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

(DOE/NETL Agreement No. DE-FE0004360**)**

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

Carbon Capture Scientific, LLC

Project Review Meeting

Pittsburgh, PA • February 15, 2013

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-6

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 after completion of the project
  - ISGS/UIUC team: Lab- and bench-scale tests of thermodynamics and reaction engineering data of major unit operations
  - CCS, LLC team: Risk mitigation analysis and techno-economic studies

Project Duration and Budget

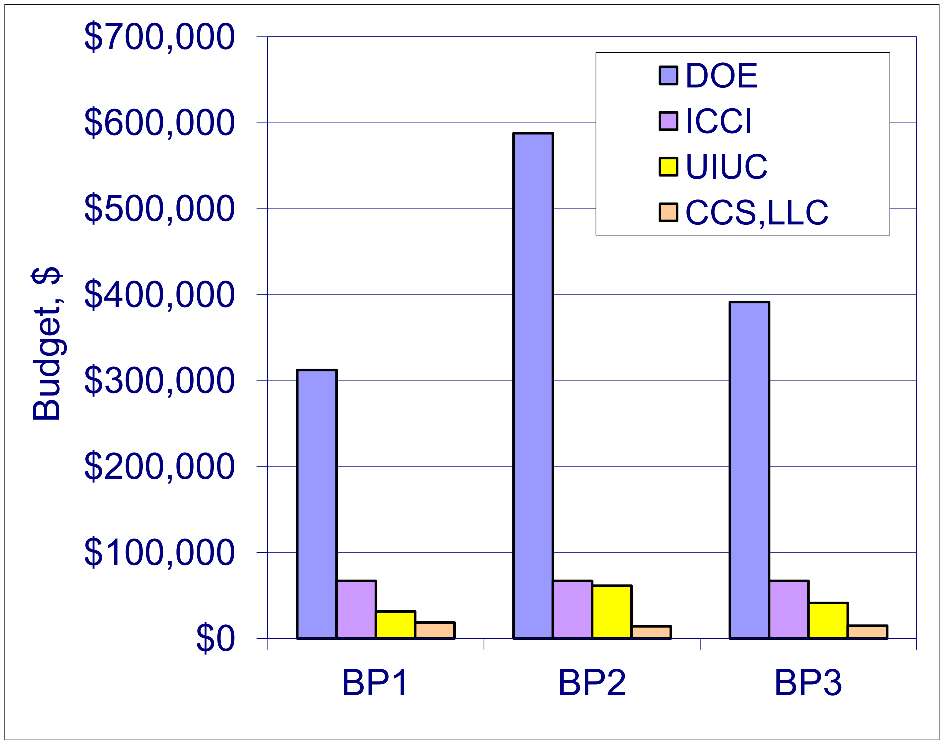
Project duration: 1/1/2011 – 3/31/2014

- BP1: 1/1/2011-12/31/2011
- BP2: 1/1/2012-3/31/2013 (3-mon extension)
- BP3: 4/1/2013-3/31/2014

Total budget:

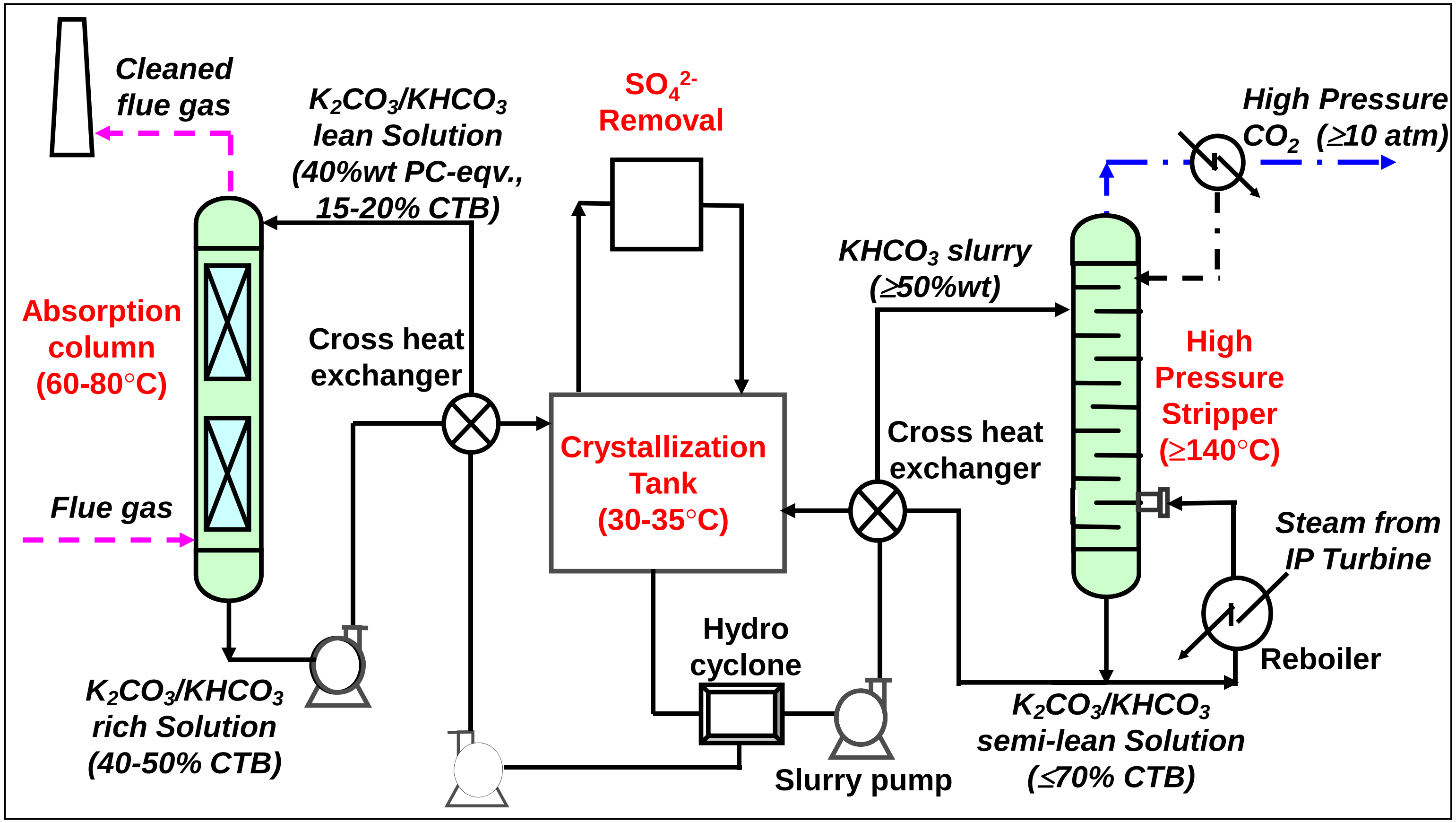
	Budget, $
DOE/NETL	**1,291,638**
ICCI (cash cost share)	**201,000**
UIUC (in kind)	**134,357**
CCS, LLC (in kind)	**47,713**
Total	**1,674,708**

(Cost share is ~23%)



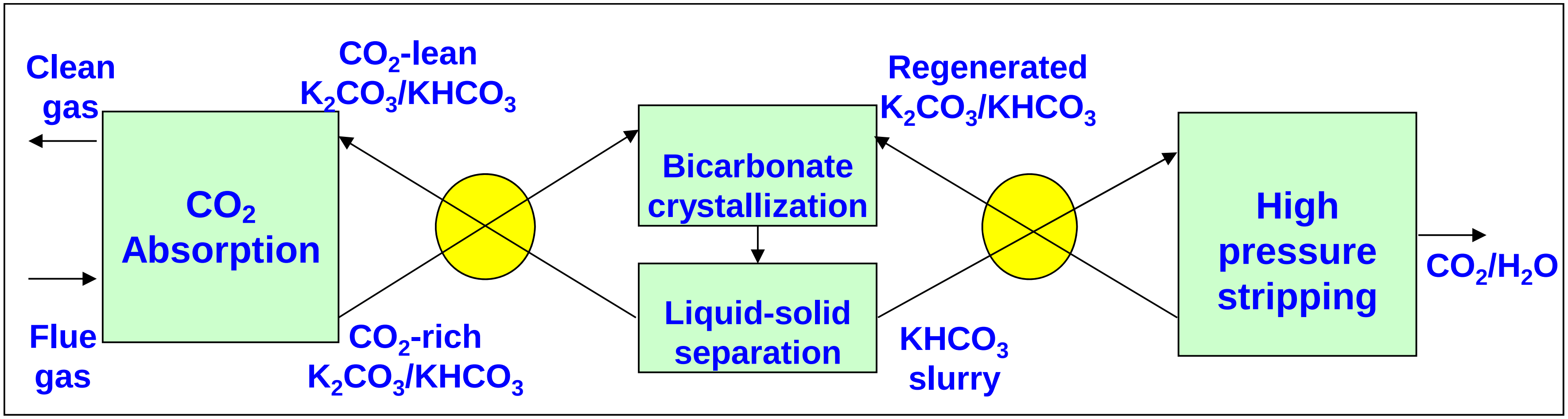
Technical background

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



- Absorption at 60−80°C
- Working capacity of 40wt% $K_2CO_3/KHCO_3$ (PC) solution: ~15 to ~40% carbonate-to-bicarbonate (CTB) conversion
- Crystallization at near room temperature (30-35°C)
- Stripping of bicarbonate slurry at 10−40 bar

Major Reactions



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

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

$$Crystalliz\,ation\ \ at \sim 35°C:$$
$$KHCO_3 = KHCO_3(s)\downarrow$$

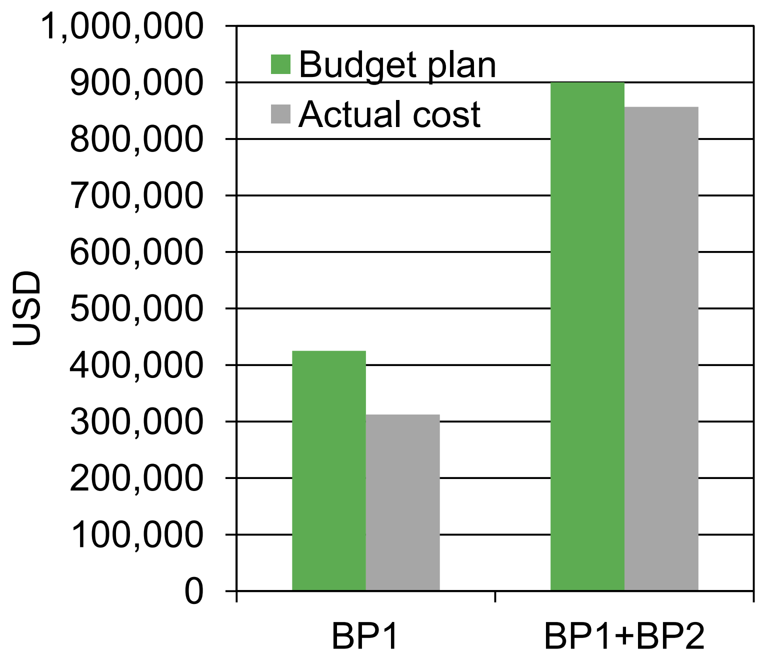
Hot-CAP Offers Major Advantages Over Traditional Amine-Based Solutions

	MEA	Hot-CAP
Solvent	30wt% MEA	40wt% K_2CO_3
Solvent degradation	Y	N
Corrosion	Y	Less significant
Absorption temperature	40-50°C	60-80°C
Stripping temperature	120°C	140-200°C
Stripping pressure	1.5-2 atm	≥10 atm
Phase change with absorption and stripping	N	Crystallization
FGD required	Y	Reduced Size

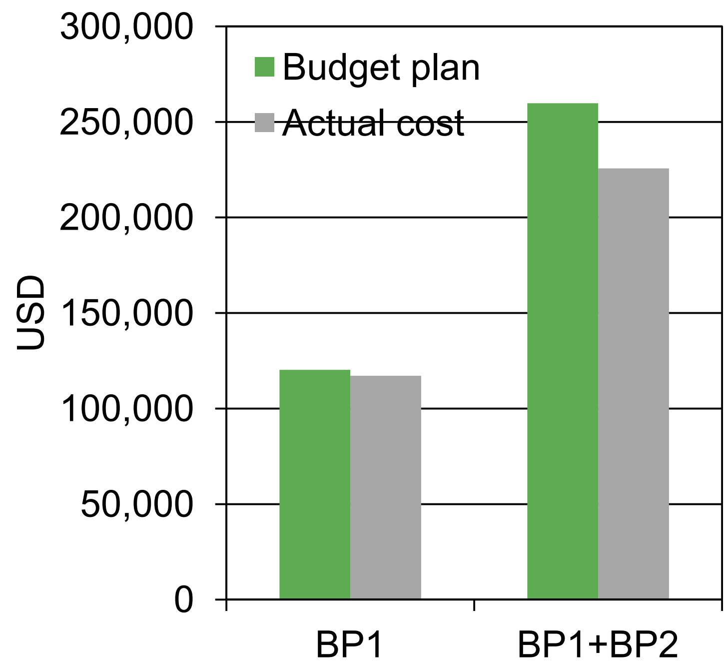
Project Progress and Current Status

Project Costs on Track at the Close of BP2

DOE/NETL actual costs as of 1/31/2013
(BP2 ends by 3/31/13)



