Development of Chemical Additives for Reducing CO_2 Capture Costs

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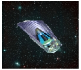
Berkeley Lab at a Glance

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 CO_2 capture rates, reduce energy demands and capital costs.

Concepts

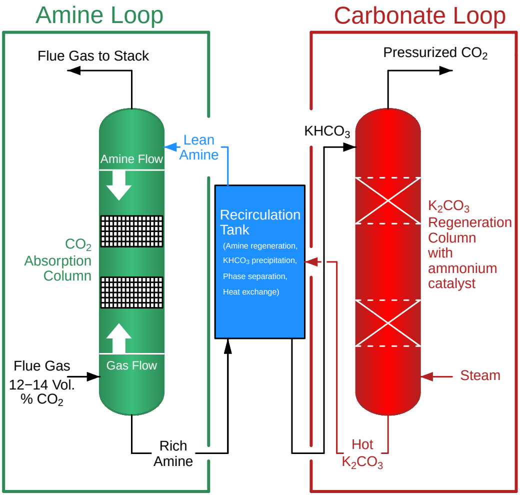
- CO_2 captured is transferred from one solvent to another by chemical methods before the final solvent is thermally regenerated

12–15% CO_2

STEP	PURPOSE
1: Amine	High CO_2 capture rate
(CO_2 →) 2: K_2CO_3	Precipitate $KHCO_3$ as a solid = much less water than amine solution
(CO_2 →) 3: $KHCO_3$/Ammonia	Enhancement of CO_2 production kinetics; low heat capacity

~100% CO_2

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.

$$\text{Amine}-CO_2 + K_2CO_3 \longleftrightarrow \text{Amine} + KHCO_3 \downarrow$$

Benefits

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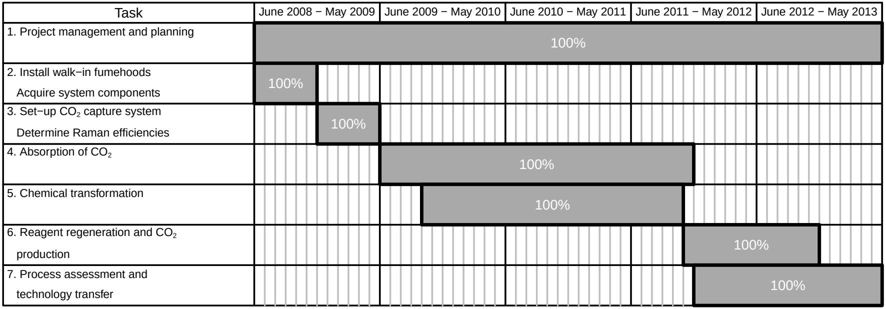
- Enhancement of CO_2 absorption kinetics, reducing absorber capital costs,
- reduction of processing water, reducing solvent regeneration energy demands,
- employment of stable and low heat capacity $KHCO_3$, reducing emissions of harmful products and sensible heat demands,
- reduction of reagent loss and equipment corrosion, reducing operation costs.

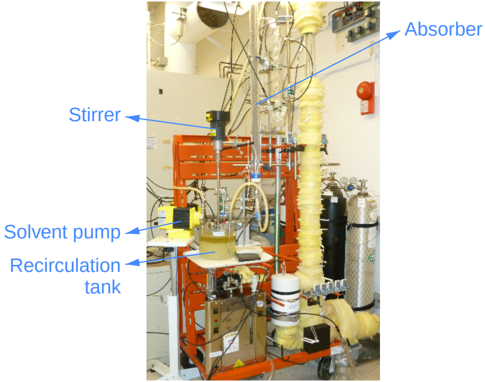
Challenges and Mitigation

Challenges	Mitigation
• Could precipitate in absorber	• Control L/G and/or amine composition
• Solid/slurry handling	• Engineering system analysis

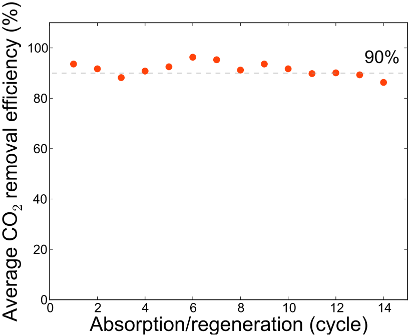
Performance Schedule



Integration of Absorption and Chemical Regeneration



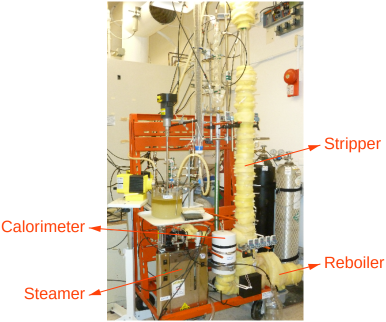
- Long-term multi-cycle run (14 cycles of absorption and chemical regeneration, and the absorption lasted at least 15min per cycle.)
- L/G: ~120 gallon/1000ft^3

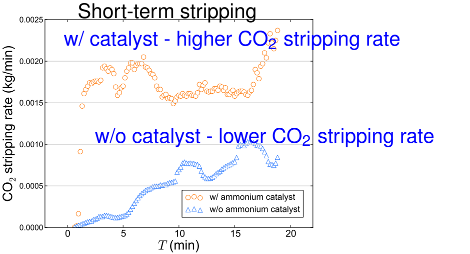


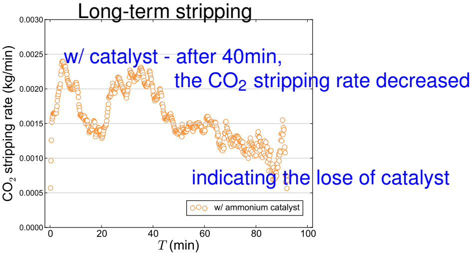
- Sustainable 90% removal efficiency indicates the efficient chemical regeneration of amine.

