Bench-Scale Development of a Hot Carbonate Absorption Process with Crystallization-Enabled High Pressure Stripping for Post-Combustion CO_2 Capture

(DOE Award No. DE-FE0004360)

Illinois State Geological Survey, University of Illinois at Urbana-Champaign

Carbon Capture Scientific, LLC

Presenter: Yongqi Lu

Project Closeout Meeting at DOE/NETL

Pittsburgh, PA • May 2, 2014

Acknowledgements

- U.S. Department of Energy / National Energy Technology Laboratory under Agreement No. DE-FE0004360

- Illinois Department of Commerce and Economic Opportunity through the Office of Coal Development and the Illinois Clean Coal Institute under Project No. 11/US-16

Project Team

Illinois State Geological Survey, University of Illinois

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Carbon Capture Scientific, LLC

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DOE/NETL COR: Andrew Jones

ICCI COR: Joseph Hirschi

Project Objectives

- Perform a proof-of-concept study aimed at generating process engineering and scale-up data to help advance a post-combustion CO_2 capture process to a pilot-scale demonstration level within three years
  - ISGS/UIUC team: Lab- and bench-scale tests to generate thermodynamic and kinetic data of major unit operations
  - CCS, LLC team: Risk mitigation analysis and techno-economic studies

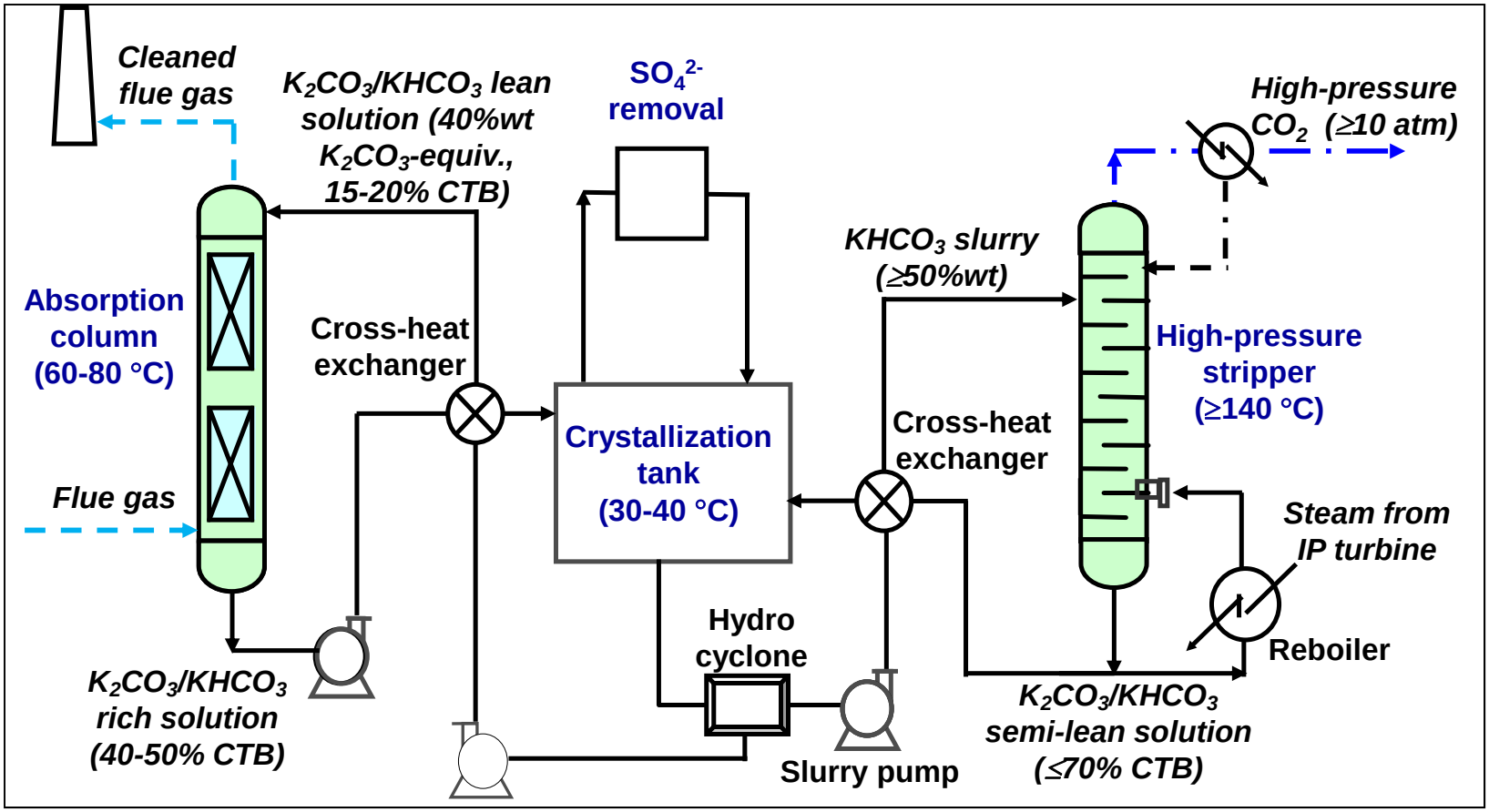
Project Duration and Budget

- Project duration: 1/1/2011 – 3/31/2014
  - BP1: 1/1/2011 - 12/31/2011
  - BP2: 1/1/2012 - 3/31/2013 (3-month extension)
  - BP3: 4/1/2013 - 3/31/2014

	Budget, $
DOE/NETL	**1,291,638**
ICCI cost share	**201,000**
Other cost share (in kind)	**182,070**
Total	**1,674,708**

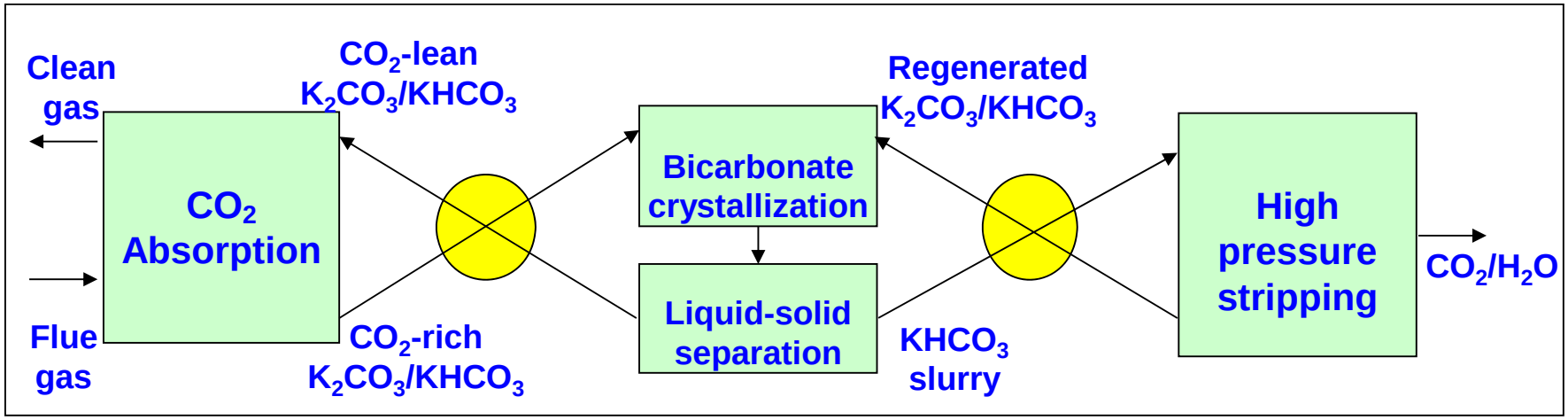
Technical background

Hot Carbonate Absorption Process with High Pressure Stripping Enabled by Crystallization (Hot-CAP)



- Absorption at 60−80°C
- Working capacity of 40wt% $K_2CO_3/KHCO_3$ (PCB) solution: 15-20% to 40-45% carbonate-to-bicarbonate (CTB) conversion
- Crystallization at near room temperature (30-40°C)
- Stripping of bicarbonate slurry at ≥ 6 bar

Major Reactions

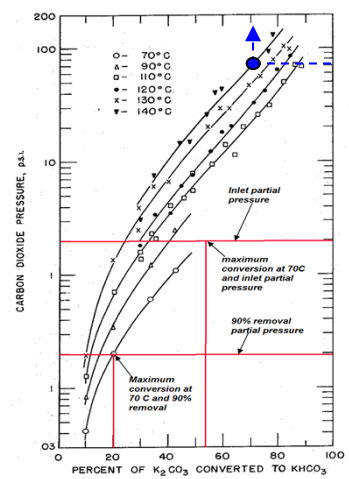


$$CO_2 \; absorption \;\; at \; 60-80°C:$$
$$CO_2 + H_2O + K_2CO_3 = 2KHCO_3$$

$$CO_2 \; desorption \; at \geq 140°C:$$
$$KHCO_3 = CO_2(g)\uparrow + H_2O + K_2CO_3$$

$$Crystallization \;\; at \sim 35°C:$$
$$KHCO_3 = KHCO_3(s)\downarrow$$

40wt%PCB



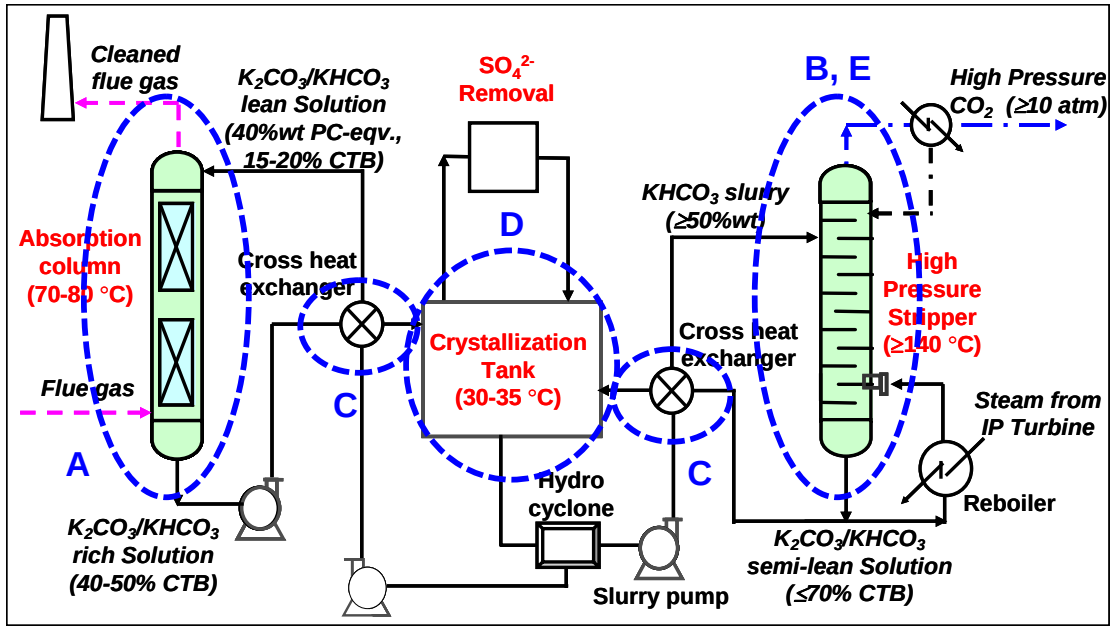
Advantages of Hot-CAP over Traditional Amine Solutions

	MEA	Hot-CAP
Solvent	30wt% MEA	40wt% K_2CO_3
Solvent degradation	Y	Less
Corrosion	Y	Less
Absorption temperature	40-50°C	60-80°C
Stripping temperature	120°C	140-200°C
Stripping pressure	1.5-2 bar	≥ 6 bar
Phase change with absorption and stripping	N	Crystallization
FGD required	Y	Reduced Size

- Lower heat of Rx, stripping heat, sensible heat (smaller Cp), compression work
- Less solvent degradation
- Less corrosion

Project Technical Risks

A. Is CO_2 absorption rate into 40wt% PCB comparable with 5M MEA?
B. Can CO_2 stripping operate at a high pressure (e.g. ≥ 10 bar)?
C. Can fouling on surfaces of heat exchangers and crystallizers caused by $KHCO_3$ crystallization be prevented?
D. Is crystallization rate fast enough (e.g., a residence time < 1 hr)?
E. Can stripper be designed to handle slurry and operate at a high pressure?
F. Can SO_2 removal be combined in Hot-CAP?



Executive Summary

- **Major reactions and unit operations are technical feasible**
  - CO_2 absorption rates into promoted PCB at 70 °C ≥2x greater than MEA at 50 °C *(Task 2)*
  - Crystallization of $KHCO_3$ is kinetically fast and completed in 15 min *(Task 3)*
  - Fouling of heat exchangers and crystallizers can be prevented through the use of multi-continuous stirred tank reactor configuration *(Tasks 3 and 6)*
  - Stripping system operated at pressures up to 12 bar *(Task 4)*
  - Optimum operating pressure 6 to 8 bar - mitigates concern of operating stripper at high pressures *(Tasks 4 and 6)*
  - Combined SO_2 removal and CO_2 capture is feasible *(Task 5)*

- **Hot-CAP is cost competitive over MEA *(Task 6)***
  - 26% lower parasitic power loss than MEA
  - 12% lower capital cost than MEA, O&M cost slightly lower
  - Increase in LCOE over non-capture case is 60% (vs. 85% for MEA)
  - Increase in LCOE is 29% lower than MEA

Major Activities and Research Findings

Major Tasks

Task 1. Project planning & management

Task 2. Kinetics of CO_2 absorption
- Promoter screening
- Absorption column testing

Task 3. Kinetics of crystallization
- Bicarbonate crystallization testing
- Crystallizer sizing calculation

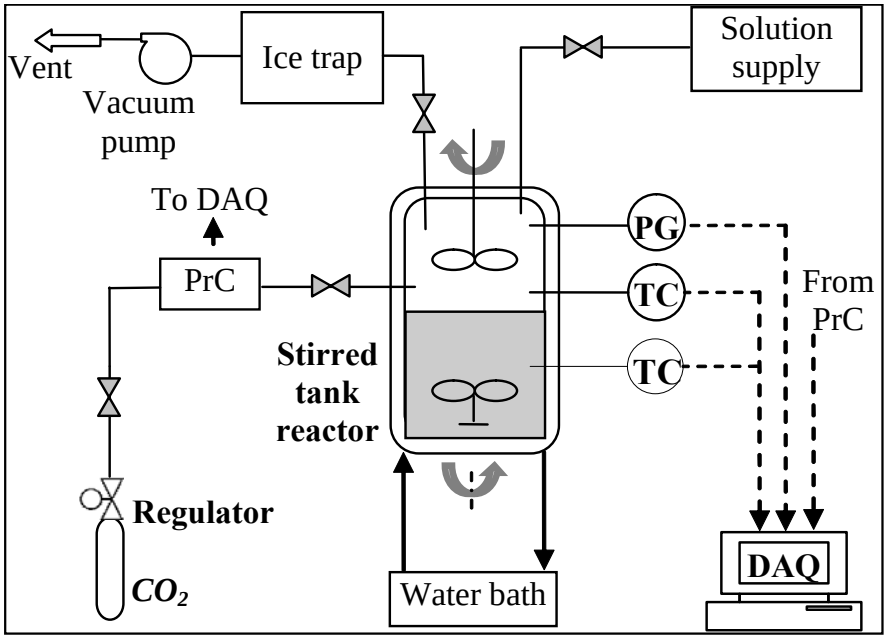
Task 4. Phase equilibrium & kinetics of high-pressure CO_2 stripping
- VLE measurement
- Stripping column testing

Task 5. Feasibility of sulfate reclamation for SO_2 removal

Task 6. Techno-economic analysis
- Risk mitigation analysis
- Process simulation
- Economic evaluation

