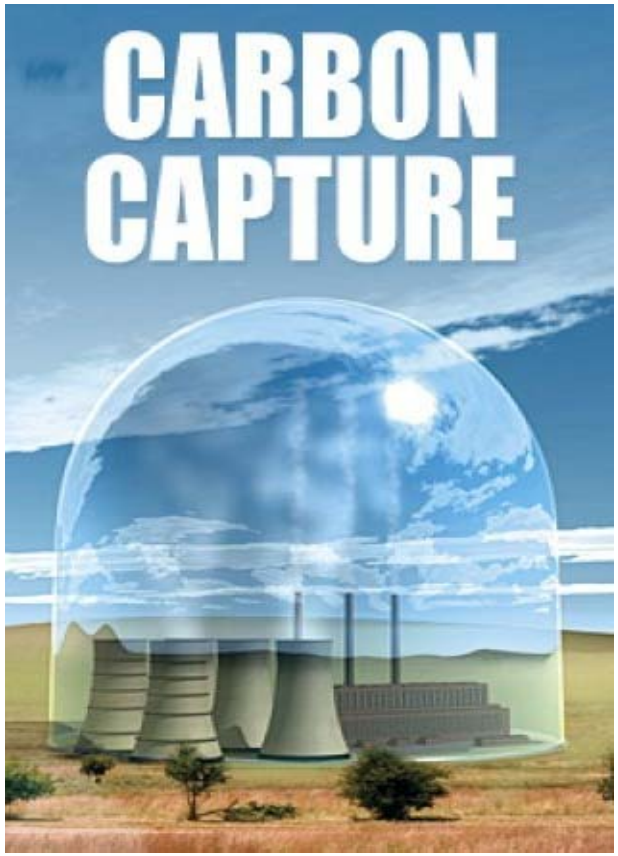
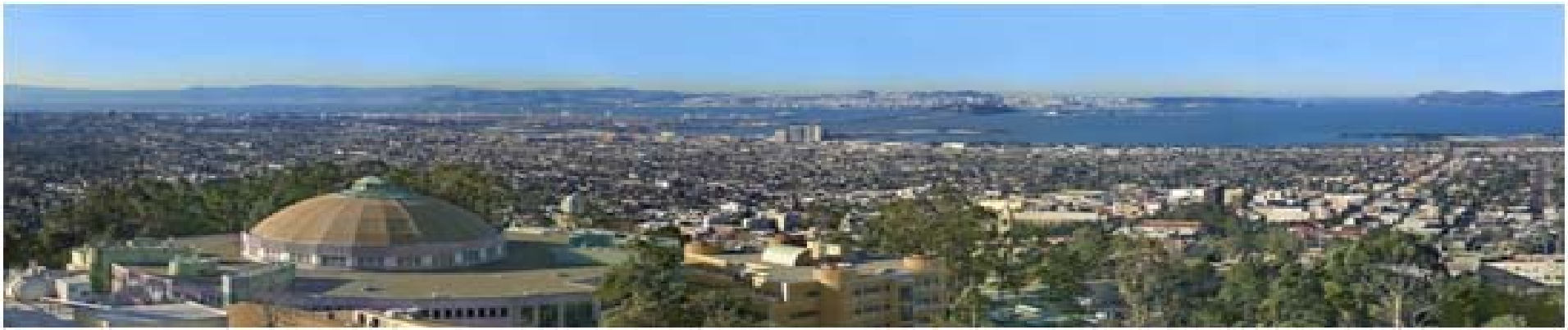
Developing Chemical Additives for Aqueous Ammonia to Reduce CO_2 Capture Cost



Lawrence Berkeley National Laboratory



The Lab at a Glance

11 — Nobel Laureates ; 55 — Nobel Laureates either trained here or had significant collaborations
13 — National Medal of Science members ; 61 — National Academy of Science members
$700 Million — Contributed to the local economy annually
800 — University students trained each year ; 4,000 — Employees ; 200 — Site acreage

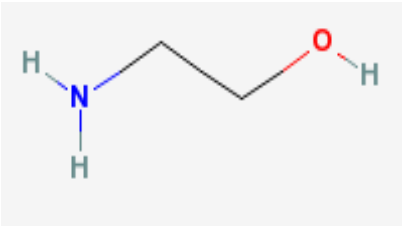
- Berkeley Lab was founded in 1931 by Ernest Orlando Lawrence, a UC Berkeley physicist who won the 1939 Nobel Prize in physics for his invention of the cyclotron.
- Berkeley Lab is a member of the national laboratory system supported by the U.S. Department of Energy. It is managed by the University of California (UC) and is charged with conducting unclassified research.
- Located in the hills above the UC Berkeley campus that offers spectacular views of the San Francisco Bay.
- Its budget for 2008 was approximately $600 million.
- Technologies developed at Berkeley Lab have generated billions of dollars in revenues, and thousands of jobs. The overall economic impact on the global economy is an estimated $1.4 billion a year.