Thermal Regeneration Tests

- Semi-continuous stripping operation: make-up water in, and K_2CO_3 solution out
- Sufficient $KHCO_3$ solid was preloaded in the stripper



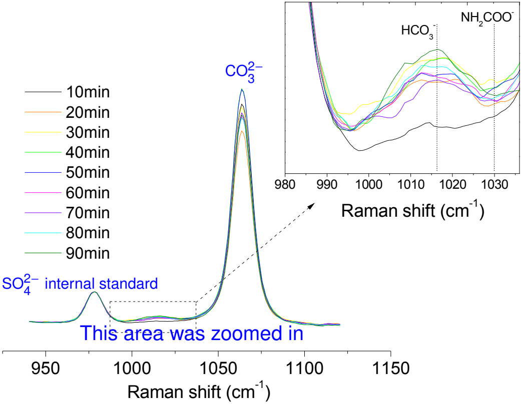




- The addition of ammonium catalyst increased the CO_2 stripping rate under the same energy input
- Ammonium catalyst has potential, but more work is needed to overcome the volatilizing problem

Raman of Regenerated K_2CO_3 from the Stripper

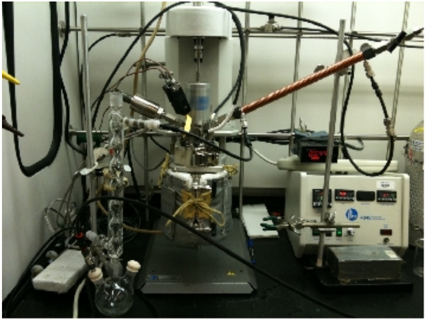
- Long-term semi-continuous stripping operation: make-up water in, and K_2CO_3 solution out, with ammonium catalyst
- Sufficient $KHCO_3$ solid was preloaded in the stripper



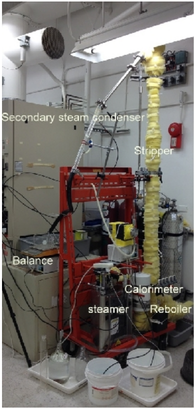
- The ammonium carbamate peaks were undetectable.
- Ammonium species won't contaminate the solvent in the absorber.

Energy Penalty Determination

Two different methods:

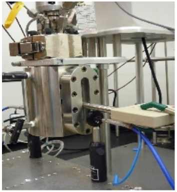


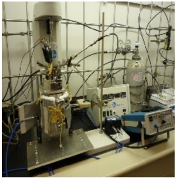
With an autoclave

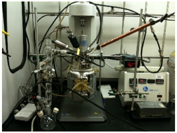


With a stripper

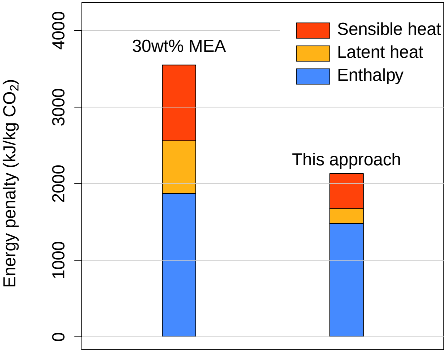
Energy Penalty Determination with Autoclave







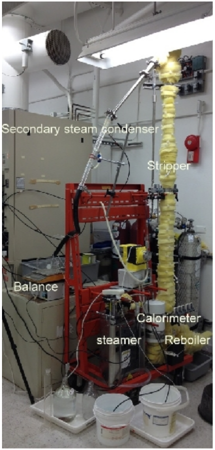
- High-pressure autoclave with functions of in-situ Raman
- Water and $KHCO_3$ were in the autoclave

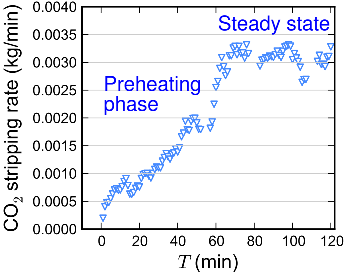


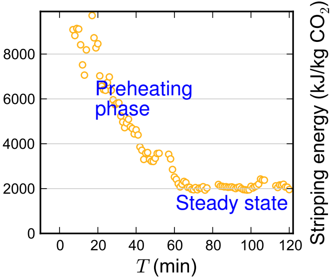
- Under 1.6bar, the stripping energy was preliminarily determined to be 2130kJ/kg CO_2

