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**)**

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

2013 NETL CO_2 Capture Technology Meeting

Pittsburgh, PA • July 8-11, 2013

Prime Contractor

- Illinois State Geological Survey (ISGS)
  - One of five scientific surveys at Prairie Research Institute, University of Illinois
  - 200 scientists and technical support staff
  - Lead organization of Midwest Geological Sequestration Consortium (MGSC) Partnership
  - ISGS's Applied Research Laboratory conducts carbon capture and other energy & environmental technology researches

Project Overview

Project Team

Illinois State Geological Survey-University of Illinois

- Bench- and lab-scale experimental studies
- Nick Devries, Yongqi Lu (PI), David Ruther, Manoranjan Sahu, Qing Ye, Xinhuai Ye, Shihan Zhang

Carbon Capture Scientific, LLC

- Risk analysis and techno-economic studies
- Scott Chen, Zhiwei Li, Kevin O'Brien (Sub-PI)

DOE/NETL (Funder)

- Project manager - Andrew Jones

Illinois Clean Coal Institute (Co-Funder)

- Project manager – Joseph Hirschi

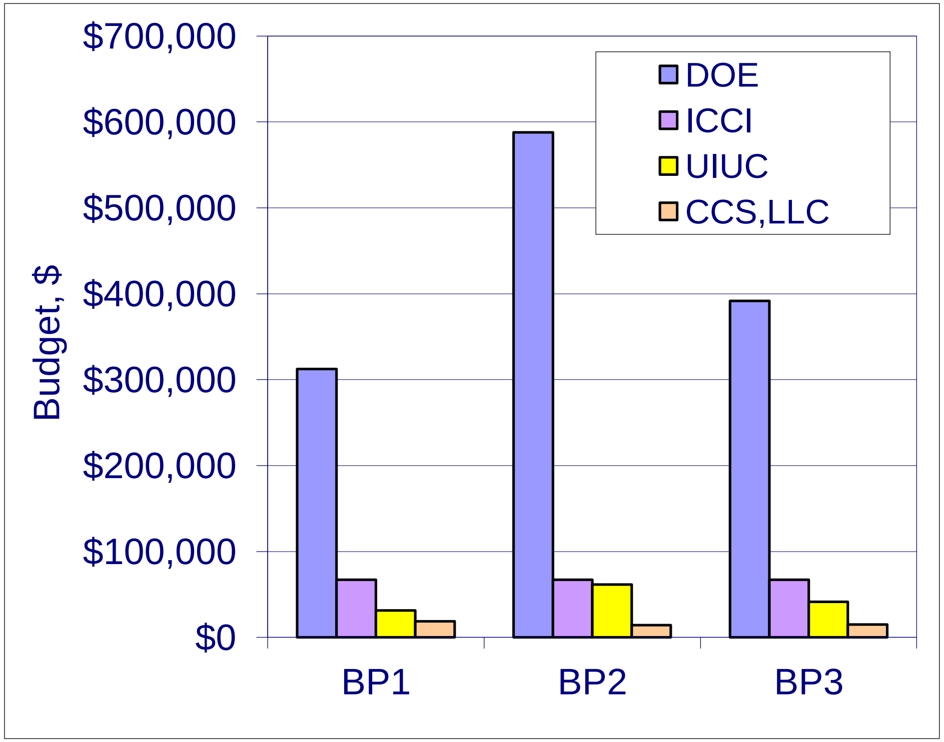
Project Performance Dates and Budget

- Project duration: 39 months
  - BP1: 1/1/11- 12/31/11
  - BP2: 1/1/12 - 3/31/13
  - BP3: 4/1/13 - 3/31/14

- Budget

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

(Cost share: ~23%)

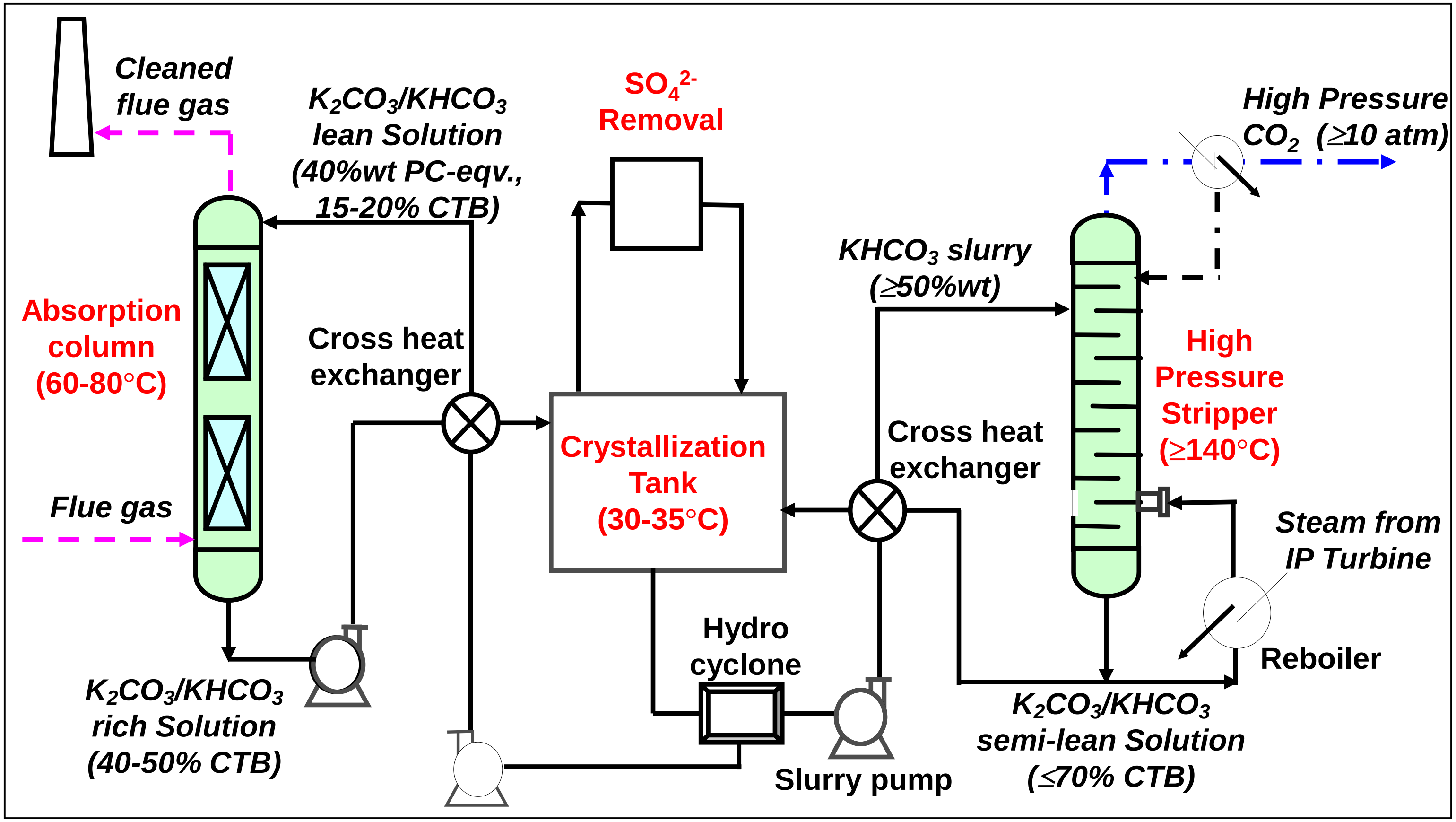


Project Objectives

- Perform a proof-of-concept study aimed at generating process engineering and scale-up data to help advance the proposed CO_2 capture process to a pilot-scale demonstration level upon completion of the project
  - ISGS/UIUC team: Lab- and bench-scale tests to generate thermodynamics and reaction engineering data for major unit operations
  - CCS, LLC team: Technical risk mitigation analysis and techno-economic studies

