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Development and Evaluation of a Novel Integrated Vacuum Carbonate Absorption Process

(DE-FC26-08NT0005498)

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Advanced Energy Technology Initiative
Illinois State Geological Survey
Institute of Natural Resource Sustainability
University of Illinois at Urbana-Champaign

2010 DOE/NETL CO_2 Capture Technology Meeting

Pittsburgh, PA • September 13-17, 2010

AETI-INRS-University of Illinois at Urbana-Champaign

- Institute of Natural Resource Sustainability (INRS)
  - Five scientific surveys including Illinois State Geological Survey (ISGS)
  - Lead organization of Midwest Geological Sequestration Consortium Partnership
  - 700 scientists and technical support staff
  - Annual budget of $50 million
- Advanced Energy Technology Initiative (AETI)
  - Carbon capture & sequestration
  - Energy-water nexus
  - Combustion-generated air pollution control
  - Materials and systems for energy and environmental applications

Project Overview

Project Objectives/ Budget/ Duration

- Proof-of-concept of the Integrated Vacuum Carbonate Absorption Process (IVCAP)
  - Identify an effective catalyst for accelerating CO_2 absorption rate
  - Identify an effective additive for reducing stripping heat
  - Evaluate a modified IVCAP for combined SO_2 and CO_2 removal
  - Demonstrate as a viable low-cost post-combustion CO_2 capture technology

- Total funding: $1,148 K
  - DOE funding: $691 K
  - Cost share
    - Illinois Clean Coal Institute (cash) : $118 K
    - Calgon Carbon Corporation (in kind): $100 K
    - UIUC-ISGS (in kind): $239 K

- Project duration: 10/1/2008-4/30/2011
  - BP1: 10/1/2008-4/30/2010 (with 7-month no cost extension)
  - BP2: 5/1/2010-4/30/2011
  - BP3: 5/1/2011-4/30/2012

Project Team

DOE/NETL: Andrew Jones (COR)

ICCI: Joseph Hirsch (ICCI manager)

UIUC: Tatiana Djukardi (BS, Chemical Engg)
Arezoo Khodayari (Graduate student, Environmental Engg)
Yongqi Lu (PhD, Chemical/Environmental Engg)
Mark Rood (Professor, Environmental Engg)
Massoud Rostam-Abadi (PhD, Chemical Engg)
David Ruhter (MS, Biology/ecology)
Xinhuai Ye (PhD, Chemical Engg)
Zhaohui Zhang (PhD, Biochemical Engg)

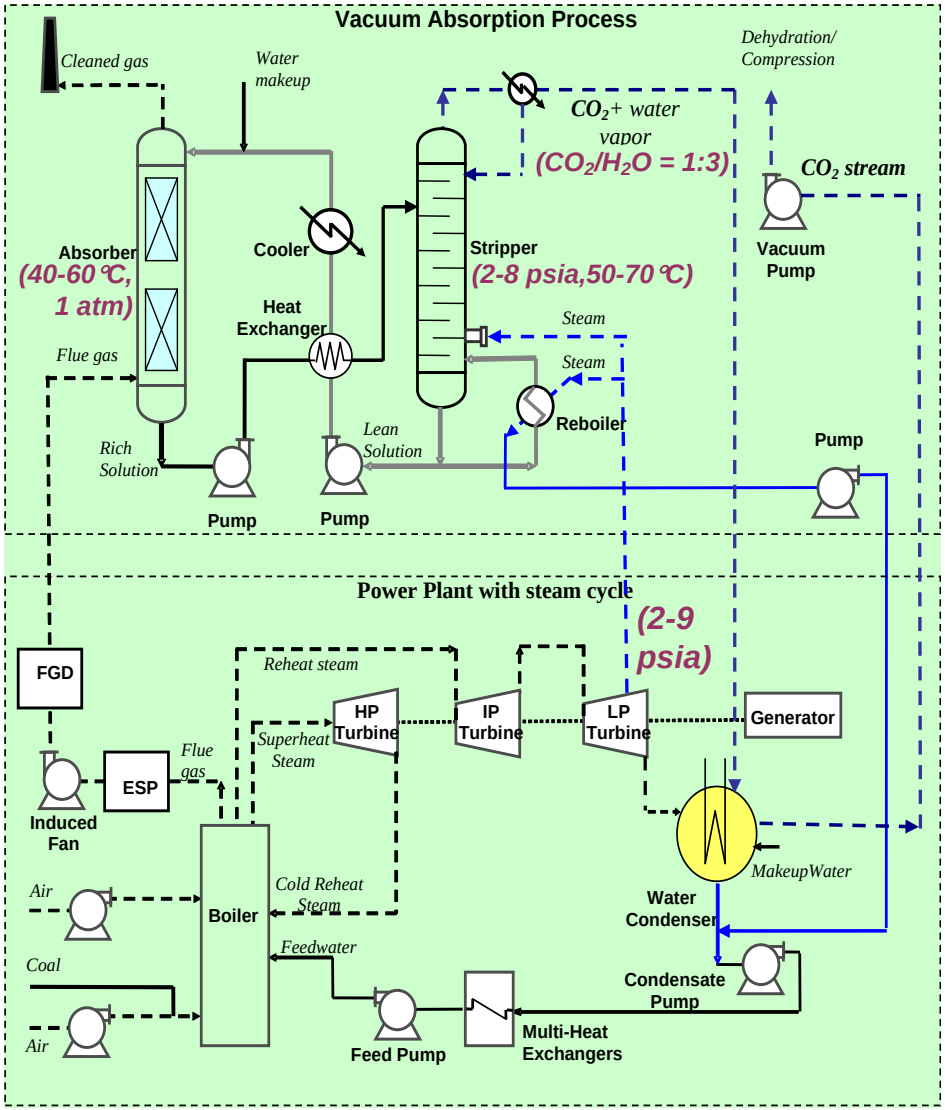
Calgon: Nick Pollack (PhD, Chemical Engg)

Enzyme Manufacturing Company: Name undisclosed

Technology Fundamentals/Background

Integrated Vacuum Carbonate Absorption Process (IVCAP)

