Post-combustion CO₂ Capture Using Metal Organic Frameworks

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Background

As part of GCEP-sponsored research:
- Develop preliminary systems-level performance and cost models for evaluation of new materials for CO₂ capture
- Incorporate these models in a broader power plant systems model such as the Integrated Environmental Control Model (IECM) to make comparative analyses

Objectives

- Develop a preliminary performance model for evaluation of metal organic frameworks (MOFs) for post-combustion CO₂ capture
- Develop a preliminary thermodynamic model for pressure/vacuum swing adsorption (PSA/VSA)
- Compare the performance results with MEA-based CO₂ capture process

Sorbents for CO₂ capture

- Zeolites – porous crystalline aluminosilicates
  - Eg. Zeolite13X, NAX
- Amine-functionalized chemisorbents
  - Eg. PEI, NETL-32D
- Metal organic frameworks (MOFs)
  - MOF-5, MOF-177, Mg-MOF-74

Work in progress!
MOFs have better CO₂ capture properties than zeolites

Metal Organic Frameworks
- Metal-containing nodes linked by organic ligand bridges
- “Tunable” properties to enhance CO₂ capture
- Over 100 MOFs reported in literature
  - Typical metals – Cu, Ni, Al, Sc, Co, Mn
- Pressure swing adsorption and regeneration

Pressure/vacuum swing adsorption (PSA/VSA)
- Adsorption occurs at high pressure (or at atmospheric pressure in VSA)
- Desorption occurs when pressure is released
- Compared with thermal swing adsorption (TSA)
  - Shorter cycle times
  - Longer sorbent life, but …
  - Lower CO₂ product purity

Single-stage PSA – Skarstorm cycle

Clean flue gas

Adsorber (High pressure)

Pressurization
Feed

Flue gas

Blower/Compressor
Single-stage PSA – Skarstorm cycle

4 steps:
• Pressurization
• Feed
• Blowdown
• Purge

Performance model
- For a given sorbent, desired CO₂ capture efficiency and operating conditions, estimate:
  - Amount of sorbent required
  - Amount of energy required
  - Purity of CO₂ product

Simplified PSA/VSA model*
- Three steps:
  - Pressurization (adsorption)
  - Feed (adsorption)
  - Blowdown (desorption)
- Atmospheric pressure adsorption, vacuum pressure desorption
- Equilibrium conditions
- Cyclic steady state
- Single-stage operation

Pressurization and blowdown steps are done in 100 increments, with equilibrium reached at each step.

A few model equations

\[
\text{Loadings calculated using Langmuir equilibrium model}
\]

\[
\begin{align*}
W_{\text{absorbed}} &= \frac{m_{\text{CO}_2}}{m_{\text{abs}}}, \\
W_{\text{desorbed}} &= \frac{m_{\text{CO}_2}}{m_{\text{des}}}, \\
W_{\text{product}} &= \frac{m_{\text{CO}_2}}{m_{\text{product}}}, \\
W_{\text{vapor}} &= \frac{m_{\text{CO}_2}}{m_{\text{vapor}}}, \\
W_{\text{pressure}} &= \frac{m_{\text{CO}_2}}{m_{\text{pressure}}}, \\
\text{Purity} &= \frac{m_{\text{product}}}{m_{\text{desorbed}}} \\
\text{Specific work} &= \frac{(W_{\text{vapor}} + W_{\text{desorbed}})}{W_{\text{CO}_2}}
\end{align*}
\]

Results from the single-stage VSA model

With single-stage VSA, high recovery and purity is possible only at very low desorption pressure.

Isotherms for Mg\textsubscript{2}(dobdc) – MOF-74

\[
\begin{align*}
m_{\text{CO}_2} &= 7.9 \text{ mol/kg}, \quad b_{0,\text{CO}_2} = 1.56 \times 10^{-6} \text{ /bar}, \quad Q_{\text{CO}_2} = 42 \text{ kJ/mol} \\
m_{\text{N}_2} &= 14 \text{ mol/kg}, \quad b_{0,\text{N}_2} = 4.96 \times 10^{-5} \text{ /bar}, \quad Q_{\text{N}_2} = 18 \text{ kJ/mol}
\end{align*}
\]
Preliminary case study

- Base plant (modeled using IECM 8.0.2)
  - 650 MWg, Appalachian Medium Sulfur coal
  - 11,310 kmol/hr CO₂ in flue gas (12% by volume)
- CO₂ capture using Mg-MOF-74 and VSA
  - 90% CO₂ capture
  - Desorption pressure 0.002 bar
  - Isothermal at 75°C
  - CO₂ product compressed to 135 bar

Case study results

<table>
<thead>
<tr>
<th></th>
<th>Base plant*</th>
<th>MOF-VSA CO₂ capture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gross power out (MW)</td>
<td>650</td>
<td>650</td>
</tr>
<tr>
<td>Thermal energy input (MWth)</td>
<td>1564</td>
<td>1564</td>
</tr>
<tr>
<td>Net power out (MW)</td>
<td>608</td>
<td>362</td>
</tr>
<tr>
<td>Net plant efficiency (%HHV)</td>
<td>39</td>
<td>23</td>
</tr>
</tbody>
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Using a single-stage VSA process, energy penalty using MOFs is much higher compared to conventional MEA-based CO₂ capture

Future work

- Improve the performance model
- Expand the model to incorporate multi-stage and advanced VSA cycles
- Explore better MOF materials
- Explore possibilities of combined PSA-VSA or TSA-VSA cycles
- Develop a cost model

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