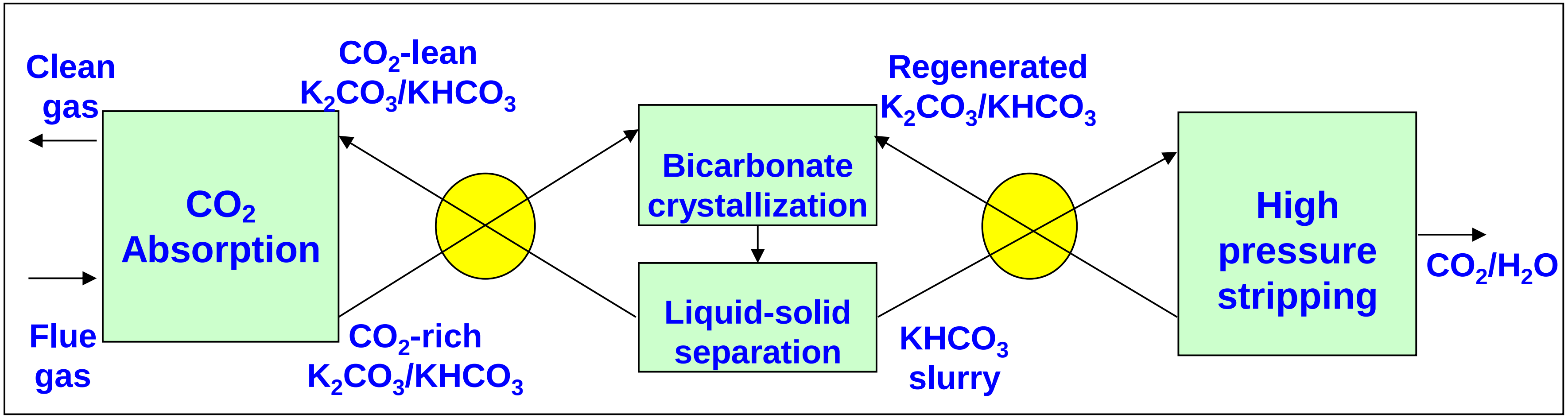
Technology Fundamentals/Background

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



- Absorption into 30-40wt% potassium carbonate (PC) solution at 60−80°C
- Working capacity of PC: 15/20% to 40/50% carbonate-to-bicarbonate (CTB) conv.
- Crystallization at near room temperature (~30°C)
- Stripping of bicarbonate slurry at ≥10 atm

Major Reactions



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

$$CO_2 \text{ desorption at } \geq 130°C:$$
$$KHCO_3 = CO_2(g)\uparrow + H_2O + K_2CO_3$$

$$\text{Crystallization at } 30°C:$$
$$KHCO_3 = KHCO_3(s)\downarrow$$

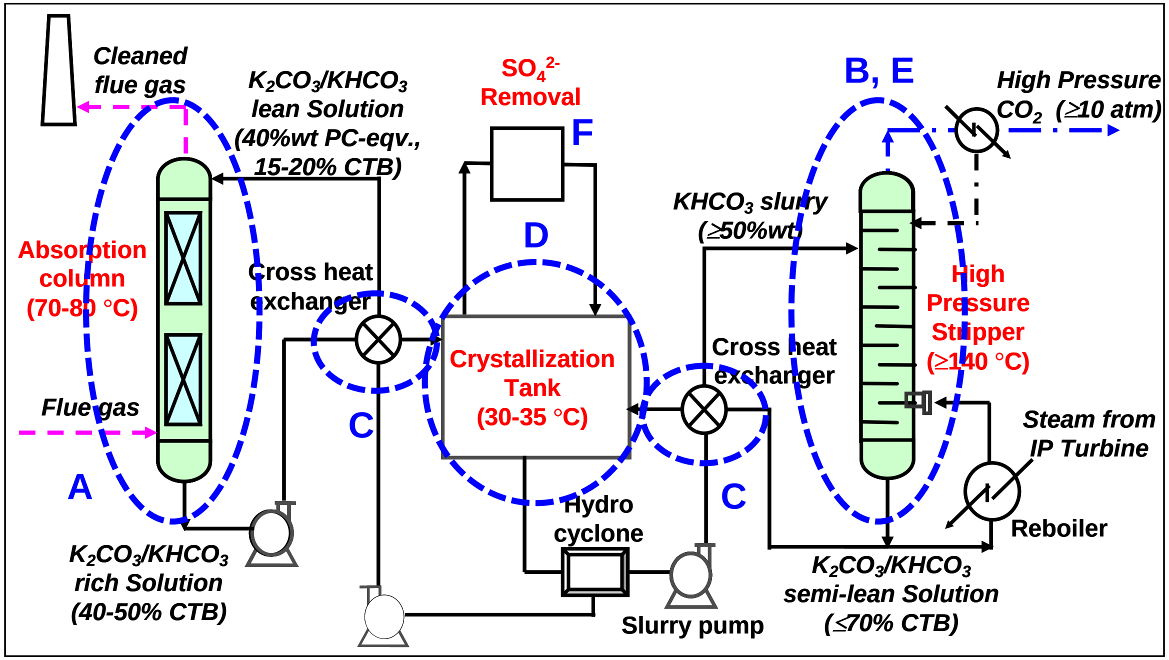
Advantages of Hot-CAP over Conventional MEA

Items	MEA	Hot-CAP
Solvent	30wt% MEA	30-40wt% K_2CO_3
Solvent degradation	Y	N
Corrosion	Y	Less significant
Absorption temperature	40-50°C	60-80°C
Stripping temperature	120°C	130-200°C
Stripping pressure	1.5-2 atm	≥10 atm
Phase change bw absorb. and stripping	N	Crystallization
FGD required	Y	N

- High stripping pressure
  - low compression work
  - low stripping heat (high CO_2/H_2O ratio)
- Low sensible heat
  - Comparable stripping working capacity to MEA
  - Lower Cp (60% of MEA)
- Low heat of absorption
  - 18 kcal/mol CO_2 (crystallization heat included) vs. 21 kcal/mol for MEA

Technical Risks/Challenges to Be Addressed

A. Is overall rate of CO_2 absorption into PC comparable to 5M MEA?
B. Can CO_2 stripping operate at high pressure (e.g. ≥10 bar)?
C. Can fouling risk due to bicarbonate precipitation on surfaces of heat exchangers and crystallizer coolers be prevented?
D. Is crystallization rate fast enough (e.g., residence time of <1 hr)?
E. Can the stripper be designed to handle slurry while operating at high pressure?
F. Can SO_2 removal be combined in Hot-CAP?



