Advanced Thermally Robust Membranes for High Salinity Extracted Brine Treatment via Direct Waste Heat Integration

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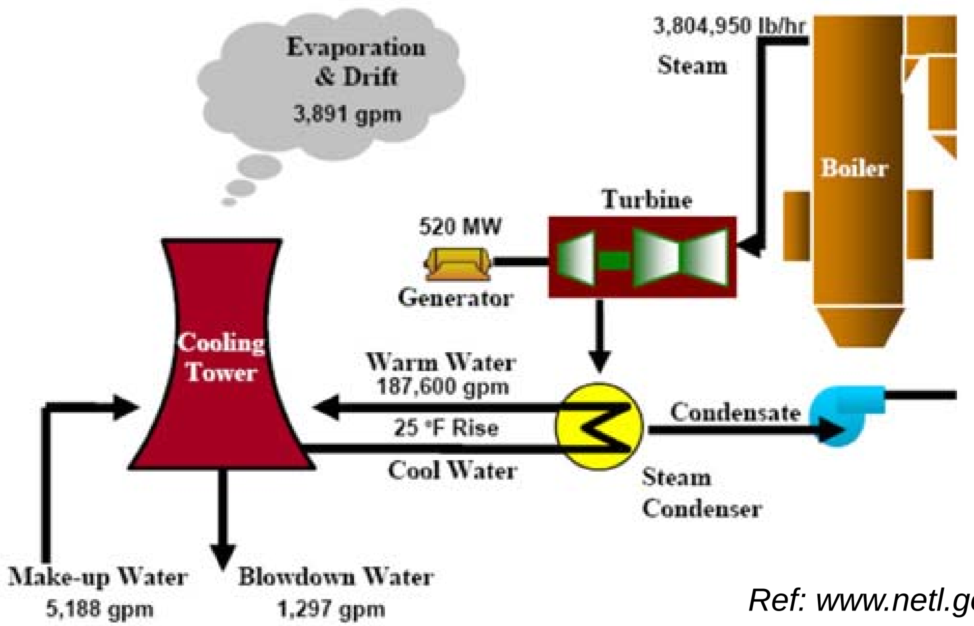
Energy-Water Nexus

- **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

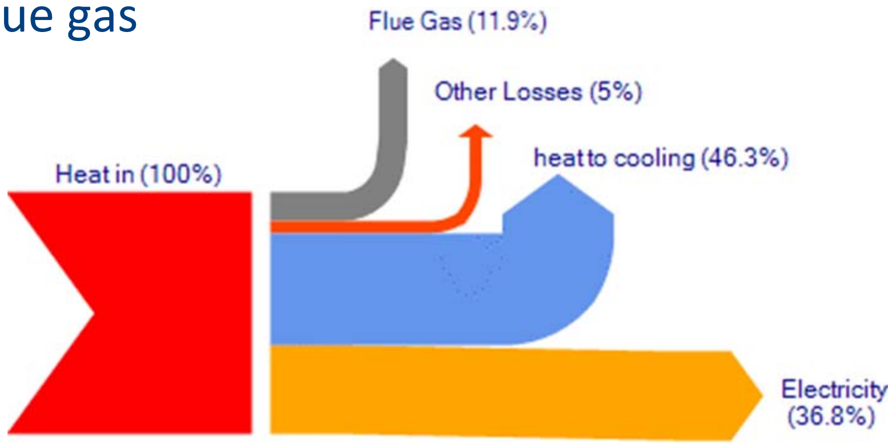
  - An estimated ½ gallon of water is consumed per kWh of electric power produced
  - Water needs will increase significantly due to carbon capture (CC)
    - 30% increase in water consumption due to CC in pulverized coal power plant

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

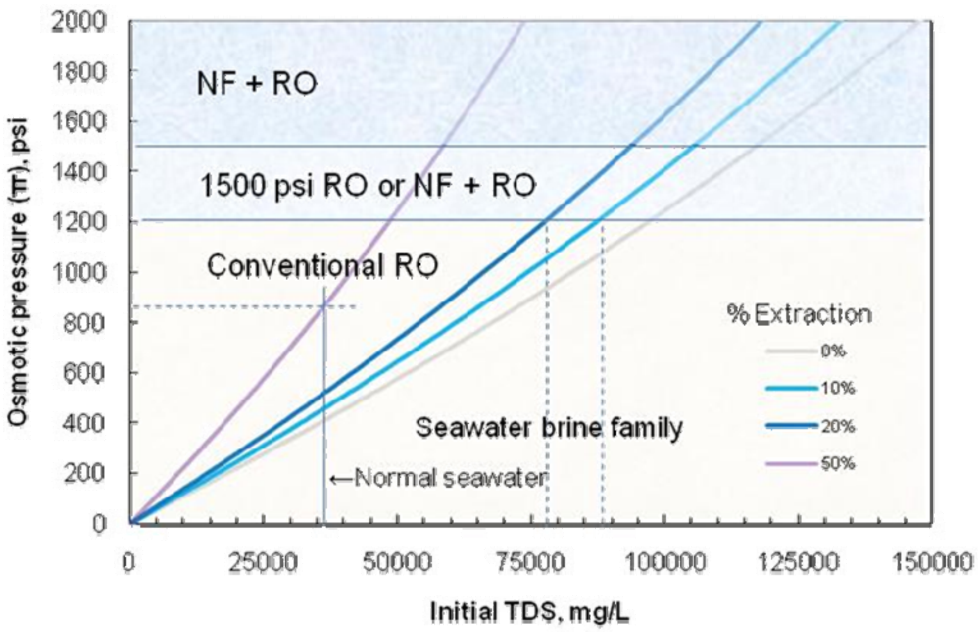
- **Lost water recovery**
  - Evaporation from cooling towers and flue gas
    - Difficult to capture: Low partial/total pressure
    - 6 to 13 % water vapor depending on the coal feedstock and FGD
    - Potential to supply 10 to 33% of boiler make-up water
    - Water vapor recovery will improve efficiency by latent and sensible heat recovery



