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Development and Evaluation of a Novel Integrated Vacuum Carbonate Absorption Process

(Contract No.: DE-FC26-08NT0005498)

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Illinois State Geological Survey
Prairie Research Institute
University of Illinois at Urbana-Champaign

Project Closeout Review

DOE/NETL, Pittsburgh, PA

July 13, 2012

Project Team

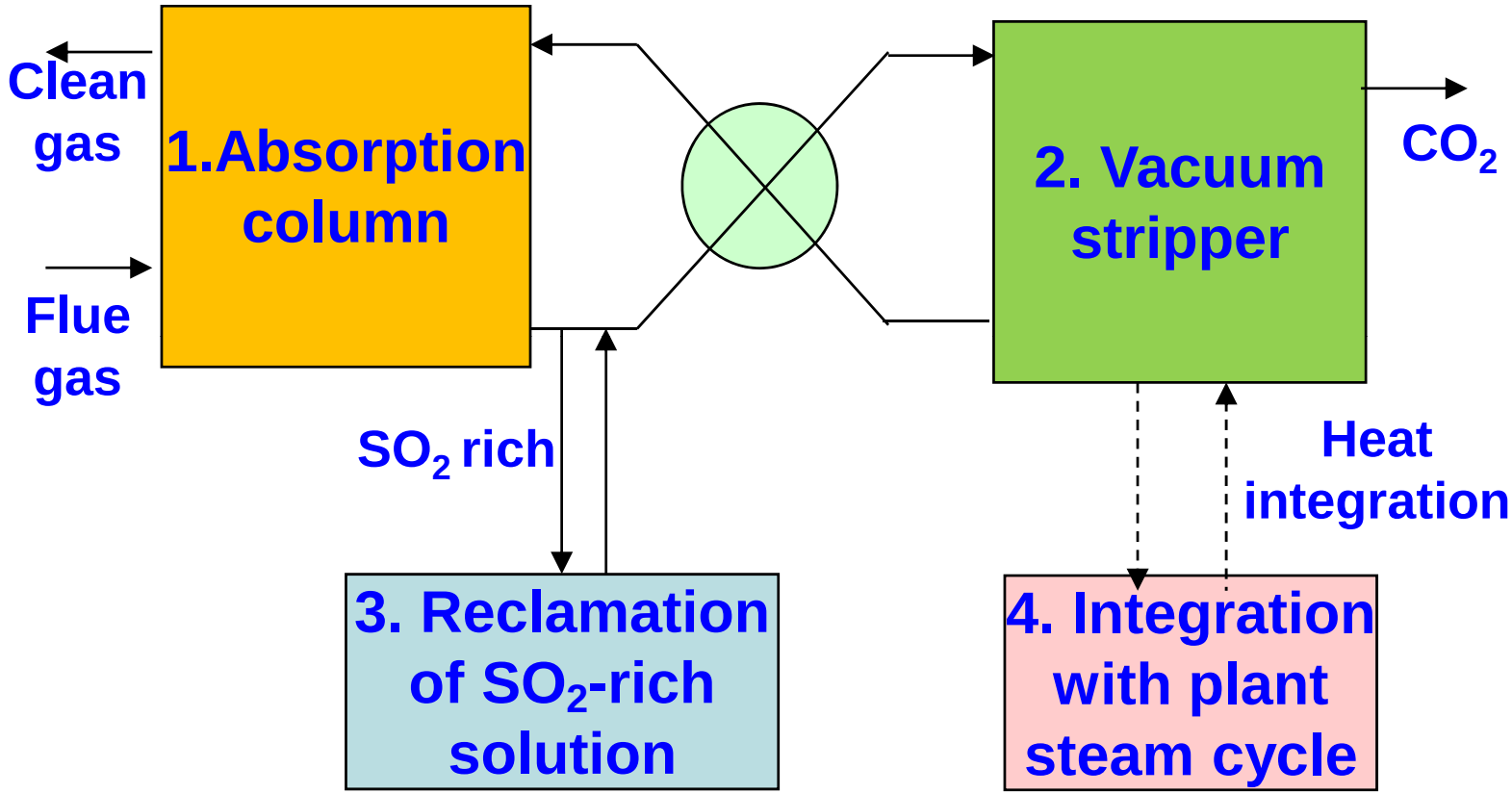
DOE/NETL:	Andrew Jones (COR)
UIUC:	Tatiana Djukardi (BS Chem E, biocatalyst stability) Arezoo Khodayari (Grad student, biocatalyst reactivity) Yongqi Lu (PhD Environmental E, PI) Mark Rood (Prof Environmental E, student supervision) Massoud Rostam-Abadi (PhD Chem E, principal technical adviser) David Ruhter (MS Biology/ecology, lab support) Priscilia Sinata (BS Chem E, process simulation) Xinhuai Ye (PhD Chem E, catalysts and additives studies) Shihan Zhang (PhD Environmental E, enzyme immobilization) Zhaohui Zhang (PhD BioChem E, enzyme immobilization)
Calgon:	Nick Pollack (PhD Chem E, material support and technical advisor for techno-economic studies)
Enzyme provider:	Two PhD scientists (technical support for enzyme research) (name not disclosed)

Lead Contractor

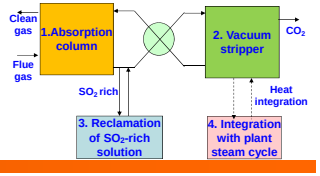
- Illinois State Geological Survey (ISGS) - University of Illinois
  - 200 scientists and technical support staff
  - One of five scientific surveys at the Prairie Research Institute (PRI)- University of Illinois
  - Lead organization of Midwest Geological Sequestration Consortium Partnership
  - A group of chemical/environmental engineers working on carbon capture and other energy & environmental technology research

Project Overview

IVCAP Process Schematic



Project Objectives

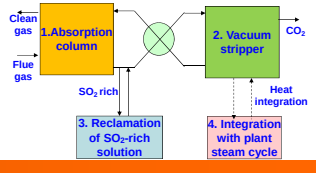


- **Overall goal**
  - Perform R&D, process engineering and techno-economic analysis to evaluate proof-of-concept and scale up of IVCAP

- **Objectives**
  - Identify catalysts to accelerate CO_2 absorption rate
  - Identify an effective additive to reduce stripping heat
  - Demonstrate combined SO_2 and CO_2 removal
  - Perform techno-economic evaluation

- **Success criteria**
  - Development of a catalyst and relevant process conditions to achieve an overall absorption rate of CO_2 into K_2CO_3 (PC) solution comparable to MEA solution (vs. project objective 1)
  - Identification of an additive to suppress water vaporization and reduce stripping heat by 20% (vs. project objective 2)
  - Effectiveness for multi-pollutant control of SO_2 and CO_2 (vs. project objective 3)

Scope of Work



- **Task 1: Screening and development of absorption catalysts**
  - **Objective: Accelerate CO2 absorption rate into PC**
    - evaluate activities of enzymes and other catalysts
    - develop immobilized enzymes on support materials

- **Task 2: Vapor-liquid equilibrium (VLE) measurement of PC with additives**
  - **Objective: Reduce stripping heat**
    - measure VLE of CO_2-PC systems with and without additives

- **Task 3: Kinetic study on reclamation of SO_2-loaded solvent**
  - **Objective: Combined SO2/CO2 capture**
    - study competitive crystallization of sulfate in SO_2 loaded PC

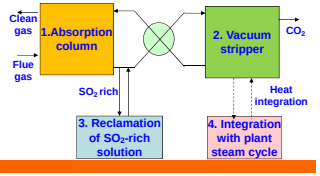
- **Task 4: Techno-economic analysis**
  - **Objective: energy performance /capture cost**
    - perform process simulation and techno-economic evaluation

- **Task 5: Project management & planning**

Project Schedule

- **Project period of 10/1/2008 through 4/30/2012**
  - BP1 including a 7-month no cost extension: 10/1/2008-4/30/2010
    - delay in personnel recruiting
    - signing non-disclosure and material transfer agreements with an enzyme manufacturer
  - BP2: 5/1/2010-4/30/2011
  - BP3: 5/1/2011-4/30/2012

Gannt Chart



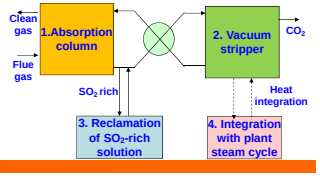
	BP1*												BP2												BP3											
Months after contract award	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
Task 1. Development of absorption catalysts																																				
1.1 Experimental set up																																				
1.2 CA activity									a	A																										
1.3 Inorganic catalysts												b	B																							
1.4 CA immobilization																		c																		
1.5 Impacts of additives from task 2																						d														
Additional tasks																																				
A1 Evaluation of thermophilic CA																														l						
A2 Dev. & evalu. of novel support material/method for CA immobilization																																	m			
Task 2. V-L equilibrium Measurement																																				
2.1 Experimental set up																																				
2.2 Reference solutions																e																				
2.3 Solutions with additives																				f	C															
3. Kinetic study of solvent reclamation																																				
3.1 Batch test																								g												
3.2 Semi-continuous test																													h							
3.3 Impact of inorganic catalysts and additives from tasks 1 and 2																															i					
Task 4. Techno-economic analysis																																				
4.1 Process simulation																																	j			
4.2 Cost analysis																																		k		
Task 5. Management &Reporting			Q			Q			Q			Q			Q			Q			Q			Q			Q			Q			Q			F

10/1/2008 4/30/2010 4/30/2011 4/30/2012

* BP1 was no-cost extended for 7 months

a, b, c, d, e, f, g, h, i, j, k, l, m: milestones; A, B, C: decision points

Project Milestones



	Title	Completion time	Verification method
a	Task 1.2 Reactivity test of enzyme	BP1-9th month	Kinetic data acquired for selected enzymes
b	Task 1.3 Reactivity test of inorganic catalysts	BP2-12th month	Kinetic data acquired for selected inorganic catalysts
c	Task 1.3 Enzyme immobilization completed and its activity	BP2-6th month	An immobilization method developed and reactivity of enzymes immobilized on 2-3 support materials evaluated
d	Task 1.4 Impact of additives on catalyst activity	BP2-10th month	Evaluation result of additives (tested in task 2.3) on the reactivity of enzymes.
e	Task 2.2 Selected V-L equilibrium measurement of solutions w/o additives	BP2-4th month	V-L equilibrium data provided
f	Task 2.3 V-L equilibrium measurement of solutions with additives	BP2-8th month	V-L equilibrium data provided
g	Task 3.1 Batch test of solvent reclamation	BP2-12th month	Kinetic data of the crystallization process from the batch test acquired
h	Task 3.2 Semi-continuous test of solvent reclamation	BP3-5th month	Kinetic data of the crystallization process under high pressure conditions acquired
i	Task 3.3 Impact of catalysts and additives on solvent reclamation	BP3-7th month	Evaluation result of the impacts of selected catalysts and additives provided
j	Task 4.1 Process simulation	BP3-9th month	Proposed process and integration with a 500 MW plant simulated
k	Task 4.2 Cost analysis	BP3-10th month	Cost results for the application in a 500 MW plant provided
l	Task A1 Evaluation of thermophilic CA	BP3-6th month	Activity and 1-2 month stability of thermophilic CA tested
m	Task A2 Development & evaluation of novel support material/method for CA immobilization	BP3-9 th month	1-2 novel support/carrier materials developed and immobilized CA prepared

All milestones completed: (1) BP1 extended for 7 mon; (2) Two milestones (h & i) delayed for 3 mon

Work Activities in Response to NETL/AIChE Peer Review Board's Recommendations/ Comments

- Project selected for NETL/AIChE Peer Review in July 2011

- Additional work tasks
  - Perform a sensitivity analysis to investigate and optimize stripping pressure and temperature conditions
  - Perform a sensitivity analysis to investigate and optimize key enzyme performance metrics
  - Refine calculations on steam pressure in the reboiler
  - Refine calculations on CO_2 pressure entering the vacuum pump
  - Conduct literature searches related to technical risks (e.g., recycle water treatment needs; corrosion inhibitors; potential air ingress into the vacuum system; potential impact of flue gas trace components on enzymes)

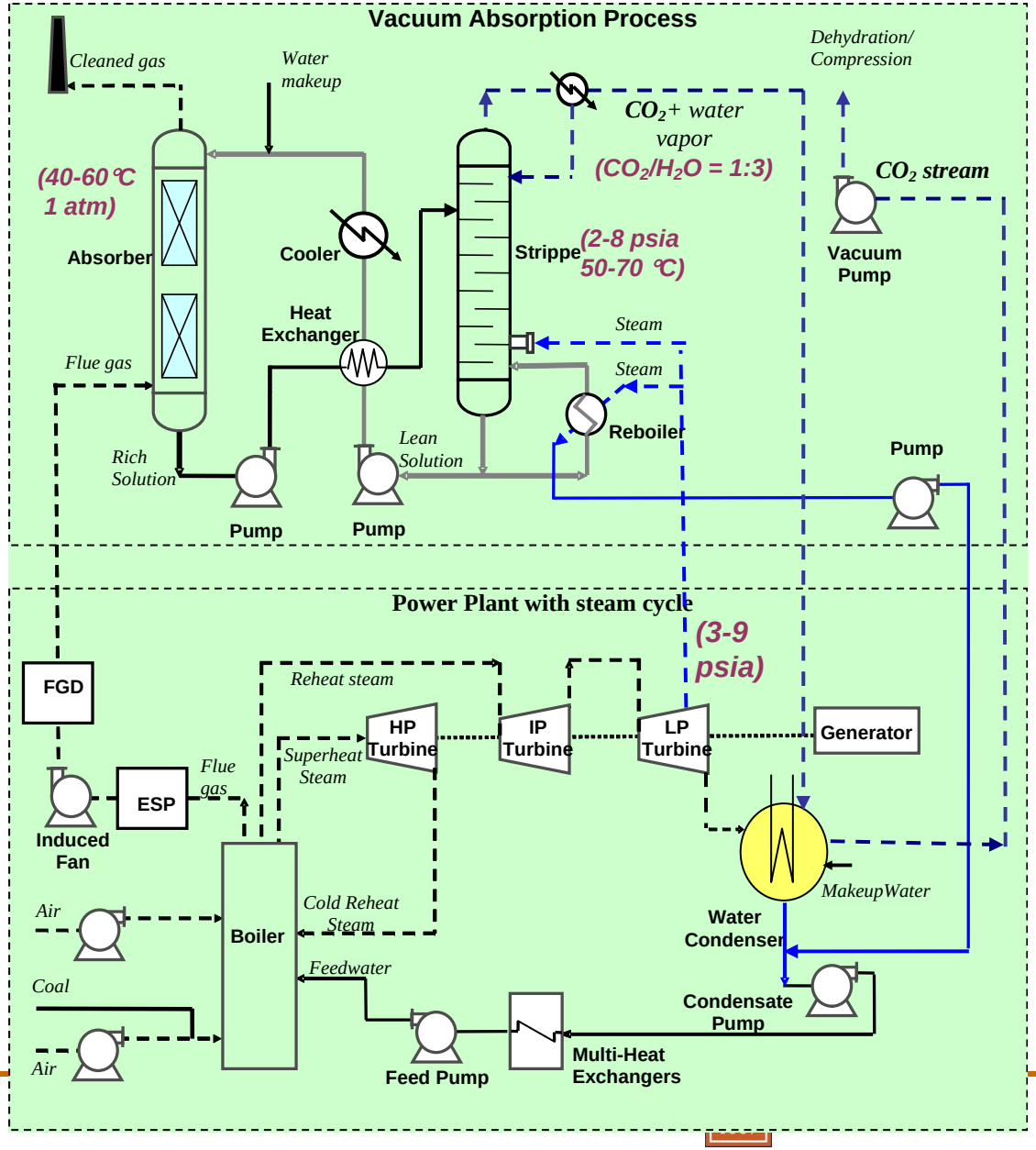
Project Cost

- **Total Budget**
  - DOE funding: $765 K
  - Cost share (33% of total budget)
    - Calgon Carbon Corporation (in kind): $100 K
    - UIUC-ISGS (in kind): $275 K

- **Expenditure as of 5/31/2012**
  - DOE share: $746K (as of 5/31/2012)
  - Cost share:
    - $309 K from Calgon and UIUC (as of 3/31/2012)
    - $118 K from ICCI

Scientific and technical background of technology

Diagram/ Concept of Integrated Vacuum Carbonate Absorption Process



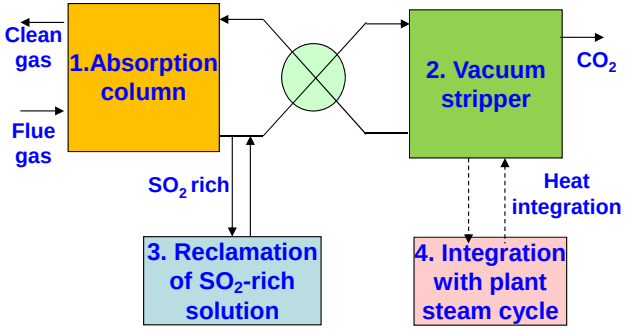
Chen, Lu, Rostam-Abadi, Patent No. US 8,062,408, Nov. 2011

