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

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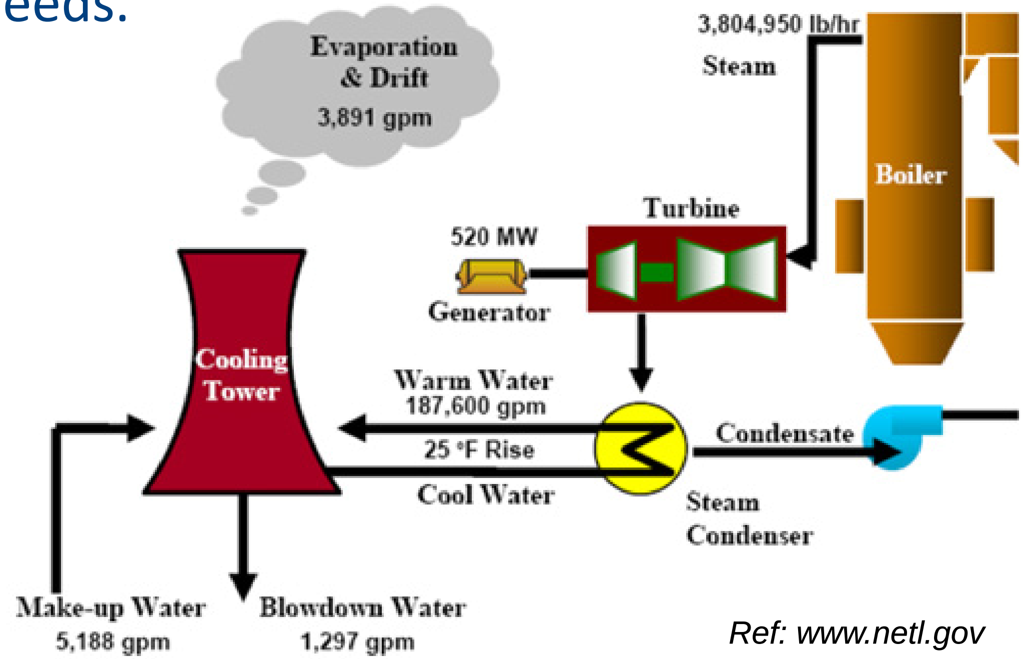
Energy-Water Nexus

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



Ref: www.netl.gov

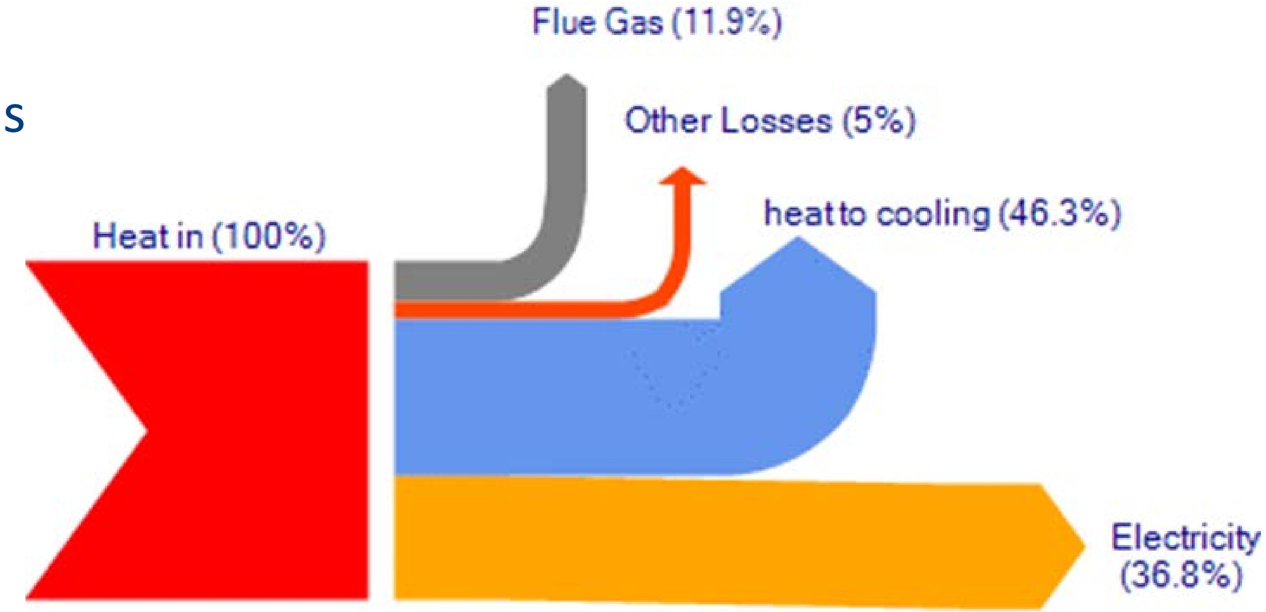
  - An estimated ½ gallon of water is consumed per kWh of electric power produced
  - Water needs will increase significantly due to carbon capture (CC)
    - 30% increase in water consumption anticipated with CC addition to pulverized coal power plant

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



- **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 & at elevated temperatures

Elevated Temperature Membrane Separations

Applications of Interest:

Flue Gas Dehydration

High Salinity Brine Treatment

PBI Membranes for Flue Gas Dehydration

Goal

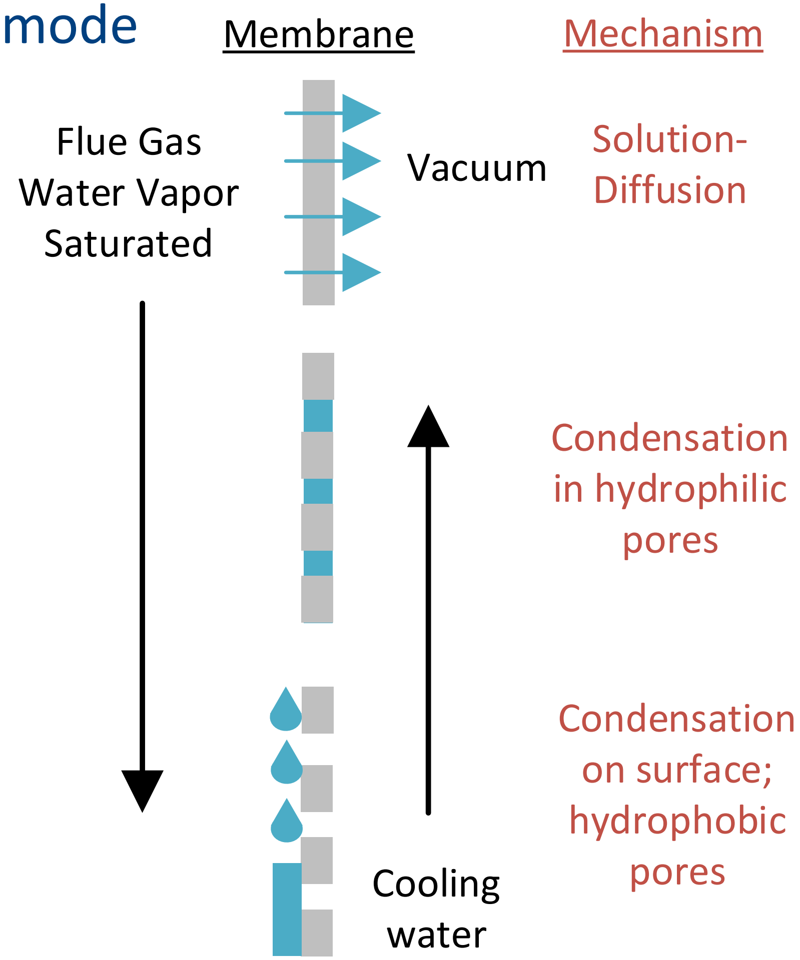
Thermo-chemically robust membrane material demonstration and fundamental performance data gathering for water vapor capture from power plant flue gas

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 cost effective but expensive (Levy, 2011)
    - Cost & benefit of CHX dependent on the flue gas temperature (135 °F downstream of the FGD scrubber & 300 °F in 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 FGD make-up
  - Dessicant drying systems are energy intensive
    - Parasitic energy losses in dessicant regeneration
    - Low quality of water produced