Project Overview and Status

June 2008	- Project received funding ($200 K)
June - December 2008	- Laboratory renovation to meet DOE safety standards
	- Equipment acquisition and calibration
January 2008 to present	- Set up apparatus
	- Perform preliminary experiments
Participants:	- Ted Chang, T.L. Hsiung, Y. Li (LBNL)
	- Chuck Miller (NETL)

Background and Objective

MEA

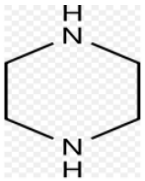


Sterically hindered amines

KS-1, 2, and 3
Castor-1
PSR
Flexsorb PS

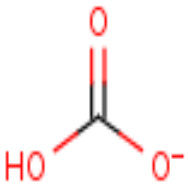
Promoted amine

MDEA
+

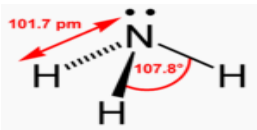


PZ

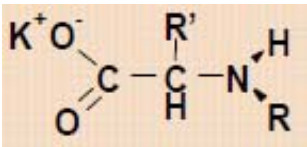
- **Existing and proposed solvents**
- **Each has advantages and challenges**
- **Project objective:**
  - **evaluate solvent systems**
  - **overcome the challenges**
- **Current focus is on Aqueous NH_3**
- **Goal:**
  - **90% CO_2 capture efficiency**
  - **< 35% increase in electricity cost**



Potassium carbonate



Ammonia

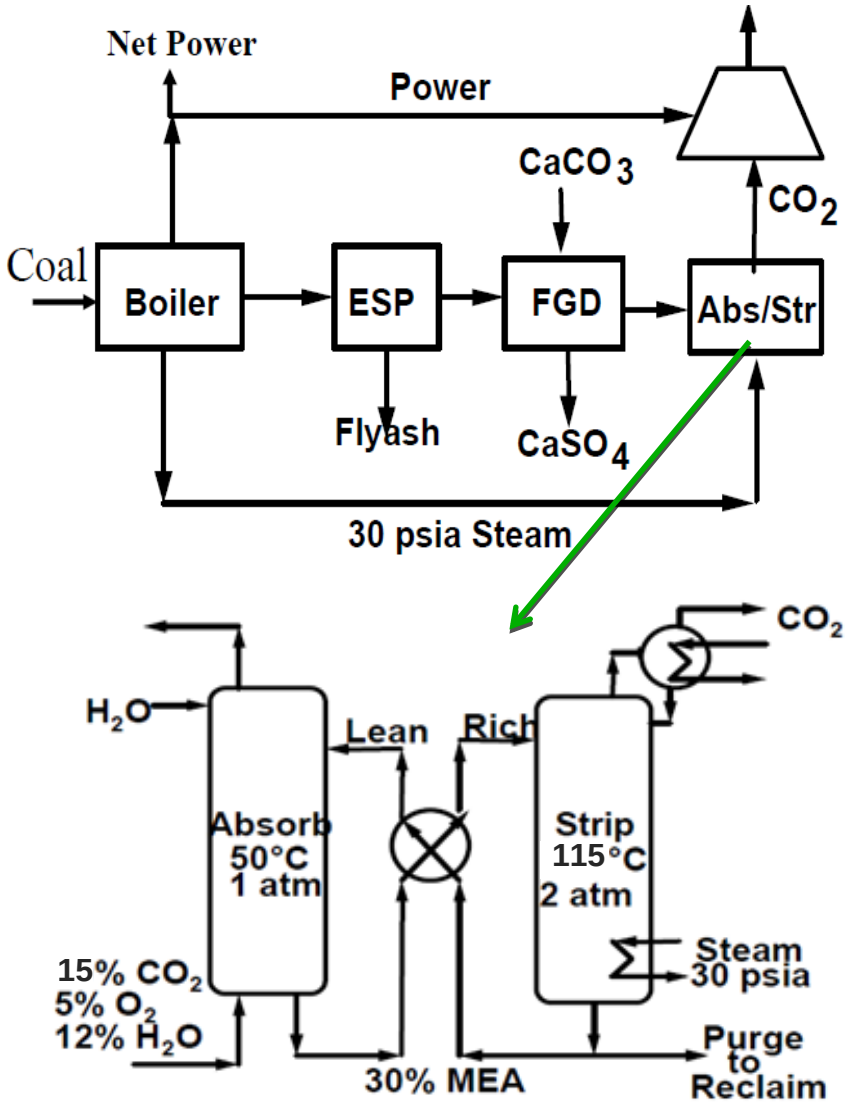


Amino acid salts

10^{18}

Ionic liquid

Baseline: MEA



Well established, but has challenges

- High energy consumption for solvent regeneration
- High equipment corrosion rate
- Amine degradation, high solvent makeup rate
- Low CO_2 loading capacity

Where are costs?

- Energy = 20-40% of power plant output
  - Steam for stripping
  - Gas pressure drop
  - CO_2 compression
- Amine degradation = 10% of cost
  - oxidative, thermal, chemical
- Capital cost

Electricity Cost:

- 65% increase if implemented

Responses to MEA's Challenges

- **Less corrosion and solvent degradation:**

  Fluor's Econamine FG process employs chemical additives as inhibitor

- **Lower energy consumption & corrosion:**

  MHI/KEPCO functionalizes MEA, forming hindered amine (KS-1, 2, 3), to weaken bonding with CO_2