Actual cost share as of 12/31/2012



- Corrective actions and adjustments taken by the team after BP1 to get project budget management back on track
- Additional funds from NETL in BP2 vital to mitigating technical risks of the process

Technical Milestones Achieved

Budget Period	Task/ Subtask No.	Milestone Description	Planned Completion Date	Actual Completion Date	Verification Method
1	2.1 (a)	Stirred tank reactor modified	4/30/2011	4/15/2011	Able to measure absorption kinetics at 60-80°C
1	3.1 (b)	Crystallization reactor system set up	6/30/2011	batch reactor on 6/30/11; continuous reactor on 9/7/11	Experimental system assembled and ready for shakedown tests
1	4.1 (c)	High pressure autoclave reactor system set up for VLE measurements	9/30/2011	9/30/2011	Experimental system assembled and ready for shakedown tests
1	2.1 (d)	Kinetic tests of absorption in $K_2CO_3/KHCO_3$ solution completed	12/31/2011	12/31/2011	Results reported in the quarterly report
2	4.1/4.2 (k)	VLE measurements for $K_2CO_3/KHCO_3$ slurry systems completed	6/30/2012	6/30/2012	Results reported in quarterly report
2	2.3 (n)	Absorption column tests completed	9/30/2012	6/30/2012	Results reported in quarterly report
2	3.3 (o)	$NaHCO_3$-$KHCO_3$ crystallization testing completed	12/31/2012	12/20/2012	Results reported in quarterly report

- 17 milestone in BP1 and BP2 (7 major ones listed in the table)
  - 15 milestones completed on schedule
  - 1 milestone extended for 3-mon
  - 1 milestone scheduled to be completed by end of BP2 (3/31/13)

Tasks Completed on Schedule

Project Tasks	Progress to date
Task 1. Project planning & management	In process
Task 2. Kinetics of CO_2 absorption • Absorption with and w/o promoters • Absorption column testing	Complete
Task 3. Crystallization kinetics & solubility of bicarbonate • $KHCO_3$ crystallization testing • $NaHCO_3$ crystallization testing	Complete
Task 4. Phase equilibrium & kinetics of high pressure CO_2 stripping • VLE measurement • Stripping column testing	VLE completed; fabrication of a stripping column extended for 3-mon in BP2 Column testing: BP3
Task 5. Reclamation of sulfate from SO_2 removal	On schedule: continues in BP3
Task 6. Techno-economic evaluation • Risk mitigation analysis • Process simulation • Economic evaluation	Risk analysis to be completed by end of BP2; Economic Evaluation : BP3

Work and Budget Plan in BP3

BP3: No Budget Changes Requested

- No change requested for either total federal budget or cost share in BP3
- Actually incurred cost as of 1/31/13 close to the BP1+BP2 budget plan

	Plan **BP1 + BP2 (USD)**	**Plan BP3** **(USD)**
DOE/NETL share	900,108	391,530
Recipient cost Share	259,788	123,282
Total	1,159,896	514,812

Major Work Activities Planned in BP3

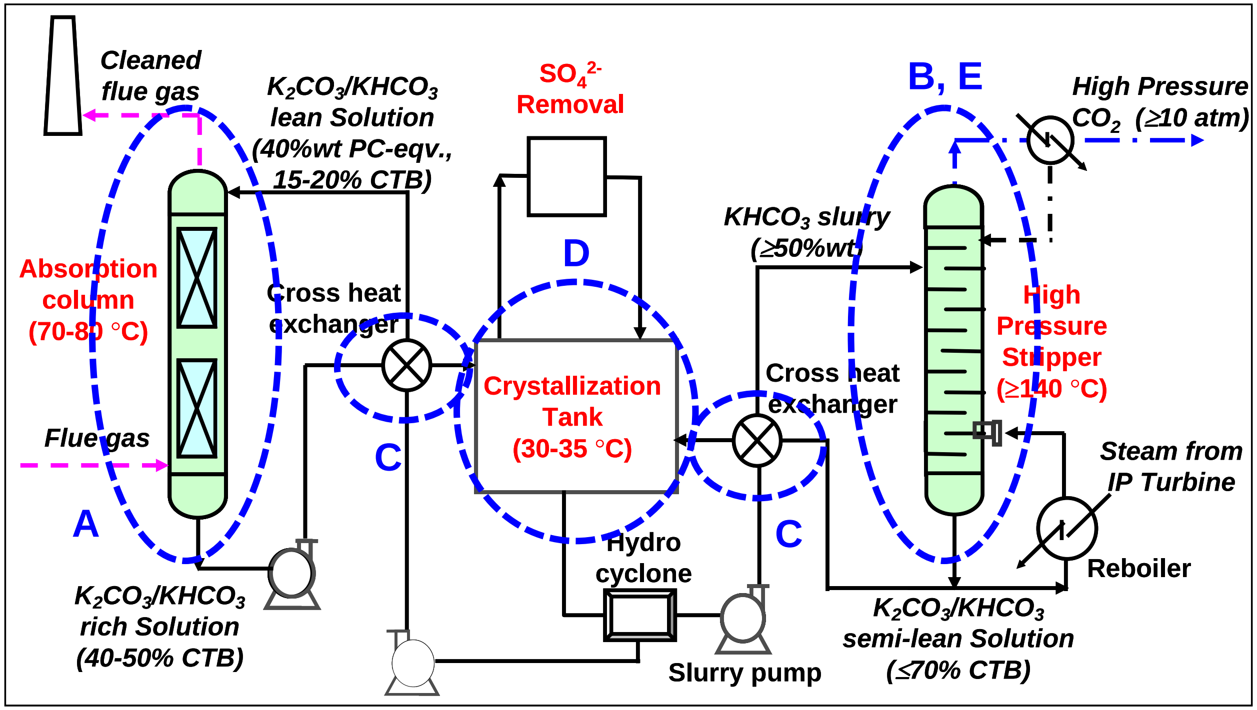
- **Task 4: High pressure CO_2 stripping testing in a bench-scale column**
  - Kinetic and hydrodynamic performances
  - Process optimization
- **Task 5: Experimental studies of combined SO_2 removal and CO_2 capture**
  - Process optimization
  - Proof-of-concept testing of a modified process option
- **Task 6: Techno-economic studies**
  - Equipment sizing
  - Cost and sensitivity analysis
- **Other work**
  - Solubility measurement

Major Activities and Research Findings

Technical Challenges to Be Addressed

- Is the overall rate of CO_2 absorption into PC solution at Hot-CAP operating conditions comparable to that into 5M MEA?
- Is the crystallization rate fast enough (e.g., equivalent to a residence time of <1 hr in a crystallizer)?
- Can the CO_2 stripper operate at high pressure (e.g. $\geq$10 bar)?
- Can SO_2 removal be combined in Hot-CAP?
- Can fouling on surfaces of heat exchangers and crystallizers due to bicarbonate crystallization be prevented?
- Can the stripper be designed to handle slurry and operate at high pressure?

Technical Risks and Mitigation Strategies



Risk	Mitigation
A. Insufficient rate of CO_2 absorption	Develop promoters/catalysts & reconfigure absorption column
B. Stripping pressure not high enough (e.g.,<10 atm)	Develop a sodium bicarbonate-based slurry
C. Heat exchanger and crystallizer fouling	Vender consultation, engineering analysis & customized design
D. Insufficient cooling rate in crystallizer affects cost/space	Same as above
E. Stripper required to handle slurry and high pressure	Same as above

Summary of Task Results

- Task 2: Kinetics of CO_2 absorption
  - High absorption rates achieved in concentrated PC + promoter at elevated T
  - Presence of precipitates didn't result in a significant decease in rates

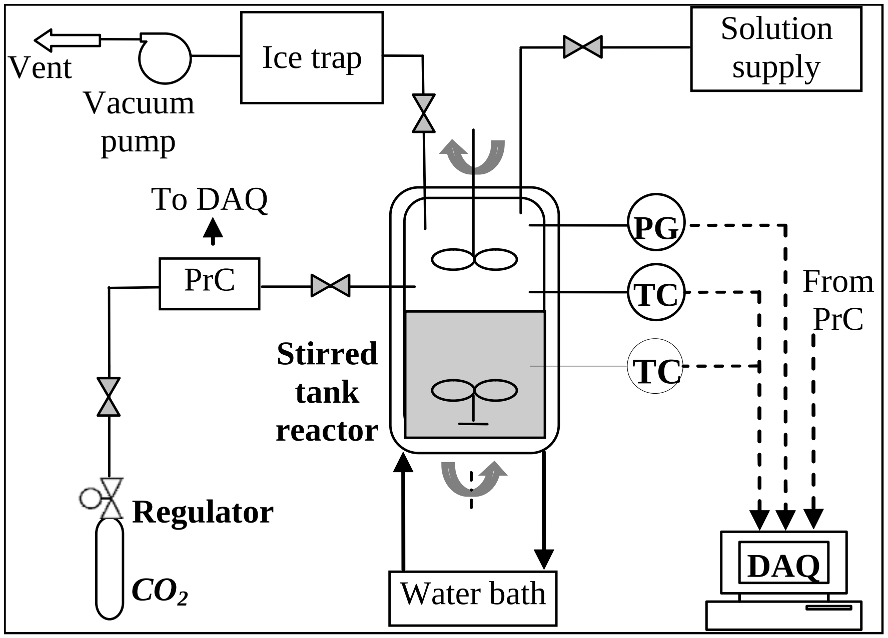
- Task 3: Crystallization kinetics & solubility of bicarbonate
  - Pure $KHCO_3$ crystal formed from cooling CO_2-rich PC; crystallization time $\leq$40 min is sufficient to obtain large particle sizes (>233 μm)
  - Crystallization of $NaHCO_3$ from K-Na mixture solutions proved feasible

- Task 4: Phase equilibrium & kinetics of high pressure CO_2 stripping
  - VLE measurement revealed thermodynamic feasibility of high-pressure stripping (both high P and low H_2O/CO_2 ratio)

- Task 5: Reclamation of sulfate from SO_2 removal
  - Sulfate reclamation testing provided guidance for developing process concepts for combined SO_2 removal and CO_2 capture

- Task 6: Risk analysis and techno-economic evaluation
  - A multi-stage crystallization configuration proposed to recover heat and address fouling risk
  - A new stripping column design proposed to generate both high stripping P and lean solution

Task 2: Studies of CO_2 Absorption Kinetics: Stirred Tank Reactor (STR) Testing

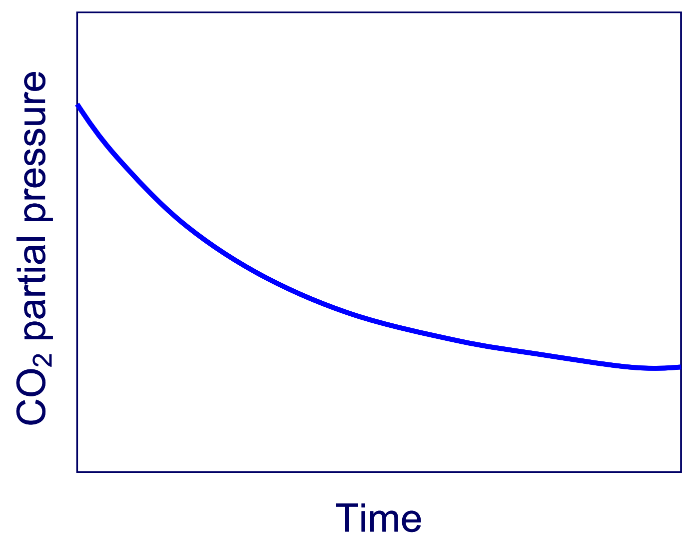


(PrC: Pressure controller; TC: Thermal couple; PG: pressure gauge DAQ: Data acquisition)