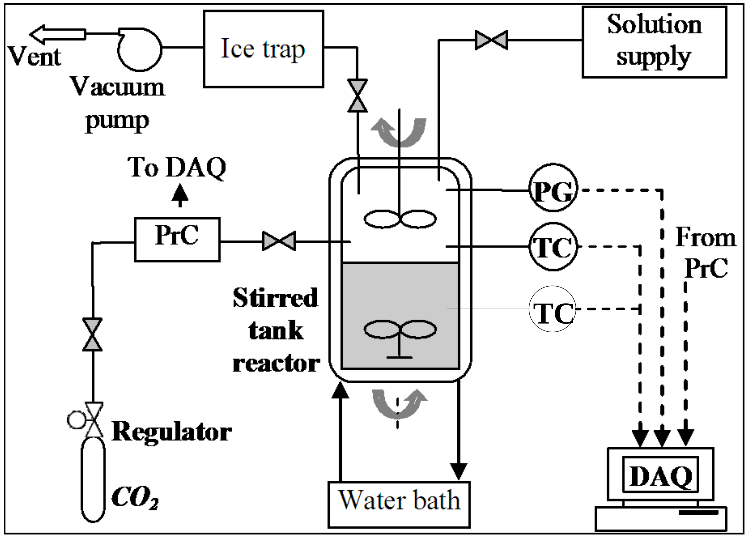
Progress and Current Status of Project

Project Major Tasks, Progress and Millstones Achieved

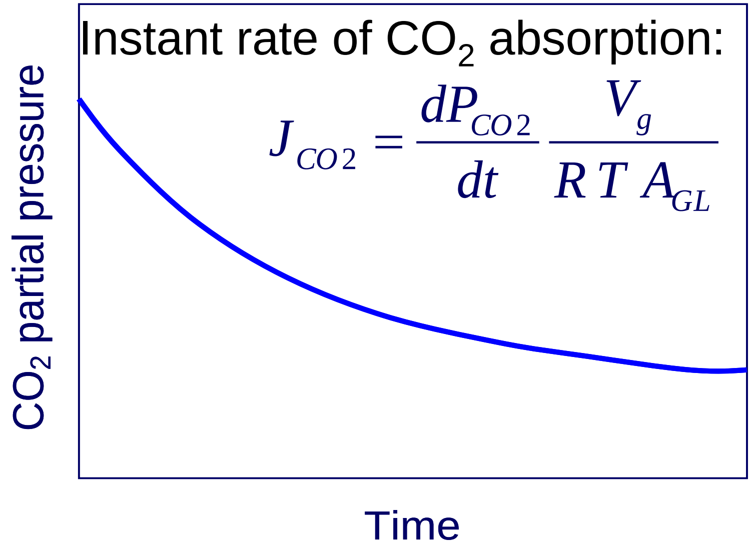
Project Tasks	Progress to date
Task 0. Project planning & management	In progress
Task 1. Kinetics of CO_2 absorption • Absorption with and w/o promoters • Absorption column tests	Completed (Supplementary tests (with Na_2CO_3) in progress)
Task 2. Crystallization kinetics & solubility of bicarbonate • $KHCO_3$ crystallization tests • $NaHCO_3$ crystallization tests	Completed
Task 3. Phase equilibrium & kinetics of high pressure CO_2 stripping • VLE measurements • Stripping column tests	VLE completed; Column tests in progress
Task 4. Reclamation of sulfate from SO_2 removal • Semi-continuous reclamation tests • Process modification/improvement	Proof-of-concept tests completed; Tests on process improvement in progress
Task 5. Techno-economic evaluation • Risk mitigation analysis • Process simulation • Economic evaluation	Risk analysis completed; Economic evaluation in progress

- Currently in 1st quarter of BP3
- 17 milestones in BP1 and BP2
  - 16 milestones completed on schedule
  - 1 milestone extended for 3 months

(1) Studies of CO_2 Absorption: Promoter Screening Tests Using a Stirred Tank Reactor (STR)



(PrC: pressure controller; TC: thermal couple; PG: pressure gauge; DAQ: data acquisition)



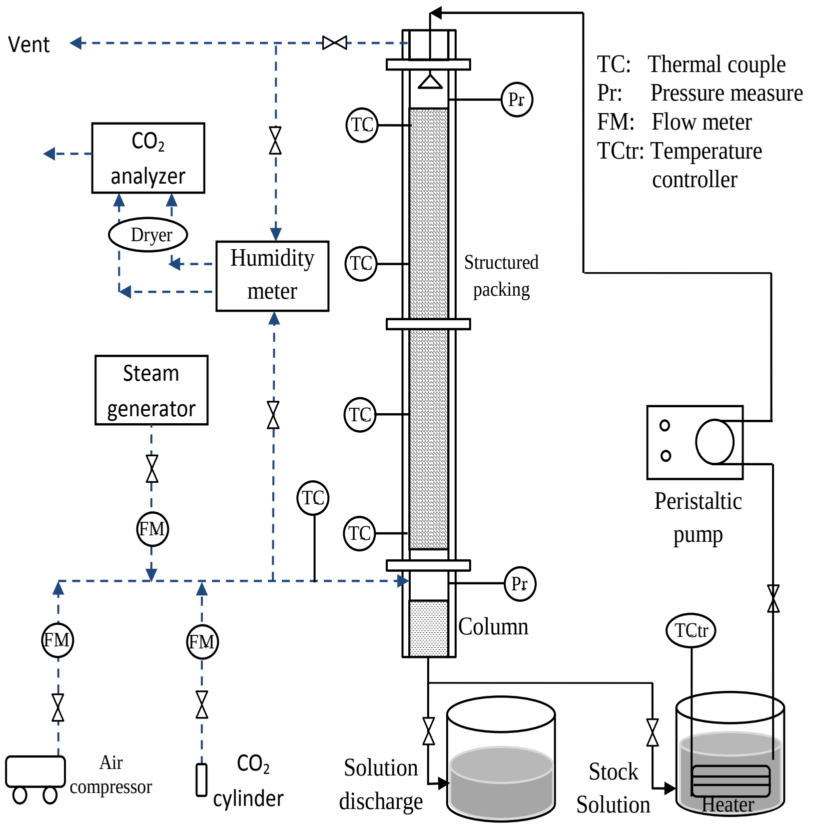
Instant rate of CO_2 absorption:

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

Screening tests using STR:

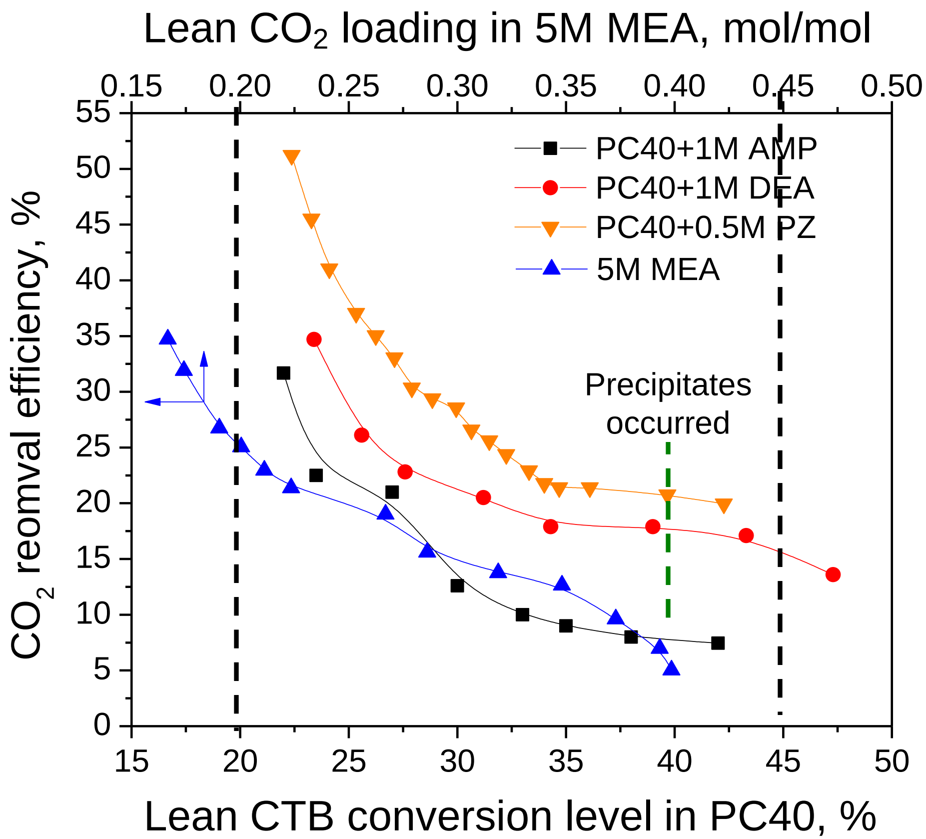
- 3 inorganic and 8 organic promoters
- 3 promoters selected for packed bed column testing