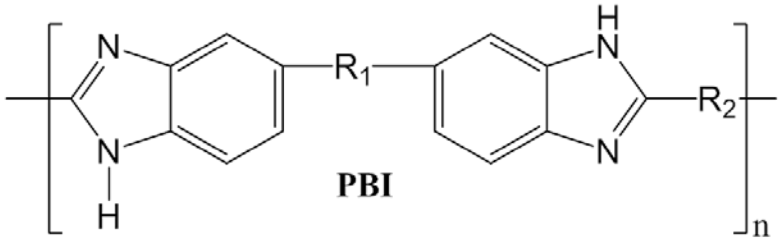
Flue Gas Dehydration: Membranes

- **Selective transport of water vapor in dense hydrophilic polymer membranes 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



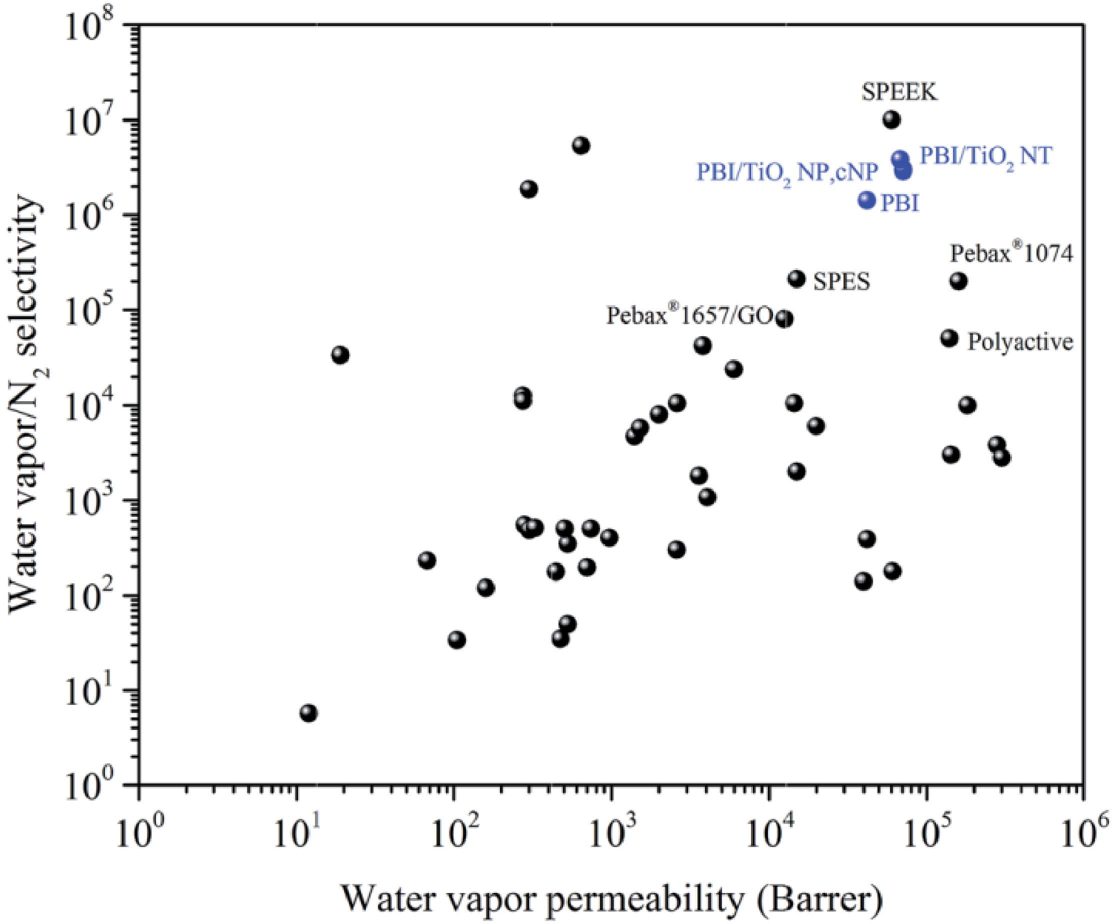
Background: PBI Based Materials/Membranes

- **PBI-based materials/membranes exhibit exceptional thermo-chemical stability**
  - T_g > 400 °C, board operating temperature opportunities
  - Chemically robust – no degradation in steam and H_2S at elevated temperatures
  - High water uptake and water vapor selectivity
    - 15 wt% water sorption
  - Demonstrated ability to tailor transport properties via materials design and processing protocols



R_1, R_2 } Bulky, large and high mobility functional groups ⇒

- Chain packing Efficiency
- Enhnace Fractional Free Volume
- High localized mobility
- Rigid and bent configurations

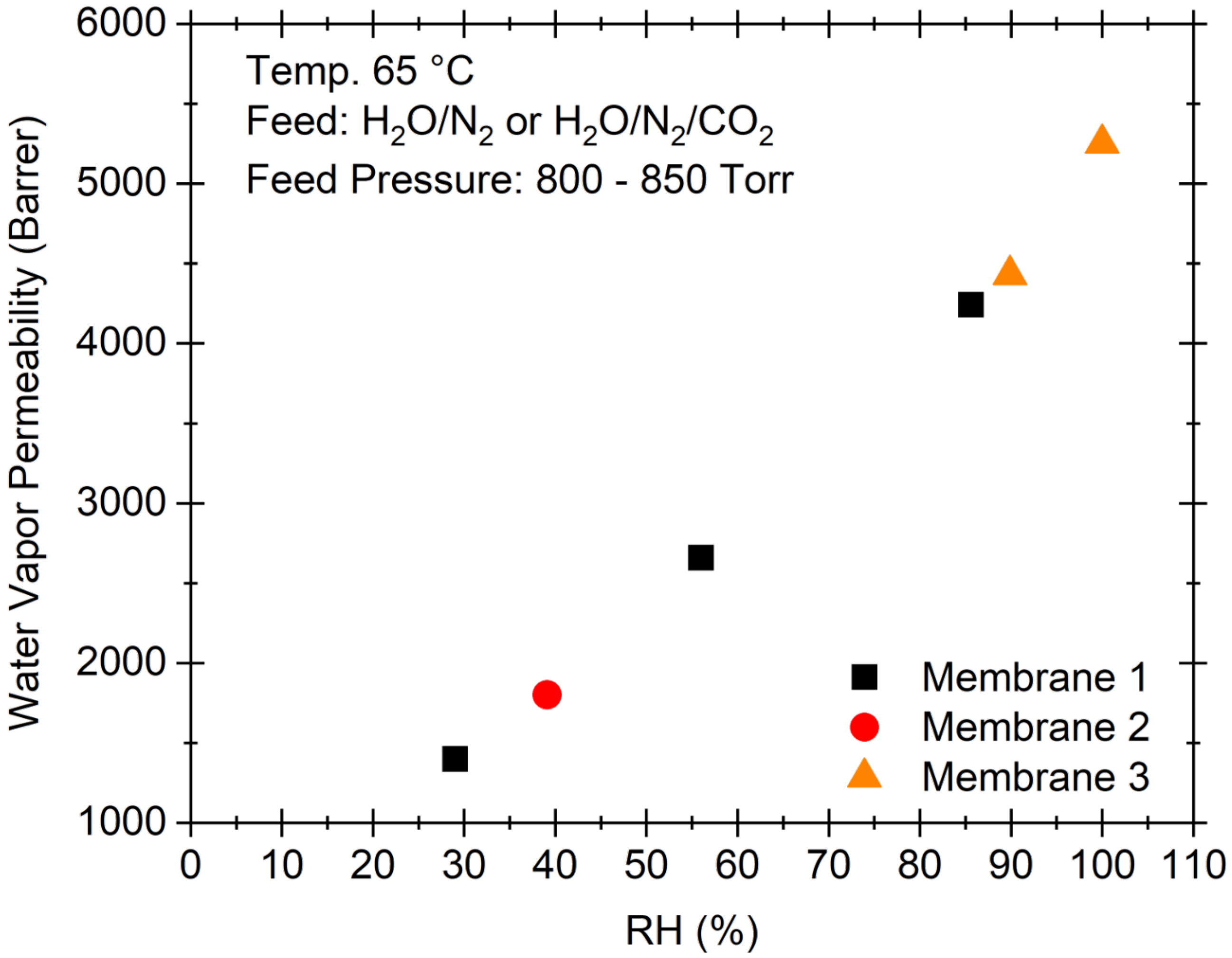


Ref: Akhtar et.al., J. of Mater. Chem. A, 2017, 5, 21807

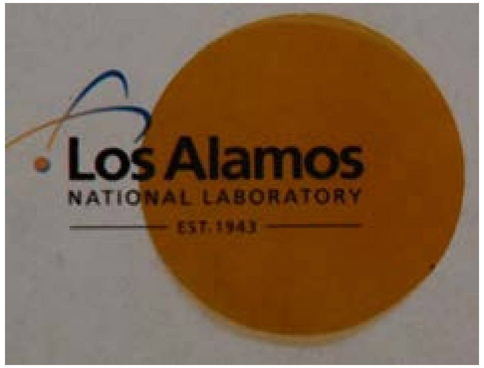
  - Processability demonstrated, industrially attractive hollow fiber platform