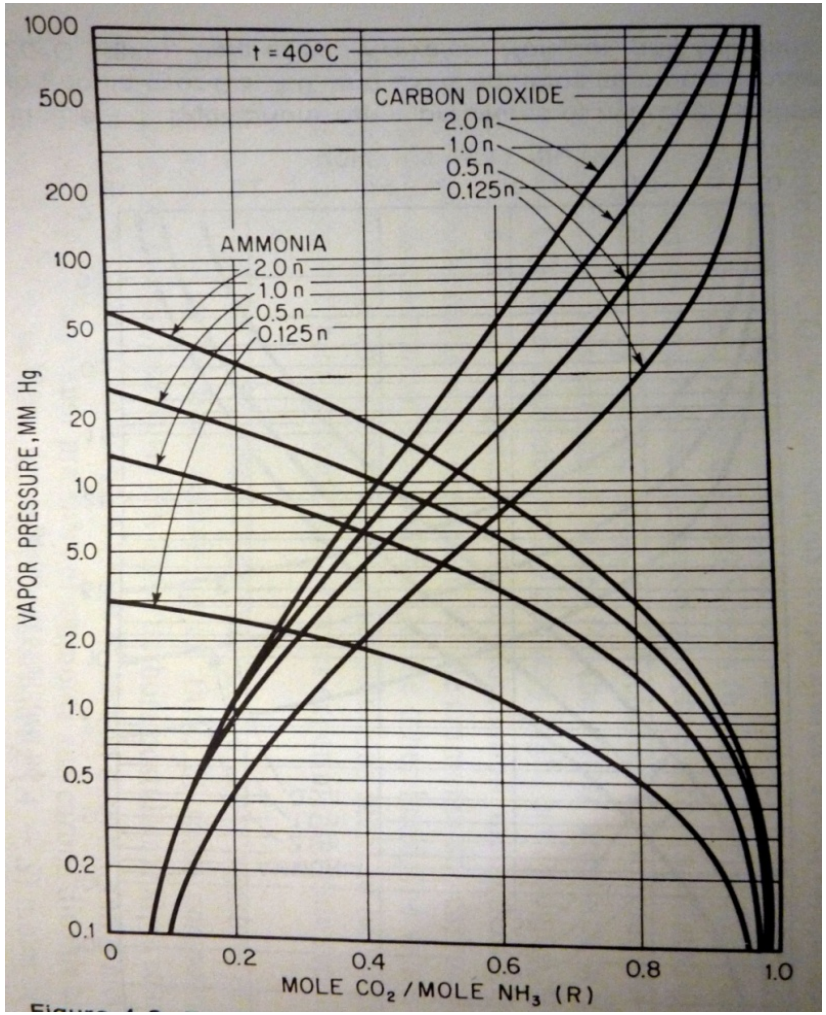
- **Lower capital cost and less energy consumption with smaller absorber and less packing/pressure drop:**

  UT Austin research blending MEA with piperazine to increase CO_2 absorption kinetics

Aqueous Ammonia (AA)

- Ciferno, et. al., performed an economic scoping study
  - Advantages:
    - low reagent cost
    - high CO_2 loading capacity
    - low heat requirement for regeneration
  - Challenges:
    - minimizing NH_3 loss
    - accommodating flue gas temperature
    - improving absorption kinetics
- This project is currently investigating methods to overcome these challenges

Recognize the challenges (High Vapor Pressure of NH_3)



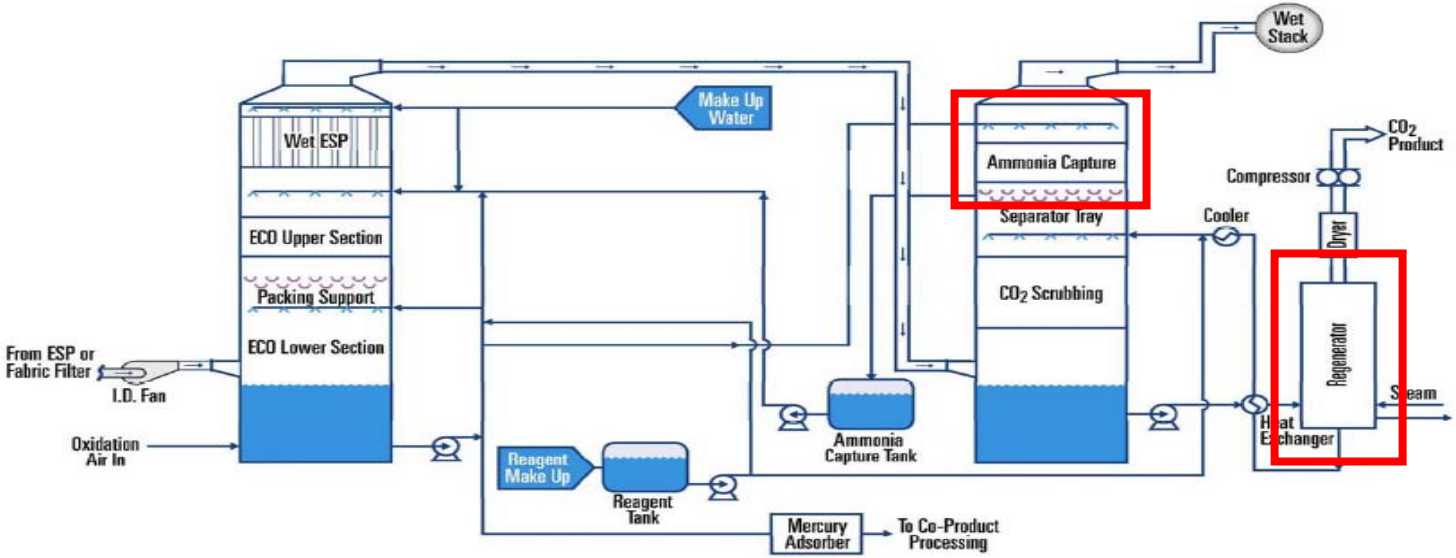
NH_4OH $(NH_4)_2CO_3$ NH_4HCO_3

Van Krevelen, DW et al., (1949)

