



I L L I N O I S

UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

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
Prairie Research Institute
University of Illinois at Urbana-Champaign

2011 DOE/NETL CO₂ Capture Technology Meeting

Pittsburgh, PA • August 22-26, 2011



Lead Contractor

- ❑ Prairie Research Initiative /University of Illinois
 - Five scientific surveys including Geological Survey (ISGS)
 - 700 scientists and technical support staff
 - Annual budget of \$50 million
 - Lead organization of Midwest Geological Sequestration Consortium Partnership
 - Advanced Energy Technology Initiative (AETI)
 - carbon capture & sequestration
 - materials and systems for energy and environmental applications
 - combustion-generated air pollution control
 - energy-water nexus



Project Overview



Project Objectives

- ❑ Proof-of-concept of the Integrated Vacuum Carbonate Absorption Process (IVCAP)
 - Identify an effective catalyst for accelerating CO₂ absorption rate
 - Identify an effective additive for reducing stripping heat
 - Evaluate a modified IVCAP for combined SO₂ and CO₂ removal
 - Techno-economic evaluation of the IVCAP as a post-combustion CO₂ capture technology

Project Budget and Duration

- ❑ Total funding: \$1,140 K
 - DOE funding: \$765 K
 - Cost share
 - Calgon Carbon Corporation (in kind): \$100 K
 - UIUC-ISGS (in kind): \$275 K

- ❑ Project duration: 10/1/2008-4/30/2012
 - 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)



UIUC:
Tatiana Djukardi (BS, Chemical eng)
Arezoo Khodayari (Graduate student, Environmental eng)
Yongqi Lu (PhD, Chemical/Environmental eng)
Mark Rood (Professor, Environmental eng)
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David Ruhter (MS, Biology/ecology)
Priscilia Sinata (BS, Chemical eng)
Xinhuai Ye (PhD, Chemical eng)
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Zhaohui Zhang (PhD, Biochemical eng)



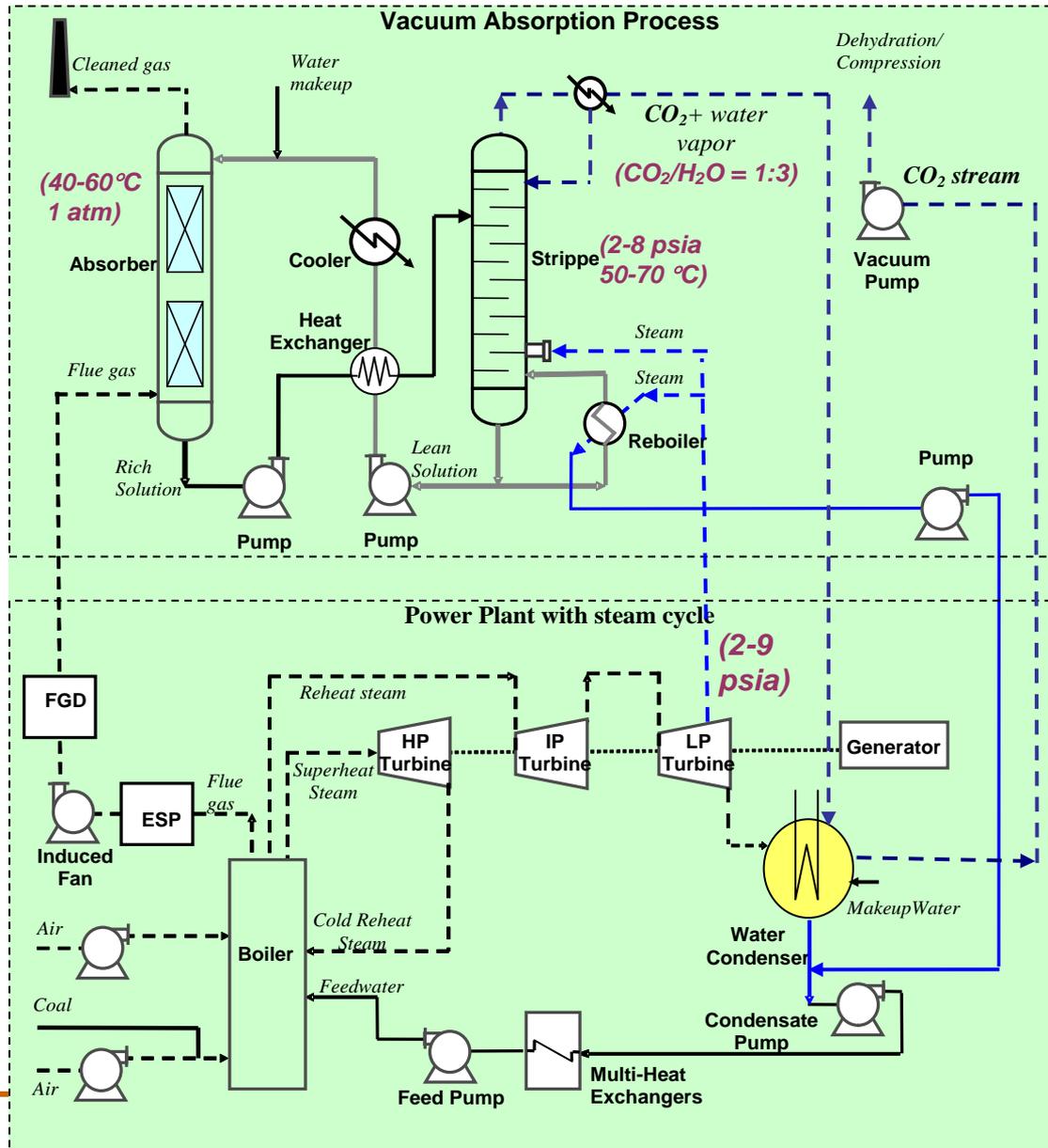
Calgon Carbon: Nick Pollack (PhD, Chemical eng)



Technology Fundamentals/Background



Flow Diagram/ Concept of Integrated Vacuum Carbonate Absorption Process (IVCAP)