Attractive Water Vapor Permeation Characteristics

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



- Thickness ≅ 55 µm
- Sweep gas: He

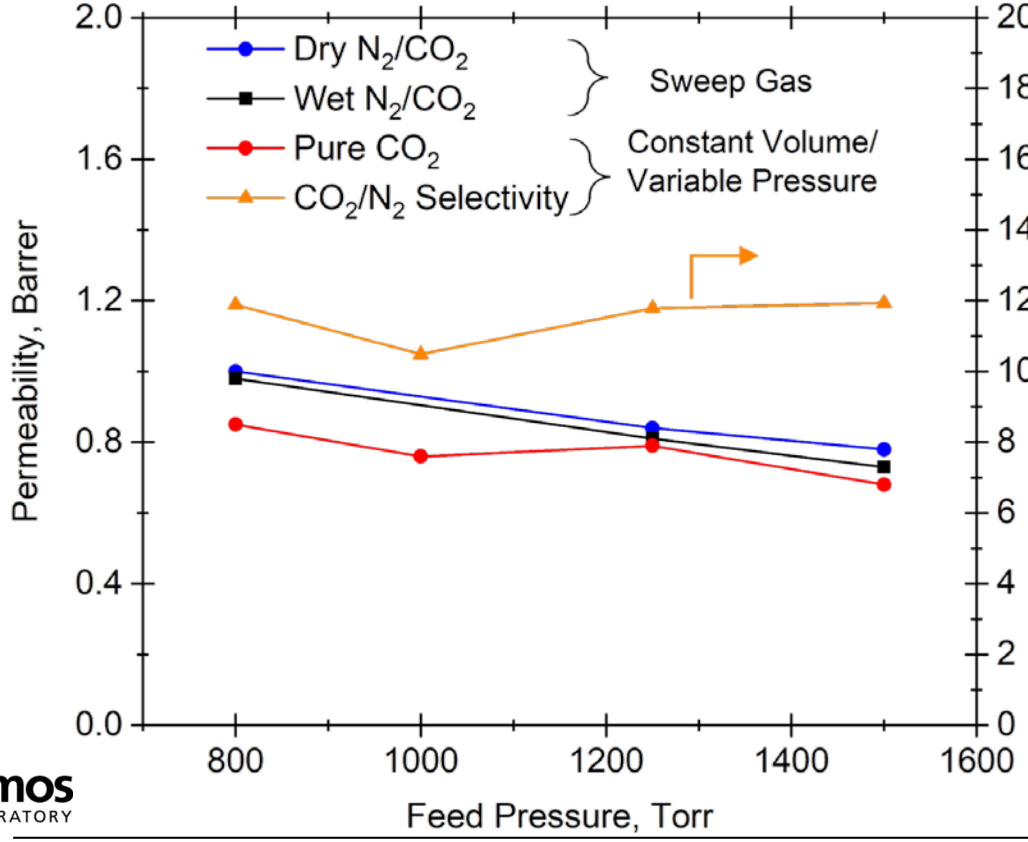


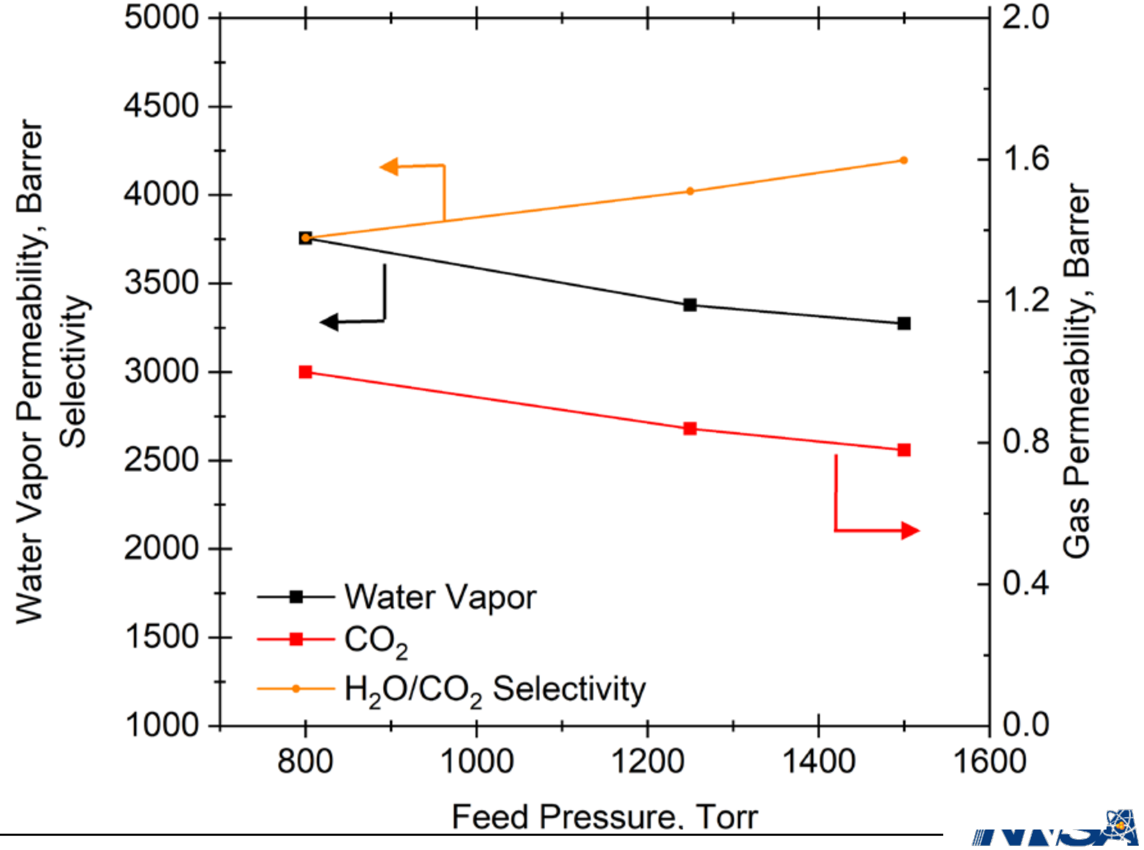
High Water Vapor Perm-Selectivity

- **PBI has high water vapor perm-selectivity over both CO_2 and N_2**
  - Water vapor permeability decreased with feed pressure
  - H_2O/CO_2 selectivity = 4000
  - H_2O/N_2 selectivity estimated at ≈ 48,000 (based on CO_2/N_2 selectivity of 12)

Test Conditions

- Feed Composition
  - CO_2 =10 to 11%
  - Water Vapor: 11 to 21%
  - Bal: N_2
- Temp: 65 °C
- Thin film ≅ 55 μm
- Sweep gas: He