Features of IVCAP

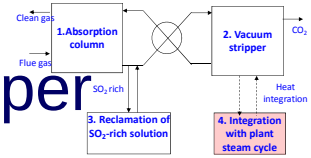
1. Stripper operates at 2-8 psia and 50-70°C
   - can use low quality steam from power plant
   - can use steam for direct heat exchange
   - can reduce parasitic power use by 25-35% compared to baseline MEA processes

2. Employs a biocatalyst to promote absorption rate

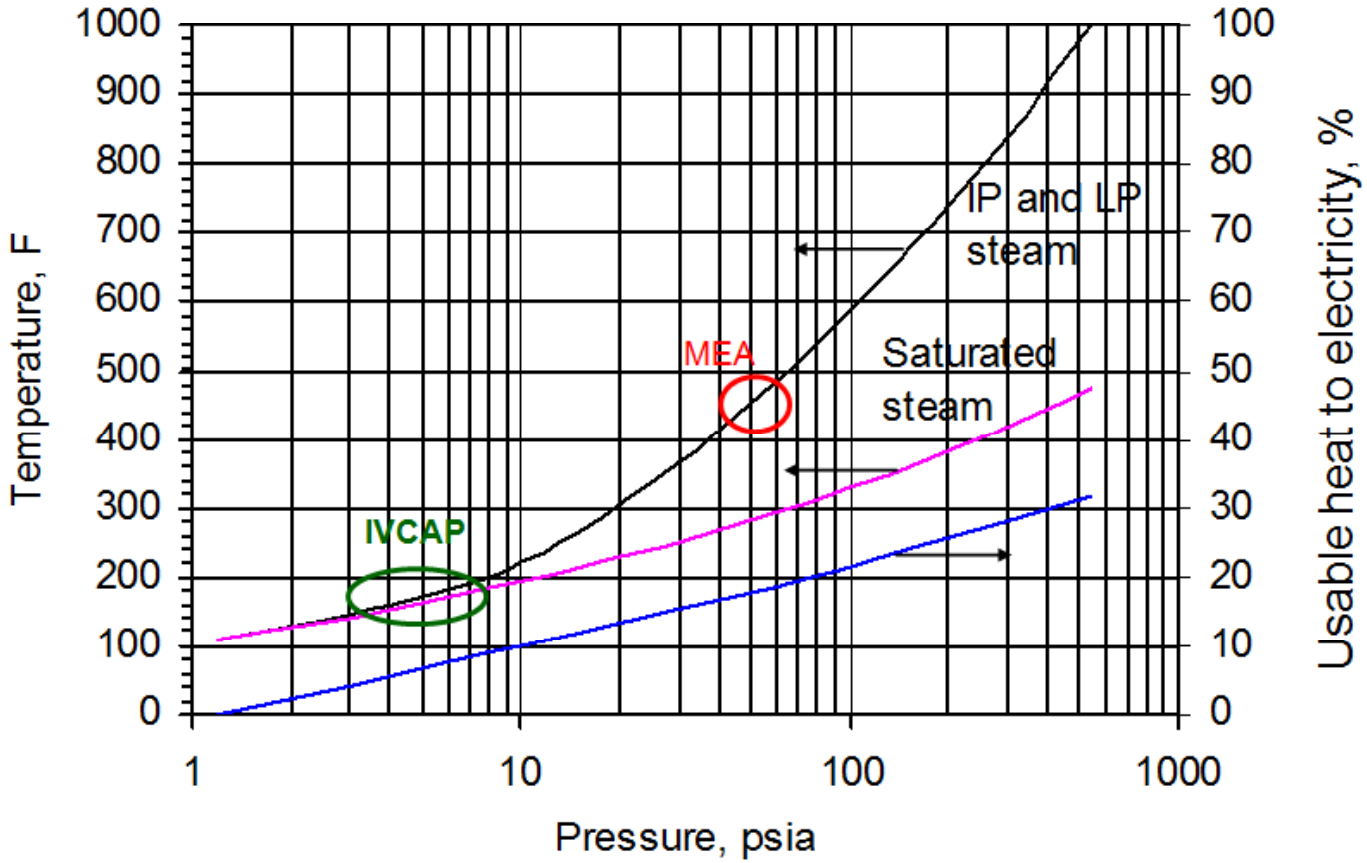
3. Combines SO_2 removal with CO_2 capture



Feature 1: Benefit of Using Low-Quality Steam in Stripper

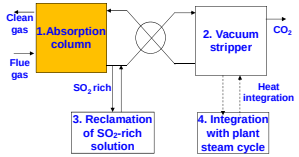


- Lower quality steam → less electricity loss
- lower stripping temperature allows use of lower quality steam



Superheated steam in power plant IP and LP turbines

Feature 2: CO_2 Absorption Promoted with a Biocatalyst



Without a catalyst:

- Reaction (1) slow in water
- Reaction (2) dominant at pH >9 (pH of $K_2CO_3/KHCO_3$ solution is 9-11)

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \qquad (1)$$

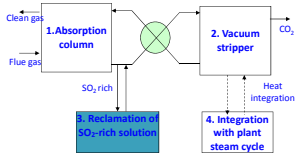
$$CO_2 + OH^- \Leftrightarrow HCO_3^- \qquad (2)$$

With ***carbonic anhydrase* (CA)** enzyme

- Reaction (1) dominant

$$CO_2 + H_2O \xrightarrow{CA} H^+ + HCO_3^- \qquad (1')$$

Feature (3): Combined SO_2 Removal in CO_2 Capture



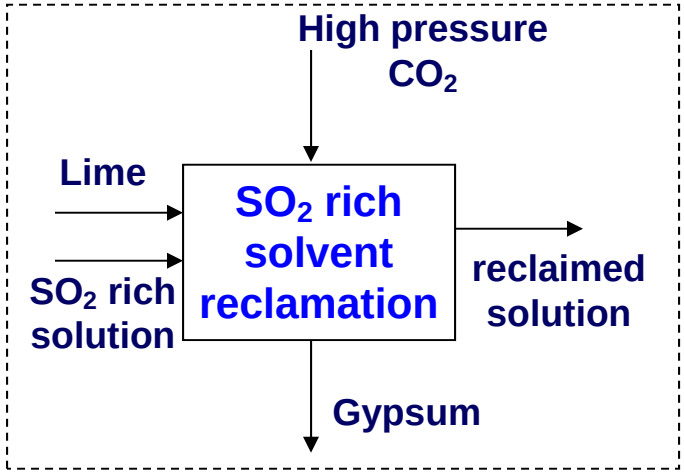
- Absorption:

$$SO_2 + 1/2O_2 + K_2CO_3 = K_2SO_4 + CO_2$$

- Sulfate reclamation:

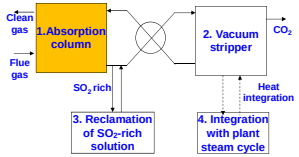
$$K_2SO_4 + Ca(OH)_2 + 2H_2O + 2CO_2 = CaSO_4 \cdot 2H_2O \downarrow + 2KHCO_3$$

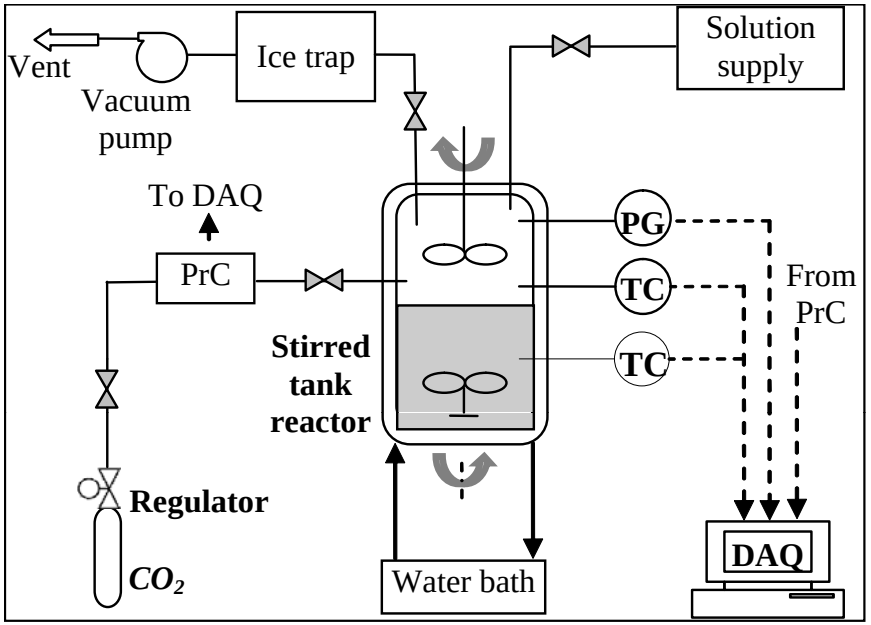
- Reducing $[CO_3^{2-}]$ favors $CaSO_4$ and limit $CaCO_3$ precipitation :
  - High pressure CO_2
  - Low pH
  - Appropriate temperature



Major Activities and Findings

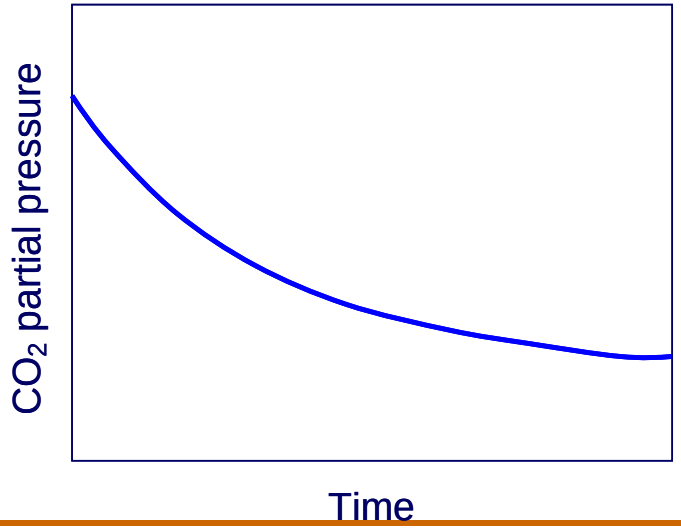
1. Evaluation of Catalysts to Promote CO_2 Absorption





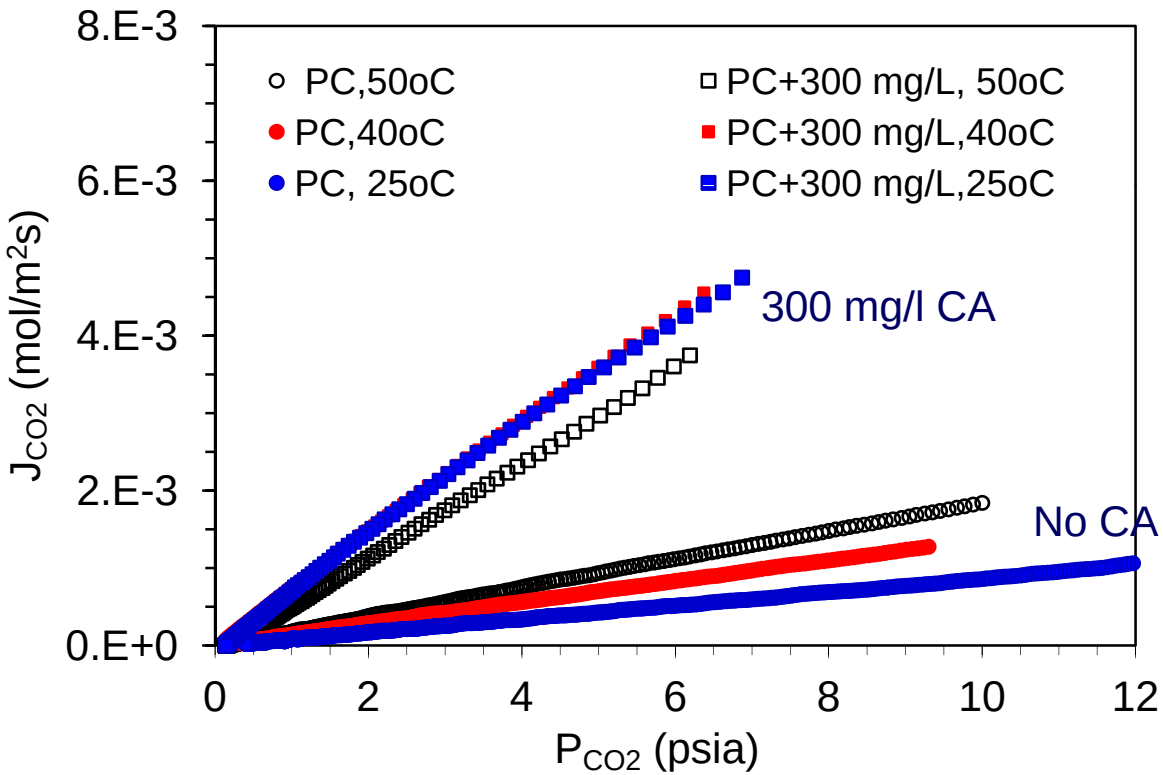
- Instant flux of CO_2 absorption

$$J_{CO2} = \frac{dP_{CO2}}{dt} \frac{V_g}{R\,T\,A_{GL}}$$



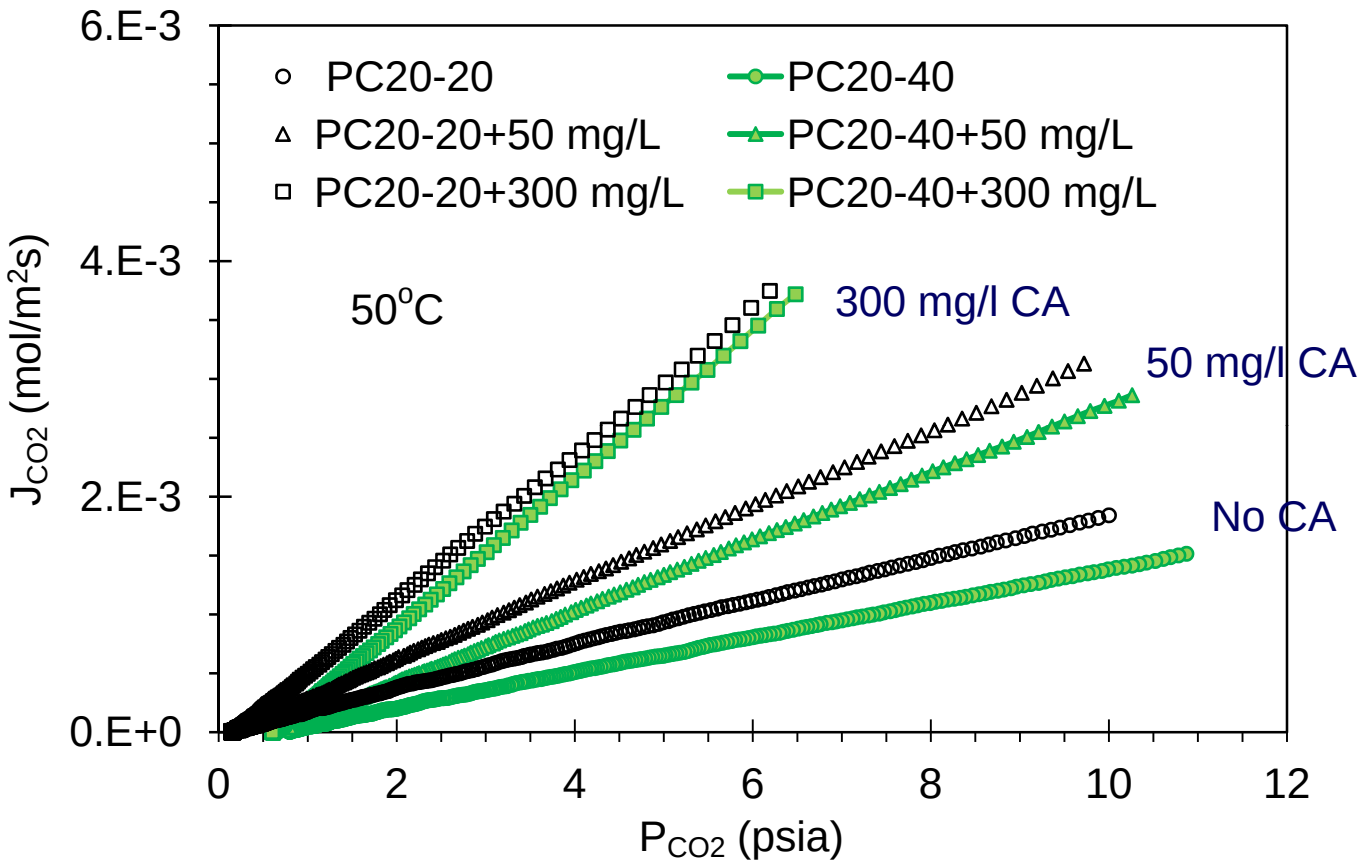
Activity of Carbonic Anhydrase (CA) Enzymes

- Two CA enzymes
  - ACA1 and ACA2 technical-grades produced in pilot units
  - As-received sample, not purified