- NH_3 vapor pressure was measured over NH_3/CO_2 solutions between 0.125 N to 2 N at 40°C
- Estimated to be 45 mm Hg ($4x10^4$ ppm) over 6 N $(NH_4)_2CO_3$ solution
- Vapor pressure increases with increasing pH
- Approaches to challenges
  - Low cost NH_3 recovery method
  - Reduce NH_3 v.p. over solutions

ECO_2 – NETL/Powerspan*

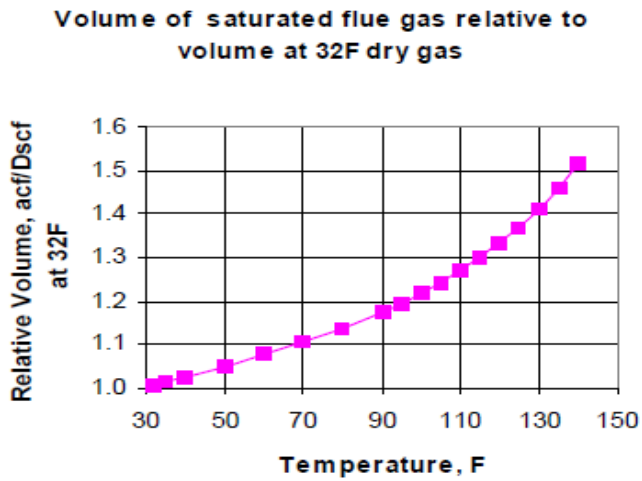
Integrated ECO-SO_2 - ECO_2 Process Flow



- CO_2 capture takes place in ECO2, which is after SO_2 removal in ECO system
- Use of ammonia in ECO makes incorporating CO_2 removal feasible
  - Provides the ability to absorb ammonia vapor and use dilute ammonia streams
  - Ammonia is not consumed in the CO_2 capture process
  - Management of ammonia vapor is key to process success and economics

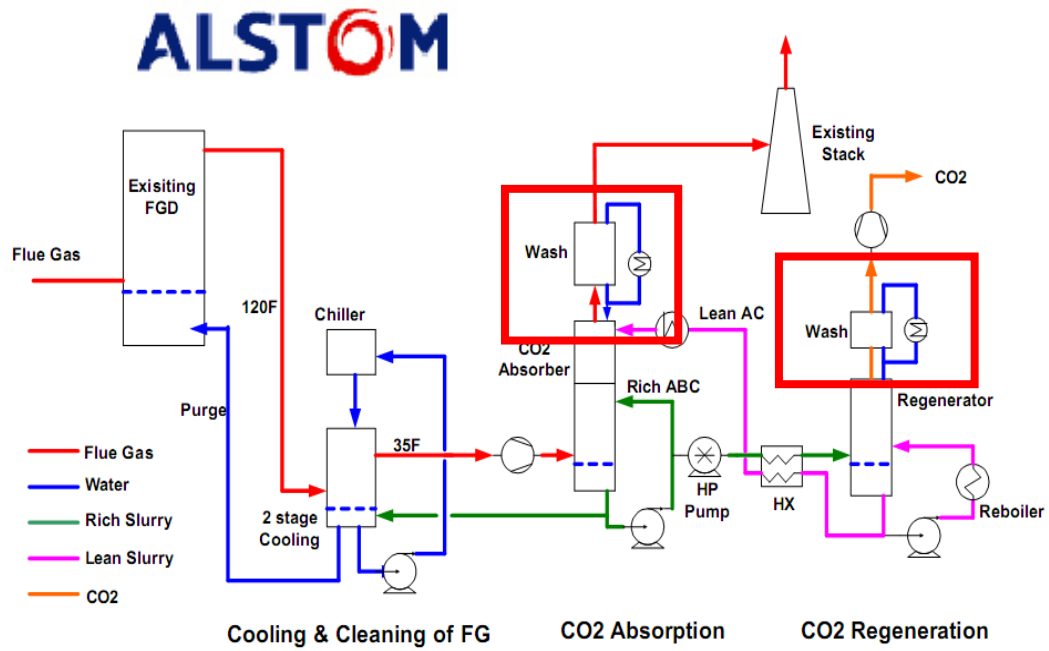
* from Powerspan

Chilled A Process – Eli Gal/Alstom*



- Flue gas cooled to low temp. before entering absorber
- Cooling flue gas to minimize NH_3 emission
- Cooling also results in volume and equipment size reduction

- CO_2 absorption at low Temp
- NH_3 regeneration at high P and T
- Flue gas cooling estimated to consume 1-2 % power output



* from Alstom

Kinetic Consideration

- **Absorber size and amount of packing required to obtain desirable CO_2 absorption efficiencies are dependent on the absorption rate**
- **Absorption rate is proportional to square root of solvent concentration and rate constant**

$$- \ln (p_{CO2\ out} / p_{CO2\ in}) = \{(k\,[C]\,D_{CO2})^{1/2}/(H / P_T)\}\{a\,Z / P_M\,V\}$$

k: rate constant
C: concentration
D_{CO2}: diffusivity of dissolved CO_2
H: Henry's constant
P_T: total pressure of flue gas
a: gas-liquid interfacial area per volume of contact zone
Z: length of gas-liquid contact zone
P_M: molar density of flue gas
V: flue gas velocity in the absorber