PBI Membranes for Flue Gas Dehydration

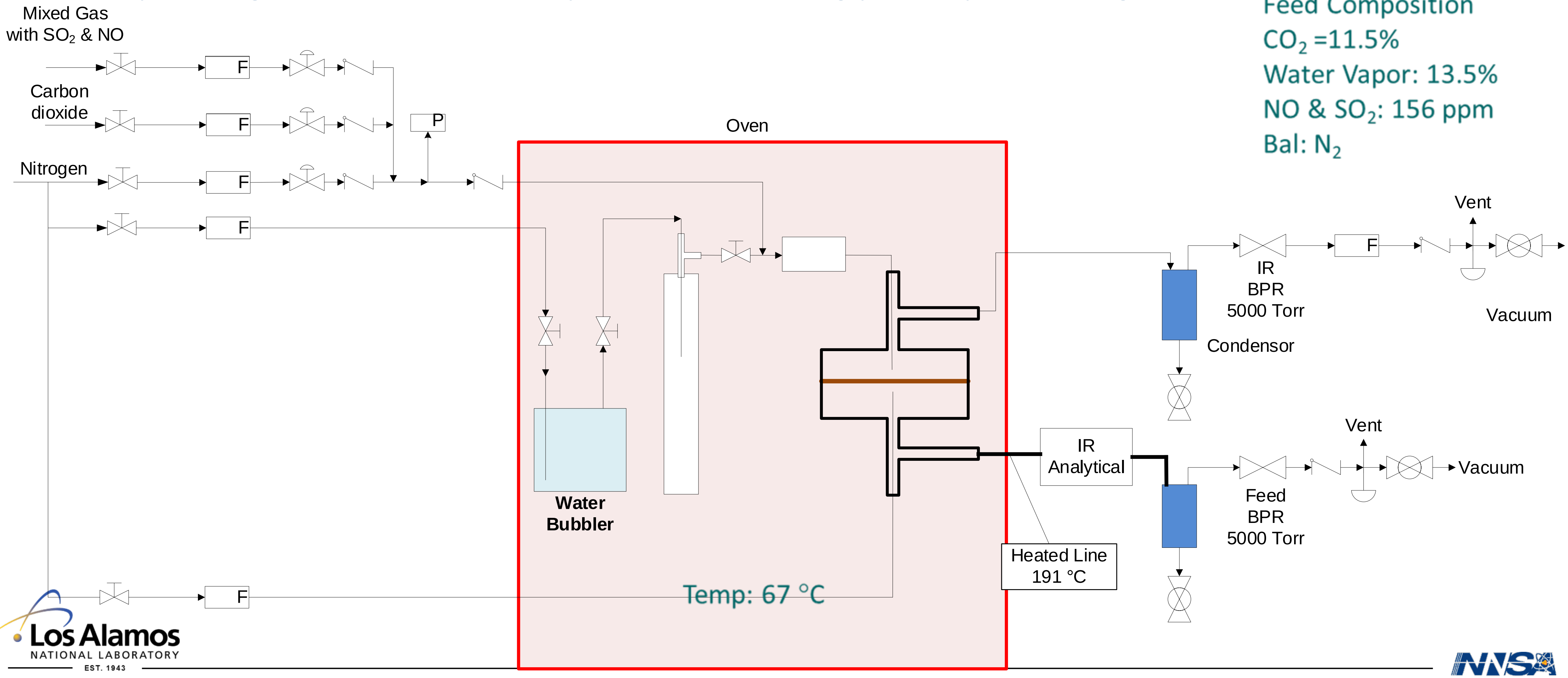
- **Measure PBI membrane performance at flue gas process conditions**

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

PBI Impurity Tolerance Evaluation

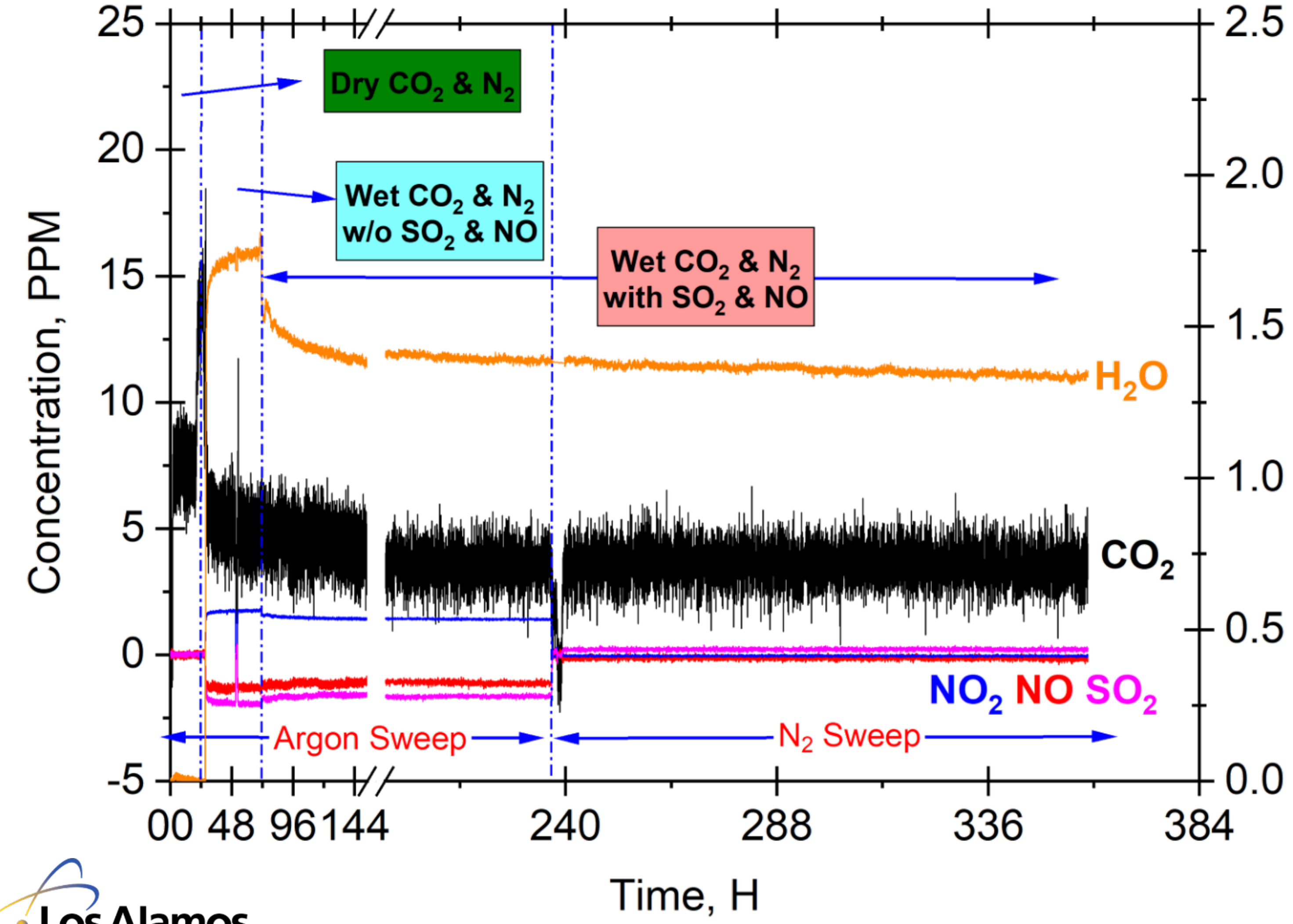
- **PBI film evaluated in SO_2 and NO containing mixed feed stream**
  - Operating conditions and composition mimicking power plant flue gas



Feed Composition
CO_2 =11.5%
Water Vapor: 13.5%
NO & SO_2: 156 ppm
Bal: N_2

Permeate Stream Analysis

Real-time permeate composition determination using in-line multi-gas FTIR analytics