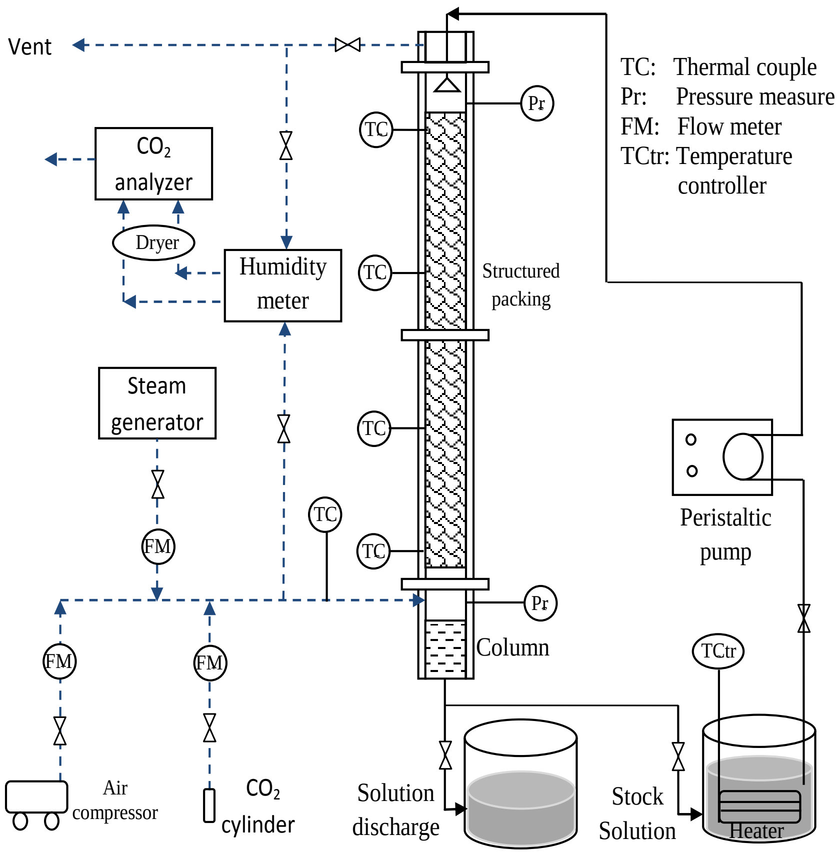
- Instant flux of CO_2 absorption

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

- STR used for kinetic screening of 3 inorganic and 8 organic promoters

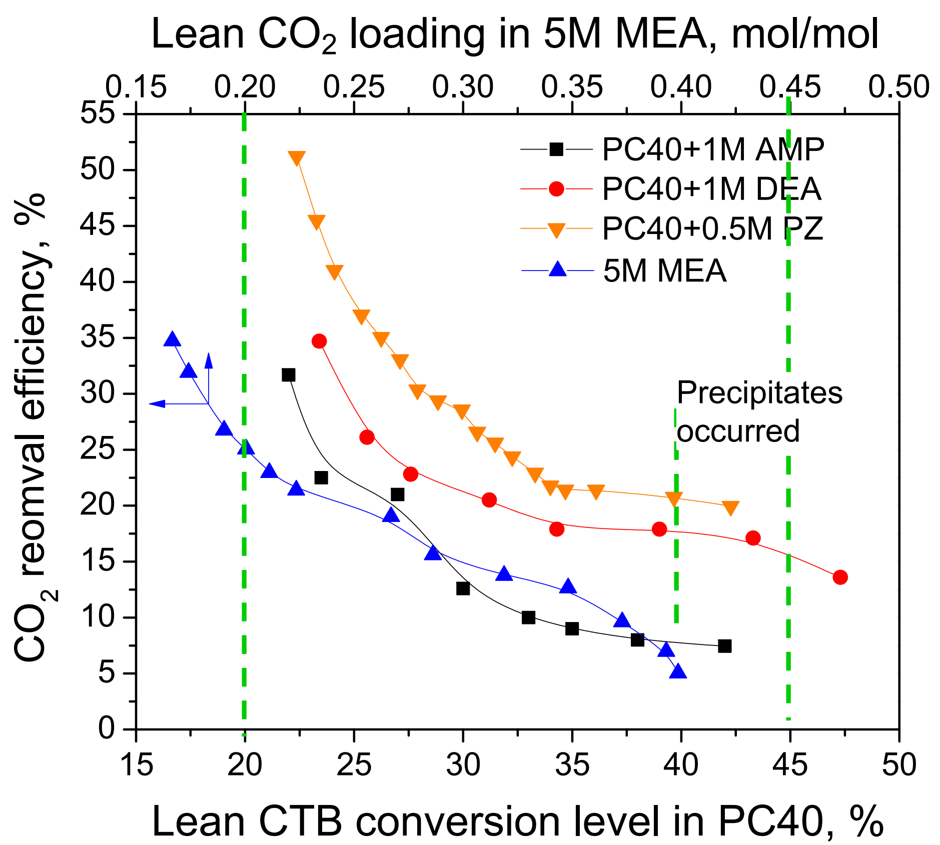


CO_2 Absorption Column Testing



	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

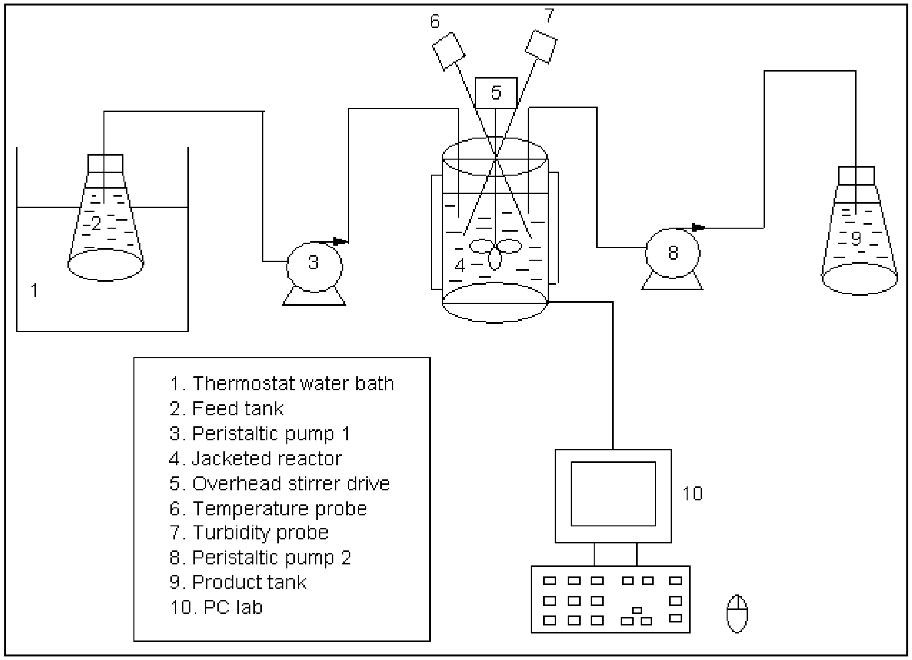
Performance Comparison bw. 40wt% PC and 5M MEA Revealed Risk A (Insufficient Rate into PC) Could Be Addressed



(70ºC absorption in PC40 and 50ºC in 5M MEA; inlet CO_2 =14 vol%, L/G=4.7 lb/lb)
(30% CO_2 removal efficiency equivalent to ~11% increase in CTB thru the column)

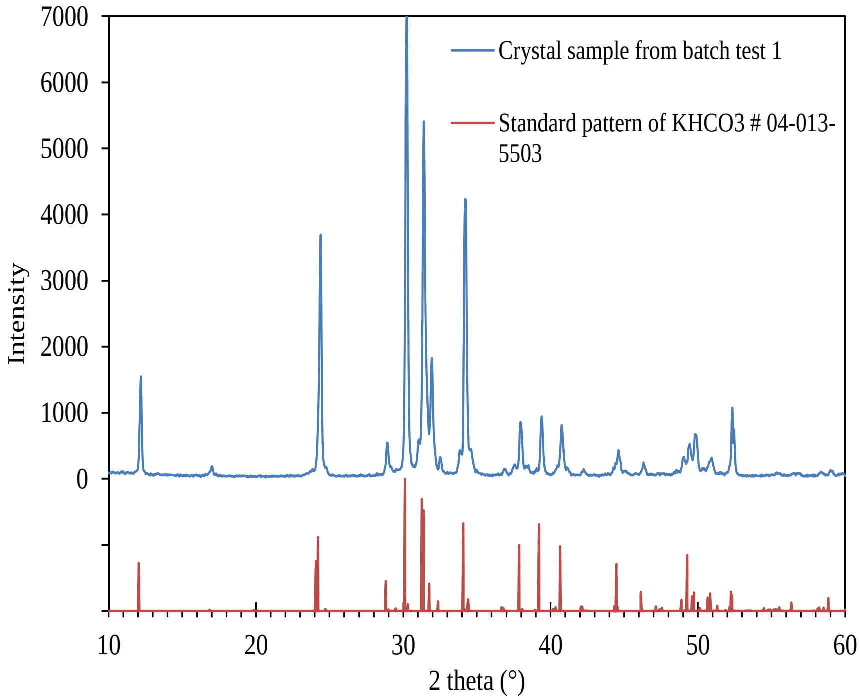
- CO_2 removal efficiency by PC40+1M DEA or 0.5M PZ at 70°C > 5M MEA at 50°C
- Without a promoter, CO_2 removal efficiency by PC was insignificant

Task 3: Studies of Bicarbonate Crystallization: Mixed Suspension-Mixed Product Removal (MSMPR) Reactor

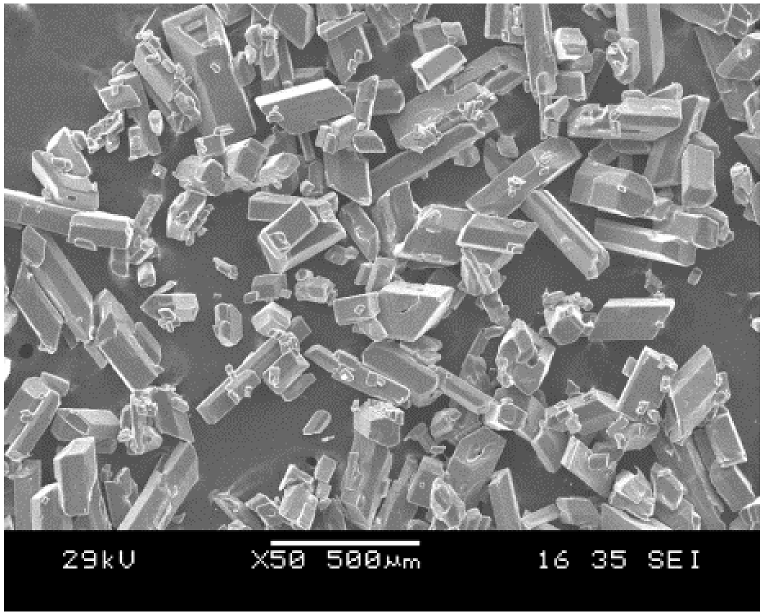


- 1-liter calorimetric CSTR (Syrris Atlas), temperature range of -20-140°C
- Operation precisely controlled by Altas software
- Two peristaltic pumps (feed and discharge)
- Sampling at steady state, filtered for crystal size distribution (CSD) analysis (Horiba)

Morphology and Composition of Crystal Particles



XRD pattern of a typical kalicinite ($KHCO_3$) sample



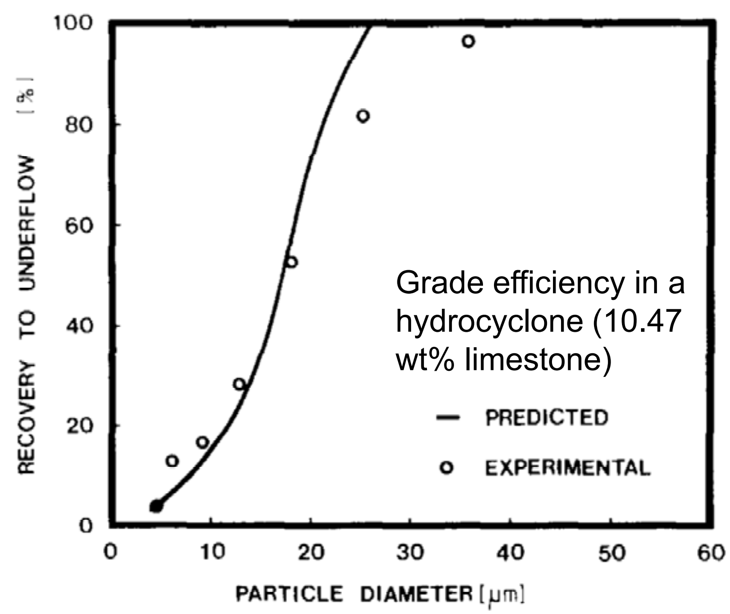
SEM image of $KHCO_3$ crystal (end T=45°C)

- High purity kalicinite ($KHCO_3$) prevailed in crystal particles
- Prism-shaped (hexagonal) morphology dominated
- Yield of $KHCO_3$ crystal consistent to its solubility at crystallization T (eg.~50% of $KHCO_3$ crystallized from PC40-40 at 35°C)

Indications from Parametric MSMPR Tests

- Crystallization process affected by agitation rate, mean residence time (MRT) and T-dependent supersaturation level (TSL)
  - High TSL, mild agitation and long MRT favored larger crystals
  - High TSL, mild agitation and short MRT favored fast crystal growth
  - Low TSL, vigorous agitation and short MRT favored nucleation

- Mean particle size of $KHCO_3$ crystal ranged between 233 and 455 μm (residence time=15, 30, 45min, T=55,45,35°C)
  - Crystal size large enough for conventional liquid-solid separation
  - Crystallization time ≤ 45 min is sufficient

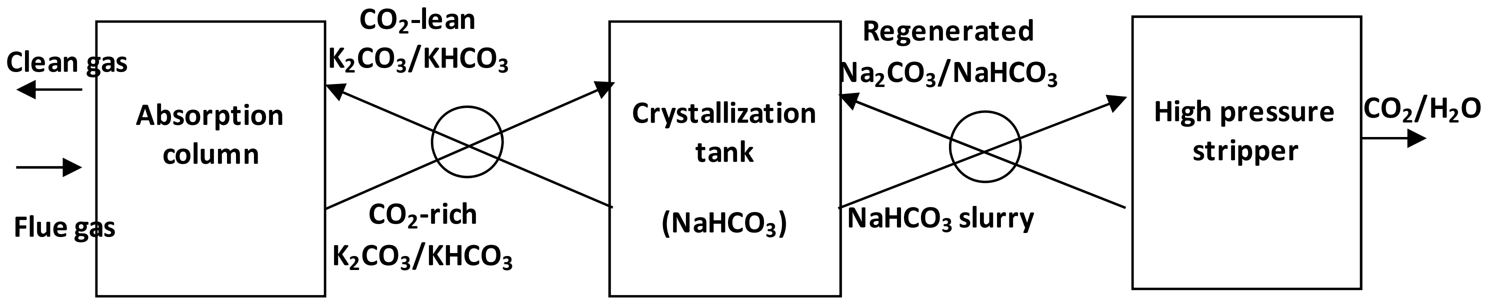


Source: Monredon et al. *Int. J. of Mineral Process. 1992,* 35: 65-83.