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

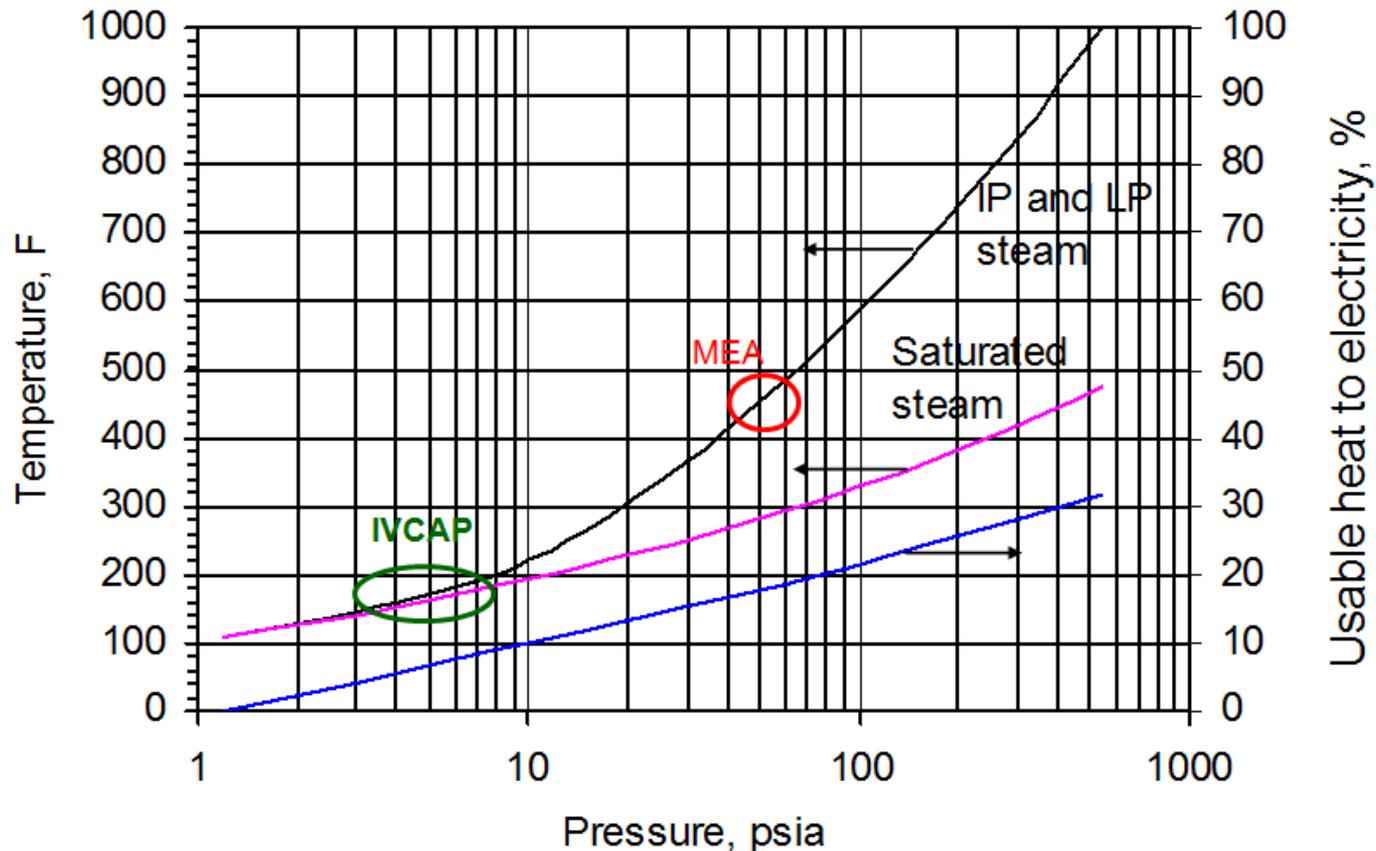
Features of IVCAP

- ❑ Absorber: $K_2CO_3 + CO_2 + H_2O \rightarrow 2KHCO_3$
- ❑ Stripper: $2KHCO_3 \xrightarrow{\text{Heat, Vacuum}} K_2CO_3 + CO_2 \uparrow + H_2O$
- ❑ Low T/P stripping (2-8 psia, 50-70°C)
 - Allows use of low quality steam from power plant
 - Part of steam used for direct heat exchange
 - Reduces energy use (parasitic power use) by 25-35% compared to baseline MEA processes
- ❑ Employs a biocatalyst to promote absorption rate
- ❑ Combines SO₂ removal with CO₂ capture



Feature (1) Benefit of Use of Low-Quality Steam for Solvent Regeneration

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



Superheated steam in power plant IP and LP turbines



Feature (2) CO₂ Absorption Reactions Promoted with a Biocatalyst

Without a catalyst:

- ❑ Reaction (1) slow in water
- ❑ Reaction (2) dominant at pH >9 (pH of K₂CO₃/KHCO₃ solution is 9-11)



With CA enzyme

- ❑ Reaction (1) dominant when promoted by **carbonic anhydrase (CA)**
- ❑ Reaction (2) plays a minor role (pH of K₂CO₃/KHCO₃ solution is 9-11)



Feature (3) Combined SO₂ Removal in CO₂ Capture Process

Absorption:



Sulfate reclamation:

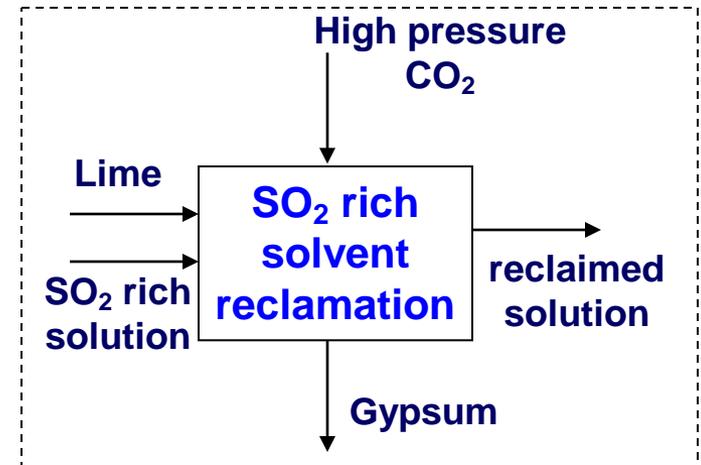


Reducing [CO₃²⁻] to favor CaSO₄ precipitation:

- High pressure CO₂
- Low pH
- Appropriate temperature

Precipitation rates of CaSO₄ and CaCO₃:

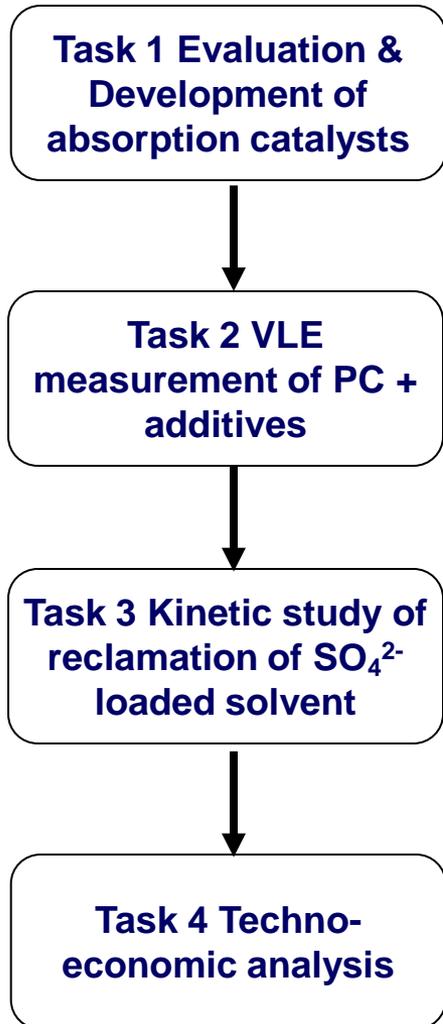
$$J = k_c (C - C^*)^m$$



Progress and Current Status



Research Activities Performed



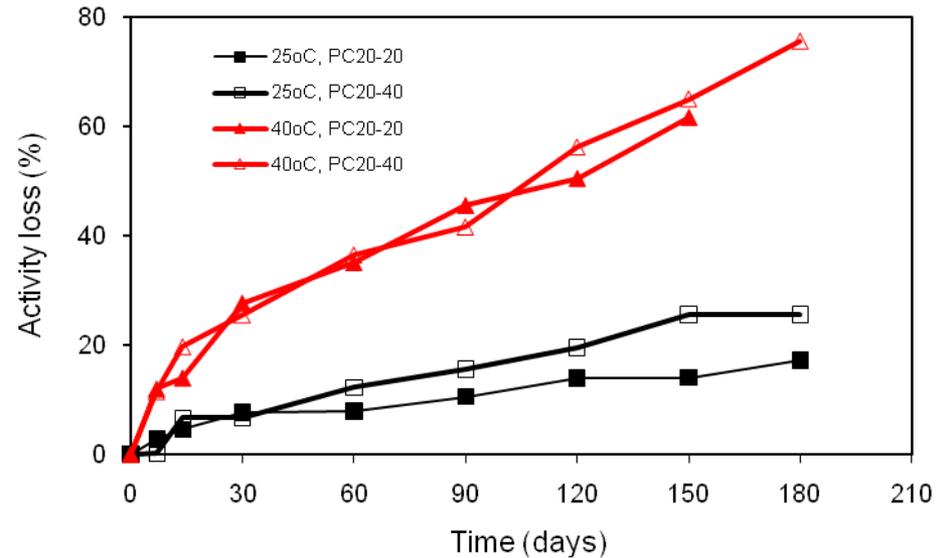
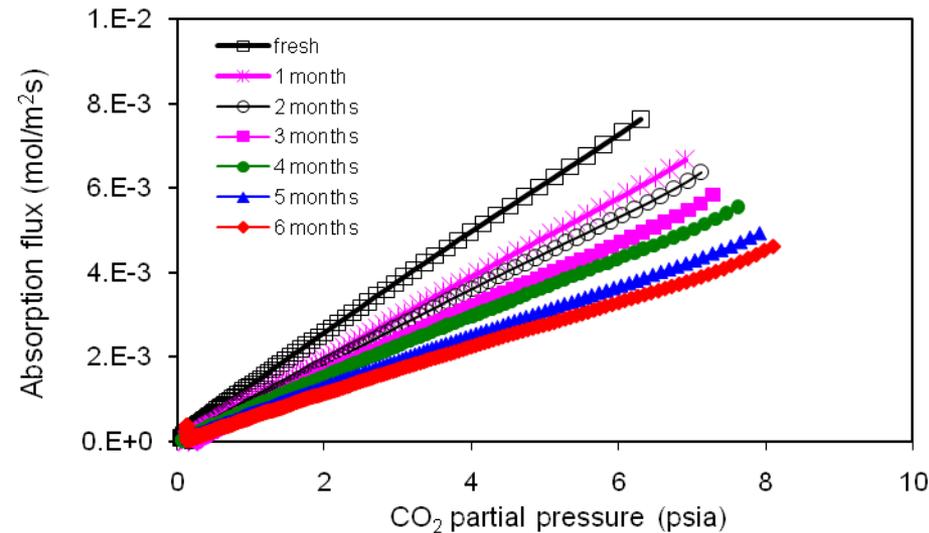
Task/subtask	Completion date
Task 1. Evaluation & develop.of catalysts	
1.1 Experimental set up	11/31/08
1.2 Activity of enzyme biocatalysts	9/30/09
1.2*Long-term stability of enzymes	12/31/10
1.3 Activity of other catalysts	12/30/09
1.4 Enzyme immobilization	10/31/10
Task 2. VLE measurement	
2.1 Experimental set up	6/30/10
2.2 VLE of PC w/o an additive	9/30/10
2.3 VLE of PC with additives	12/31/10
Task 3. SO ₂ -loaded solvent reclamation	
3.1 Batch test of solvent reclamation	4/30/11
3.2 Semi-continuous test	In progress
A1. Evaluation of new thermophilic CAs	In progress
A2. Develop. & evaluation of novel support material/method for CA immobilization	In progress

Note: Work completed after Sep, 2010 or currently in progress are updated here

(1) Stability of CA Enzyme – Long Term Thermal Stability

CA enzyme from Provider A (ACA1)

- A technical-grade CA enzyme produced in a pilot unit
- As received sample not purified

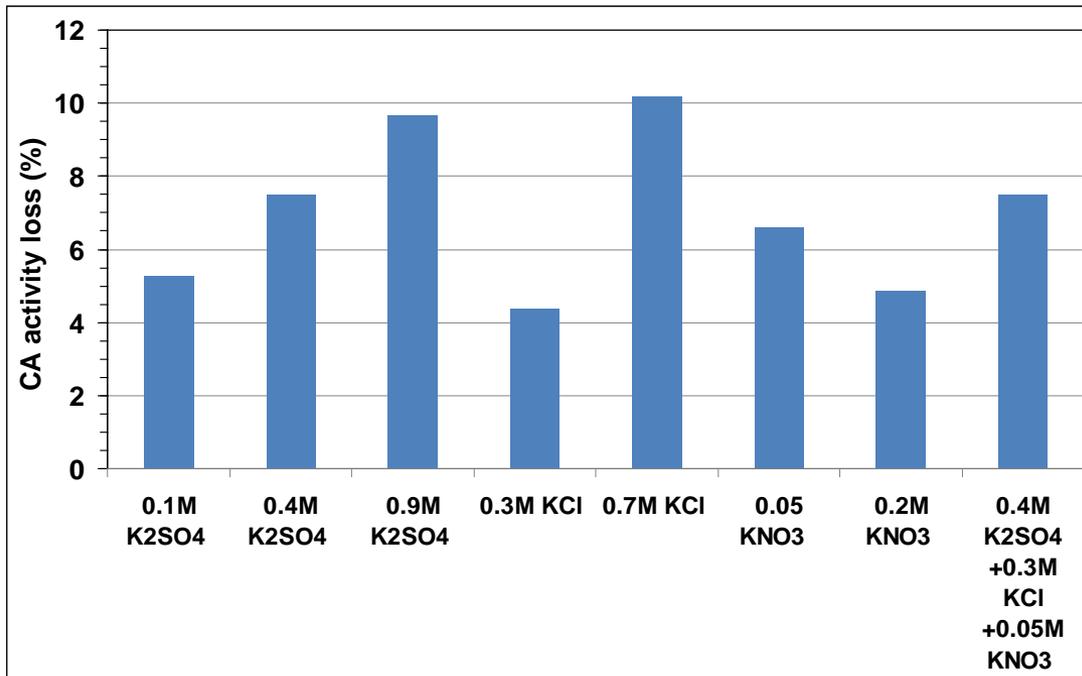


$$\text{Activity loss} = \frac{E_{CA,0} - E_{CA,t}}{E_{CA,0} - 1.0} \times 100\%$$

- CA Relatively stable at 25°C (20% loss in 6 months)
- CA Stability loss at 40°C (70% in 6 months)
 - 2.5-3 times annual enzyme makeup



Stability of CA Enzyme – Chemical Stability with Flue Gas 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)

