



Development of Chemical Additives for Reducing CO₂ Capture Costs

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Lawrence Berkeley National Laboratory

Presented at 2011 NETL CO₂ Capture Technology Meeting

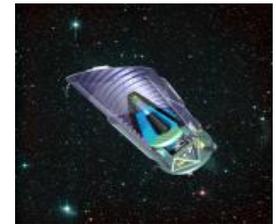
August 22-26, 2011

Berkeley Lab at a Glance

11 — Nobel Laureates; 55 — Nobel Laureates trained here ; 13 — National Medal of Science members;
800 — University students trained each year; 4,000 — Employees; 200 — 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**



Overview



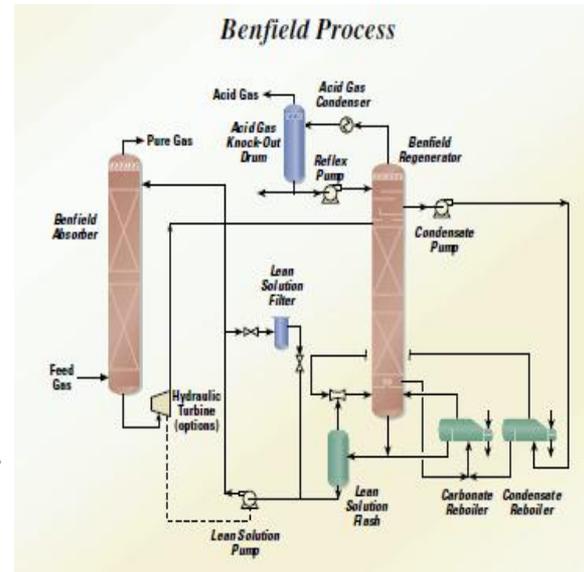
- **Funding: DOE \$ 1,250 K**
- **Dates: June 1, 2008 – May 31, 2013**
- **Participants: Ted Chang, PI**
Y. Li, C.Y. Liao, and Ray Dod
- **DOE/NETL Manager: David Lang**

Project Objective

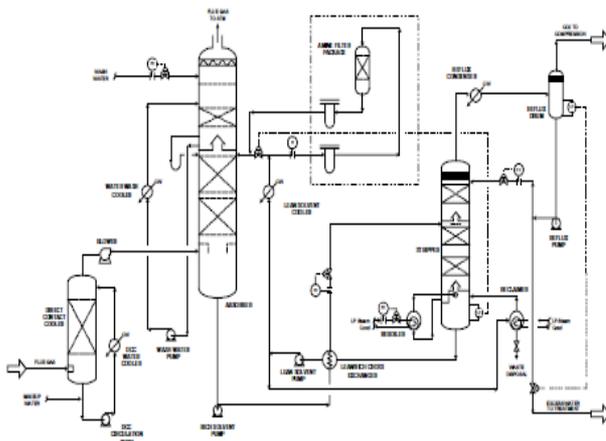


- Develop a novel solvent system that will integrate amine, potassium carbonate, and ammonium solvents to obtain as much CO₂ absorption and as little solvent regeneration energy demand as possible.

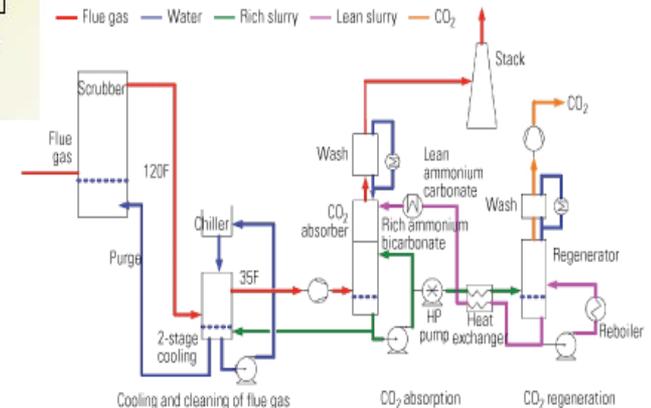
Benfield Process



Econoamine Process



Chilled Ammonia Process



Project Tasks

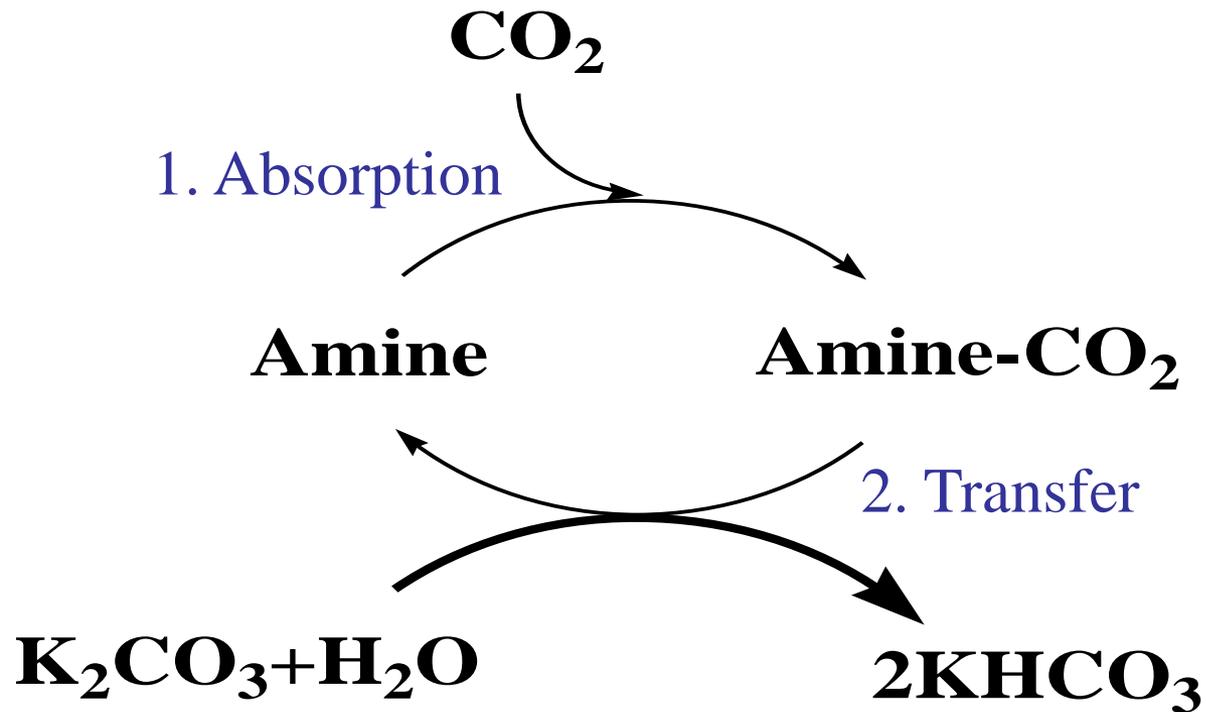


- **Task 1: Absorption of CO₂ – Identify additives to enhance CO₂ absorption**
- **Task 2: Chemical transformation – Transfer absorbed CO₂ from additives to K₂CO₃ and then to ammonium species, and finally to produce concentrated CO₂ gas**
- **Task 3: Reagent regeneration – Regenerate additives, K₂CO₃ and ammonium species**
- **Task 4: Process assessment and technology transfer – Evaluate process chemistry, configuration, and energy demand; Transfer technology to industry for scale-up development**