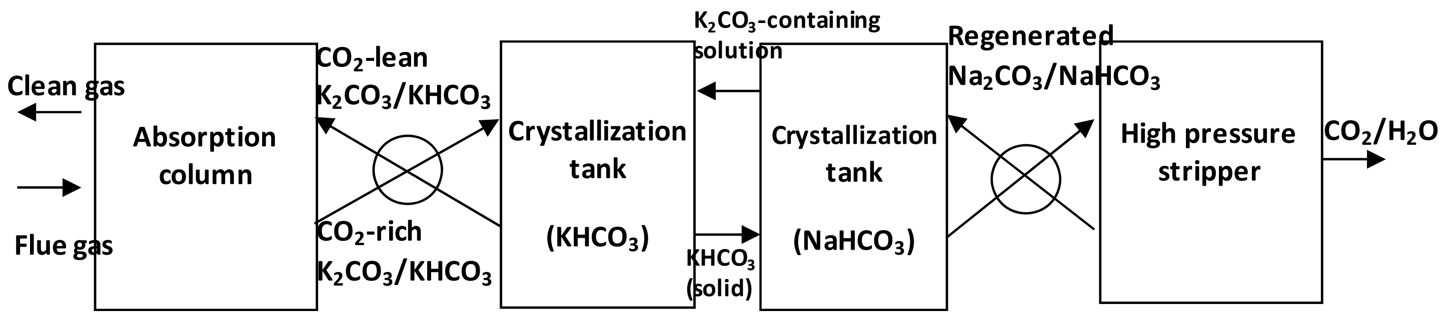
$NaHCO_3$ Crystallization from $K_2CO_3/KHCO_3/Na_2CO_3/NaHCO_3$ Mixture Solutions in MSMPR Reactor

- Stripping pressure could be further increased by using $NaHCO_3$ slurry for CO_2 stripping
  - Solubility of $NaHCO_3$ is ~1/3 of $KHCO_3$
  - Equilibrium pressure of CO_2 over $Na_2CO_3/NaHCO_3$ (SC) system is higher

- Two process options proposed

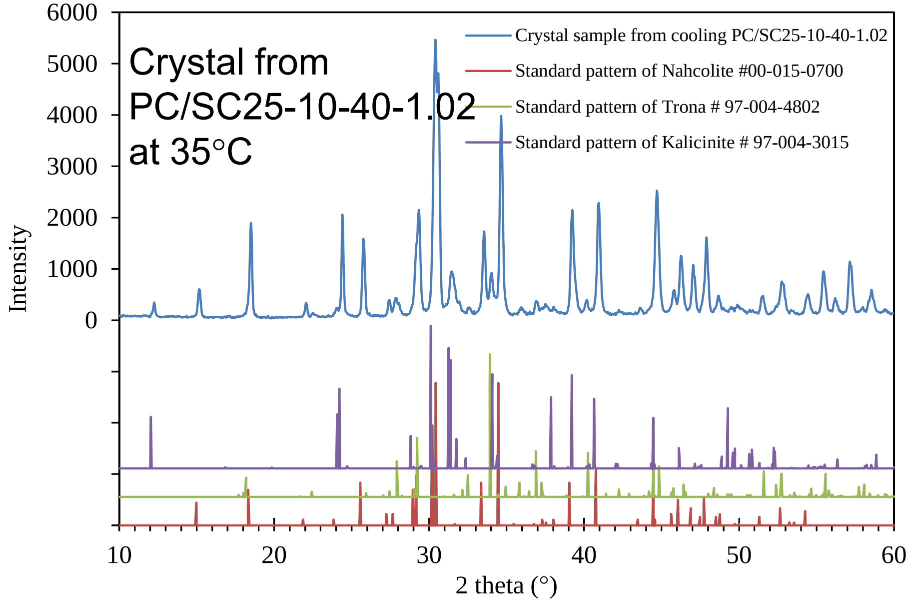


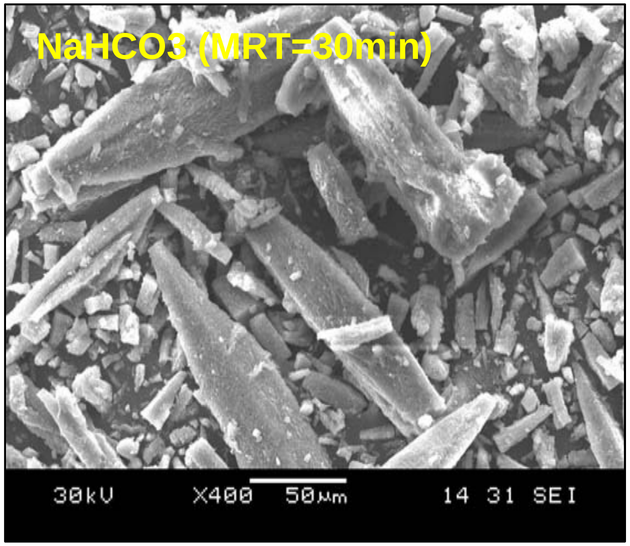
(A) $HCO_3^- + Na^+ = NaHCO_3$ (s)



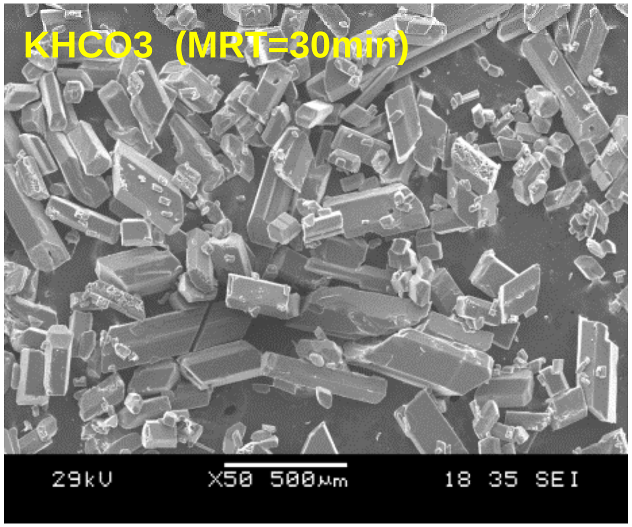
(B) $KHCO_3$ (s) + Na^+ = $NaHCO_3$(s) + K^+

$NaHCO_3$ from Cooling Crystallization of PC/SC Mixture Solutions (Option A)





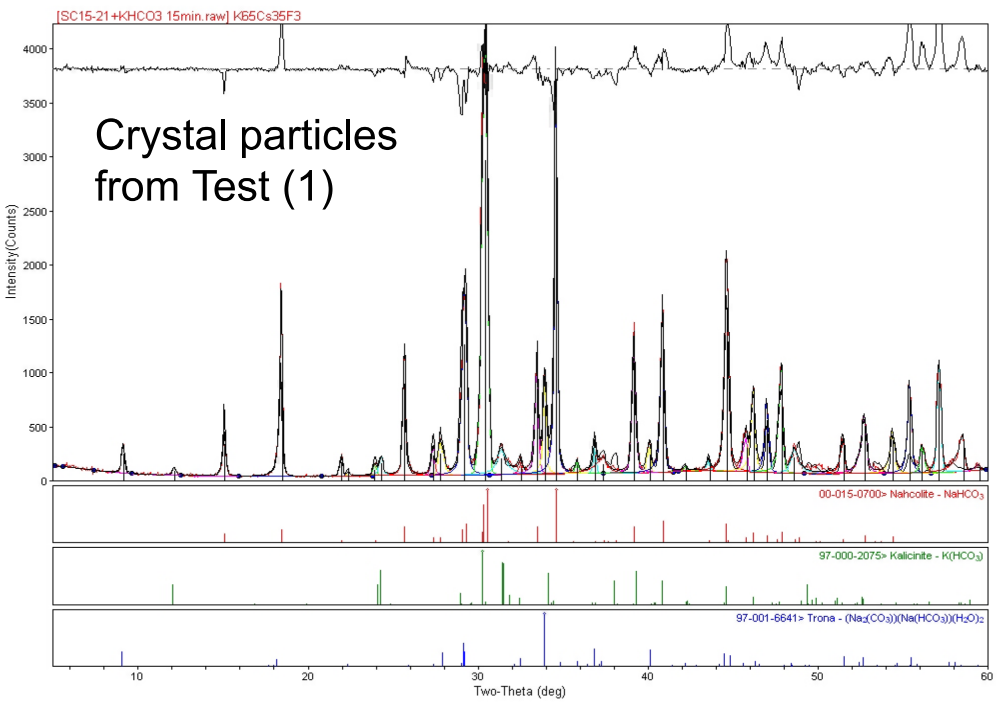
Feed	PC/SC 20-12-40-1.02	PC/SC 25-10-40-1.02			PC/SC 30-5-40-1.02
Crystal phase	Nahcolite	Nahcolite	Trona	Kalicinite	Kalicinite
Composition	100%	85.7%	7.4%	6.9%	100%



- Crystal composition depended on feed solution; Nahcolite ($NaHCO_3$) could be a dominant crystal phase
- Mean size of $NaHCO_3$ crystal particles from PC/SC smaller than $KHCO_3$ from PC

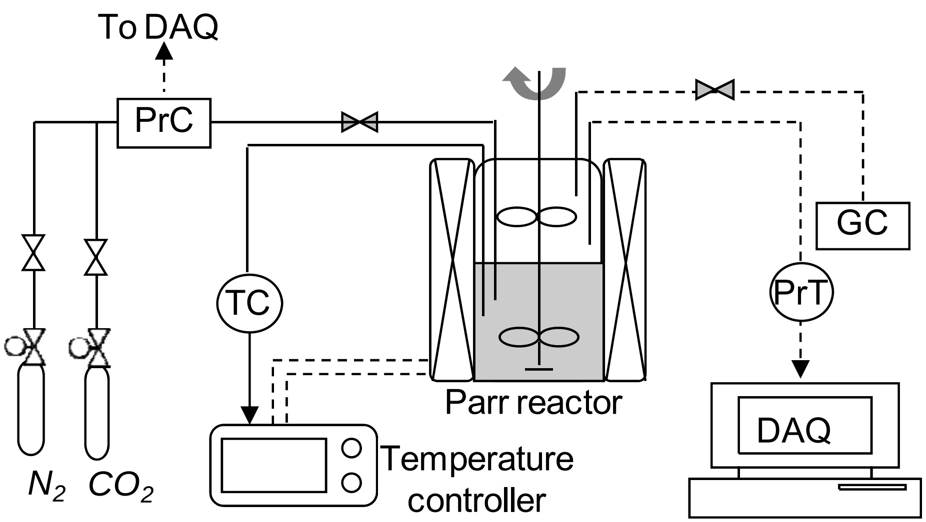
$NaHCO_3$ from Reactive Crystallization between Solid $KHCO_3$ and SC Solutions (Option B)