CO_2 Absorption Column Tests: Experimental Setup



	Specification
Column height, m	**10 ft**
Packed bed height	**7 ft**
Absorber diameter, cm	**4 in**
Height of packing element	**4 in**
Diameter of packing element	**4 in**
Specific surface area	**800 m^2/m^3**
Void fraction (ε)	**0.66**

Column Tests Revealed More Favorable Rate of CO_2 Absorption into 40wt% PC + Promoter than 5M MEA



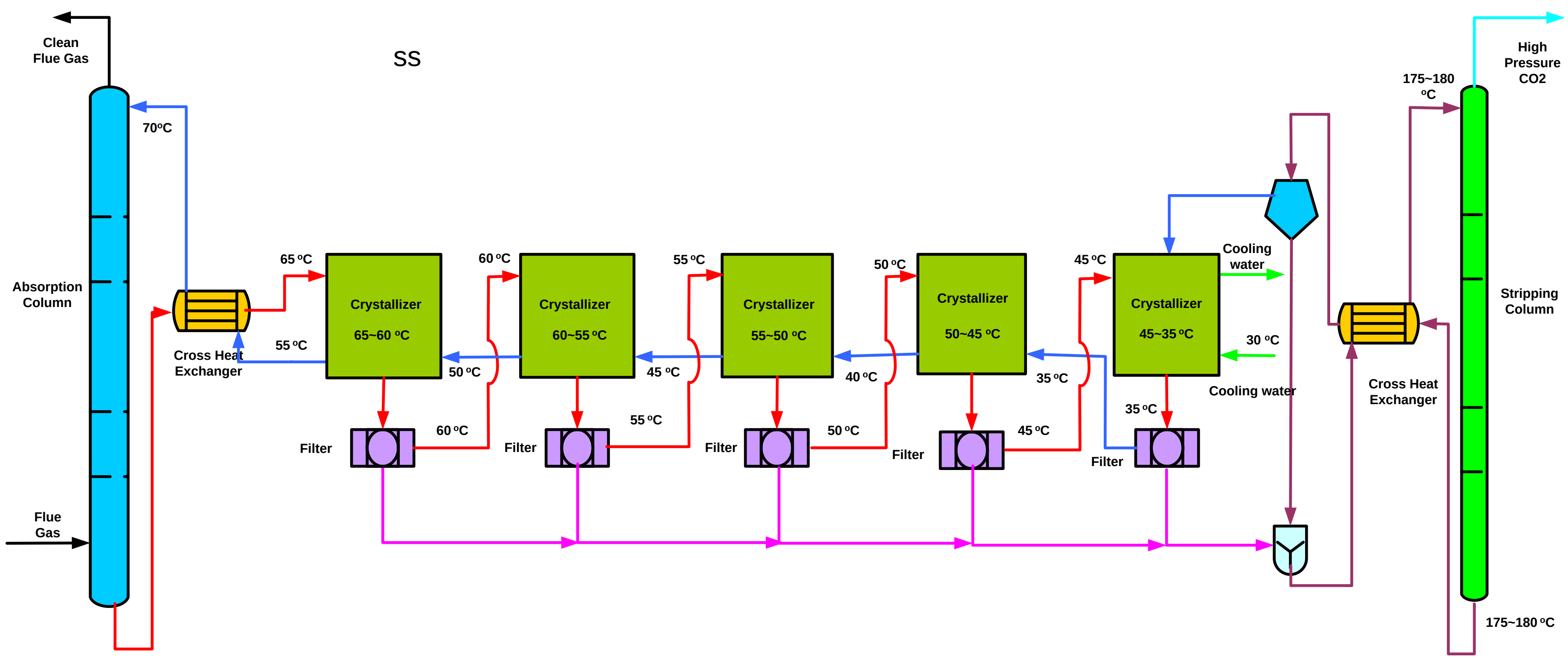
(70ºC absorption in 40wt% PC and 50°C in 5M MEA; inlet CO_2 =14 vol%, L/G=4.7 lb/lb)
(30% CO_2 removal efficiency equivalent to ~11% increase in CTB thru the column)

- CO_2 removal by PC40+1M DEA or 0.5M PZ at 70°C > 5M MEA at 50°C
- W/o promoter, CO_2 removal efficiency by 40wt% PC was insignificant

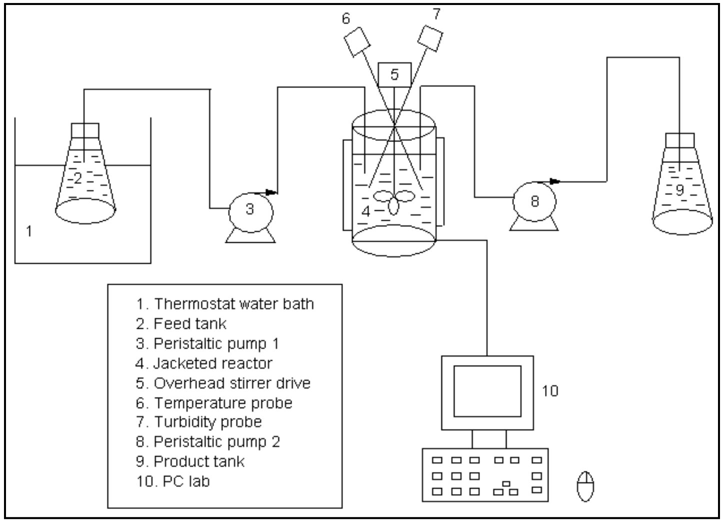
(2) Studies of Bicarbonate Crystallization

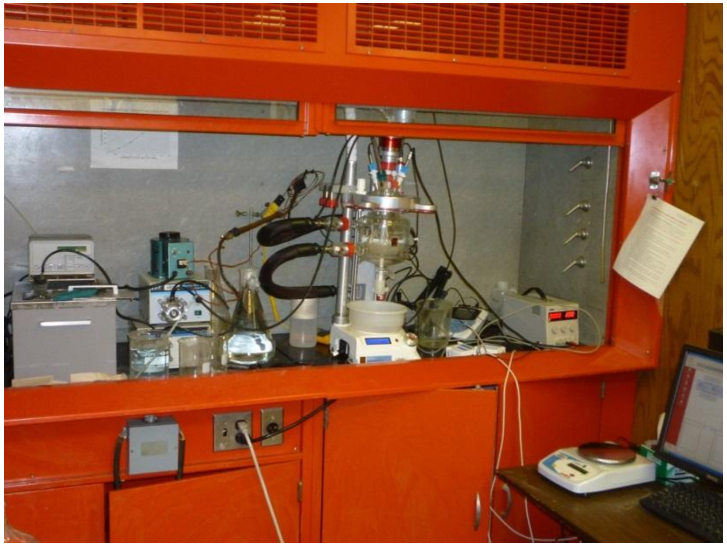
A process configuration developed to address fouling risk and heat recovery:

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



Crystallization Tests in a Continuous Mixed Suspension-Mixed Product Removal (MSMPR) Reactor



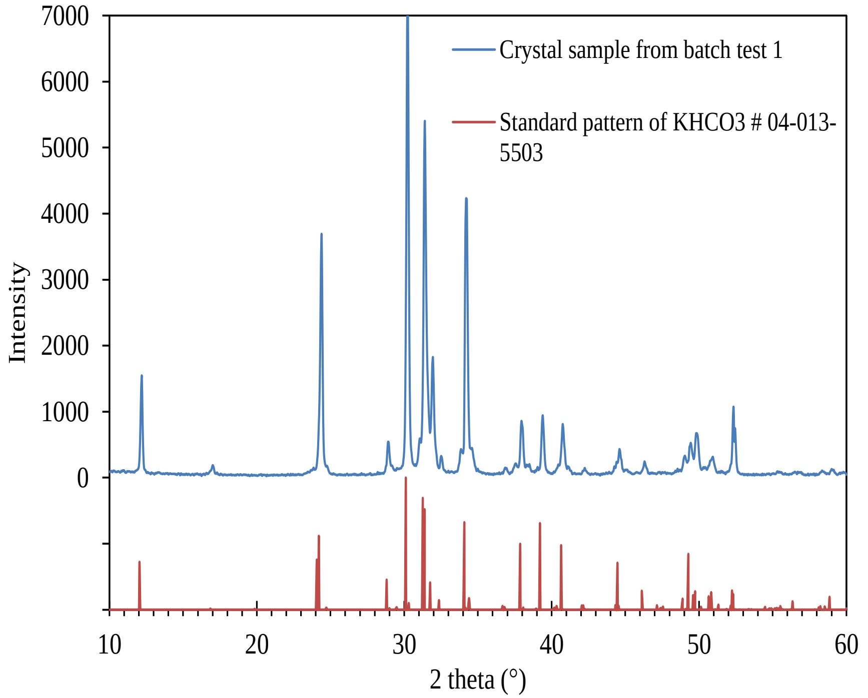


- CO_2-rich feed solution:
  - Temperature: 70°C
  - Composition: $K_2CO_3/KHCO_3$ (PC40-40)
- Test conditions selected to simulate multiple-CSTR process
  - 70-55°C
  - 55-45°C
  - 45-35°C
- Crystallization rate constants (nucleation and growth) determined

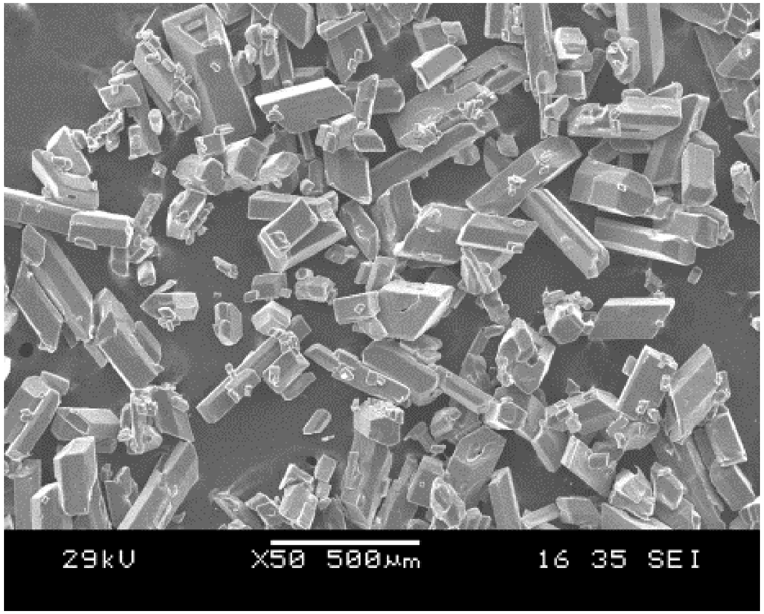
1-liter calorimetric CSTR (Syrris Atlas);

Crystal size distribution analysis (Horiba LA-950)

Morphology and Composition of Crystal Particles



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

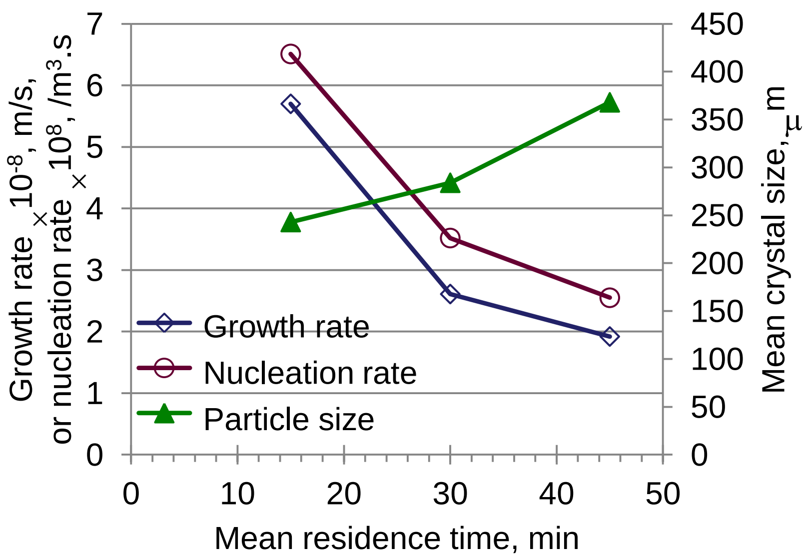


SEM image of $KHCO_3$ crystal (end T=45 C)

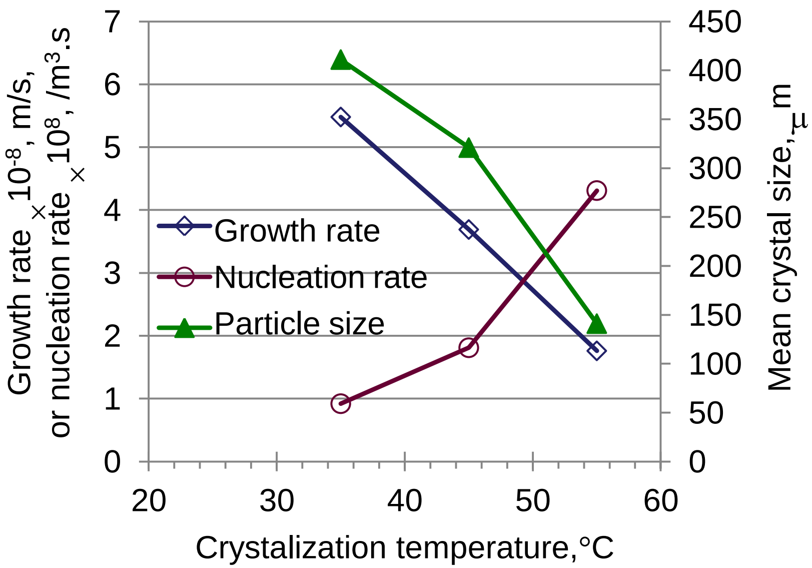
- High-purity kalicinite ($KHCO_3$) prevailed in crystal phase
- Prism-shaped (hexagonal) morphology
- Yield of $KHCO_3$ crystals consistent to its solubility at crystallization T