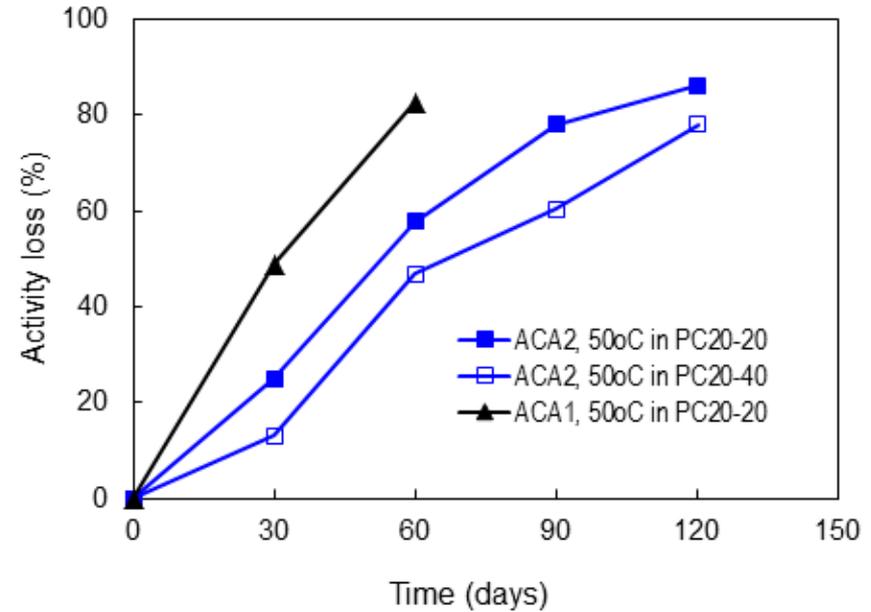
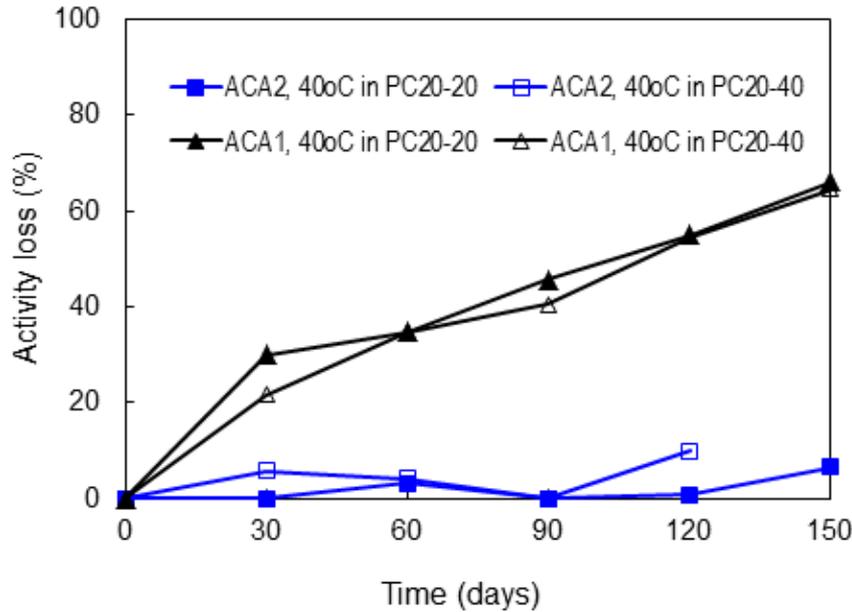
0.9M SO₄²⁻, 0.2M NO₃⁻, and 0.7M Cl⁻ are ~20, 100, and 1 times higher than FGD wastewater (high S/Cl coal)

- Presence of SO₄²⁻, NO₃⁻, and Cl⁻, either alone or a mixture, in PC+CA solution resulted in <10.2% loss of initial CA activity

CA Enzyme with Improved Thermophilic Performance

ACA2

➤ As-received liquid sample not purified



- ❑ Fresh ACA2 exhibited comparable activity at 40°C; ~30% higher activity at 50°C (data not shown)
- ❑ ACA2 stable at 40°C and stability improved at 50°C
- ❑ BCA retained 40% activity after 1 month at 60°C vs. ACA1 lost activity in days (data not shown)

(2) Enzyme Immobilization

CA enzymes

- Sigma-Aldrich (SCA)
- ACA1

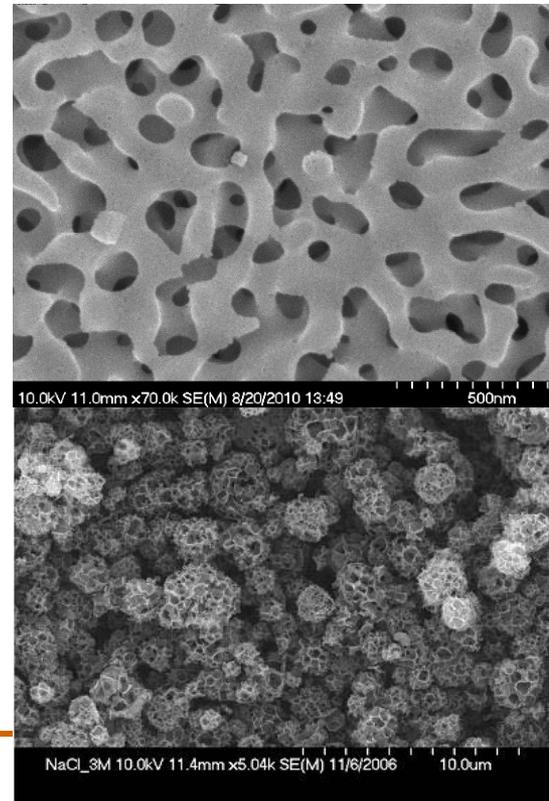
Support materials

- Controlled pore glass
 - CPG100 (200-400 mesh)
 - CPG38
 - Porous AC



	Average pore size, nm	BET surface, m ² /g	Pore volume, cm ³ /g
AC	3.8	1007.0	0.50*
CPG38	38.1	64.5	1.06
CPG100	100	21.8	0.79

* Pores of 2-20 nm contributed 20%



Enzyme Loading onto Support and Activity of Immobilized CA Enzyme

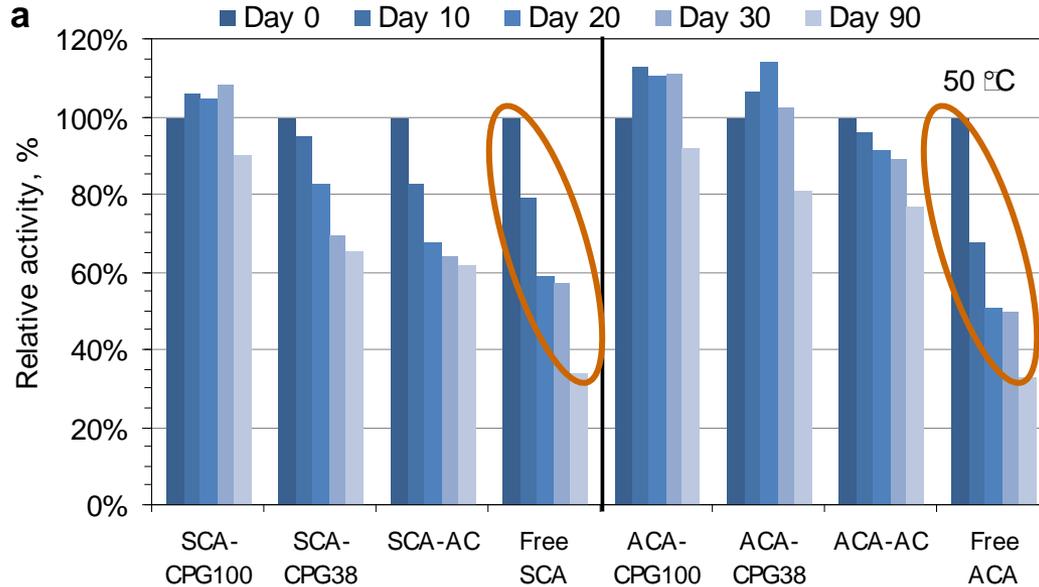
Sample	Enzyme loading (mg CA/g support)	Immobilization factor (IF)	CA activity
SCA-CPG100	18.3	0.383	<i>p</i> -NPA hydrolysis
		0.159	CO ₂ hydration
SCA-CPG38	32.6	0.351	<i>p</i> -NPA hydrolysis
		0.209	CO ₂ hydration
SCA-AC	10.7	0.229	CO ₂ hydration
ACA-CPG100	14.2	0.279	CO ₂ hydration
ACA-CPG38	27.1	0.345	CO ₂ hydration
ACA-AC	9.6	0.217	CO ₂ hydration

$$IF = \frac{\text{Specific activity of immobilized enzyme}}{\text{Specific activity of free enzyme}}$$