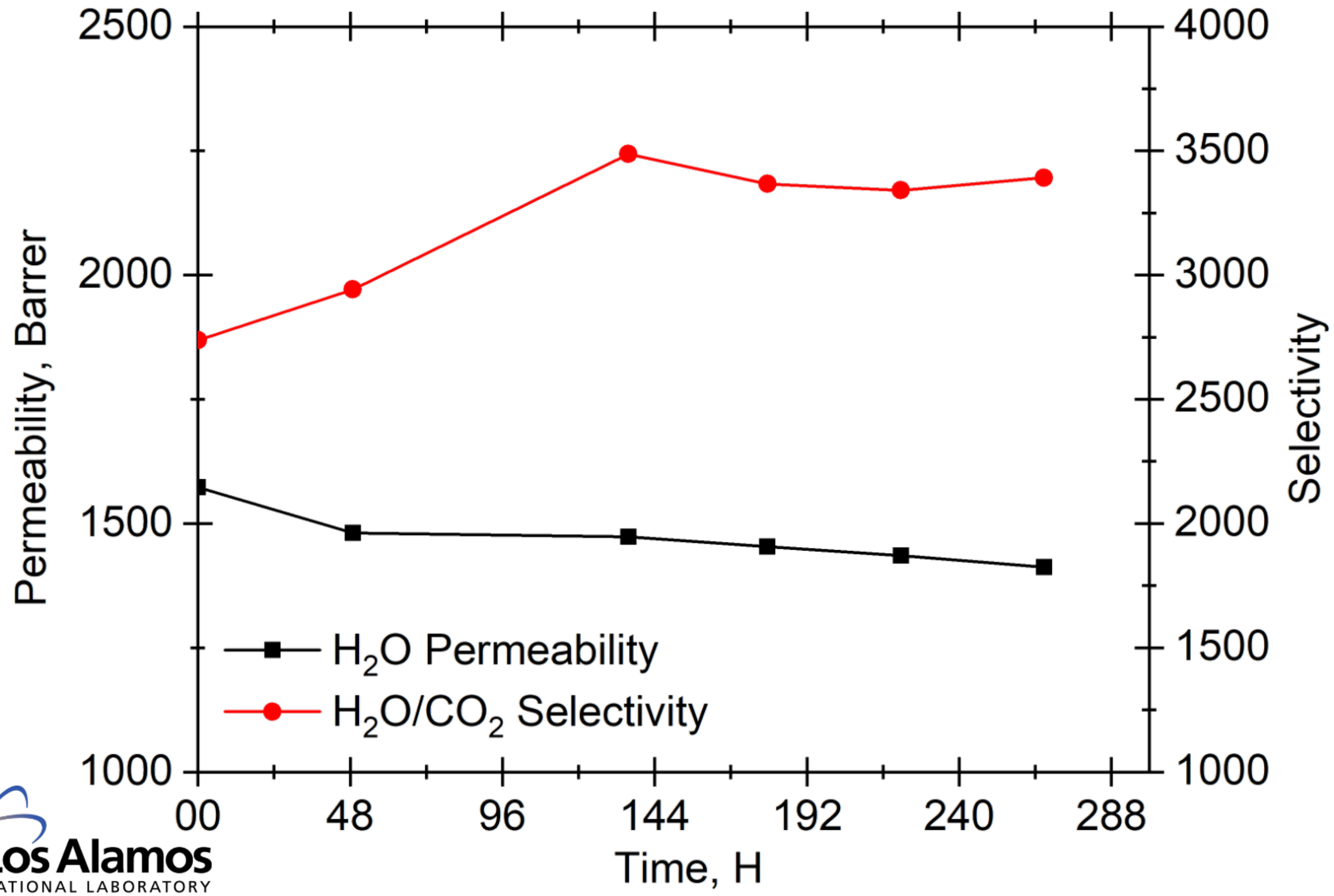


- Water vapor and CO_2 concentrations stable over the test period.
- No evidence of SO_2 and NO in the product stream
- Trace analysis of condensed water will be conducted to ascertain purity.

*Switched to N_2 sweep due to absence of proper calibration data in Argon

Long Term Durability

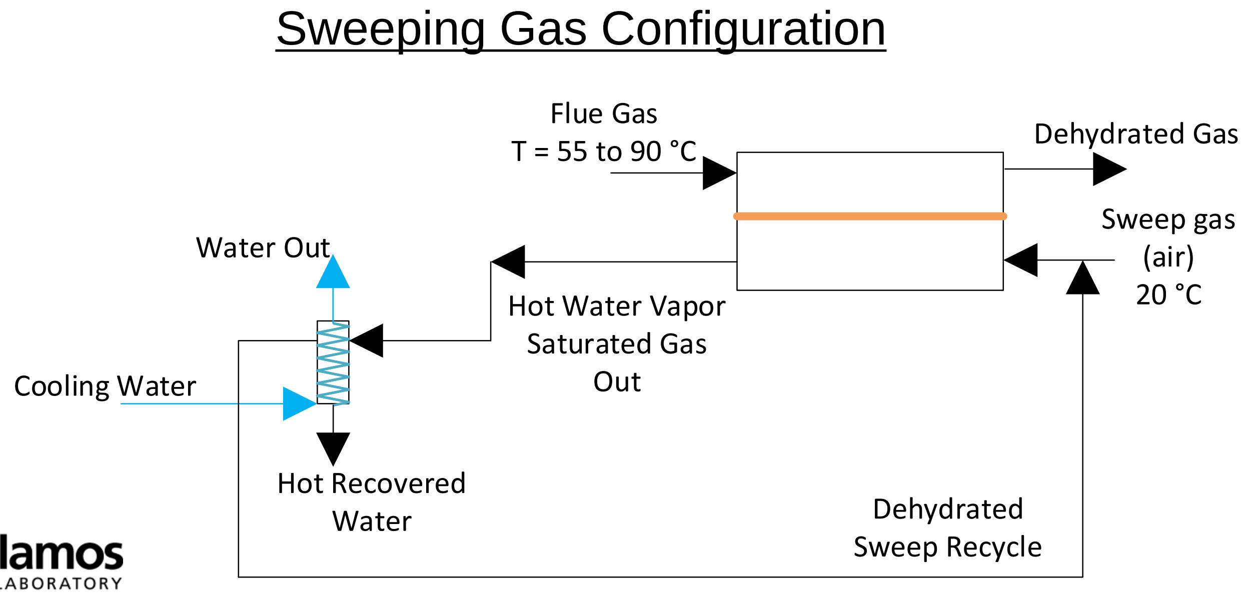
- **High water vapor transport characteristics maintained in the presence of SO_2 and NO**
  - H_2O/CO_2 initial increased prior to attaining a stable value
  - Water vapor permeability seems to decreasing very slowly

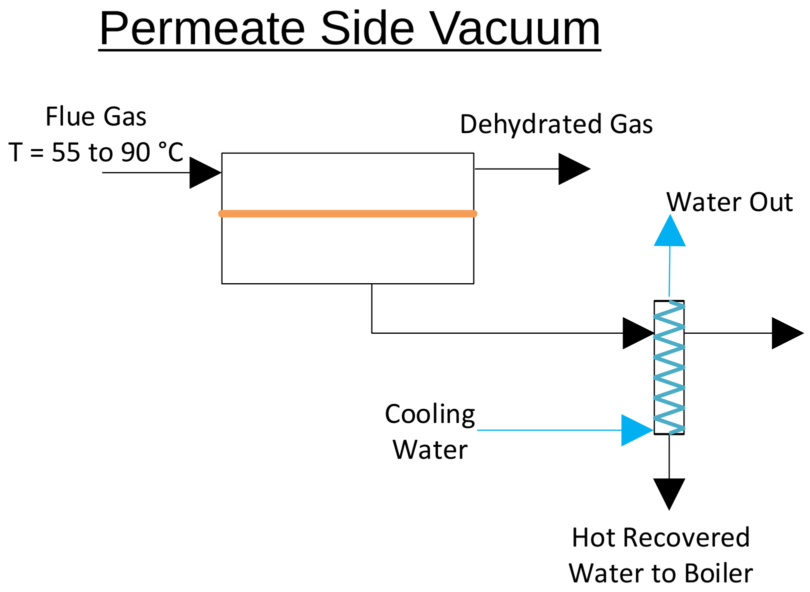


- 11% reduction in water vapor permeability over 12 days of exposure to SO_2 and NO
- Water vapor permeability decrease may be due to SO_2 and/or NO sorption or reaction with PBI
  - Re-evaluation with feed gas without SO_2 and NO, and pure gas will be conducted
  - Post-evaluation chemical functionality analysis of membrane may provide evidence of reaction between membrane and feed stream components