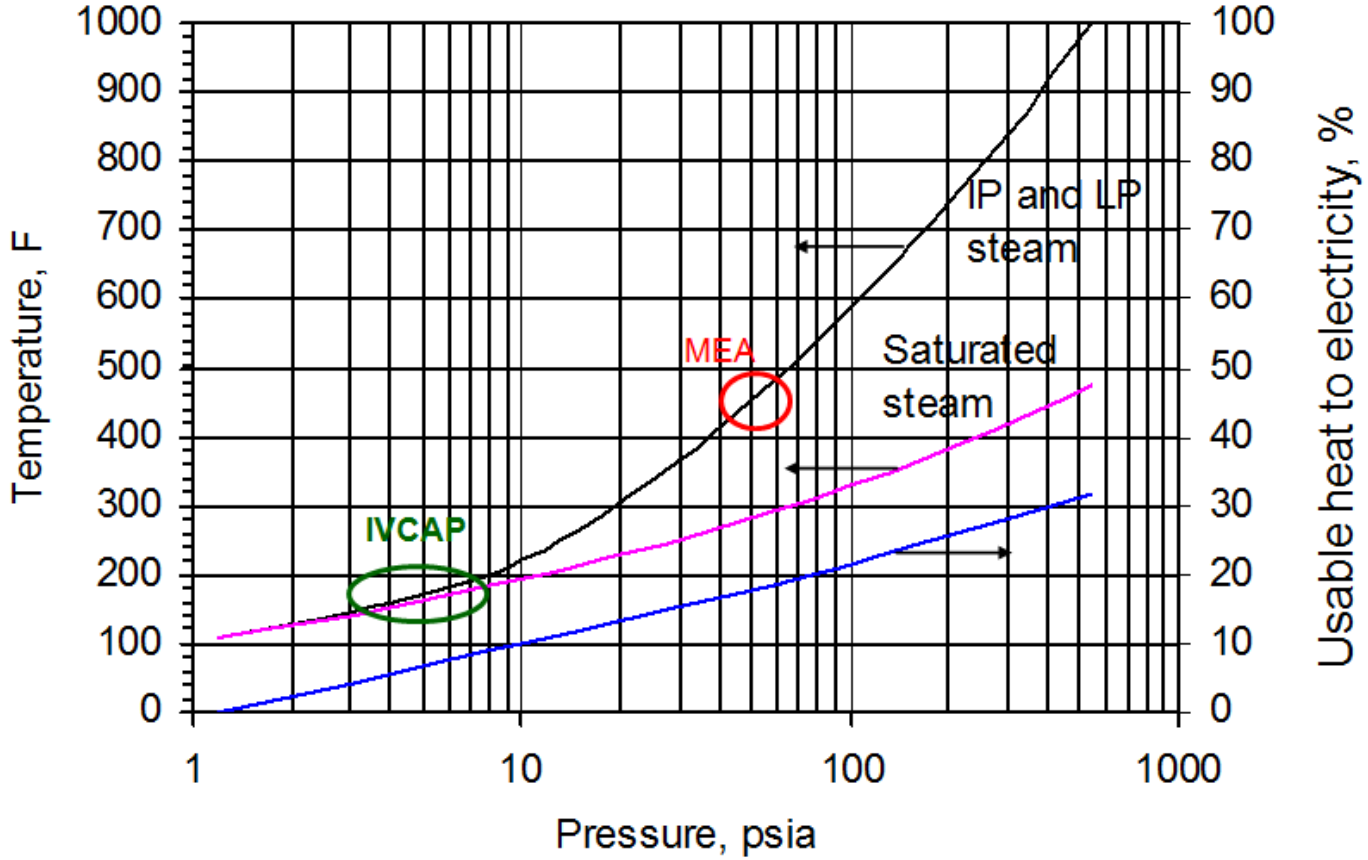
- K_2CO_3 (PC) solvent
  - Low heat of absorption (600 kJ/ kg)
  - Low T/P stripping
  - Biocatalyst to promote absorption
- Integration with power plant
  - Uses low quality steam under vacuum stripping
  - Increases heat transfer efficiency by direct injection of steam into stripper



Chen, Lu, Rostam-Abadi, Patent Application No. 60/798,489, May 2007

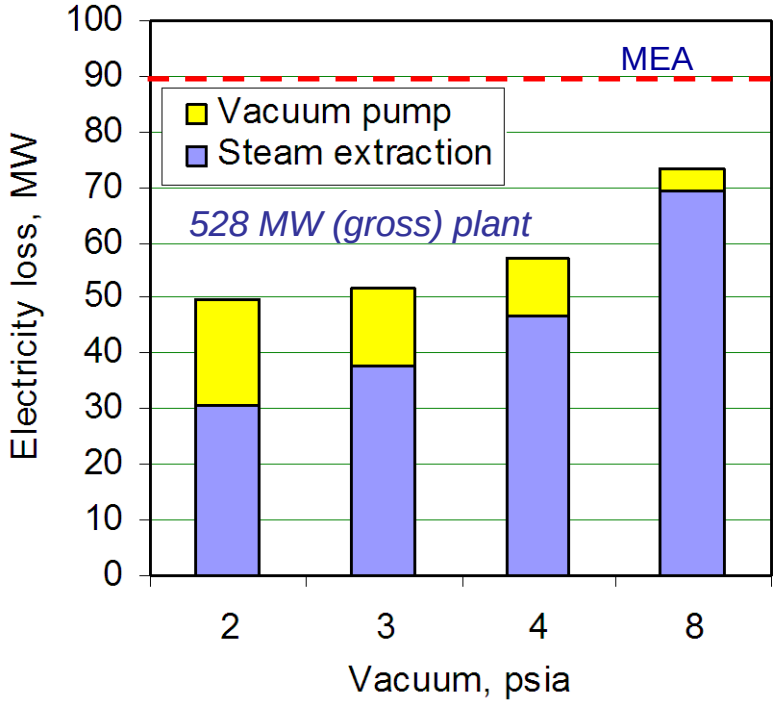
Use of Low-Quality Steam for Solvent Regeneration

- Lower stripping temperature → use lower quality steam
- Lower quality steam → less electricity loss



Superheated steam in power plant IP and LP turbines

Energy Use Performance of IVCAP



MW	PCP W/O CO_2	PCP+ MEA	PCP+ IVCAP
Net output	**492.9**	**358.9**	**390.1**
Aux. electricity use	34.7	32.0	33.8
Steam extraction	**0**	**89.4**	**37.8**
Fan/pump in CO_2 capture process	0	11.8	12.8
CO_2 compression	0	35.4	39.7
Vacuum pump	**0**	**0**	**14.0**

*** A case study based on 3 psia stripping pressure, 1%wt CO2 lean loading, 20%wt PC, L/G=1.2 (L/G)min, and 50ºC absorption**