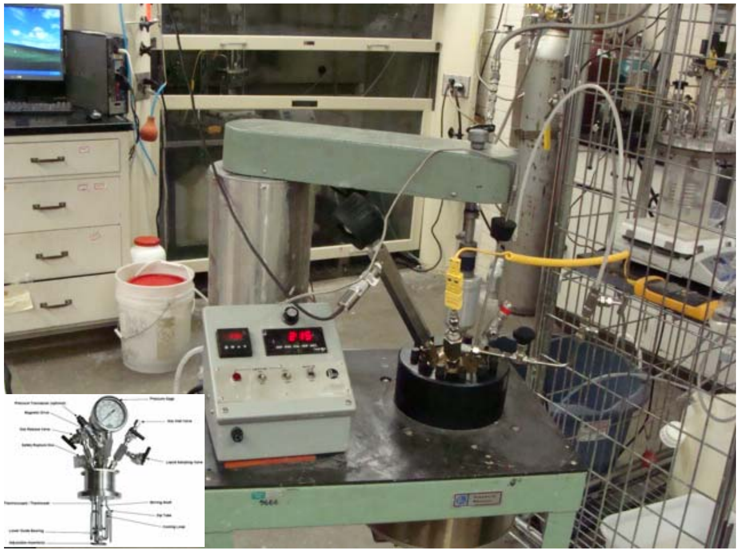
Initial solution	SC 15-21 (1.14 kg/l)		SC 12-30 (1.11 kg/l)	
MRT (min)	15	30	15	30
Crystallization T (ºC)	35	35	35	35
XRD analysis				
Nahcolite	88.8%	81.4%	84.3%	84.7%
Kalicinite	2.2%	3.9%	4.7%	3.1%
Trona	9.0%	14.7%	11.0%	12.2%
Mean particle size (μm)	71.6	105.0	92.9	124.8



- Crystal phases dominated by nahcolite (>81wt%)
- Predicted yield of $NaHCO_3$ crystals comparable to $KHCO_3(s)+Na^+$ reaction stoichiometry

Task 4: Studies of Phase Equilibrium and Kinetics of High Pressure CO_2 Stripping

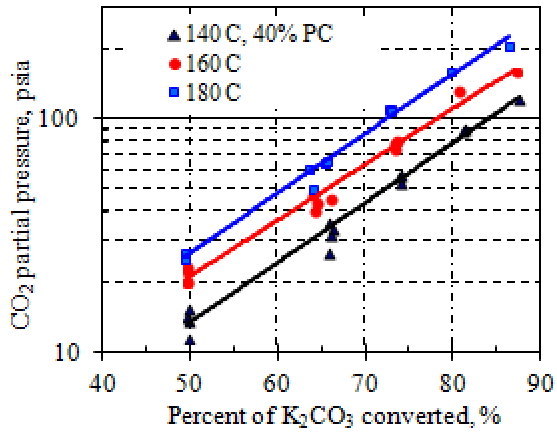


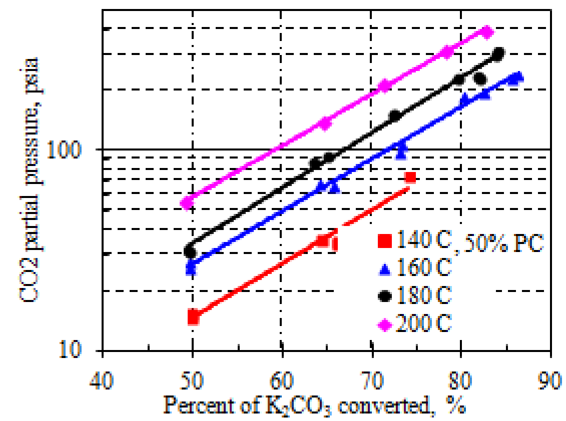


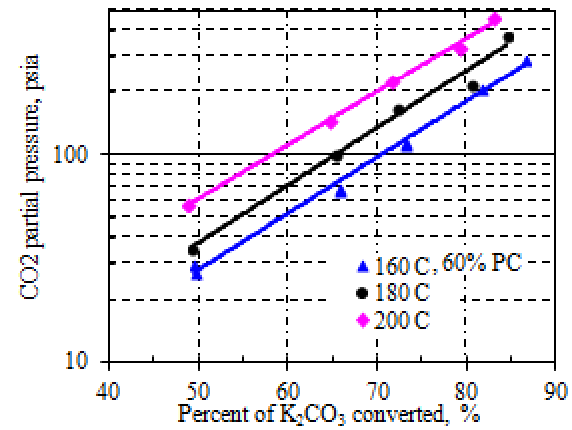
1-liter Parr reactor (model 4531, rated at 1,900 psi and 275°C)

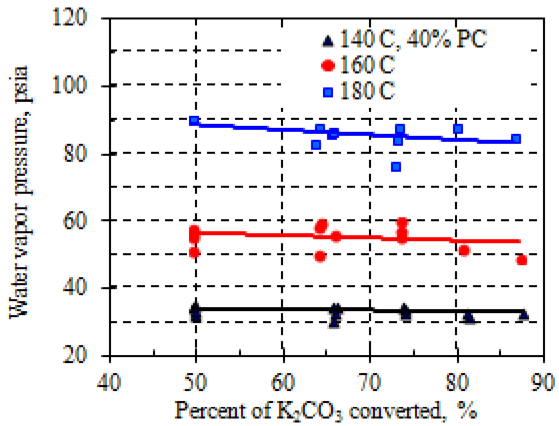
- Gas analysis using a GC-based method
- Liquid analysis using a back-titration method
- 40-70wt% $KHCO_3/K_2CO_3$ slurry at 120-200°C

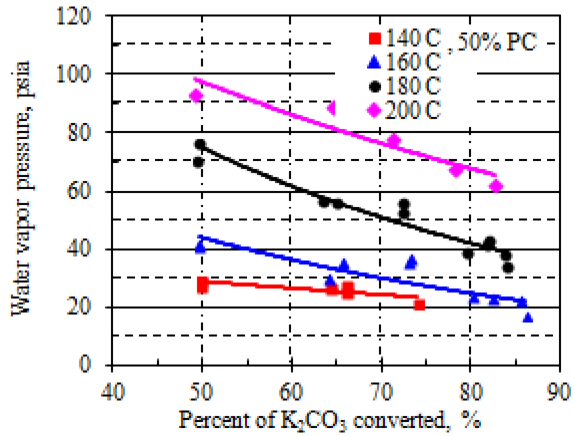
VLE Data for 40, 50, 60wt% PC Solutions at 140-200°C

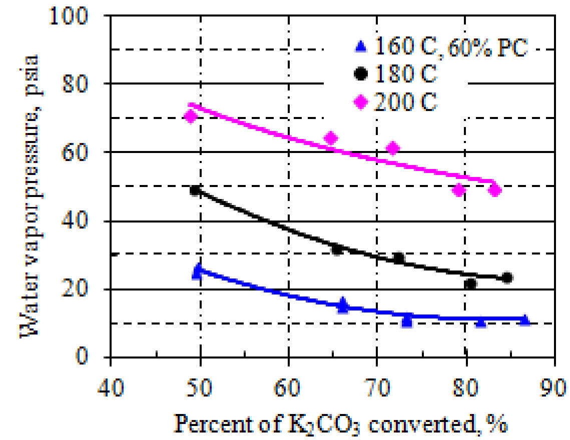












VLE Results Indicated that High Stripping Pressure is Thermodynamically Feasible in Hot-CAP (Risk B)

- A high stripping pressure and a lower water vapor/CO_2 partial pressure ratio can result in a significant reduction in stripping heat (water vaporization) during CO_2 stripping and compression work

- VLE data confirmed feasibility of high pressure CO_2 stripping in Hot-CAP

  - Total P and water vapor/CO_2 ratio reached 31 bar and 0.16:1 for 50wt%(K_2CO_3-equivalent) PC of 85% CTB conversion at 200°C, and 34 bar and 0.11:1 for 60 wt% PC

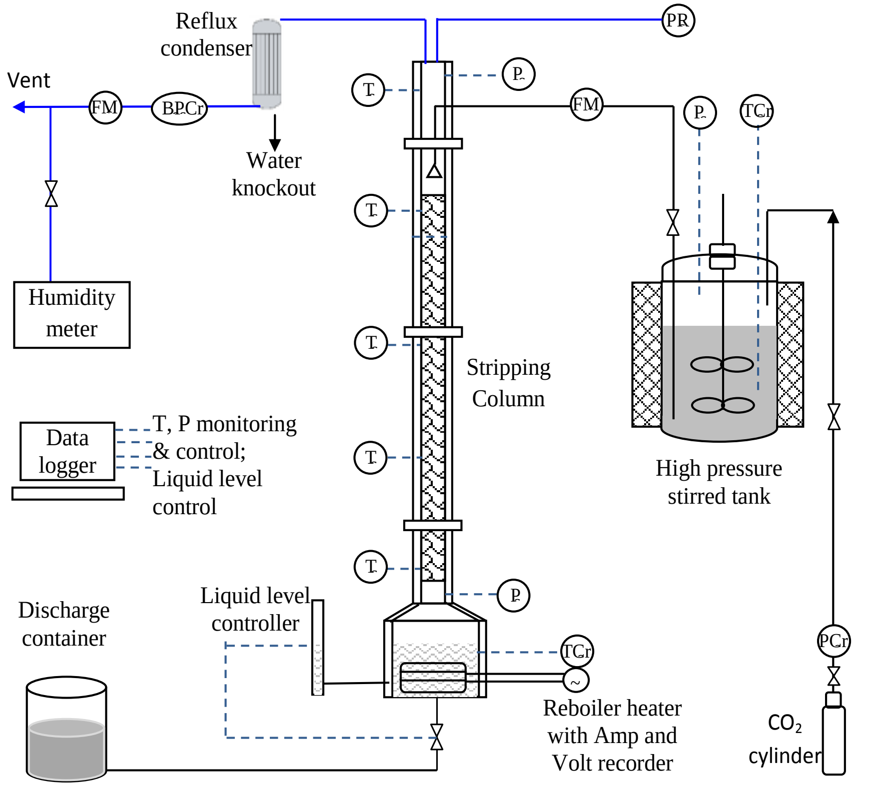
- Higher stripping T, higher CTB conversion, and higher PC concentration led to higher stripping P and lower water vapor/CO_2 ratio

  - P_{CO2} increased substantially with increasing CTB conversion and T

  - P_{H2O} decreased with decreasing T and increasing CTB conversion (especially at PC concentration ≥50 wt%)

  - 50 or 60wt% PC could generate sufficiently high stripping pressures at elevated temperatures

A Bench-Scale High Pressure Stripping Column



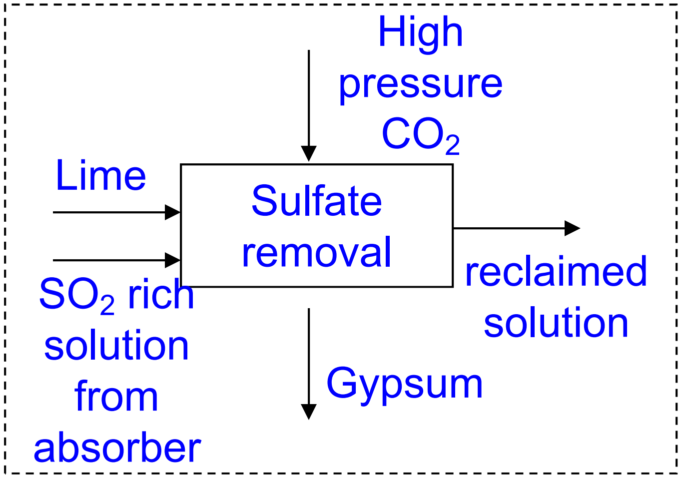
T: Thermal couple;
TCr: Temperature controller;
BPCr: back pressure controller
P: Pressure transducer;
PR: pressure rupture disk;
FM: Flow meter
PCr: pressure regulator;

- Stripping column of 7 ft high x 1 inch diameter
- 15-gal liquid supply tank with heater and T/P control
- Designed after considering Risk E
- Both rated at 200 °C and 500 psia (34bar)
- Shake-down tests in progress, and stripping testing continues in BP3

Task 5: Reclamation of Sulfate for SO_2 Removal in Hot-CAP

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 reactions

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

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

(Solubility values differ by 4 orders of magnitude)

