# 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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2012 NETL $CO_2$ Capture Technology Meeting

Pittsburgh, PA • July 9-12, 2012

# Prime Contractor

- Illinois State Geological Survey (ISGS)
  - 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 Team

DOE/NETL

- Project manager- Andrew Jones

Illinois Clean Coal Institute

- Project manager – Joseph Hirschi

Illinois State Geological Survey-University of Illinois

- Bench- and lab-scale experimental studies
- Nick Devries, Yongqi Lu, Manoranjan Sahu, Massoud Rostam-Abadi, David Ruther, Qing Ye, Xinhuai Ye

Carbon Capture Scientific, LLC

- Risk analysis and techno-economic studies
- Kevin O’Brien, Scott Chen, Zhiwei Li

# 1. Project Overview: Project Objectives

- Perform a proof-of-concept study aimed at generating process engineering and scale-up data to help advance the Hot-CAP process to a pilot-scale demonstration level within three years
    - Lab- and bench-scale tests of thermodynamics and reaction engineering data of major unit operations
    - Risk and techno-economic analysis studies

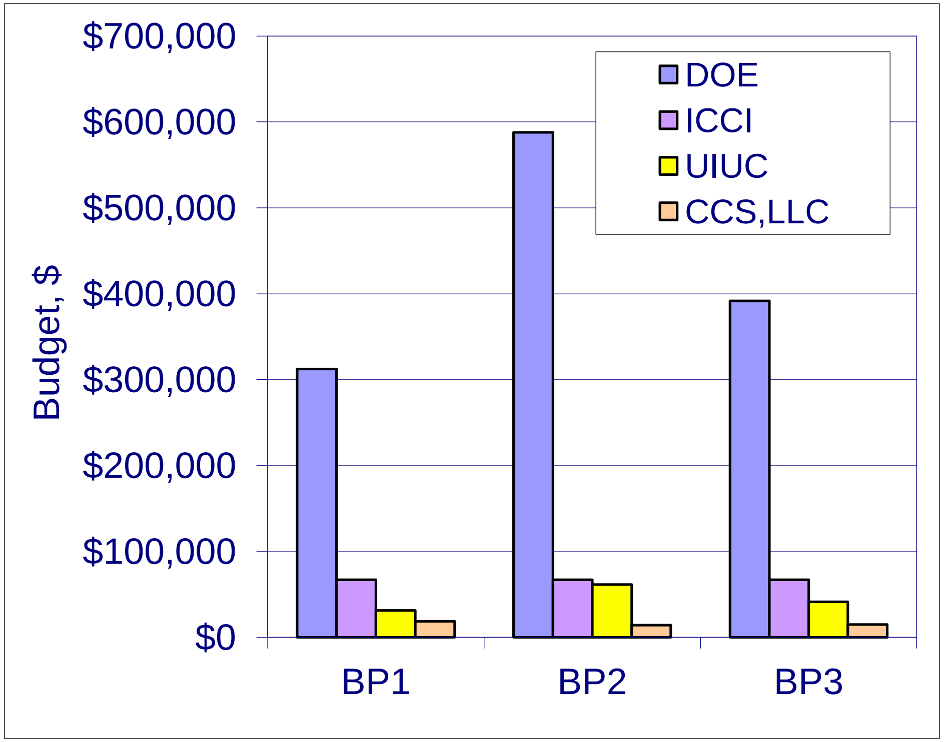
# Project Duration and Budget

Project duration: 1/1/2011 – 12/31/2013

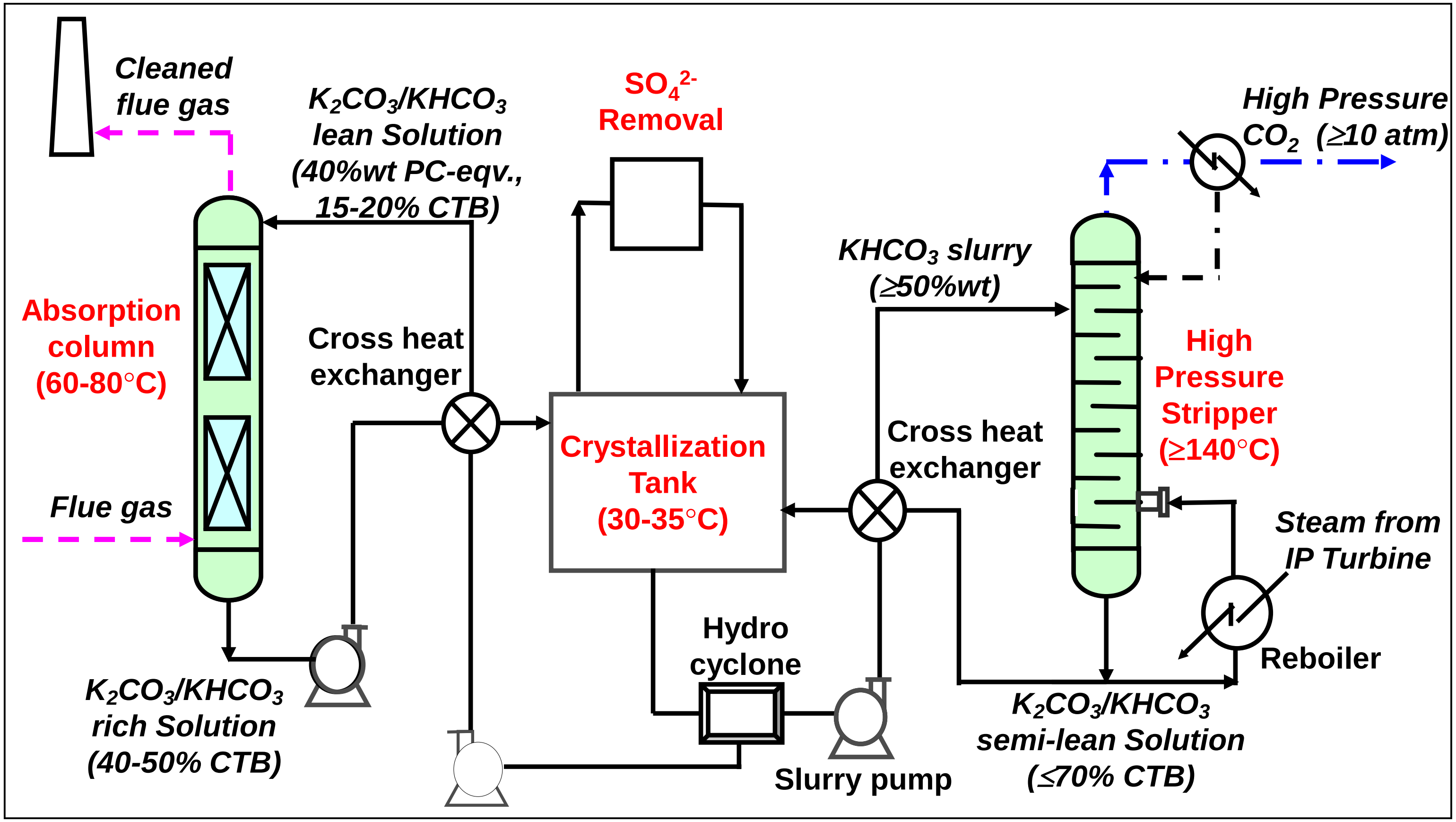
Budget:

| | **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 is ~23%)