Technology Fundamentals

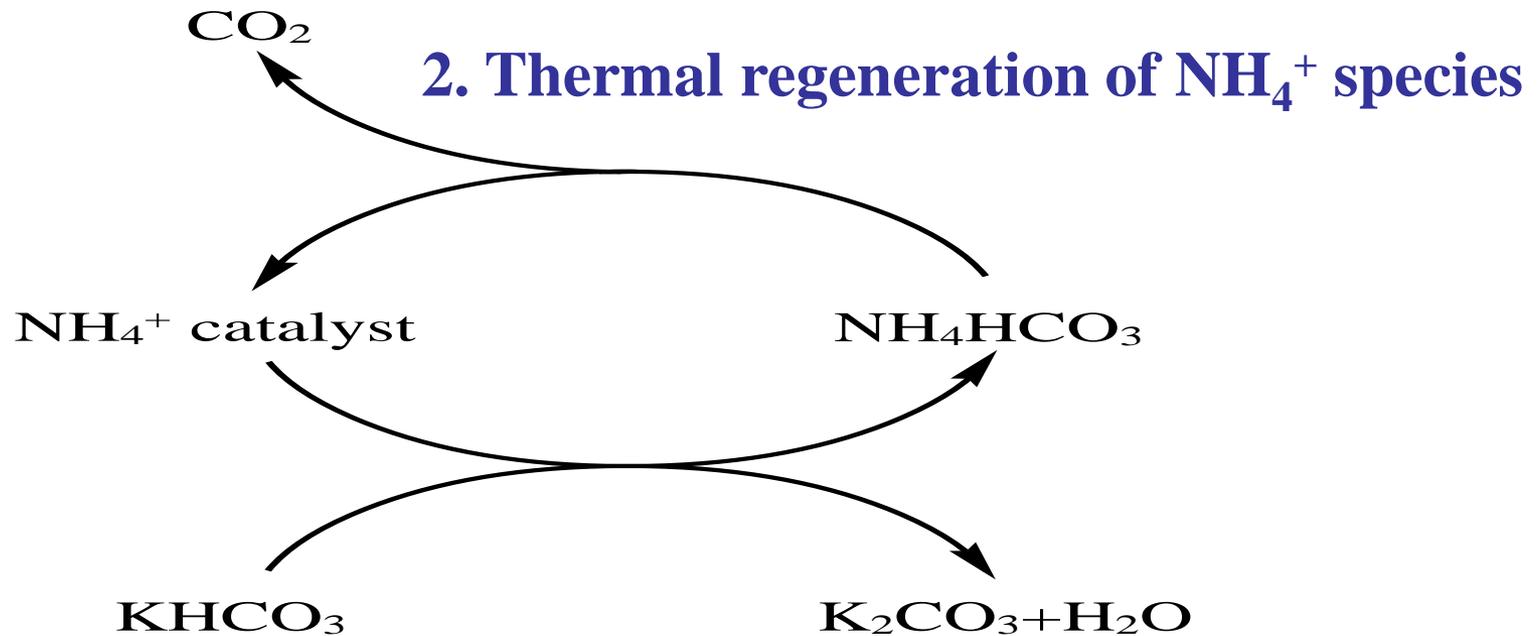
Next 5 slides

CO₂ Transformation Pathway



- Fast CO₂ absorption and transfer kinetics
- Favorable thermodynamics → chemical regeneration

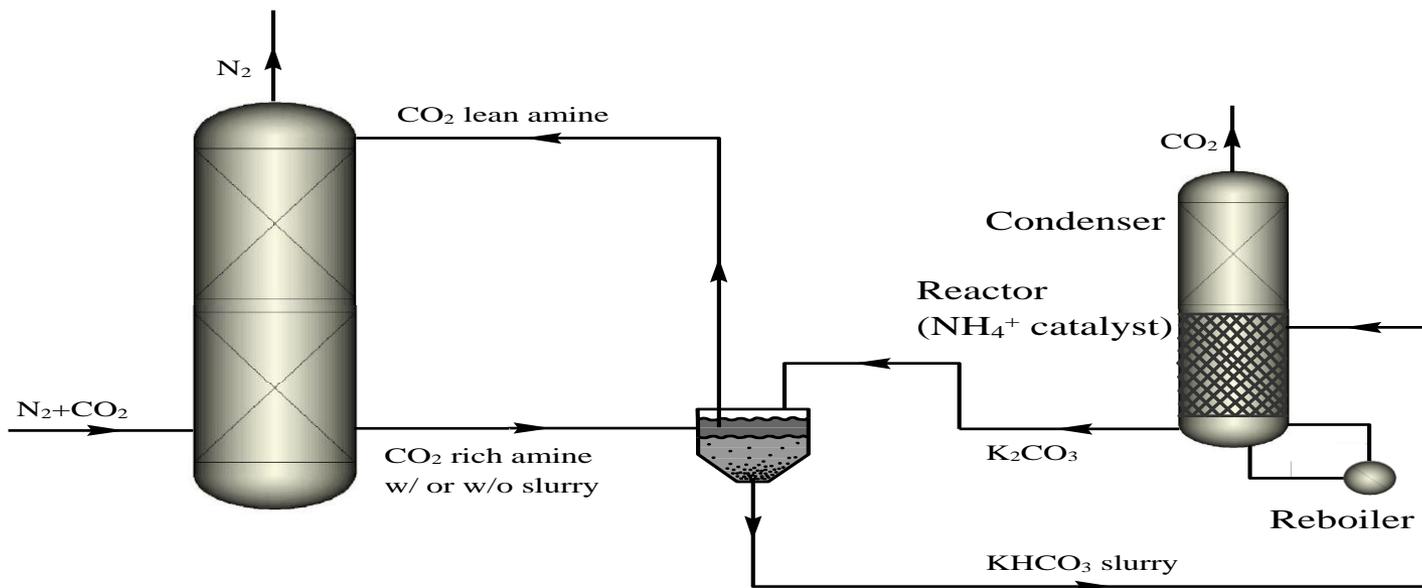
Transfer of CO₂ from KHCO₃ to NH₄⁺



1. Chemical regeneration of K₂CO₃



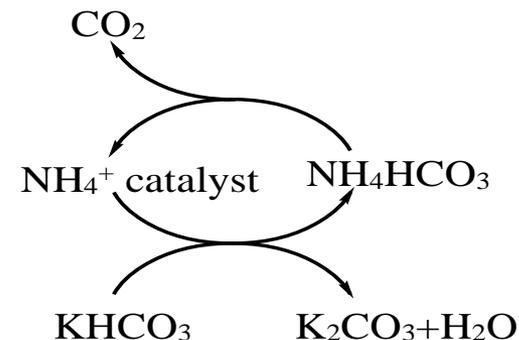
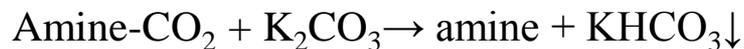
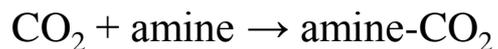
Conceptual Process Configuration



Absorber

Amine regenerator

K₂CO₃ regenerator



Technical and Economic Advantages



- **Reduce energy demand**
 - * **Slurries** → reduce sensible and latent heat
 - * **NH_4HCO_3** → low decomposition temperature → small ΔT
 - * **Heat capacity** → 1/3 MEA → small C_p
 - * **Waste heat** → CO_2 production
- **Reduce reagent loss and equipment corrosion**
 - * **Reduce amines exposed to stripping step**
- **Reduce capital costs in solvent regeneration**
 - * **Rapid reaction kinetics and CO_2 production**
- **Employ benign, low cost, and thermal stable chemicals**

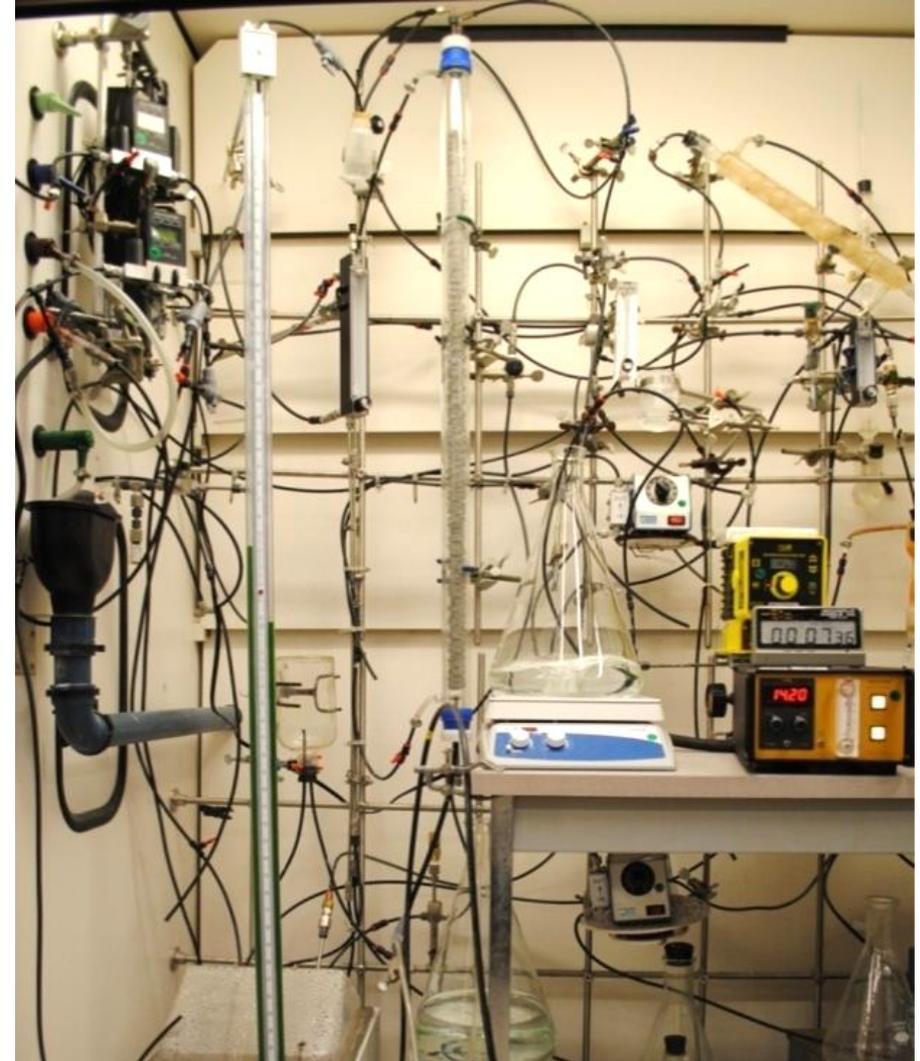
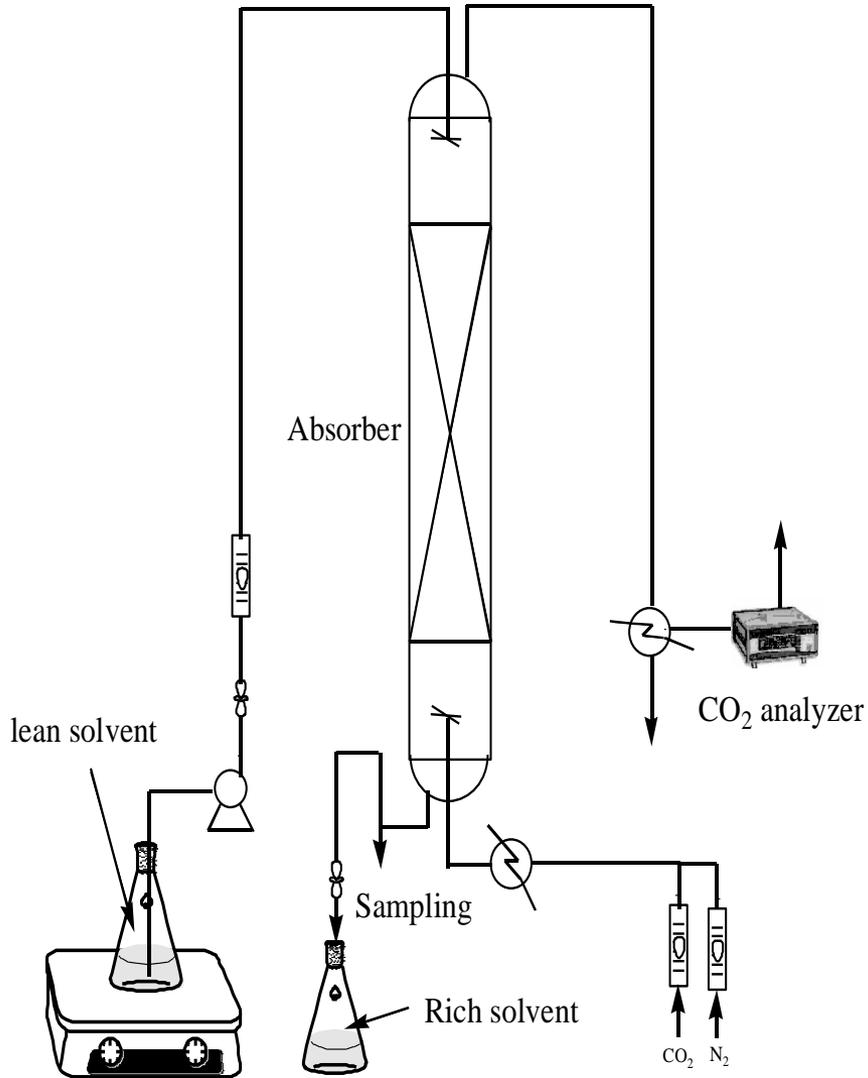