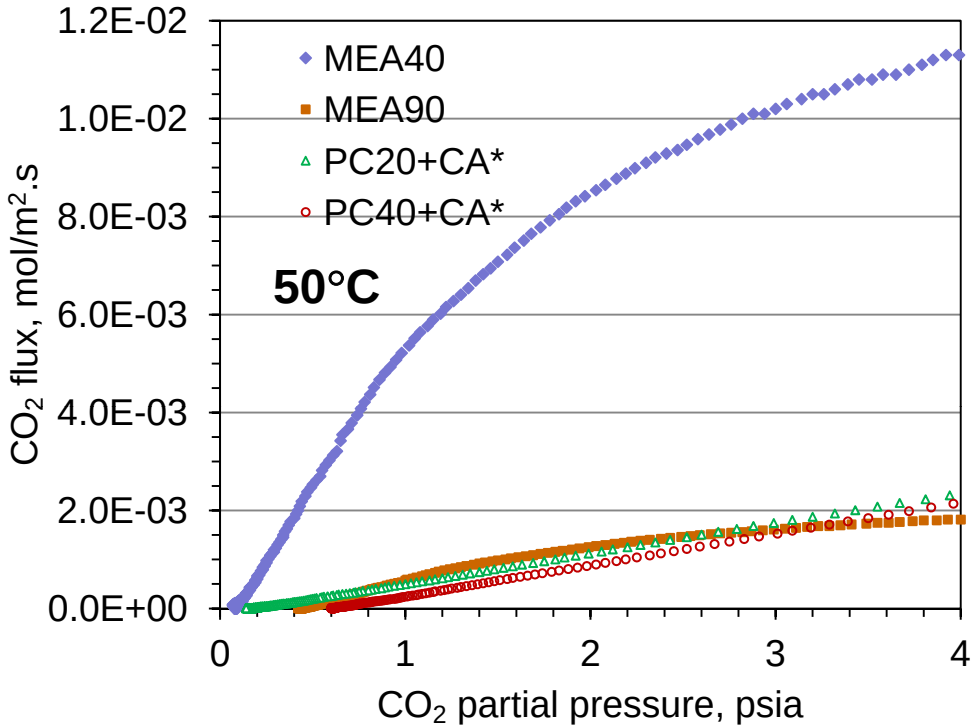
- **Rates increased by ~10 times at 25°C, ~5 times at 40°C, ~3 times at 50°C at 300mg CA/L**
- **Rates comparable at 25-50°C with CA (CO_2 solubility vs. kinetics dependence on T)**

Activity of Carbonic Anhydrase (CA) Enzymes



- Rates comparable at different CO_2 loading levels

Comparison between PC+CA and MEA



PC20+CA* (lean): 20wt% PC with 40% conversion + 300mg/L CA

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

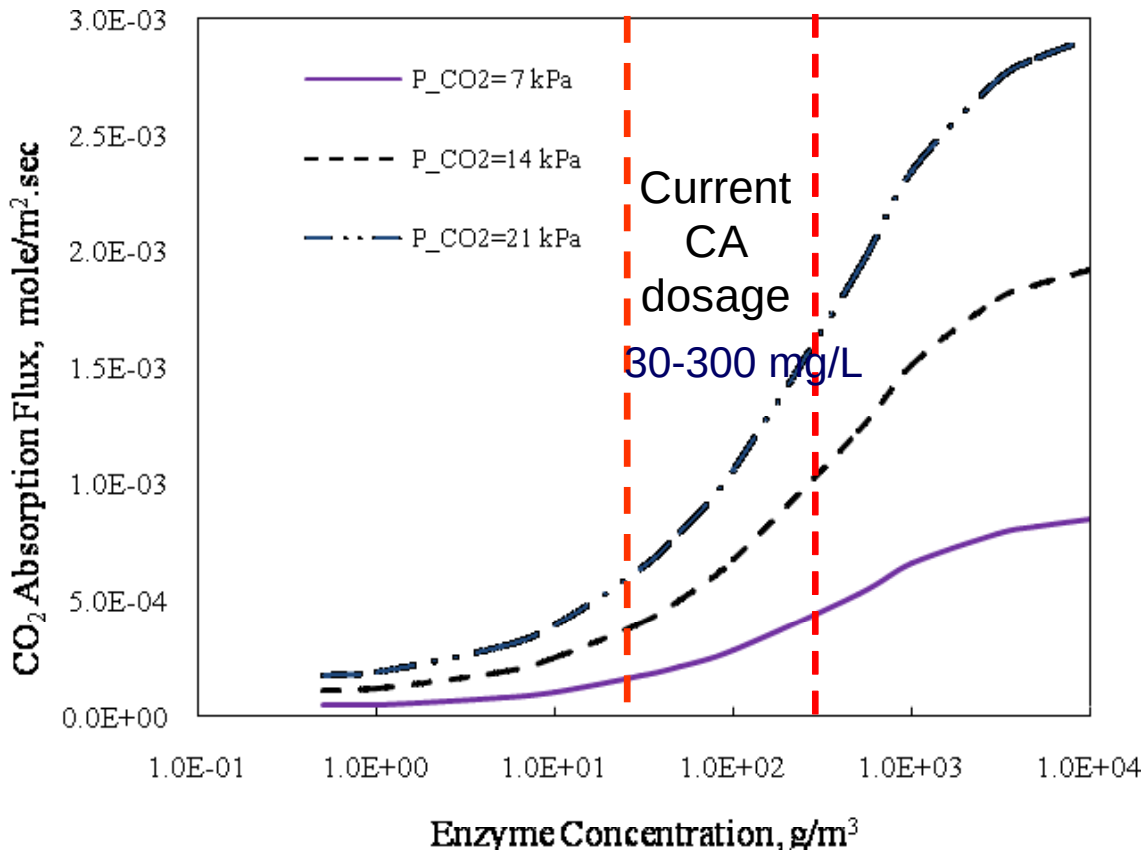
MEA40 (lean): 5M MEA with 40% conversion (0.2 mol CO_2/mol MEA)

MEA90 (rich): 5M MEA with 90% conversion (0.45 mol CO_2/mol MEA)

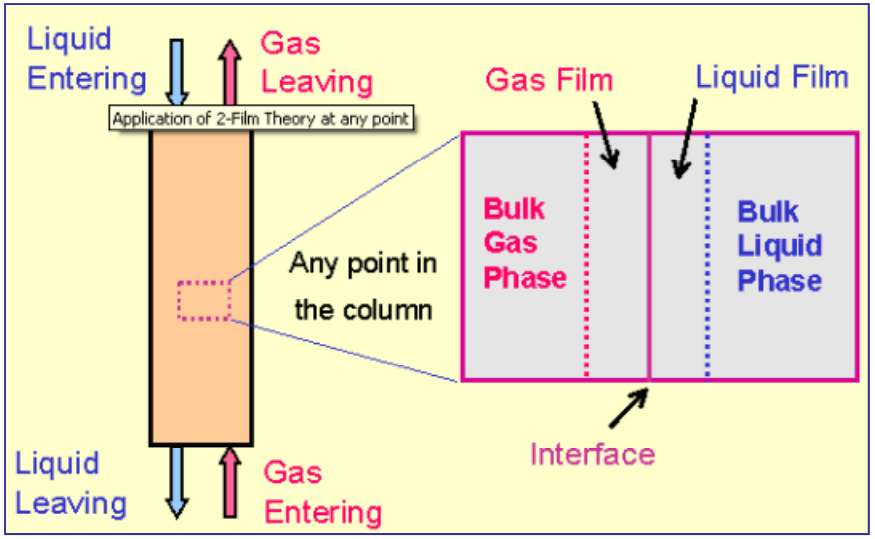
- Rates into PC + CA(300mg/L) at 50°C
  - Rates in lean solution: PC20+CA is 4-9 times slower than MEA40
  - Rates in rich solution: PC40+CA is comparable to MEA90

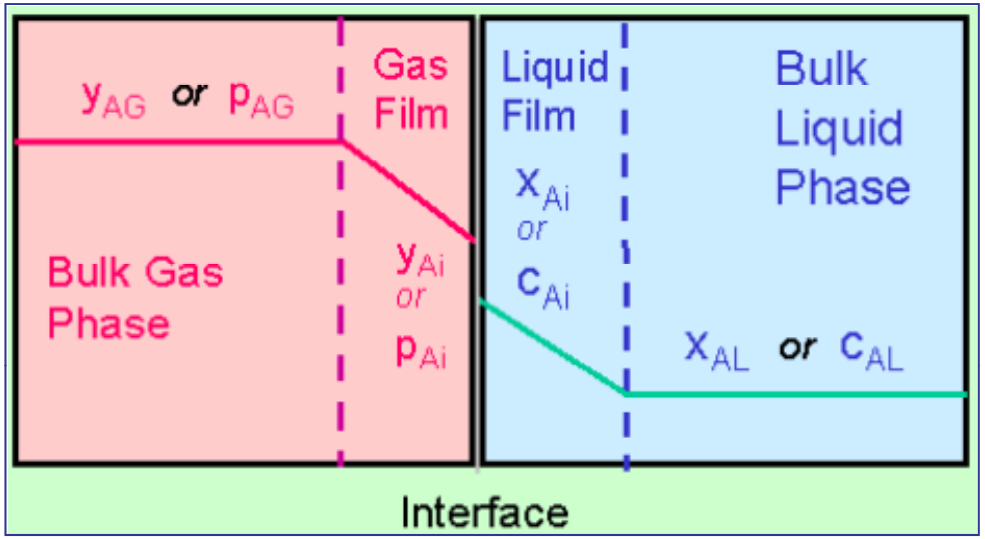
Predicted Rates Promoted at Different CA Dosage Levels

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



Diffusion and Reaction in Packed Bed Absorber

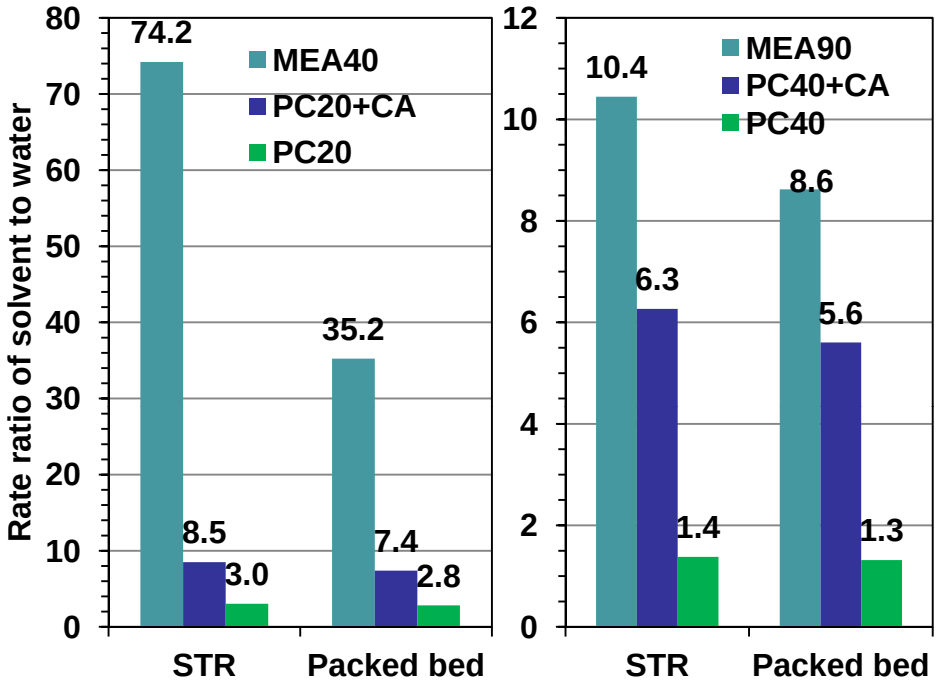




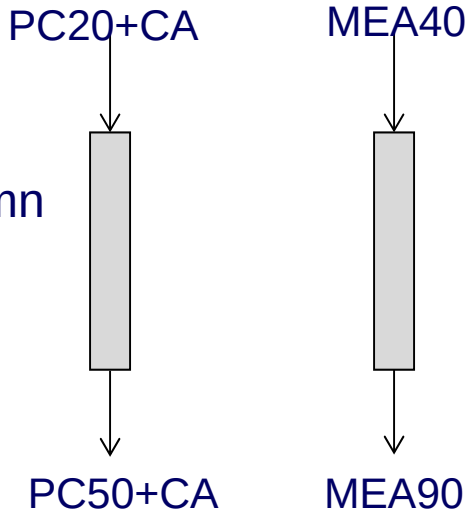
Schematic of absorption based on two-film theory

- CO_2 gas-phase mass transfer negligible in STR test
- Gas- and liquid-phase mass transfers in absorption column

Comparison of Modeled Rates in Packed-Bed Column

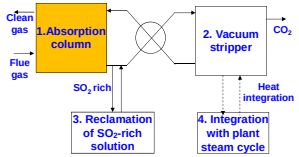


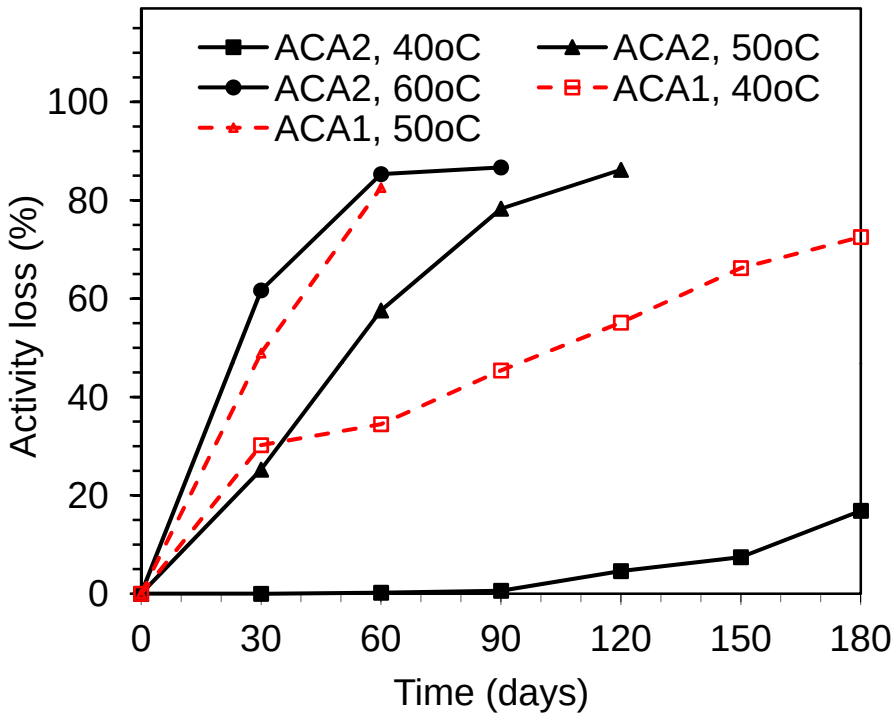
50 °C	Gas-phase resistance	Liquid-phase resistance
Column top		
MEA40	49.5	50.5
PC20+CA*	10.4	89.6
PC20	4.0	96.0
Column bottom		
MEA90	12.1	87.9
~PC40+CA*	7.9	92.1
PC40	1.9	98.1



- Gas diffusion resistance significant in MEA at the top of column
- Liquid phase resistance dominants in PC+CA
- Rate into PC+300mg CA/L is 1.5-4.8 times lower than MEA
  - A smaller difference between PC+CA and MEA rates at higher CO_2 loading

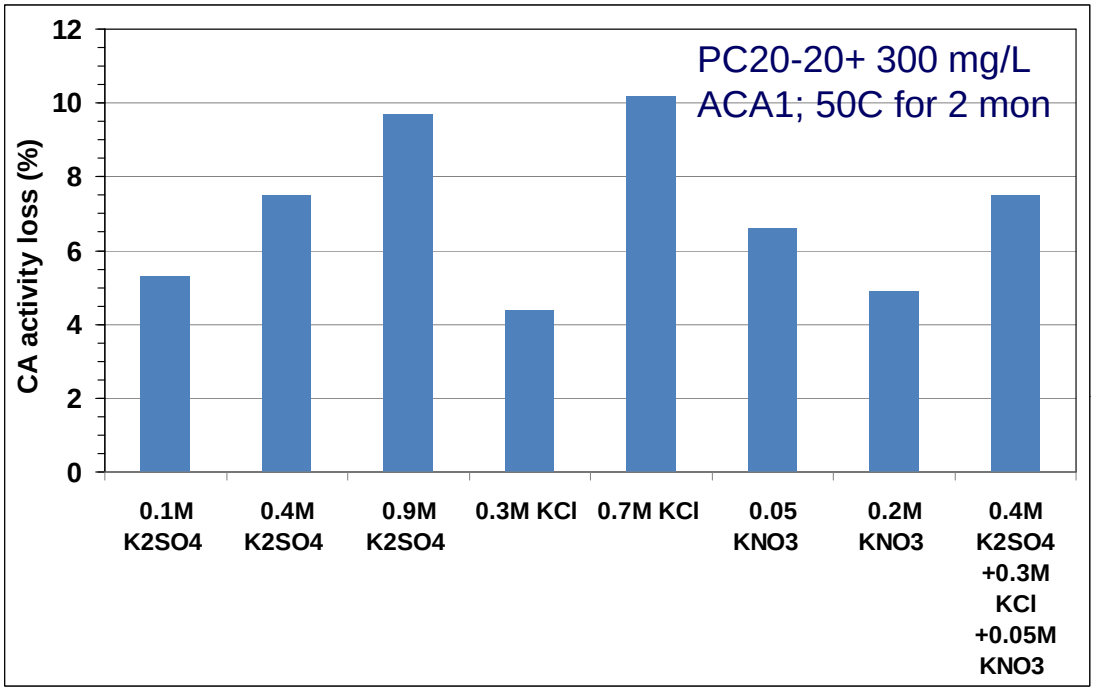
2. Stability of CA Enzyme - Thermal Stability