Flue Gas Dehydration Process Design

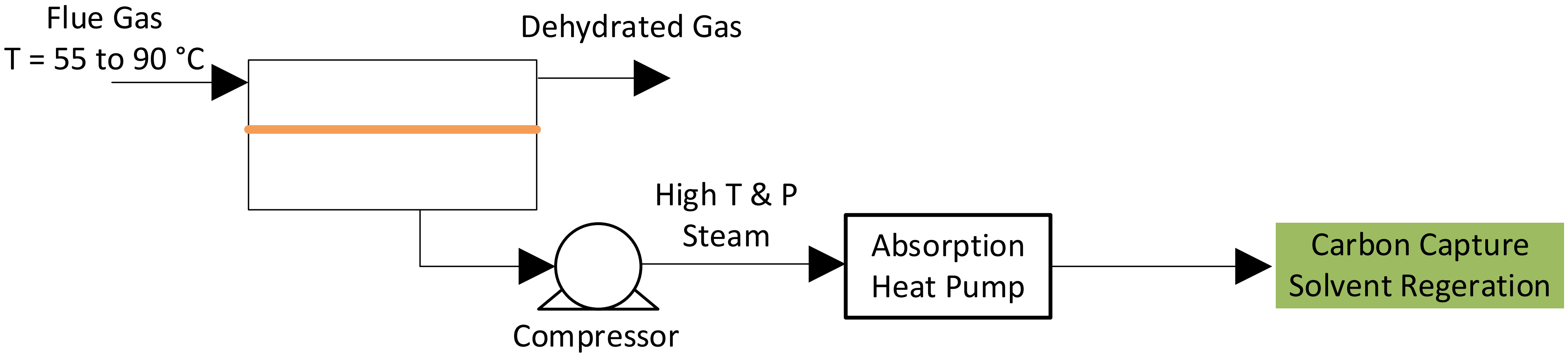
- **Preliminary process design envisioned to capture water vapor from power plant flue gas aimed at:**
  - High purity water recovery for use as boiler make-up water
  - Water vapor latent heat recovery to improve power plant efficiency
- **PBI membrane process using sweep gas or vacuum to provide driving force for water vapor transport**
  - Power plant cooling water for condensation of captured water vapor





Flue Gas Dehydration Process Design (cont.)

- **Vapor compression and upgrading for increased plant integration opportunities**
  - Water vapor is compressed to increase temperature and pressure followed by further upgrading in an absorption heat pump for generating steam suitable for carbon capture solvent regeneration



  - Wang et.al. 2017 showed that integration of a dual heat adsorption pump can potentially reduce power consumption for carbon capture by 10.5%
  - Clean water vapor (w/o SOx and NO) after membrane separation would enable low cost materials for compressor and heat pump construction

Summary: Flue Gas Dehydration

- **Water vapor transport characteristics of PBI materials are 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
  - Stable performance reported in SO_2 and NO containing feed gas at flue gas operating conditions
- **Future work**
  - Continue PBI membrane evaluation for water vapor perm-selectivity at flue gas representative conditions in the presence of SO_2 and NO.
    - Demonstrate longer term performance stability and durability
  - Perform process design and energy calculations to develop a PBI membrane based process for energy and water vapor recovery from flue gas meeting the DOE/NETL – Fossil Energy program goal of improved power plant efficiency.

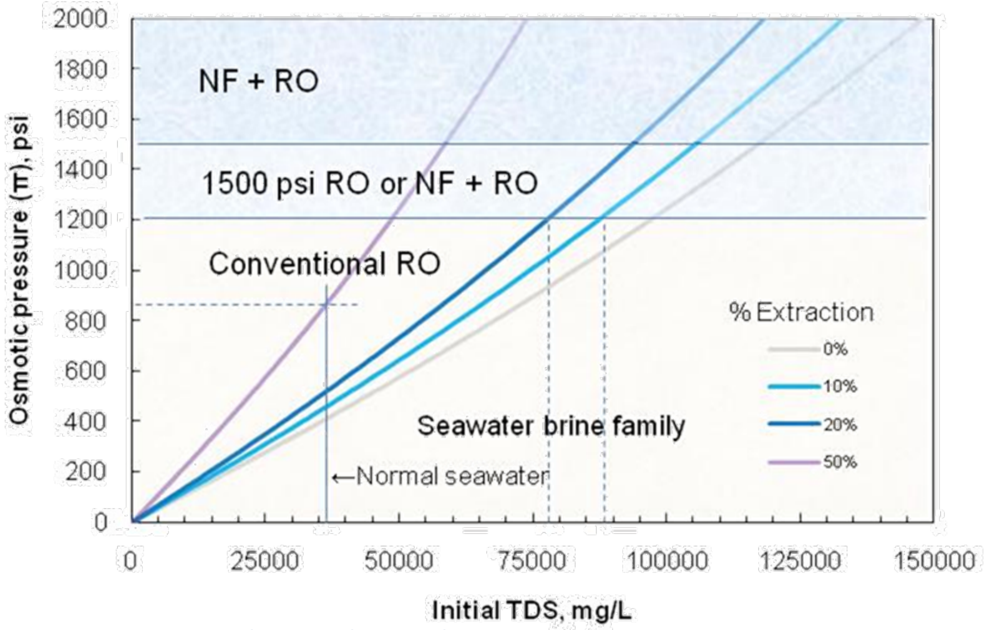
High Salinity Brine Treatment

Goal

Thermo-chemically robust membrane material demonstration and fundamental performance data gathering for 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



TDS Limitations

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

Temperature Limitations

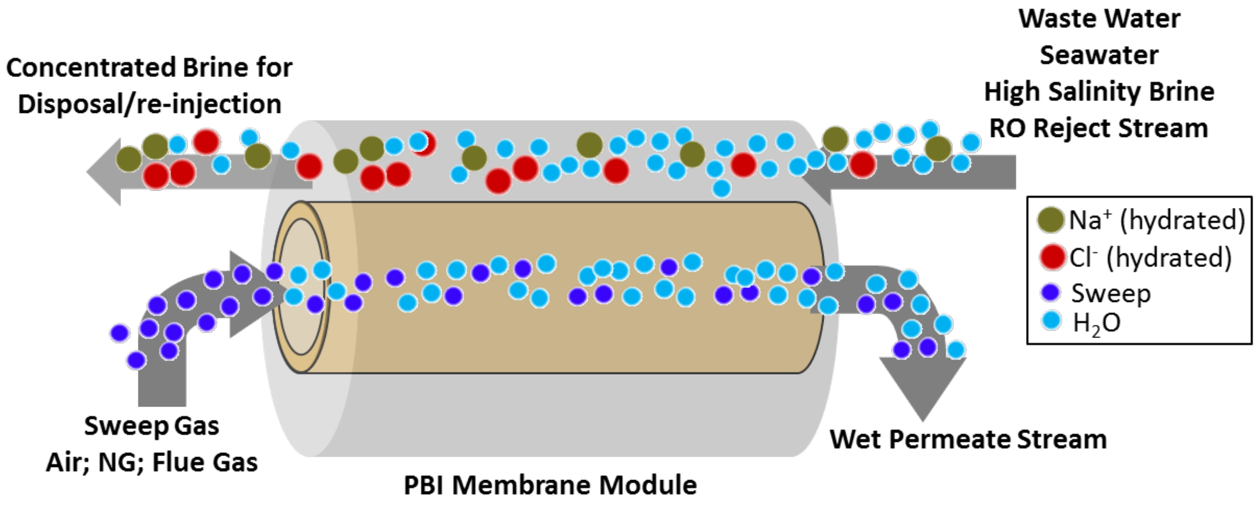
- The low operating temperatures of current RO membranes (typ. < 50 °C) limits energy efficient integration into high temperature high salinity streams (70 to > 150 °C) and power plant waste streams (120 to 140 °C).