- **Develop new process configurations**
- **Identify new additives to go beyond current CO₂ absorption and transfer rates**
- **Determine kinetics and thermodynamics of reactions involved**

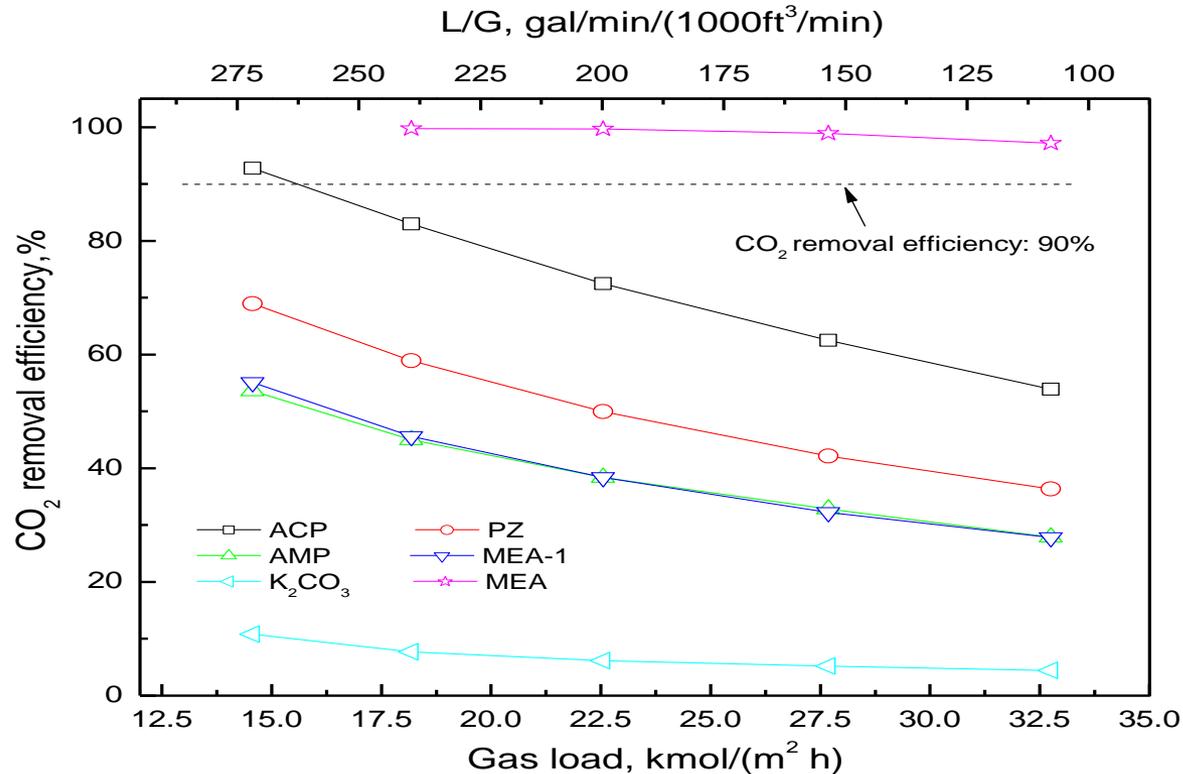
Progress and Current Status

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Apparatus for CO₂ Absorption



CO₂ Absorption by Chemically Regenerated Solvents



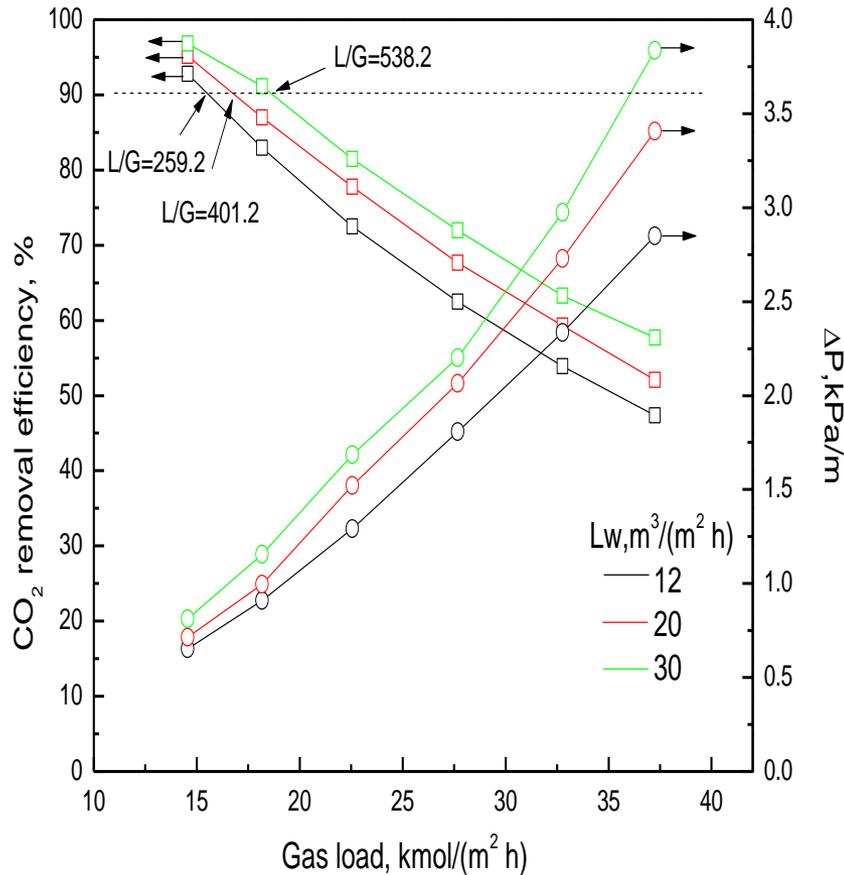
- Chemically regenerated solvents were not as good as thermally regenerated MEA
- ACP was the best among all chemically regenerated additives tested

