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

2018 Crosscutting Review Meeting
11th April 2017, Pittsburg

Rajinder P. Singh & Kathryn A. Berchtold
Carbon Capture and Separations for Energy Applications Laboratories
Material, Physics and Applications Division
Los Alamos National Laboratory
Elevated Temperature Membrane Separations

Applications of Interest:

Flue Gas Dehydration

Water Treatment
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
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
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 $\text{H}_2\text{O}/\text{N}_2$ selectivity
  - Water quality was not high enough for boiler make-up; significant transport of $\text{SO}_2$ and $\text{NO}_2$

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 H₂S 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

PBI Membrane Flue Gas Dehydration

- Measure PBI membrane performance at flue gas process conditions

**Typical Flue Gas Composition**

<table>
<thead>
<tr>
<th>Gas</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>70-72% (vol.)</td>
</tr>
<tr>
<td>CO₂</td>
<td>13-14%</td>
</tr>
<tr>
<td>O₂</td>
<td>3-4%</td>
</tr>
<tr>
<td>H₂O</td>
<td>6 to 20%</td>
</tr>
<tr>
<td>SOx</td>
<td>~200 ppm</td>
</tr>
<tr>
<td>NOx</td>
<td>~200 ppm</td>
</tr>
<tr>
<td>HF/HCL</td>
<td>&lt;10 ppm</td>
</tr>
<tr>
<td>Temp.</td>
<td>50 to 180 °C</td>
</tr>
</tbody>
</table>

- Permeability & selectivity at varied operating conditions
- H₂O, SO₂ and NO detection using FTIR multi-gas detector
- N₂ and CO₂ 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

- Temp. 65 °C
- Feed: H_2O/N_2 or H_2O/N_2/CO_2
- Feed Pressure: 800 - 850 Torr

- Film Thickness ≈ 55 µm
- Sweep gas: He

Membrane 1
Membrane 2
Membrane 3
PBI has high vapor perm-selectivity over CO₂ and N₂ at flue gas representative conditions

- Water vapor permeability decreased with feed pressure
- H₂O/CO₂ selectivity = 5000
- H₂O/N₂ selectivity estimated at > 20,000 based on GC N₂ detection limit

**Test Conditions**
- Feed RH: 89.9%, CO₂ = 10 to 11%, Bal: N₂
- 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

<table>
<thead>
<tr>
<th>Component</th>
<th>Permeability (Barrer)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PBI</td>
</tr>
<tr>
<td>Single Gas$^b$:</td>
<td></td>
</tr>
<tr>
<td>Temp, °C</td>
<td>30</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.0231</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.342</td>
</tr>
<tr>
<td>Mixed Gas:</td>
<td></td>
</tr>
<tr>
<td>Temp, °C</td>
<td>65</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>4000$^a$</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.05 (est.)$^1$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.8</td>
</tr>
</tbody>
</table>

$^a$ Measured using N$_2$/CO$_2$/H$_2$O 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
Four preliminary process configurations possible

- Permeate sweep (water or gas) process configuration

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

Sweeping Gas Configuration
Sweep gas to create partial pressure driving force followed by condensation of water from sweep gas to get clean water
Permeate vacuum process configurations

**Pervaporation**
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.

**Vapor-Compression**
A variation of pervaporation configuration using vapor compression to condense water vapor. Very low gas ($\text{N}_2$ & $\text{CO}_2$) 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 N₂ and CO₂ 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 SO₂ and NO.
  - Multi-gas FTIR flue gas test system enables direct H₂O, CO₂, SO₂ 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

**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 an 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 (HGSBMBS)

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
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
PBI membranes evaluated in semi-continuous pervaporation mode

- High temperature and pressure membrane stir cell with feed injection to maintain steady feed concentration
Water transport of PBI membranes measured for NaCl/water solution measured in pervaporation mode

Influence of Salt Solution Exposure

- Water Vapor Flux, Kg m\(^{-2}\) h\(^{-1}\)
- Temperature, °C

Feed: 53,000 PPM NaCl in Water
55 μm Film
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\(^{-1}\)
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$_2$O, 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

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

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.