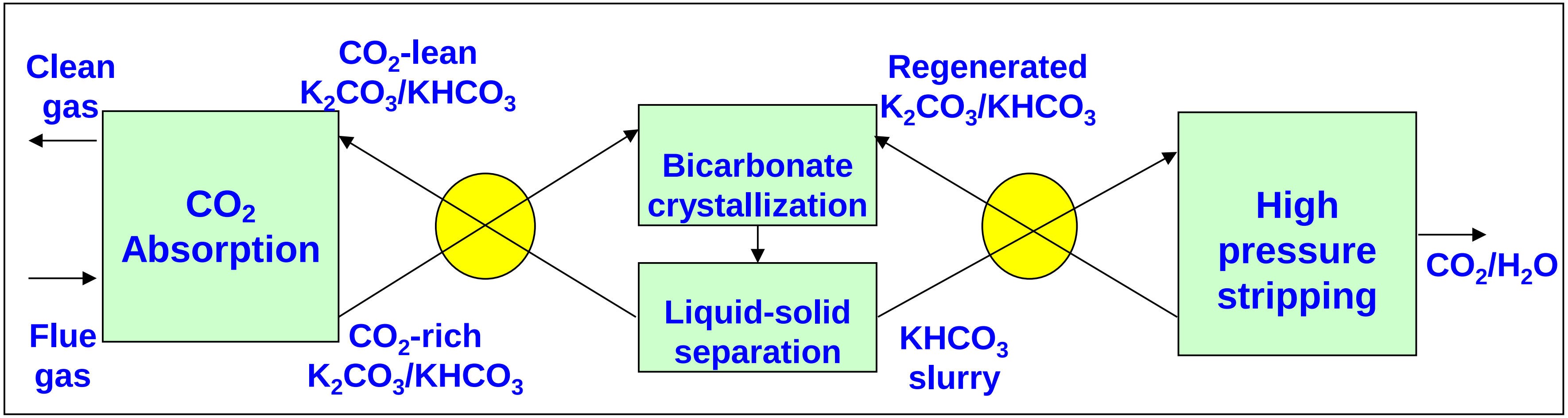


# 2. Technology Fundamentals/ Background: Hot Carbonate Absorption Process with High Pressure Stripping Enabled by Crystallization (Hot-CAP)



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

# Major Reactions



Clean gas

Flue gas

$CO_2$ Absorption

$CO_2$-lean $K_2CO_3/KHCO_3$

$CO_2$-rich $K_2CO_3/KHCO_3$

Bicarbonate crystallization

Liquid-solid separation

Regenerated $K_2CO_3/KHCO_3$

$KHCO_3$ slurry

High pressure stripping

$CO_2/H_2O$

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

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

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

# Hot-CAP vs. MEA

| Items | 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 bw absorb. and stripping | N | Crystallization |
| | | |
| FGD required | Y | N |

- ❑ Low compression work and low stripping heat (high $CO_2/H_2O$ ratio)
- ❑ Low sensible heat
  - ➢ Comparable working capacity to MEA but low Cp (1/2)
- ❑ Low heat of absorption
  - ➢ 7-17 kcal/mol (crystallization heat included) vs. 21 kcal/mol for MEA

# Energy Use Comparison between Hot-CAP and MEA

| Items | MEA | Hot-CAP |
|---|---|---|
| Energy Consumption | | |
| $CO_2$ desorption | | |
| Heat of absorption (kJ/kg$CO_2$) | 1,870 | 1,600 |
| Sensible heat (kJ/kg$CO_2$) | 990 | 300 |
| Stripping heat (kJ/kg$CO_2$) | 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

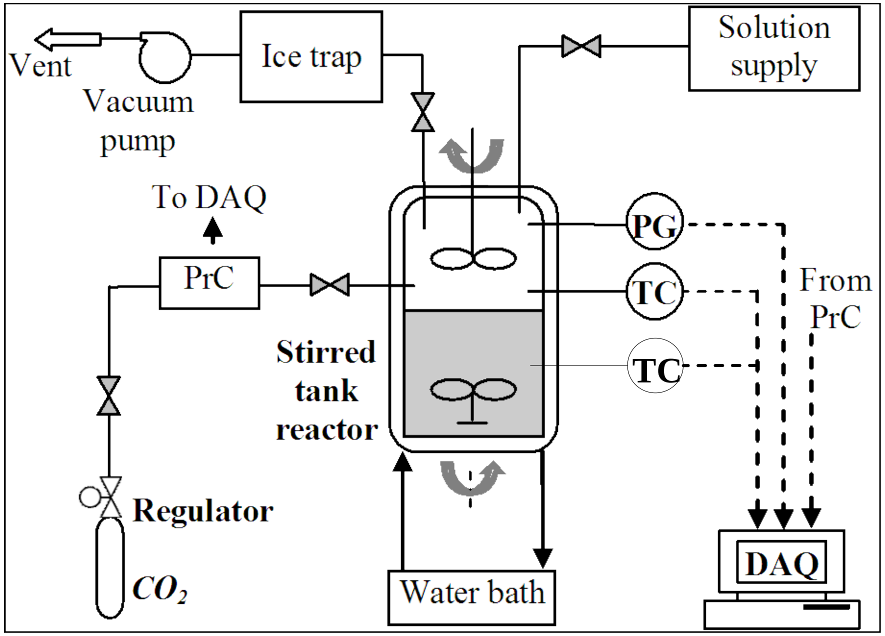
# 3. Project Progress and Current Status: Project Tasks

| | |
|---|---|
| **Task 1. Project planning & management** | **Task 4. Phase equilibrium & kinetics of high pressure stripping**<br>• VLE data of slurry system<br>• Stripping column test |
| **Task 2. Kinetics of $CO_2$ absorption**<br>• Absorption kinetics<br>• Absorption column test | **Task 5. Kinetics of sulfate reclamation** |
| **Task 3. Crystallization kinetics & solubility of bicarbonate**<br>• $KHCO_3$ crystallization test<br>• $NaHCO_3$ crystallization test | **Task 6. Techno-economic evaluation**<br>• Risk mitigation study<br>• Process modeling/ simulation<br>• Economic evaluation |