  - 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

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



TDS Limitations

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

Temperature Limitations

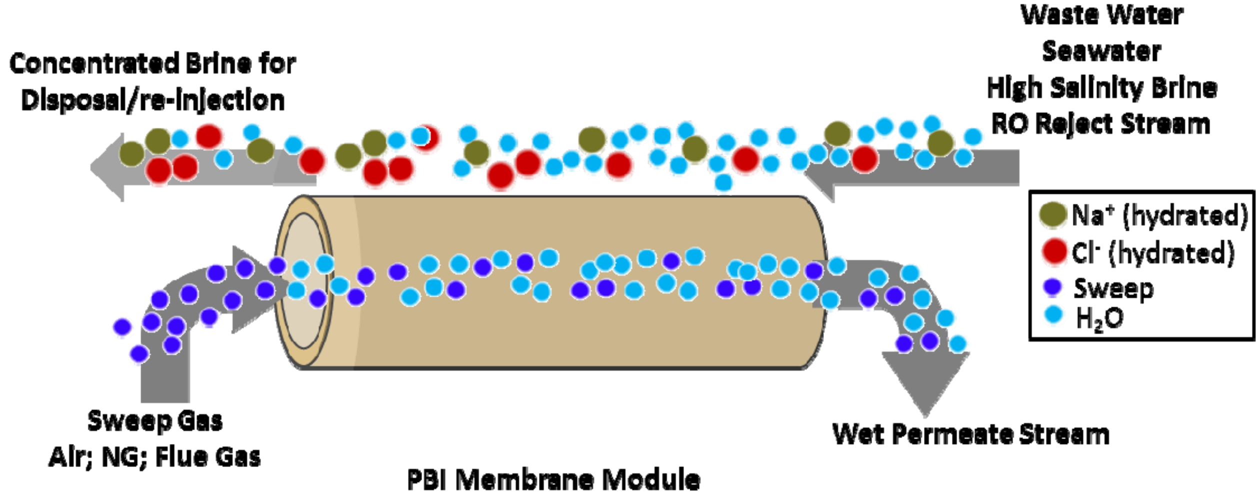
- The low operating temperatures of current RO membranes (typ. < 50 °C) limits energy efficient integration into high temperature high salinity streams (70 to > 150 °C) and power plant waste streams (120 to 140 °C).

- **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 brine disposal costs.



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

Thermo-chemically Robust Membrane Material Development & Demonstration

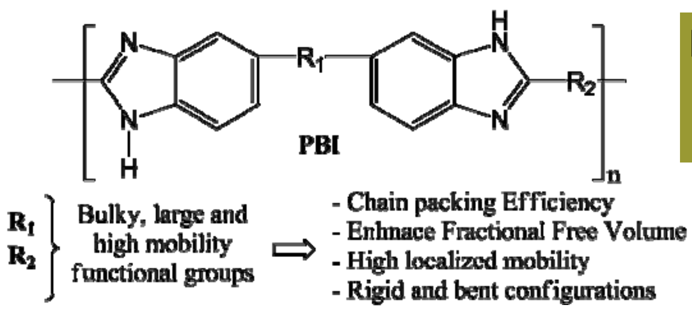
Background: PBI Based Materials/Membranes

- Polybenzimidazole-based materials/membranes exhibit exceptional thermo-chemical stability
  - Tg > 400 °C, presented board temperature operating regime
  - Tolerance to “bad actors” such as steam and H_2S
- Known syngas separation performance indicates potential for excellent salt rejection performance for PBI materials

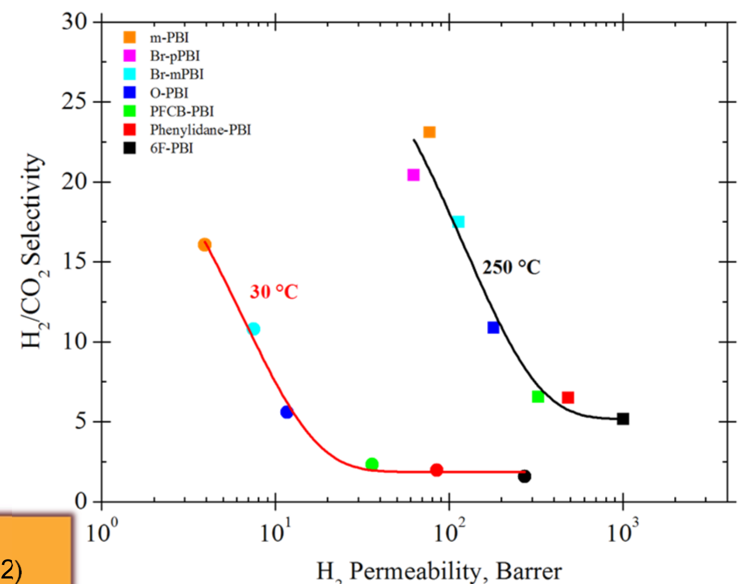
Species	H_2O	H_2	CO_2	N_2	Hydrated Na^+	Hydrated Cl^-
Kinetic Diameter (Å)	2.65	2.89	3.30	3.64	7.2	6.6
α (H_2O/X)	-	3	69	300	>>300*	>>300*

* estimated

- Demonstrated ability to tailor transport properties via materials design and processing protocols



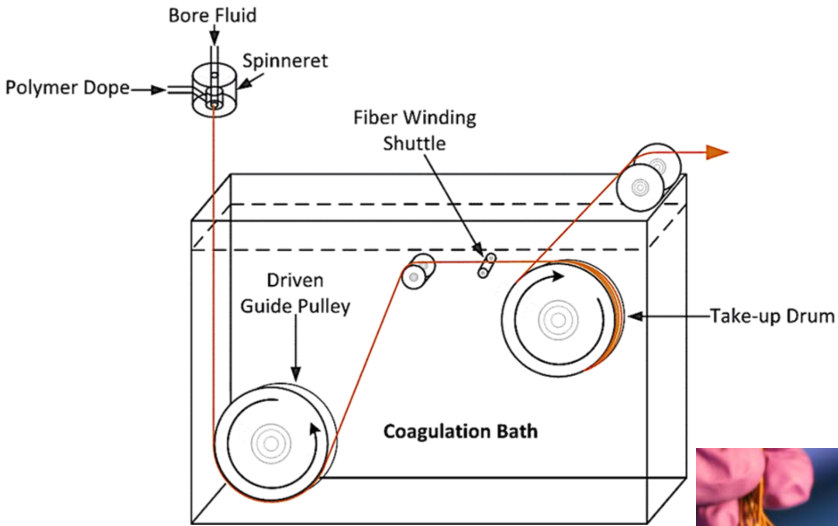
Material Design to Tailor Structure-Property Relationships