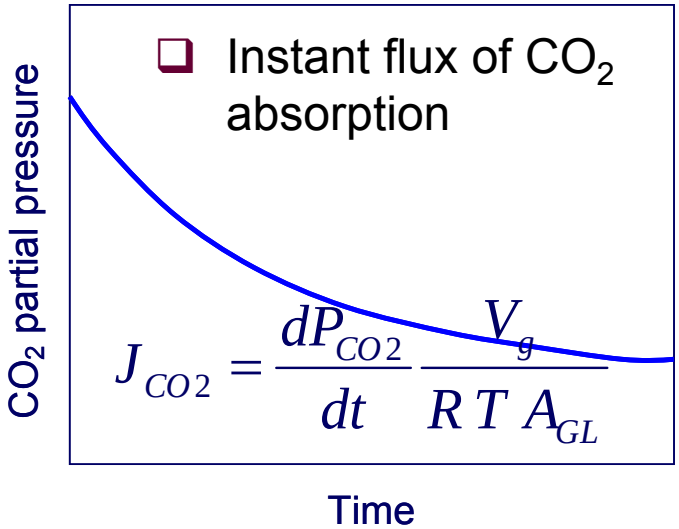
Task 2. Kinetics of CO_2 absorption

CO_2 Absorption into PCB: Promoter Screening



Promoters tested:

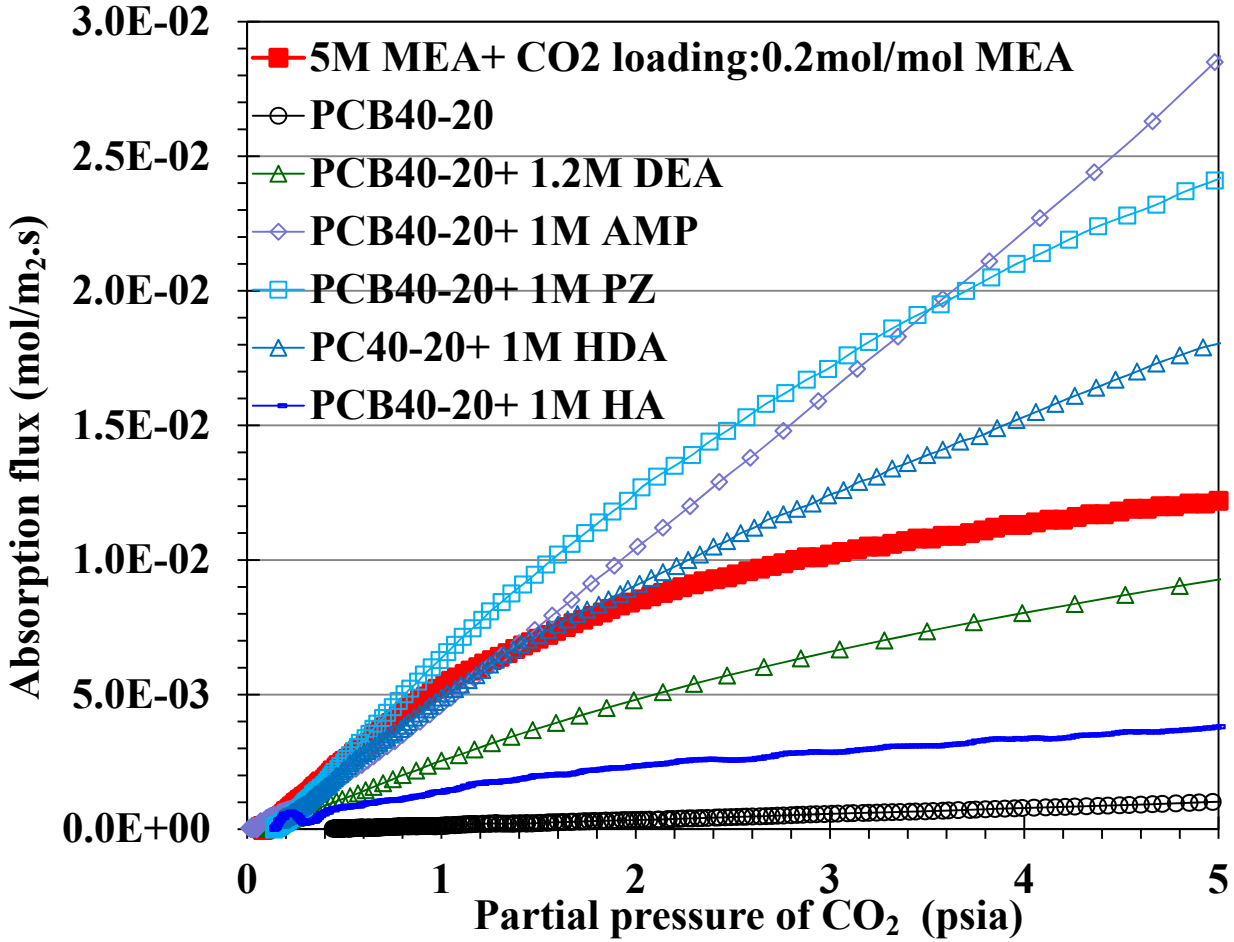
- 3 inorganic catalysts
- 5 amino acid salt promoters
- 5 amine promoters



- Instant flux of CO_2 absorption

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

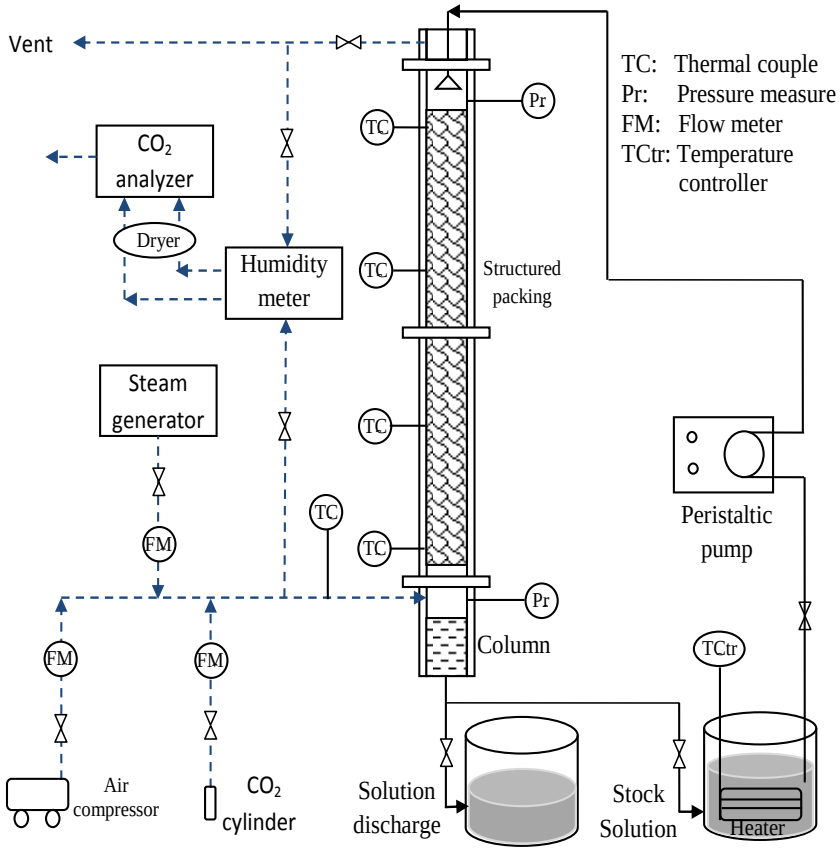
CO_2 Absorption into 40 wt% PCB with Amine Promoters



- Rates into PCB40-20 with 1M PZ, AMP, or HDA at 70 °C comparable with 5M MEA at 50 °C

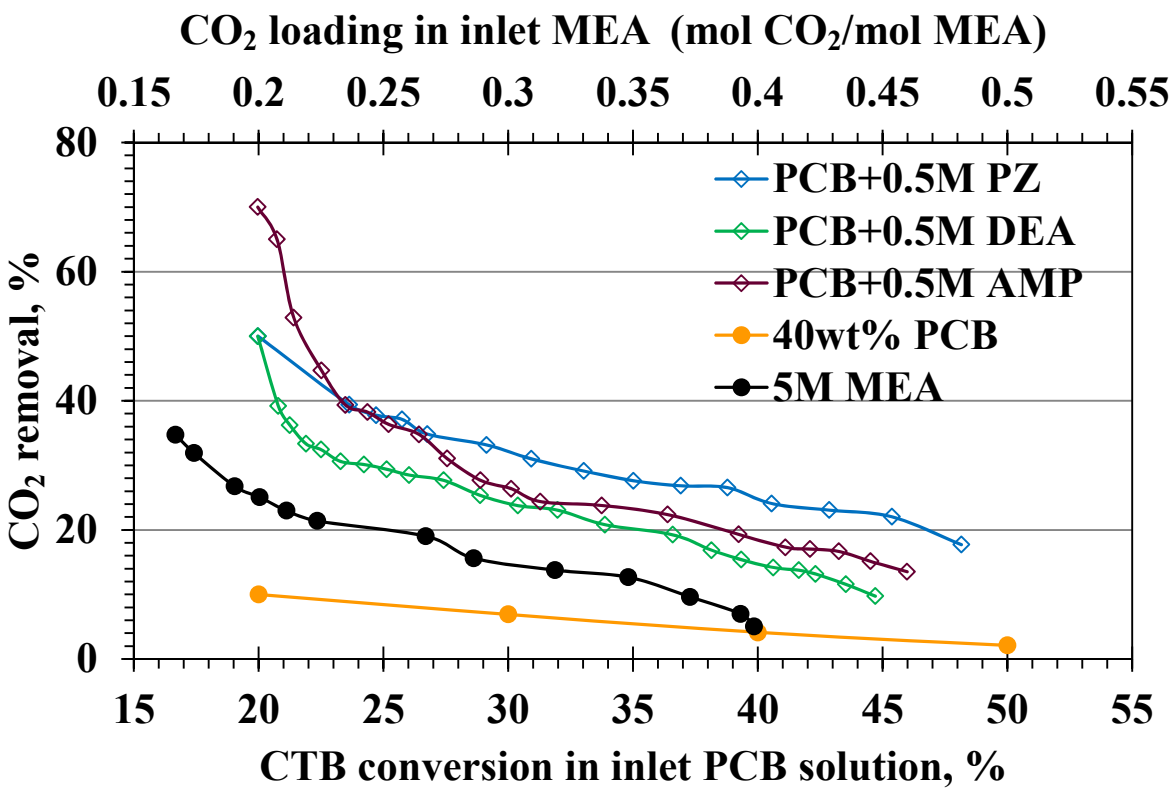
piperazine (PZ), aminomethyl propanol (AMP), hexamethylenediamine (HDA), diethanolamine (DEA), hexylamine (HA)

CO_2 Absorption into PCB: Column Testing



	Specification
Column height, m	3
Packed bed height, m	2
Absorber diameter, cm	10
Height of packing element, cm	10
Diameter of packing element, cm	10
Specific surface area (a), m^2/m^3	800
Void fraction (ε)	0.66

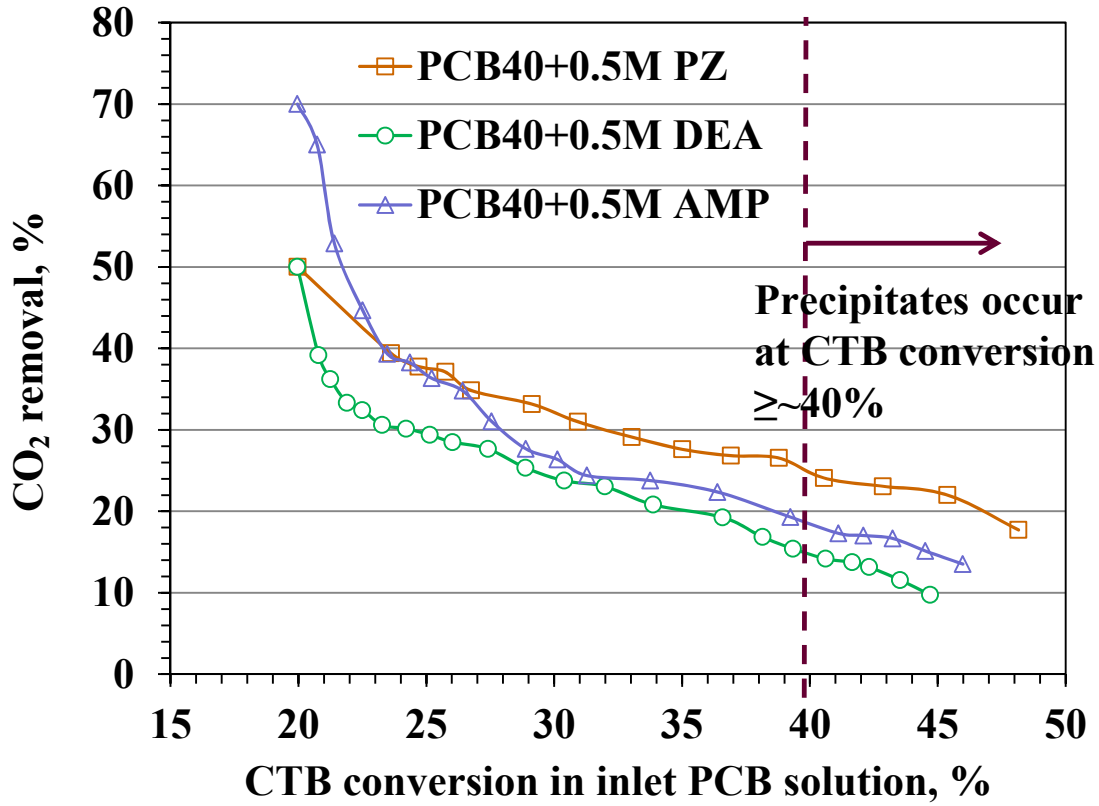
Comparison of CO_2 Absorption into 40wt% PCB vs. 5M MEA



(70ºC ab. in 40wt% PCB and 50 ºC in 5M MEA; inlet 14vol% CO_2, L/G=4.0 L/m^3)
(30% CO_2 removal efficiency equivalent to ~11% increase in CTB thru the column)

- CO_2 removal efficiency by 40wt% PCB with a promoter at 70°C:
  - 1-3 times > 5M MEA at 50°C (under lean or rich conditions)
  - 3-7 times > PCB without a promoter

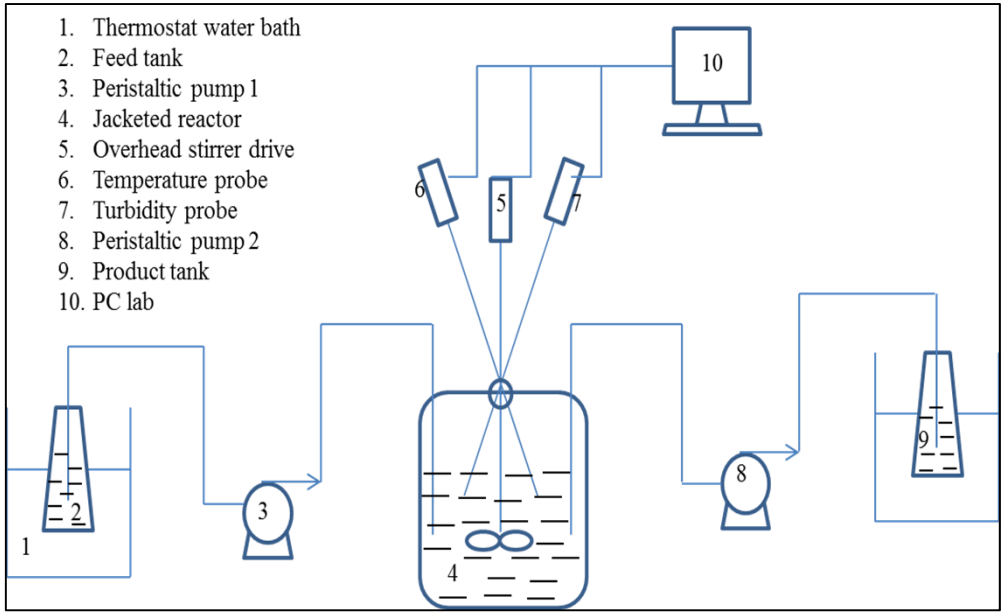
Effect of Precipitation in Packed-Bed Column



- Precipitation occurred with feed PCB of ≥40% CTB conversion, but didn't noticeable affected CO_2 removal
- PZ > AMP > DEA for promoting CO_2 removal in PCB