Parametric Tests Indicated Fast Crystallization of $KHCO_3$

- Crystal growth and nucleation rates measured at different agitation rates, mean residence times (MRT, 15, 30, 45 min) and T-dependent super-saturation levels (TSL, T=35, 45, 55°C)



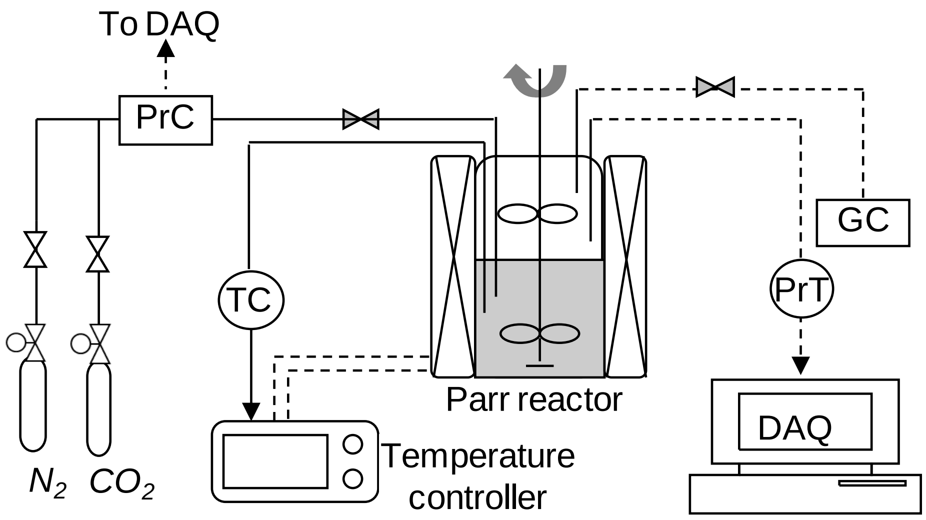
Example 1: 70°C PC40-40 feed, crystallization at 55°C, 350 rpm



Example 2: 70°C PC40-40 feed, MRT=30min, 700 rpm

- Mean particle size of $KHCO_3$ crystals under test conditions: 233-455 µm
  - Crystal size large enough for ~100% liquid-solid separation in conventional hydrocyclone
  - Crystallization time ≤ 45 min is sufficient

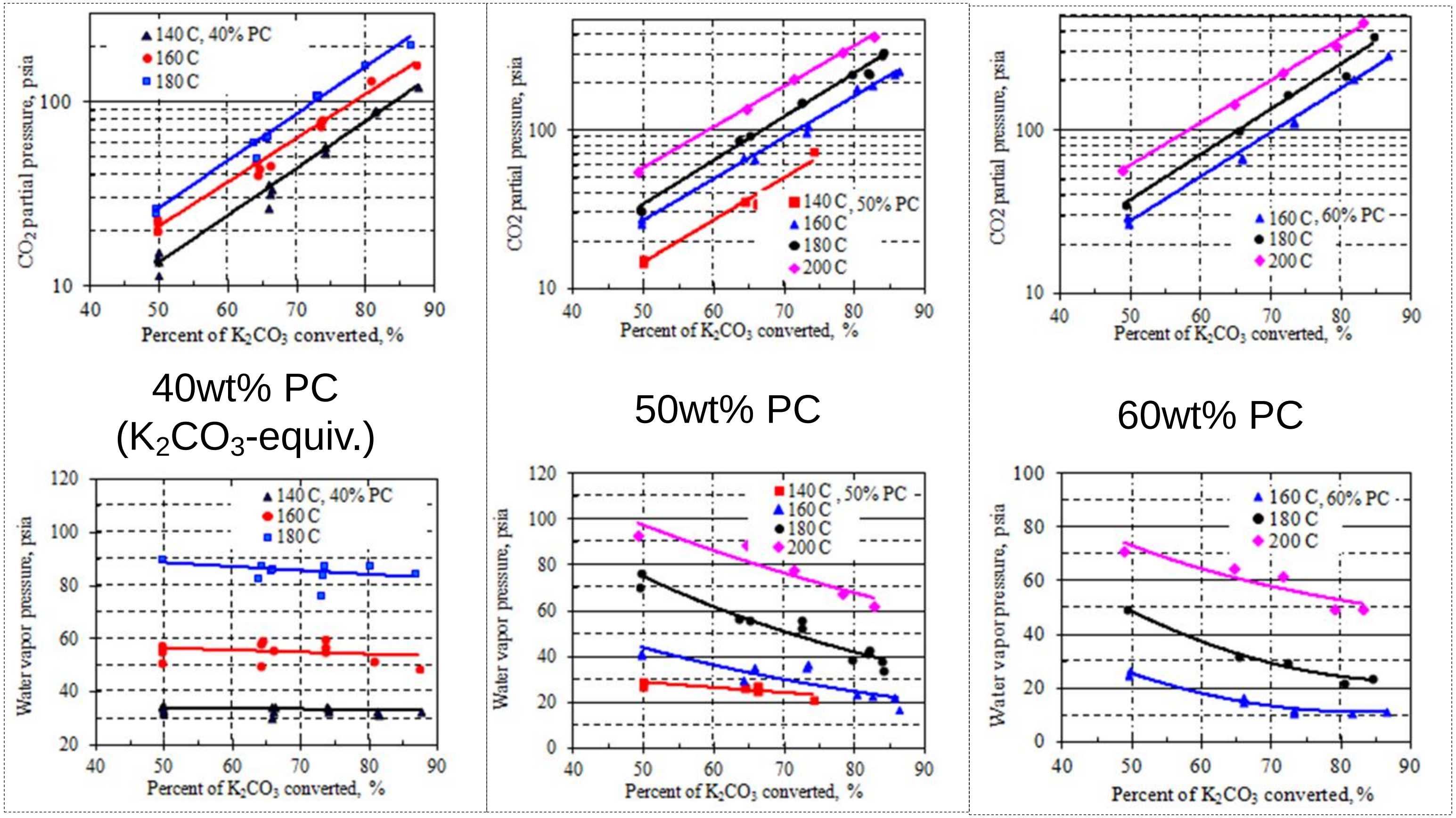
(3) Studies of CO_2 Stripping: VLE measurement for $K_2CO_3/KHCO_3$ Slurry



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

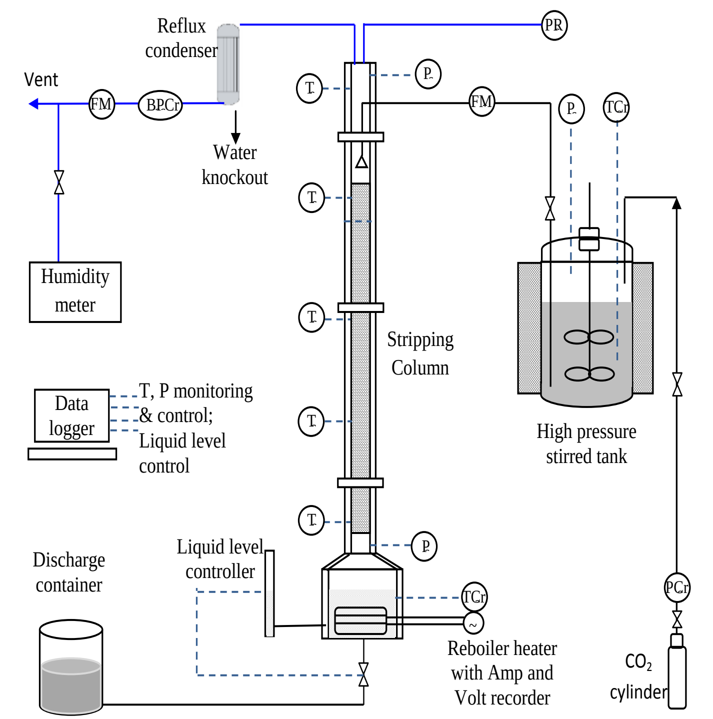
- Gas analysis using GC and liquid analysis using a back-titration method
- 40-70wt% $KHCO_3/K_2CO_3$ slurry at 120-200°C