Li, *J Membrane Sci* 461(2014)
Berchtold, *J Membrane Sci* 415 (2012)
Pesiri, *J Membrane Sci* 415 (2003)

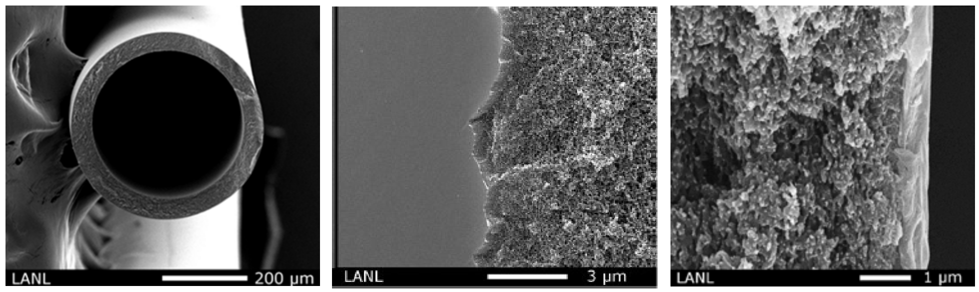
Background: PBI Membrane Deployment

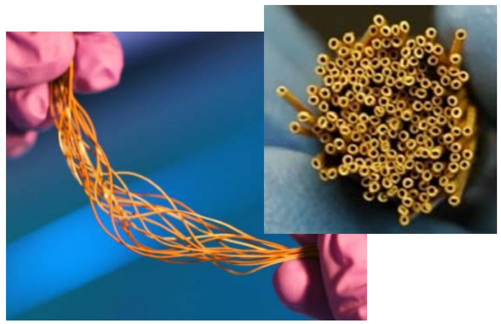
- Next generation thermo-chemically robust high performance PBI hollow fiber membrane platform developed & demonstrated for gas separation applications



Liquid-liquid de-mixing based phase inversion hollow fiber spinning process

High Performance Mechanically Robust Composite Structures Developed for Operation in High T&P Conditions





First generation multi-fiber modules under development

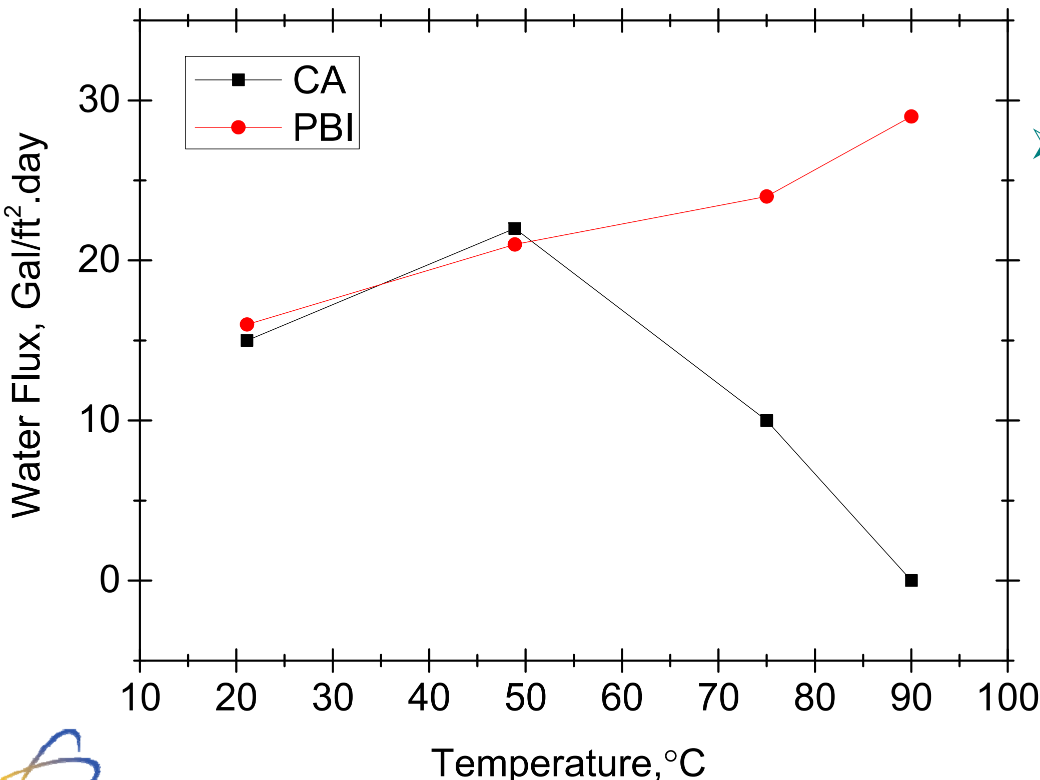
- Rapid translation to high TRL platform enabled by prior work (follow-on effort)

Patent Application: 20160375410

Salt Rejection Characterization

- **PBI (Hollow fiber membranes) has been explored as a:**
  - Reverse osmosis membrane for low concentration (≤0.5%) brine separation at temperatures up to 90℃

PBI as a "High Temperature" RO Membrane



- PBI membranes showed significant improvement in water flux compared to that of CA at elevated temperatures
  - Salt rejection ≥ 95%
  - Cellulose acetate completely degraded at elevated temperatures

Model, FS; LA Lee, 1972, Reverse Osmosis Membrane Research, 285

Objectives

- Realize high performance PBI-based membranes for high salinity brine separation
  - Optimize materials selection to tailor water vapor transport and maximize salt rejection at process relevant conditions
  - Characterize membrane thermo-chemical stability characteristics at process relevant conditions with a specific focus on oxidative stability and stability in high salinity brine environments
  - Characterize membrane flux and salt rejection characteristics at process relevant conditions

