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

2017 Crosscutting Review Meeting
22nd March 2017, Pittsburg

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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.

- 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: www.netl.gov
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

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.

HGSBSM can be thought of as MD in extreme operating environments
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
  - $T_g > 400 \, ^\circ C$, 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

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

<table>
<thead>
<tr>
<th>Species</th>
<th>$H_2O$</th>
<th>$H_2$</th>
<th>$CO_2$</th>
<th>$N_2$</th>
<th>Hydrated $Na^+$</th>
<th>Hydrated $Cl^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic Diameter (Å)</td>
<td>2.65</td>
<td>2.89</td>
<td>3.30</td>
<td>3.64</td>
<td>7.2</td>
<td>6.6</td>
</tr>
<tr>
<td>$\alpha (H_2O/X)$</td>
<td>-</td>
<td>3</td>
<td>69</td>
<td>300</td>
<td>$\gg300^*$</td>
<td>$\gg300^*$</td>
</tr>
</tbody>
</table>

Background: PBI Membrane Deployment

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

- 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°C

**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
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 N₂ & Air
  - FTIR: No degradation evident in N₂ 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

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Measured Dense Film Water Flux, kg m² hr⁻¹</th>
<th>Estimated for Industry Relevant 200 nm Selective Layer, kg m² hr⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>0.67</td>
<td>185</td>
</tr>
<tr>
<td>Exposed to 100,000 mg/L salt solution</td>
<td>0.48</td>
<td>132</td>
</tr>
<tr>
<td>Exposed to 200,000 mg/L salt solution</td>
<td>0.36</td>
<td>99</td>
</tr>
</tbody>
</table>

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 N₂ sweep stream
- Custom laboratory set-up using FTIR multi-gas detector for composition analysis
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

![Graph showing flux versus temperature](image)

Calculated using
Permeate side
Feed side
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

![Graph showing flux vs. temperature for 6F-PBI membrane](image-url)
Two PBI material chemistries evaluated

- 6F-PBI has approximately one order of magnitude higher H₂ permeability as compared to m-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

![Graph showing water vapor fraction over time](image)

- Switch to Dry Gas for Analytics Background
Other Potential Applications Development

Goal

Develop process intensification strategies to deploy PBI membranes for solving water treatment challenges in power plants
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 SO₂ and NO₂
- 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 N₂ permeability (0.01 barrer)
- Previously evaluated for steam/H₂ feed mixtures at 250 °C
  - H₂O/H₂ selectivity = 3
  - H₂O/N₂ (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
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

**PBI Membranes for Flue Gas Dehydration**

**Condensing Membrane HX**

**Flue Gas**
- T = 55 to 180 °C
- Water Vapor = 7 to 17%

**Dry Flue Gas**

**Hot Boiler Make-up Water**

**Cold Water**
- 15 to 28 °C

**Dry Flue Gas**

**Flue Gas**
- T = 55 to 180 °C
- Water Vapor = 7 to 17%

**Permeate collector**

**Vacuum**

**Pervaporation**
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.
Acknowledgement

Department of Energy
Office of Fossil Energy (FE)/NETL – The Crosscutting Research Program

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