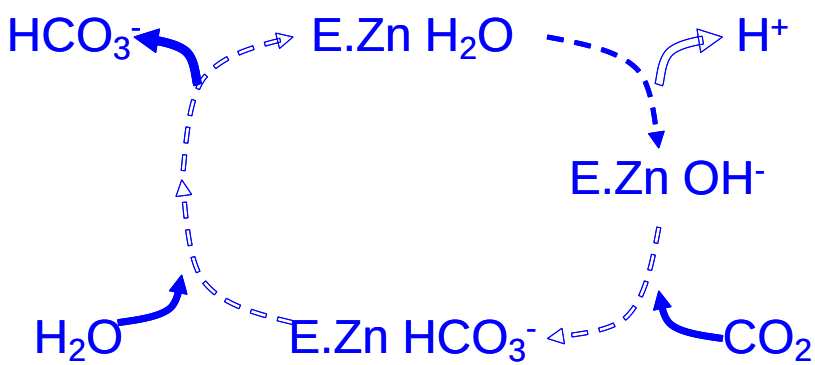
- Energy use in CO_2 stripping reduced by 20-45% compared to MEA
- Total energy use reduced 20%-30% compared to MEA

Main Reactions

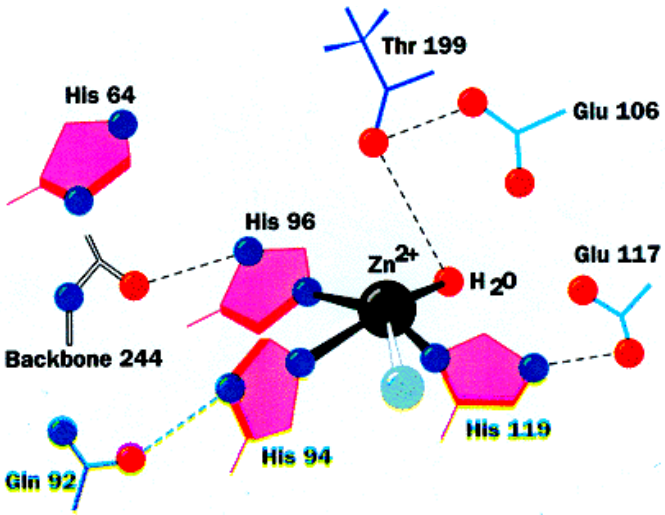
- Reaction (1) is slow without a catalyst;
  Carbonic anhydrase (CA) enzyme promotes Rx (1)
- Reaction (2) is not fast enough in PC solution (low [OH^-])

$$(1)\ CO_2 + H_2O \underset{k_{12}}{\overset{k_{11}}{\Leftrightarrow}} HCO_3^- + H^+$$

$$(2)\ CO_2 + OH^- \underset{k_{22}}{\overset{k_{21}}{\Leftrightarrow}} HCO_3^-$$



CA catalytic mechanism for Rx(1)



Histidine residues (pink), hydroxide group (red), coordinating zinc ion (black)

Progress and Current Status

Research Tasks

BP1 & 2

10/2008-2/2011

Task 1 Evaluation & Development of absorption catalysts

BP2

5/2010-12/2010

Task 2 Screening of additives for reducing stripping heat

BP3

2/2011-11/2011

Task 3 Kinetic study of combined SO_2 removal in IVCAP

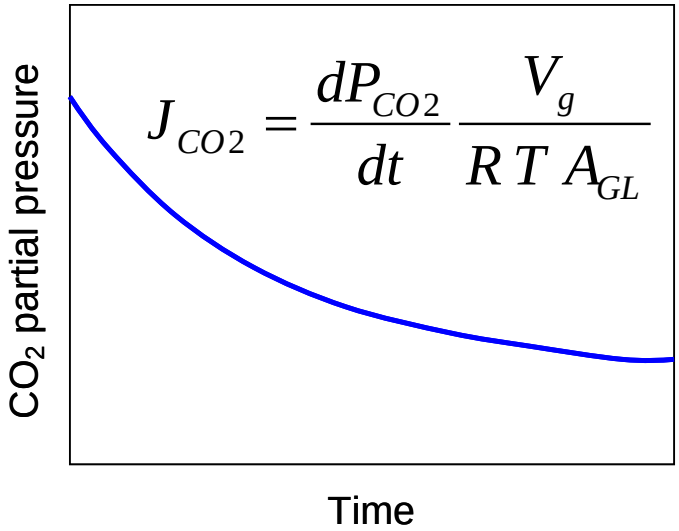
BP3

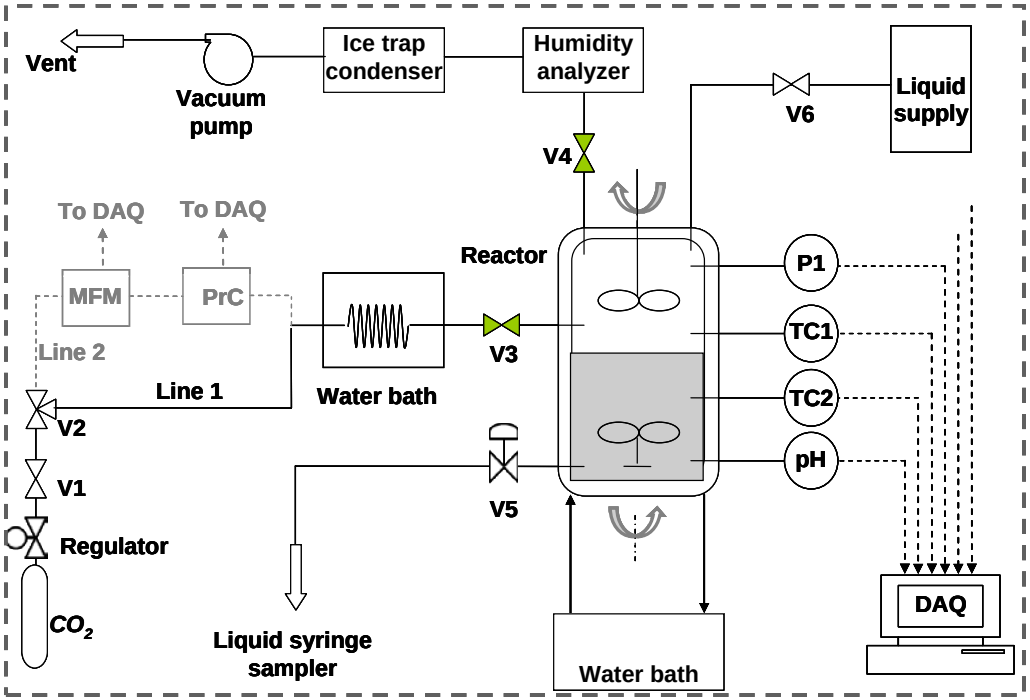
11/2011-2/2012

Task 4 Techno-economic analysis

Task 1	Status
1.1 Experimental set up	Completed
1.2 Activity of CA enzyme	Completed
CA stability with flue gas impurities	Completed
CA long term stability	In progress
1.3 Activity of other catalysts/ additives	Completed
1.4 CA enzyme immobilization	In progress
1.5 Impacts of additives from Task 2	Planned in Q3/BP2