Thermo-Chemical Stability

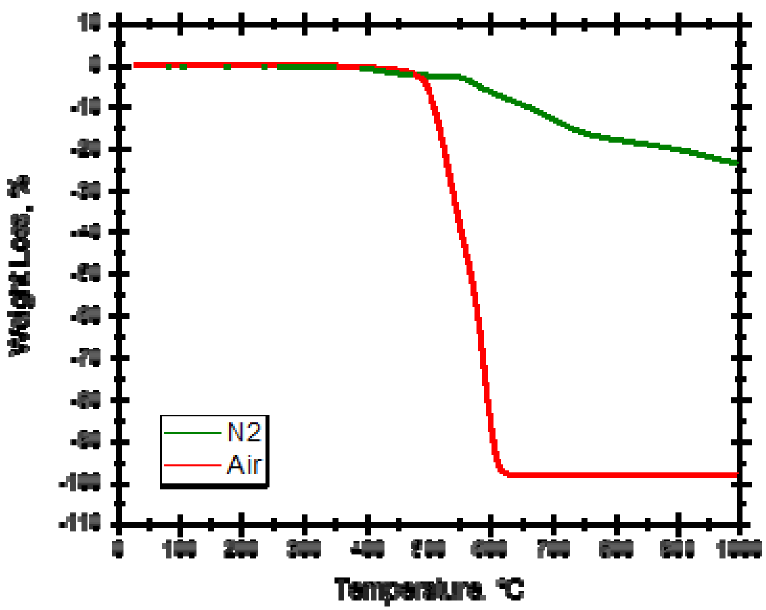
Goals

Characterize membrane thermo-chemical stability characteristics at process relevant conditions

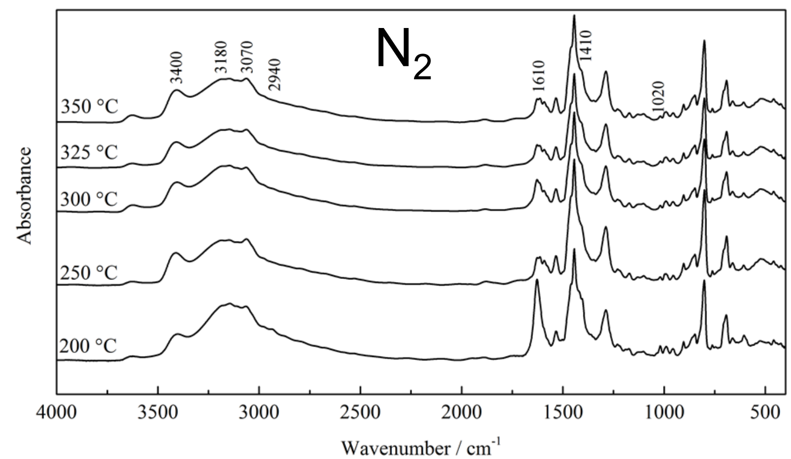
- in oxidative environments and
- in high salinity brine environments

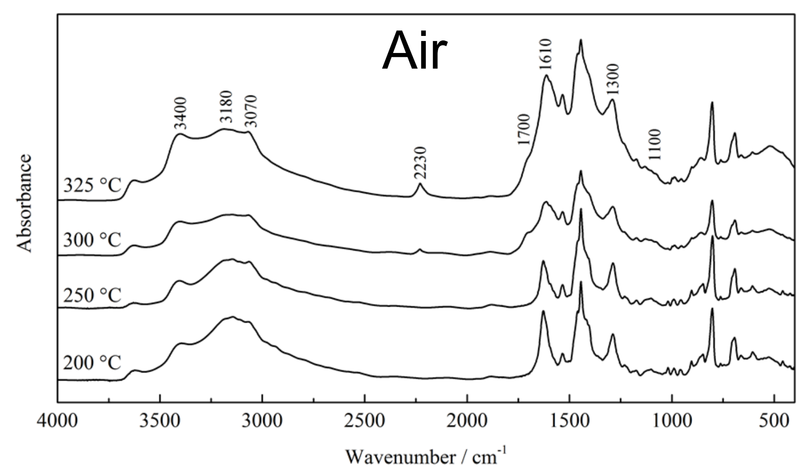
Thermo-Chemical Stability

- **PBI materials have exceptional thermal stability in inert and oxidizing environments**
  - Spectroscopic evaluation conducted to understand the thermo-chemical stability of PBI
    - TGA: Exceptional thermal stability up to 400 °C in N_2 & Air



    - FTIR: No degradation evident in N_2 and air in films exposed for 24 hours at temperatures up to 350 and 250 °C, respectively





Influence of Salt Solution Exposure

- **Pure water transport of PBI membranes measured after high salinity exposure at elevated temperatures**
- **Performance studies conducted at 120 °C in pervaporation mode**
  - Membrane samples exposed to high salinity solutions at reflux conditions (90 to 96 °C) for 24 hours followed by pure water flux evaluation
    - Decrease in water flux after salt solution exposure (thermal annealing & slow water sorption saturation not factored in these experiments)
    - Water flux levels measured for exposed membranes attractive for industrial applications

Membrane	Measured Dense Film Water Flux, kg m^2 hr^{-1}	Estimated for Industry Relevant 200 nm Selective Layer, kg m^2 hr^{-1}
Pristine	0.67	185
Exposed to 100,000 mg/L salt solution	0.48	132
Exposed to 200,000 mg/L salt solution	0.36	99

  - Membrane evaluation in higher exposure temperatures & subsequent longer term stable flux measurement on-going.

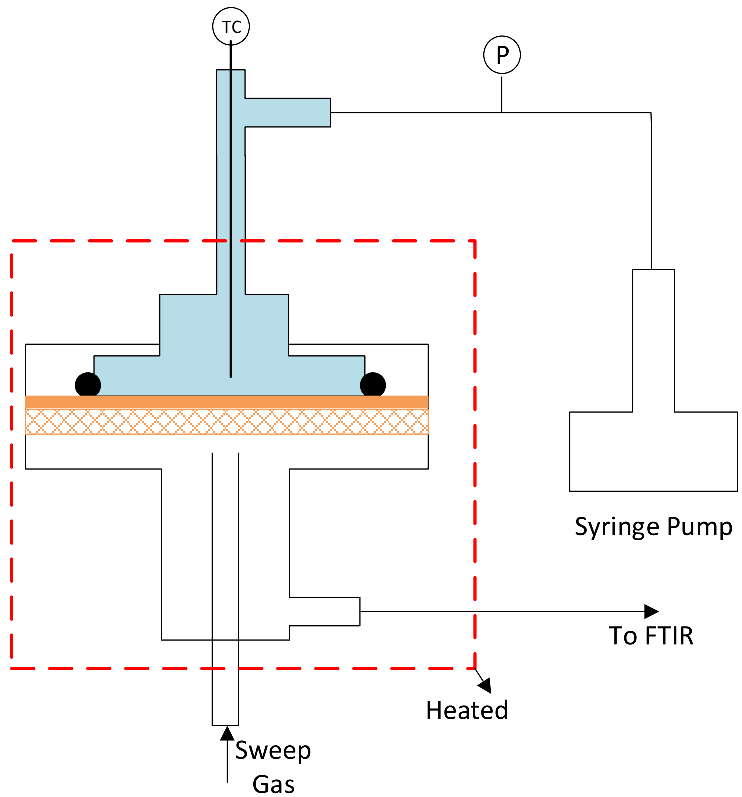
Water/Water-Vapor Transport Characterization