VLE Results Indicated that High Stripping Pressure is Thermodynamically Feasible in Hot-CAP

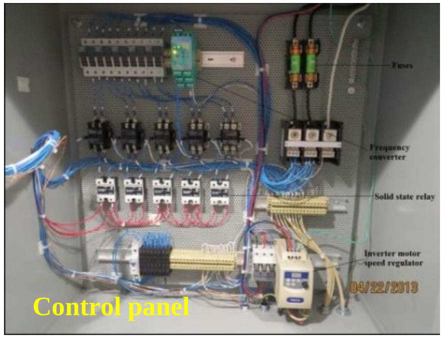


- High P_{total} and low P_{H2O}/P_{CO2} ratio attained
- Higher P_{total} and lower P_{H2O}/P_{CO2} ratio at higher temperature, CTB conversion, or PC concentration

CO_2 Stripping Experimental System



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: 7 ft high x 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

Initial Results Indicated Good Performance of CO_2 Stripping Even with Less Concentrated Feed Slurry

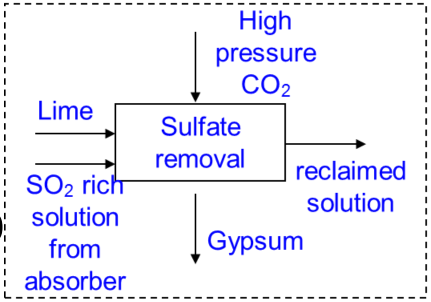
Temperature in reboiler (ºC)	Rich solution*	Lean solution	Feed flow rate (LPM)	CO_2 flow rate (ml/min)	P_{total} in column (psia)
140	PC40-40	PC40-33	0.1	660	39
160	PC40-40	PC40-20	0.1	2,022	81
160	PC30-60	PC30-54	0.1	270	89
140	PC32-80	PC32-55	0.1	1,900	69
170	PC32-80	PC32-48	0.1	2,435	97
180	PC50-60	PC50-48	0.1	1,700	108

*** PC X-Y stands for X wt% K_2CO_3-equivalent concentration and Y% carbonate-to-bicarbonate (CTB) conversion**

- Initial results with relatively low concentration slurry (30-50 wt%) confirmed that high P_{total} and low P_{H2O}/P_{CO2} were possible
- Increasing feed CTB% conversion and reboiler temperature favored performance of CO_2 stripping
- Parametric tests in progress to investigate:
  - Effects of CTB% in feed, slurry concentration, stripping T, slurry flow rate, etc.

(4) Reclamation of Sulfate for SO_2 Removal in Hot-CAP: Process Proof-of-Concept Tests

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



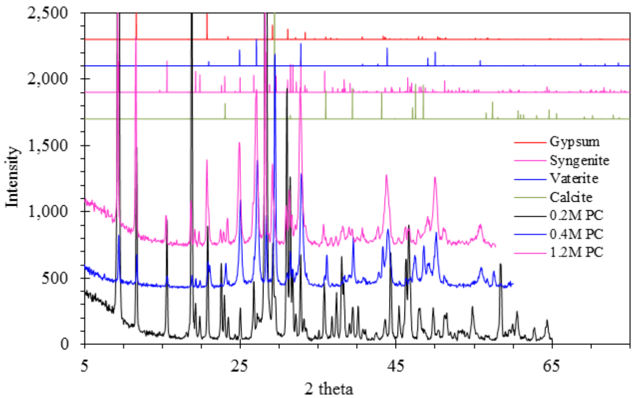
K_2SO_4 reclamation process:

- Reaction with lime: $K_2SO_4 + CaO + 2H_2O + CO_2 = K_2CO_3 + CaSO_4 \cdot 2H_2O(\downarrow)$
- Competitive reaction: $Ca^{2+} + CO_3^{2-} \Rightarrow CaCO_3(\downarrow)$

  Inhibition by high-P CO_2: $CaCO_3(s) + CO_2 + H_2O = Ca(HCO_3)_2(aq)$

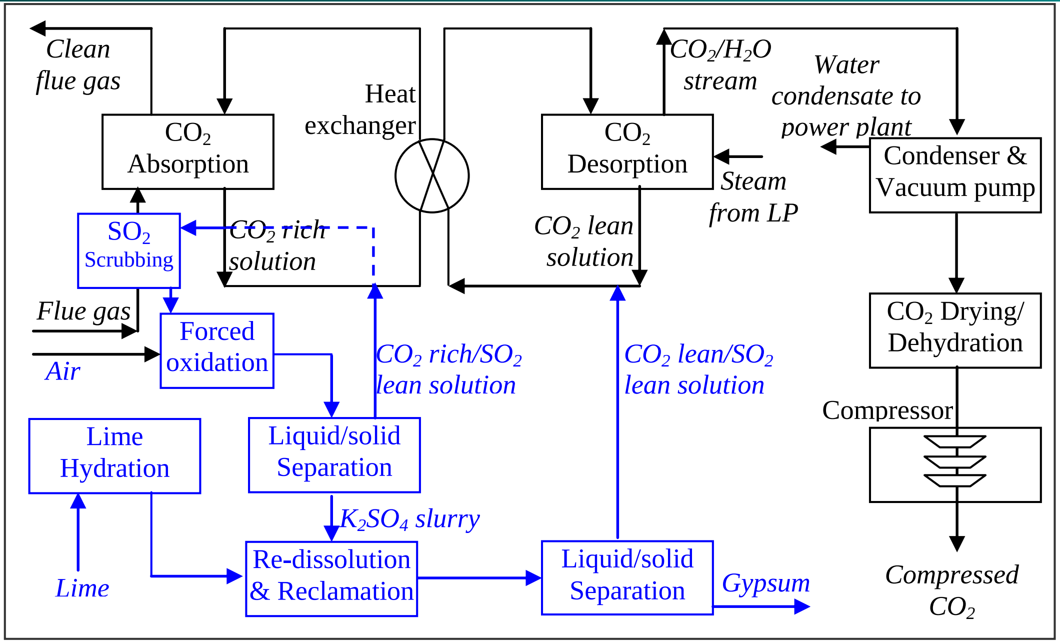
Semi-continuous experimental results :

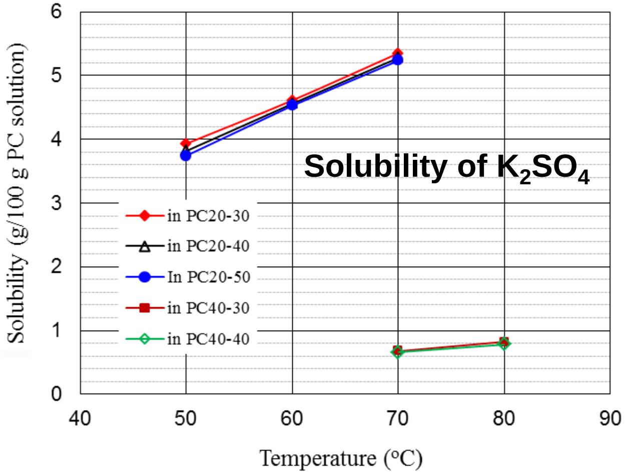
- Precipitates: gypsum (0-58wt%), syngenite (0-91%), vaterite/calcite (0-100%)
- Precipitates from most tests contained >30% vaterite/calcite
- Precipitation of $CaSO_4$ favored over $CaCO_3$ at lower T or lower PC concentration



Example: XRD of precipitates from three PC-0.4M K_2SO_4-0.4M $CaCl_2$ systems.