Reaction Rates of CO_2 with Solvents

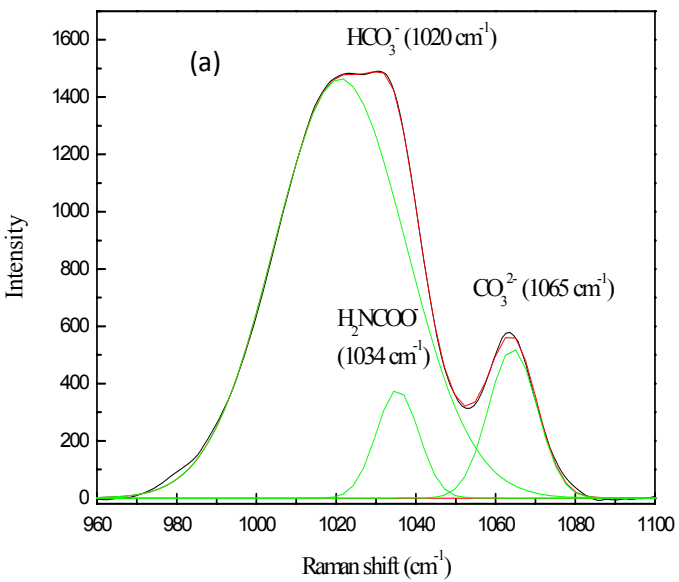
Solvent	C (M)	k @ 25°C (M^{-1} s^{-1})	$(kC)^{1/2}$
NH_3[a]	7 (12%)	3.98×10^2	5.20×10^1
MEA[b]	7 (30%)	4.70×10^3	18.10×10^1
OH^-[c]	10^{-1} (pH=13)	1.40×10^4	3.74×10^1
PZ[d]	2	1.02×10^5	45.20×10^1
Alanine[e]	3	2.99×10^3	9.47×10^1
Methionine[e]	3	1.61×10^3	6.95×10^1
Glutamate[e]	3	2.83×10^3	9.21×10^1
Sarcosine[e]	3	5.96×10^3	13.37×10^1
Proline[e]	3	1.43×10^4	20.71×10^1

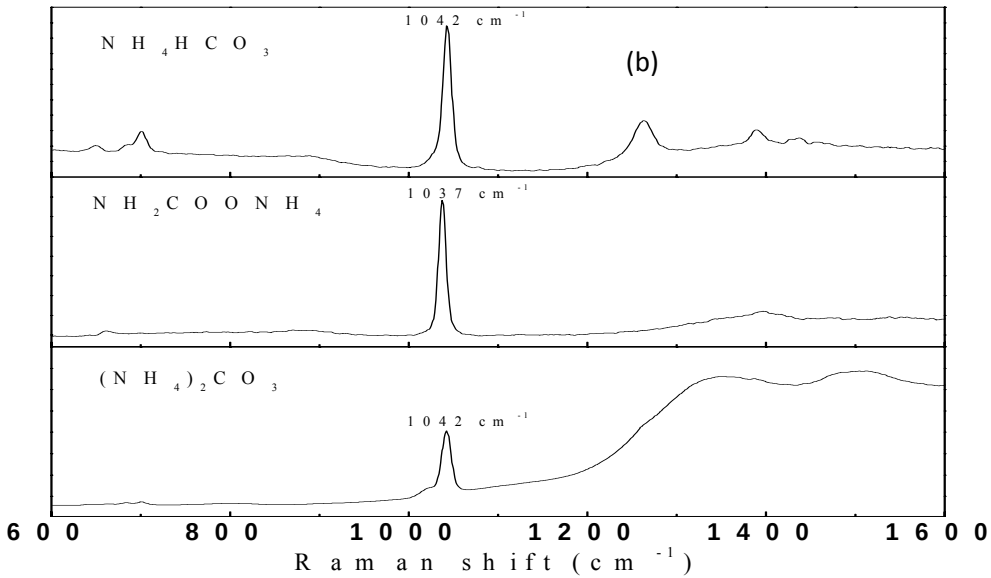
- **About 3 times more packing needed for AA, compared with MEA**

a: Pinsent et.al; b: Barth et.al.; c: Cents et.al.; d: Rochelle et.al.; e: Versteeg et.al.