  - 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 extracted water disposal costs by reducing volumes



Waste Water
Seawater
High Salinity Brine
RO Reject Stream

Concentrated Brine for
Disposal/re-injection

● Na^+ (hydrated)
● Cl^- (hydrated)
● Sweep
● H_2O

Sweep Gas
Air; NG; Flue Gas

Wet Permeate Stream

PBI Membrane Module

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 (e.g. cellulose acetate, polyamide, polyimide) have low hydrolytic stability
  - Fouling and degradation in high salinity feed streams

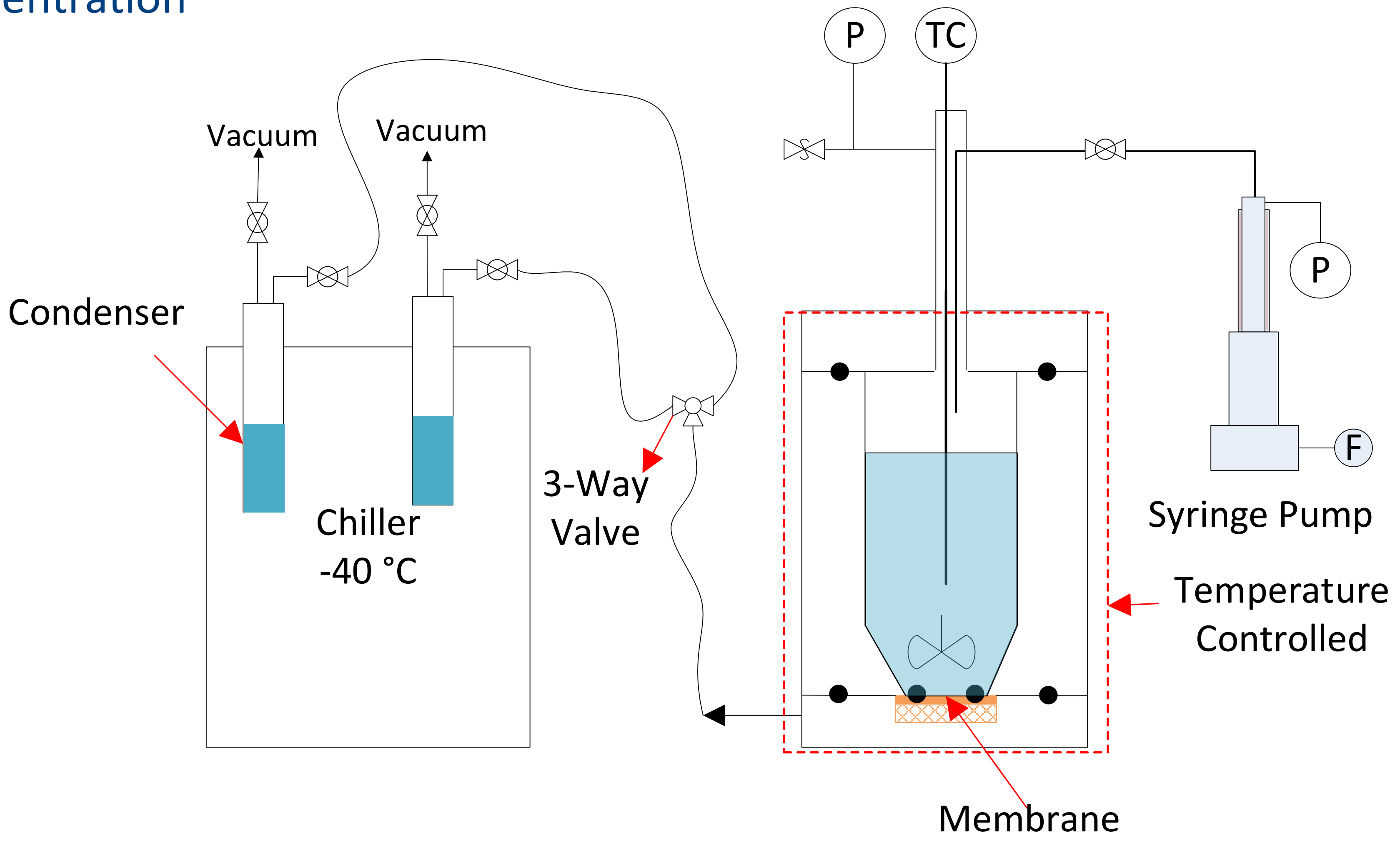
PBI Membranes for High Salinity Brine Treatment

Goal

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

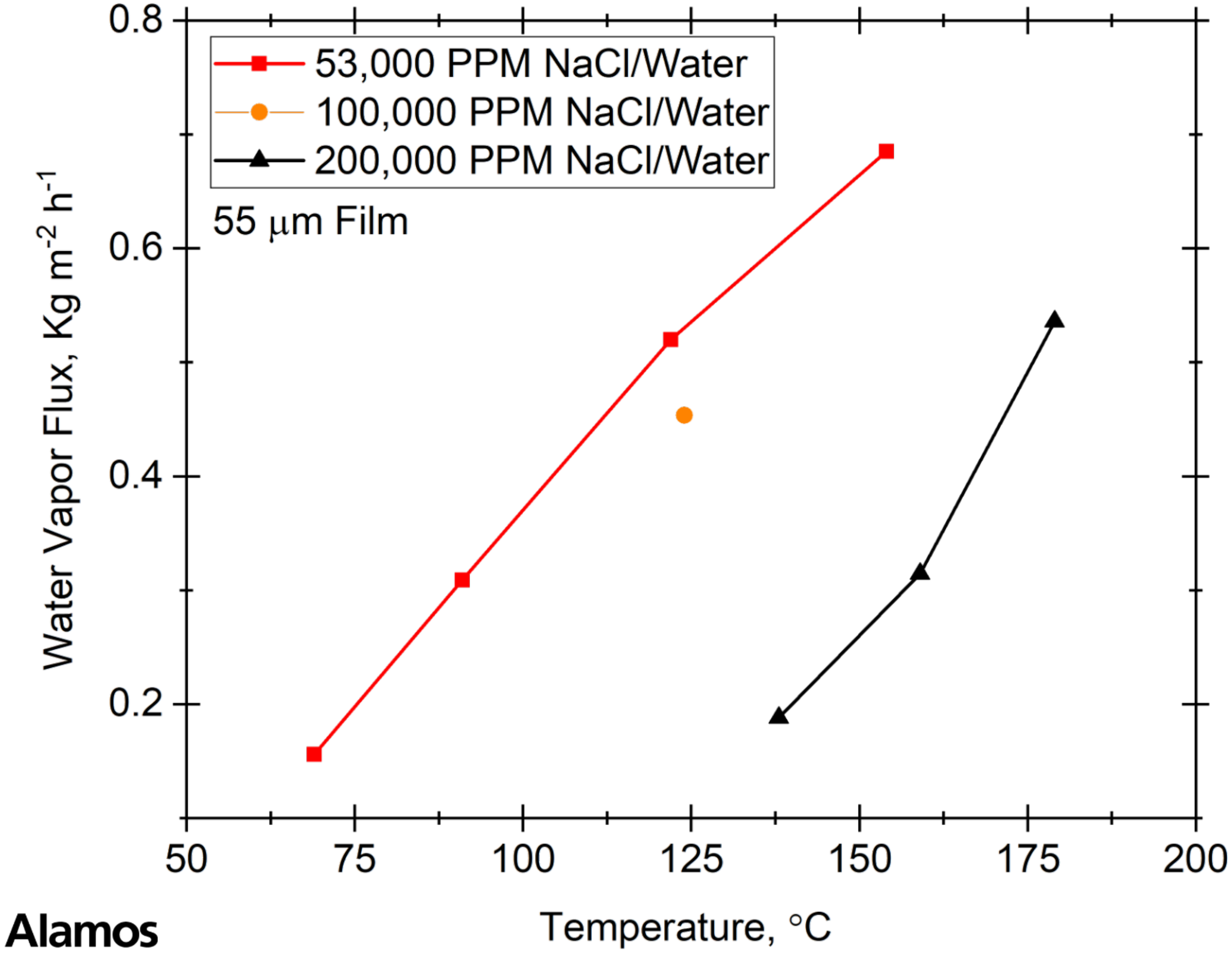
High Salinity Brine: Vapor Permeation Evaluation