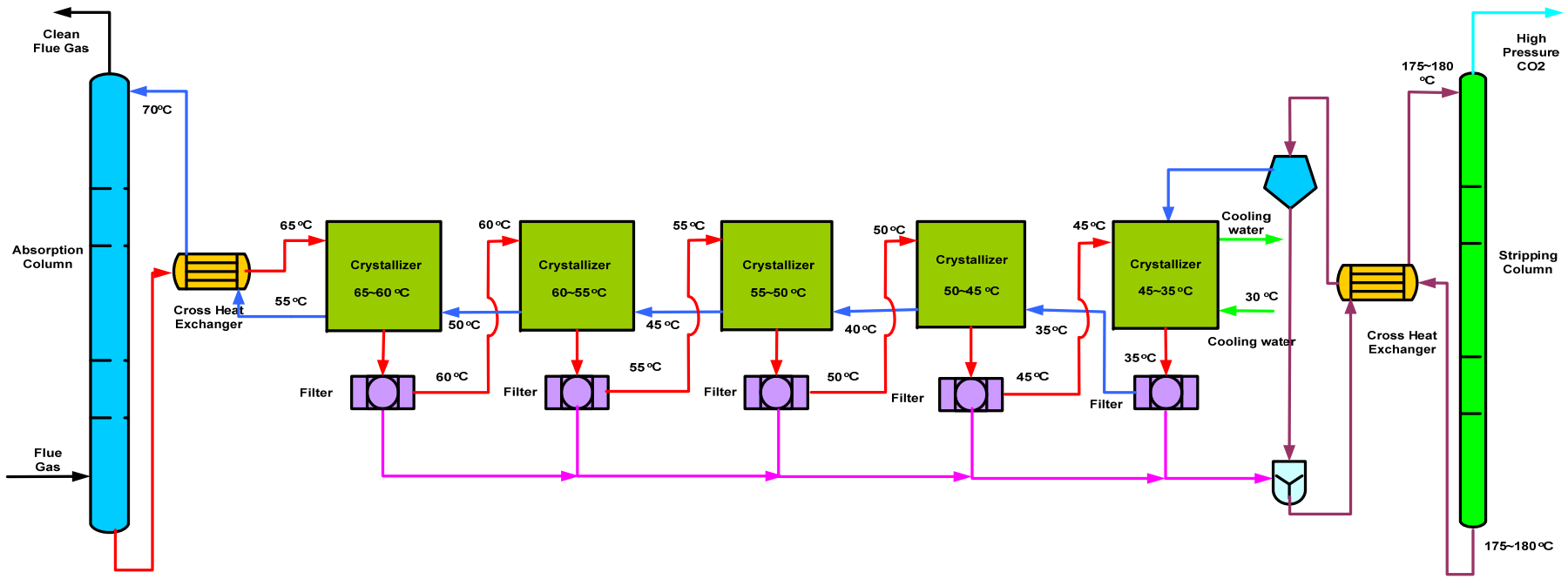
Task 3. Kinetics of crystallization

Studies of Bicarbonate Crystallization: Mixed Suspension-Mixed Product Removal (MSMPR) Reactor



- 1-liter calorimetric CSTR (Syrris Atlas), precise temperature control (-20–140 °C)
- In-situ turbidity detection
- Operation controlled by software
- Two peristaltic pumps (feed and discharge)
- Sampling at steady state, filtered for crystal size distribution (CSD) analysis (Horiba LA-950)

Experiment Conditions for Bicarbonate Crystallization



- Simulating CO_2-rich solution from Hot-CAP absorber:
- Crystallization temperature:
  - 70-55°C → 55-45°C → 45-35°C to simulate a multiple-CSTR crystallization process
- Data used to develop a kinetic model for crystal growth and nuclearation

Kinetic Model Developed for Crystallizer Sizing

- Crystallizer size was estimated by:

$$\tau = L_M / (3.67 G_{av})$$

τ: residence time, L_M : mass median size;

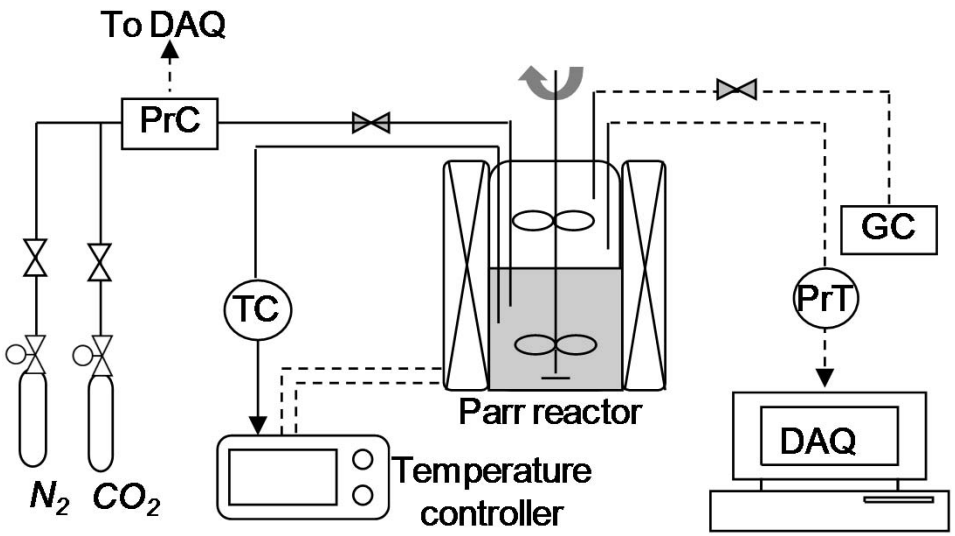
G_{av} (m/s): average growth rate over an entire particle size range

(a correlation with operating conditions regressed based on experimental data)

Unit no.	Average growth rate G_{av} (m/s)	Total nucleation rate B_{TOT} (1/s·m^3)	Residence time τ (s)	Crystallizer volume V (m^3)
1	6.89E-08	1.33E+08	108	555
2	5.92E-08	1.25E+08	126	633
3	5.70E-08	1.10E+08	131	644
4	5.46E-08	0.97E+08	137	660
5	4.83E-08	0.89E+08	154	734
Total			656 (11 min)	3,226

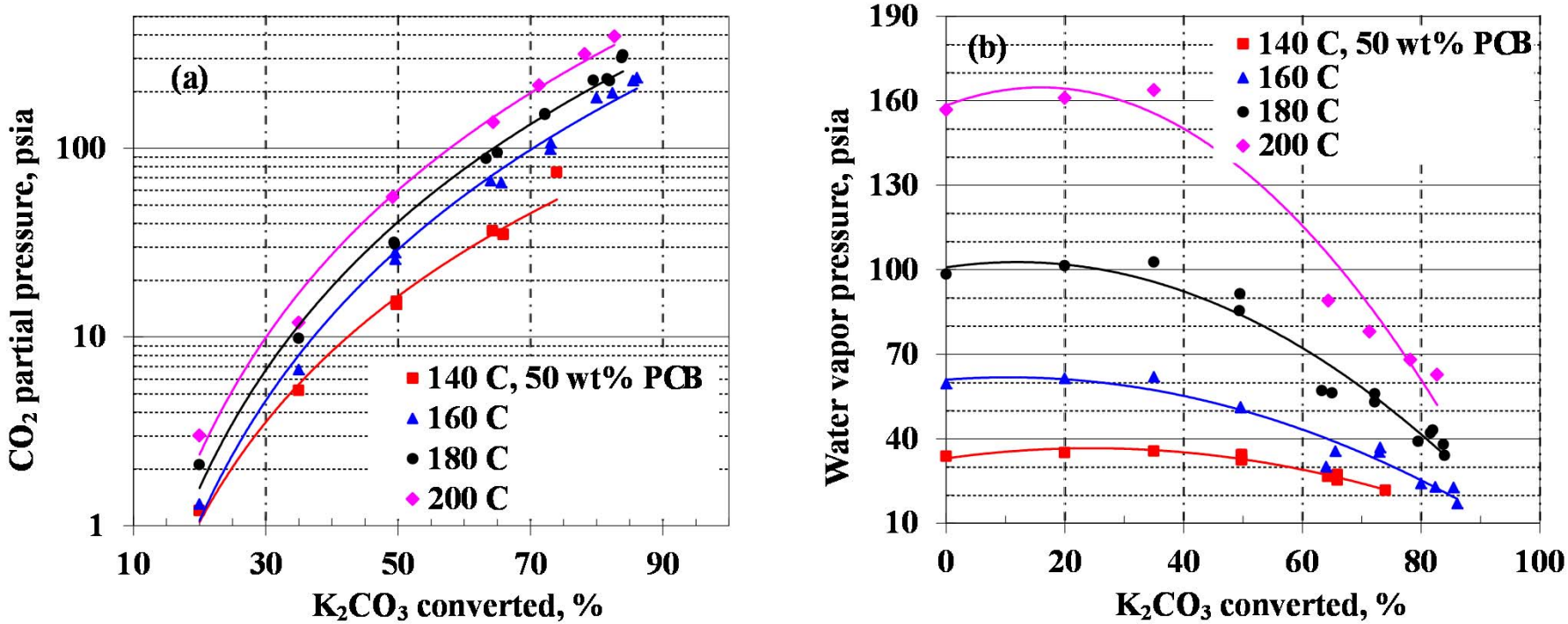
Task 4. Phase equilibrium & kinetics of high-pressure CO_2 stripping

Vapor-Liquid Equilibrium Measurement at High Temperatures



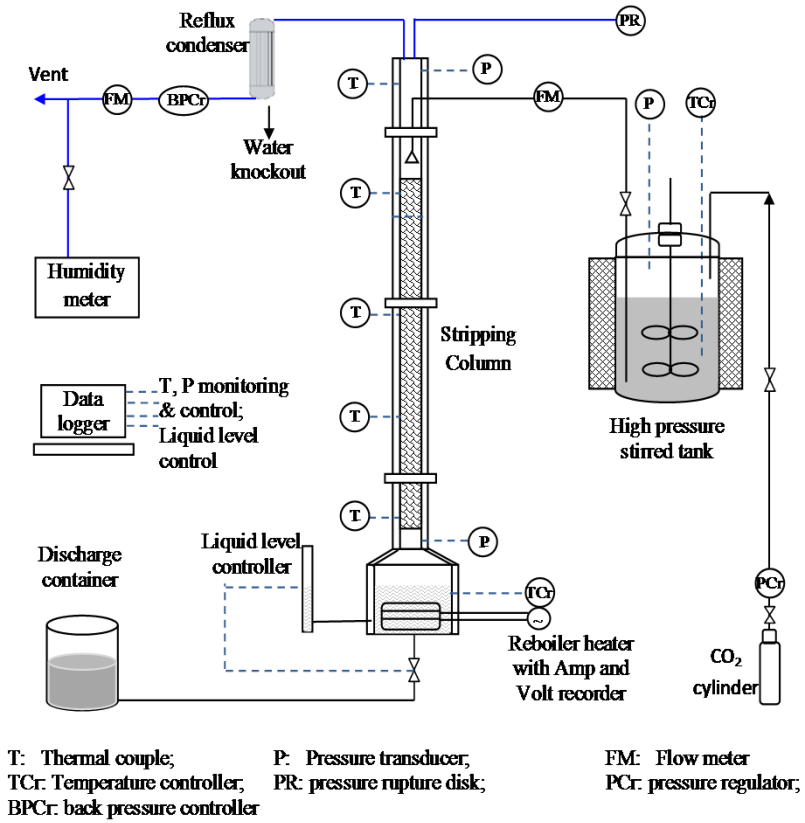
- 40-60wt% $KHCO_3/K_2CO_3$ slurry at 120-200°C
- Gas analysis using a GC-based method (N_2 as a trace gas)
- Liquid analysis using a back-titration method

VLE Data for 40, 50, 60wt% PCB at 140-200°C



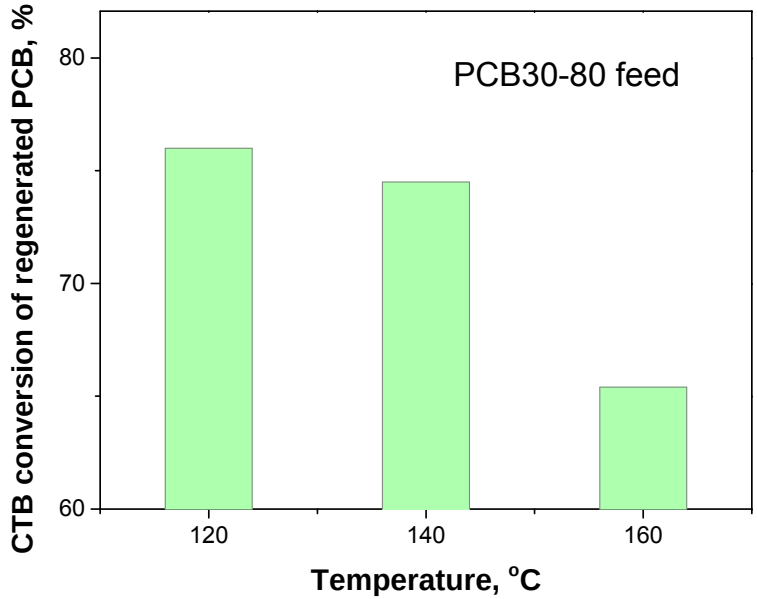
- High stripping pressures attained at high CTB conversions and temperatures (e.g., P = 31 bar and P_{H2O}/P_{CO2} = 0.16:1 for 50wt% PCB with 83% CTB conversion at 200°C)
- Lower P_{H2O}/P_{CO2} ratios attained at higher CTB conversion or higher PCB concentration

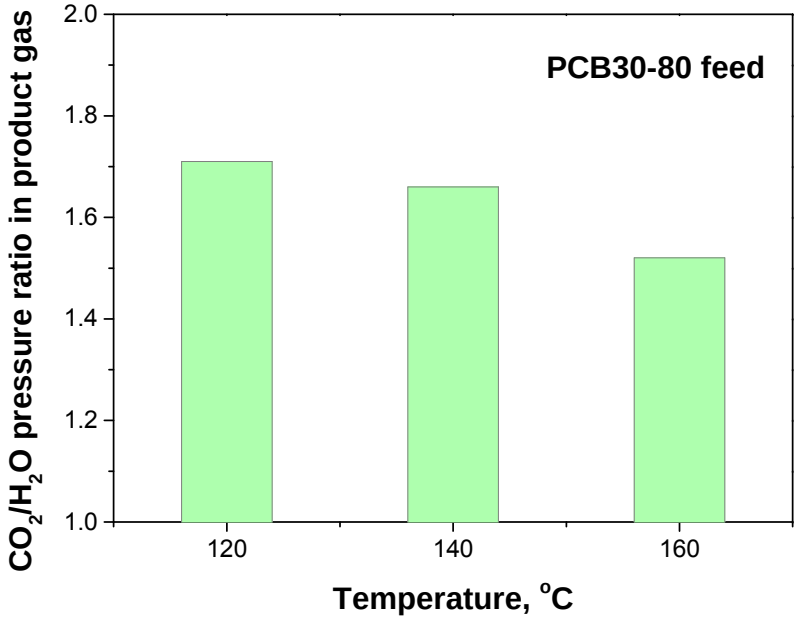
CO_2 Stripping Tests: Bench-Scale System

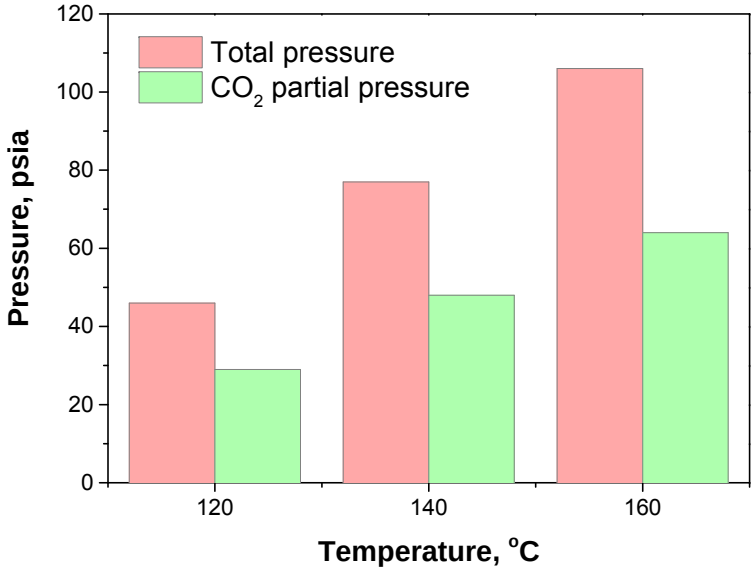


- Stripping column: 7-ft high by 1-in ID; 3 kW electrically heated reboiler
- Slurry supply tank: 10-gallon vol., 5 kW electrical heater
- Control panel and monitoring (T, P, rpm, flow rate, etc.)
- System rated at 200 °C and 500 psia