- ACA2 relatively stable at 40°C
- ACA2 better stability than ACA1

Stability of CA Enzyme – in Presence of Flue Gas Impurities



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

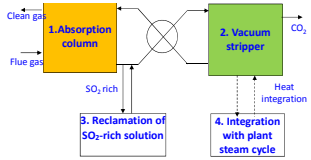
$(E_{cat,pur}\ enhancement\ factor\ w/o\ impurity)$

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

0.9M 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)

- <11% loss of initial CA activity in presence of SO_4^{2-}, NO_3^-, and Cl^-

3. Enzyme Immobilization



Advantages

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

Support materials

- Porous materials
  - Macro-porous particles (e.g., controlled pore glass (CPG)
  - Meso-porous particles (e.g., activated carbon, CPG)
- Non-porous nanoparticles (e.g., silica)

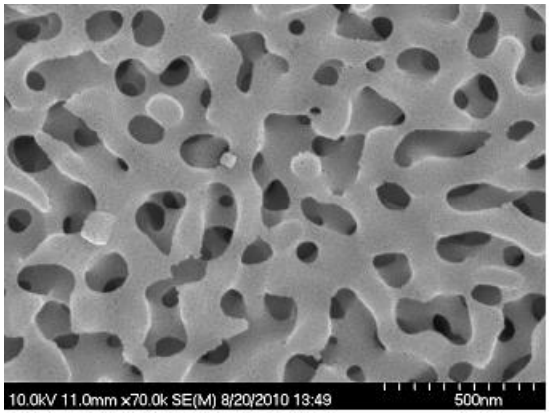
3.1 CA Immobilization onto Porous Materials

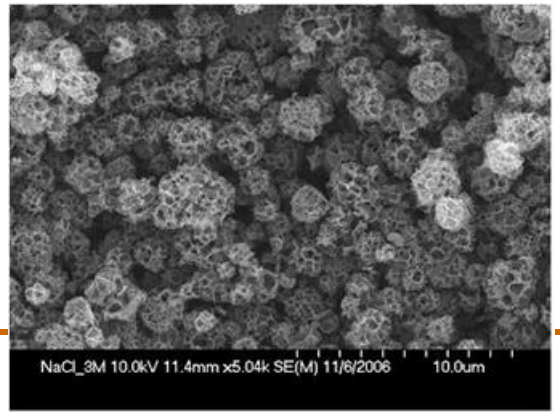
Support materials

- Controlled pore glass
  - CPG100 (200-400 mesh)
  - CPG38 (40-60 mesh)
- Porous AC

Enzymes

- SCA (sigma CA)
- ACA1

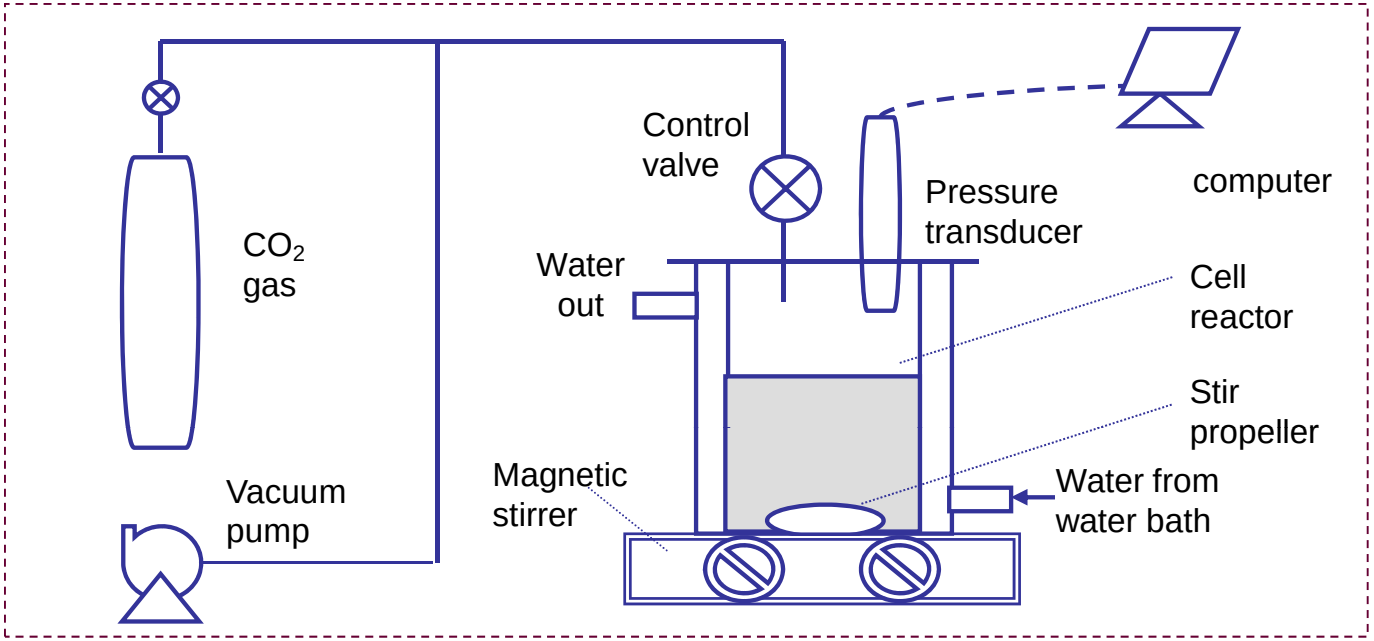




	Average pore size, nm	BET surface, m^2/g	Pore volume, cm^3/g
AC	3.8	1007.0	0.50*
CPG38	38.1	64.5	1.06
CPG100	100	21.8	0.79

* Pores of 2-20 nm contributed 20%

CA Activity Assay: Manometric Method



- CO_2 hydration activity
  - CA in 15 mL of 0.1 M Na_2HPO4–NaH_2PO4 buffer solution (pH 7.4) (or: 15 ml of 0.1M K_2CO_3/$KHCO_3$ solution (pH10.0))
  - CO_2 pressure drop monitored at 4°C

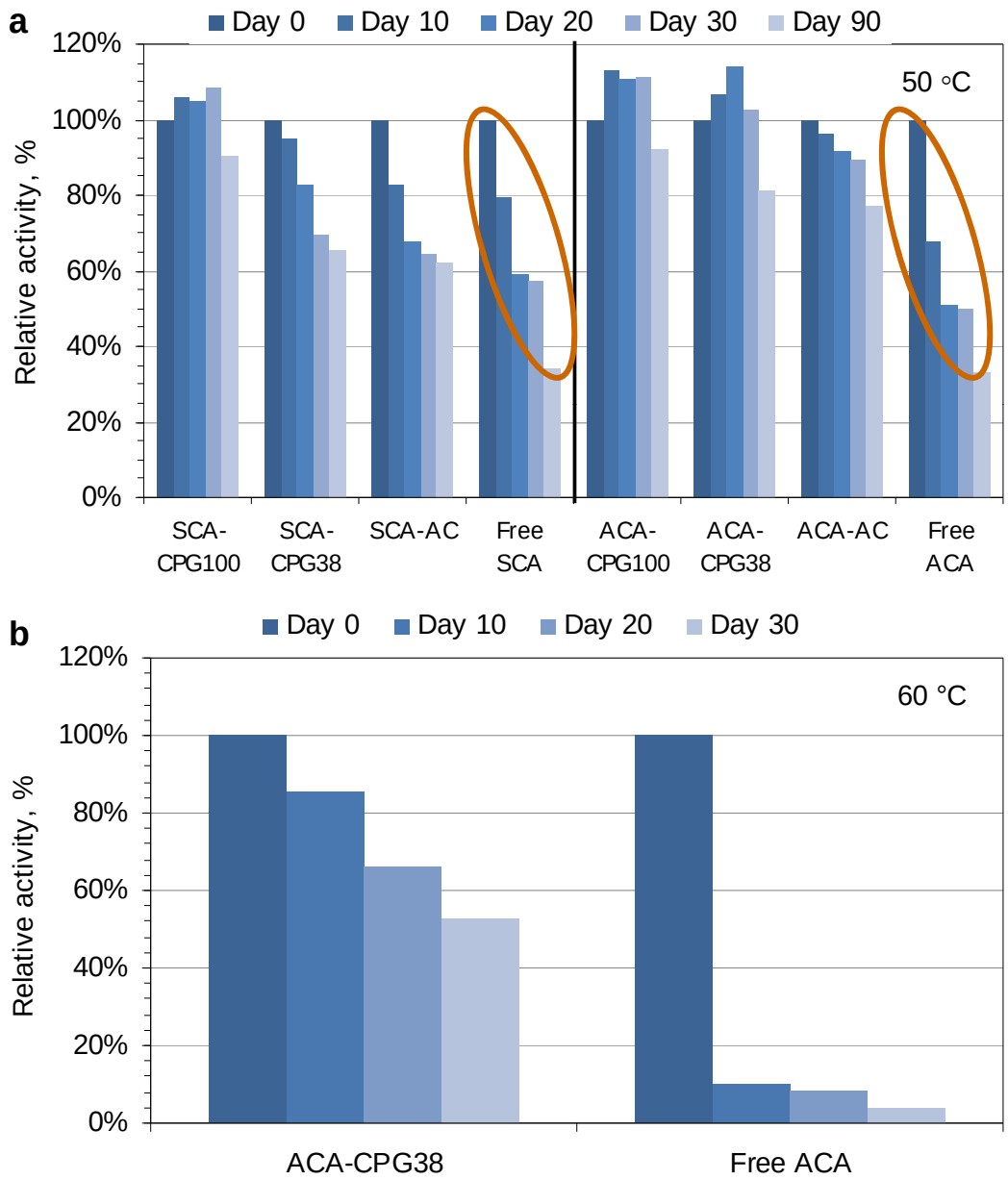
Activity of Immobilized CA Enzyme

Sample	Enzyme loading (mg CA/g support)	Immobilization factor (IF)	CA activity
SCA-CPG100	18.3	0.383	*p*-NPA hydrolysis
		0.159	CO_2 hydration
SCA-CPG38	32.6	0.351	*p*-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

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

- **Mesoporous support (CPG38) provided a good tradeoff between pore size and pore volume for achieving high CA loading and CO_2 activity**

Thermal Stability of Immobilized CA Enzymes

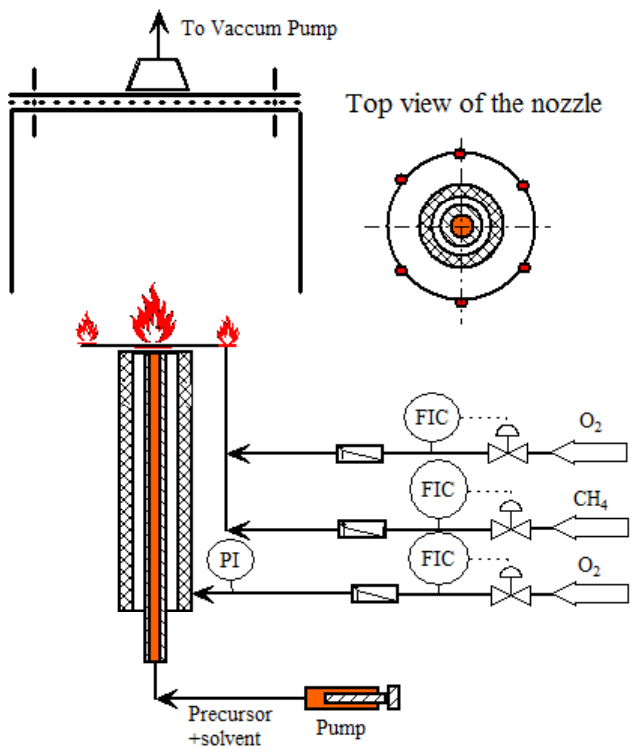


- 60-300% better thermal stability than **free CAs**

3.2 CA Enzyme Immobilization onto Nonporous Nanoparticles

- Nonporous nanoparticles as support matrices:
  - large external surface area for enzyme attachment
  - no intra-particle diffusion for CO_2 substrate
  - Can be separate-ready (e.g., adding magnetic components)

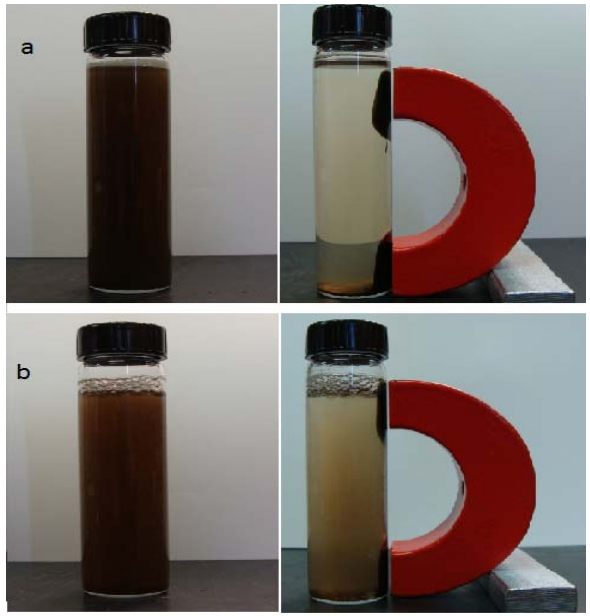
Synthesis of Silica Nanoparticles by Flame Spray Pyrolysis (FSP)



- Easy to scale up
- Controlled sorbent properties (size, composition, etc)
- Suitable for massive production

Support synthesized:

- Silica nanoparticles: SN1 (15nm), SN2 (25), SN3 (35)
- SiO_2-ZrO_2 composite: SZ1 (Si/Zr=4), SZ2 (Si/Zr=1)
- SiO_2- γ-Fe_2O_3 composite: SF1 (Si/Fe=4), SF2 (Si/Fe=8)



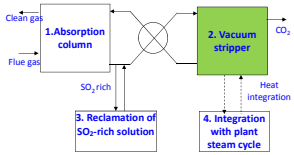
Magnetic SiO_2-Fe_2O_3 nanoparticles

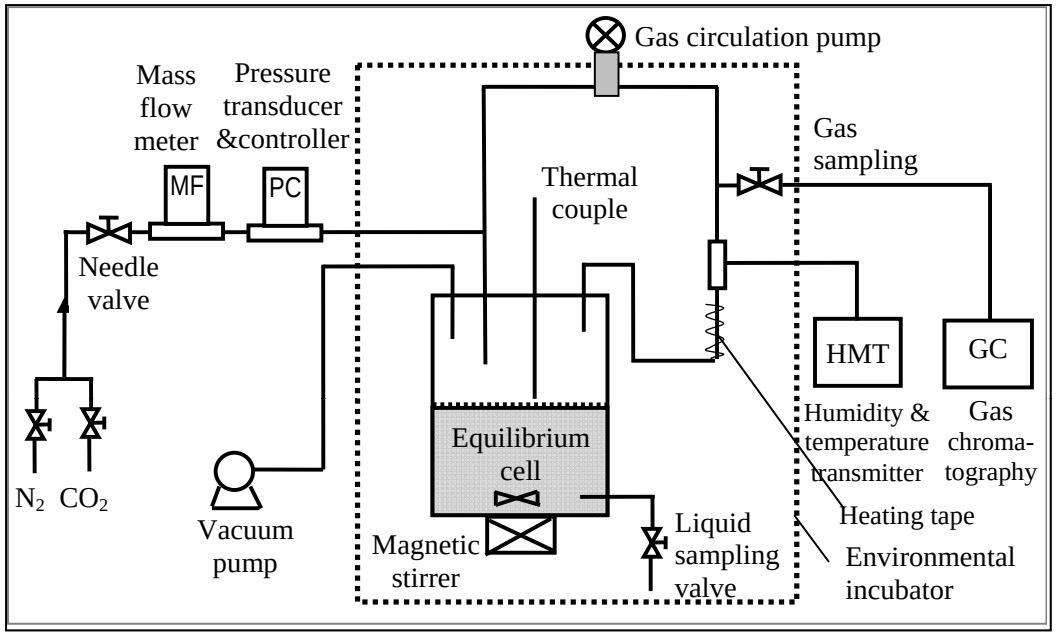
Loading and Activity of CA Enzyme Immobilized onto Nanoparticles