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

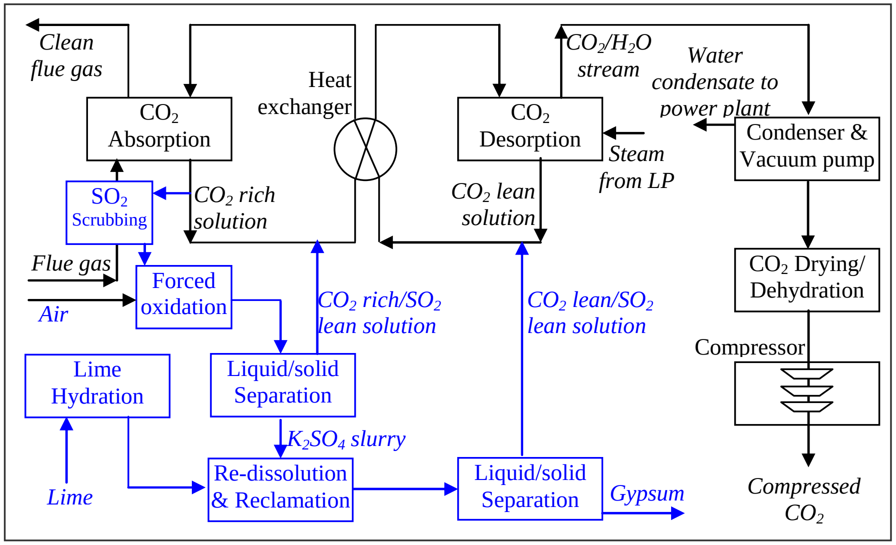
$$CO_3^{2-} + CO_2 + H_2O = 2HCO_3^-$$

Results of Semi-Continuous Reclamation Tests

Group	Experiments	Temp. (°C)	Flow mode	Reaction time	Product composition
I. Effect of temperature	PC0.2M-100-0.4M K_2SO_4+ 0.2M Ca^{2+}	70	Batch	1 hr	100% $CaCO_3$
	PC0.2M-100-0.4M K_2SO_4+ 0.2M Ca^{2+}	50	Batch	1 hr	100% $CaCO_3$
II. Effect of CO_2 flow mode	PC0.2M-100-0.4 M K_2SO_4+ 0.2M Ca^{2+}	25	Batch	1 hr	1.5% gypsum + 42.3% syngenite
	PC0.2M-100-0.4 M K_2SO_4+ 0.2M Ca^{2+}	25	Bubbling	1 hr	8.6% gypsum +91.4% syngenite
III. Effect of initial PC concentration	PC1.2M-100-0.4 M K_2SO_4+ 0.4M Ca^{2+}	25	Bubbling	1 hr	100% calcite
	PC0.4M-100-0.4 M K_2SO_4+ 0.4M Ca^{2+}	25	Bubbling	1 hr	3.3% gypsum +9.9% syngenite +54.6% vaterite +32.3% calcite
IV. Effect of reaction time at 0.2M PC	PC0.2M-100-0.4 M K_2SO_4+ 0.2M Ca^{2+}	25	Bubbling	40 min	58.0% gypsum +10.9% syngenite +31.2% vaterite
	PC0.2M-100-0.4 M K_2SO_4+ 0.2M Ca^{2+}	25	Bubbling	20 min	14.7% gypsum +28.6% syngenite +56.7% vaterite
V. Effect of reaction time at 0.4M PC	PC0.4M-100-0.4 M K_2SO_4+ 0.4 M Ca^{2+}	25	Bubbling	6 hr	5.1% gypsum +28.3% syngenite +57.3% vaterite +9.3% calcite

- Competitive precipitation of $CaSO_4$ over $CaCO_3$ favored at lower temperature
- Increasing SO_4^{2-}/CO_3^{2-} increased formation of syngenite and gypsum
- Increasing reaction time and gas mixing increased yield of syngenite and gypsum
- Composition of precipitates might be controlled by kinetics of $CaCO_3$ conversion into $Ca(HCO_3)_2$ in high pressure CO_2: $CaCO_3+CO_2+H_2O = Ca(HCO_3)_2$

A Modified Process Option for K_2SO_4 Reclamation



Solubility of pure chemicals in water, g/100 water:

	20ºC	30ºC	40ºC	60ºC	70ºC	80ºC
Potassium carbonate (K_2CO_3)	111	114	117	127	-	140
Potassium bicarbonate ($KHCO_3$)	33.7	39.9	47.5	65.6	-	-
Potassium sulfate (K_2SO_4)	11.1	13	14.8	18.2	-	21.4
Potassium sulfite (K_2SO_3)	>100	-	-	-	-	-
$KHSO_4$	49	-	-	-	-	-
$KHSO_3$	-	-	-	-	-	-

Major reactions:

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

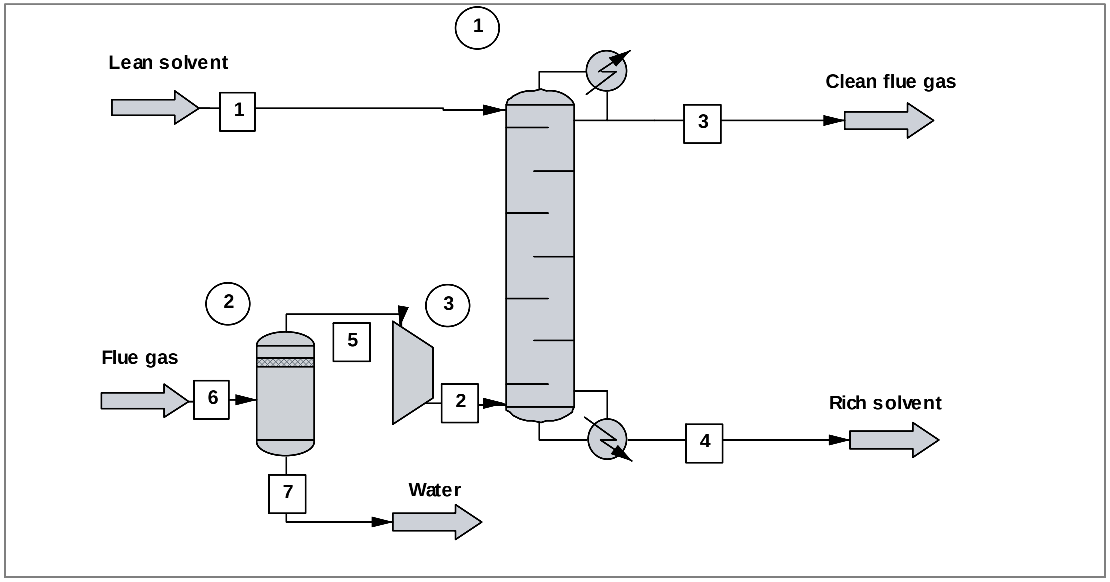
$2KHCO_3 + SO_2 + H_2O \rightarrow K_2SO_3 + 2H_2CO_3$

Oxidation: $K_2SO_3 + \frac{1}{2} O_2 \rightarrow K_2SO_4\downarrow$

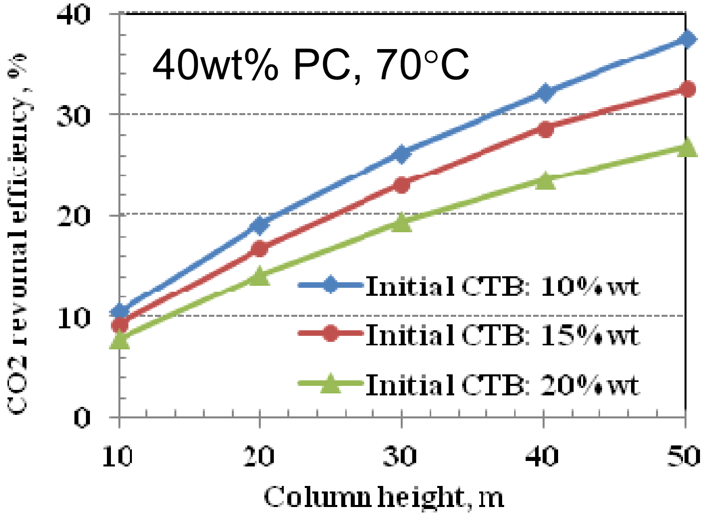
Reclamation: $K_2SO_4 + Ca(OH)_2 \rightarrow 2KOH + K_2SO_4\downarrow$

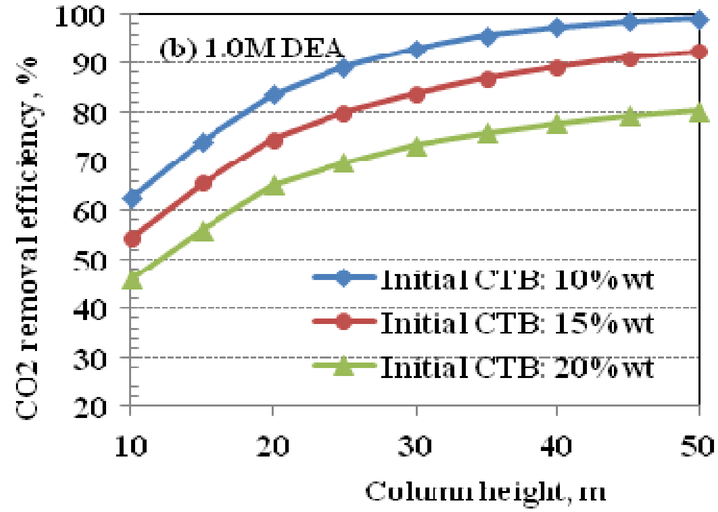
Task 6: Technical Risks Mitigation Analysis and Process Simulation Studies

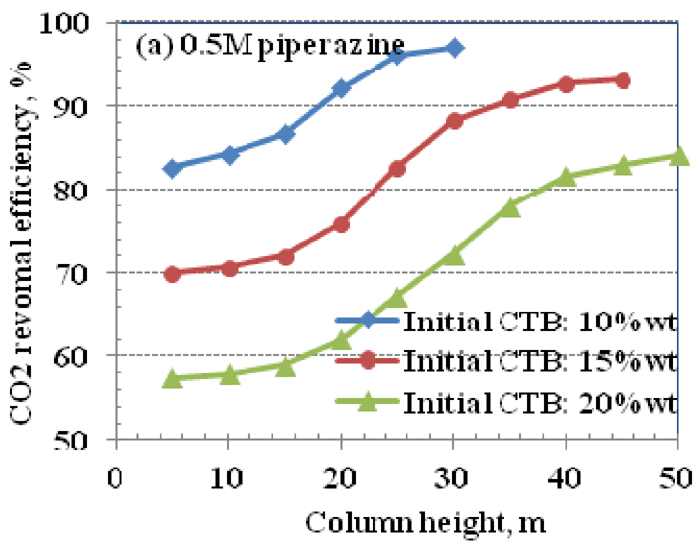
- ChemCad software used for equilibrium-based process simulation
- ProTreat software used for rate-based simulation
- Flue gas conditions referred to a 550 MWe sub-critical power plant in Case 10 of a DOE/NETL study

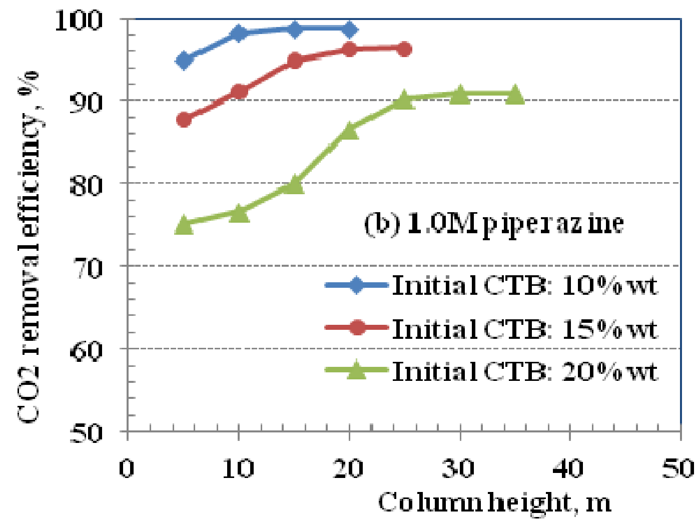


Risk A: System Simulation of CO_2 Absorption in PC w/ and w/o Promoters







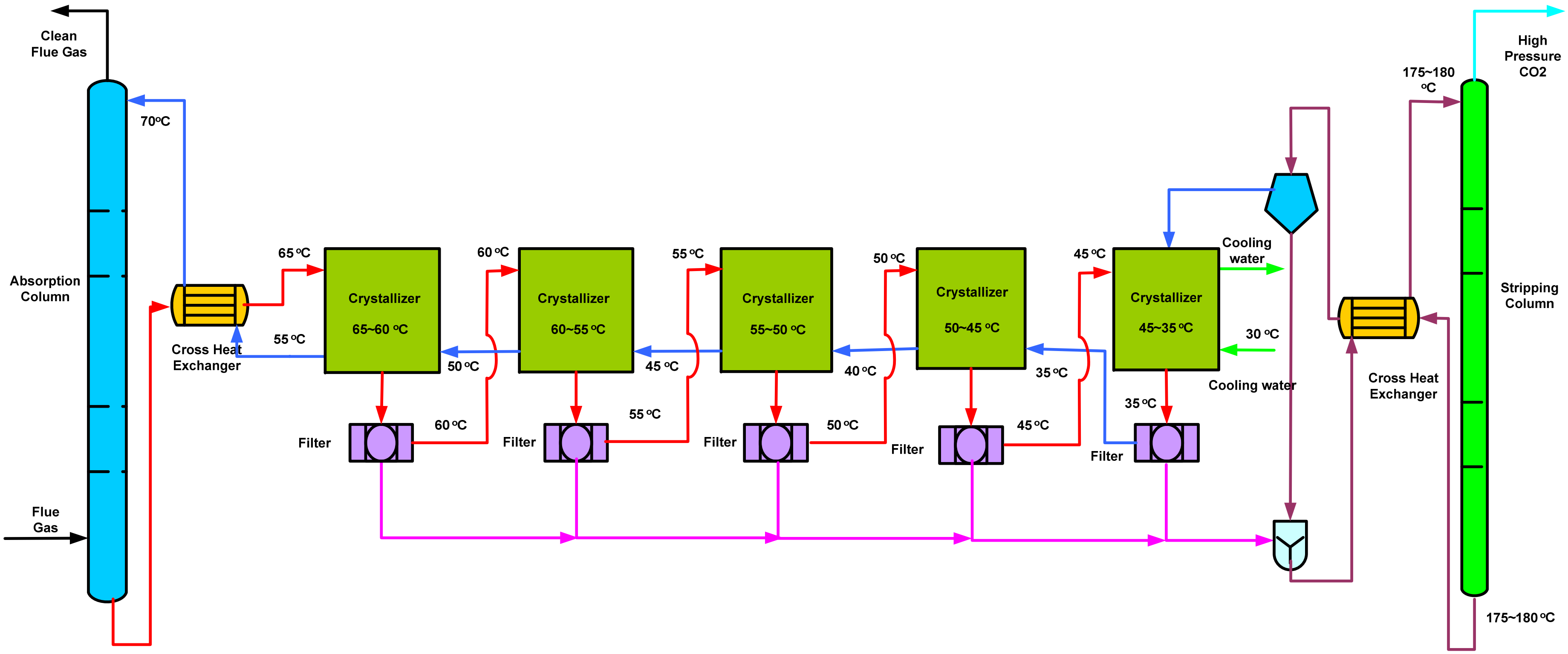


- CO_2 removal efficiency greatly increased by addition of DEA or PZ promoter, consistent to experimental findings