Effect of Stripping Temperature

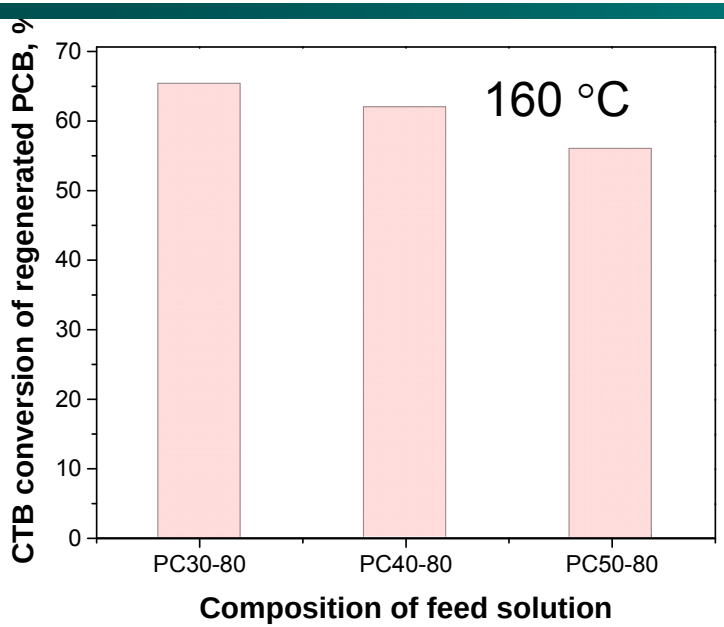


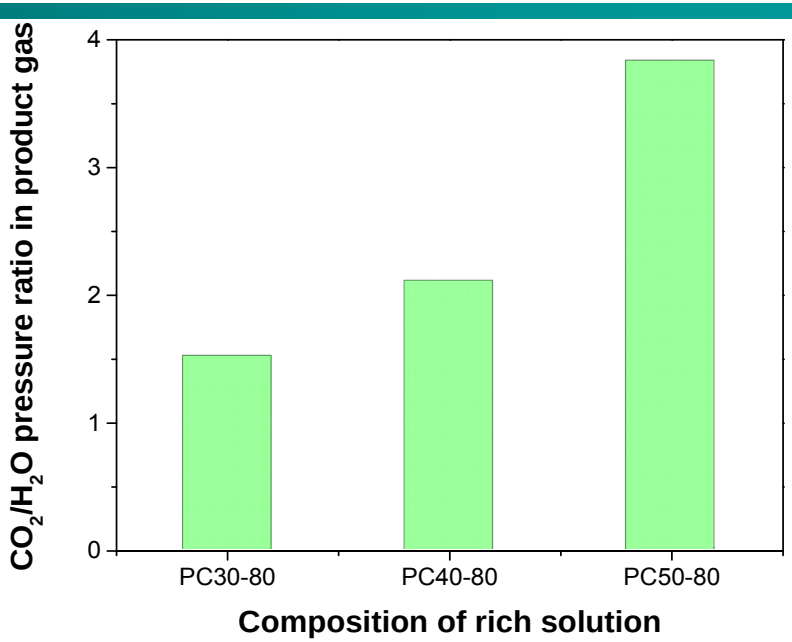


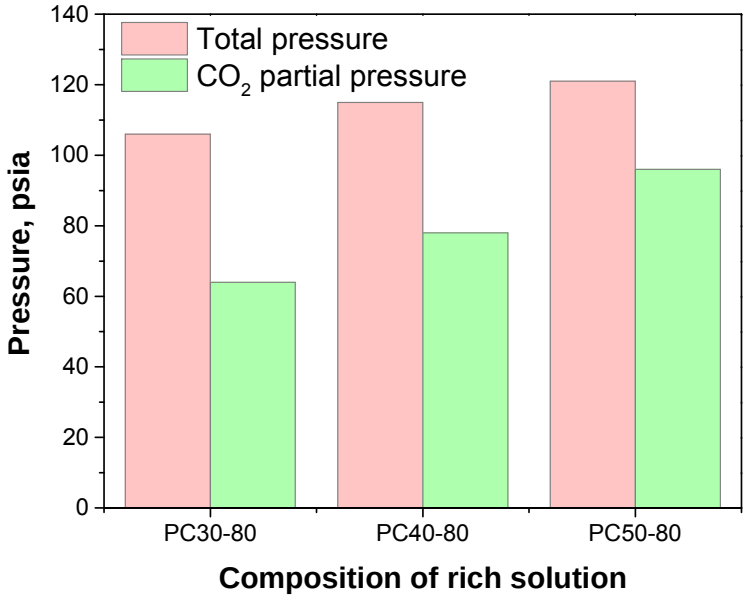


- More PCB regeneration and higher P achieved at higher T
- CO_2/H_2O ratio decreased slightly with increasing stripping T

Effect of PCB Concentration

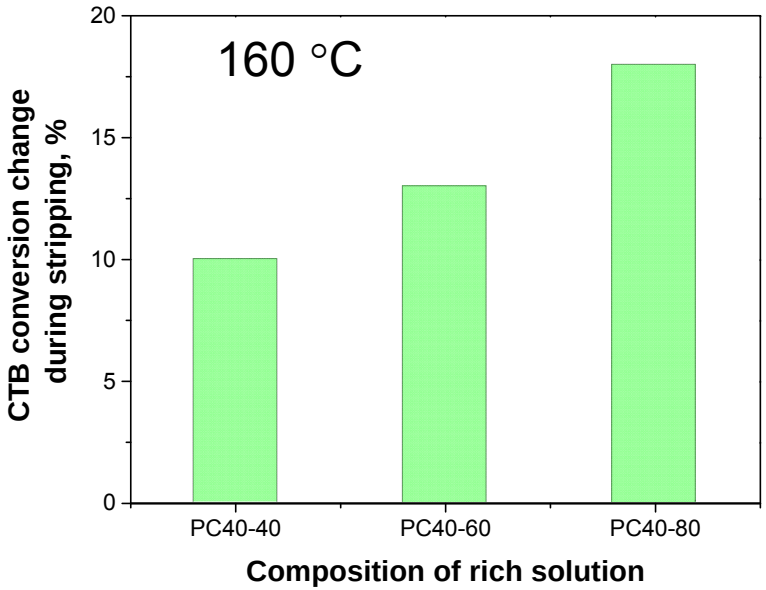


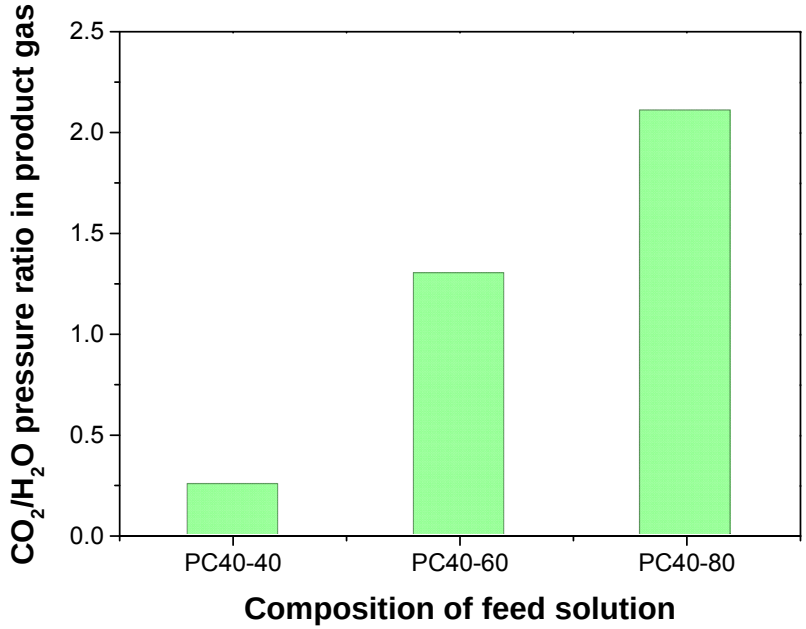


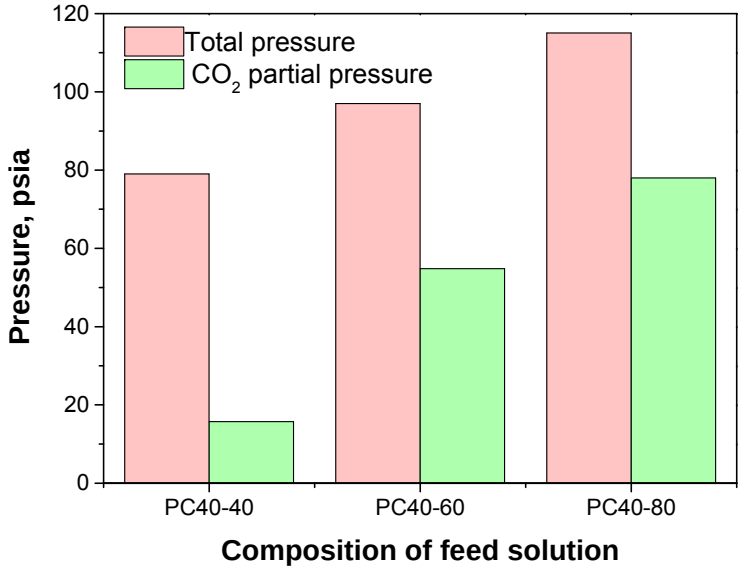


- Increasing PCB concentration increased PCB regeneration, P, and CO_2/H_2O ratio

Effect of CO_2 Loading in Feed Solution

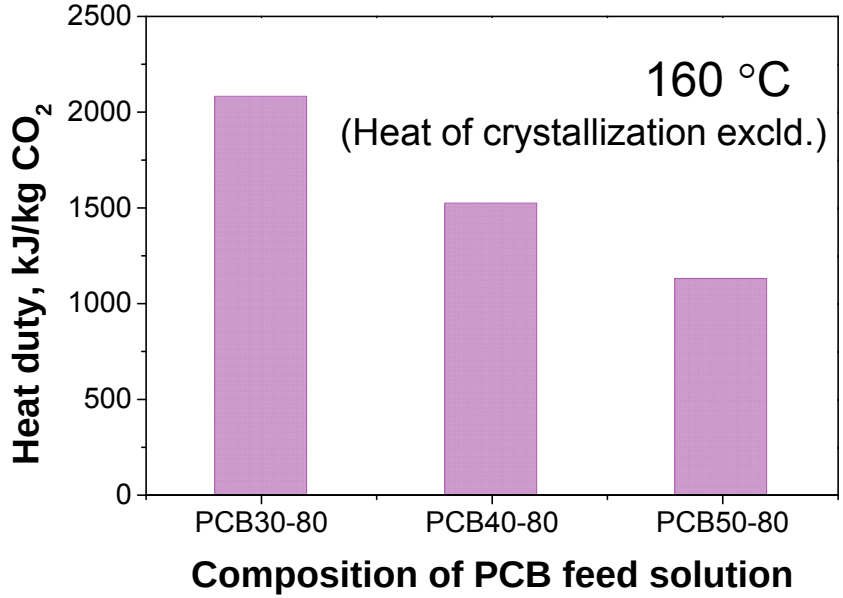


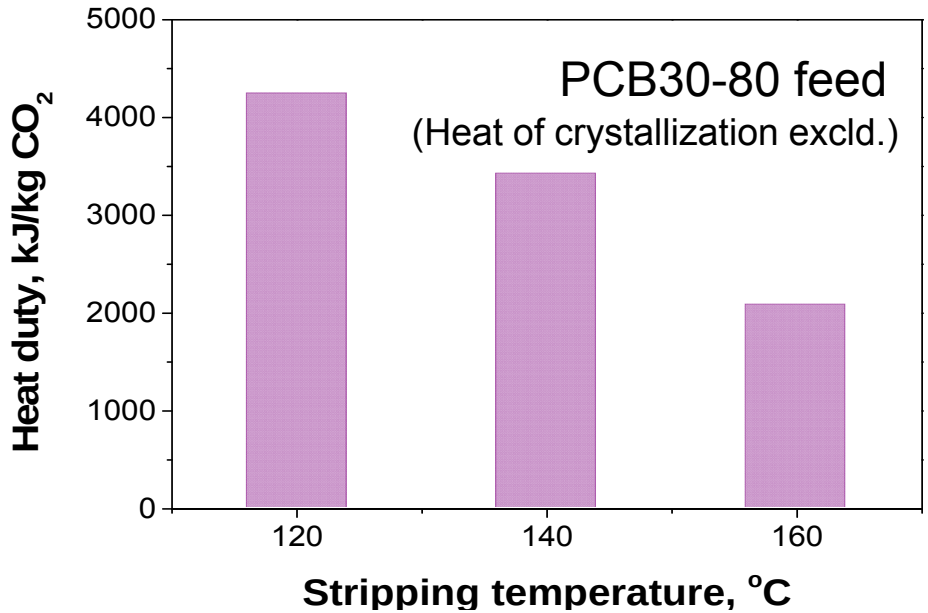


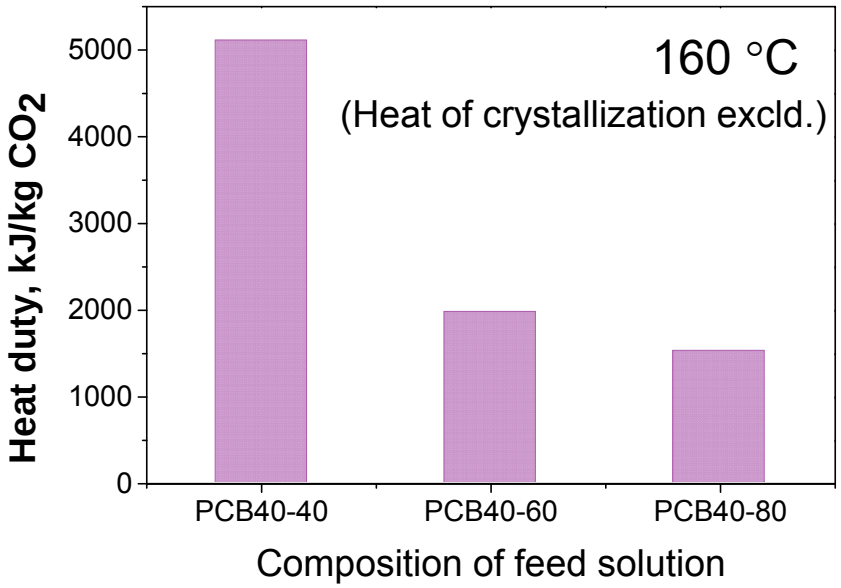


- Higher CO_2 loading in feed solution resulted in more PCB regeneration, higher P, and higher CO_2/H_2O ratio

Heat Duty for CO_2 Stripping







- Heat duty decreased with increasing feed CTB, PCB concentration, and T
- Heat duty for PCB at 160 °C (best 1,791 kJ/kg CO_2 including heat of crystallization) was 2-3 times < 5M MEA (best 4,300 kJ/kg for lean loading of 0.37-0.2 mol CO_2/mol MEA)

