The importance of transport processes in silica-supported, polyethyleneimine-impregnated CO$_2$ sorbents

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Carbon Capture Simulation Initiative

- Identify promising concepts
- Reduce the time for design & troubleshooting
- Quantify the technical risk, to enable reaching larger scales, earlier
- Stabilize the cost during commercial deployment

National Labs

Academia

Carnegie Mellon

PRINCETON UNIVERSITY

West Virginia University

BOSTON UNIVERSITY

Industry

FLUOR

ADA

B&W

GE

Duke Energy

ALSTOM

Burns & McDonnell

SOUTHERN COMPANY

WorleyParsons

Boeing

ExxonMobil

ENERGY
Carbon Capture Challenge

- The traditional pathway from discovery to commercialization of energy technologies can be quite long, i.e., ~2-3 decades.

- President’s plan requires that barriers to the widespread, safe, and cost-effective deployment of CCUS be overcome within 10 years.

- To help realize the President’s objectives, new approaches are needed for taking carbon capture concepts from lab to power plant, quickly, and at low cost and risk.

- CCSI will accelerate the development of carbon capture technology, from discovery through deployment, with the help of science-based simulations.

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**Diagram:**

- **bench research** ~ 1 kWe
- **small pilot** < 1 MWe
- **medium pilot** ~ 5 MWe
- **semi-works pilot** 20-35 MWe
- **first commercial plant** ~ 100 MWe
- **deployment** > 500 MWe > 300 plants
the sorbent: silica support

- mesoporous silica forms the substrate
- silica xerogels (sol-gel process) most economical
- substrate particles agglomerates of micron-sized mesoporous particles

the sorbent: PEI loading

- substrate impregnated with polyethyleneimine, or PEI
- PEI tends to fill the mesopores, reducing porosity and internal surface area
- some amines bind with silanol sites that cover the surface of the substrate

An IR peak associated with silanol (3747 cm\(^{-1}\)) disappears when PEI is loaded onto the substrate.

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<table>
<thead>
<tr>
<th>sample</th>
<th>BET surface area (m² g⁻¹)</th>
<th>pore volume (cm³ g⁻¹)</th>
<th>pore diameter (nm)</th>
<th>CO₂ cap. (mg/g of sorb)</th>
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</thead>
<tbody>
<tr>
<td>MCM-41</td>
<td>1229</td>
<td>1.15</td>
<td>2.7</td>
<td>6.3</td>
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<tr>
<td>PEI(50)/MCM-41</td>
<td>11</td>
<td>0.03</td>
<td>0</td>
<td>89.2</td>
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<tr>
<td>(MBS-1)</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>SBA-15</td>
<td>950</td>
<td>1.31</td>
<td>6.6</td>
<td>5.0</td>
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<tr>
<td>PEI(50)/SBA-15</td>
<td>80</td>
<td>0.20</td>
<td>6.1</td>
<td>140</td>
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<tr>
<td>(MBS-2)</td>
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</tbody>
</table>

Sorbent NETL-196C, ~44.1 wt-% PEI, Dry atmosphere. Sorbent synthesis: McMahan Gray, NETL; Sorbent characterization: Daniel Fauth, NETL.
anhydrous model

- two-step formation of carbamic acid:
  \[ R_2NH + CO_2(g) \rightleftharpoons R_2NH^+ - CO_2^- \]
  \[ R_2NH^+ - CO_2^- + R_2NH \rightleftharpoons R_2NCOOH : R_2NH \]

- three modes of mass transport:
  - gas phase bulk
  - gas phase Knudsen
  - solid state (zwitterion-mediated hopping)
anhydrous model

(Left) Sample calculated output of the sorbent model showing diffusion effects (right) average model response for different entropies and enthalpies of zwitterion formation:
bot.-left: low-high; top-left: low-low; bot.-right: high-high; top-right: high-low
anhydrous model

(left) total variance metric for all model parameters
(right) average model response for different entropies and enthalpies of zwitterion formation:
bot.-left: low-high; top-left: low-low; bot.-right: high-high; top-right: high-low
anhydrous model

(left) scatter plot of model sensitivity to formation enthalpy of zwitterions
(right) scatter plot of model sensitivity to formation enthalpy of carbamate
quantum chemistry

CO$_2$-DMA zwitterion

zwitterion stability (DFT-B3LYP)

$\varepsilon_r = 1$ \hspace{1cm} $\Delta E = +147.0$ kJ/mol

$\varepsilon_r = 3$ (DPA) \hspace{1cm} $\Delta E = +96.6$ kJ/mol

$\varepsilon_r = 80$ (H$_2$O) \hspace{1cm} $\Delta E = -12.6$ kJ/mol
quantum chemistry

(Left) MMA + H₂O + CO₂
(Middle) linear topology
(Right) ring topology

- linear topology: \[ \Delta E = -16.2 \text{ kJ/mol} \]
- ring topology: \[ \Delta E = -34.4 \text{ kJ/mol} \]
anhydrous model

(left) TGA data for NETL-196C in 10% CO₂ and nominally dry conditions
(right) TGA data for NETL-196C in 10% CO₂ (blue) and 0% CO₂ (red) with 9% H₂O
conclusions

• Transport of CO₂ within the amine bulk controls not only the kinetics but the apparent capacity of PEI-impregnated silica sorbents.

• These sorbents depend on water to open up the bulk amine sites for CO₂ adsorption.

• Adsorption measurements in nominally dry conditions will therefore be misleading, significantly underestimating the capacity for carbamate formation in H₂O-saturated flue gas.
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