# Work Activities from 1/1/2011 thru 6/30/2012

| Tasks/subtasks on project schedule | Comments |
|---|---|
| 1.1/1.2 Absorption in $K_2CO_3$/$KHCO_3$ (PC) solution without and with promoters<br>(3/1/11-3/31/12) | (1) Kinetics obtained for reference PC; (2) effective promoters/catalysts identified; (3) impact of sulfate investigated |
| 2.1/2.2 $KHCO_3$ crystallization equipment setup, test, impact of $K_2SO_4$ on crystallization<br>(4/1/11-6/30/12) | (1) Results proved feasibility of $KHCO_3$ crystallization under Hot-CAP conditions; (2) morphology and crystal PSD analysis provided guideline for crystallizer design; (3) impact of promoters and sulfate identified |
| 3.1/3.2 VLE measurement of $K_2CO_3$/$KHCO_3$ slurry (7/1/11-6/30/12) | (1) A high pressure setup and experimental approach established; (2) VLE data obtained |
| 5.1/5.2 Risk mitigation studies and process simulation/modeling.<br>(1/1/11-12/31/13) | (1) Vendor discussions resulted in a new process design to mitigate fouling risk in heat exchanger and crystallizer cooler; (2) process simulation studies in progress as scheduled |

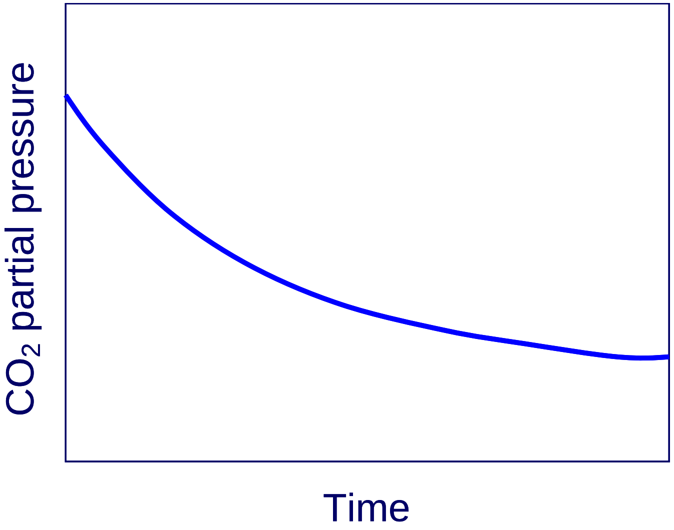
# 3.1 Studies of Absorption Kinetics: Stirred Tank Reactor (STR) Setup