Goals

Optimize materials selection to tailor water vapor transport and to performance benchmark membrane water flux

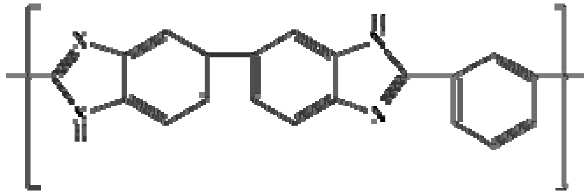
Transport in Permeate Sweep Mode

- **Ideal water vapor transport characteristics of PBI measured using N_2 sweep stream**
  - Custom laboratory set-up using FTIR multi-gas detector for composition analysis

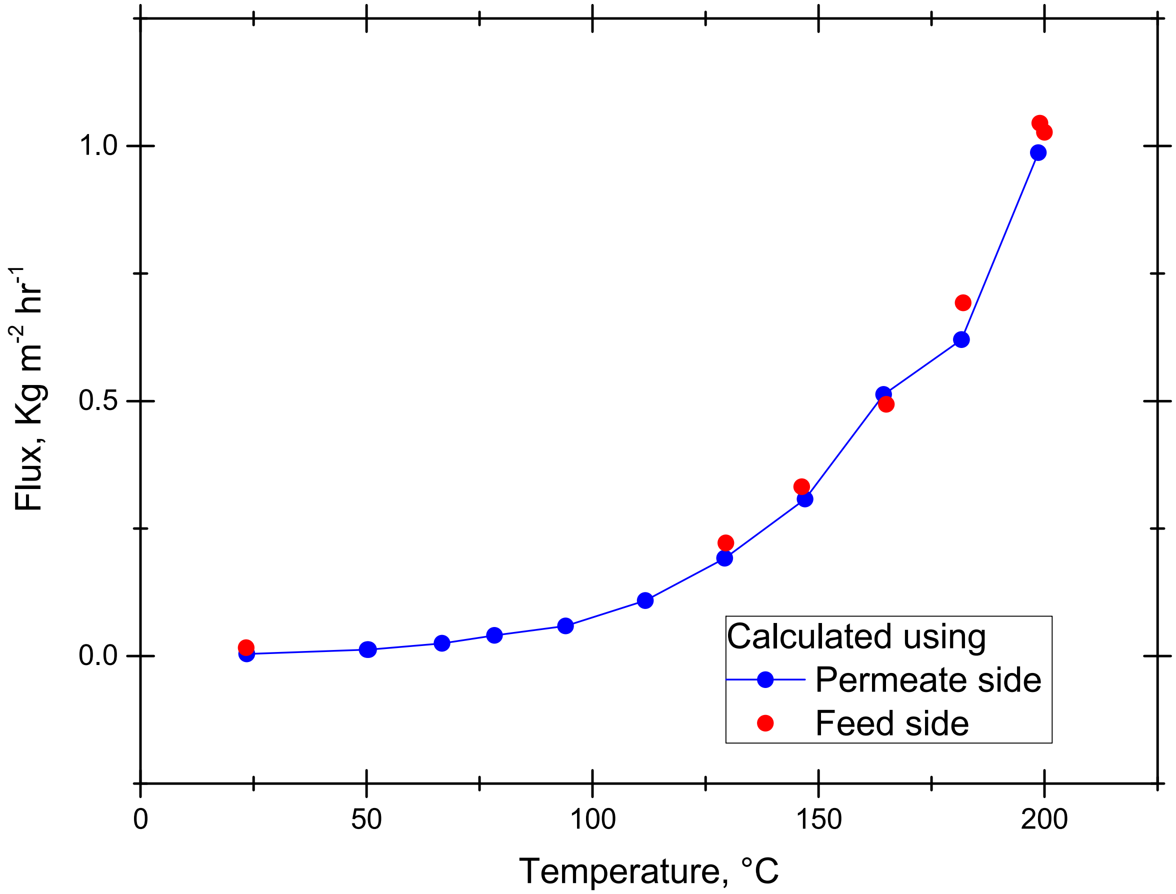


High Water Permeation Rate

- **H-bonding characteristics and presence of N-H group results in high water vapor transport characteristics**
  - Exponential increase in water vapor permeation rate at temperatures > 100 °C

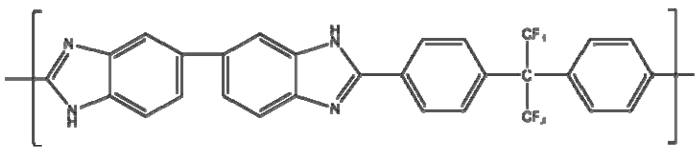


- 55 µm film
- Feed pressure = 250 psi
- Consistent flux calculated using feed side water volume decrease rate or water fraction measured in permeate stream