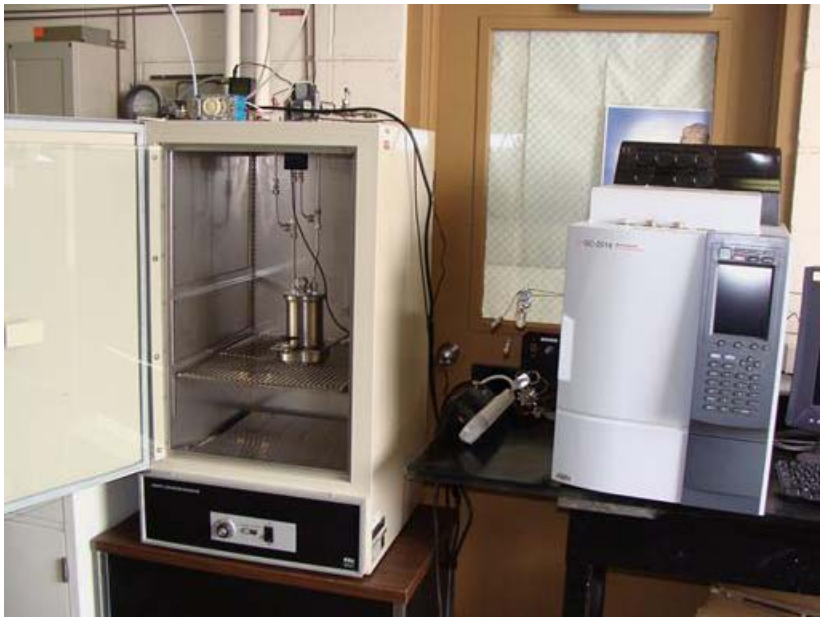
Samples*	Enzyme loading, mg/g	IF, %
SCA	-	-
ACA1	-	-
SCA-SN1	54.9	47.0
SCA-SN2	49.4	44.6
SCA-SN3	45.1	36.3
ACA1-SN1	50.2	37.5
ACA1-SZ1	35.9	41.2
ACA1-SZ2	22.7	32.5
ACA1-SF2	52.5	46.8
ACA1-SF1	47.3	40.3

- Enzyme loading and activity of CA enzyme on nanoparticles improved compared to micro-sized porous materials

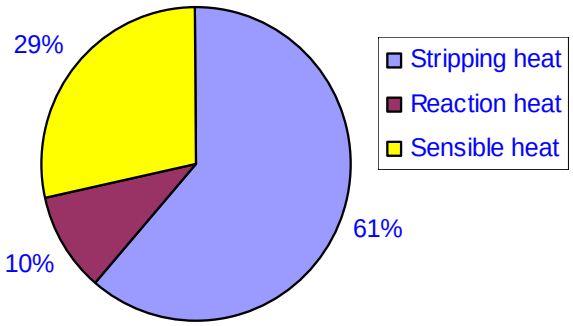
4. Additives to Reduce Stripping Heat





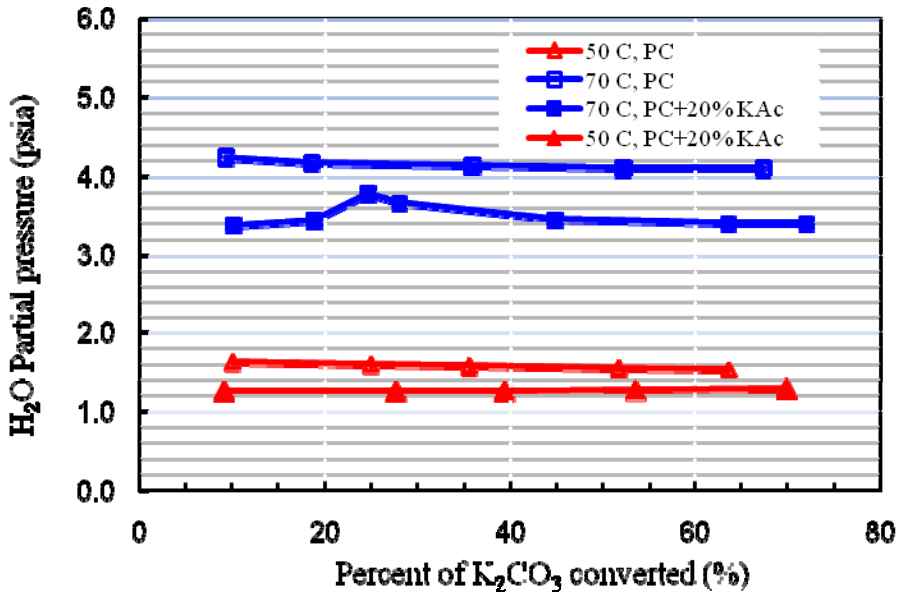


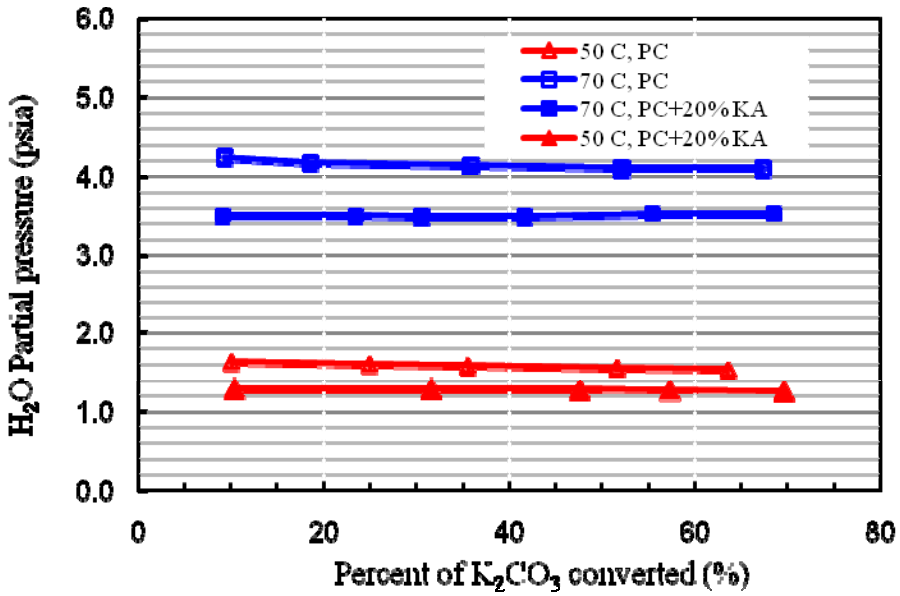
- VLE measurements of PC+ additives
- Gas analysis using GC and RH analyzers
- Liquid analysis using a back-titration method



Breakdown of heat use in IVCAP

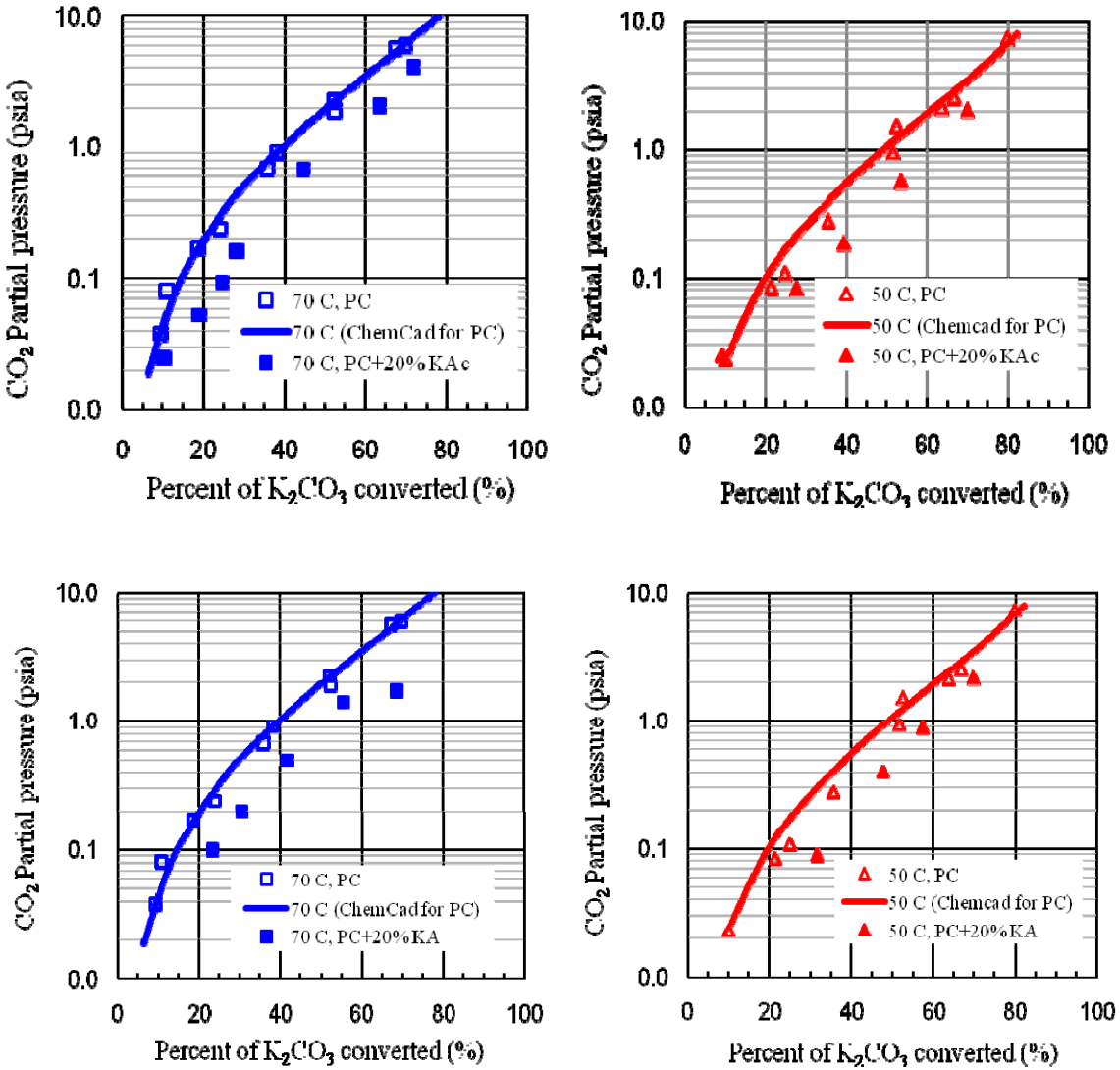
Equilibrium Pressure of Water Vapor over 20wt% PC + Additives





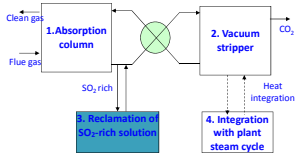
- KAc and KA were effective in lowering water vapor pressure
- Saturation pressure of water vapor reduced by ~20% at 70°C and >20% at 50°C with 20wt% additives

Equilibrium Pressure of CO_2 over 20wt% PC + Additives



- Increase in CO_2 solubility in PC+KAc (or KA) favors CO_2 absorption
- KAc, KA only slightly volatile at 70ºC
- Stripping heat of IVCAP could be reduced
- Addition of 20wt% KAc reduced CA activity by 40%

5. Study of Process Concept for Combined SO_2 Removal and CO_2 Capture in IVCAP



SO_2 absorption into PC: $K_2CO_3 + SO_2 + 1/2O_2 = K_2SO_4 + CO_2$

Reclamation process

- Reclamation of K_2SO_4 using lime

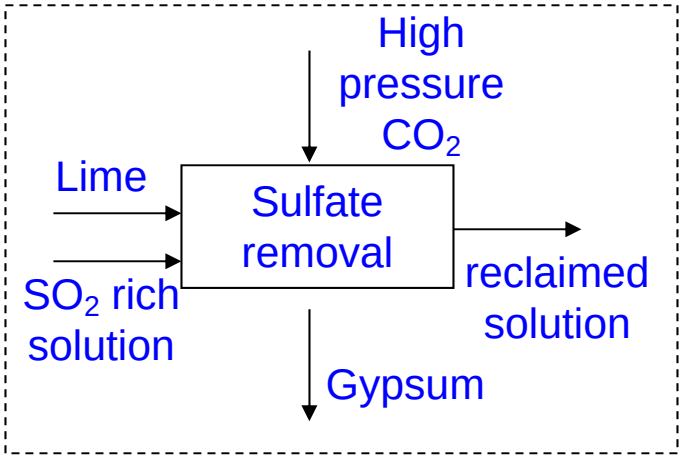
$$K_2SO_4 + CaO + 2H_2O + CO_2 = K_2CO_3 + CaSO_4 \cdot 2H_2O(s)\downarrow$$

- Two competitive precipitation reactions

$$Ca^{2+} + SO_4^{2-} \Rightarrow CaSO_4(\downarrow)$$

$$Ca^{2+} + CO_3^{2-} \Rightarrow CaCO_3(\downarrow)$$

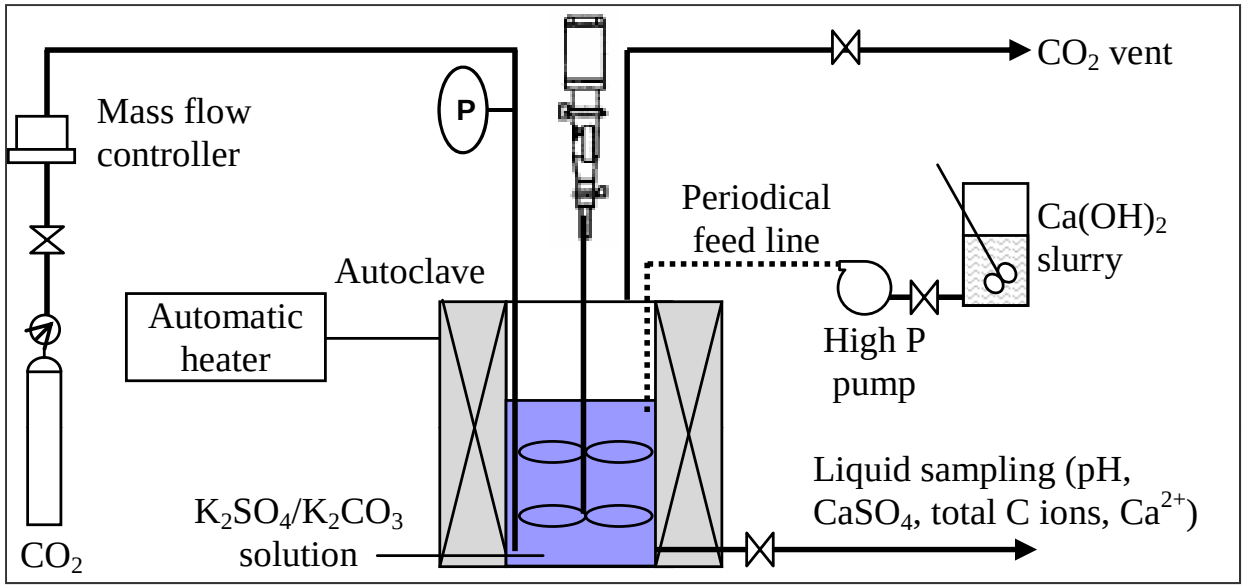
(Solubilities differ by 4 orders of magnitude)



- Prevent $CaCO_3$ precipitation
  - High pressure CO_2 to lower $[CO_3^{2-}]$

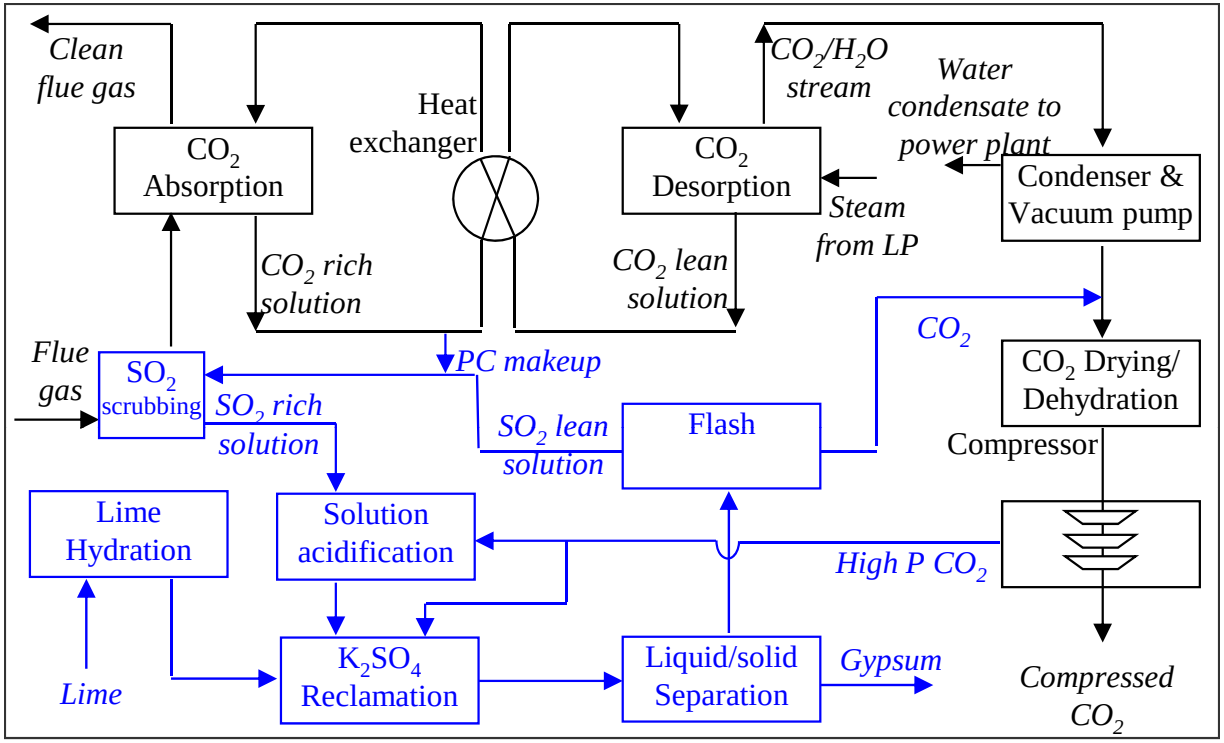
$$CO_3^{2-} + CO_2 + H_2O = 2HCO_3^-$$

Semi-Continuous Tests for Sulfate Reclamation



- XRD analysis of precipitate samples
  - For 5-20 wt% PC, vaterite was the only crystal phase
  - For <5 wt% PC, up to 47%wt syngenite and gypsum was present in crystal products
- Low PC concentration favors SO_2 removal and K_2SO_4 reclamation