Methodology

- Solution and solid species: analyzed by Laser Raman and/or NMR
- Gaseous species: CO_2 and NH_3 analyzed by infrared and/or UV



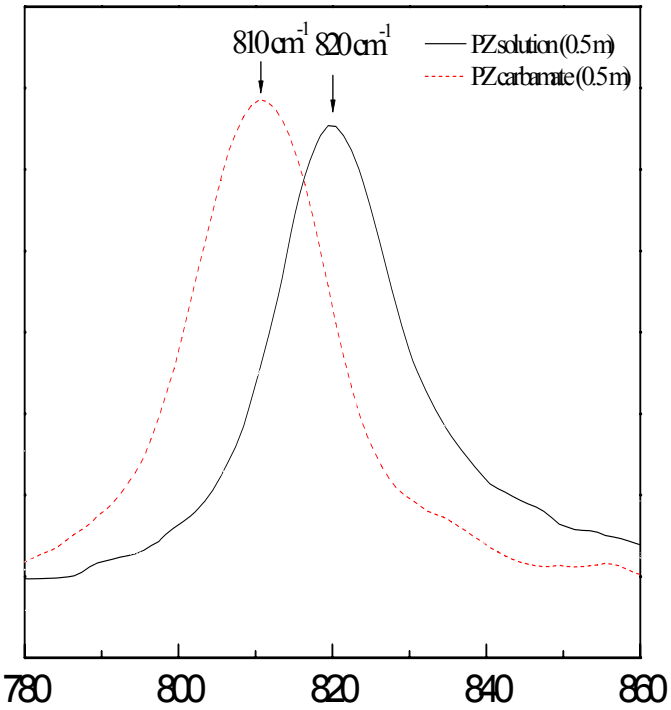


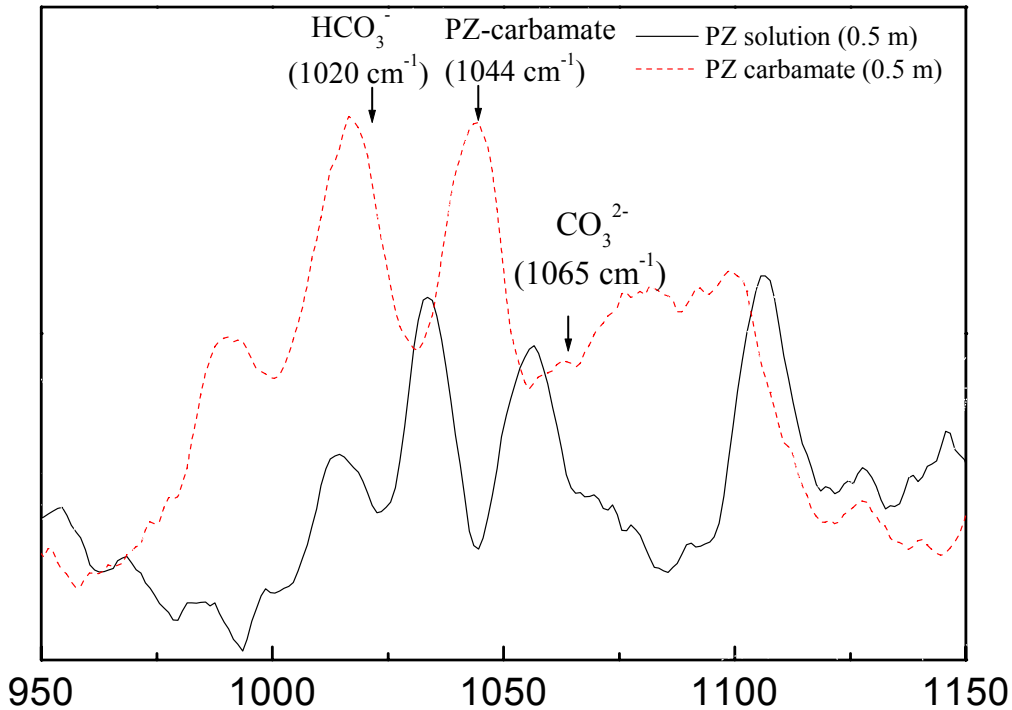
Raman spectra of ammonium species in (a) solutions and (b) precipitates

Solution species - HCO_3^-: 1020 cm^{-1}; H_2NCOO^-: 1034 cm^{-1}; CO_3^{2-}: 1065 cm^{-1}
Precipitates - NH_4HCO_3: 1042 cm^{-1}; NH_2COONH_4: 1037 cm^{-1}; $(NH_4)_2CO_3$: 1042 cm^{-1}

Methodology

- **Promoted K_2CO_3 with PZ system**





Raman shift (cm^{-1})

Raman spectra of PZ and PZ carbamate species

Solution species: PZ: 810 cm^{-1} ; PZ carbamate: 820 cm^{-1}; HCO_3^-: 1020 cm^{-1}; CO_3^{2-}: 1065 cm^{-1}

Project Research Direction

- **Chemical additives were employed as inhibitors for equipment corrosion and reagent degradation in the MEA system, and activators to improve CO_2 absorption kinetics in the MDEA or K_2CO_3 system.**

- **This project will investigate chemical additives and appropriate process configuration for aqueous ammonia to reduce NH_3 loss and improve CO_2 absorption kinetics.**

Acknowledgments

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- LBNL would like to thank Chuck Miller of NETL for technical guidance and feedbacks to the project.