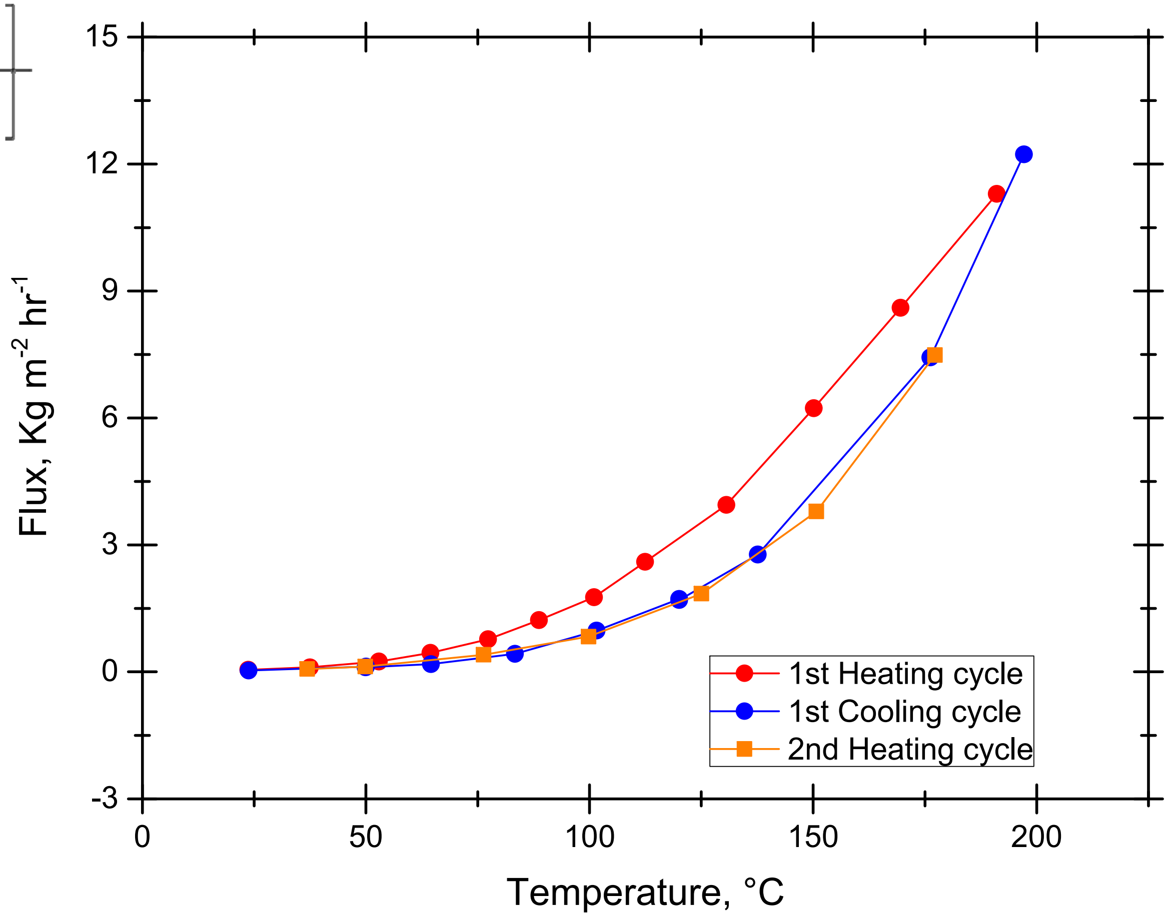


6F-PBI Membrane

- **Water vapor transport of 6F-PBI similar to m-PBI**
  - Similar trend in water flux as a function of temperature as observed for m-PBI



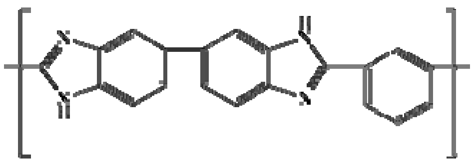
- 7 µm film
- Feed pressure = 250 psi
- Water flux decreased after membrane exposure to 200 °C. Polymer structure re-arrangement or loss of residual solvent



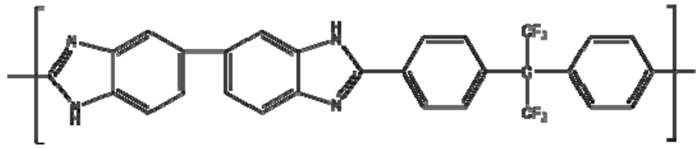
Influence of Material Chemistry

Two PBI material chemistries evaluated

- 6F-PBI has approximately one order of magnitude higher H_2 permeability as compared to m-PBI