ACP Parametric Study

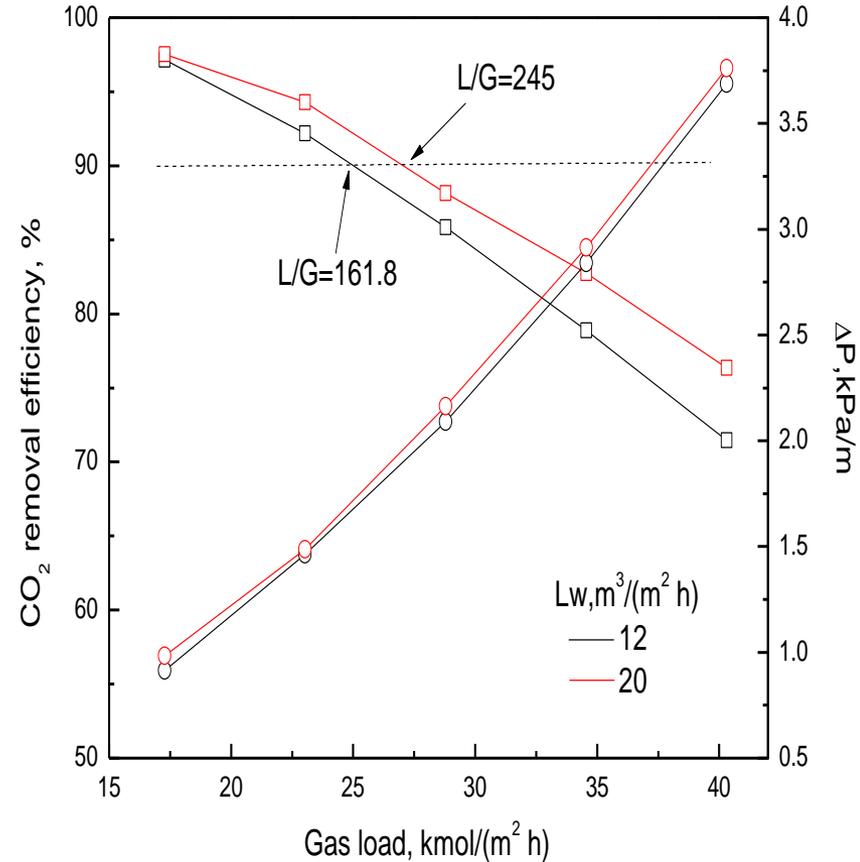
Effect of CO₂ Concentration on Absorption



15%

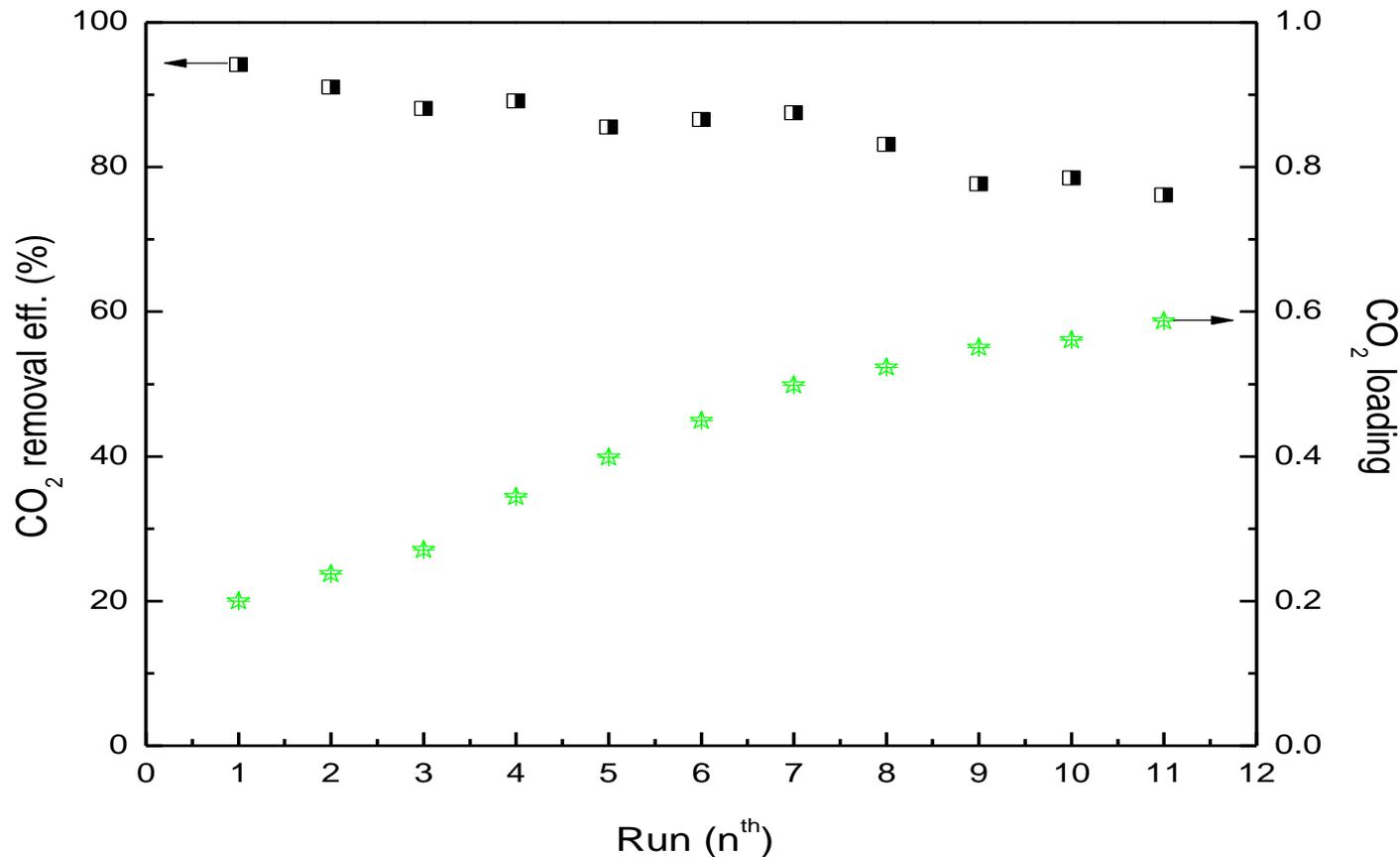


5%



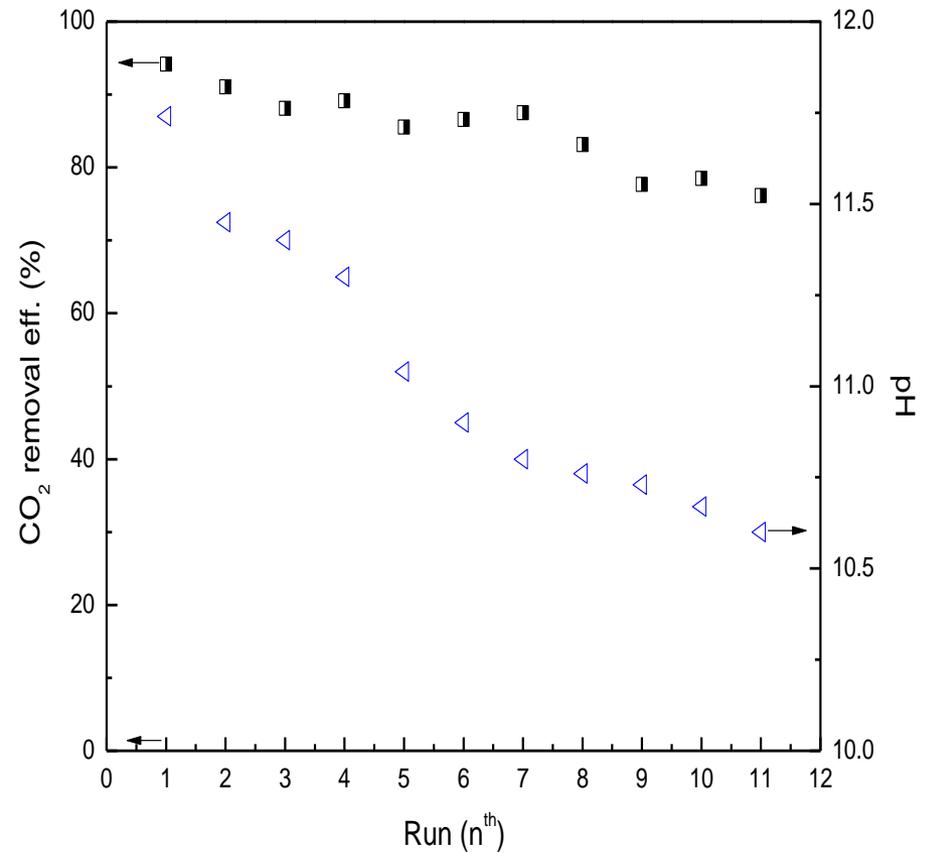
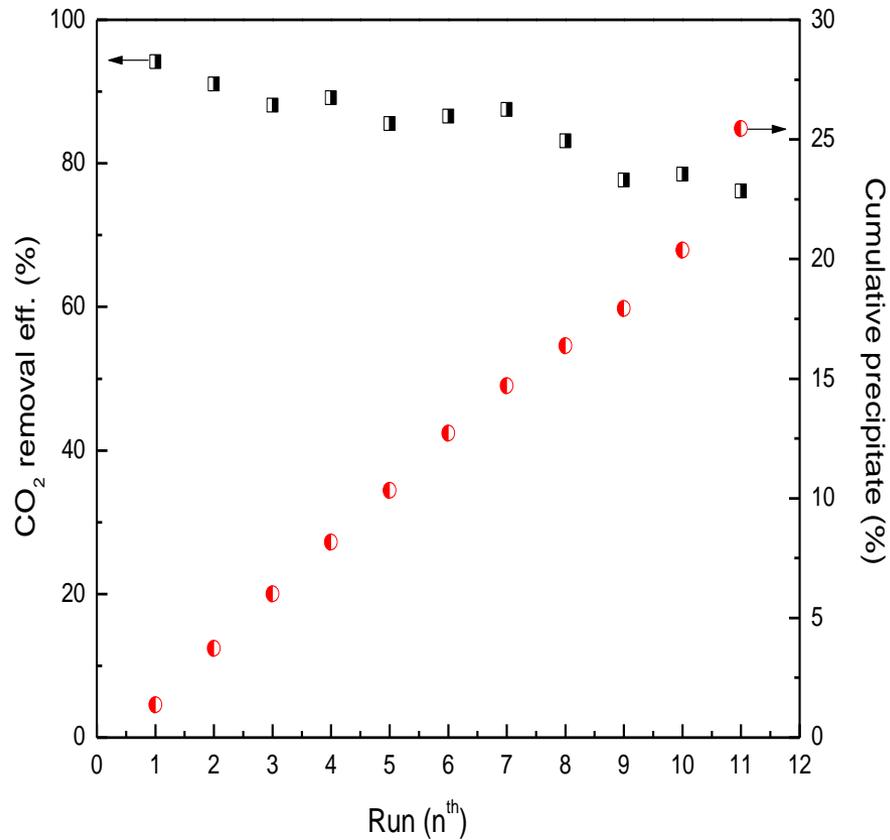
- CO₂ removal efficiency increases with decreasing CO₂ concentrations