Immobilization factor (*IF*) represents efficiency of enzyme immobilization

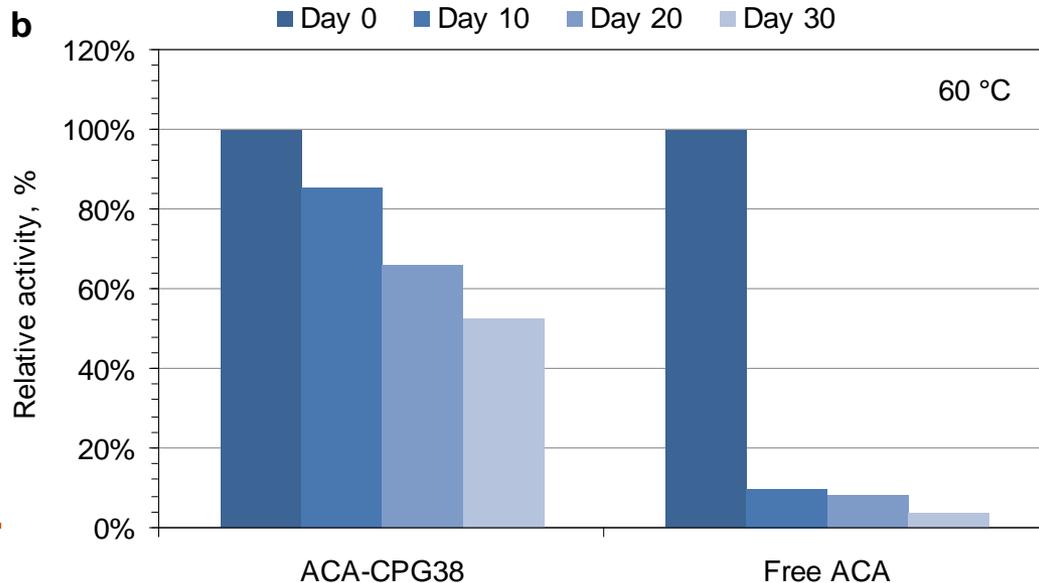


Stability of Immobilized CA Enzymes



Immobilized CA enzymes exhibited significantly improved thermal stability

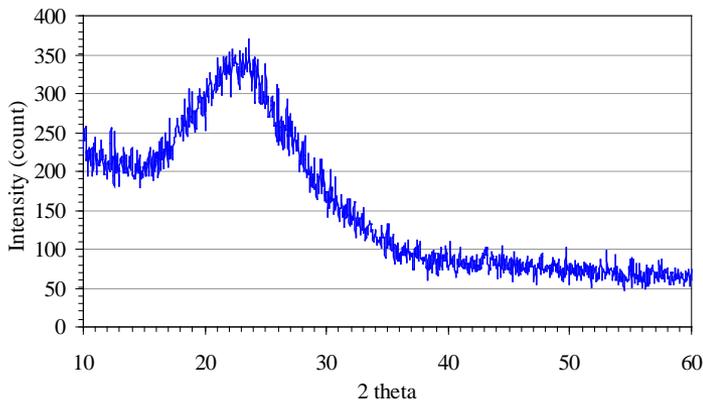
- Immobilized CAs retained 62-92% of initial activities after 90 days at 50°C vs. ~33% for free CAs
- ACA-CPG38 retained 53% activity after 30 days at 60°C vs. ~0% for free ACA



Development of New Support Materials for CA immobilization

- ❑ Nano-sized (<100 nm) support/carrier particles
 - Minimize intra-particle diffusion
 - Offer a large external surface area for high CA loading
 - Can be separation-ready
 - Synthesis using flame spray pyrolysis (FSP)
- ❑ Current work on synthesis of silica-based materials

SCA immobilized onto FSP silica at different pH



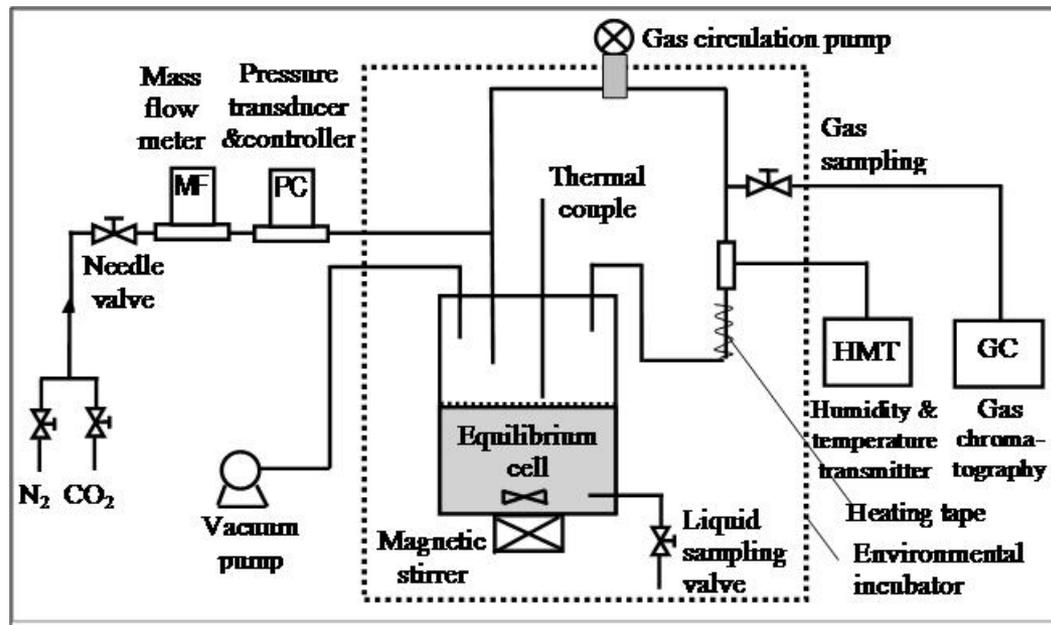
Amorphous phase,

BET=115 m²/s, size=25 nm

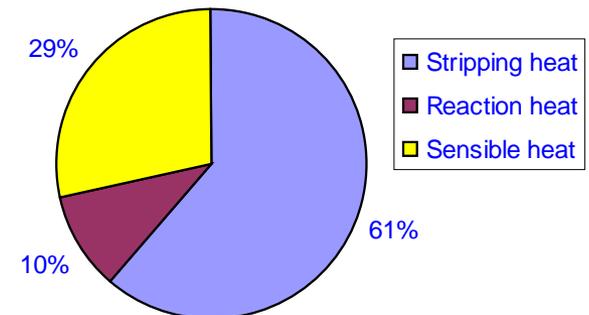
Immobilization pH	CA loading (mg CA/g support)
10	30.5
8	67.5
7	45.4
5	30.8

- CA loading tripled that onto CPG or AC
- Work in progress to improve activity (IF=~40% currently)