Process Concept (1)



- SO_2 is absorbed into a separate PC (0.2M) with high CTB conversion level (>40%) prior to CO_2 capture
- Similar to a dual-alkali FGD
  - Absorption

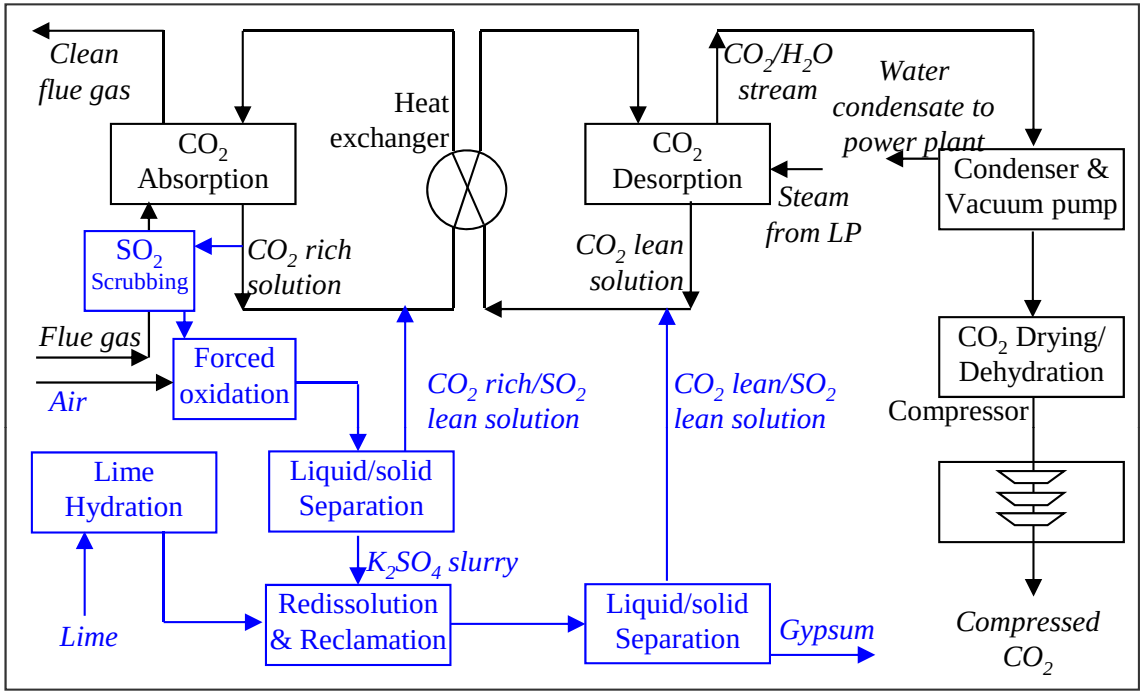
    $KHCO_3 + SO_2 \rightarrow KHSO_3 + CO_2$

    $K_2SO_3 + SO_2 + H_2O \rightarrow 2\ KHSO_3$
  - Regeneration

    $2\ KHSO_3 + Ca(OH)_2 \rightarrow K_2SO_3 + CaSO_3 \cdot 1/2\ H_2O_{\downarrow} + 3/2\ H_2O$

    $Ca^{2+} + SO_4^{2-} + x\ H_2O \rightarrow CaSO_4 \cdot xH_2O_{\downarrow}$

Process Concept (2)

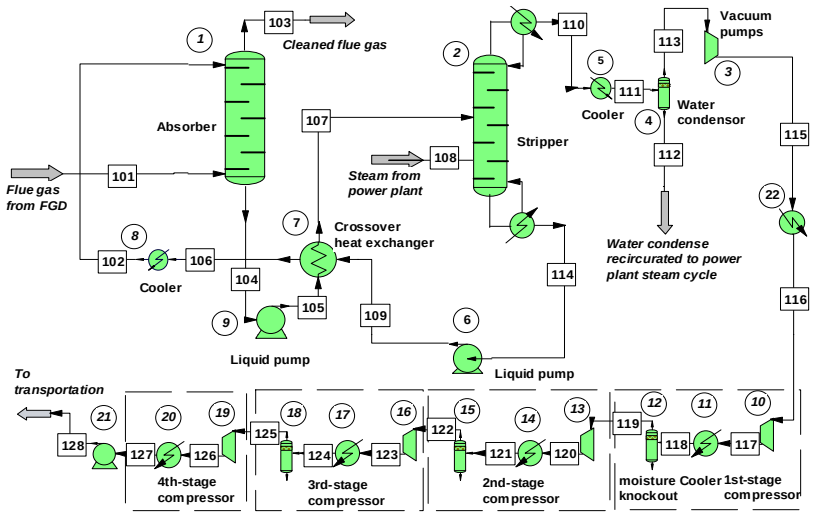


Solubility	20 ºC	30 ºC	40 ºC	60 ºC
Potassium carbonate (K_2CO_3)	111	114	117	127
Potassium bicarbonate ($KHCO_3$)	33.7	39.9	47.5	65.6
Potassium sulfate (K_2SO_4)	11.1	13	14.8	18.2
Potassium sulfide (K_2SO_3)	n/a (>>K_2SO_4)	n/a (>>K_2SO_4)	n/a (>>K_2SO_4)	n/a (>>K_2SO_4)

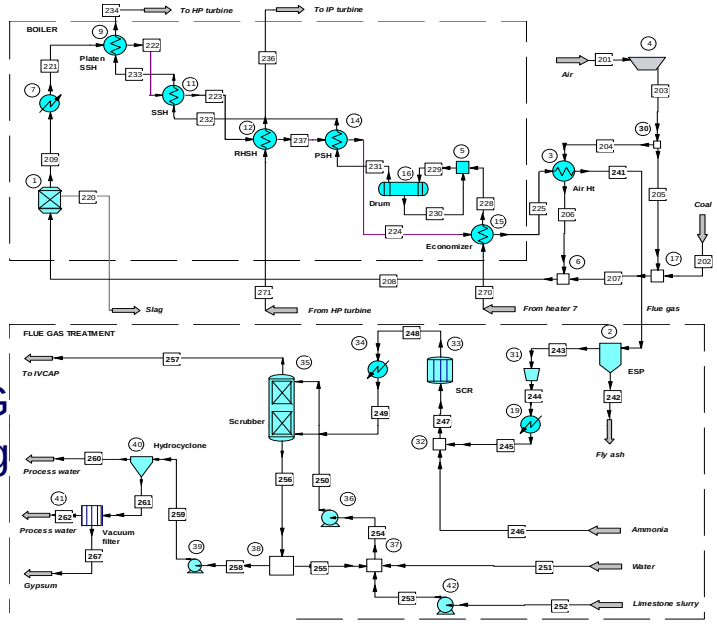
- Absorption: $2K_2CO_3 + SO_2 + H_2O \rightarrow K_2SO_3 + H_2CO_3$ (PC containing ~0.85M [SO_3^{2-}])
- Oxidation: $K_2SO_3 + ½\ O_2 \rightarrow K_2SO_4\downarrow$
- Regeneration: $K_2SO_4 + Ca(OH)_2 + 2\ H_2O \rightarrow CaSO_4 \cdot 2\ H_2O\downarrow + 2KOH$

6. Techno-Economic Study

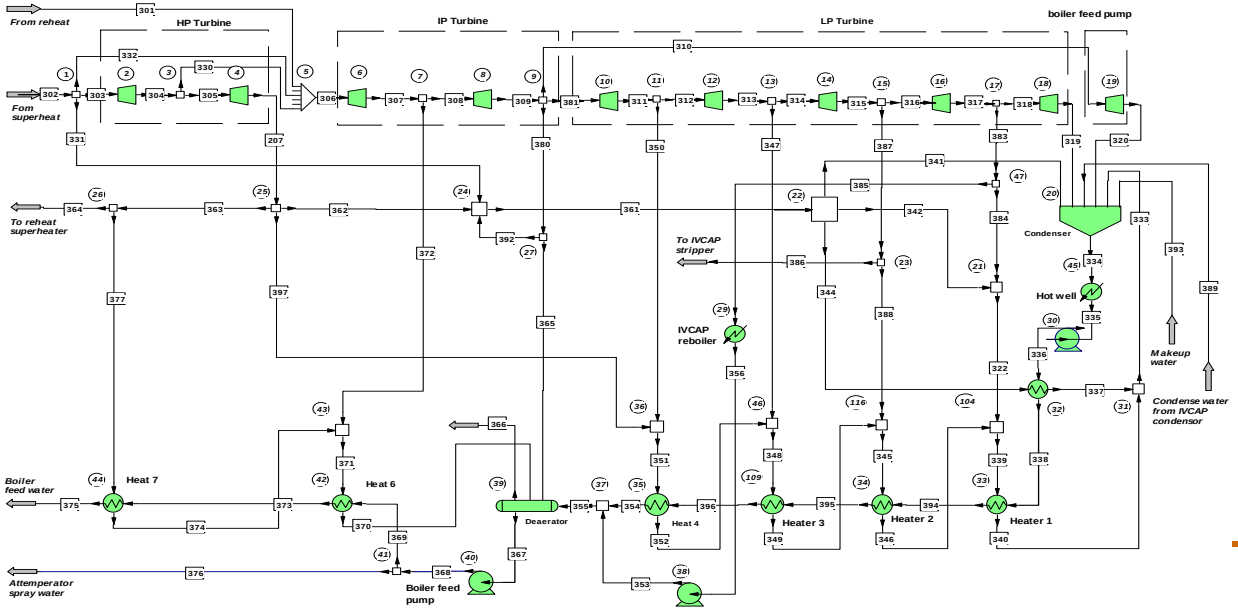
- Chemcad used in mass/energy balance cal.



IVCAP



Boiler and FG cleaning



Steam cycle

Assumptions Used in Simulations

Pulverized coal-fired power plant		
Gross output, MWe	528	
Unit type	Sub-critical	
Coal	IL bituminous #6	
Excess Air, %	15%	
Gas temperature exiting air preheater, °F	295	
Main steam condition	2,415 psia/1000 °F	
Reheat steam condition	545 psia/1000 °F	
Turbine efficiency, %	88.5%	
SO_2 removal in wet FGD, %	98%	
CO_2 capture and compression	MEA process	IVCAP process
Solvent concentration, %wt	30% MEA	20%wt K_2CO_3-equivalent
Pressure drop in absorber, psia	2	2
Temp. of flue gas entering absorber, °F	129	129
Temp. of solvent entering absorber, °F	104	122 (104-140)
Liquid to gas ratio, lb/lb	3.86	1.2 $(L/G)_{min}$ (1-1.5)
Lean CO_2 loading, %wt	5.5%	1% (0.5%-2%)
Pressure at the top of stripper, psia	25	3 (2-8)
Pressure drop in stripper, psia	2	1
Vacuum pump efficiency, %	-	85%
CO_2 removal, %	90%	90%
Compressor efficiency, %	82%, 4-stage with inter-stage cooling	
Inter-stage cooling temperature, °F	104	
Compression end pressure, psia	2,000	

Energy Performances of MEA and IVCAP Reference Plants

Electricity, MWe	Power plant w/o CO_2 cap	Power plant with MEA	Power plant with IVCAP*
CO_2 capture process:			
Steam extraction loss	n/a	89.4	37.8
Gas blower	n/a	10.0	11.5
Liquid pump	n/a	1.8	2.7
Vacuum pump	n/a	n/a	14.0
CO_2 compression	n/a	35.42	37.8
Auxiliary energy use in power plant	34.7	32.0	33.3
Net electricity output	492.9	358.9	390.5
Thermal efficiency, %	37.6%	27.2%	29.6%

*** IVCAP baseline conditions**

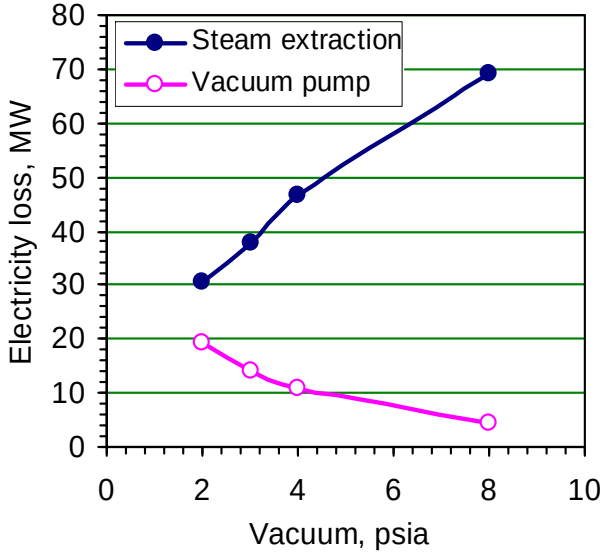
20%wt K_2CO_3-equivalent;
L/G =1.2 times $(L/G)_{min}$;
Stripping pressure = 3 psia at stripper top;

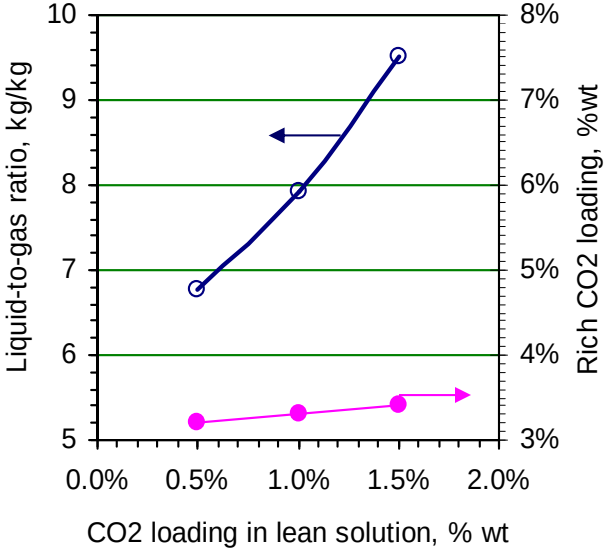
CO_2 lean loading =1 wt%
ΔT in reboiler = 10 °F
stripper ΔP = 1 psia

DOE/NETL Case 9 (subcritical): net plant efficient = 36.8%
DOE/NETL Case 10: (subcritical plant + MEA): net plant efficient = 24.9%

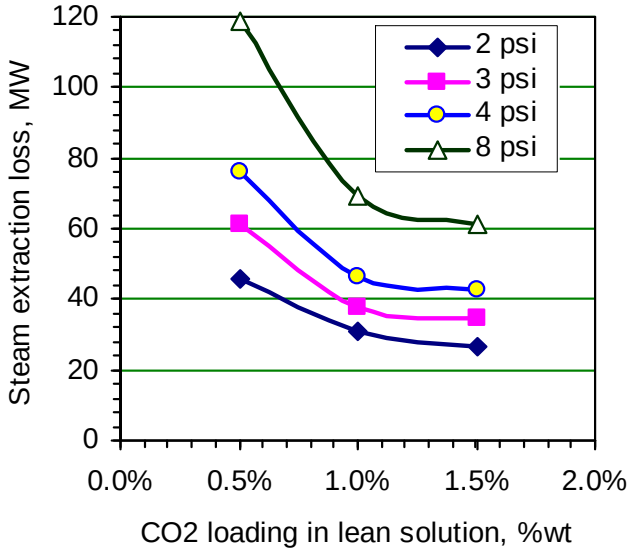
Effects of Major IVCAP Parameters on Energy Use Performance

- Increasing stripping P increases steam usage and quality and decreases electricity use for vacuum pump; Overall electricity loss increases with increasing stripping P