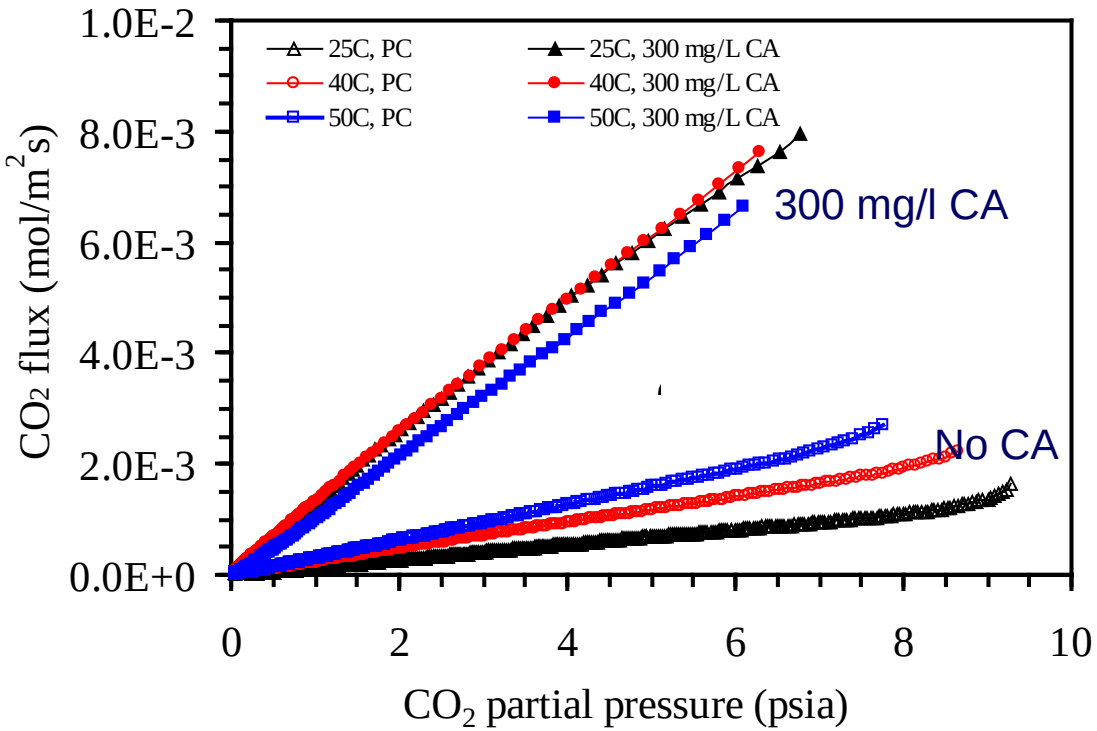
1.1 Stirred Tank Reactor (STR) Experimental System





Batch-mode tests

1.2 Activity of CA Enzyme

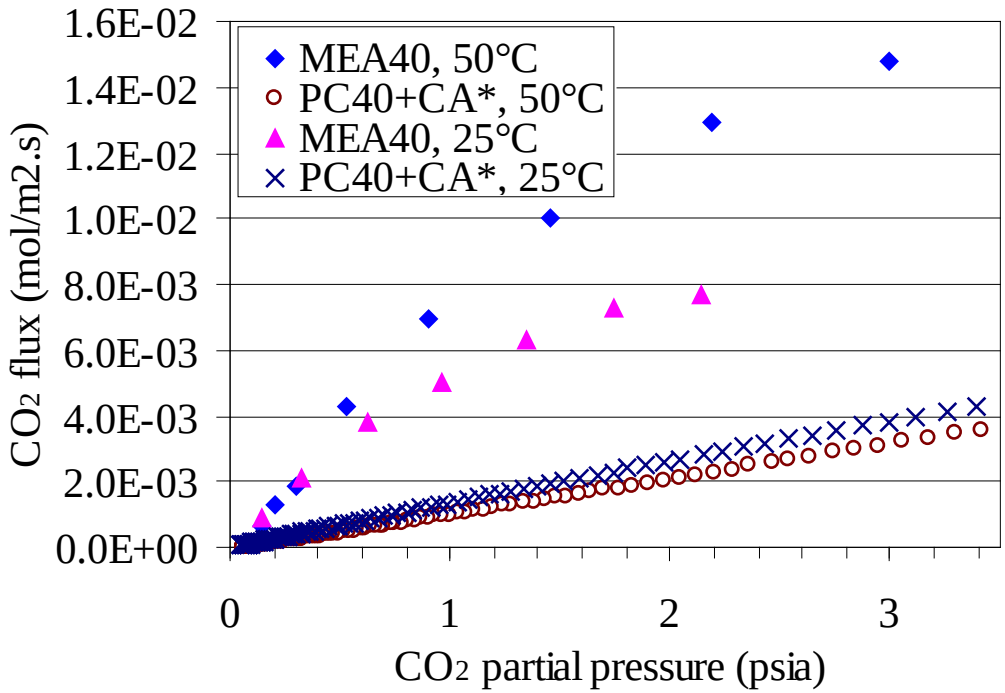


Solvent:

20wt%PC with 20% conversion

- Rate increased by 8.8-11.3 times at 25°C (5.2-6.4 times at 40°C, 3.4-4.0 times at 50°C)
- Comparable rates into PC+CA at 25-50°C due to lower CO_2 solubility and faster rate at higher T
- Rates comparable at different carbonate-to-bicarbonate conversion levels (data not shown)