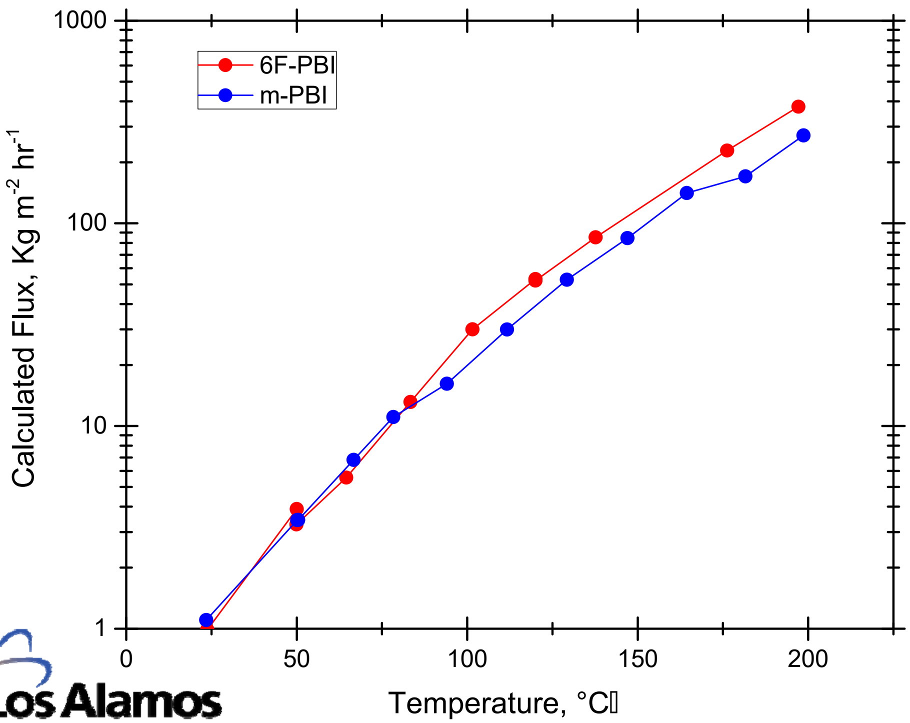
m-PBI



6F-PBI

m-PBI 6F-PBI

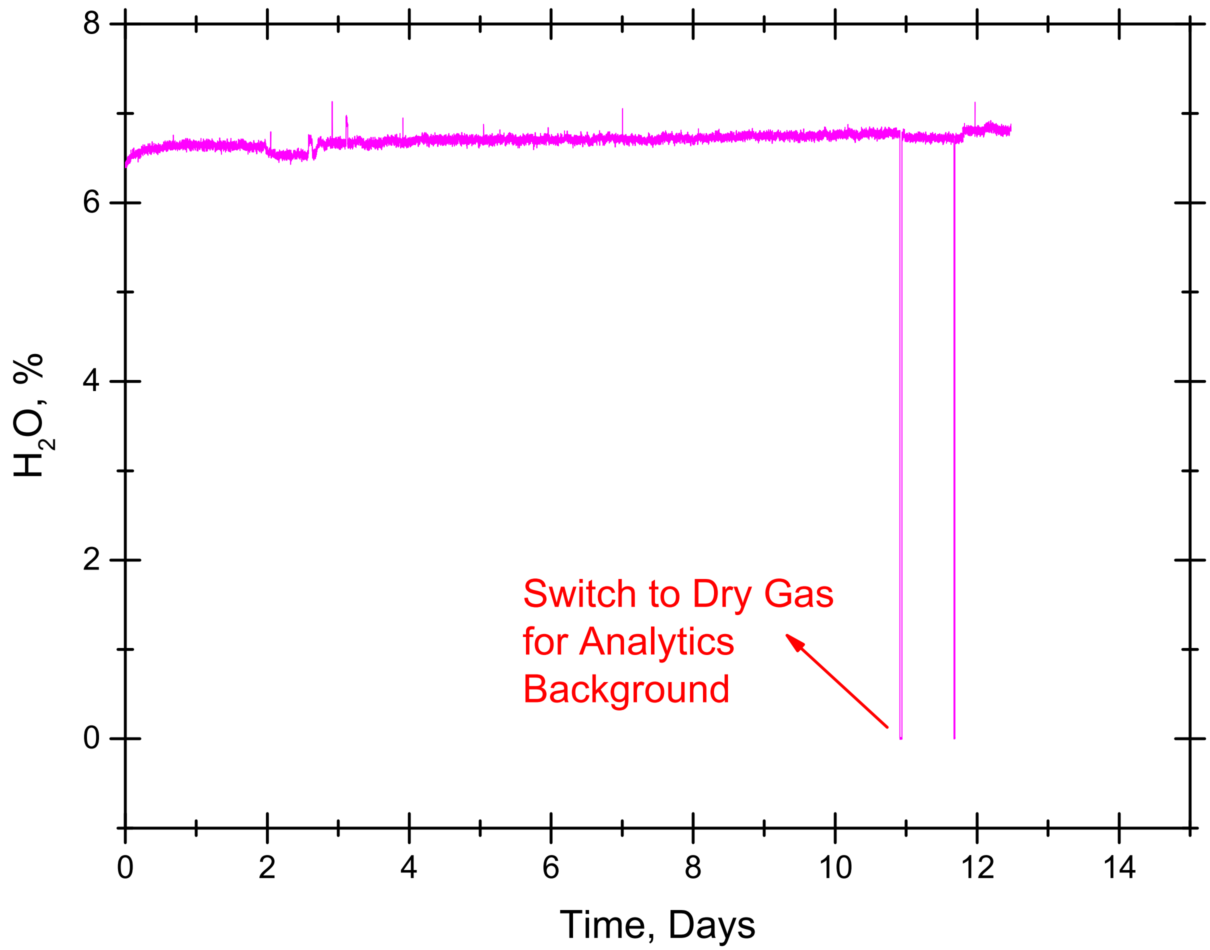
6F-PBI is more hydrophobic than m-PBI



- Calculated flux derived assuming an industrially relevant, 200 nm thick membrane selective layer
- 6F- and m-PBIs exhibit similar fluxes at temperatures < 100 °C
  6F-PBI has a 30% higher water flux than m-PBI at 200 °C

Exceptional Hydrolytic Stability Demonstrated

- **PBI membrane demonstrated exceptional hydrolytic stability**
  - Stable water vapor fraction in permeate stream measured for pure water feed at 178 °C at 250 psi for 6F-PBI membrane



Other Potential Applications Development

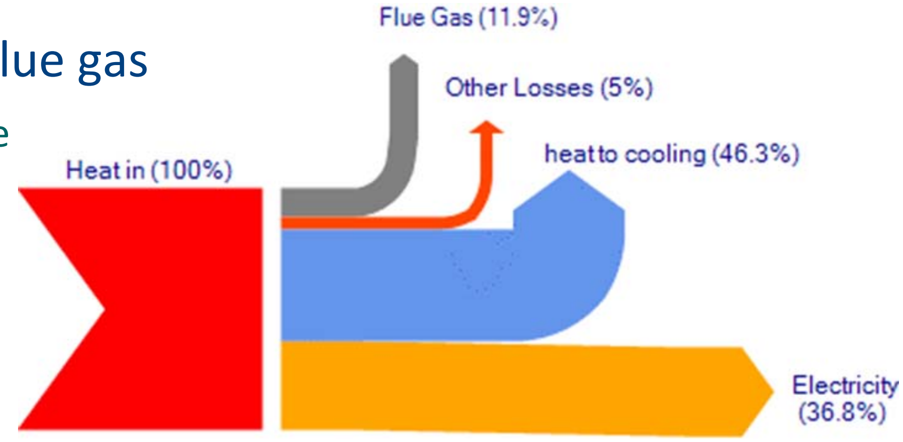
Goal

Develop process intensification strategies to deploy PBI membranes for solving water treatment challenges in power plants

Flue Gas Dehydration

Lost water recovery

- Evaporation from cooling towers and flue gas
  - Difficult to capture: Low partial/total pressure
  - 6 to 13 % water vapor depending on the coal feedstock and FGD
  - Potential to supply 10 to 33% of boiler make-up water
  - Water vapor recovery will improve efficiency by latent and sensible heat recovery



No industry standard process to capture water from flue gas

- Condensing heat exchangers, membranes and liquid desiccant based dehumidification techniques proposed for flue gas dehydration
- Chemically challenging stream due to the presence of SOx & NOx
  - Acid formation during condensation mandates the use of expensive alloys to minimize corrosion