Backup Slides

Econamine Costs

- **Steam consumption** – most important component of operating cost
  - Less than 4.2 GJ/t CO_2 (3.6×10^6 Btu/t CO_2)
- **Solvent loading and circulation rate** – max. 0.5 mole CO_2/mole MEA
  - Remove ¼ mole CO_2/mole MEA between lean and rich loading
- **Power consumption**
  - Major component: flue gas blower

    Blower + Pumps (circulation and absorber): consume 60 kWh /ton CO_2

    (for 8% CO2 containing flue gas; inversely proportional to CO_2 conc.)
- **Solvent consumption** – 1.6 kg/ton CO_2 for gas-fired
- **Additive consumption** – 20% of cost of makeup amine

* J. Widgetbucks, Recovery of CO_2 from Flue Gases: Commercial Trends, Dec. 28, 2007

Promising Areas for Cost Reduction*

- **Operating Cost**
  - Reduction of steam consumption
  - Integration of power generation with stripper reboiler
  - Reduction of absorber packing pressure drop

- **Capital Cost**
  - Absorber vessel size
  - Absorber and flue gas cooling vessel materials

- **Challenges**
  - New Chemical solvents
  - More sophisticated process design to reduce steam consumption and solvent circulation rate

* J. Widgetbucks, Recovery of CO_2 from flue gases: Commercial trends, Dec. 28, 2007

Gas Absorption Kinetics

- For CO_2 to be absorbed, it has to pass through a gas film and then a liquid film on each side of the gas-liquid interface.

  Their resistances to mass transfer are in series

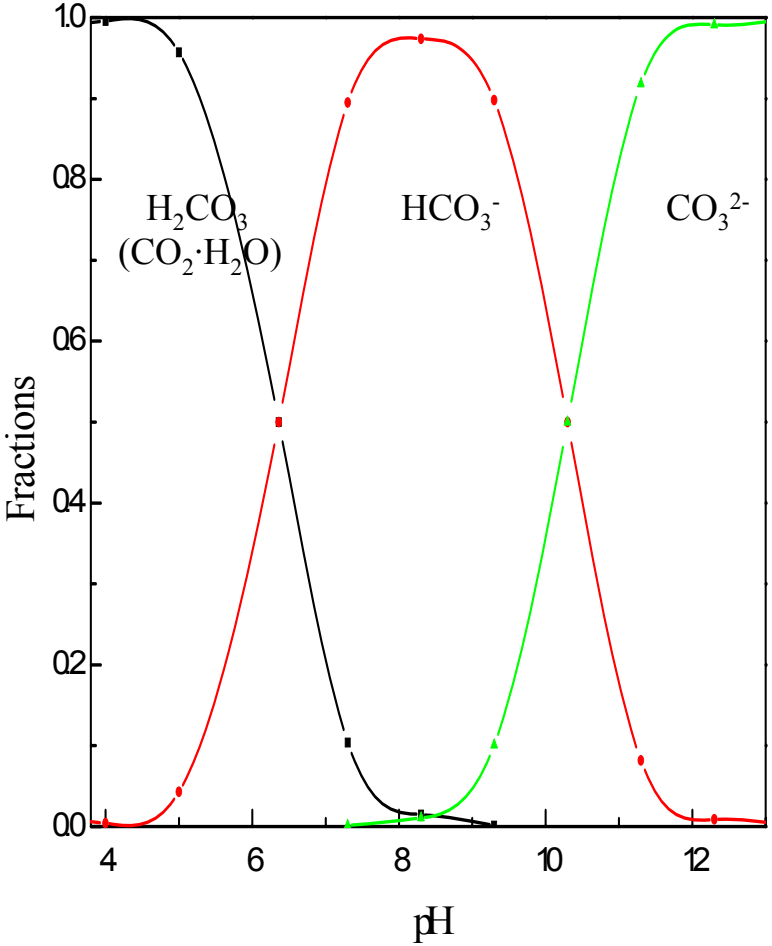
Overall resistance = gas film resistance + liquid film resistance