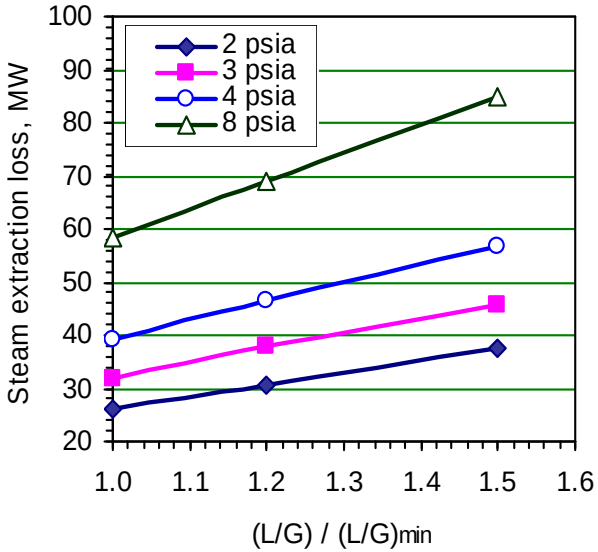




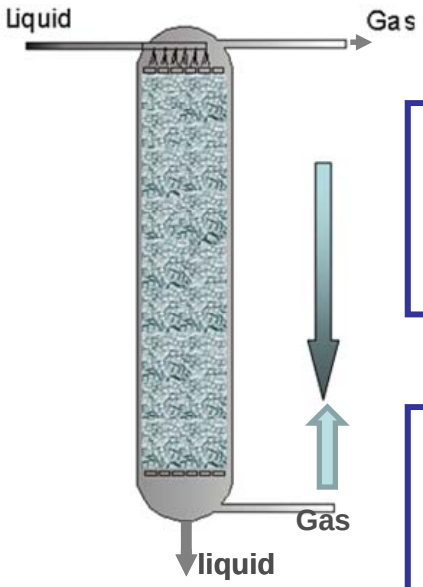
- Decreasing CO_2 lean loading from 0.5% to 1.5% halved steam extraction loss



- Increasing L/G ratio from 1.0 to 1.5 times $(L/G)_{min}$ increased steam extraction loss by 45%



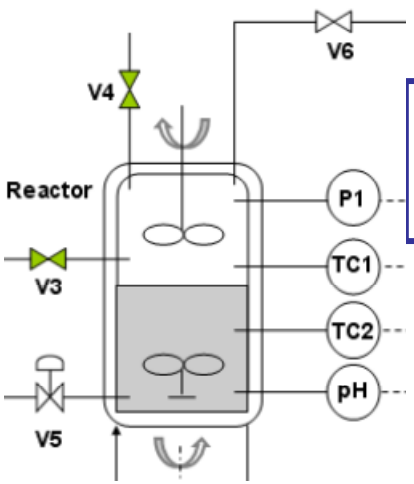
Equipment Sizing: (1) Absorber



Estimation of overall liquid phase mass transfer coefficient in packed bed K_L

Estimation of gas and liquid phase mass transfer coefficients in packed bed k_g, k_L

Estimation of enhancement factor E from STR test (Task 1)



$$\frac{1}{K_L} = \frac{H}{k_G} + \frac{1}{Ek_L}$$

Overall resistance | Gas-phase resistance | Liquid-phase resistance

K_L: overall gas-phase mass transfer coefficient;
H: Henry's constant
E: enhancement factor (for a fast reaction):

$$E \approx Ha = \frac{\sqrt{D_L k_{ov}}}{k_L}; \quad k_{ov} = k_{OH} C_{OH^-} + k_{CA} C_{CA}$$

Calculation of the bed height based on mass balance equation:

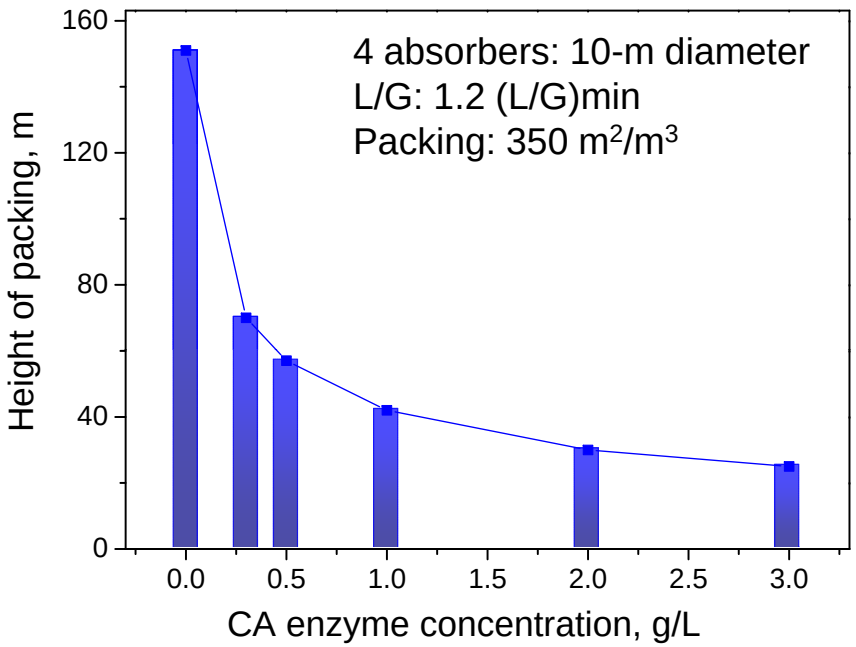
$$-\frac{L}{A} dC_{CO_3^{2-}} = K_L a (C^* - C^b) dh$$

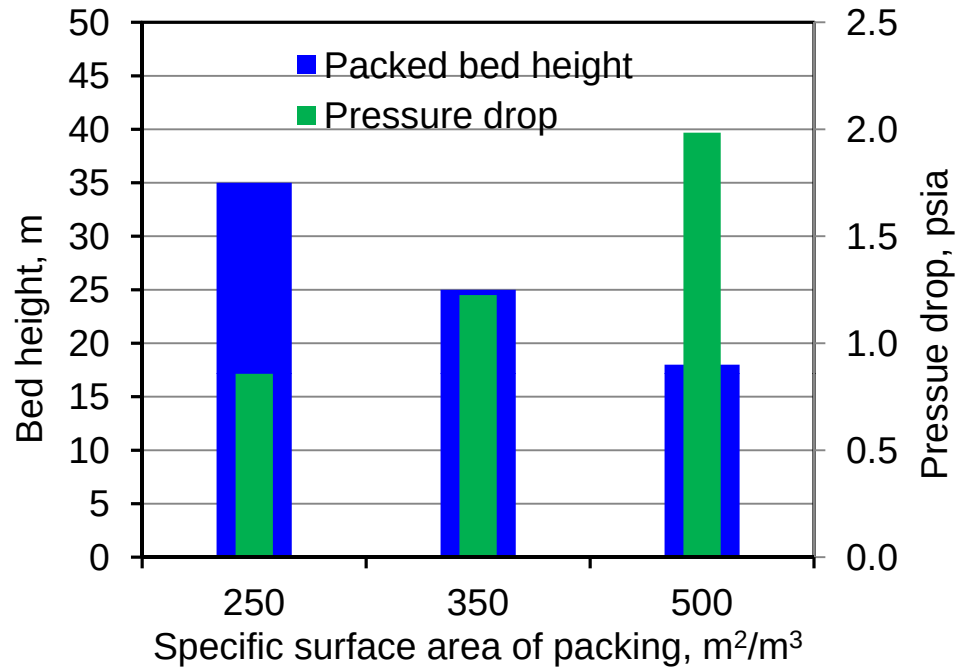
Assumptions Used in Packed Bed Absorber Sizing (528 MWe Gross Power Plant)

	Condition	Specification
Feed gas	CO_2 concentration (vol%)	13.9%
	Gas flow rate (ft^3/hr @ 300°F)	14,576,780 × 4
	CO_2 removal efficiency (%)	90%
Feed liquid	K_2CO_3/$KHCO_3$ concentration (wt%)	20% (K_2CO_3-equivalent)
	CO_2 loading	Equivalent to 20% K_2CO_3 conversion
	CA concentration (g/L)	0.3 - 3
Packed bed	Operation temperature (°C)	50
	Specific surface area of packing	350 m^2/m^3 (250-500)

*** 4 trains**

Absorption Column





- IVCAP's absorption column with 2 g/L CA dosage and 350 m^2/m^3 packing
  - 40% > MEA absorber (DOE/NETL 2002 report)
  - 23% > MEA absorber (DOE/NETL 2007, Conesville #5 unit retrofitting)
  - 3% > MEA absorber (calculated by Aspen)

Equipment Sizing: (2) Desorber

- Two major desorption reactions:

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

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

k_{12} obtained from k_{11} (enzymatic kinetic study, Task 1) and equilibrium constant K (literature)

k_{21} and k_{22} referred to Aspen Plus

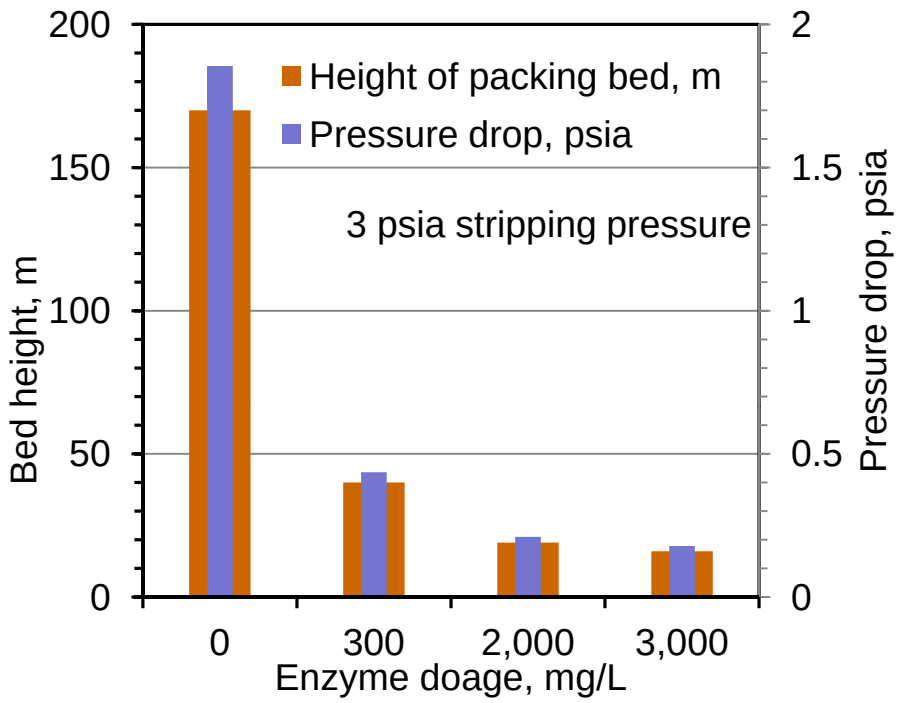
- Coupled rate equations (mass and heat transfer), with liquid- and gas-phase thermodynamics calculations using NRTL model and R-K equation of state

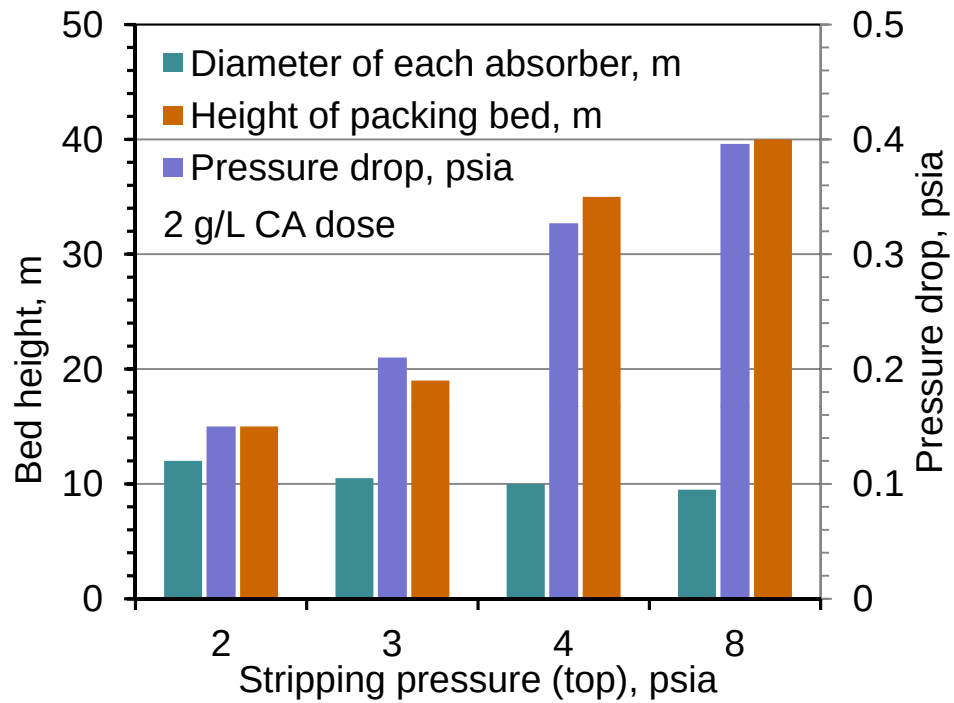
Assumptions Used in Stripper Column Sizing (528 MWe Gross Power Plant)

	Condition	Value or specification
CO_2-rich solution	CO_2 loading, wt%	3.30%
	Liquid flow rate (tonne/hr)	4,019*4
	Temperature (°C)	64
Direct steam injection	Temperature (°C)	67
	Pressure (psia)	4
	Steam flow rate (tonne/hr)	115*4
CO_2 recovery	CO_2 flow rate (tonne/hr)	96*4
	Pressure at stripper top (psia)	3
CO_2-lean solution	CO_2 loading, wt%	1.0%
Packing	Specific surface area, m^2/m^3	350

*** 4 trains**

Stripper Column





- IVCAP's stripper column size at 2 g/L CA dosage and 3 psia stripping
  - 3.8 times > MEA (DOE/NETL 2002 report)
  - 5.4 times > MEA (DOE/NETL 2007, Conesville #5 unit retrofitting)
  - 1.4 times > MEA (calculated by Aspen)

Cost Analysis: Capex and Opex for Baseline IVCAP

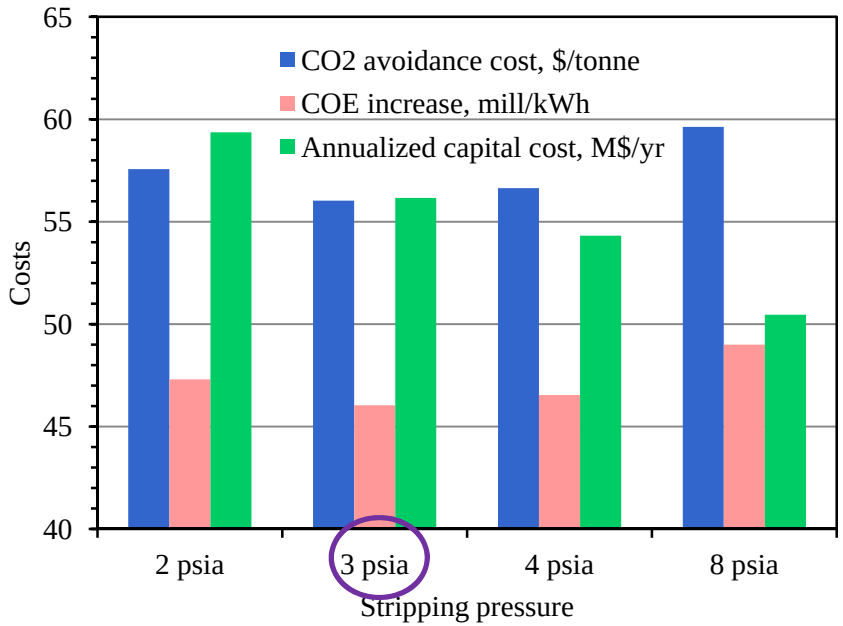
Total capital cost, M$		
	MEA	IVCAP
Flue gas blower	5.71	5.71
CO_2 absorber vessel	80.70	98.75
Heat exchangers	6.76	2.53
Circulation pumps	13.92	21.61
Solvent regenerator	50.99	113.59
Reboiler	17.57	10.85
Steam extractor	4.40	4.40
Solvent reclaimer	8.20	n/a
Solvent processing	7.99	n/a
Drying & compress. unit	48.27	48.27
Vacuum pump	n/a	20.00
Total process facilities capital	244.51	325.72
Total capital requirement	373.80	497.94
Annualized capital cost, M$/year	42.16	56.16
Annual O&M cost, M$/year		
Solvent (MEA or PC)	17.42	1.74
CA enzyme	n/a	5.79
Corrosion inhibitor	3.48	0.35
Activated carbon	0.42	n/a
Caustic (NaOH)	0.33	n/a
Reclaimer waste disposal	3.82	n/a
Water	0.04	0.04
Total variable costs (energy costs not included)	25.47	7.92
Operating labor	0.68	0.68
Maintenance labor	3.35	4.46
Maintenance material	5.02	6.69
Admin. & support labor	1.21	1.54
Total fixed costs	10.26	13.38