(3) Vapor-Liquid Phase Equilibrium (VLE) Measurement Cell

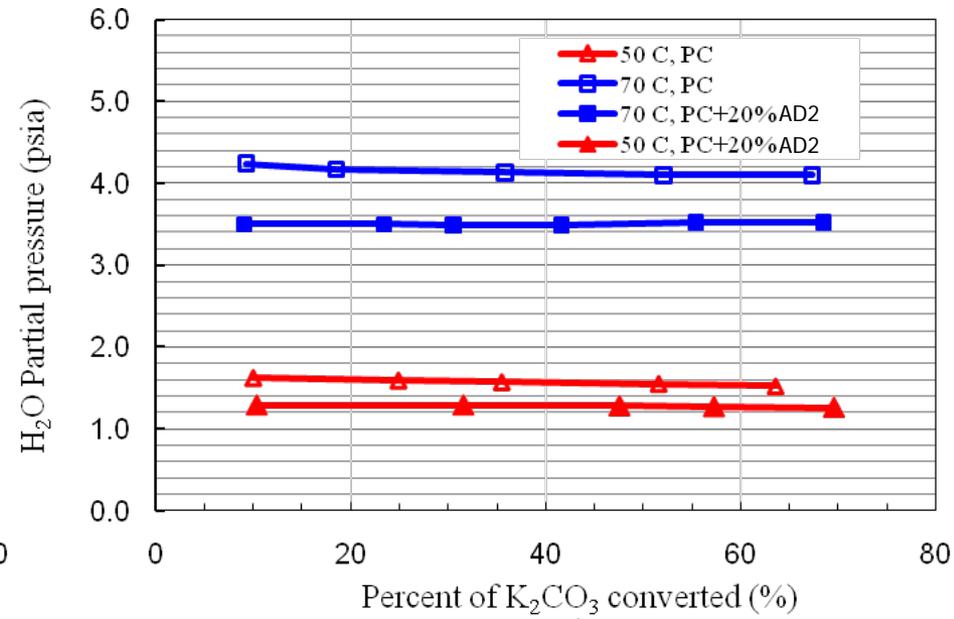
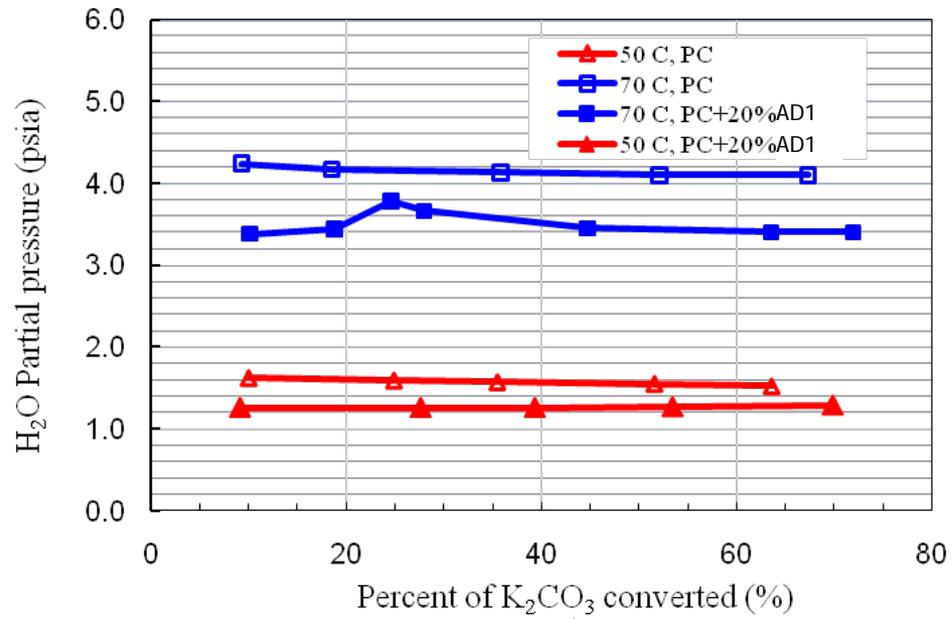


- ❑ Screening and VLE measurements of additives
- ❑ Gas analysis using GC and RH analyzers
- ❑ Liquid analysis using a back-titration method



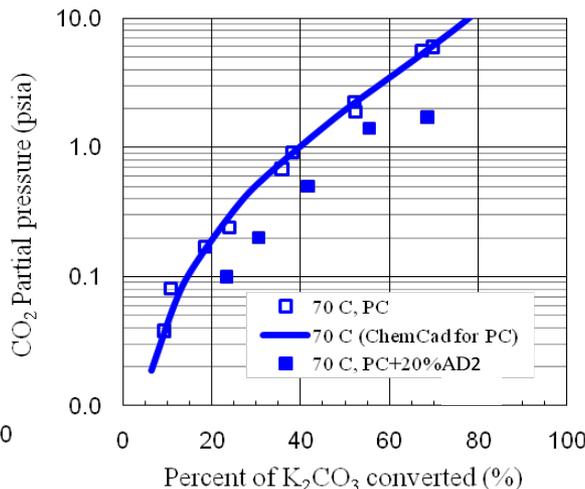
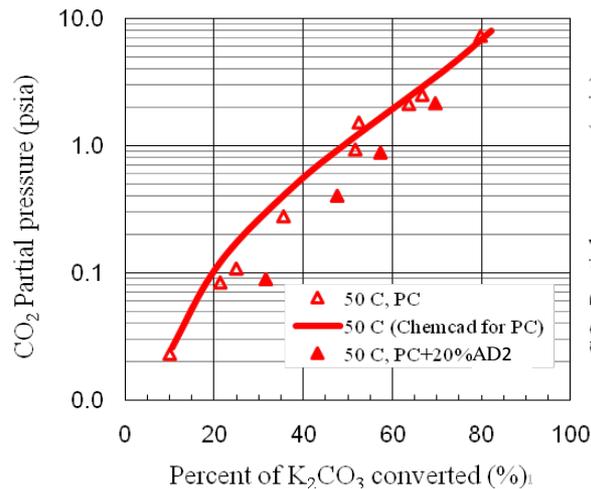
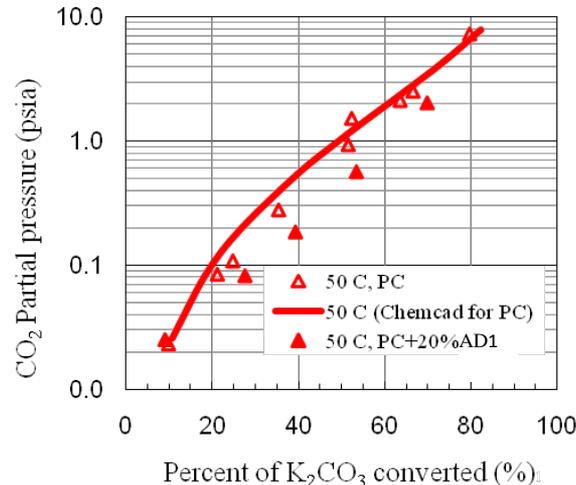
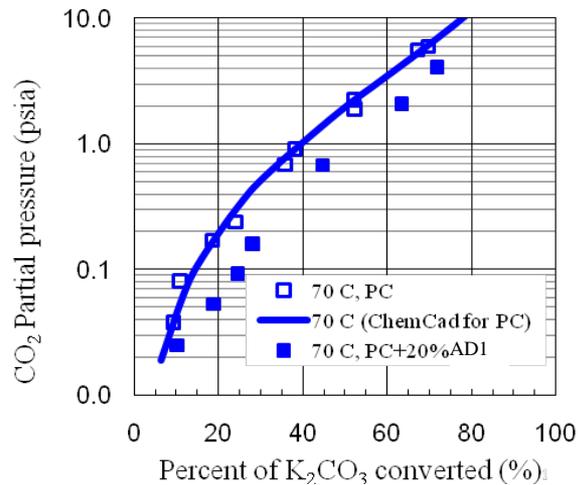
Breakdown of heat use in IVCAP