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

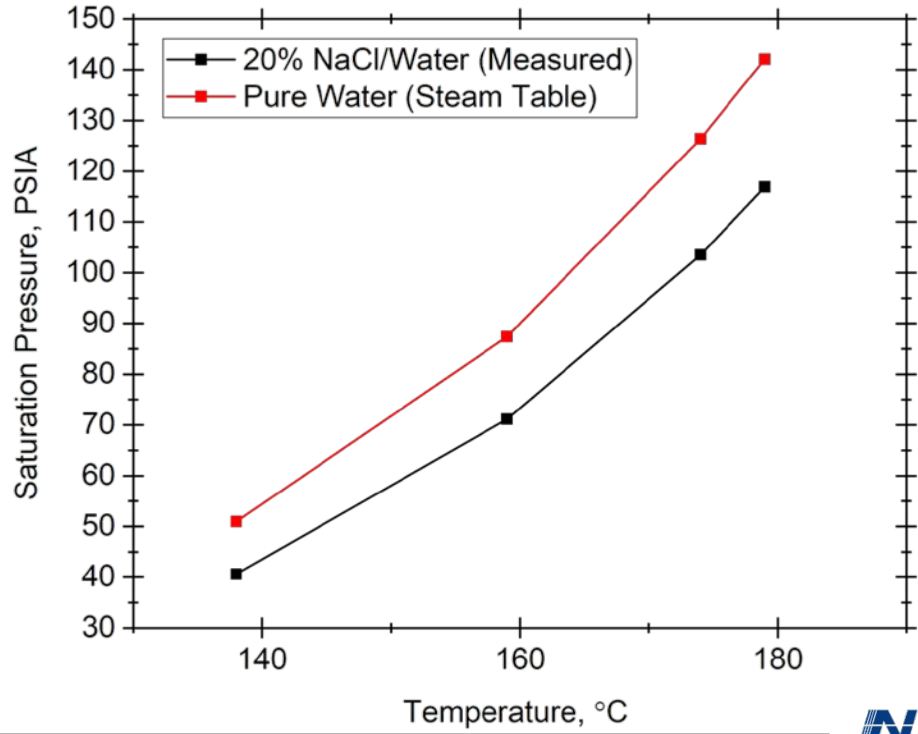


Influence of Salt Solution Exposure

- **Water transport of PBI membranes measured for NaCl/water solution measured in pervaporation mode at elevated temperatures approaching 200 °C**

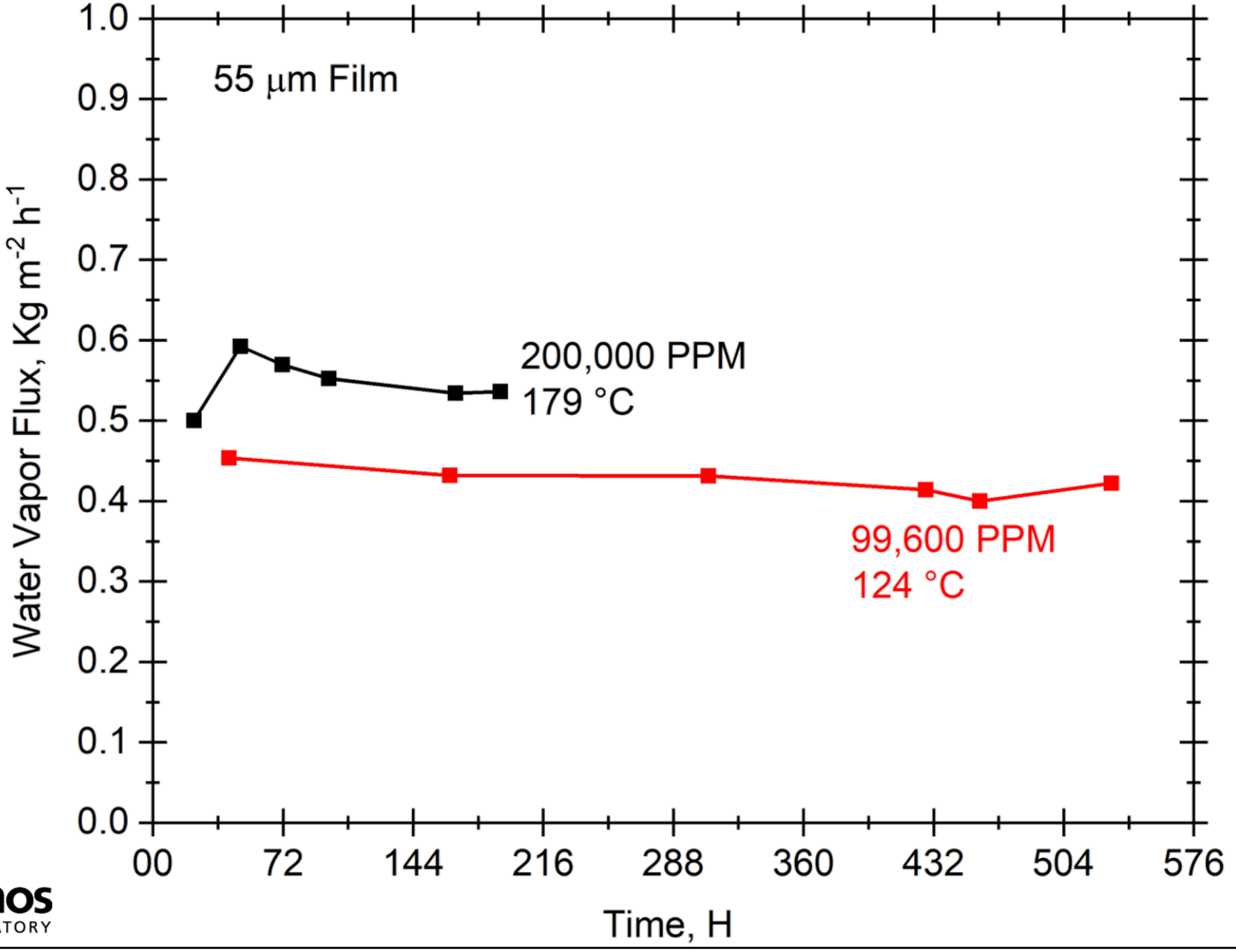


- Higher temperature generates higher vapor pressure resulting in larger driving force for water vapor permeation while higher salt concentration reduces the vapor pressure

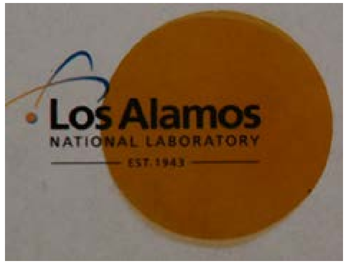


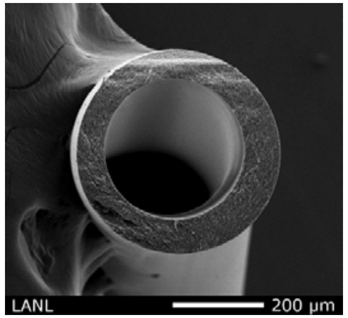
PBI Material Durability

- **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 materials in high salinity brine



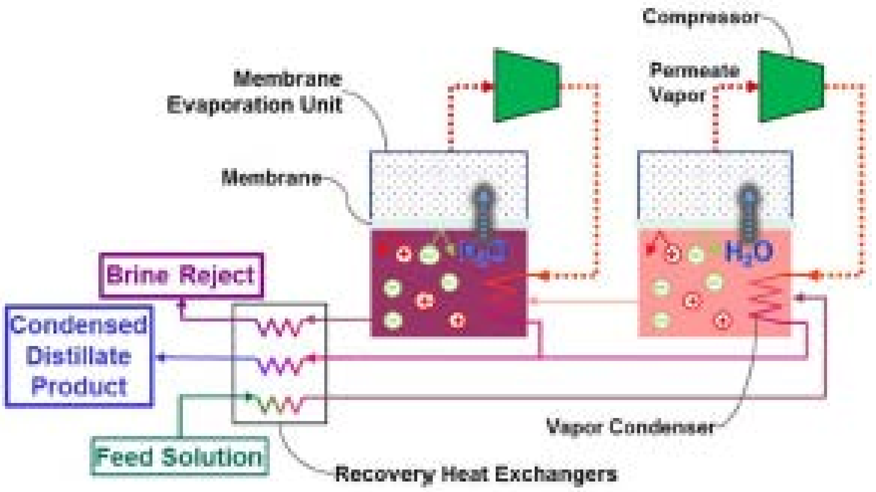
Water vapor flux calculated for industrially representative thickness (200 nm) = 116 to 150 kg m^{-2} h^{-1}





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 200,000 PPM and 200 °C, respectively
- **Future Work**
  - Develop process design and optimization for water treatment relevant to power plant generated waters
    - Integration of membrane pervaporation process with available power plant waste heat
    - Hybrid membrane evaporation + vapor compression process to zero liquid discharge



Vane et.al., J Chem Technol Biotechnol. 2017, 92(10): 2506–2518

Acknowledgement

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