Risk C: Reducing Scaling / Fouling

- Addressed in BP1 by vendor discussions
- Various engineering solutions to prevent $KHCO_3$ fouling
  - Reducing the temperature difference in the cross heat exchanger
  - Pre-seeding of the crystallization solution
  - Using plate and frame type of heat exchangers
  - Using a vacuum cooling crystallizer or a surface cooling crystallizer that is equipped with scrappers
  - Adding an extra heat exchanger

Risks D: Addressing Heat Recovery



- Addressed in BP1 through vendor discussions
- Conventional single-crystallizer design requires a large ΔT between inflow and outflow, undesirable for heat recovery from inflow solution
- Multiple crystallization tanks/modules developed with a crystallizer vendor to reduce ΔT to ~ 5°C

Risk E: Considerations of Stripping Column Design

- Technical challenges
  - Conventional stripping processes required high bicarbonate content (high CO_2 loading) in the stripper lean solution to attain high stripping pressure
  - High bicarbonate content in the stripper lean solution leads to re-crystallization risk in cooling process
  - High bicarbonate content in the stripper lean solution leads to low CO_2 working capacity

- An innovative stripping column design has been proposed to address such challenges

THANK YOU ALL!

Additional Slides

Potential Advantages of Hot-CAP

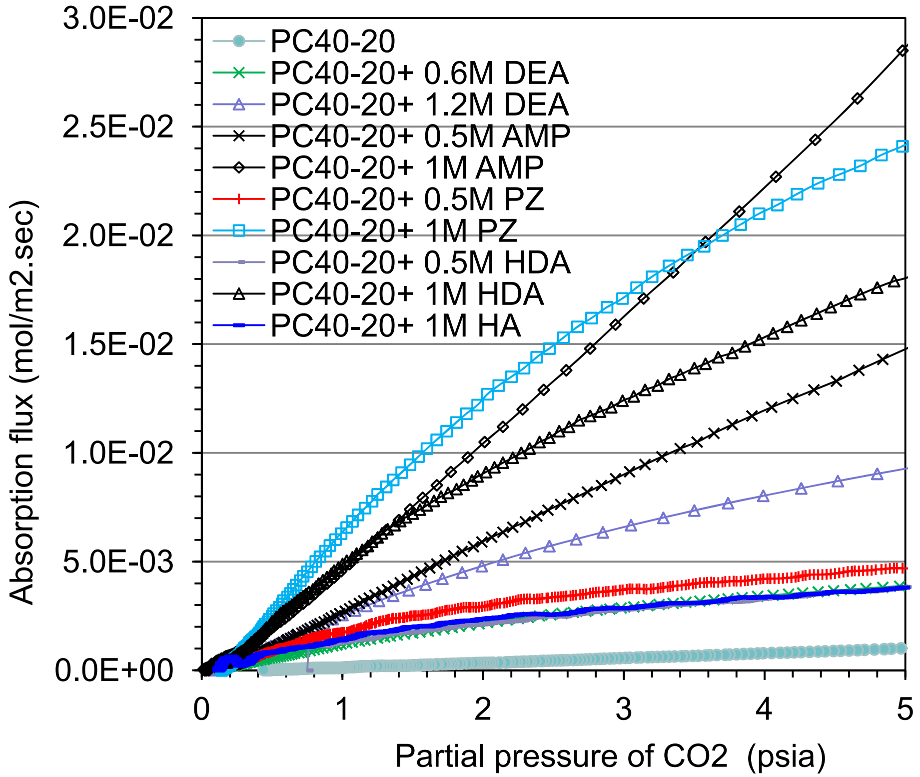
- High stripping pressure
  - low compression work
  - low stripping heat (high CO_2/H_2O ratio)
- Low sensible heat
  - Higher working capacity to MEA
  - Low Cp (1/2)
- Low heat of absorption
  - 7-17 kcal/mol CO_2 (crystallization heat incld.) vs. 21 kcal/mol for MEA
- No solvent degradation and less corrosiveness
- Low solvent cost
- FGD may be eliminated

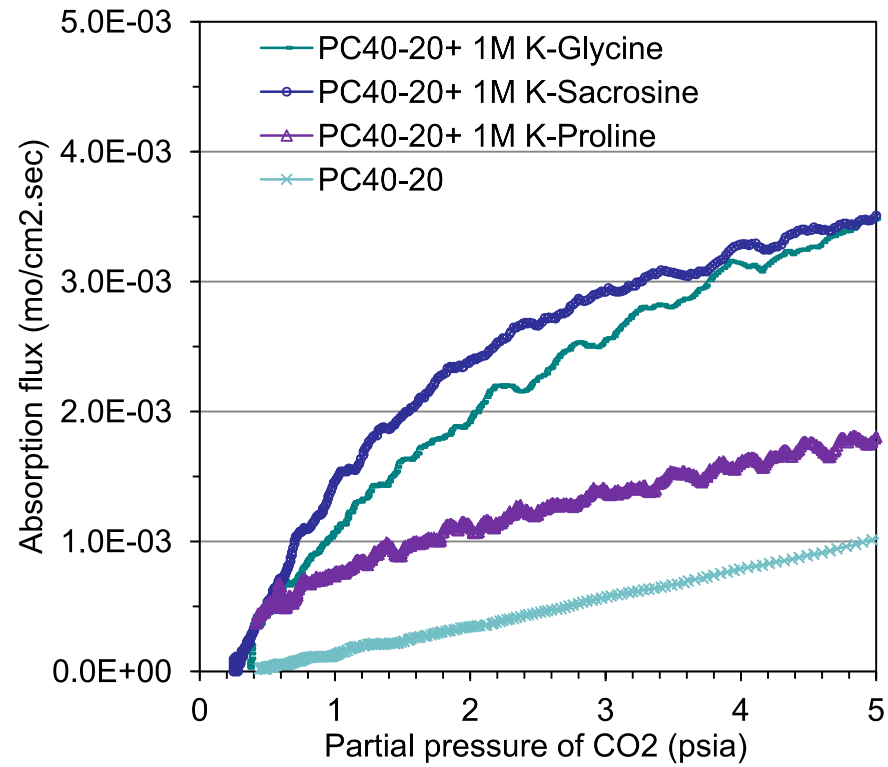
Energy Use Analysis of Hot-CAP

Items	MEA	Hot-CAP
Energy Consumption		
CO_2 desorption		
Heat of absorption (kJ/kgCO_2)	1,870	1,600
Sensible heat (kJ/kgCO_2)	990	300
Stripping heat (kJ/kgCO_2)	690	200
Electricity equivalent (kWh/ kg CO_2)	0.22	0.13
Compression work (kWh/ kg CO_2)	0.09	0.03
Other load (kWh/ kg CO_2)	0.04	0.04
Total electricity use(kWh/kg CO_2)	0.35	0.20

- A reduction of ~40% electricity losses compared to MEA

Risk A: CO_2 Absorption into 40wt% PC with Organic Promoters

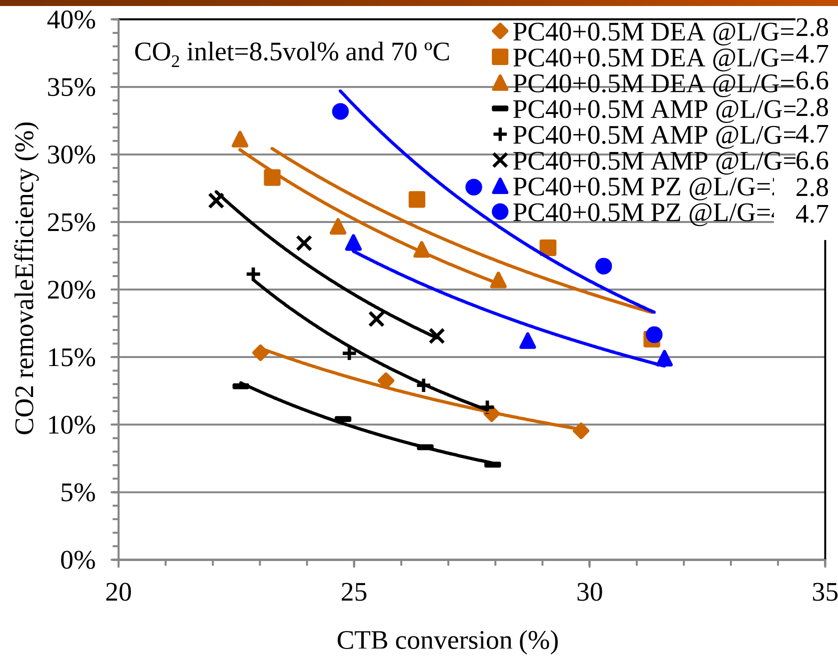


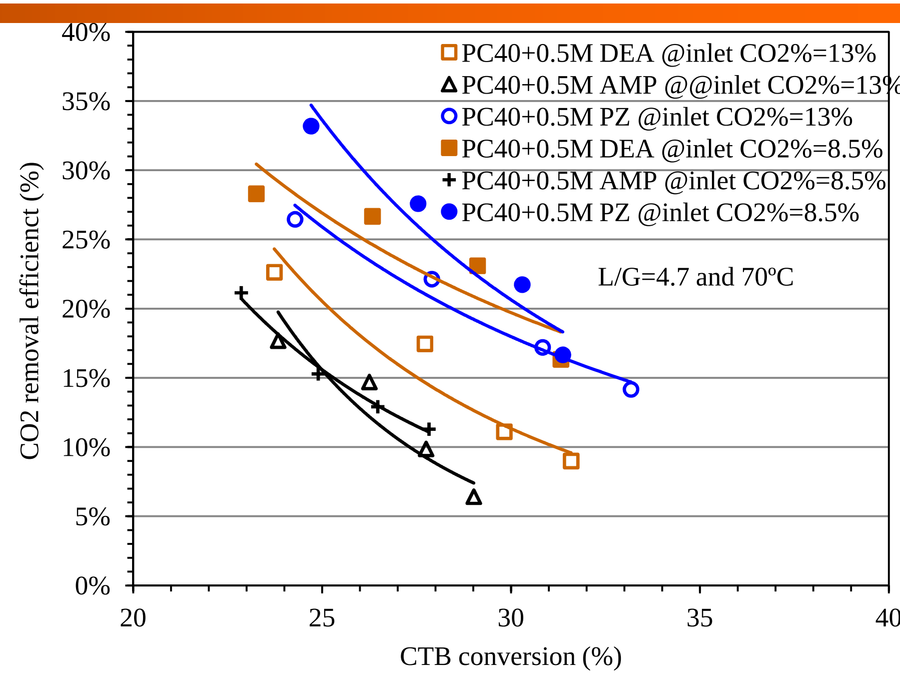


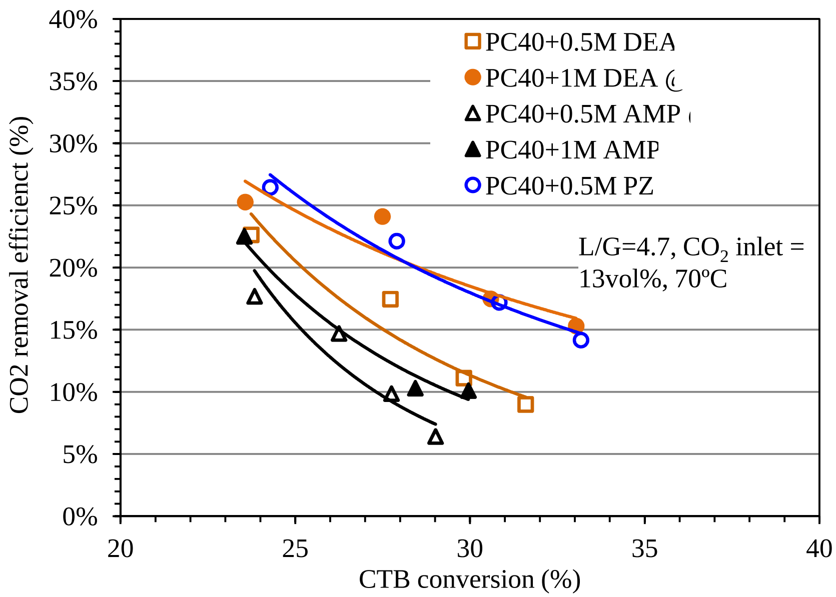
- Rates promoted by amine promoters 3.5-30 times compared to reference PC
- Rates promoted by amino acid salts by 3-11 times
- Rates most effectively promoted with 1M PZ, 1M AMP and 1M HDA