Task 5. Feasibility of sulfate reclamation for SO_2 removal

Reclamation of Sulfate for SO_2 Removal in Hot-CAP

SO_2 absorption into PCB

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

Reclamation process

- Reclamation of K_2SO_4 using lime

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

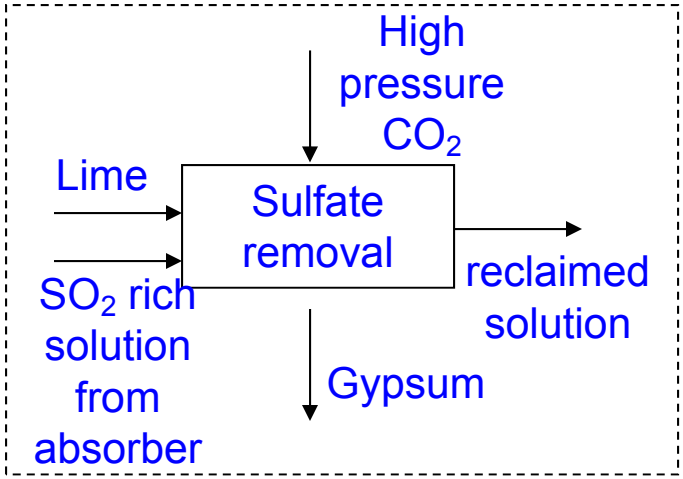
- Two competitive reactions

$$Ca^{2+} + SO_4^{2-} \Rightarrow CaSO_4(\downarrow)$$
$$Ca^{2+} + CO_3^{2-} \Rightarrow CaCO_3(\downarrow)$$

(Solubility products differ by 4 orders of magnitude)

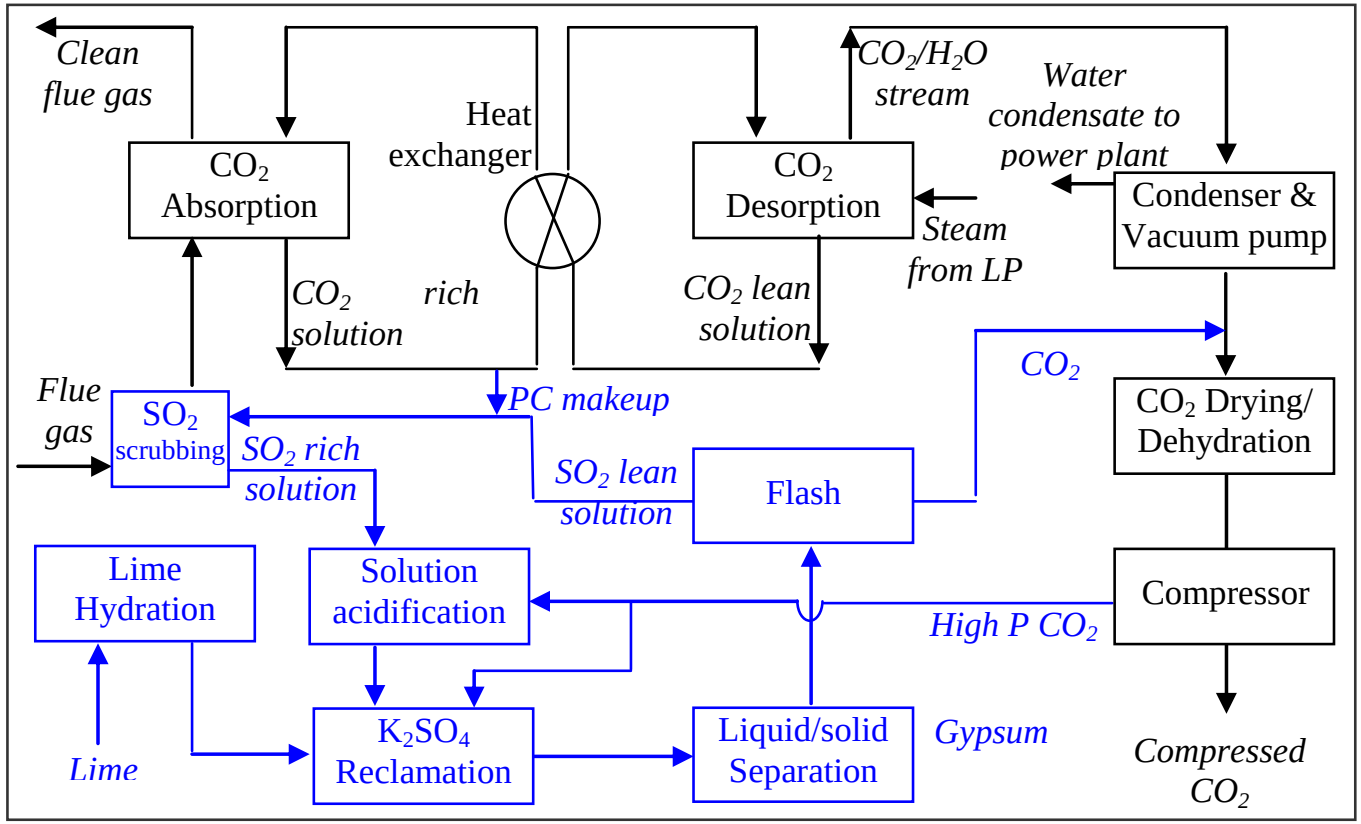
- High pressure CO_2 to lower $[CO_3^{2-}]$ and prevent $CaCO_3$ precipitation:

$$CO_3^{2-} + CO_2 + H_2O = 2HCO_3^-$$
$$CaCO_3(s) + CO_2 + H_2O = Ca^{2+} + HCO_3^-$$

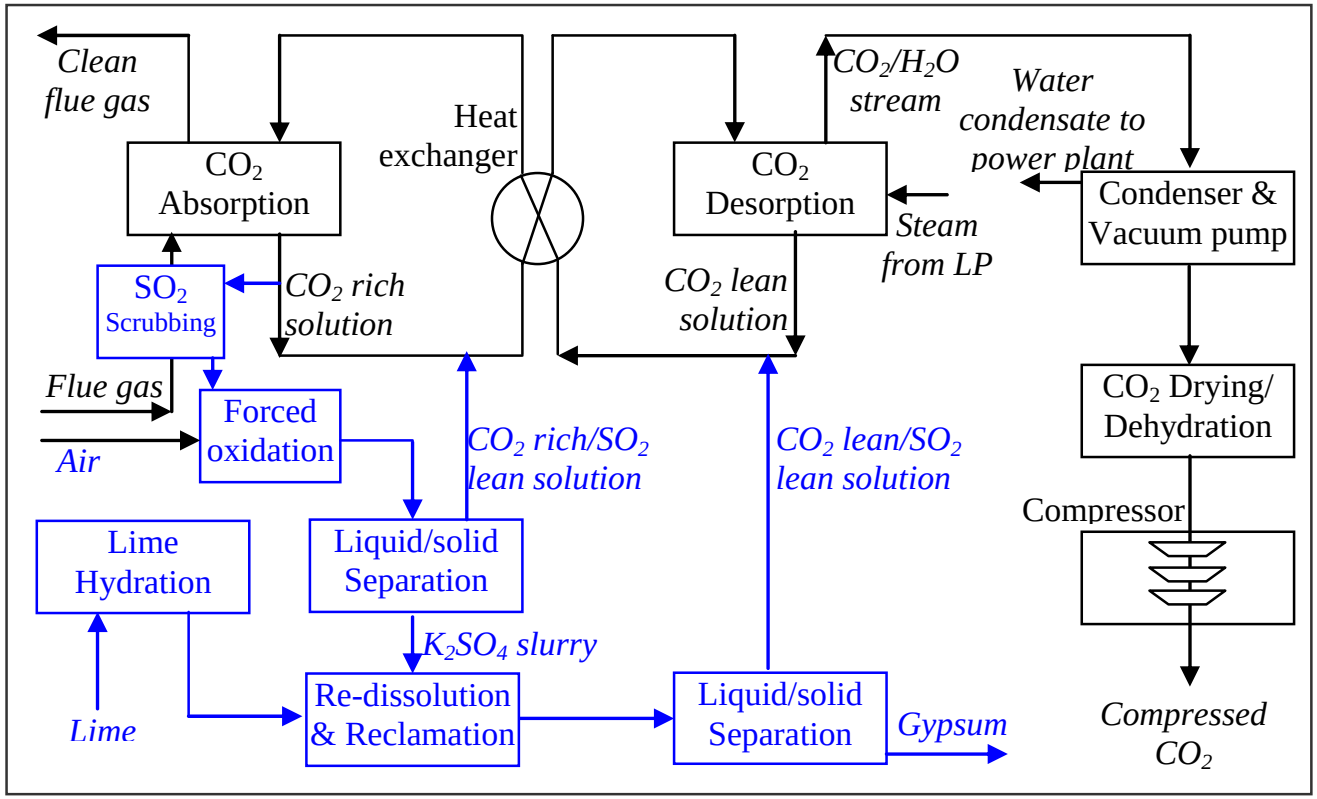


A Modified Process I for SO_2 Removal in Hot-CAP

- Calcite/vaterite ($CaCO_3$) dominant in precipitates with ≥0.2 M PCB and at ≥50 °C
- Process modified to use:
  - A dilute PCB (≤ 0.2 M and CTB > 40%) in a separate scrubber, and lime to reclaim K_2SO_4 (similar to a dual-alkali FGD)
  - T < 50 °C and a high-pressure CO_2 gas



A Modified Process II for SO_2 Removal in Hot-CAP



Absorption: $2K_2CO_3 + SO_2 + H_2O \rightarrow K_2SO_3 + H_2CO_3$

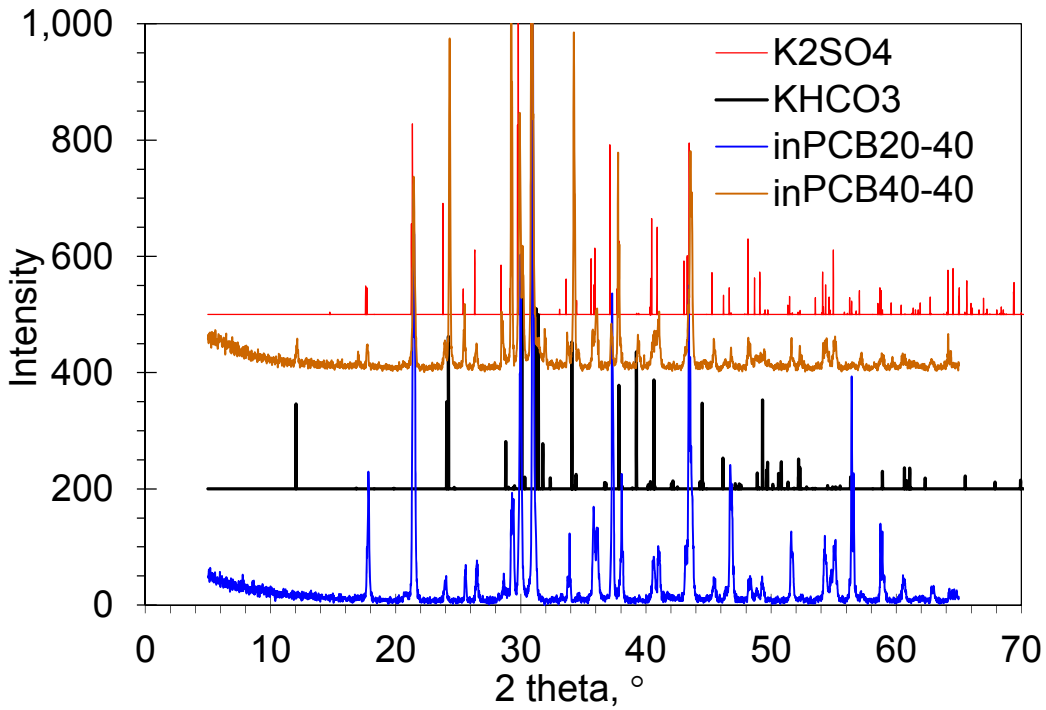
$2KHCO_3 + SO_2 + H_2O \rightarrow K_2SO_3 + 2H_2CO_3$

Oxidation: $K_2SO_3 + ½\ O_2 \rightarrow K_2SO_4\downarrow$

Reclamation: $K_2SO_4 + Ca(OH)_2 \rightarrow 2KOH + CaSO_4\downarrow$

Solubility of $K_2SO_4 << KHCO_3 << K_2CO_3$ and K_2SO_3

Equilibrium Composition of Sulfide Oxidation



Precipitate solids from oxidation of 5wt% K_2SO_3 in PCB20-40 and PCB40-40 at 70 °C

Feasibility demonstrated by:

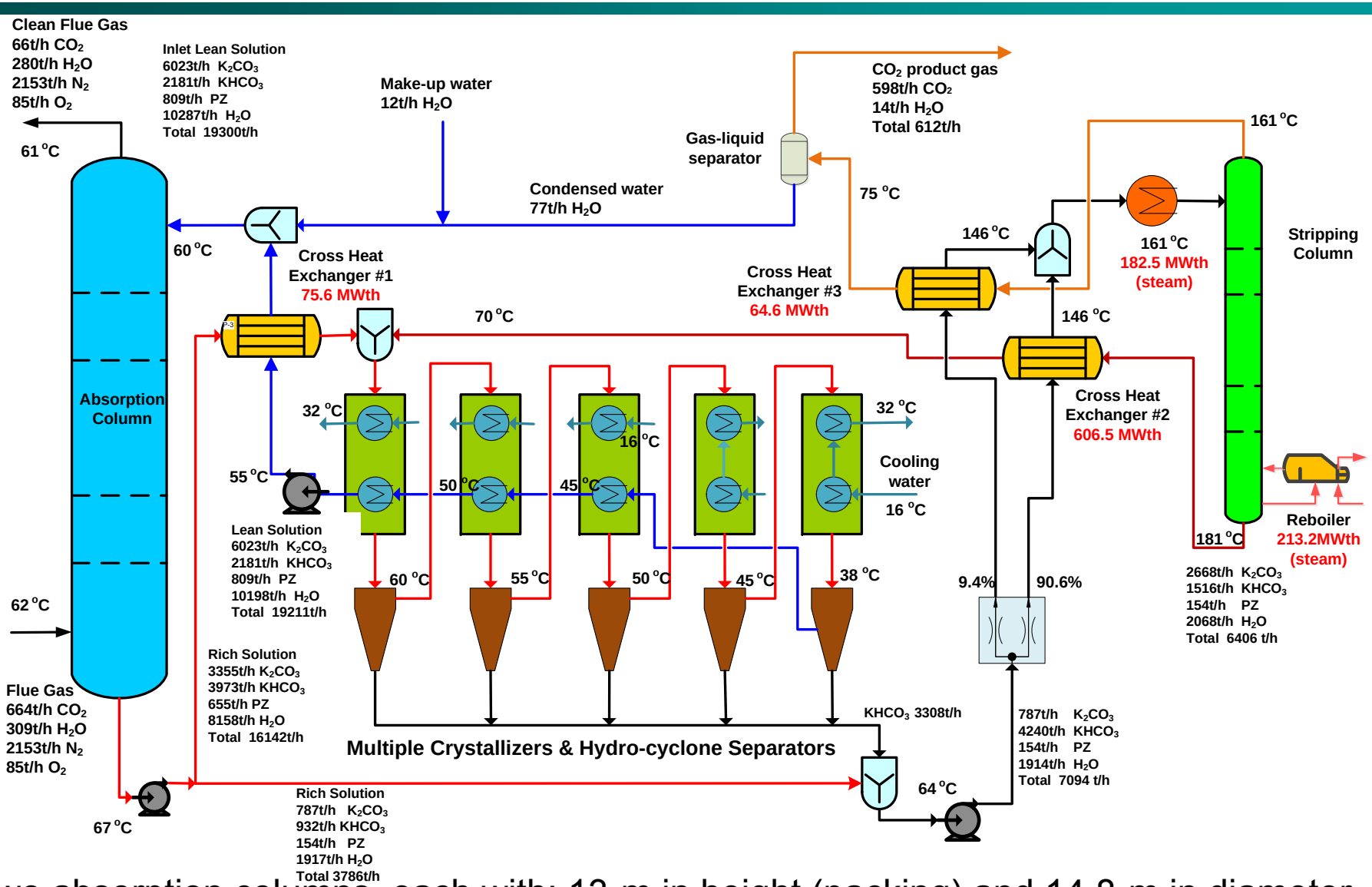
- Precipitates from PCB20-40 contained 100 wt% K_2SO_4
- Precipitates from PCB40-40 contained ~70 wt% K_2SO_4 and ~30 wt% $KHCO_3$