Equilibrium Pressure of Water Vapor over 20wt% PC + Additives



- Two additives, AD1 and AD2, identified to be effective for lowering water vapor pressure
- Equilibrium pressure of water vapor reduced by ~20% at 70°C and >20% at 50°C with 20wt% additives

Equilibrium Pressure of CO₂ over 20wt% PC + Additives



- CO₂ solubility in PC+AD1 (or AD2) increased, which favors the absorption of CO₂
- AD1, AD2 and their dissociation species in PC are only slightly volatile (<1 ppmv at 70°C, data not shown)
- Energy use (stripping heat) of IVCAP could be reduced by using additives
- Addition of 20wt% AD1 or AD2 exhibited some degree of inhibition on enzyme activity; further evaluation needed to identify tradeoff between activity impact and energy saving

(4) SO₂-Loaded Solvent (Sulfate) Reclamation

□ Batch test

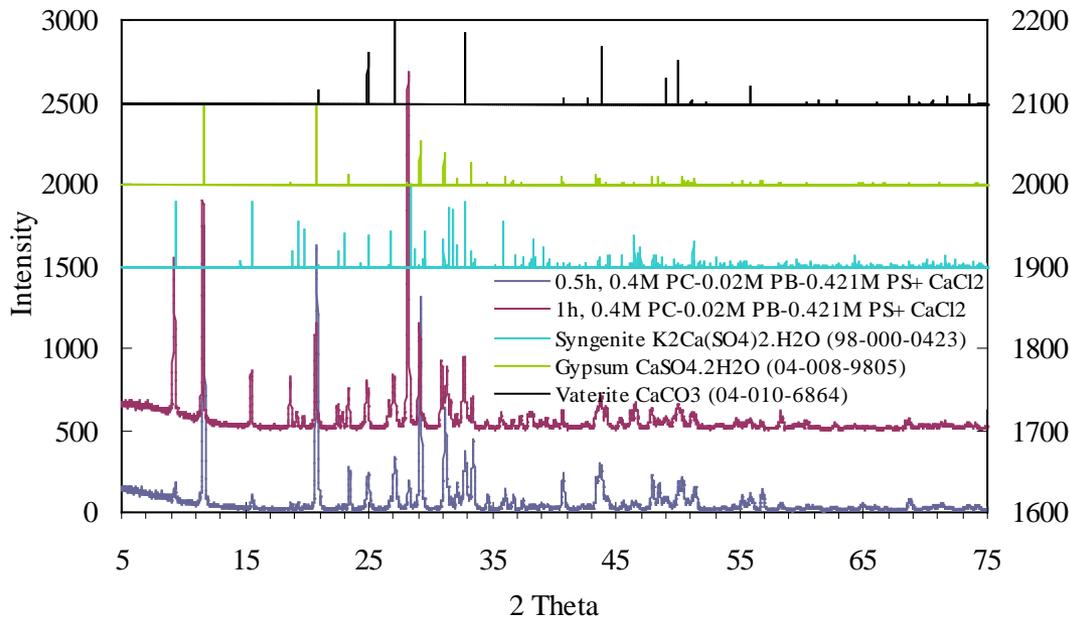
- Reaction of CaCl₂ with KHCO₃-K₂CO₃-K₂SO₄ in solution to simulate Ca(OH)₂ in real application
- Reduced initial K₂CO₃ concentration to partly simulate solution after reaction with high pressure CO₂ (CO₃²⁻+CO₂+H₂O=2HCO₃⁻)

25°C Initial solution makeup (M)				Equilibrium ratio based on initial makeup	SR* of CaSO ₄	SR of CaCO ₃
KHCO ₃	K ₂ CO ₃	K ₂ SO ₄	CaCl ₂			
2	0	0.12	0.12	5.3	459	809,407
2	0.006	0.12	0.12	4.7	459	919,238
2	0.1	0.12	0.12	1.2	459	3,730,195
0.4	0.02	0.421	0.421	20.2	5,645	2,617,354
0.2	0.01	0.211	0.211	20.2	1,418	655,893