DEA: diethanolamine; AMP: 2-amino-2-methyl-1-propanol; PZ: piperazine; HDA: hexamethylene diamine; HA: hexylamine

Risk A: Parametric Tests of CO_2 Absorption



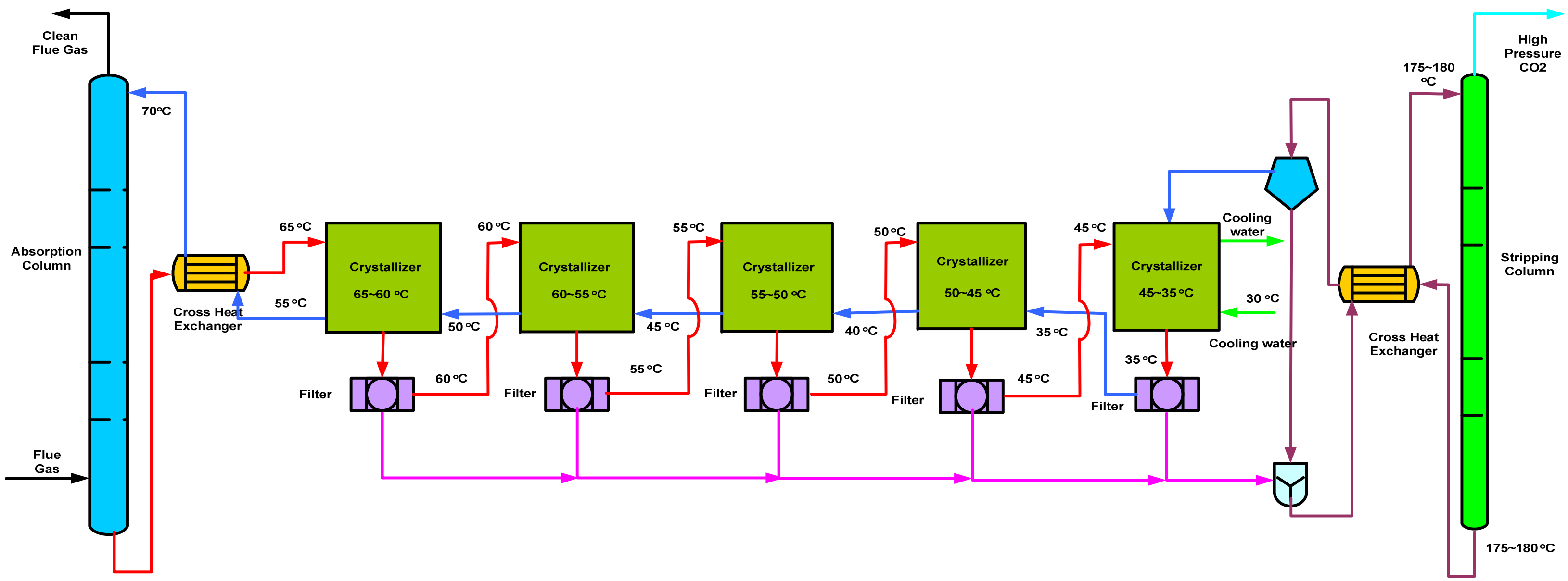




- CO_2 removal efficiency increased with increasing L/G and promoter dosage; decreased with increasing inlet CO_2 concentration and CO_2 loading
- Higher CO_2 removal efficiency attained by PC+PZ than others

Bicarbonate Crystallization Testing in Continuous MSMPR Reactor

- CO_2-rich solution typical of Hot-CAP absorber:
  - Temperature: 70°C
  - Composition: $K_2CO_3/KHCO_3$ (PC40-40)
- Crystallization temperature:
  - 70-55°C → 55-45°C → 45-35°C to simulate a multiple-CSTR crystallization process
  - Kinetic data required for design of CSTR crystallizers



Kinetics of $KHCO_3$ Crystallization

- Kinetic parameters determined based on CSD (q_i) and suspension density (M_T) measured
  - Population density n(L)

    $$n(L_i) = \frac{M_T q_i}{k_v \rho_s \overline{L_i}^3 \Delta L_i}$$

  - Mean crystal size (L)

    $$\overline{L} = \frac{\int_0^\infty n(L) L^4 dL}{\int_0^\infty n(L) L^3 dL}$$

  - Average growth rate G_{av}

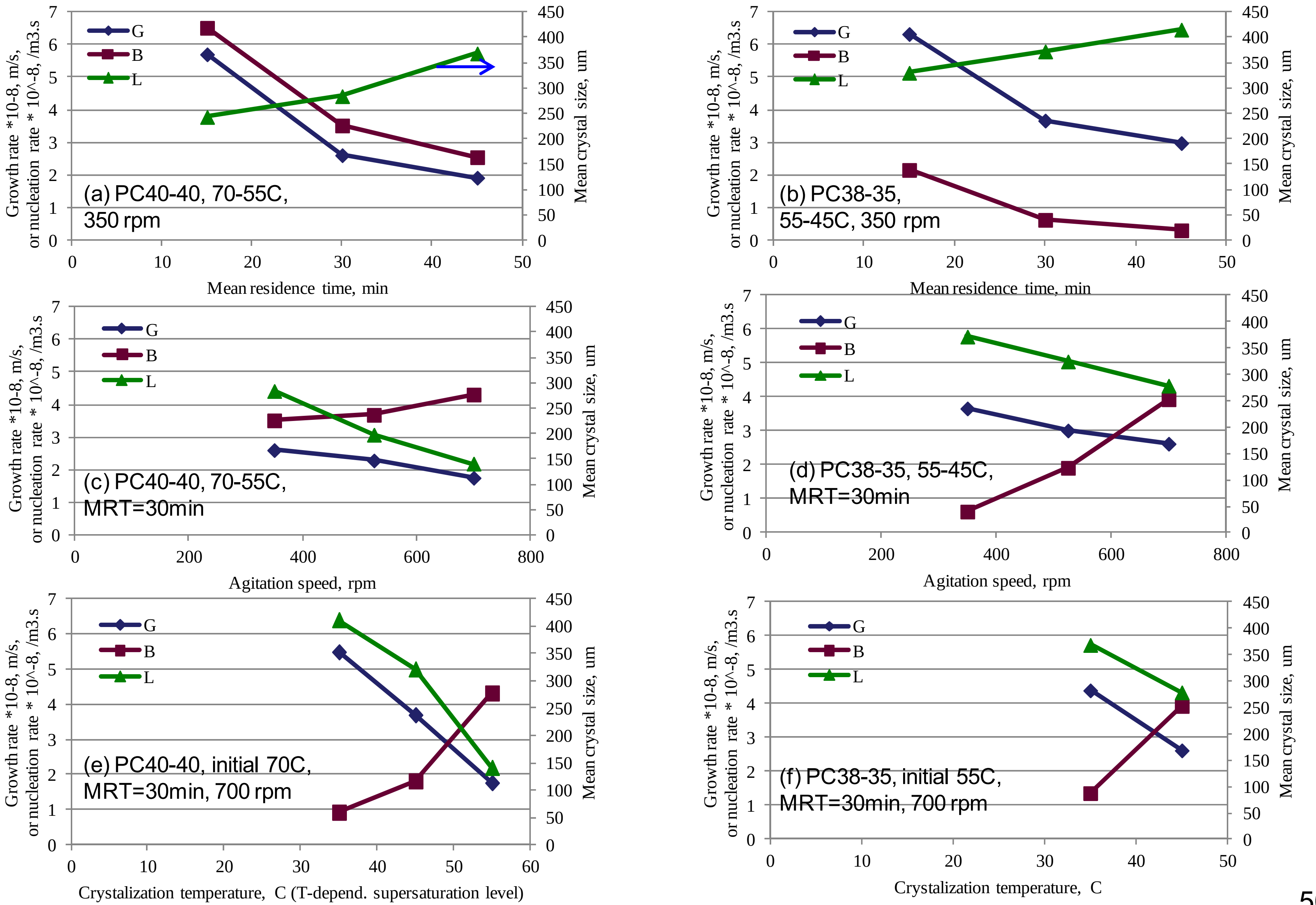
    $$G_{av} = \frac{M_T}{3\rho_s \tau k_v \int_0^\infty n(L) L^2 dL}$$

  - Total nucleation rate B_{TOT}

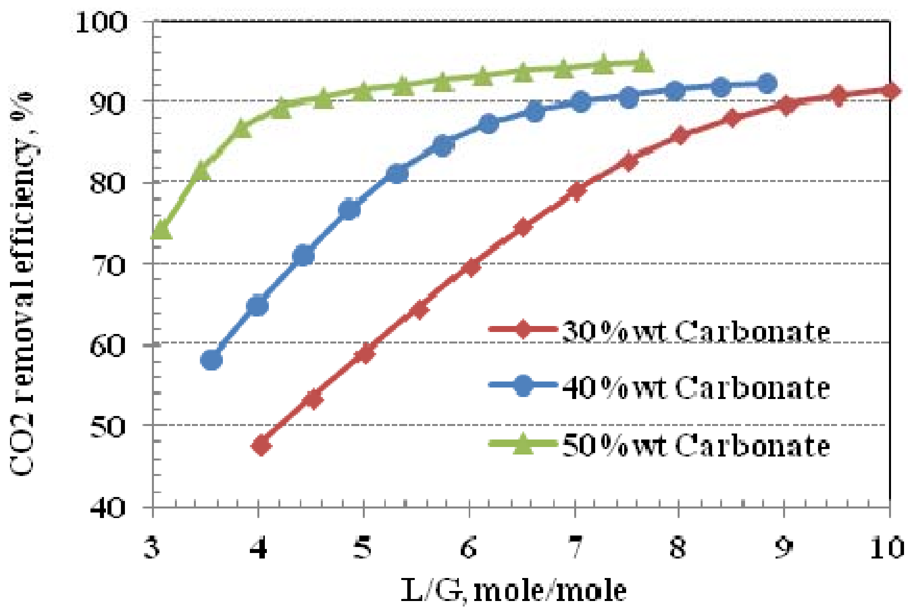
    $$B_{TOT} = \frac{\int_0^\infty n(L) dL}{\tau}$$

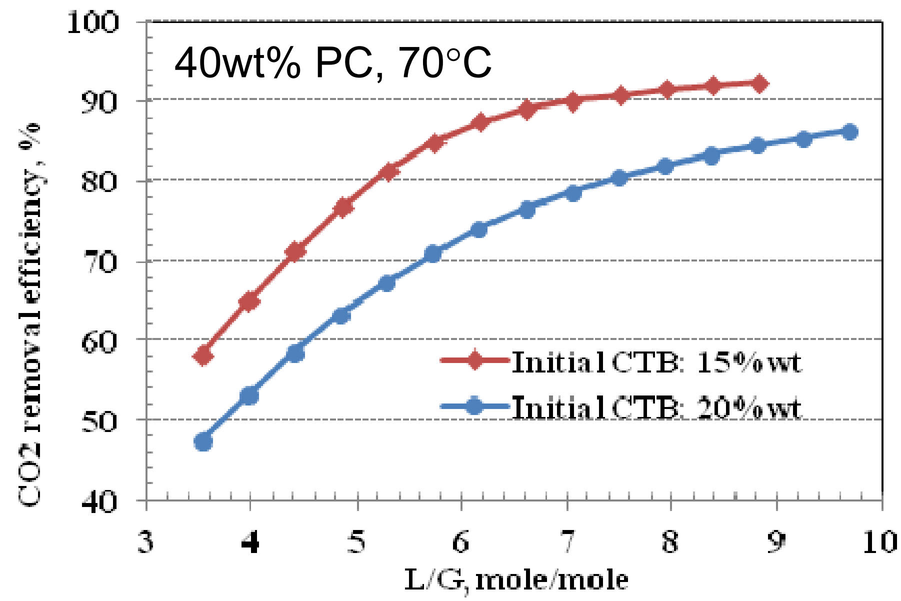
- Size-dependent crystal growth observed
  - Log-n(L) curve not linear with crystal dimension L (for $L \leq L_c$)
  - Growth rate (G) not constant with increasing L (for $L \leq L_c$)

Parametric Tests of $KHCO_3$ Crystallization from PC Solutions



Risk A: Equilibrium-Based Simulation of CO_2 Absorption in PC w/o a Promoter





- A higher PC concentration favored higher CO_2 removal efficiency
- 90% CO_2 removal achieved by 40wt% PC with 15% initial CTB conversion without a promoter at L/G >7