Membrane engineering for CO₂ separation by gas separation systems

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³° Trondheim Gas Technology Conference (TGTC-3)
June 4th-5th, 2014
### Main sources of CO₂

<table>
<thead>
<tr>
<th>Source</th>
<th>Separation</th>
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</thead>
<tbody>
<tr>
<td><strong>Flue gas streams</strong></td>
<td><strong>CO₂/N₂</strong></td>
</tr>
<tr>
<td>Power plants,</td>
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<tr>
<td>coal gasification plants,</td>
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<tr>
<td>Steel factory,</td>
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<tr>
<td>Cement factory,</td>
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<tr>
<td>Transportation</td>
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<tr>
<td><strong>Natural Gas</strong></td>
<td><strong>CO₂/CH₄</strong></td>
</tr>
<tr>
<td>Sweetening of Natural gas, etc.</td>
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<tr>
<td><strong>Biogas</strong></td>
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<tr>
<td>Various</td>
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</tbody>
</table>

*Inventory of U.S. Greenhouse Gas Emissions and Sinks (2008), EPA*
Flue gas emissions from:

- Power plant
- Steel factory
- Cement factory
- Coal gasification plant
CO$_2$/CH$_4$ mixtures from....

BIOGAS

NATURAL GAS SWEETENING
**ABSORPTION**

Absorption is a process that relies on a solvent's chemical affinity with a solute to dissolve preferably one species into another. It is widely proposed for CO₂ separation where generally, monoethanolamine or a solid absorbent is used. High amount of energy consumed is for solvent(MEA) recovery (3-4 units).

**ADSORPTION**

The PSA process is based on the capacity of some adsorbents (zeolites, etc.) in adsorbing such gases at high gas-phase partial pressure. Proper selection of the adsorbents is critical for both the performance of the unit and adsorbent life-time. For instance, the CO₂ is adsorbed at higher partial pressure and then desorbed at lower partial pressure. High pressure is required (3-4 units).

**CRYOGENIC**

Low temperature separation process. The difference in boiling temperatures of the feed components affects the separation. One of the main advantages is the ability to produce separated hydrocarbon streams rich in C₄+, ethane/propane, etc. One of the main drawbacks is the presence of H₂O in the gaseous stream that can strongly affect the separation performance; the gaseous stream to be treated needs to be completely dehydrated prior to be cooled. High energy intensity. Pre-treatment stages of the up-stream. (2 units)
Membrane-assisted Gas Separation

- Simplicity
- Modularity
- Equipments: reduced in size & number
- Low investment costs
- The required gas compression is much smaller than that of PSA
- Temperature not as extreme as cryogenic

One stage plant

1.2 \times 10^6 \text{Nm}^3/\text{h}

10\%\text{CO}_2

55 \text{bar}

2\%\text{CO}_2

44\%\text{CO}_2

1.7 \text{bar}

Use for fuel or flare
- **CO$_2$/N$_2$ Streams**
  - No value
  - Pressure is required for separation
  - The final stream of interest is the permeate
  - Low CO$_2$ concentration (10-30%)

- **CO$_2$/CH$_4$ Streams**
  - Value due to the CH$_4$ content
  - Pressurised stream
  - The final stream is the retentate (high pressure)
Polymeric membranes generally undergo a trade-off limitation between permeability and selectivity: as permeability increases, selectivity decreases, and vice-versa.

**Membrane materials**

<table>
<thead>
<tr>
<th>Membrane materials</th>
<th>CO$_2$/N$_2$ Selectivity ranges</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA, SPEEK, PSF, TRLON, HYFLON, MATRIMID 5218, PMMA, PPO, PEI+zeolite, CTA, PDMS modified, TR polymers, Polyarilates, Polycarbonates</td>
<td>20-30</td>
</tr>
<tr>
<td>PI modified, PEO, PES, PMEEP, PEI</td>
<td>30-60</td>
</tr>
<tr>
<td>Sieving selective carbon, PEO, PEBAX, PEBAX+silica, PEG+Silica, PI+zeolite, PVAm (Facilitated transport membranes)</td>
<td>50-100</td>
</tr>
<tr>
<td>PVAm (Facilitated transport membranes)</td>
<td>150-300</td>
</tr>
</tbody>
</table>


*TR, thermally rearranged*
Simple tool for a preliminary analysis on the prospects for membranes in CO\textsubscript{2} capture from flue gas

Dimensionless 1D mathematical model for the multi-species steady-state permeation in no-sweep mode and co-current configuration