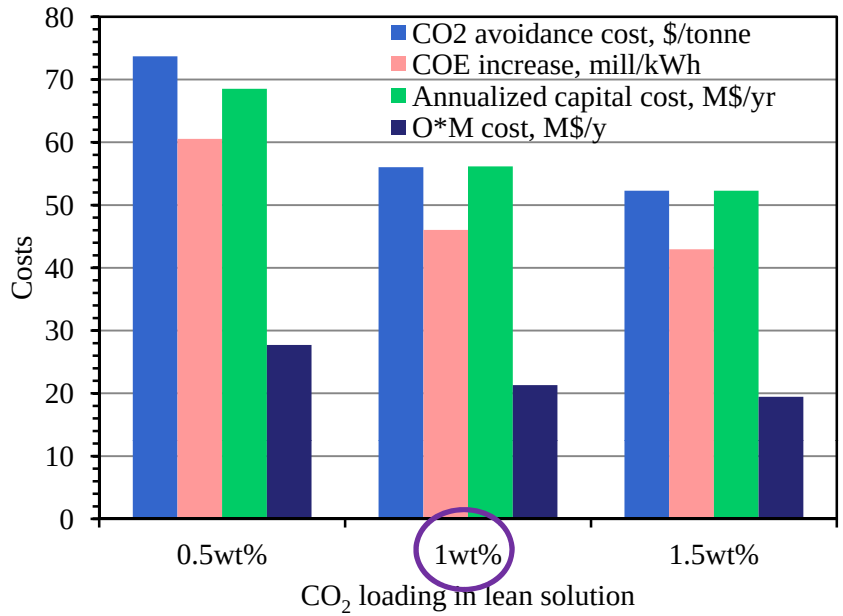
Cost Comparison between MEA and baseline IVCAP

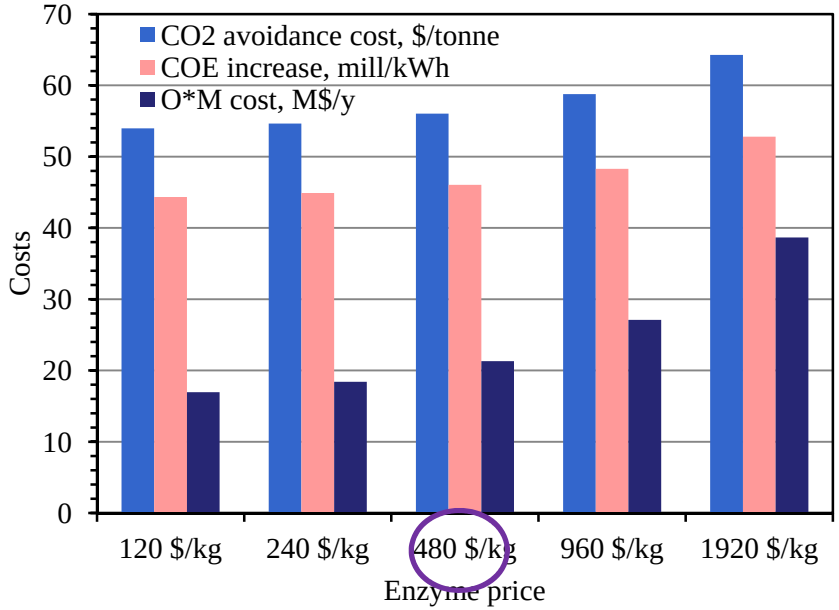
	MEA process	IVCAP process
Cost of electricity increase, $/MWh		
Capital cost	17.88	21.91
Fixed O&M	4.35	5.22
Variable O&M: non-energy	10.80	3.09
Variable O&M –energy losses	22.40	15.81
Subtotal	55.43	46.04
Net electricity, MW	358.9	390.5
Loading factor, %	75%	75%
Reference CO_2 emissions, lb/kWh	1.88	1.88
CO_2 emissions with control, lb/kWh	0.26	0.24
COE increase, $/MWh	55.42	46.04
CO_2 avoidance cost, $/tonne	68.47	56.03

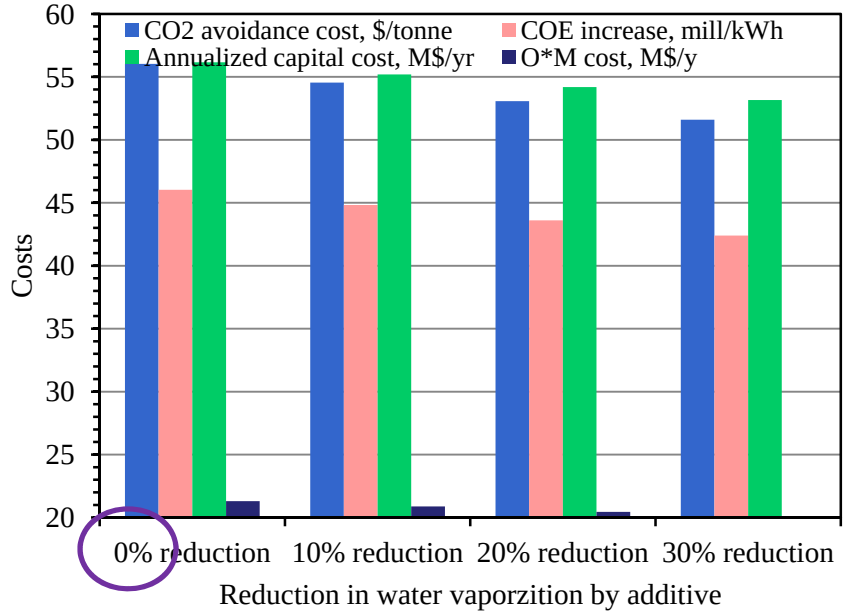
- Assuming COE of a reference power plant w/o CO2 capture is $65/MWh
  - MEA : 85% COE increase
  - Baseline IVCAP: 71% COE increase

Cost Sensitivity Analysis for IVCAP

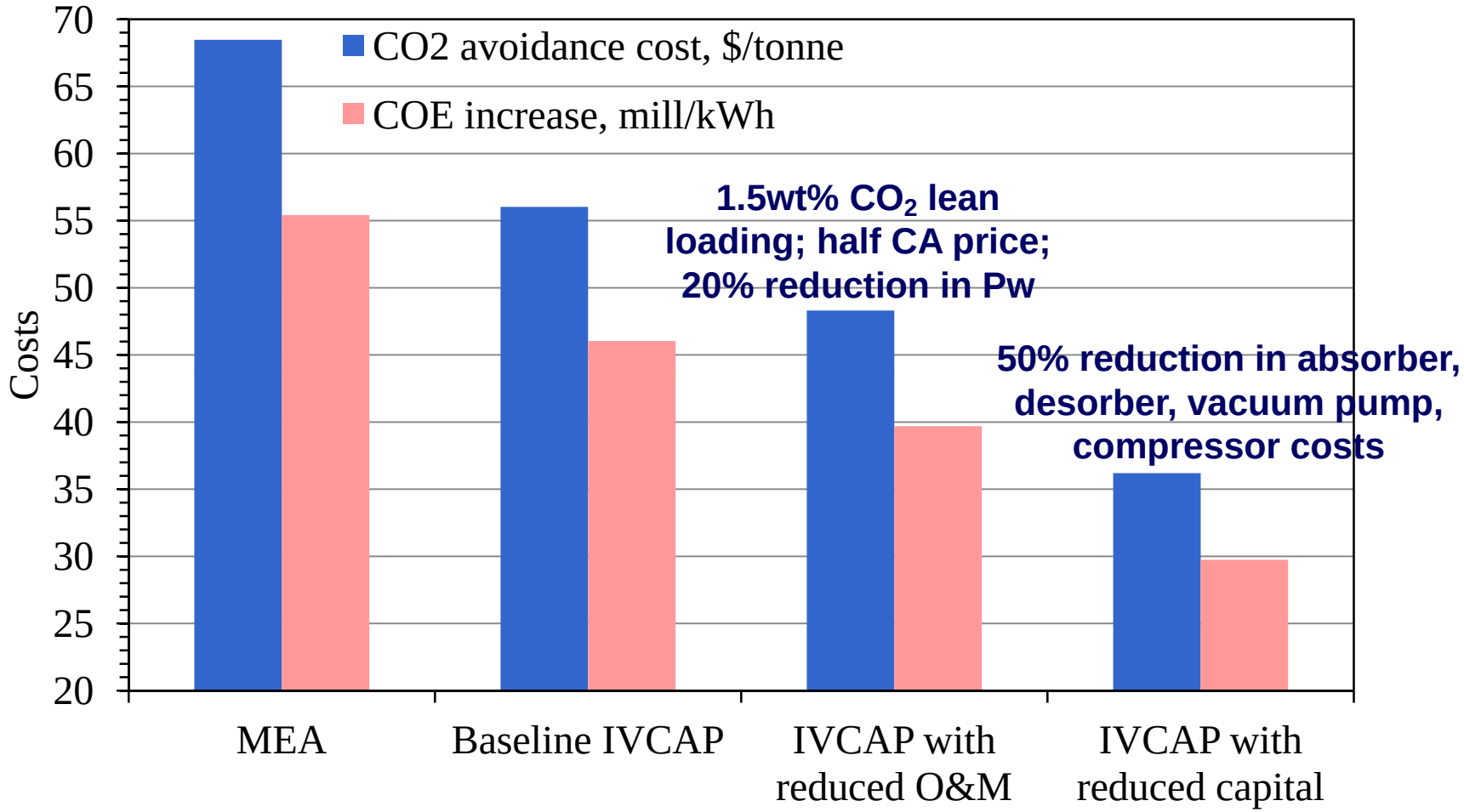








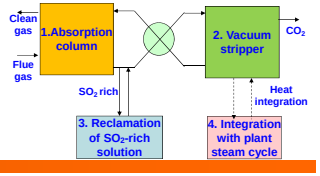
Cost Summary



- Baseline IVCAP: 71% COE increase
- IVCAP with Opex reduction: 61% COE increase
- Hypothetical case with Capex reduction: 46% COE increase

Conclusions and Recommendations

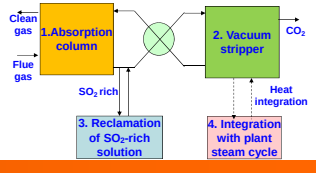
Conclusions



CO_2 absorption into PC solution

- CA can effectively promote CO_2 absorption into PC
  - In a packed bed absorption column, rates into PC+CA (300 mg/L) ~5 times lower than MEA at column's top and comparable at column's bottom
- CAs tested were stable in presence of flue gas components SO_2, HCl and NOx
- Existing CA enzymes suitable for absorption conditions but require better stability at stripping conditions

Cont'd



CA enzyme immobilization

- Enzyme immobilization can effectively improve enzyme's stability
  - CA enzymes immobilized on porous glass and mesoporous activated carbon increased stability by 60-300% at 50°C over 90 days
  - Nano-sized (<100 nm) FSP particles support further improved the enzyme's loading, activity, and stability

Stripping Heat

- KAc and KA are effective additives to reduce stripping heat requirement

Combined SO_2 removal and CO_2 capture

- IVCAP can integrate SO_2 removal by a dual-alkaline process or by precipitation of K_2SO_4 from PC solution

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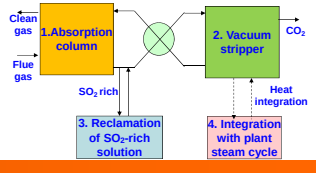


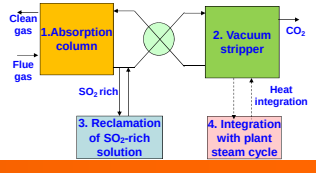
Techno-economics of IVCAP

- 24% lower parasitic power loss than MEA
- Capital cost ~1/3 higher and O&M cost ~40% lower than MEA
- 71% increase in COE
- Potential to lower COE to 61% increase

Other major technical risks of IVCAP

- Less severe operating conditions (P_{CO2} and T) than "Hot Potassium Carbonate" processes
- Activity and stability of CA enzyme are not significantly impacted by major impurities and trace elements in flue gas
- Degasification may be needed to remove dissolved CO_2 prior to recycling water from stripper to boiler
- Precipitation of $KHCO_3$ is unlikely under IVCAP conditions

Cont'd



Major conclusion

- IVCAP is a technically feasible (e.g., rates of absorption and desorption) and economically competitive (e.g., 61-71% COE increase) post-combustion CO_2 capture process compared to conventional MEA processes

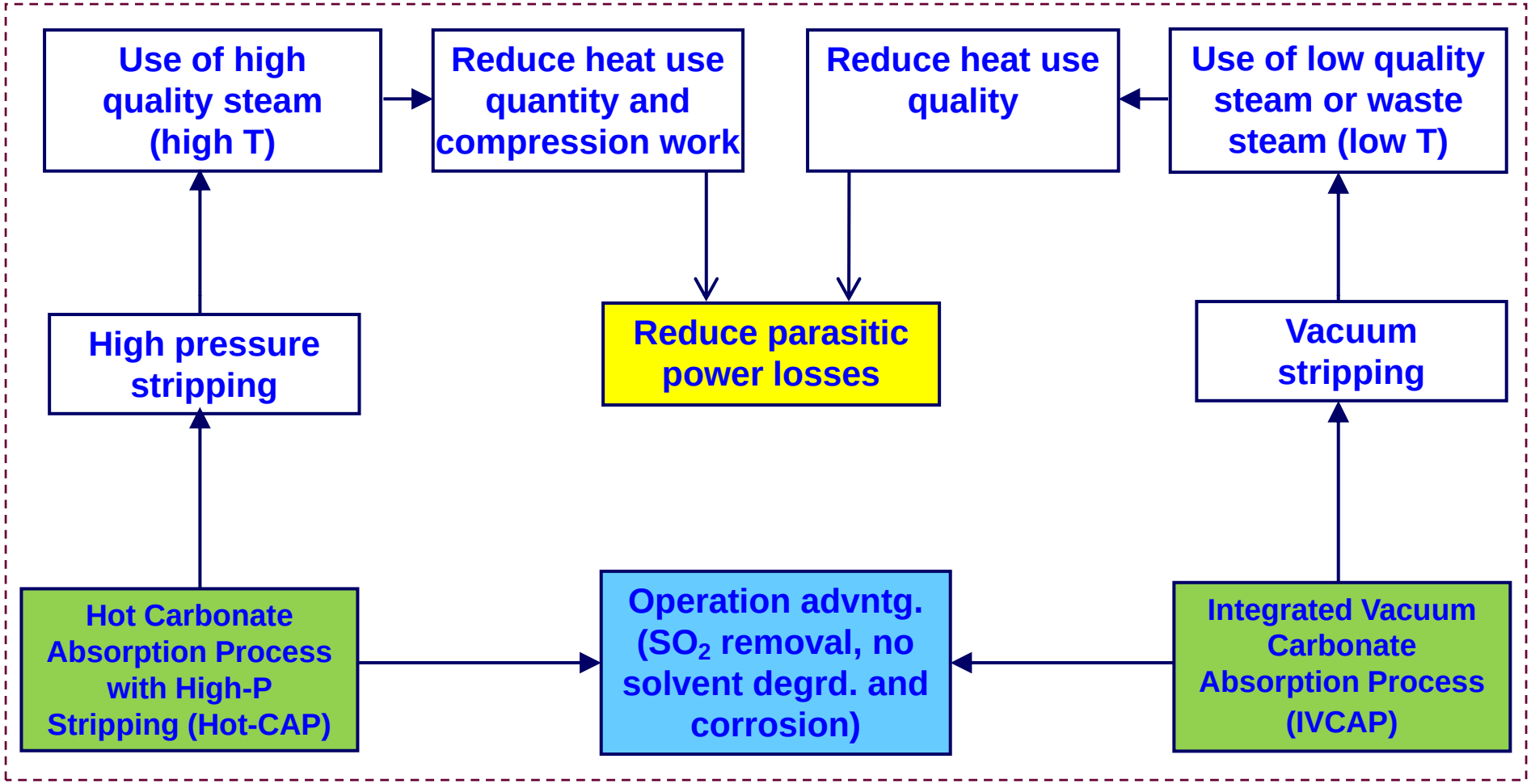
Recommendations

Based on process engineering results from the bench-scale study, process simulation, and techno-economic studies, a scale-up study using a slipstream of an actual flue gas at a pilot-scale is recommended to advance IVCAP to the next stage of development

- Slipstream test (0.5-2 MW)
  - Employ a continuous adsorption-desorption system
  - Improve process design with pilot test data
  - Long-term operation (months)
- Enzyme development
  - Codexis/CO_2 Solutions and Novozymes are potential industrial participants with capabilities to develop/provide thermophilic CA (stable at 70 °C) for pilot-scale demo tests
- Collaborators
  - A utility and an engineering company are included as participants
  - Cost-sharing opportunities from DOE, industries and the State of Illinois

Acknowledgements

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

- U.S. DOE/NETL project manager Andrew Jones

IVCAP vs. Hot-CAP: Two Ways to Minimize Energy Usage