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**Presentation Objective**
- Provide guidance, based on NETL perspective, to developers of membrane materials and CO$_2$-membrane capture systems for post-combustion CO$_2$ capture
- Summarize results: details in supporting documentation

- Review polymeric CO$_2$-membrane current and potential performance characteristics
- Consider the influences of alternative PC power plant CO$_2$-membrane process configurations and operating conditions
- Estimate PC power plant CO$_2$-membrane post-combustion performance factors: membrane area, permeate CO$_2$ purity, power plant efficiency
- Generate cost of electricity results that inform the potential impacts of the membrane material performance, and process configurations
• Potential benefits of membrane-based post-combustion CO₂ capture
  • No power plant steam extraction is needed
  • No circulating medium is needed (solvent, adsorbent, sorbent)
  • Low-cost, polymer-based membrane materials are commercially available for small-scale applications

• Goals of membrane-based post-combustion CO₂ capture development
  • Reduce the large membrane surface area currently needed
  • Reduce the large number of membrane modules currently needed
  • Improve the low CO₂-permeate purity that results for high (90%) CO₂ separation efficiency
  • Eliminate the need for process enhancement by an air-sweep membrane, and/or minimize the negative impacts on the PC furnace performance that may result
**CO₂-Membrane Characteristics**

- Important CO₂-membrane material characteristics are the CO₂ permeance, \( K_{\text{CO}_2} \), and the selectivity, \( \alpha \), of CO₂ relative to the other gas constituents (N₂, H₂O, O₂, and Ar).
- Robeson [1] provides a correlation relating membrane permeability and selectivity, based on collected test data.
- Performance data for membranes assumed in this study is characterized by the Robeson upper bound.
- \( K_{\text{CO}_2} \) is corrected for application at our power plant operating temperature (53-63°C) in this assessment [2].

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### Robeson Upper Bound Permeance

<table>
<thead>
<tr>
<th>Selectivity ($\alpha_{CO_2/N_2}$)</th>
<th>Membrane Film Thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>25</td>
<td>2,022</td>
</tr>
<tr>
<td>50</td>
<td>273</td>
</tr>
<tr>
<td>100</td>
<td>37</td>
</tr>
<tr>
<td>200</td>
<td>5</td>
</tr>
</tbody>
</table>
**CO₂-Membrane Study Characteristics**

- PC flue gas contains CO₂, N₂, O₂, Ar, and significant water vapor
- Polymeric membranes are generally sensitive to water vapor: Rubbery polymers are less sensitive; glassy polymers are more sensitive (permeance decreases with increased water vapor) [3]
  - A sensitivity study on the impact of water showed that for a single, counter-current membrane configuration, membrane area requirements per mole of CO₂ to achieve 90% CO₂ capture could vary by as much as 35%, with permeate purity varying by 7%
- Polymeric membrane $K_{CO₂}$ and selectivity assumptions applied in study
  - $\alpha_{CO₂/H₂O} = 0.2$ (water vapor permeates rapidly)
  - $\alpha_{CO₂/N₂} = \alpha_{CO₂/O₂} = \alpha_{CO₂/Ar}$
  - Permeance or selectivity are not influenced by operating pressure, or interactions with other flue gas constituents (including gas contaminants and water vapor)

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This study considers polymeric membranes having $\alpha_{\text{CO}_2/\text{N}_2}$ ranging from 25 to 100. Permeance values above the Robeson upper bound represent advanced membrane materials of unknown properties and cost.
Membrane-Module Design

• The “membrane-module” is a commercial packaging of membrane surface (hollow fiber bundles, spiral-wound units, flat plate units, tubular units) within a containment structure

• These would be deployed as a large array of parallel membrane-modules (possibly hundred to thousands, depending on the membrane-module gas flow capacity)

• The array of membrane-modules requires a distribution system of headers, manifolds, valves, and piping to transition the gas flows between the membrane-module array and the large power plant gas ducting
  • We account for this membrane-module sub-system cost in a simplified manner
Any membrane-surface configuration (spiral-wound, hollow fibers, plate, tubular) can be used so long as it can promote counter-current contacting, can operate with acceptable pressure drop, can tolerate the membrane-surface pressure difference, and can be housed as a sufficiently large membrane-module.
The DOE/NETL baseline conventional PC power plant with conventional capture serves as the reference plant for this study [4].