SR: supersaturation ratio



Composition of Precipitation Products

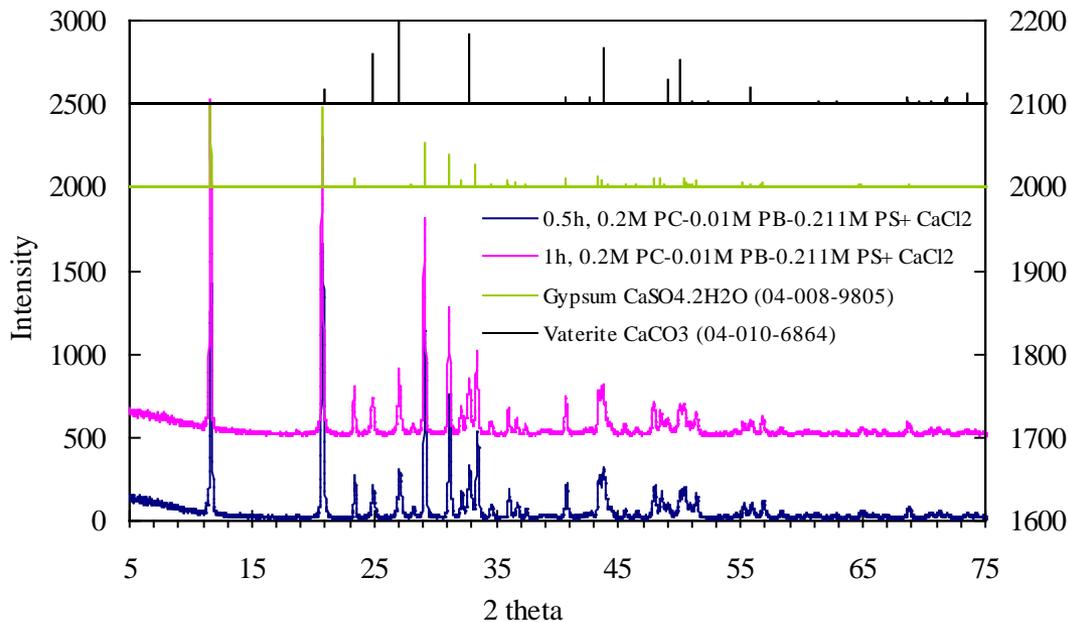


Composition of precipitates, wt%

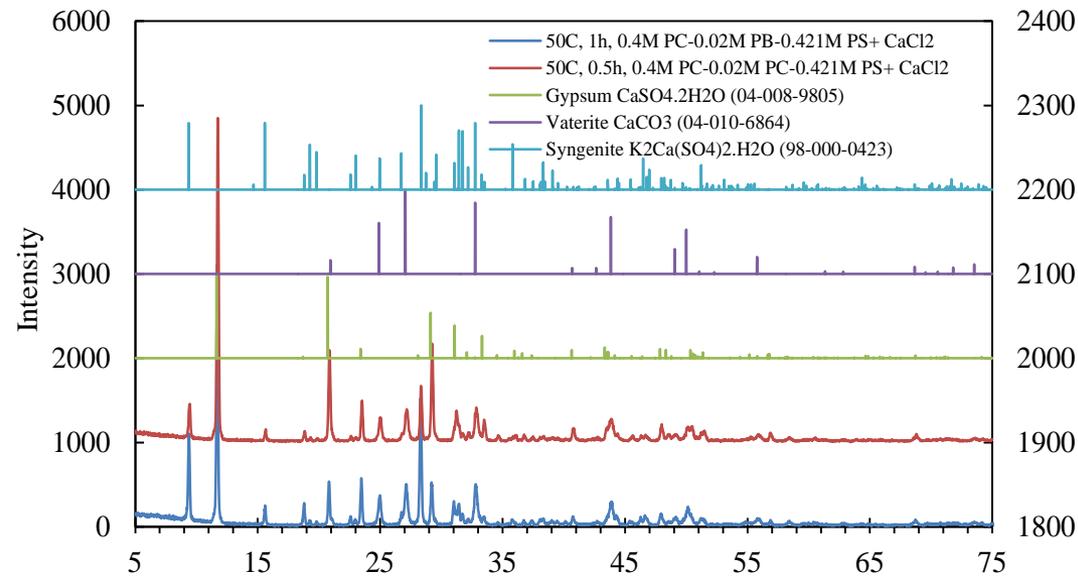
Crystal phase	0.5hr	1hr
Vaterite ($CaCO_3$)	30.8	25.6
Gypsum ($CaSO_4 \cdot 2H_2O$)	54.9	28.1
Syngenite ($K_2Ca(SO_4)_2 \cdot H_2O$)	14.3	46.3
Gypsum Equiv.*	67.0	67.2

Initial 0.4M $KHCO_3$ -0.02M K_2CO_3 -0.421M K_2SO_4 solution, 25°C (initial equilibrium $SO_4^{2-}/CO_3^{2-}=20.2$)

- ❑ Calcite/vaterite crystal dominant in precipitate at $SO_4^{2-}/CO_3^{2-} = 5.3, 4.7, 1.2$
- ❑ Gypsum and syngenite shared 60-70 wt% at $SO_4^{2-}/CO_3^{2-} = 20.2$
- ❑ Precipitation of $CaSO_4$ competitive to $CaCO_3$ at high SO_4^{2-}/CO_3^{2-} ratio



Initial 0.2M KHCO₃-0.01M K₂CO₃-0.211M K₂SO₄ solution, 25°C



Initial 0.4M KHCO₃-0.02M K₂CO₃-0.421M K₂SO₄ solution, 50°C

Reduced “salting-out” effect in diluted solution eliminated syngenite formation

Solution less saturated at 50°C than at 25°C, wt% of syngenite reduced

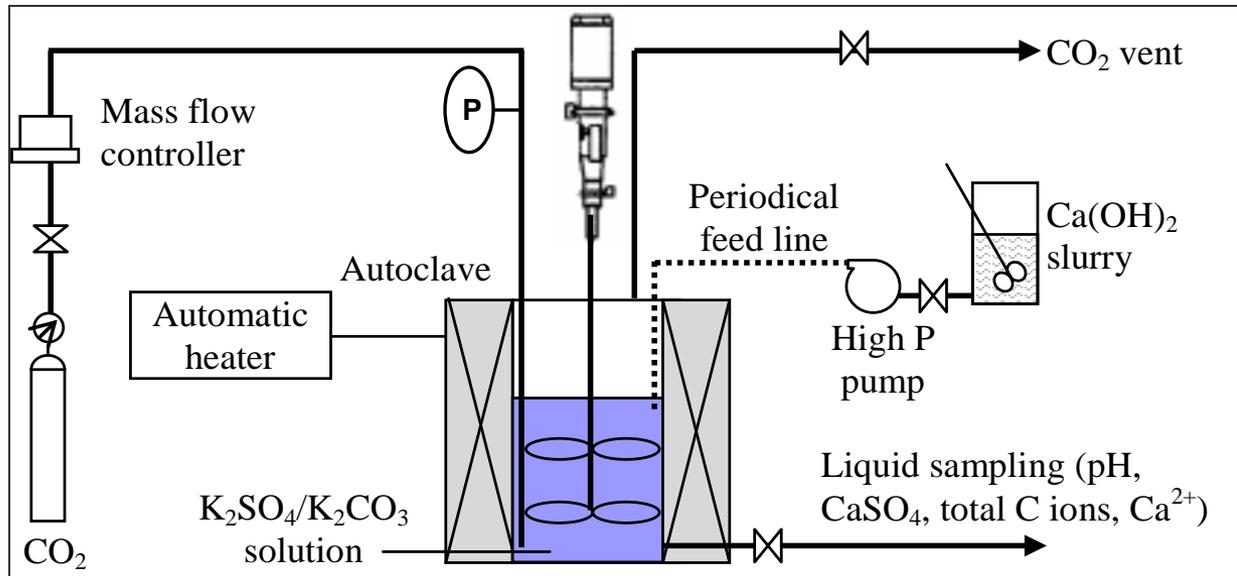
Semi-Continuous Tests Using a High Pressure Autoclave System for Sulfate Reclamation

❑ Batch test (atmospheric pressure)

- All $\text{KHCO}_3\text{-K}_2\text{CO}_3\text{-K}_2\text{SO}_4$ solutions were basic ($\text{pH} > 8.0$); impossible to obtain high $\text{SO}_4^{2-}/\text{CO}_3^{2-}$ ratio

❑ Semi-continuous test

- high pressure CO_2 gas employed to convert CO_3^{2-} to HCO_3^- (eg. at 40 atm, $\text{pH} < 6$ and $[\text{CO}_3^{2-}] = \sim 10^{-3} \text{ M}$ under equilibrium)
- Work in progress



Main Conclusions/Findings

- ❑ ACA is stable in presence of major flue gas impurities (SO_4^{2-} , NO_3^- , and Cl^-).
- ❑ ACA1 is stable at 25°C , but lost 70% of initial activity at 40°C in 6 months.
- ❑ ACA2 exhibited improved activity and higher stability compared to ACA (at $\geq 40^\circ\text{C}$)
- ❑ Immobilization of CAs had significantly improved thermal stability compared to free CAs
- ❑ New support materials under development; immobilized CA onto a new support tripled enzyme loading
- ❑ Two additives reduced equilibrium pressure of water vapor over 20wt% PC by $\sim 20\%$ at 70°C and $>20\%$ at 50°C with 20wt% addition; stripping heat could be reduced by using the additives
- ❑ In batch test, gypsum and syngenite products shared 60-70 wt% at $\text{SO}_4^{2-}/\text{CO}_3^{2-} = 21$; precipitation of CaSO_4 competitive to CaCO_3 at high $\text{SO}_4^{2-}/\text{CO}_3^{2-}$ ratio; semi-continuous test in progress to improve CaSO_4 yield



Plans for future testing/ development/ commercialization



Research Plan in the Future

- ❑ Evaluation of new thermophilic CA enzymes; Development and evaluation of new immobilization support/carrier materials and approaches
- ❑ Semi-continuous tests for reclaiming SO₂-loaded solvent to enable combined SO₂ removal with CO₂ capture
- ❑ Conduct techno-economic studies for the IVCAP installed in a 500MWe power plant

Pathways for next stage technology development

- Conduct techno-economic analysis studies
- If techno-economically viable,
 - Seek federal, state, and industrial support for a pilot-scale test (0.5-3 MWe)
 - Identify industrial partners (engineering companies, enzyme manufactures) for pilot-scale demonstration



Acknowledgements

- ❑ U.S. Department of Energy/ National Energy Technology Laboratory under Agreement No. DE-FC26-08NT0005498