ACP Multiple Runs



- Solutions filtered to remove solids from each run and filtrate used for next run
- Absorption efficiency decreased with the increase of CO₂ loading
- CO₂ removal efficiency of 85% with a loading range of 0.4, by averaging all runs

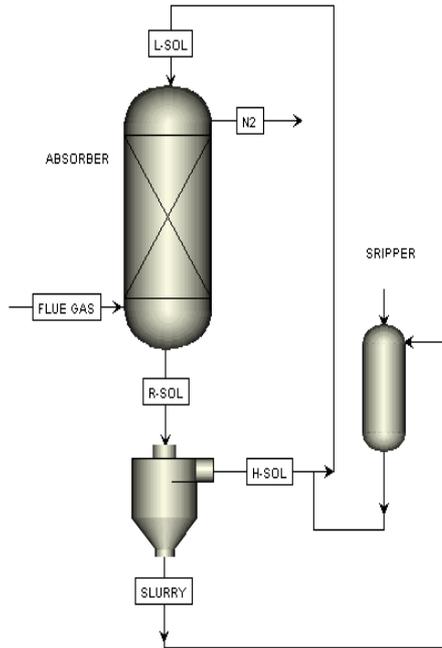
ACP Multiple Runs Solid Formation & Solvent pH



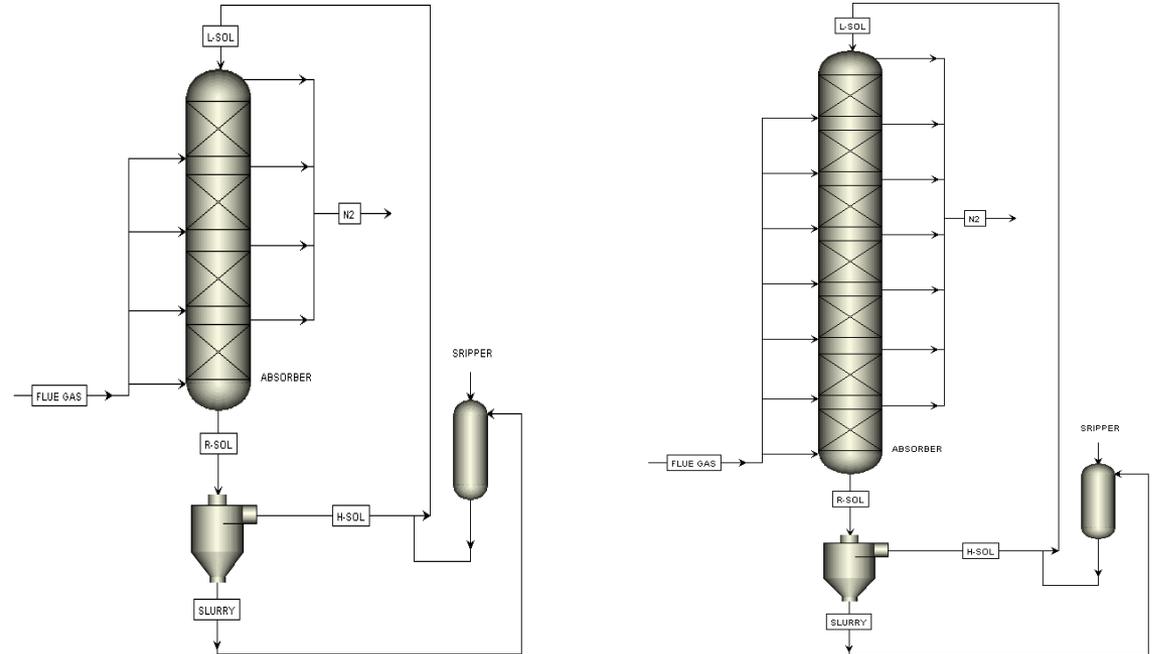
- KHCO₃ solid produced building up from 1st to 11th run
- pH decreased with increasing CO₂ absorption runs

ACP Absorption Results

Single gas feed absorption column



Multi gas feed absorption column



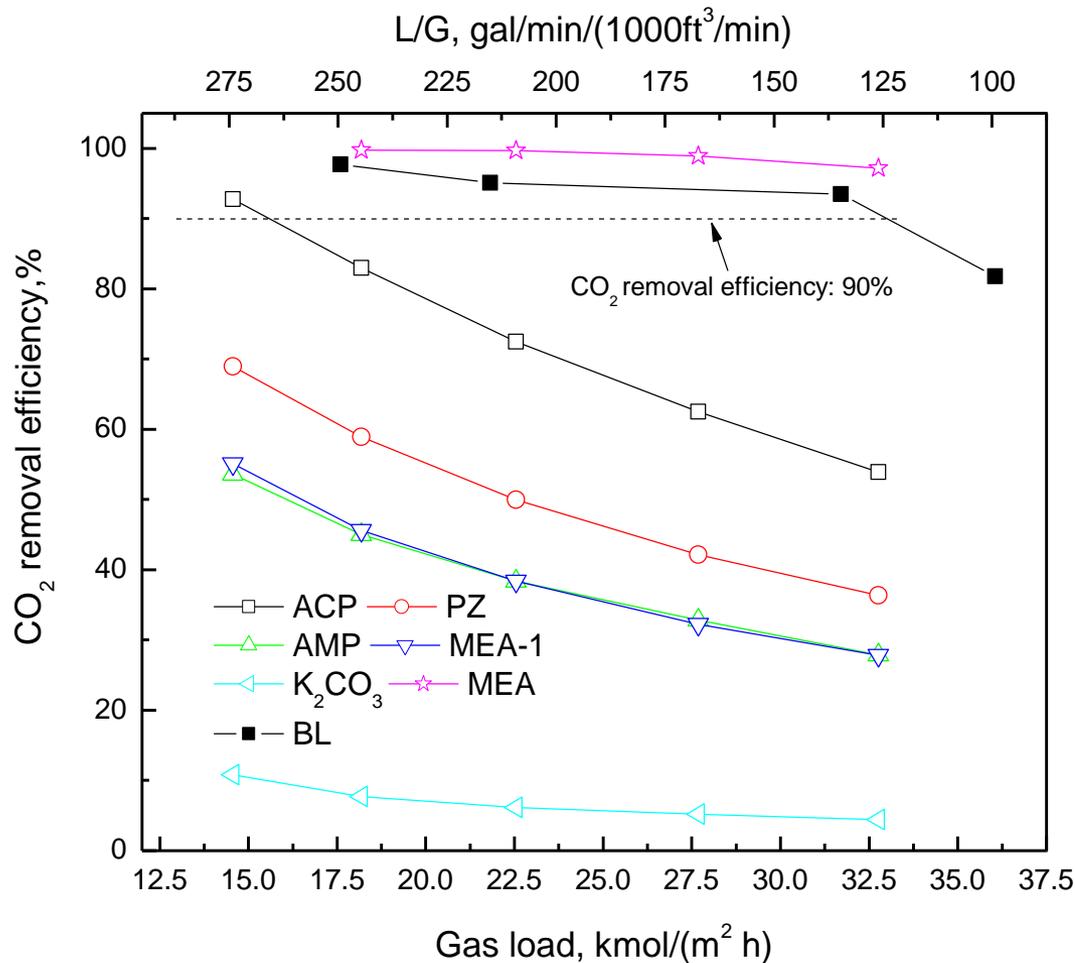
CO₂ ab. 94%
L/G 275
Slurry/solvent 2% w.

91%
 69
 11.5% w.

89%
 40
 20.6% w.