Task 6. Techno-economic analysis

Techno-Economic Analysis

- A 773 MWe (w/o CO_2 capture) Illinois #6 coal-fired power plant
  - With Hot-CAP
  - With MEA (550 MWe net) – DOE/NETL Case 10
- Process simulation and equipment sizing
  - ProTreat software used for absorber and stripper sizing
  - Measured crystallization kinetics for crystallizer sizing
  - Measured VLE data incorporated in the simulation
- Cost analysis
  - DOE/NETL methodology used for capital and O&M cost estimation
  - A Nexant study was referred

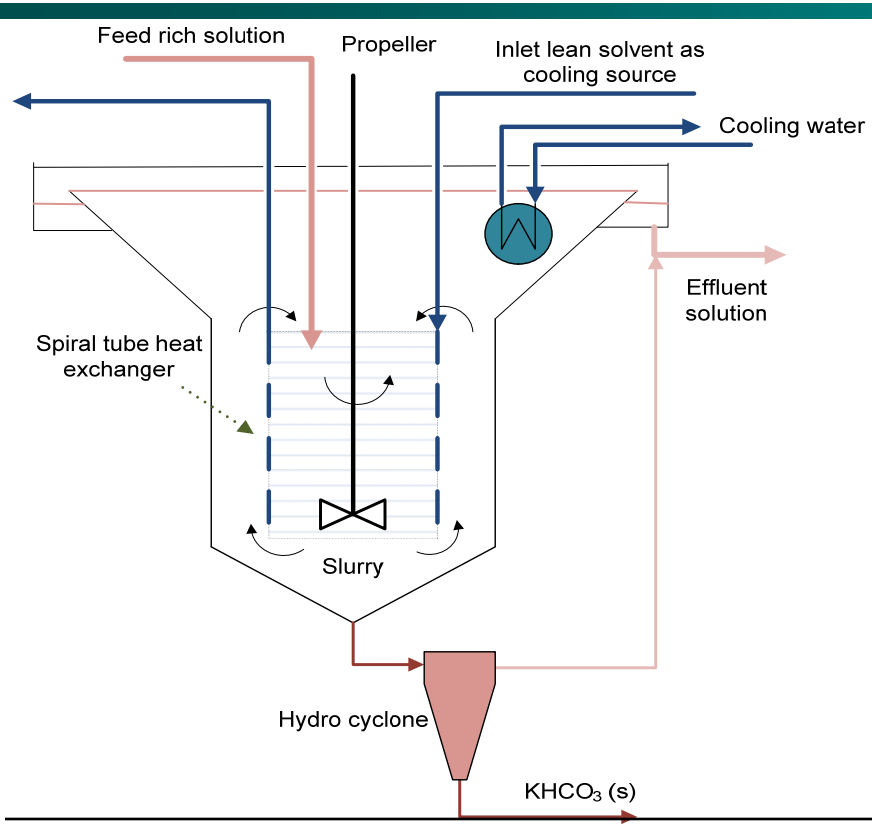
Process Mass and Energy Balances



Two absorption columns, each with: 13-m in height (packing) and 14.8-m in diameter

One stripping column, with 10-m in height and 7.3-m in diameter

Design and Sizing of Crystallizers



- Configuration of five consecutive crystallizers
  - Facilitates heat recovery
  - Reduces ΔT to ~5°C
- Concrete tank crystallizers with submerged coils

Stage	1st	2nd	3rd	4th	5th	Total
Total cooling duty, MW_{th}	88.6	143.9	127.7	123.6	159.3	643.1
by mother liquor, MW_{th}	74.5	73.4	101.7	0.0	0.0	249.6
by cooling water, MW_{th}	14.1	70.4	26.1	123.6	159.3	393.5
Crystallizer volume, m^3	555	633	644	660	734	3,226
Mean residence time, sec	108	126	131	137	154	656

Energy Use Performance: Hot-CAP vs. MEA

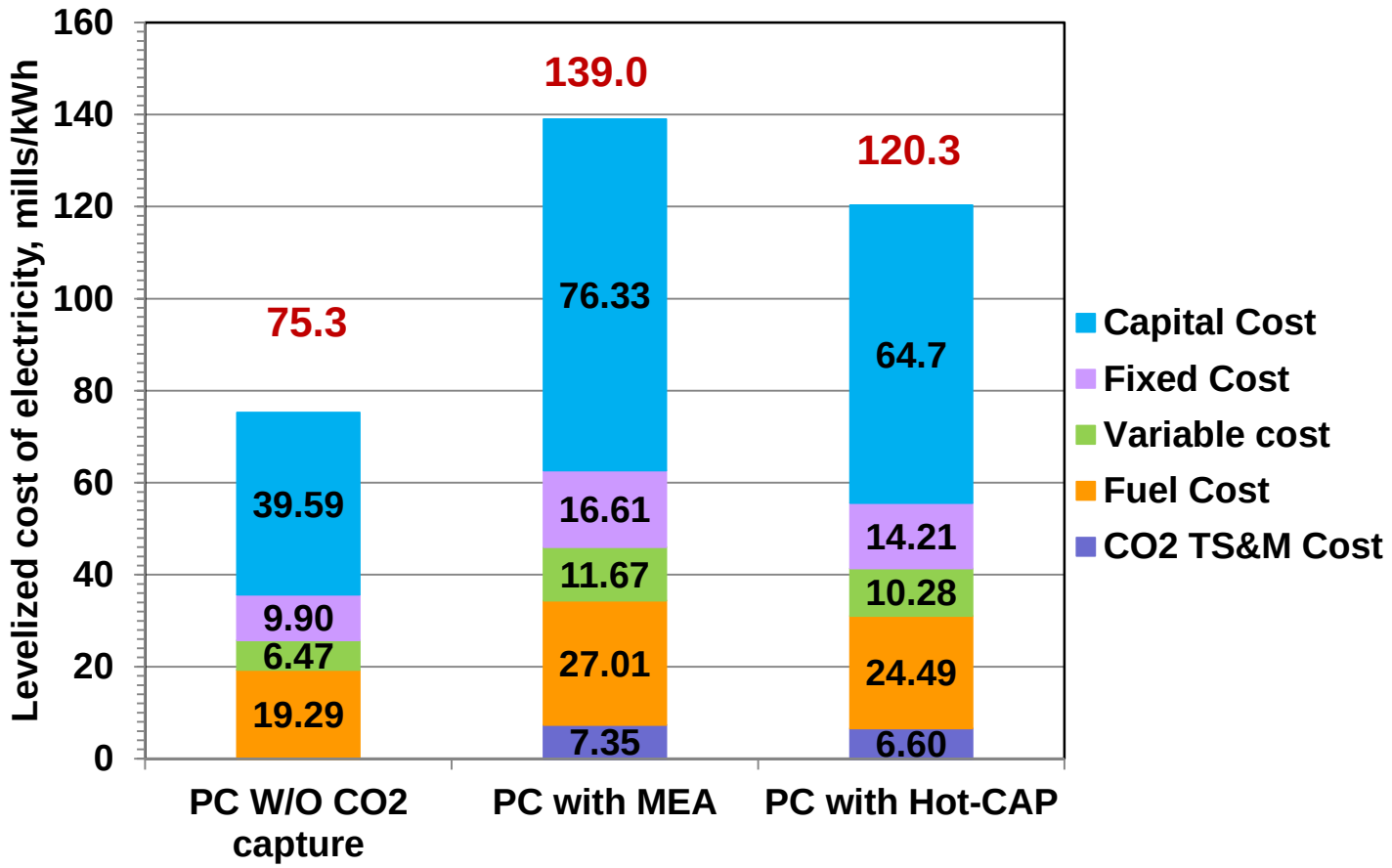
Plant Performance Summary	Case 10 with MEA	Case 10 with Hot-CAP
Consumables:		
As-Received Coal Feed, kg/hr	278,956	278,956
Thermal Input, kW_{th}	2,102,643	2,102,643
Power Generation Summary, kW:		
Steam Turbine Gross Power	672,700	722,695
Auxiliary Load Summary, kW:		
Cooling Water Circulation Pumps	11,190	8,693
Cooling Tower Fans	5,820	4,521
Transformer Losses	2,350	2,600
CO_2 Capture Plant Auxiliaries	22,400	26,541
CO_2 Compression	48,790	39,307
Others	32,190	32,190
Total Auxiliaries, kW	122,740	113,852
Net Power Export, kW	549,960	608,843
Net Plant Efficiency, % HHV	26.2%	29.0%

- PC w/o capture: 773 MW
- PC plant with Hot-CAP: 609 MWe net output vs. 550 MWe with MEA
- 26.4% reduction in parasitic power losses

LCOE Comparison between Hot-CAP and MEA

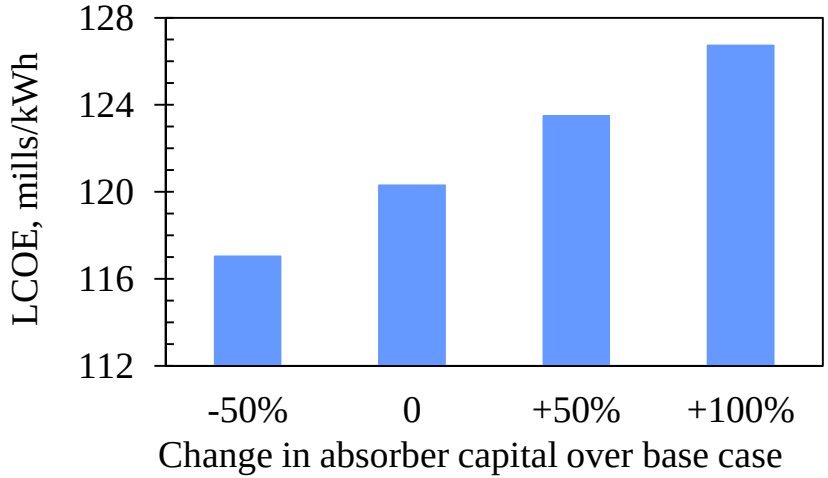
Postcombustion Case Description	Subcritical PC w/o CO_2 Capture	Subcritical PC w/ CO_2 Capture	
Case Number	**Case 9**	**Case 10**	**This Study**
Type of CO_2 Capture Technology	**N/A**	**Econoamine**	**Hot CAP**
Capital Cost Year	2007	2007	2007
CO_2 Capture	0%	90%	90%
Power Production, MW			
Gross Power	583	673	723
Net Power	550	550	609
Cost			
Total Plant Cost, 2007$/kW	1,662	2,942	2,518
Total Overnight Cost, 2007$/kW	1,996	3,610	3,085
Bare Erected Cost	1,317	2,255	1,946
Home Office Expenses	124	213	183
Project Contingency	182	369	311
Process Contingency	0	105	78
Owner's Costs	374	667	567
Total Overnight Cost, 2007$ x 1000	1,098,124	1,985,432	1,878,100
Total As Spent Capital, 2007$/kW	2,264	4,115	3,517
COE (mills/kWh, 2007$)	59.4	109.6	94.8
CO_2 TS&M Costs	0.0	5.8	5.2
Fuel Costs	15.2	21.3	19.3
Variable costs	5.1	9.2	8.1
Fixed Costs	7.8	13.1	11.2
Capital Costs	31.2	60.2	51.0
LCOE (excld. CO_2 TS&M), mills/kWh	**75.3**	**139.0**	**120.3**
% of Case 9 LCOE - Compare to 2007	**100%**	**185%**	**160%**

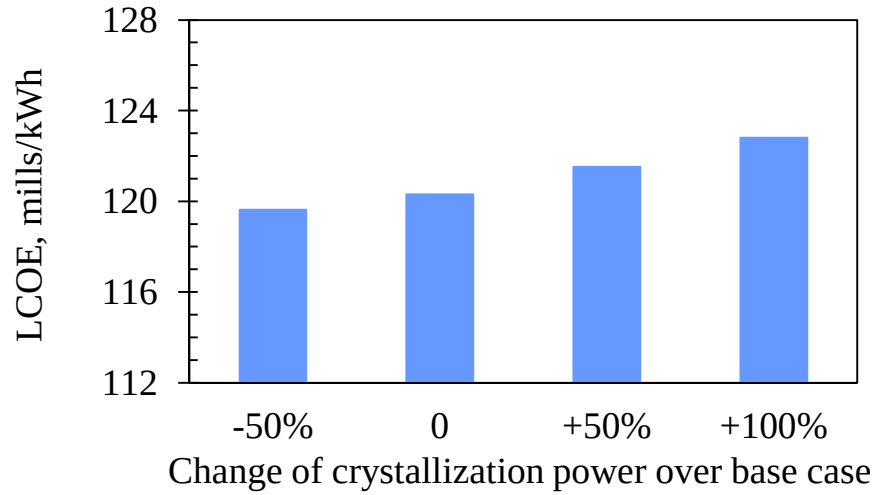
Cost Performance: Hot-CAP vs. MEA

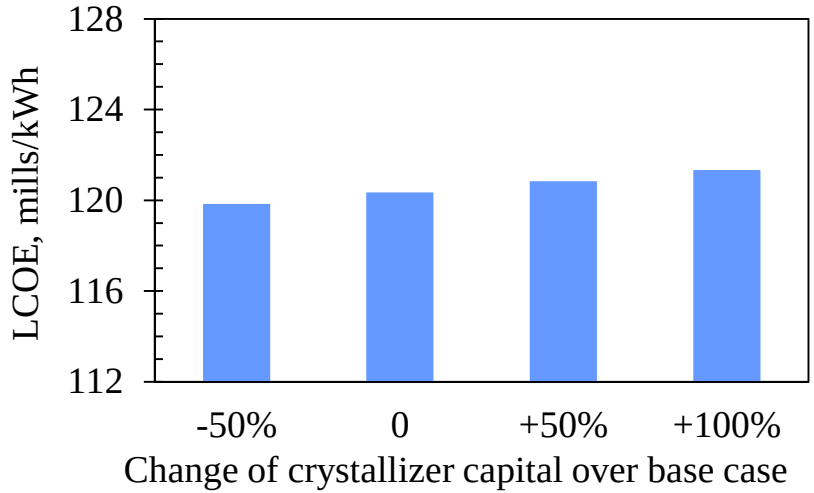


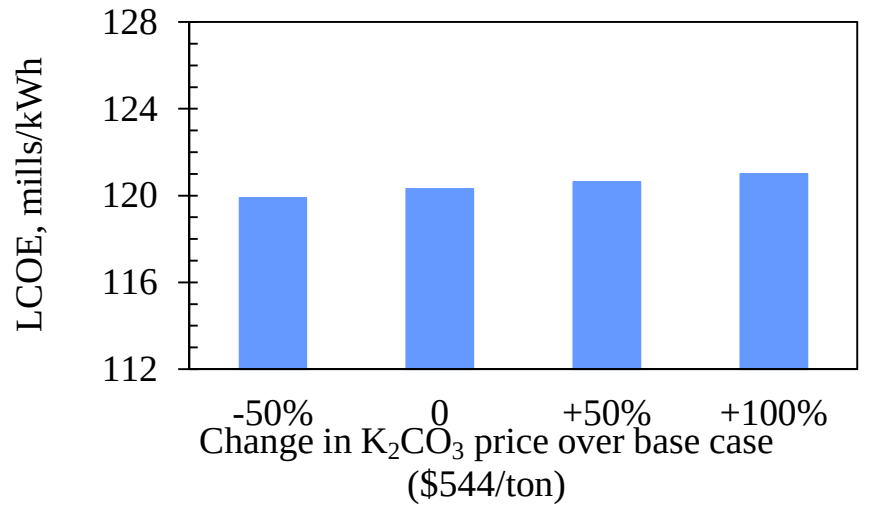
- LCOE is 120.3 mills/kWh, a 60% increase over PC w/o CO_2 capture
- LCOE increase by Hot-CAP is 29% lower than MEA

Cost Sensitivity









- LCOE very sensitive to absorber capital (+6.4 mills/kWh if capital doubles)
- LCOE sensitive to addition of a new polishing scrubber (+4.6 mills/kWh) and crystallization power use (+2.5 mills/kWh if power doubles)
- LCOE not sensitive to K_2CO_3 price, crystallizer capital, and stripping pressure increase

Main Conclusions

- **Major reactions and unit operations are technical feasible**
  - Rates of CO_2 absorption into PCB+PZ at 70 °C were 2-3 times > MEA at 50 °C
  - Crystallization of $KHCO_3$ was kinetically fast and completed within 15 min; Presence of PZ accelerated $KHCO_3$ crystallization.
  - High stripping pressure and high CO_2/H_2O ratio attained with high CO_2 loading in feed and high PCB concentration
  - Heat duty for 160 °C stripping with 30-50 wt% PCB feed of 80% CTB conversion was 2-3 times less than those for 5M MEA at 120 °C stripping
  - A process concept for combined SO_2 removal and CO_2 capture was demonstrated to be feasible
- **Hot-CAP is cost competitive over MEA**
  - 26% lower parasitic power loss than MEA
  - Increase in LCOE over non-capture case is 60% (vs. 85% for MEA)
  - Increase in LCOE is 29% lower than MEA
  - Cost more sensitive to absorber capital and addition of a SO_2 polisher than other variables

Plan for Future Work

- Process improvement
  - Absorber improvement
  - New PCB-based solvents
  - Recovery of heat of crystallization
  - New stripper configuration
- Scale-up testing of an integrated system
  - Using a slipstream flue gas
  - Investigating operational reliability issues such as slurry handling
- Testing of effects of SOx, NOx, and other contaminants in flue gas

THANK YOU ALL !