**Feed/Retentate side**

\[
\frac{d\phi_{\text{CO}_2}^{\text{Retentate}}}{d\zeta} = -\Theta_{\text{CO}_2} \left( \phi_{\text{CO}_2}^{\text{Retentate}} - x_{\text{CO}_2}^{\text{Permeate}} \right)
\]

\[
\frac{d\phi_{\text{N}_2}^{\text{Retentate}}}{d\zeta} = -\frac{x_{\text{CO}_2}^{\text{Feed}}}{x_{\text{N}_2}^{\text{Feed}}} \frac{1}{\alpha_{\text{CO}_2/\text{N}_2}} \Theta_{\text{CO}_2} \left( \phi_{\text{N}_2}^{\text{Retentate}} - x_{\text{N}_2}^{\text{Permeate}} \right)
\]

**Permeate side**

\[
\phi_{\text{CO}_2}^{\text{Permeate}}(\zeta) = \phi_{\text{CO}_2}^{\text{Feed}} - \phi_{\text{CO}_2}^{\text{Retentate}}(\zeta)
\]

\[
\phi_{\text{N}_2}^{\text{Permeate}}(\zeta) = \phi_{\text{N}_2}^{\text{Feed}} - \phi_{\text{N}_2}^{\text{Retentate}}(\zeta)
\]

**Flue gas composition**

13% CO\textsubscript{2}; 87% N\textsubscript{2}

**Flue gas pressure**

1 bar

**Selectivity**

30, 50; 100; 150; 300

**Pressure ratio**

5; 10; 20; 50

**Number of stages**

1
Simple tool for a preliminary analysis on the prospects for membranes in CO$_2$ capture from flue gas

In the equations $\varphi_{CO_2}$, $\varphi_{N_2}$ are the dimensionless molar flow rate, for CO$_2$ and N$_2$, respectively and $\zeta$ is the dimensionless module length.

$$\varphi_i = \frac{Q_i}{Q_{Feed}} \quad \zeta = \frac{Z}{L}$$

$\Theta_i$ and $\phi$ are the parameters affecting the performance of a one stage membrane system, the permeation number and the feed to permeate pressures ratio, respectively.

$$\Theta_{CO_2} = \frac{Permeance_{CO_2} A_{Membrane} P^{Feed}}{x_{CO_2}^{Feed} Q^{Feed}}$$

$$\phi = \frac{P^{Feed}}{P^{Permeate}}$$

$\Theta_i$ expresses a comparison between the two main mass transport mechanisms involved: the permeating one through the membrane and the convective flux of the feed stream.
The maps could be the starting point in the carbon capture and storage process design. In fact, global economic considerations on the final electricity cost and CO₂ storage technology allow the optimal performance to be univocally individuated on the maps.

For instance, 64% CO₂ purity and 61% recovery corresponds to a system having a pressure ratio of 20 and a permeation number ($Q_{CO₂}$) of 0.2. For a given geometry and membrane (Permeance$_{CO₂}$) this pair of parameters can be obtained by means of infinite different couples of operating conditions.

The effect of the selectivity on the performance of the membrane module is negligible at low pressure ratios.
Increasing the pressure ratio....
Increasing the pressure ratio....
The low concentration of CO₂ in the feed does not allow to achieve high purity streams in the permeate, even increasing the pressure ratio. More separation stages are necessary.
Also at higher selectivity, the low concentration of CO₂ in the feed does not allow achieving high purity streams in the permeate, even increasing the pressure ratio.
Another limiting parameter for the module performance is the membrane area (Permeation number). For a set feed flow rate, a set membrane type and defined pressure ratio, a low $\Theta$ indicates low recovery and high permeate purity, and vice versa.

$$\Theta_{CO_2} = \frac{\text{Permeance}_{CO_2} A^{\text{Membrane}} p^{\text{Feed}}}{x_{CO_2}^{\text{Feed}} Q^{\text{Feed}}}$$
The low feed pressure ratio strongly affects the performance of the membrane module even at a high selectivity of the membrane.

Also, the variation of $\theta$ does not affect the module performance.
For a high value of selectivity, the double of the pressure ratio implies a recovery 2-3 times higher and also improvements in the CO$_2$ purity.
Membrane engineering, together with material science, has a crucial role for the real application of membrane technology in CO\textsubscript{2} separation, that means integrated process design and optimization of the operating conditions are really important.

In addition to the feed conditions, the main variables affecting the performance of the membrane module are the feed pressure ratio and the permeation number.

The low concentration of CO\textsubscript{2} in the feed does not allow achieving high-purity streams in the permeate, even increasing the pressure ratio. More separation stages are necessary.

The effect of the selectivity on the performance of the membrane module is negligible at low pressure ratios but it is important at higher values of driving force.

Another limiting parameter for the module performance is the permeation number. For set feed flow rate, membrane type and pressure ratio, a low \( \theta \) provides low recovery and high permeate purity.
Thank you for your attention

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