Comparison between PC+CA and MEA



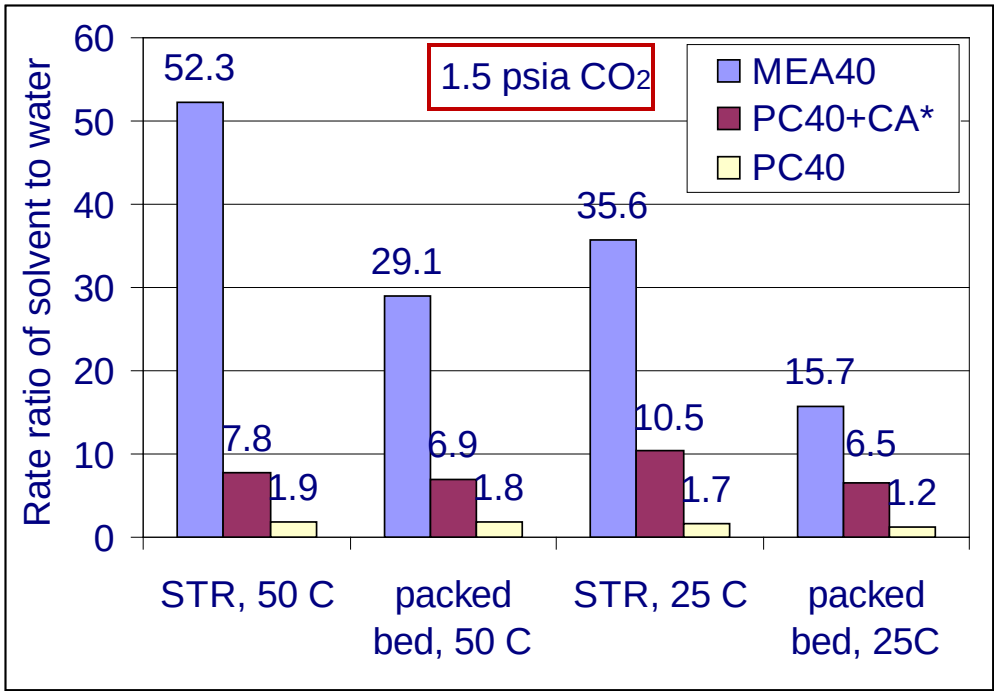
PC40+CA*: 20wt% PC with 40% conversion mixed with 300mg/L CA

MEA40: 3M MEA with 40% conversion

No gas diffusion resistance in STR system

- Absorption rate into PC40+CA slower than MEA40
  - by 5-9 times at 50°C
  - by 3-5 times at 25°C

Comparison of Modeled Rates in Packed-Bed Column



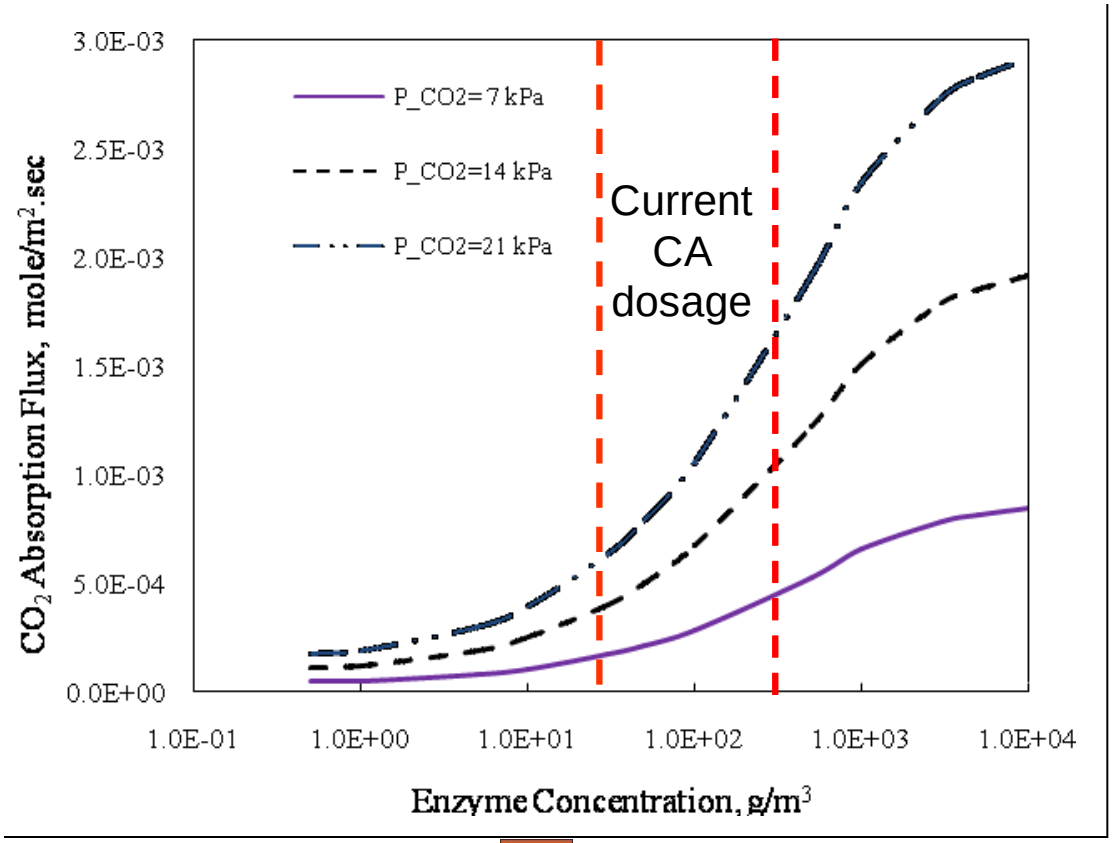
	Gas-phase resistance (50°C/ 25°C)	Liquid-phase resistance (50°C/ 25°C)
MEA40	**40.8 / 38.0**	**59.2/ 62.0**
PC40+CA*	**9.7/ 15.8**	**90.3/ 84.2**
PC40	**2.6/ 2.9**	**97.4/ 97.1**

(MEA40: 3M MEA with 40% conversion
PC40+CA*: 20wt% PC with 40% conversion mixed with 300mg/L CA
PC40: 20wt% PC with 40% conversion)