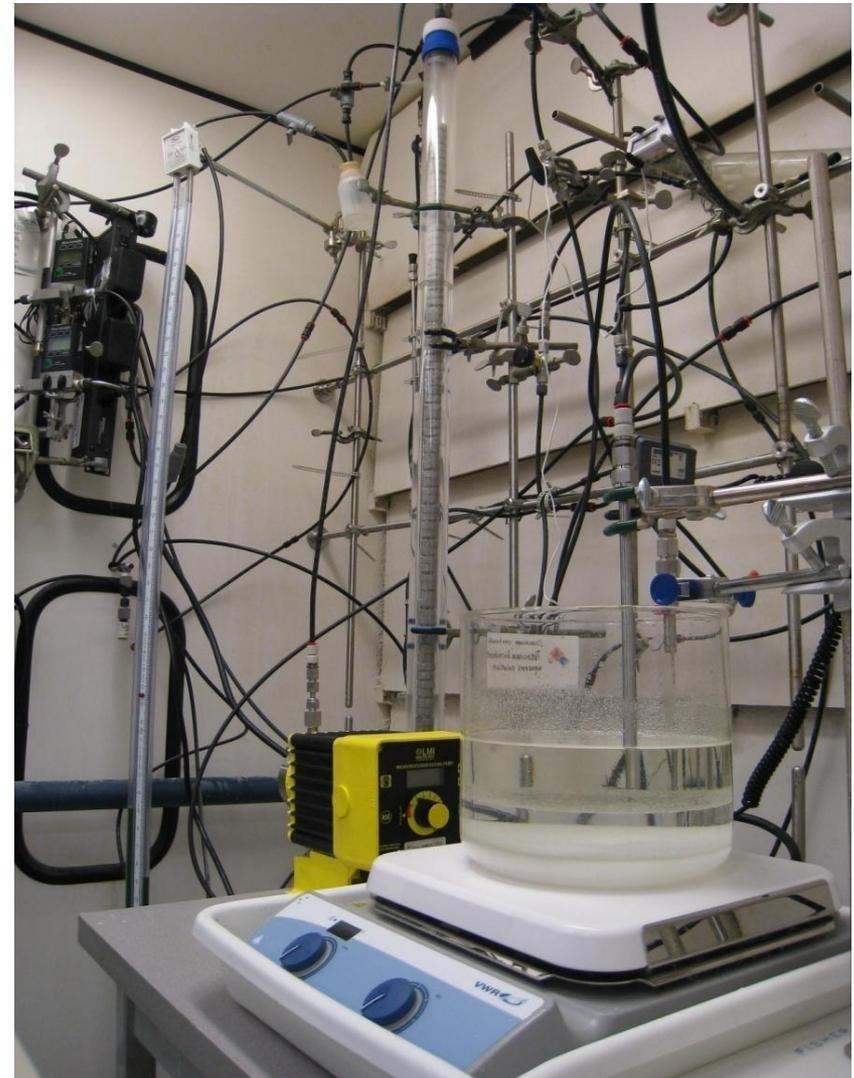
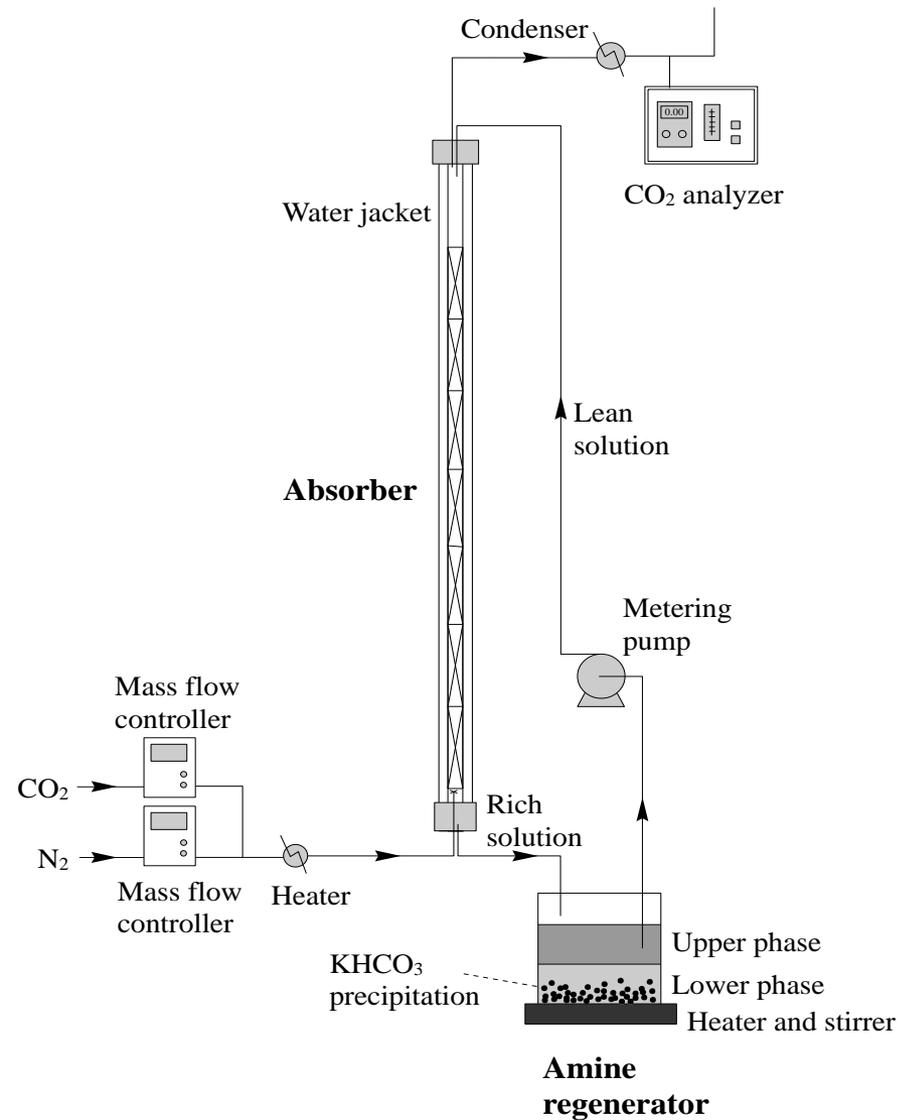
- Problems may occur if too much solid formed in the absorber → control loading & temp.

CO₂ Absorption by Chemically Regenerated Solvents

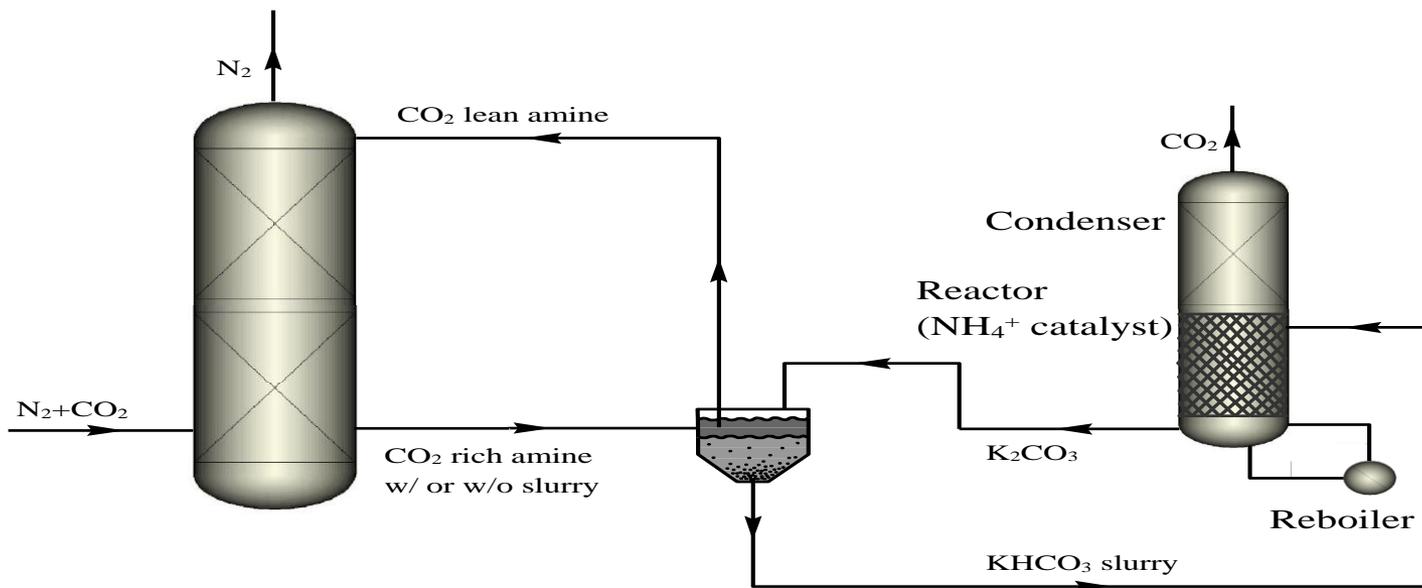


- BL regenerated by chemical methods in amine regenerator:
 - * exhibited CO₂ removal efficiency near MEA regenerated by steam stripping
 - * forming two phases,
 - * w/o producing solid in absorber

Apparatus and Phase Separation



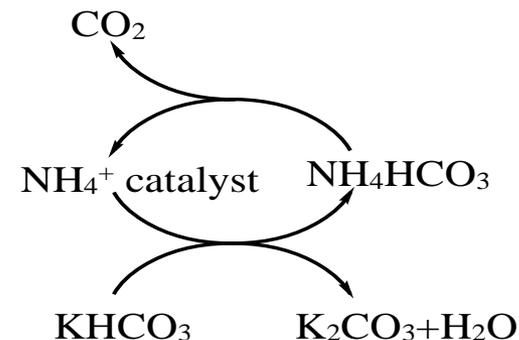
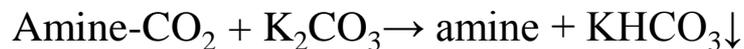
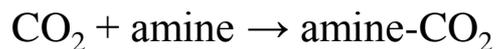
Conceptual Process Configuration