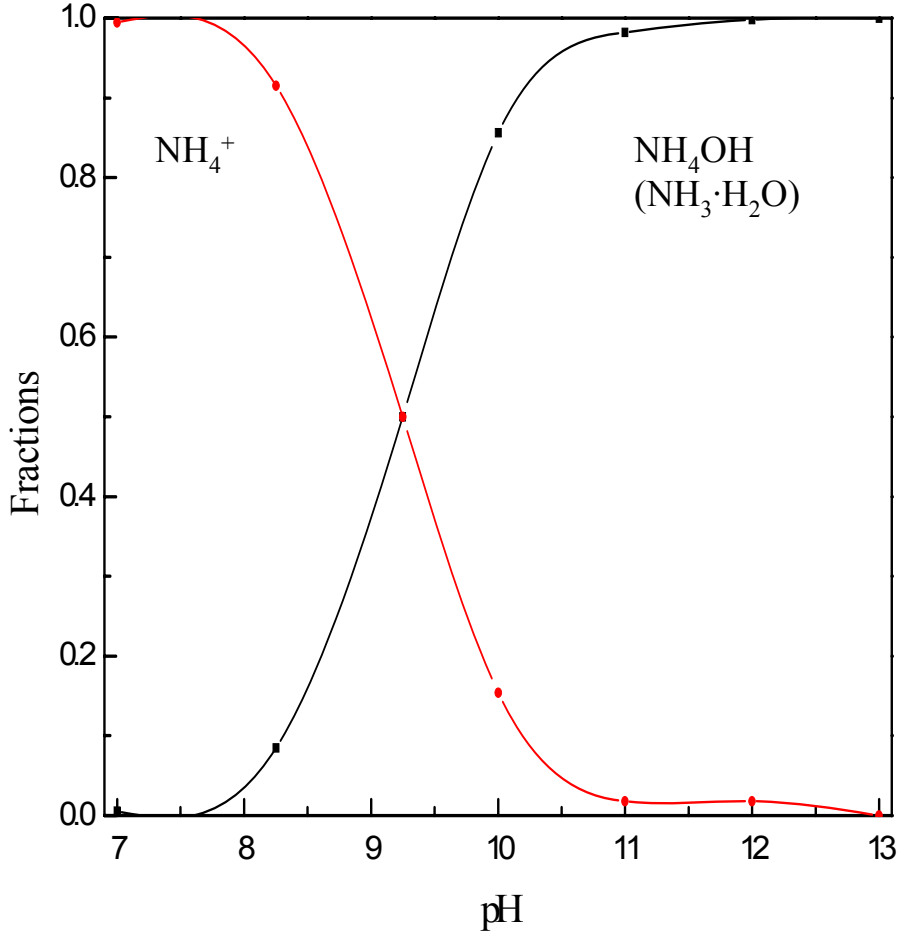
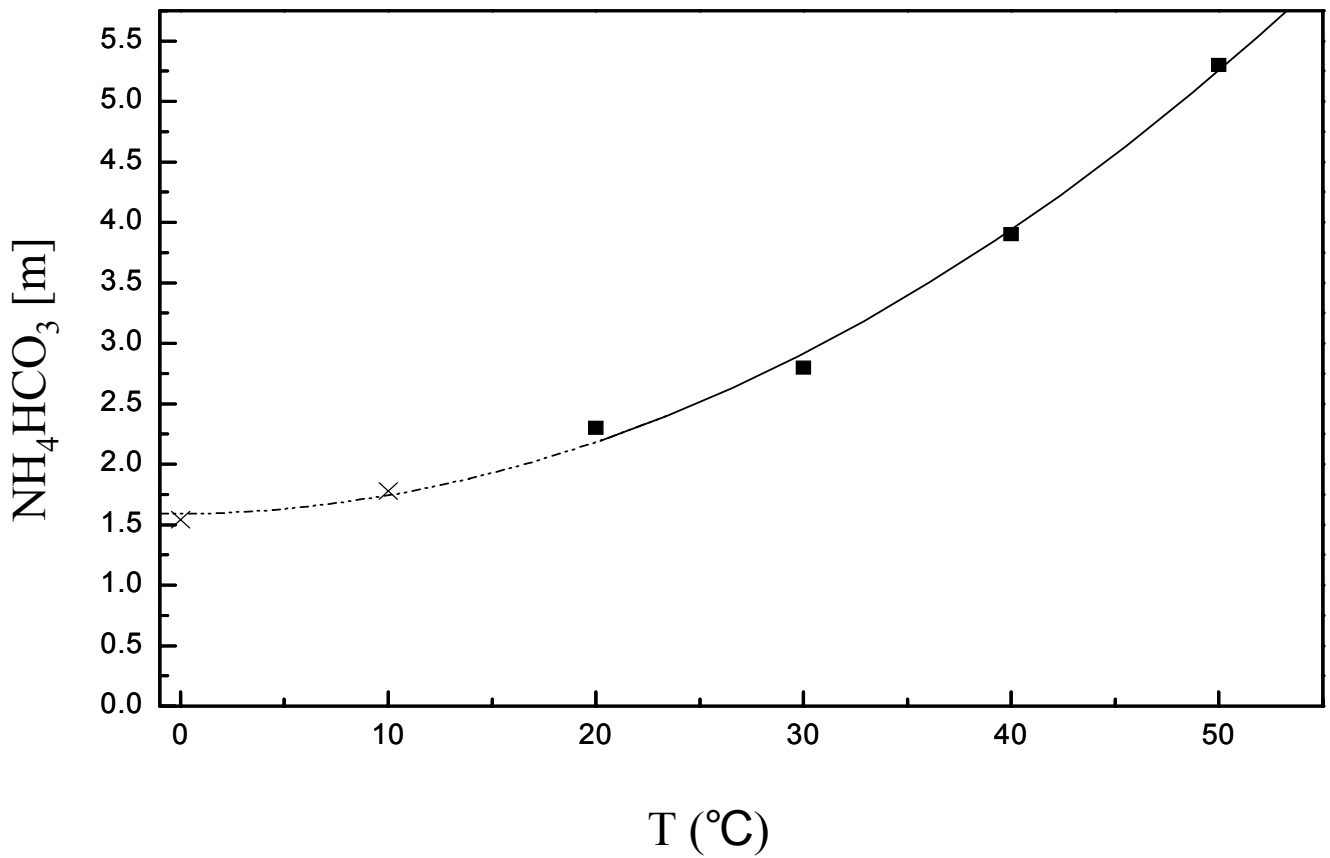
- $NTU = \ln (p_{CO2\ in} / p_{CO2\ out}) = -\ln (p_{CO2\ out} / p_{CO2\ in})$

  $= -\ln (1 - \%\ removal/100)$

  $= \{(k\,[C]\,D_{CO2})^{1/2} / (H / P_T)\}\{a\,Z / P_M\,V\}$

% removal and NTU are about equal for removal of less than 20%


1.0
0.8
0.6
0.4
0.2
0.0
Fractions
H_2CO_3
$(CO_2 \cdot H_2O)$
HCO_3^-
CO_3^{2-}
4
6
8
10
12
pH


1.0
0.8
0.6
0.4
0.2
0.0
Fractions
NH_4^+
NH_4OH
$(NH_3 \cdot H_2O)$
7
8
9
10
11
12
13
pH

Solubility of NH_4HCO_3 vs Temperature