Intrinsic Rates of Absorption: PCB vs. Amines

- Rates into PCB vs. amines
  - Intrinsic rate into 40wt% PCB at 70°C is ~6 times lower than 5M MEA
  - CO_2 solubility (Henry's law constant) at 70°C is ~4 times lower than 25°C

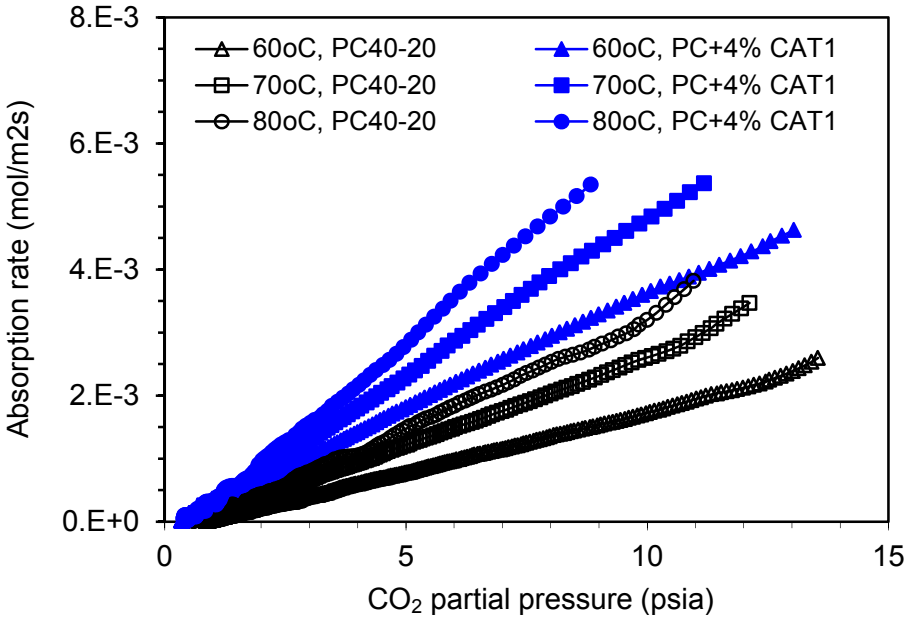
Reactant	Rate constant *k*, L/mol/s	Concentration, mol/L	Rate (*k* [Reactant]), 1/s
OH^-	1.57×10^6 (at 70°C)	4.33×10^{-3}	k_1 *[OH]* = 6,820
MEA*	7,600 (at 25°C)	5	k_2 *[MEA]* = 38,000
MDEA	4.3 (at 25°C)	5	k_3 *[MDEA]* = 21.5

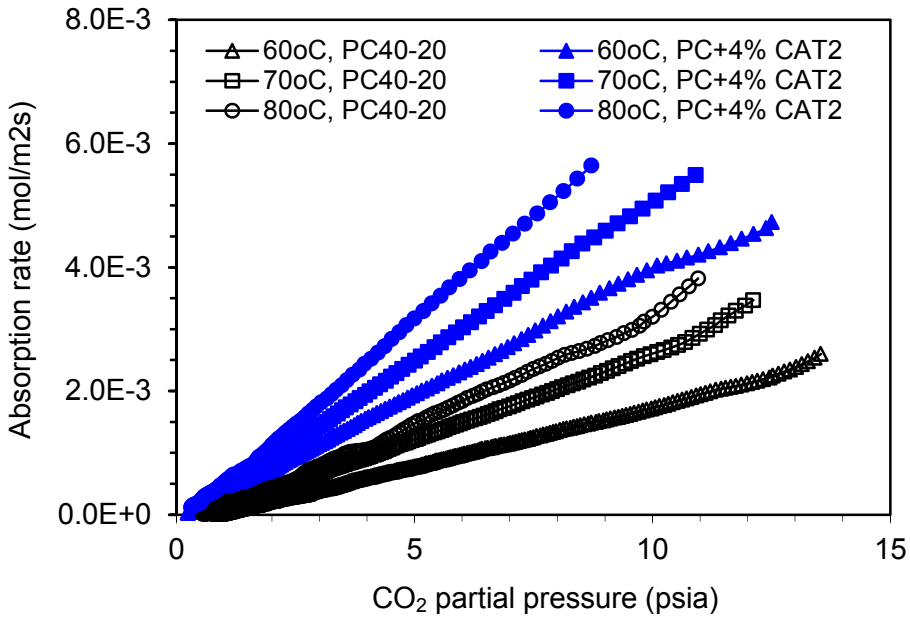
$$CO_2 + OH^- \xrightarrow{k_1} HCO_3^- \qquad \text{rate}: r_1 = k_1[CO_2][OH^-]$$

$$CO_2 + RNH_2 \xrightarrow{k_2} H^+ + RNHCOO^- \qquad \text{rate}: r_2 = k_2[CO_2][MEA]$$

$$CO_2 + RRCH_3N + H_2O \xrightarrow{k_3} RRCH_3NH^+ + HCO_3^- \qquad \text{rate}: r_3 = k_3[CO_2][MDEA]$$

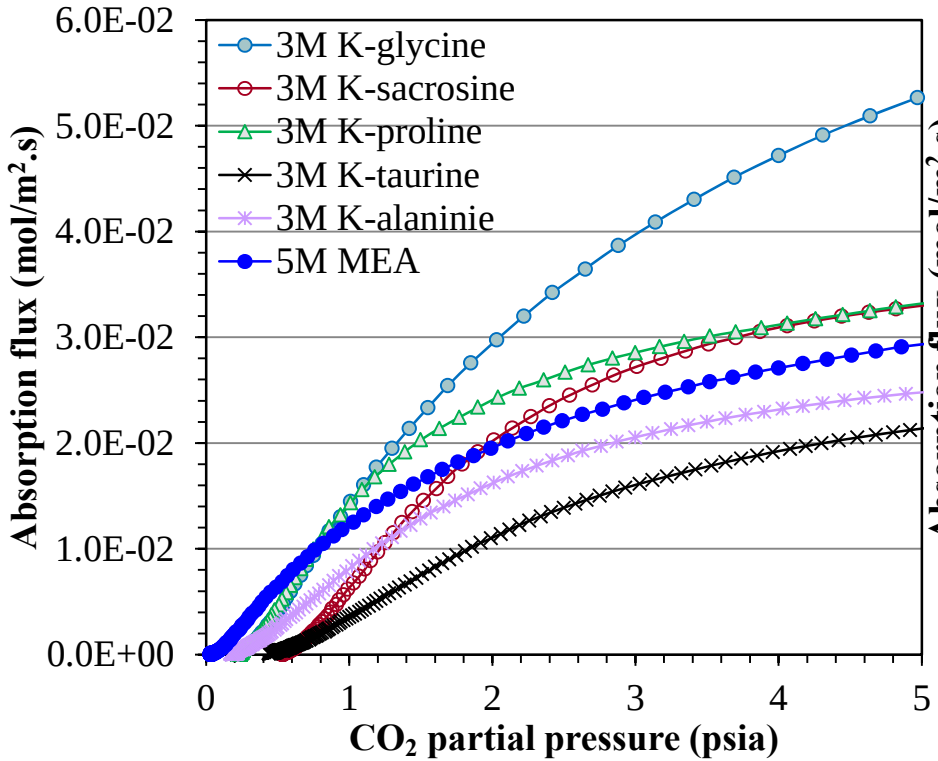
CO_2 Absorption into 40wt% PCB with Catalysts

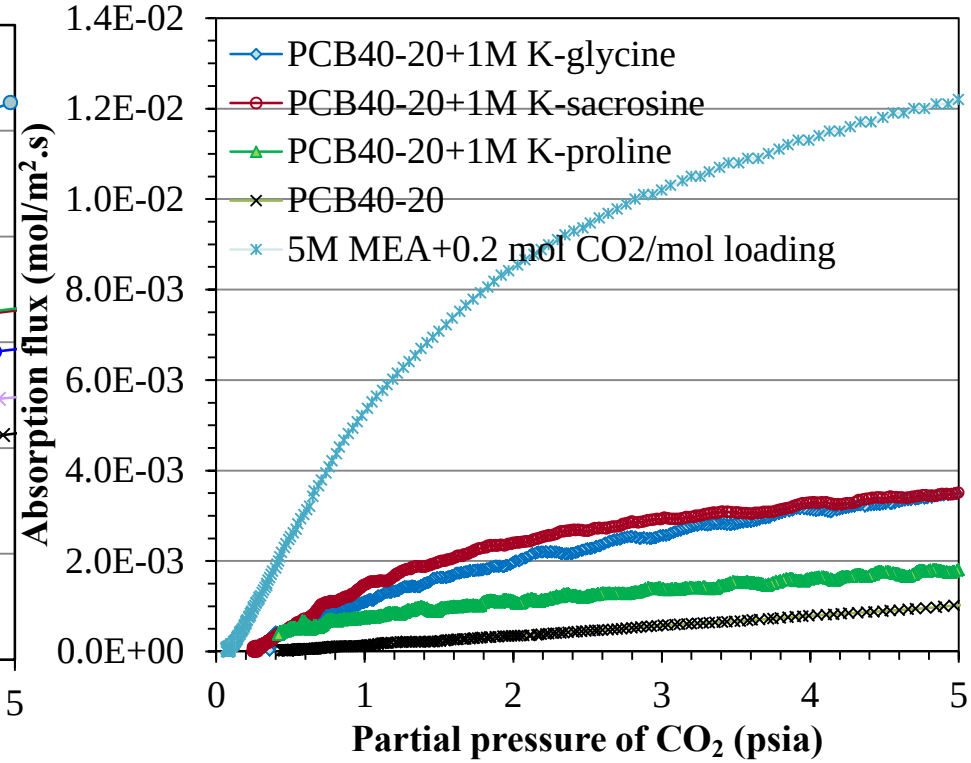




- Two inorganic catalysts, CAT1 and CAT2, identified more effective than other inorganic catalysts
- Addition of 4 wt% CAT1 or CAT2 increased rates by ~2 times at 60, 70, 80°C

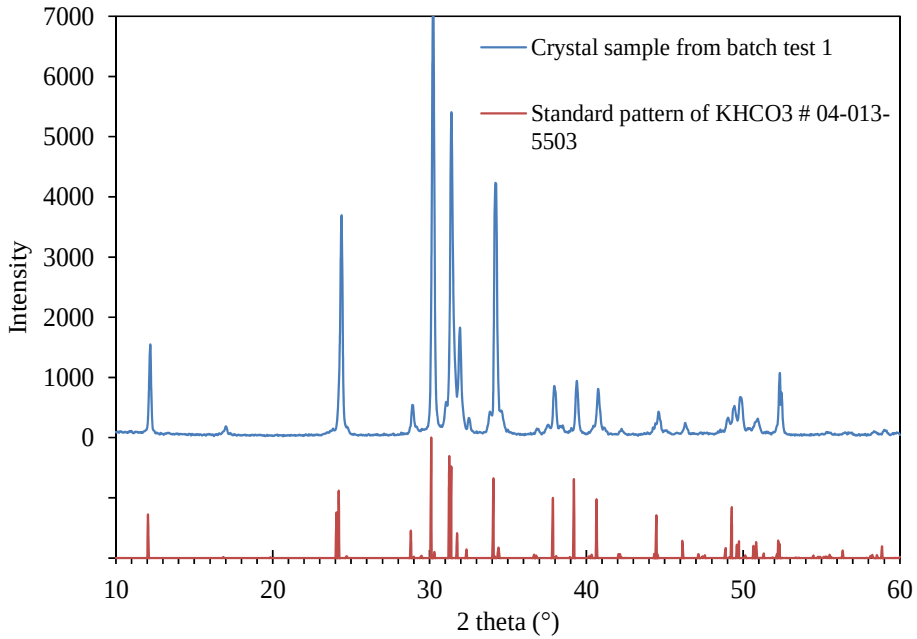
CO_2 Absorption into 40wt% PCB with Amine Acid Salt Promoters



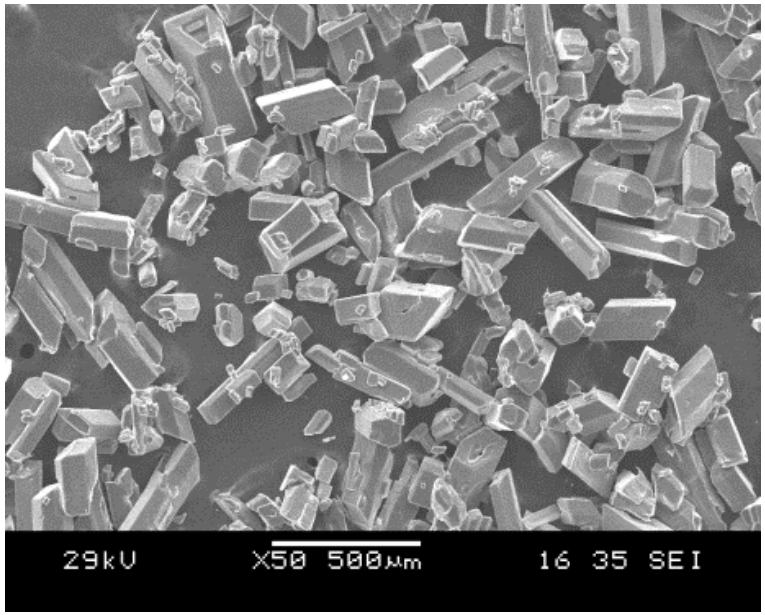


- Rates into 3M K-glycine, K-sacrosine and K-proline solutions at 70 ºC higher than or comparable to 5M MEA at 50 ºC
- Rates into PCB promoted by K-glycine and K-sacrosine increased by 3-11 times but still < MEA

Morphology and Composition of Crystal Particles



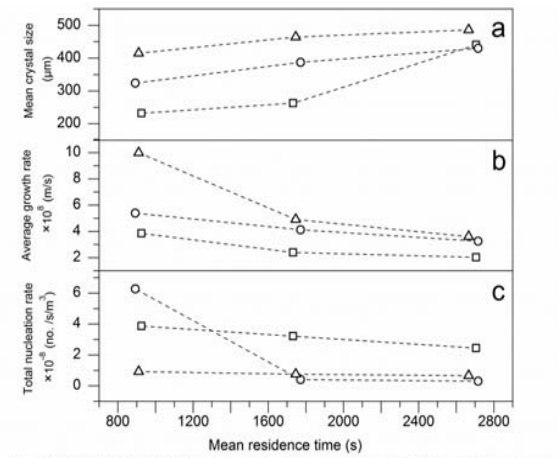
XRD pattern of a typical crystal sample



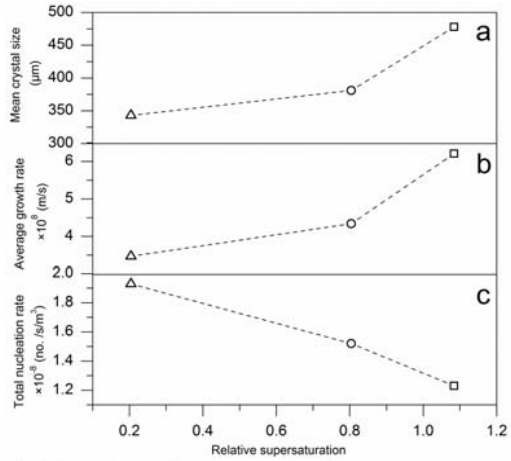
SEM image of $KHCO_3$ crystal

- Kalicinite ($KHCO_3$) was the only phase formed in all tests (w or w/o absorption promoter)
- Hexagonal prism morphology