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

- Instant flux of $CO_2$ absorption

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



# Intrinsic Rates of Absorption Determined from STR Experiments: PC vs. Amines

- Major absorption reaction of $CO_2$ in PC solution

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

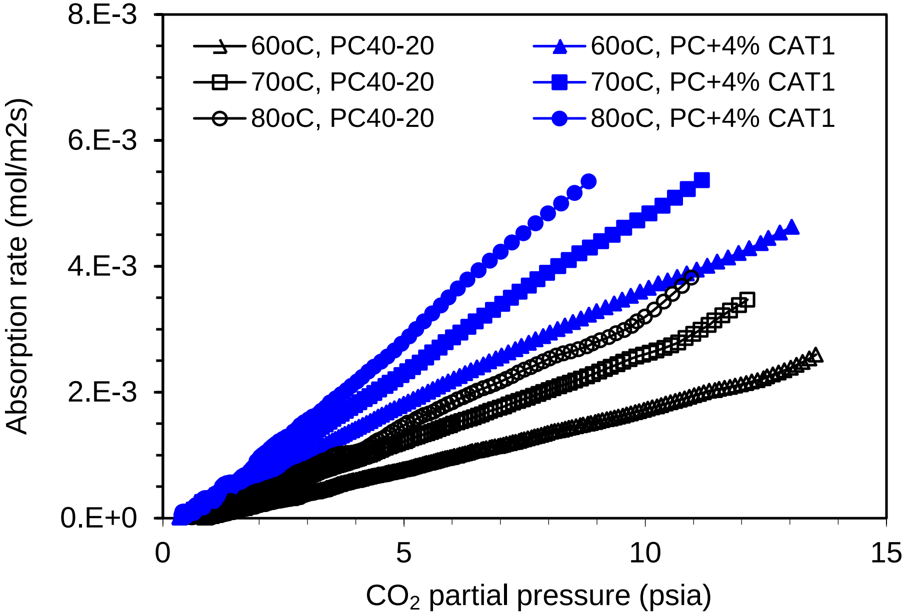
| Reactant | Rate constant *k*, L/mol/s | Concentration, mol/L | Rate (*k* [Reactant]), 1/s |
|---|---|---|---|
| $OH^-$ | $1.57 \times 10^6$ (at 70°C) | $4.33 \times 10^{-3}$ | $k_1\,[OH] = 6{,}820$ |
| MEA* | 7,600 (at 25°C) | 5 | $k_2\,[MEA] = 38{,}000$ |
| MDEA | 4.3 (at 25°C) | 5 | $k_3\,[MDEA]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

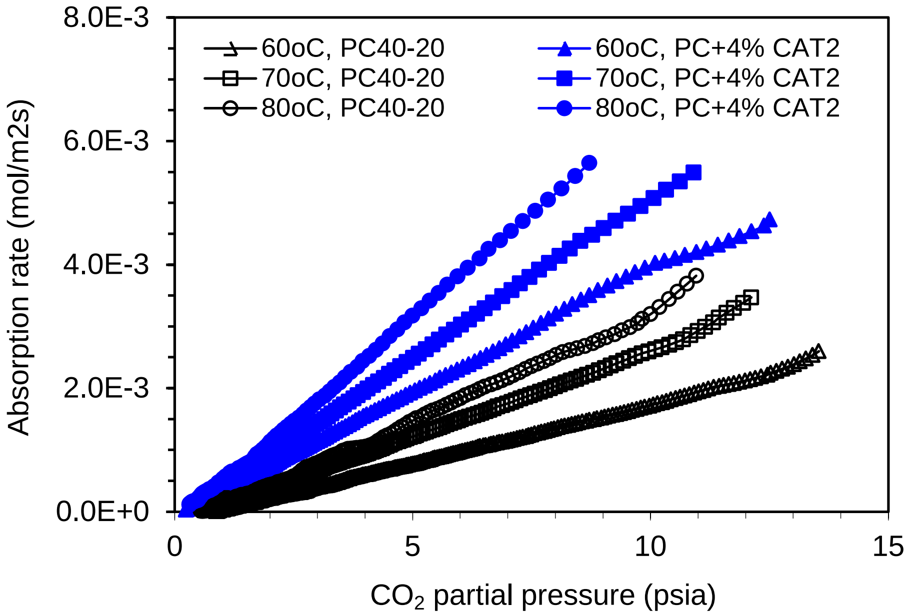
$$CO_2 + RNH_2 \xrightarrow{k_2} H^+ + RNH\,COO^- \qquad \text{rate}: r_2 = k_2[CO_2][MEA]$$

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

- Rates into potassium carbonate (PC, $K_2CO_3$) vs. amines
  - Intrinsic reaction rate into 40wt% PC at 70°C is ~6 times lower than 5M MEA
  - Henry's constant of $CO_2$ (solubility) is 4 times lower at 75°C than 25°C