The DOE/NETL baseline flue gas flow, composition, temperature, and pressure (using a fixed coal feed rate for all cases) are applied in the study.

**CO₂ capture process performance requirements**

- Net CO₂ capture: 90% of coal feed carbon
- CO₂ product minimum purity: 95 vol% CO₂ with ≤10 ppmv O₂
- CO₂ product delivery pressure: 2200 psig
- PC furnace secondary air O₂ content: 18 vol% [5] (for air-sweep membrane applications)

- Range of membrane CO₂ permeance and selectivity considered: 500 to 20,000 gpu; \( \alpha_{\text{CO}_2/\text{N}_2} \) 25 to 100

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PC Power Plant Assessment Basis: CO$_2$ Capture Process Alternatives

Five CO$_2$ Separation Process Configurations Considered

- Independent flue gas membrane modules with low-pressure flue gas and permeate-side vacuum ("independent FG membrane" configuration)

- Flue gas membrane modules coupled with air-sweep membrane modules, with low-pressure flue gas and permeate-side vacuum ("combined air-sweep" configuration)

- Both configurations above with flue gas pressurization

- Independent FG membrane modules with added membrane module stages for permeate-side enrichment, with low-pressure flue gas
Processes with Low-Pressure Flue Gas

Independent FG Membrane Configuration with Low-Pressure Flue Gas
Combined Air-Sweep Configuration with Low-Pressure Flue Gas
Processes with Low-Pressure Flue Gas (cont’d)

Configuration Influence on Power Plant Efficiency Results

- CO₂ permeance does not influence the power plant efficiency
- Increased selectivity increases the power plant efficiency
- The combined air-sweep configuration results in higher power plant efficiency than the independent FG membrane configuration
- Advanced membrane materials having very high selectivity (>100) might minimize this difference
**Processes with Low-Pressure Flue Gas (cont’d)**

**Independent FG Membrane Configuration Area Results**

Values 1, 0.5, 0.25, and 0.1 are membrane film thickness (μm) located at corresponding maximum polymer membrane CO₂ permeance for each selectivity.

- CO₂ permeances >1,000 gpu are limited to α_{CO₂/N₂} of 25 to 50.
- Higher selectivity (>50 - 100) will require advanced polymeric materials.
- The curves show a trend for increased membrane area with higher selectivity.
- Limited area benefit for permeances > 8,000 gpu.
Processes with Low-Pressure Flue Gas (cont’d)

Combined Air-Sweep Configuration Area Results

• The curves are similar in trend to the independent flue gas membrane configuration.

• The combined air-sweep configuration results in slightly higher total membrane area than the independent FG membrane configuration.
Processes with Low-Pressure Flue Gas (cont’d)

Cost Results

Independent Membrane Configuration

- Membrane module cost 50 $/m²; Membrane replacement cost 20 $/m²; Membrane life 5 years

Combined Air-Sweep Membrane Configuration

Membrane module cost 50 $/m²; Membrane replacement cost 20 $/m²; Membrane life 5 years
For low pressure operation using current membrane materials, the air sweep configuration offers cost benefits over the independent membrane configuration; as membrane performance improves, the system configuration benefits approach an equivalent cost result.

Flue gas pressurization reduces the total membrane area, and plant efficiency; not cost-effective development options.

Membrane staging increases permeate purity, gas flow rate to the membrane and the compression work, reducing the power plant efficiency—not a cost-effective development option.

Based on the results, developer focus should be on:

- Low-pressure membrane CO₂ capture processes
- Options to eliminate the air-sweep membrane, or to minimize its PC furnace impacts, especially for power plant retrofit applications
- Development of membrane materials having higher CO₂ permeance (>3,000 gpu) and with selectivity approaching 100
Findings (cont’d)

• A general COE reduction graph has been developed that allows the COE reduction for low-pressure configurations to be estimated as a function of:
  • The type of membrane configuration (independent membrane, or combined air-sweep)
  • The cost of the membrane-unit \((C_{\text{mem}})\)
  • The cost of membrane-unit replacement \((C_{\text{replace}})\)
  • The membrane-unit life \((T_{\text{life}})\)
  • The membrane \(CO_2\) permeance \((K_{CO2})\)
  • The membrane selectivity \((\alpha_{CO2/N2})\)

• This general graph can be applied as a sensitivity study tool
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