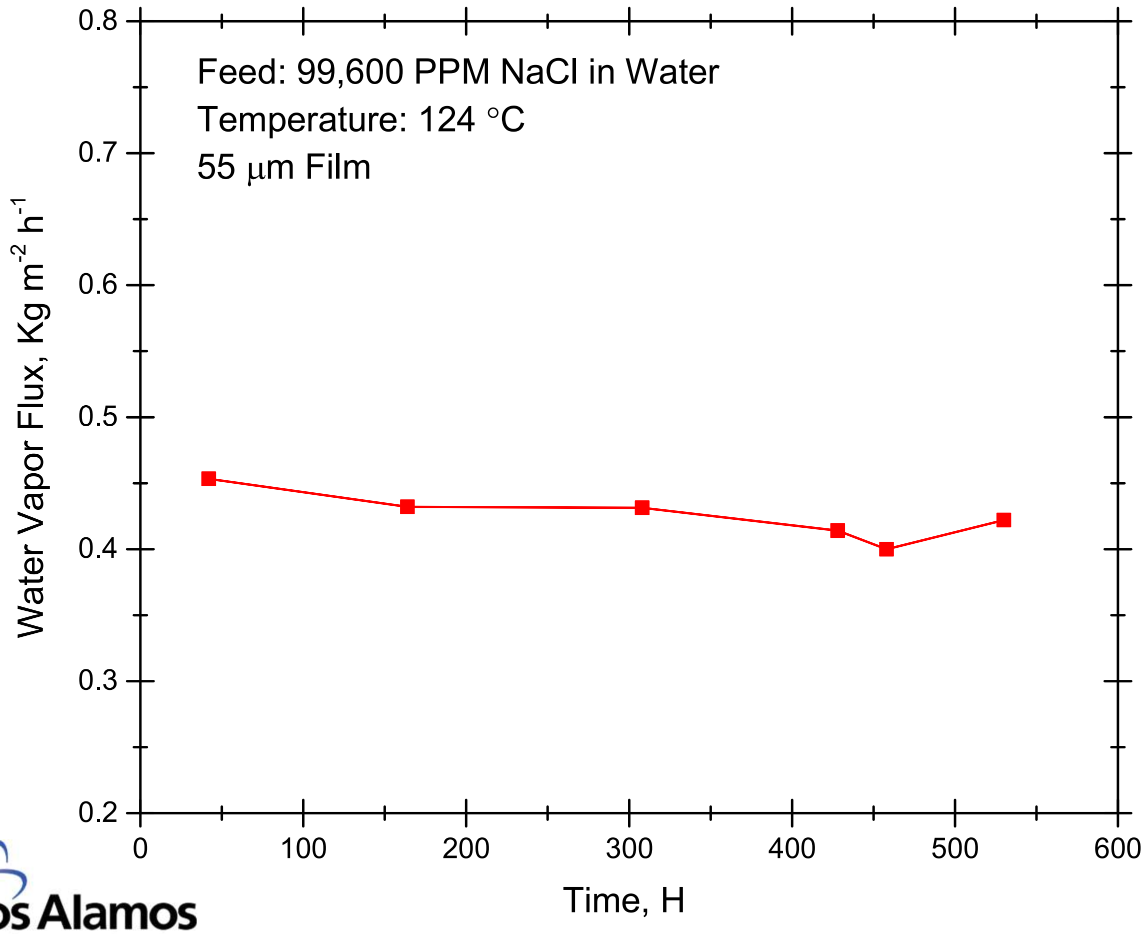
Influence of Salt Solution Exposure

- **Water transport of PBI membranes measured for NaCl/water solution measured in pervaporation mode**

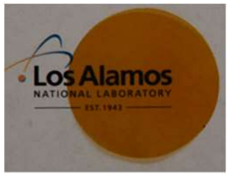


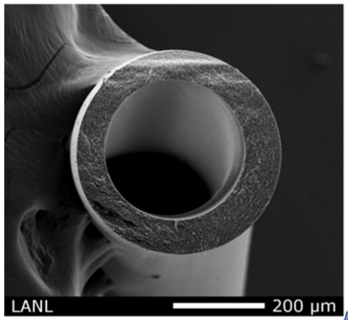
PBI Material Durability

- **Steady water vapor permeation rate demonstrated over extended operating period at 120 °C and 100,000 PPM NaCl feed**
  - Demonstrates thermo-chemical robustness of PBI in high salinity brine



Water vapor flux calculated for industrially representative thickness (200 nm) = 116 kg m^{-2} h^{-1}





Summary: High Salinity Brine Treatment

- **Thermo-chemically robust polybenzimidazole-based membranes having high water/water-vapor transport characteristics are attractive for brine treatment**
  - Water transport rate of PBI membrane increases at elevated temperatures providing opportunities for power plant waste heat utilization
  - Demonstrated tolerance of PBI membrane to NaCl solutions at concentrations and temperatures approaching 100,000 PPM and 150 °C, respectively
- **Future Work**
  - Demonstrate PBI tolerance to high salinity brines at temperatures up to 200 °C and salt concentrations up to 300,000 ppm

Future Work

Flue Gas Dehydration:

- **Evaluate PBI membranes for water vapor perm-selectivity at flue gas representative conditions in the presence of SO_2 and NO.**
  - Multi-gas FTIR flue gas test system enables direct H_2O, CO_2, SO_2 and NO analysis
- **Perform preliminary energy calculations to estimate energy needs for the envisioned PBI membrane flue gas processes.**

High Salinity Brine Treatment:

- **Demonstrate PBI tolerance to high salinity brines at temperatures up to 200 °C and salt concentrations up to 300,000 ppm**

Acknowledgement

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