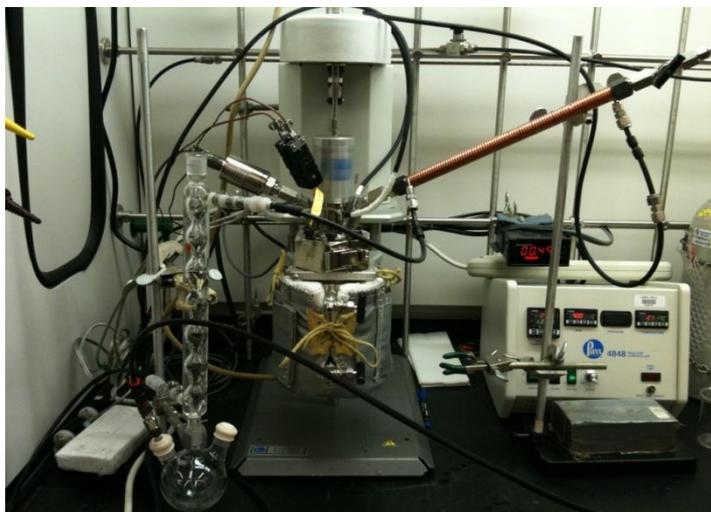
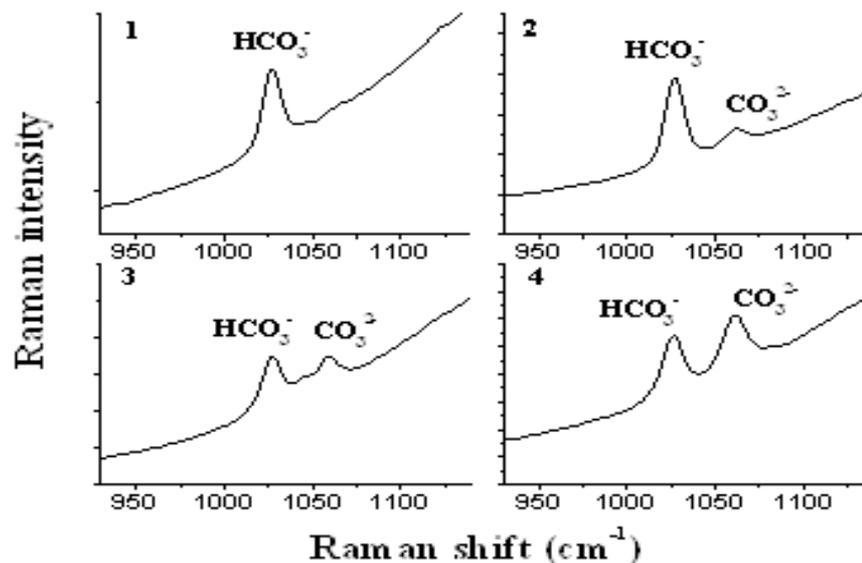
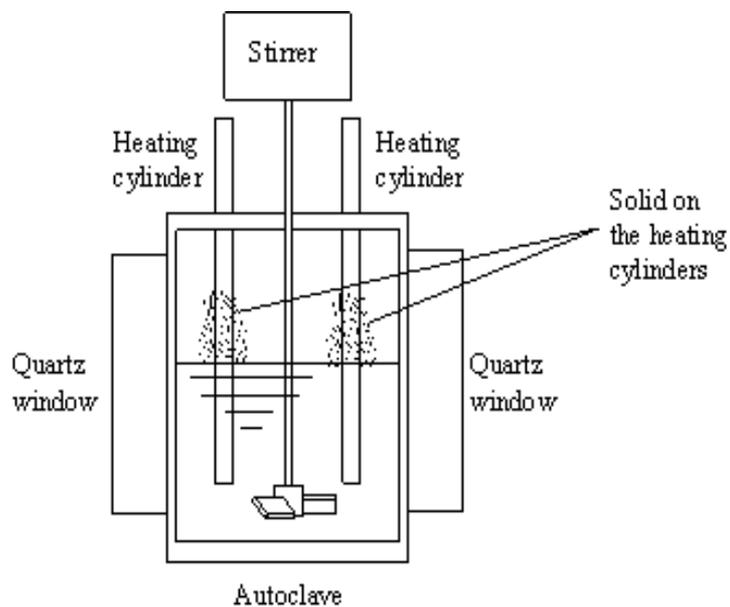
Absorber

Amine regenerator

K₂CO₃ regenerator



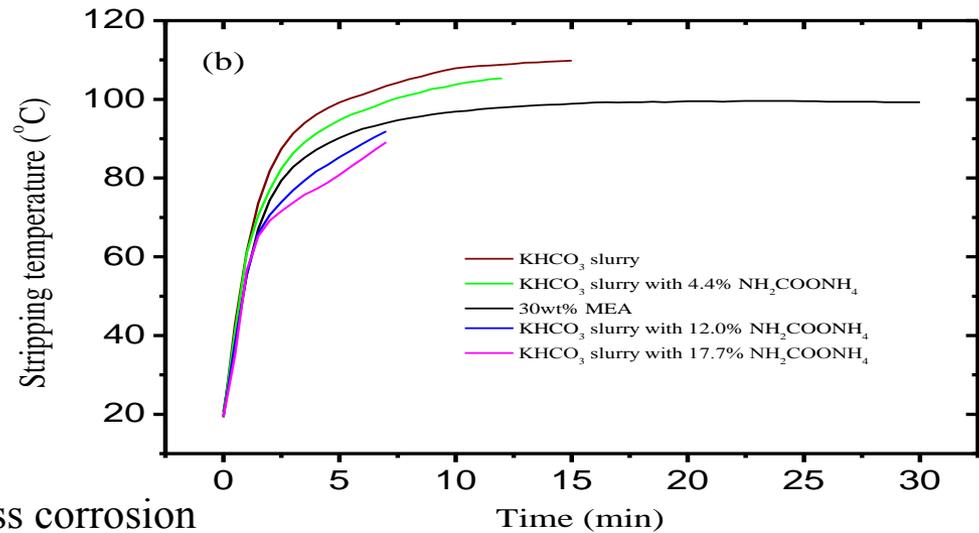
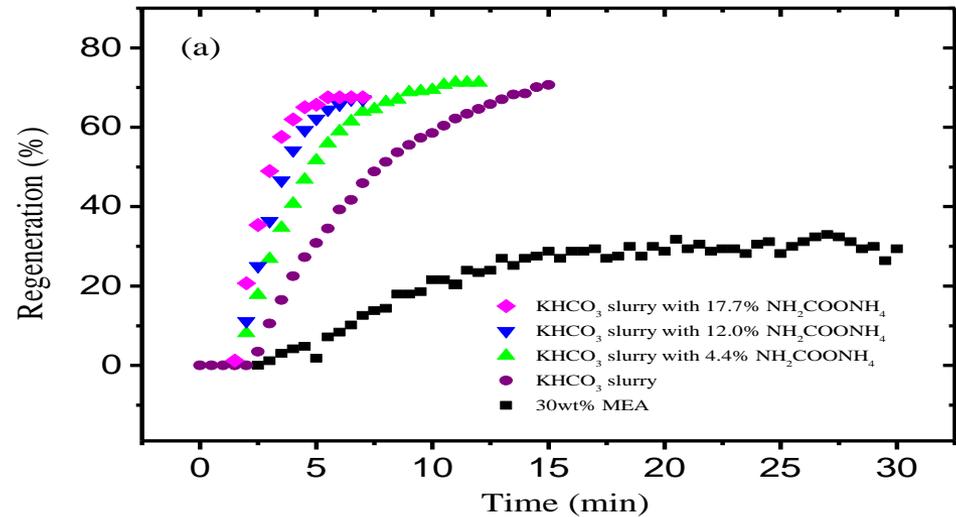
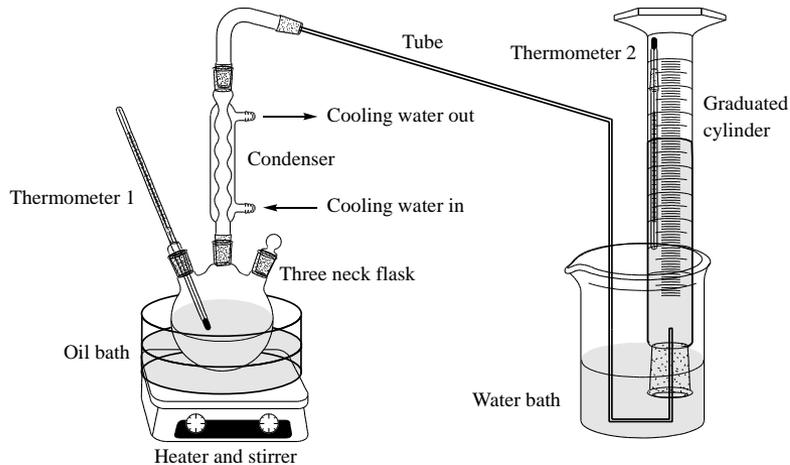
High Pressure Chemical Regeneration of K_2CO_3