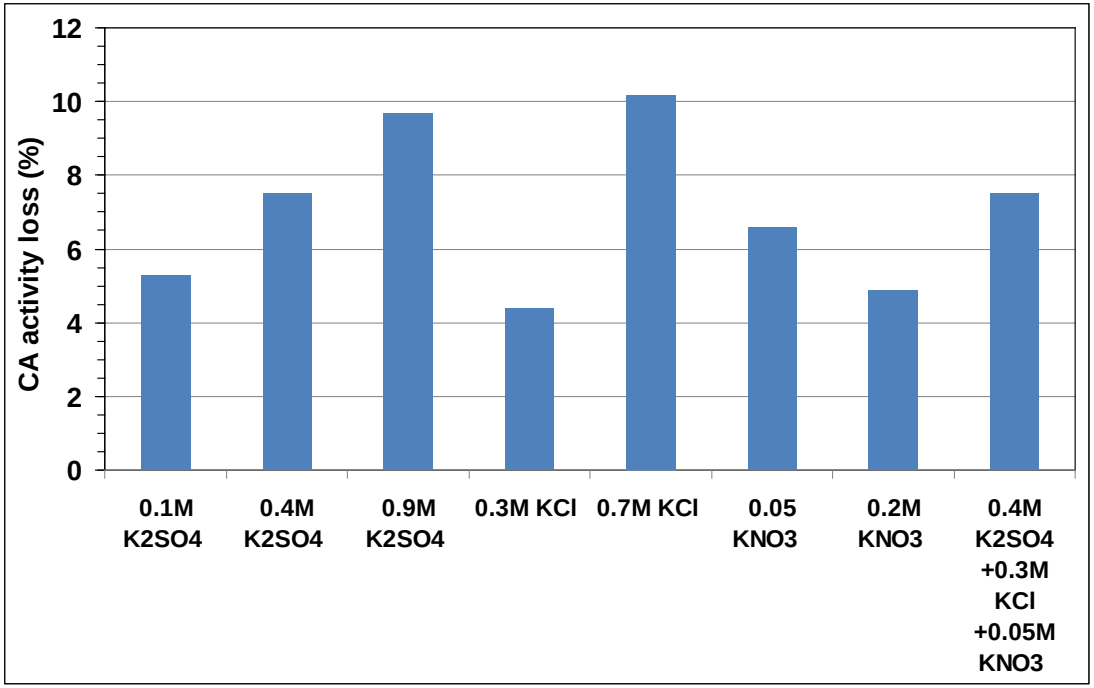
- Gas diffusion resistance significant in MEA solution
- Liquid phase resistance dominants in PC+CA (300mg/L)
- Rate into PC+CA (300 mg/L) is 2-5 times lower than MEA
  - A smaller difference between PC+CA and MEA rates at higher CO_2 loading

Predicted Rates at Different CA Dosage Levels

- Rate increases by 2 times from 300 to 3,000 mg/l CA
- Rate levels off at 3,000 mg/l CA dosage



CA Enzyme Stability in Presence of Anion Impurities



$$Activity\ loss,\% = \frac{E_{cat,pur} - E_{cat,imp}}{E_{cat,pur} - 1.0}$$

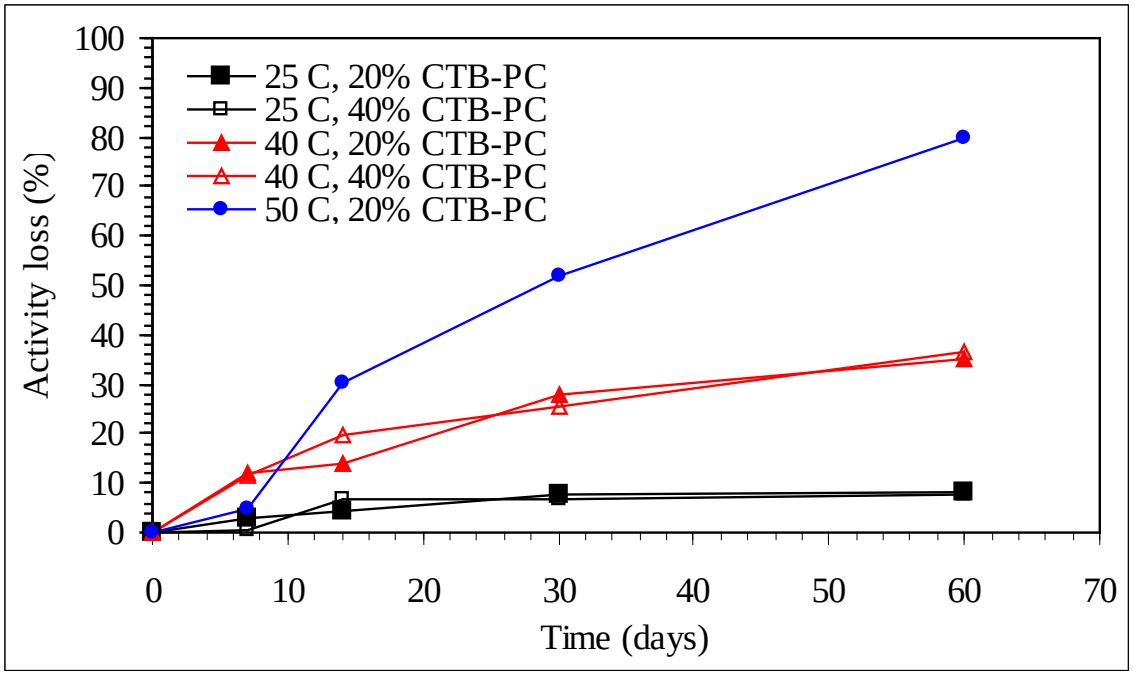
$(E_{cat,pur}$ *enhancement factor w/o impurity*$)$

$E_{cat,imp}$ *enhancement factor with impurity*$)$

0.9M SO_4^{2-}, 0.2M NO_3^-, and 0.7M Cl^- are ~20, 100, and 1 times higher than FGD wastewater (high S/Cl coal)

- Presence of SO_4^{2-}, NO_3^-, and Cl^-, either alone or a mixture, in PC+CA solution resulted in <10.2% loss of initial CA activity