A Modified Process Option for K_2SO_4 Reclamation





- Major reactions:

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

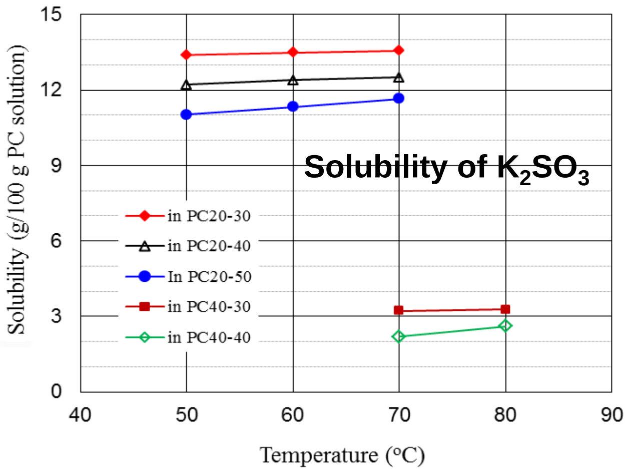
$2KHCO_3 + SO_2 + H_2O \rightarrow K_2SO_3 + 2H_2CO_3$

Oxidation: $K_2SO_3 + ½ O_2 \rightarrow K_2SO_4 (s)\downarrow$

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

- Solubility:

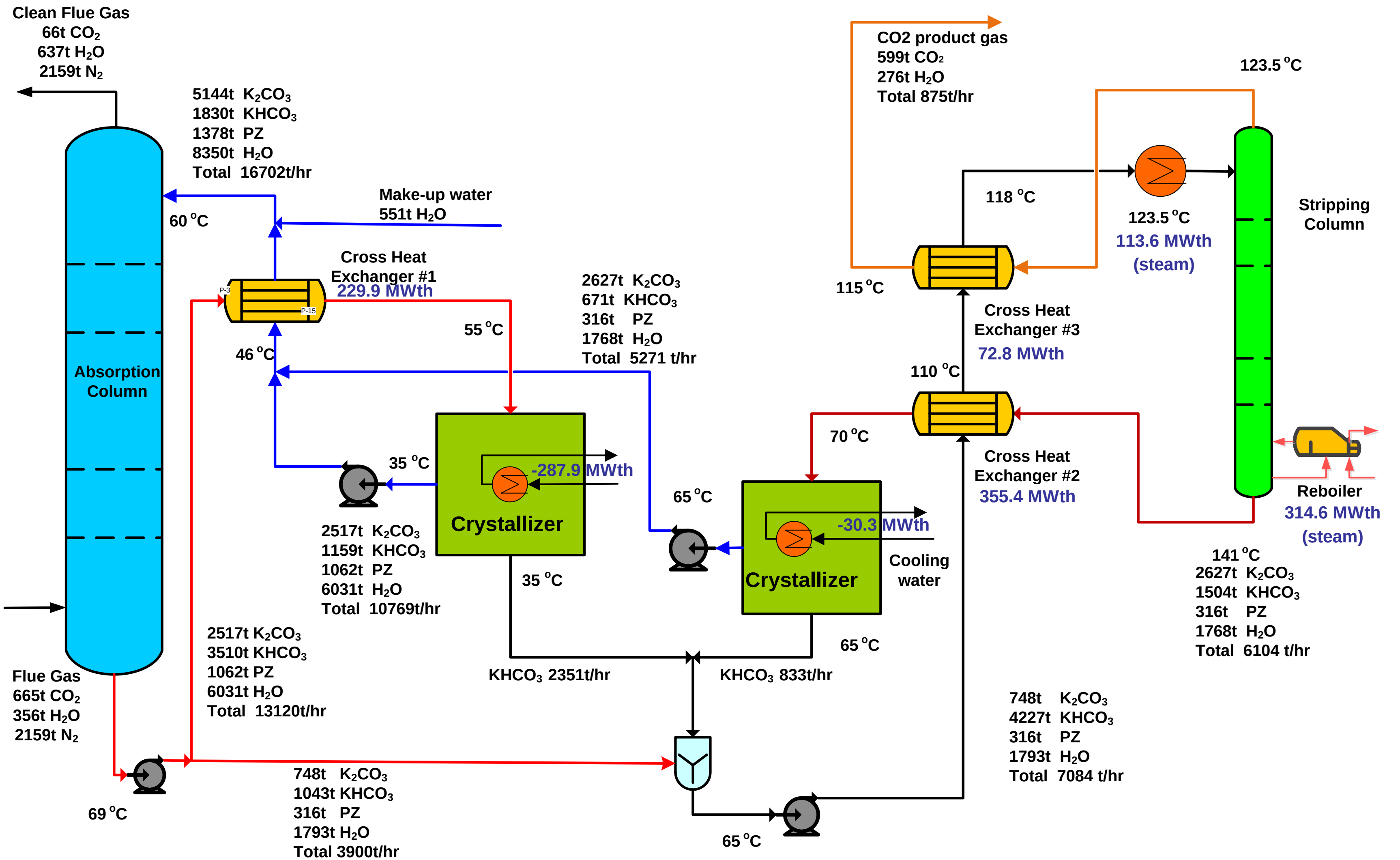
K_2SO_3, K_2CO_3, $KHCO_3$ >> K_2SO_4



- Tests of K_2SO_3 oxidation and K_2SO_4 precipitation in progress

(5) Techno-Economic Analysis: Process Simulation and Sizing of Columns Using ProTreat

- 773 MWe power plant (gross w/o CO_2 capture) equipped with Hot-CAP



Preliminary Results of Process Simulation and Sizing

Column sizing:

- 2 absorbers, each of 14.7-m ID x 25-m height
- 1 stripper, 7.3-m ID x 10-m height
- Packed with Mellapak M250.Y

Energy performance:

CO_2 Stripping (kWh/ kg CO_2)	0.155
Compression work (kWh/ kg CO_2)	0.075
Other loads (kWh/ kg CO_2)	0.04
Total electricity use (kWh/kg CO_2)	0.27

Current simulation based on a low stripping P (2 bar) due to lack of data at T>140°C in ProTreat software

- Higher stripping P and better energy performance expected at T>140°C due to high adsorption + crystallization heat (~18 kcal/mol)
- High stripping-P scenarios (>>2 bar) will be simulated by incorporating measured VLE data into software

Plans for future testing/ development/ commercialization

Work Plan in BP3

- High pressure CO_2 stripping tests
  - Stripping performance tests
  - Stripping process optimization
- Proof-of-concept testing of a modified process option for combined SO_2 removal and CO_2 capture
- Techno-economic studies
  - Process optimization study
  - Equipment sizing and cost analysis

Technology Scale-up Development

- Process optimization and improvement to reduce technical risks and enhance performance
- Detailed techno-economic analysis
- If technically and economically viable,
  - Seek federal, state, and industrial support for a pilot-scale test (0.5-3 MWe)
  - Identify industrial partners (design, manufacturing and field testing) for pilot-scale demonstration

Acknowledgements

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