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

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Berkeley Lab at a Glance

13 - Nobel Laureates; 55 - Nobel Laureates trained here;
13 - National Medal of Science members;
900 - University students trained each year;
4,200 - Employees; 202 - Site acreage

Bringing Science Solutions to the World

Research areas

Climate Change and Environmental Sciences
Energy Efficiency and Sustainable Energy
Biological Sciences for Energy Research and Health
Computational Science and Networking
Matter and Force in the Universe
Soft X-Ray Science for Discovery
Project Status

- Funding: DOE $ 1,250 K
- Project period: 6/1/08 - 5/31/13
- Participants: Ted Chang - PI
  - Y. Li - Chemist Project Scientist/Engr
  - C. Y. Liao - Graduate student
- DOE/NETL Manager: Elaine Everitt/Dave Lang
- Objectives:
  Developing 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.
Concepts

- 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>
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<tbody>
<tr>
<td>1: Amine</td>
<td>12–15% CO₂</td>
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<tr>
<td>2: K₂CO₃</td>
<td>CO₂</td>
</tr>
<tr>
<td>3: KHCO₃/Ammonia</td>
<td>~100% CO₂</td>
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Process Description

• Amine Loop: Capturing CO$_2$ by amine aqueous solution, increasing absorption kinetics.

• Recirculation tank: Connecting Amine Loop and Carbonate Loop, transferring CO$_2$ from amine to carbonate to precipitate bicarbonate.

• Carbonate Loop: Transferring CO$_2$ from bicarbonate to ammonium catalysts, increasing kinetics & producing pressurized CO$_2$. 

Amine−CO$_2$ + K$_2$CO$_3$ ← Amine + KHCO$_3$↓
Benefits

- Enhancement of CO$_2$ absorption kinetics, reducing absorber capital costs,
- reduction of processing water, reducing solvent regeneration energy demands,
- employment of stable and low heat capacity KHCO$_3$, reducing emissions of harmful products and sensible heat demands,
- reduction of reagent loss and equipment corrosion, reducing operation costs.
### Challenges and Mitigation

**Challenges**
- Could precipitate in absorber
- Solid/slurry handling

**Mitigation**
- Control L/G and/or amine composition
- Engineering system analysis
## Performance Schedule

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<tbody>
<tr>
<td>1. Project management and planning</td>
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<td>100%</td>
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<td>2. Install walk-in fumehoods</td>
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<td>100%</td>
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<tr>
<td>Acquire system components</td>
<td>100%</td>
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<tr>
<td>3. Set-up CO₂ capture system</td>
<td>100%</td>
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<tr>
<td>Determine Raman efficiencies</td>
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<td>4. Absorption of CO₂</td>
<td>100%</td>
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<tr>
<td>5. Chemical transformation</td>
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<td></td>
<td>100%</td>
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<td>6. Reagent regeneration and CO₂ production</td>
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<td>100%</td>
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<tr>
<td>7. Process assessment and technology transfer</td>
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Integration of Absorption and Chemical Regeneration

- Long-term multi-cycle run (14 cycles of absorption and chemical regeneration, and the absorption lasted at least 15min per cycle.)
- L/G: \( \sim 120 \text{ gallon/1000ft}^3 \)
- Sustainable 90% removal efficiency indicates the efficient chemical regeneration of amine.

![Diagram of absorption and regeneration system with labels: Absorber, Stirrer, Solvent pump, Recirculation tank.]

![Graph showing average CO\(_2\) removal efficiency (%).]
Thermal Regeneration Tests

- Semi-continuous stripping operation: make-up water in, and K$_2$CO$_3$ solution out
- Sufficient KHCO$_3$ solid was preloaded in the stripper

The addition of ammonium catalyst increased the CO$_2$ stripping rate under the same energy input
- Ammonium catalyst has potential, but more work is needed to overcome the volatilizing problem
Raman of Regenerated $\text{K}_2\text{CO}_3$ from the Stripper

- Long-term semi-continuous stripping operation: make-up water in, and $\text{K}_2\text{CO}_3$ solution out, with ammonium catalyst
- Sufficient $\text{KHCO}_3$ solid was preloaded in the stripper

The ammonium carbamate peaks were undetectable.

Ammonium species won’t contaminate the solvent in the absorber.
Energy Penalty Determination

Two different methods:

With an autoclave

With a stripper
Energy Penalty Determination with Autoclave

- High-pressure autoclave with functions of in-situ Raman
- Water and KHCO$_3$ were in the autoclave

Under 1.6bar, the stripping energy was preliminarily determined to be 2130kJ/kg CO$_2$
Energy Penalty Determination with Stripper

- Long-term continuous stripping test
- The input energy by steam was measured
- From CO\textsubscript{2} stripping rate (left), and assuming the sensible heat recovery, the stripping energy was estimated (right)

- The stripping energy was preliminarily determined to be 2079kJ/kg CO\textsubscript{2} on average at steady state.
- Further parametric optimization and energy penalty demonstration are needed.
CO₂ Absorption and Chemical Regeneration of Amine

- **1ˢᵗ absorption:**
  Fresh BL aqueous solution
- **2ⁿᵈ absorption:**
  The solution in which K₂CO₃ was replenished after the KHCO₃ solid was filtrated
- **3ʳᵈ absorption:**
  The solution in which K₂CO₃ was replenished for the second time after the KHCO₃ solid was filtrated

Samples were collected and analyzed by NMR.
CO$_2$ Absorption and Chemical Regeneration of Amine

\[
\delta(\text{ppm}) \propto \frac{\text{RNH}_2^+}{\text{RNH} + \text{RNH}_2^+}
\]

- The concentration of carbamate increased, and then decreased during the 2$^{\text{nd}}$ and 3$^{\text{rd}}$ absorption processes.
Degradation and EH&S Impact

- Ammonium species were undetectable in the absorber;
- only trace amount of amine exists in the high-temperature stripper;
- amine doesn’t have to undergo huge temperature swing.

- Mitigating ammonia emission problems
- Mitigating thermal degradation problems of amine
- Mitigating the formation of nitrosamine in high temperature zone

- Nitrosamine’s formation rate constant:
  - about $10^3$ less at 50°C than 135°C.

Conceptual Process Configuration

FLUE GAS TO EXISTING STACK

FLUE GAS
BLOWER
ABSORBER
STRIPPER COMPLEX

layan AMINE
SOLVENT
PUMP

LEAN AMINE
SOLVENT
PUMP

RECIRCULATION TANK

SOLID- LIQUID
SEP A RATION UNIT
W/ AMMONIUM
CATALYSTS

CO₂
KHCO₃
K₂CO₃

REBOILER

ABSORBER

STRIPPER COMPLEX
- Berkeley Lab has licensed a worldwide patent to Jiantawn LLC
- Jiantawn LLC is teaming with Nexant, Alstom, IHI, and UCB to push the technology forward
Plans for Future Development

After this project - team approach:

- Scale-up demonstration, a proposal was submitted in response to DE-FOA-0000785
- Techno-economic analysis
- EH&S implications
Acknowledgment

- The project was accomplished by Shih-Ger (Ted) Chang (PI), Yang Li (Chemist Project Scientist/Engr), and Chang-yu Liao (graduate student)
  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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