Development of Chemical Additives for Reducing CO$_2$ Capture Costs

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Project Status

• Funding: DOE $ 1,250 K

• Project period: 6/1/08 – 5/31/13

• Participants: Ted Chang – PI
  Y. Li – Postdoc
  C.Y. Liao – Graduate student

• DOE/NETL Manager: Elaine Everitt/Dave Lang
Basic Principles

- **Concept** → A novel aqueous solvent system that will integrate amine, potassium carbonate, and ammonia to attain high CO₂ capture rates, reduce energy demands and capital costs

- **Principles** → CO₂ captured is transferred from one solvent to another by chemical methods before the final solvent is thermally regenerated

<table>
<thead>
<tr>
<th>STEP</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>12-15% CO₂</td>
<td>1: Amine → High CO₂ capture rate</td>
</tr>
<tr>
<td>CO₂</td>
<td>2: K₂CO₃ → Precipitate KHCO₃ as a solid = much less water than amine solution</td>
</tr>
<tr>
<td>~100% CO₂</td>
<td>3: KHCO₃/Ammonia → Low regeneration temperature; low heat capacity</td>
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</tbody>
</table>
Project Objective

- Develop a solvent system that will reduce both energy demands and capital costs aiming at attaining DOE’s goal of no more than 35% increase in COE

Typical Amine Solvent Systems

Non-conventional Solvent System
Project Tasks

• Additives
  – Capable of capture CO\textsubscript{2} and transfer absorbed CO\textsubscript{2} to potassium carbonate with fast rates
  – Inexpensive, low vapor pressure, stable, and benign (low toxicity)

• Transformation
  – Chemistry of CO\textsubscript{2} transformation

• Energy demands
  – Solvent regeneration mass/energy balance

• Process Assessment and technology transfer
  – Integrated absorption and regeneration
  – Preliminary techno-economic analysis

Additives

Energy demands

Transformation

Process assessment and technology transfer
• CO₂ capture rates can be maintained with repetitive absorption/regeneration cycles
• Samples taken: 1. during absorption, 2. after absorption/before regeneration, and 3. after regeneration/before absorption
• Upper and lower liquid phases analyzed by NMR (Bruker AVB-400 & 600)
• Solid precipitates analyzed by laser Raman Spectroscopy
Phase Diagrams

Benefits of phase separation:
• Increase capture efficiency due to smaller bicarbonate and carbonate conc. in upper lean solvent
• Prevent amine from degradation due to its confinement in chem. transformation loop

Total concentrations

Upper phase concentrations
• Carbonate and bicarbonate can mostly be excluded from upper phase

Lower phase concentrations
• Amines can mostly be excluded from lower phase

* 0.443 mole CO₂/mole BL

0 1 2 3 4 5 6 7

Conc. (M)

0 2 4 6 8

Conc. (M)

K⁺ CO₃²⁻ HCO₃⁻ BLH₂⁺ BLCOO⁻ BLH

[BL]

Total (M)

0 4 8 12 16 20

Conc. (M)

[HCO₃⁻]+[CO₃²⁻] (M)
Regeneration of K$_2$CO$_3$

<table>
<thead>
<tr>
<th>Pathway</th>
<th>$\Delta H^\circ$ (kJ/kg CO$_2$)</th>
<th>Drawback</th>
<th>Benefits</th>
</tr>
</thead>
<tbody>
<tr>
<td>2KHCO$_3$(s)$\rightarrow$K$_2$CO$_3$(l)+H$_2$O(l)+CO$_2$(g)</td>
<td>1479</td>
<td>Slurry handling</td>
<td>Reduce sensible, latent to &lt; 1000;</td>
</tr>
<tr>
<td>2KHCO$_3$(s)$\rightarrow$K$_2$CO$_3$(l)+H$_2$O(g)+CO$_2$(g)</td>
<td>2479</td>
<td></td>
<td>Reagent stable</td>
</tr>
<tr>
<td>2KHCO$_3$(s)$\rightarrow$K$_2$CO$_3$(s)+H$_2$O(l)+CO$_2$(g)</td>
<td>2180</td>
<td></td>
<td>Low heat capacity</td>
</tr>
<tr>
<td>2KHCO$_3$(s)$\rightarrow$K$_2$CO$_3$(s)+H$_2$O(g)+CO$_2$(g)</td>
<td>3180</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Water < 40%

2KHCO$_3$+NH$_2$CO$_2$NH$_4$+H$_2$O$\leftrightarrow$K$_2$CO$_3$+2NH$_4$HCO$_3$

2NH$_4$HCO$_3$$\rightarrow$NH$_2$CO$_2$NH$_4$+CO$_2$+2H$_2$O

MEA carbamate $\rightarrow$ MEA + CO$_2$(g)

Water $\sim$ 70%

KHCO$_3$ decomposition rates:

<table>
<thead>
<tr>
<th>Steam only</th>
<th>w/ NH$_4$ species 1</th>
<th>w/ NH$_4$ species 2</th>
</tr>
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<tbody>
<tr>
<td>Avg. CO$_2$ production rate (kg/h)</td>
<td>0.0487</td>
<td>0.0621</td>
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</tbody>
</table>

- May reduce stripper size
Advantages

• Reduce energy penalty
  – Low sensible and latent heat
    Solid/slurry, small heat capacity, Low regeneration temp.
  – Using low quality steam and/or waste heat

• Reduce capital costs
  – High regeneration rates

• Reduce reagent loss and equipment corrosion
  – Amines not exposed to high temp.
  – Employ benign, low cost, and thermal stable chemicals
### Challenges

<table>
<thead>
<tr>
<th>Challenges</th>
<th>Mitigation</th>
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<tbody>
<tr>
<td>Could precipitate in absorber</td>
<td>Control L/G and/or temp.</td>
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<tr>
<td>Solid/slurry handling</td>
<td>Engineering system analysis</td>
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</table>
### Performance Schedule

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</thead>
<tbody>
<tr>
<td>1. Project management and planning</td>
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<td>2. Install walk-in fumehoods</td>
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<tr>
<td>Acquire system components</td>
<td>100%</td>
<td></td>
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<tr>
<td>3. Setup CO2 capture system</td>
<td></td>
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<tr>
<td>Determine Raman efficiencies</td>
<td>100%</td>
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<tr>
<td>4. Absorption of CO2</td>
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<tr>
<td>5. Chemical transformation</td>
<td></td>
<td>100%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. Reagent regeneration and CO\textsubscript{2} production</td>
<td></td>
<td></td>
<td>85%</td>
<td></td>
<td>60%</td>
</tr>
<tr>
<td>7. Process assessment and technology transfer</td>
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<td></td>
<td>40%</td>
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</table>

- **Chemical transformation**: slightly behind schedule as additional effort required to figure out the chemistry
- **Reagent regeneration and CO\textsubscript{2} production**: slightly ahead of schedule
- **Process assessment and tech transfer**: on schedule
Plans for Future Development

- **In this project**
  - Mass and energy balance
  - Integrated absorption and regeneration tests
  - Process chemistry and assessment
  - Industrial collaboration and technology transfer

- **After this project – team approach**
  - Scale up demonstration
  - Techno-Economic analysis
  - EH&S implications
Acknowledgment

• Coworkers: Yang Li and Chang-yu Liao, LBNL
  NMR instrument support: Chris Canlas, College of Chemistry, U.C. Berkeley

• Special thanks to DOE/NETL project managers: Elaine Everitt and David Lang for their guidance and management

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