CA Enzyme Stability in Long-Term



$$Activity\ loss,\% = \frac{E_{cat,0} - E_{cat,t}}{E_{cat,0} - 1.0}$$

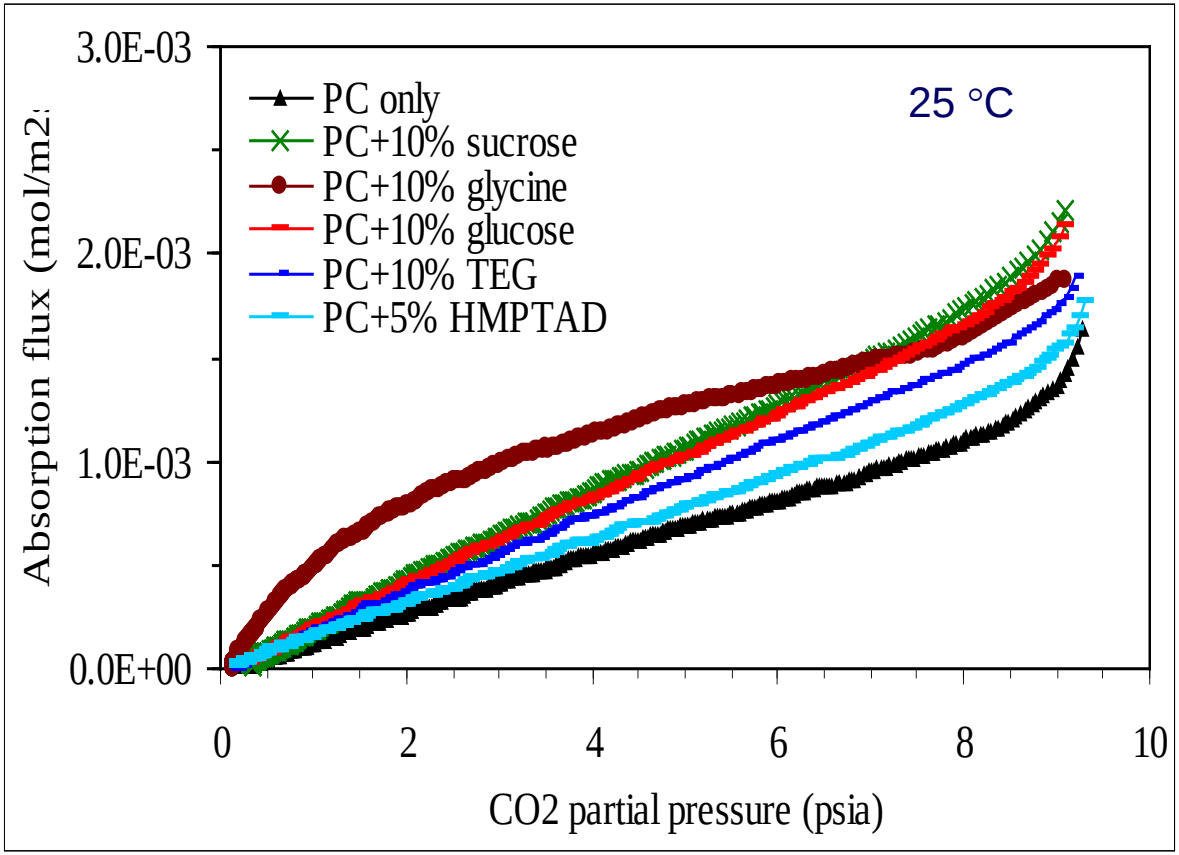
$(E_{cat,0}$ *enhancement factor at* $t = 0$

$E_{cat,t}$ *enhancement factor at* $t)$

- CA activity loss <8% at 25°C; ~35% at 40°C, ~80% at 50°C after 60 days
- Comparable CA stability in PC solutions with different carbonate-to-bicarbonate conversions (CO_2 loading)
- Low temperature (25-40°C) beneficial for CA stability while not impacting absorption rate

1.3 Test of Selected Catalysts/ Additives

- Additives promote PC rate by ≤ 70% at 25°C and ≤39% at 40°C



(TEG: triethylene glycol;
HMPTAD: hexamethyl phosphoric triamide)

1.4 Enzyme Immobilization

Advantages

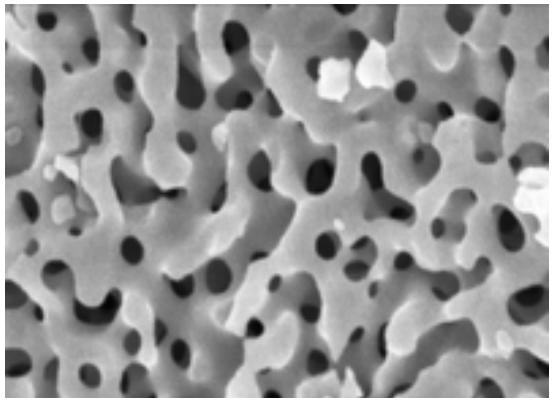
- Improve enzyme stability
- Reduce enzyme elution in a flow system

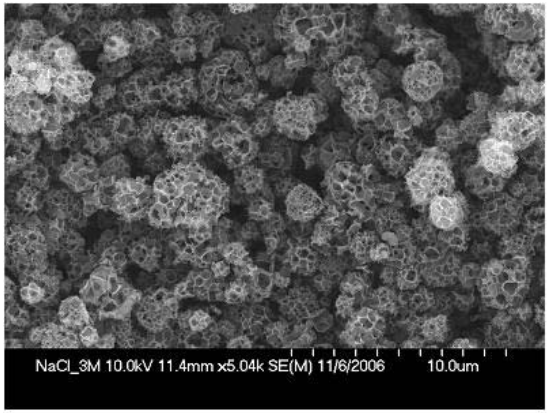
Support materials

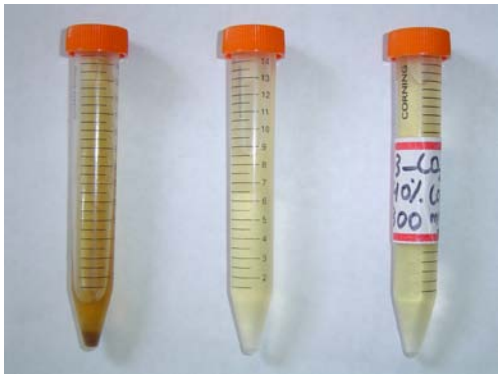
- Controlled pore glass (CPG, 100nm macro-pore, SA=25m^2/g, 200-400 mesh)
- Ceramic materials
- Porous carbon materials

CA enzymes

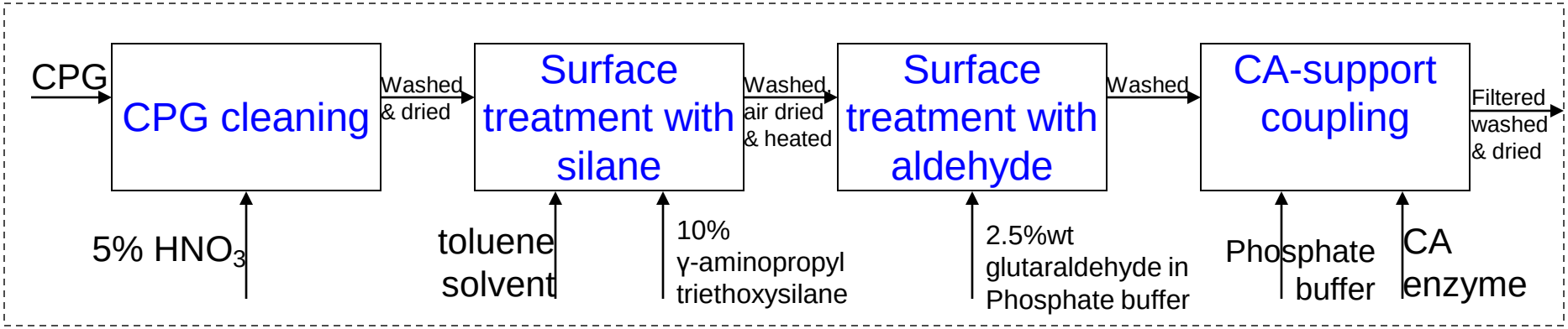
- Sigma-Aldrich (SCA)
- CA from Company A (ACA)