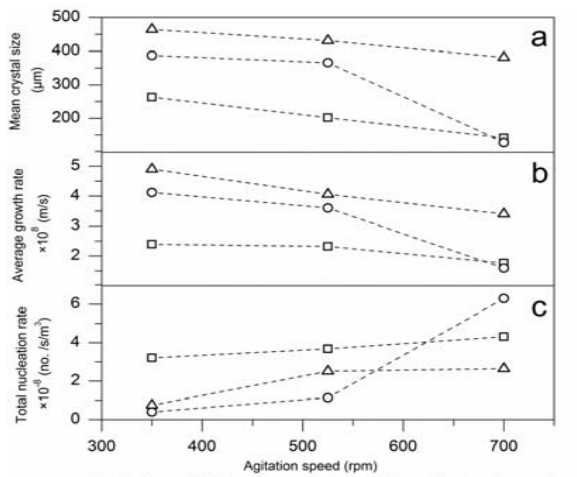
Parametric Effects on $KHCO_3$ Crystallization Kinetics



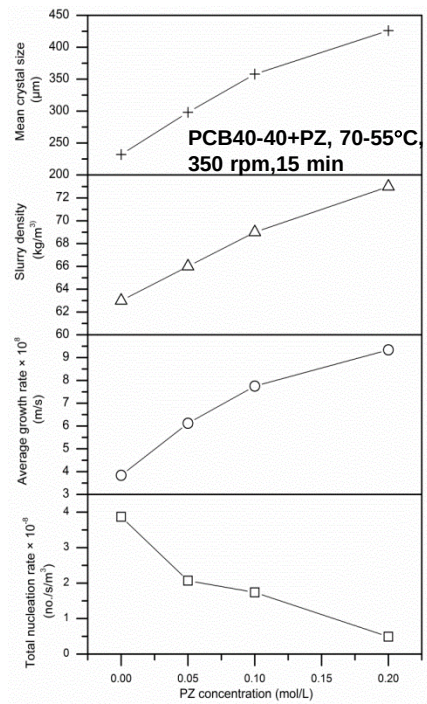
- □ - PCB 40-40 fed at 70 °C, and crystallization at 55 °C and 350 rpm agitation speed.
- ○ - PCB 38-35 fed at 55 °C, and crystallization at 45 °C and 350 rpm agitation speed.
- △ - PCB 37-31 fed at 45 °C, and crystallization at 35 °C and 350 rpm agitation speed.



- △ - PCB 35-32.5 fed at 70 °C, and crystallization at 35 °C, 700 rpm agitation speed for 30 min.
- ○ - PCB 37.5-36.5 fed at 70 °C, and crystallization at 35 °C, 700 rpm agitation speed for 30 min.
- □ - PCB 40-40 fed at 70 °C, and crystallization at 35 °C, 700 rpm agitation speed for 30 min.



- □ - PCB 40-40 fed at 70 °C, and crystallization at 55 °C and 30 min residence time.
- ○ - PCB 38-35 fed at 55 °C, and crystallization at 45 °C and 30 min residence time.
- △ - PCB 37-31 fed at 45 °C, and crystallization at 35 °C and 30 min residence time.

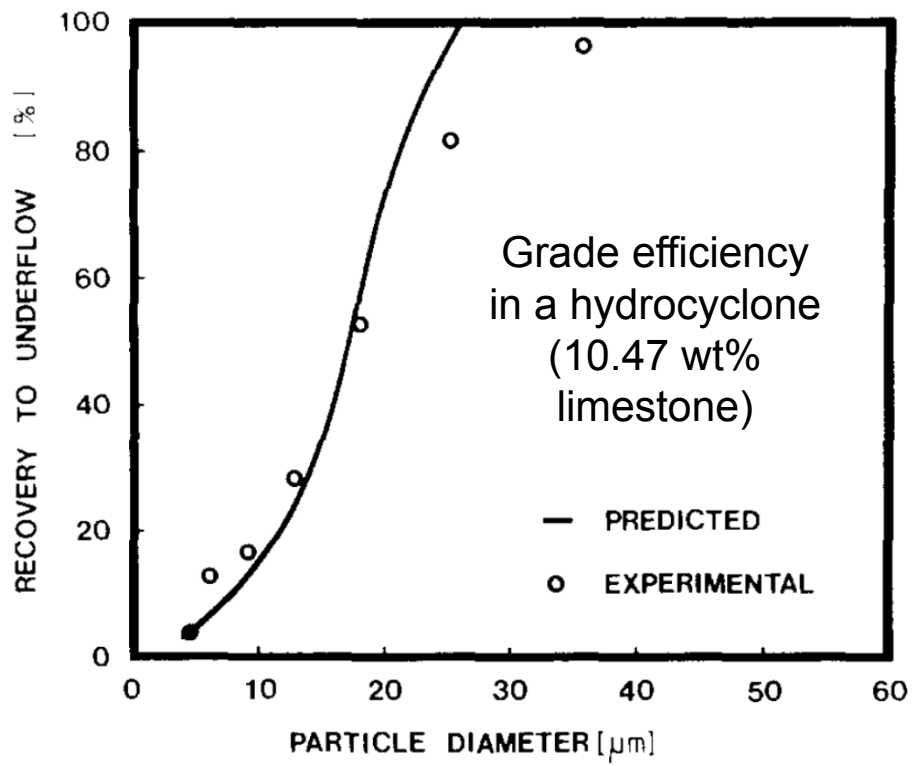


- Higher σ, milder agitation and longer τ resulted in larger crystals
- High σ, mild agitation and short τ favored fast crystal growth
- Low σ, vigorous agitation and short τ favored fast nucleation
- Presence of PZ accelerated $KHCO_3$ crystallization

(σ: supersaturation
τ: mean residence time)

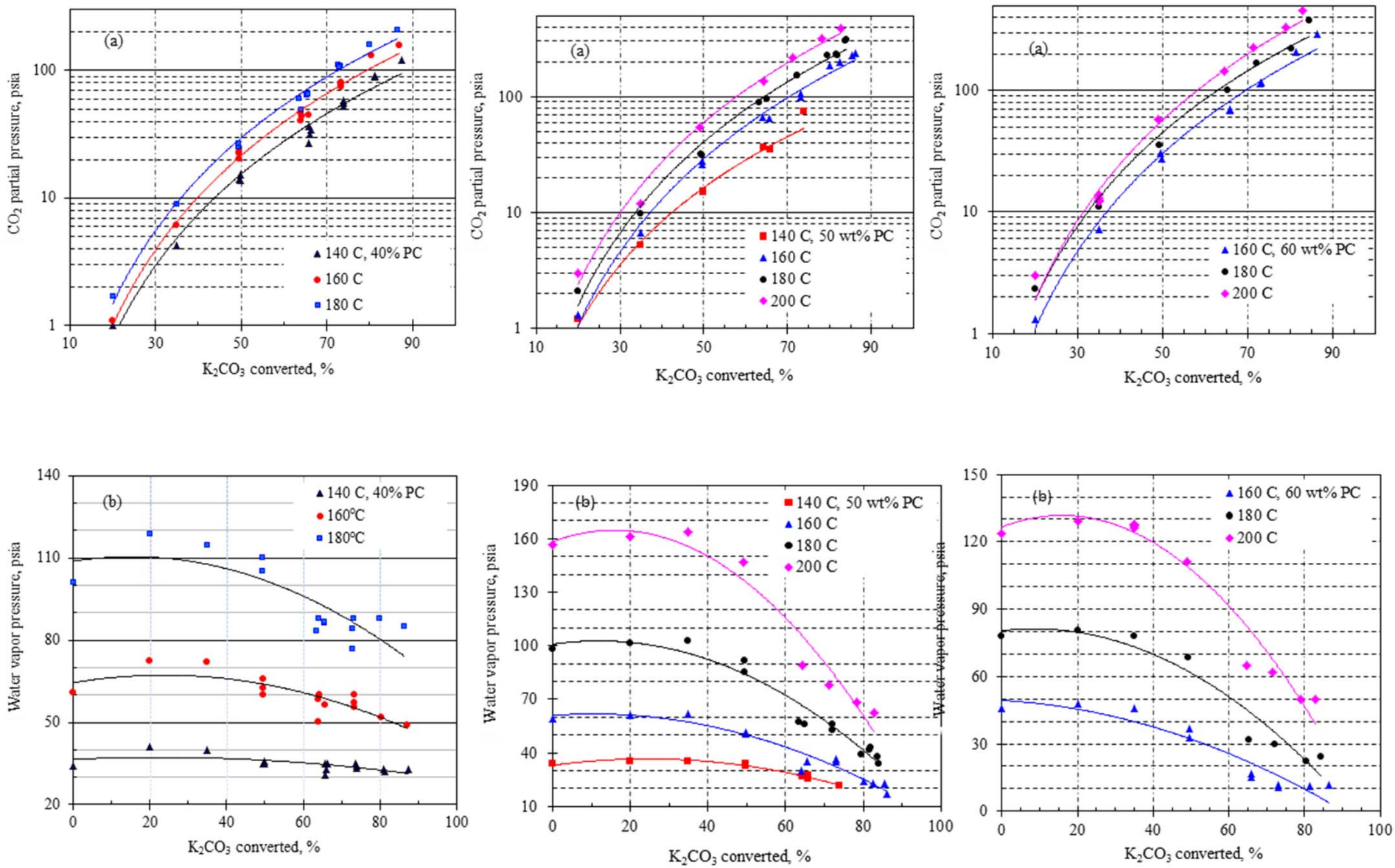
Separation Efficiency of Crystal Particles

- Mean particle size of $KHCO_3$: 233 - 455 μm
  (τ =15, 30, 45 min, crystallization T= 55, 45, 35°C)
  - Crystal size large enough for conventional liquid-solid separation
  - Crystallization ≤ 15 min is sufficient

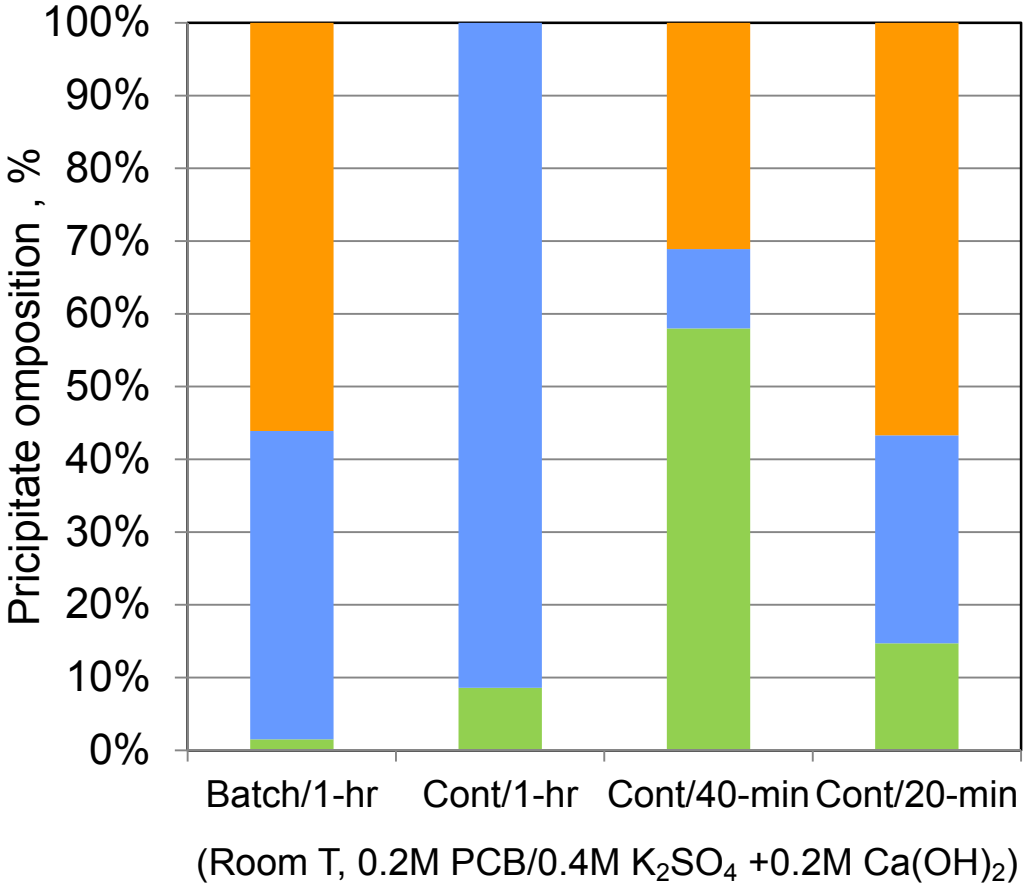


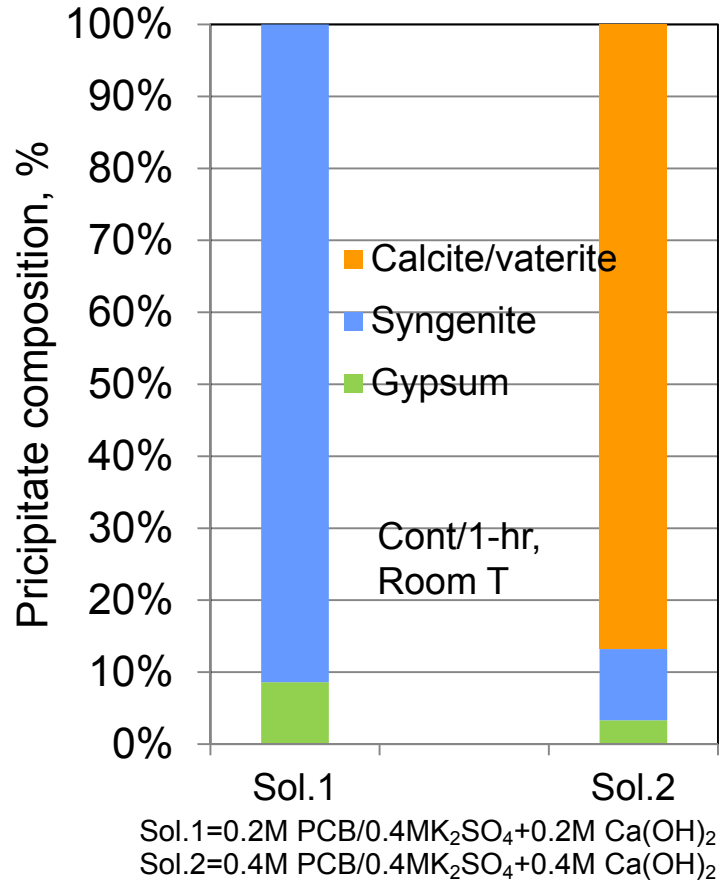
Source: Monredon *et al*. *Int. J. of Mineral Process. 1992,* 35: 65-83.

VLE Data for 40, 50, 60wt% PCB at 140-200°C



Compositions of Precipitates Produced





- Gypsum/syngenite dominant in precipitates with ≤0.2 M PCB and at <50 °C
- Gypsum/syngenite favored by increasing mixing, [K_2SO_4], or reaction time

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3\downarrow \qquad CaCO_3\downarrow + CO_2 + H_2O \leftrightarrow Ca(HCO_3)_2$$

$$Ca(HCO_3)_2 \leftrightarrow Ca^{2+} + 2\,HCO_3^- \qquad Ca^{2+} + SO_4^{2-} \leftrightarrow CaSO_4\downarrow$$

Design and Sizing of Absorber and Stripper

- Two absorption columns, each with:
  - 13-m in height (effective packing)
  - 14.8-m in diameter

- One stripping column:
  - 10-m in height
  - 7.3-m in diameter