Energy Penalty Determination with Stripper

- Long-term continuous stripping test
- The input energy by steam was measured
- From CO_2 stripping rate (left), and assuming the sensible heat recovery, the stripping energy was estimated (right)

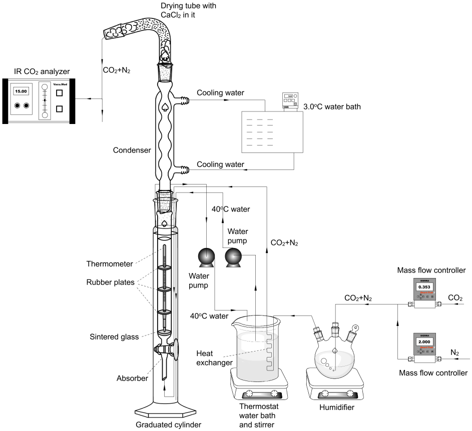






- The stripping energy was preliminarily determined to be 2079kJ/kg CO_2 on average at steady state.
- Further parametric optimization and energy penalty demonstration are needed.

CO_2 Absorption and Chemical Regeneration of Amine

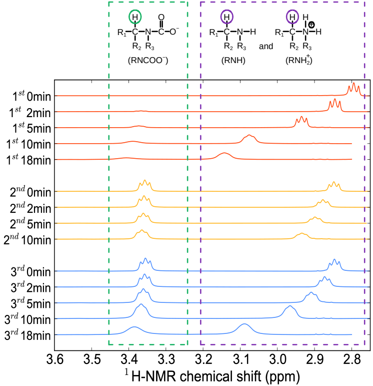


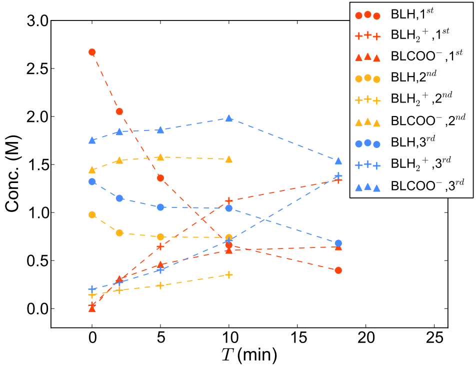
- 1^{st} absorption:
  Fresh BL aqueous solution
- 2^{nd} absorption:
  The solution in which K_2CO_3 was replenished after the $KHCO_3$ solid was filtrated
- 3^{rd} absorption:
  The solution in which K_2CO_3 was replenished for the second time after the $KHCO_3$ solid was filtrated

Samples were collected and analyzed by NMR.

Process Chemistry

CO_2 Absorption and Chemical Regeneration of Amine





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

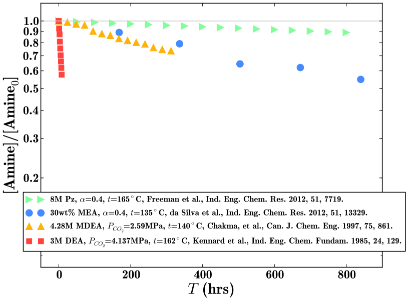
- The concentration of carbamate increased, and then decreased during 2nd and 3rd absorption processes

Degradation and EH&S Impact

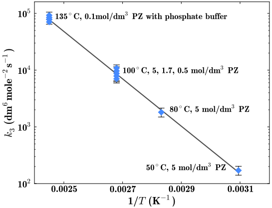
- Ammonium species were undetectable in the absorber;
- only trace amount of amine exists in the high-temperature stripper;
- amine doesn't have to undergo huge temperature swing.

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

Thermal Degradation



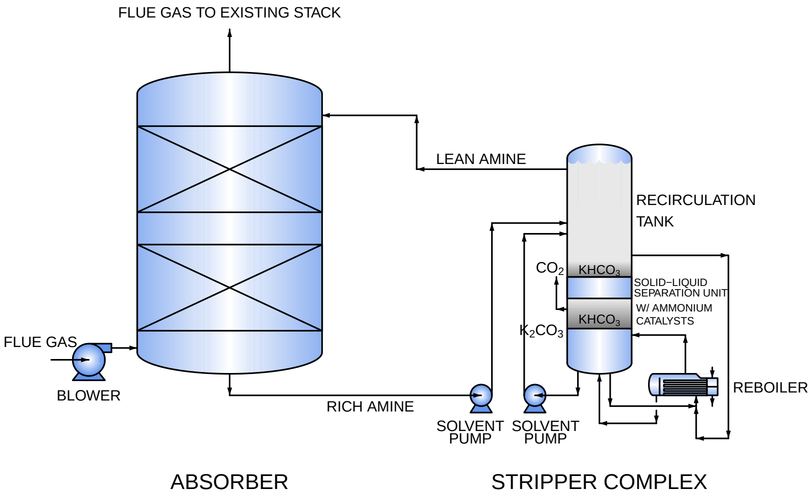
Nitrosamine Formation



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

Goldman et al. *Environ. Sci. Technol.* **2013**, 47, 3528-3534.

Conceptual Process Configuration



Technology transfer

- 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

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  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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