- KHCO_3 slurry was heated and stirred under NH_3 pressure in the autoclave
- Solid material continued to build up around the heating rods above the surface of the slurry
- Raman spectra exhibited increasing $\text{K}_2\text{CO}_3/\text{KHCO}_3$ over time

Regeneration of K_2CO_3 @ ~1 atm

Batch System CO_2 stripping Kinetics



- CO_2 production rate and solvent temperature change over heating time
- Ammonia additives increased the conversion rate of $KHCO_3$ to K_2CO_3 and decreased solvent temperature

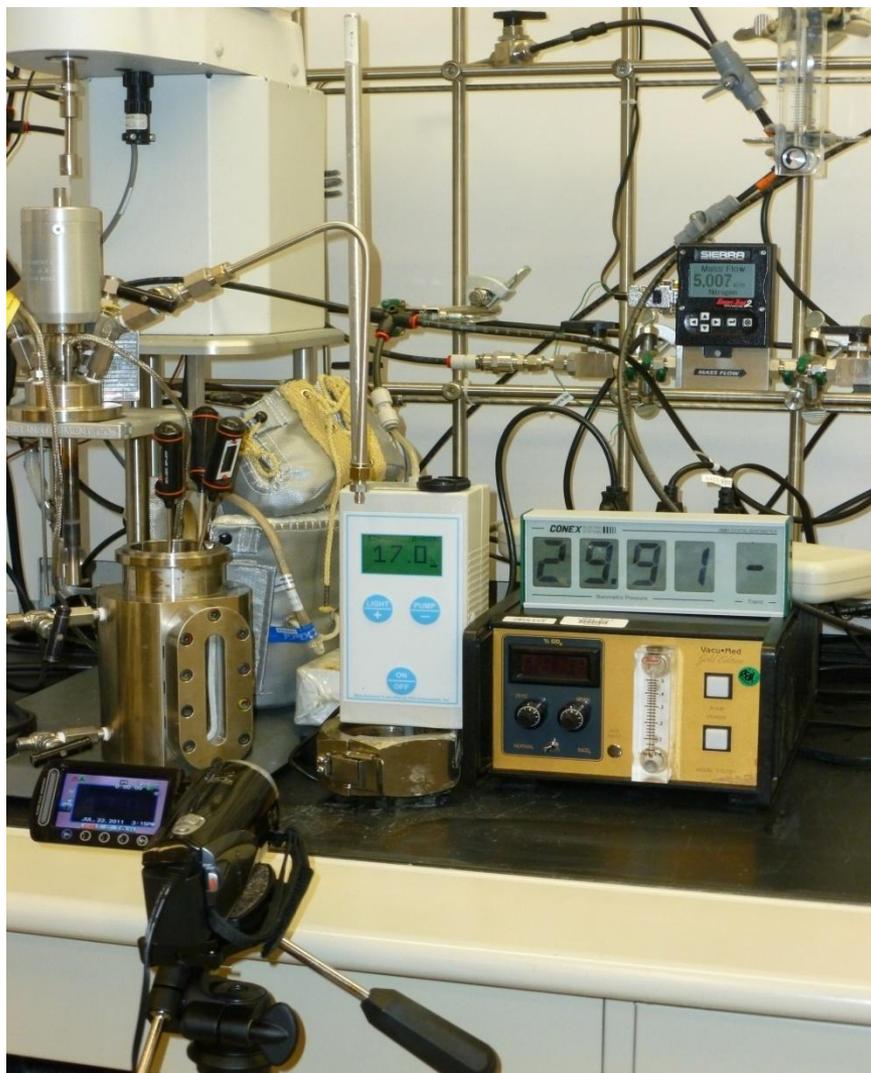
Benefits:

- Reduce regenerator size
- Lower temp results in less sensible heat and less corrosion

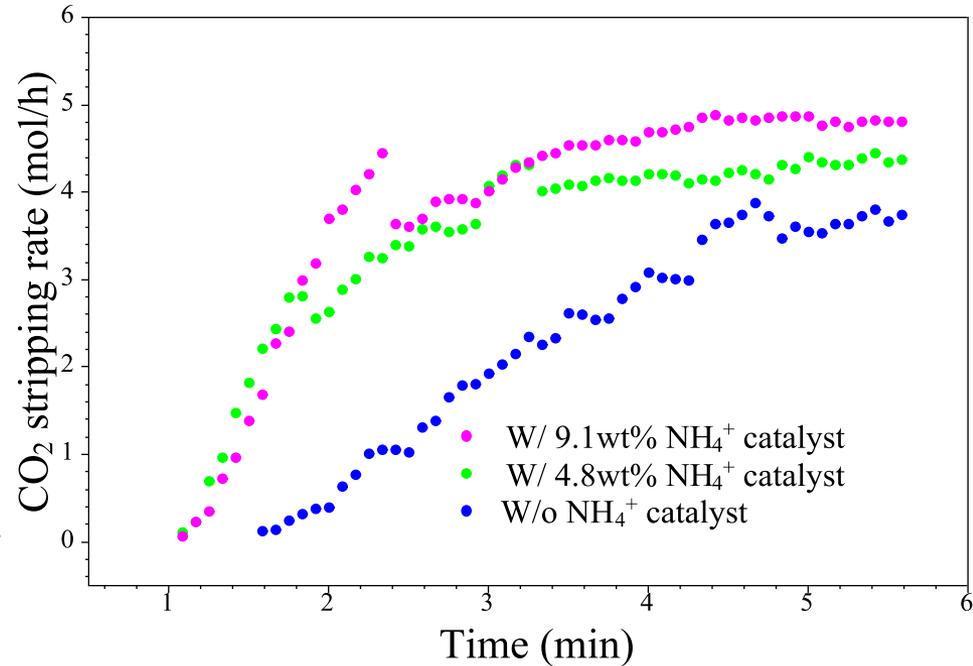
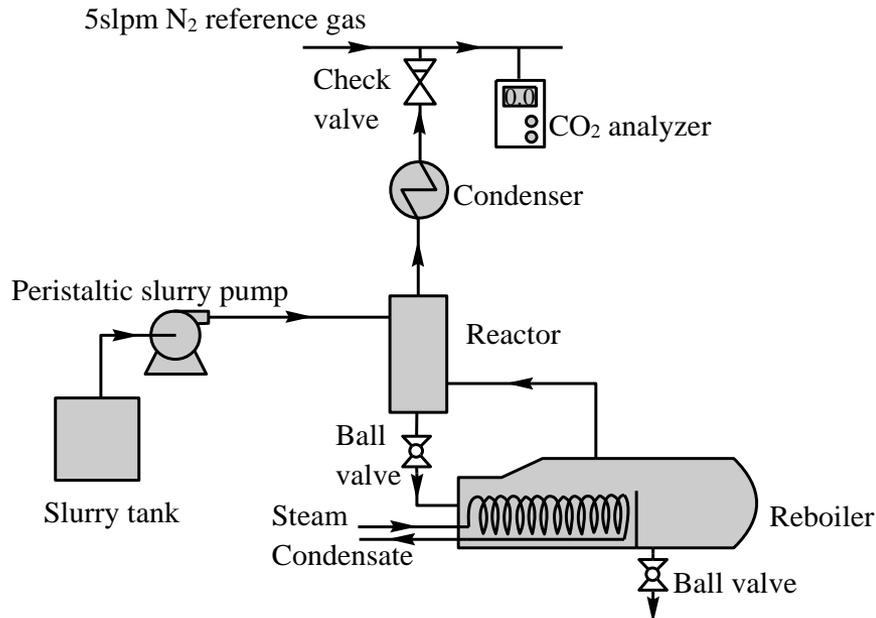
Flow System Stripping Apparatus



CO₂ Production & K₂CO₃ Regeneration



Flow System CO₂ stripping Kinetics



Reactor temperature (°C)	Steam flowrate (g/min)	m(KHCO ₃)/m(water) in slurry	Slurry inlet rate (g/min)	Volume of reactor (ml)	Volume of reboiler (ml)
75~85	25	1	60	135	300

Performance Levels



Task	June 2008 - May 2009	June 2009 - May 2010	June 2010 - May 2011	June 2011 - May 2012	June 2012 - May 2013
1. Install walking humhoods Acquire system components	100%				
2. Setup CO2 capture system Determine Raman efficiencies		100%			
3. Test CO2 absorption promoters for K2CO3 aqueous and organic solutions			85%		
4. Investigate conversion of KHCO3 to K2CO3 and ammonium species			80%		
5. Study conditions for NH4 specices regeneration and CO2 production					
6. Conduct system integration and technology transfer					

- The progress of all tasks proceeds according to the schedule.

Plans for Future Development



- **In this project**
 - * Look for better additives
 - * Perform mass and energy balance
 - * Conduct integrated absorption and regeneration tests
 - * Investigate chemistry involved
 - * Computer modeling
 - * Technology Transfer
- **After this project**
 - * Scale up demonstration

Contact & Acknowledgement



- **Lawrence Berkeley National Laboratory**
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