Membrane for Flue Gas Dehydration

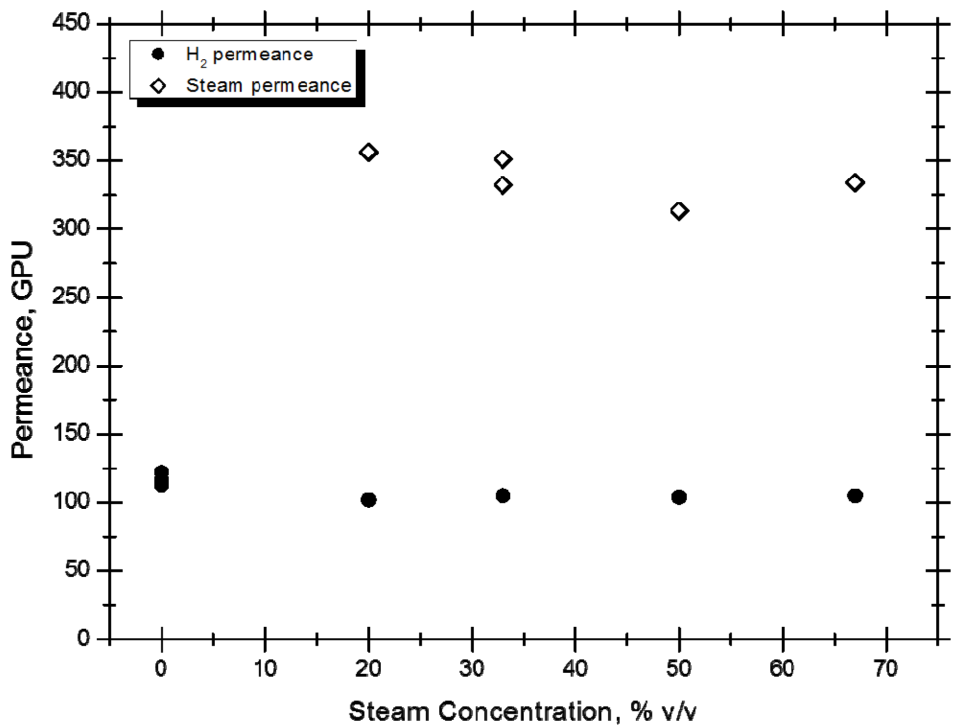
- Sulfonated PEEK (Sijbesma, 2008) evaluated in pervaporation mode
  - Water quality was not high enough for boiler make-up; significant transport of SO_2 and NO_2
- Inorganic transport membrane condensers (Wang, 2012) enabled 40% water vapor capture & 5% increase in efficiency.
  - Presence of minor amount of sulfate and carbon in permeate water reported.

PBI membrane potential for flue gas dehydration

- Low N_2 permeability (0.01 barrer)
- Previously evaluated for steam/ H_2 feed mixtures at 250 °C

  H_2O/H_2 selectivity = 3

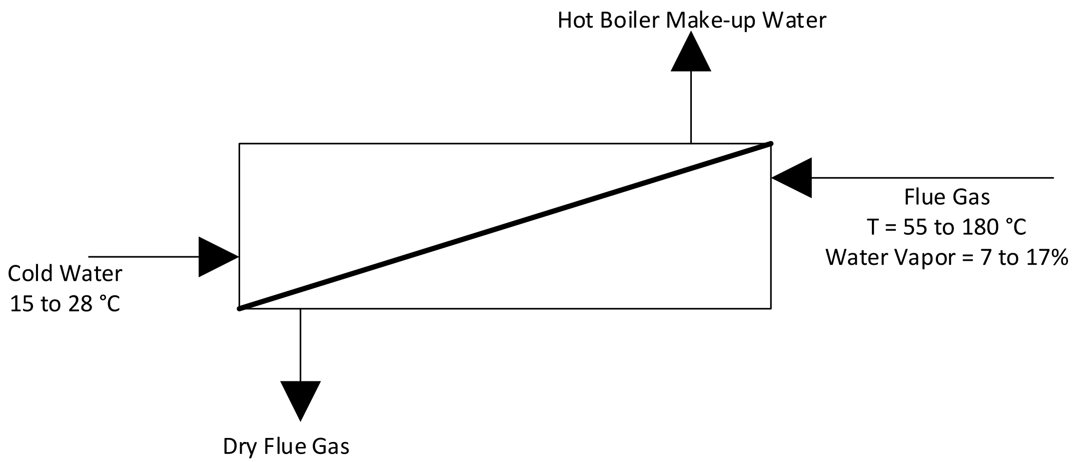
  H_2O/N_2 (est.) ≈ 300
- Higher selectivity expected at lower flue gas relevant temperatures (60 to 180 °C)
- Thermo-chemically robust to withstand SOx & NOx
- High surface area platform



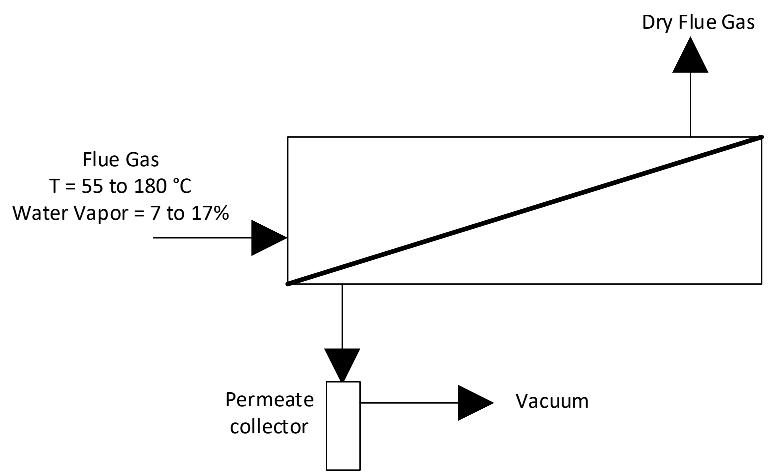
PBI Membranes for Flue Gas Dehydration

Leveraging high water vapor perm-selectivity & exceptional thermo-chemical tolerance of PBI membranes for water and heat recovery from flue gas?

- **Heat/water recovery from flue gas**
- **Additional flue gas cooling to near ambient temperatures may improve efficiency of carbon capture technology**



Condensing Membrane HX



Pervaporation

Conclusions & Future Work

- **Thermo-chemically robust polybenzimidazole-based membranes having high water/water-vapor transport characteristics are attractive for brine treatment**
- **Water transport rate of PBI membrane increase exponential at elevated temperature exceeding 100 °C provide opportunities for power plant waste heat utilization**
- **Demonstrated tolerance of PBI to oxidizing and hydrolytic conditions at elevated temperatures**
- **Potential to achieve industrially relevant water flux even after exposure to high salinity conditions**
- **Future work: Demonstrate tolerance to high salinity brines and measure salt rejection characteristics at higher temperatures.**

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