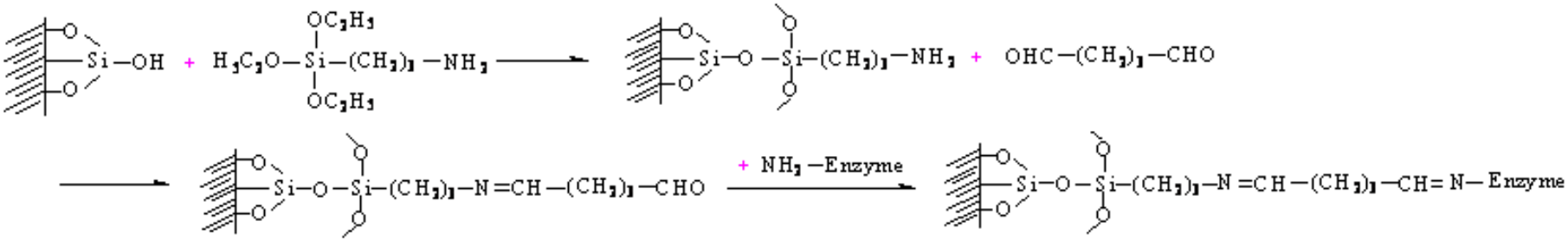




CA Immobilization onto CPG

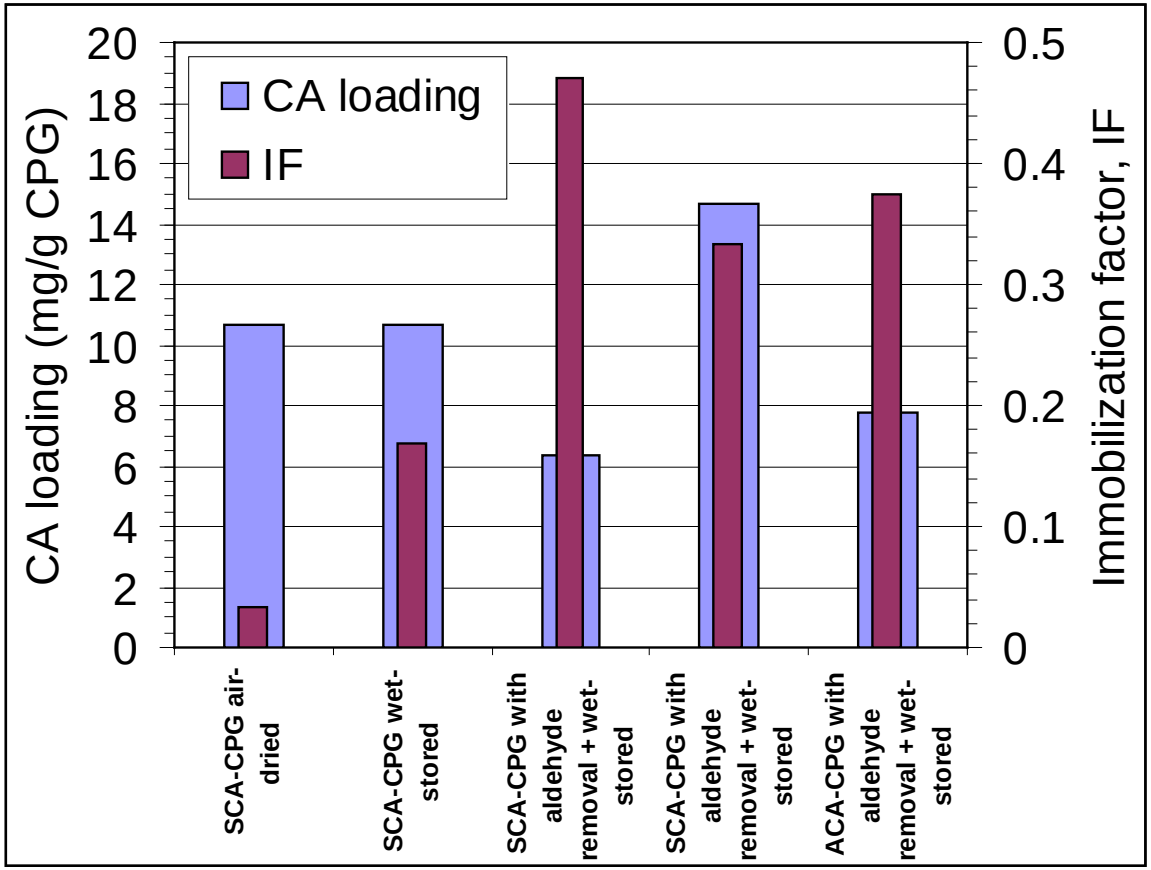


CPG activation and CPG-CA covalent coupling reactions



Comparison between Immobilized and Free CAs

Immobilization factor: $IF = \dfrac{Specific\ activity\ of\ immobilized\ enzyme}{Specific\ activity\ of\ free\ enzyme}$



Main Conclusions/Findings

- CA enzyme
  - Effective catalyst to promote CO_2 absorption into PC
  - 300 mg/l CA promotes rate by 2-20 times
  - Activity comparable at 25°C-50°C
  - Rates comparable at different CO_2 loadings
  - Rate could further increase at higher CA dosage (>300 mg/l)
  - Stable at tested pH range (9-11.5)
- Rate into PC+CA (at 300 mg/l) 2-5 times < MEA in a packed-bed column
- Presence of flue gas impurities resulted in <11% loss of initial CA activity
- CA activity loss <8% in 60 days at 25°C, ~35% at 40°C, and ~80% at 50°C
- CA immobilized onto silica/glass materials with high IF

Research Planned in BP2 and BP3

- Focus 1: Improvement of enzyme activity and stability
  - Prolonged enzyme stability tests
  - Tests of additives synergic to CA in PC (CO_2 solubility and kinetic effect)
  - CA immobilization for improved activity and stability (methods and supports)

- Focus 2: Additives for suppressing water vaporization in stripper
  - >60% of the process heat use in IVCAP stripper is due to water vaporization
  - VLE measurements to screen additives

- Focus 3: Combined SO_2 Removal in CO_2 Capture Process
  - Combining SO_2 removal with CO_2 capture is possible in IVCAP
  - Precipitation kinetic studies and process development

    Absorption ($SO_2 \rightarrow K_2SO_4$)

    Sulfate reclamation

Acknowledgements

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