# $CO_2$ Absorption into 40wt% PC with Inorganic Catalysts

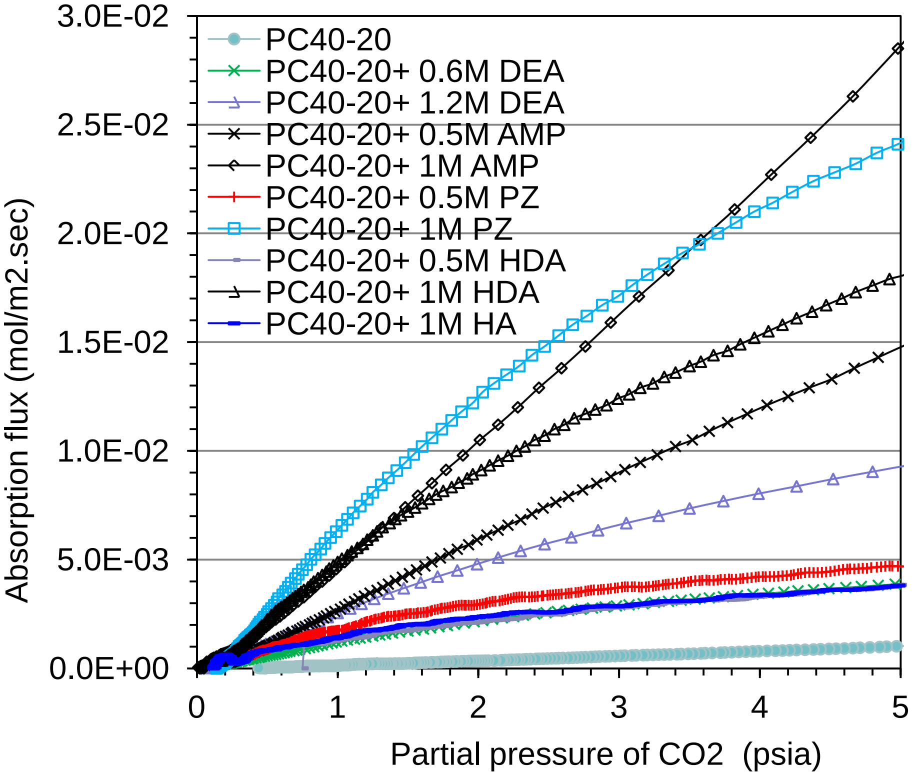


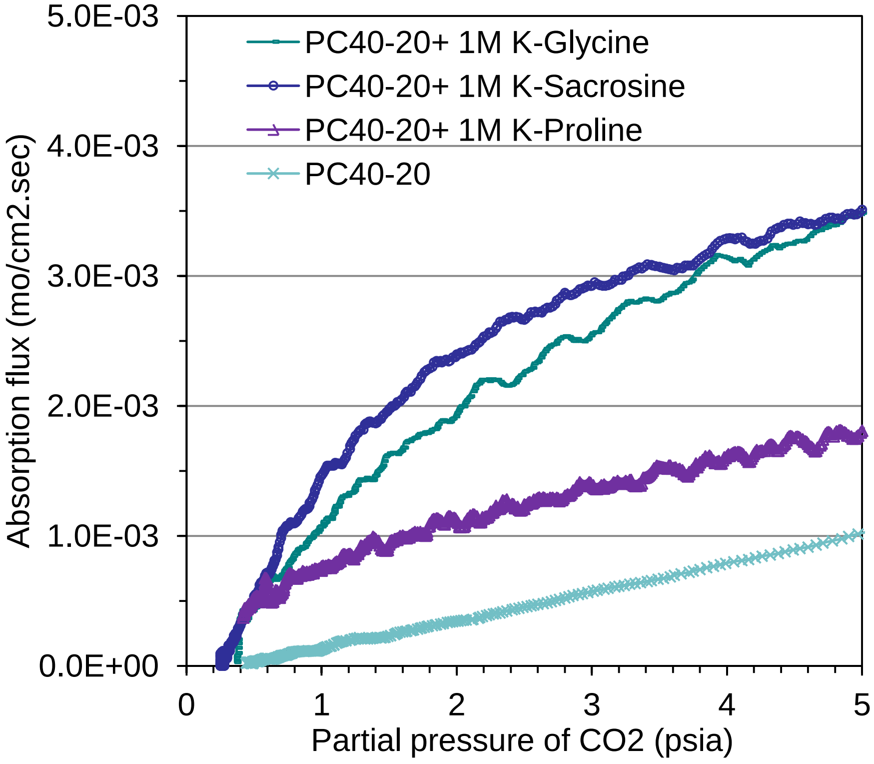


| Enhancement factor (E) | 4wt% CAT1 | 4wt% CAT2 |
|---|---|---|
| E (60°C) | 2.16 | 2.36 |
| E (70°C) | 1.86 | 2.00 |
| E (80°C) | 1.88 | 2.12 |

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

# $CO_2$ Absorption into 40wt% PC with Organic Promoters

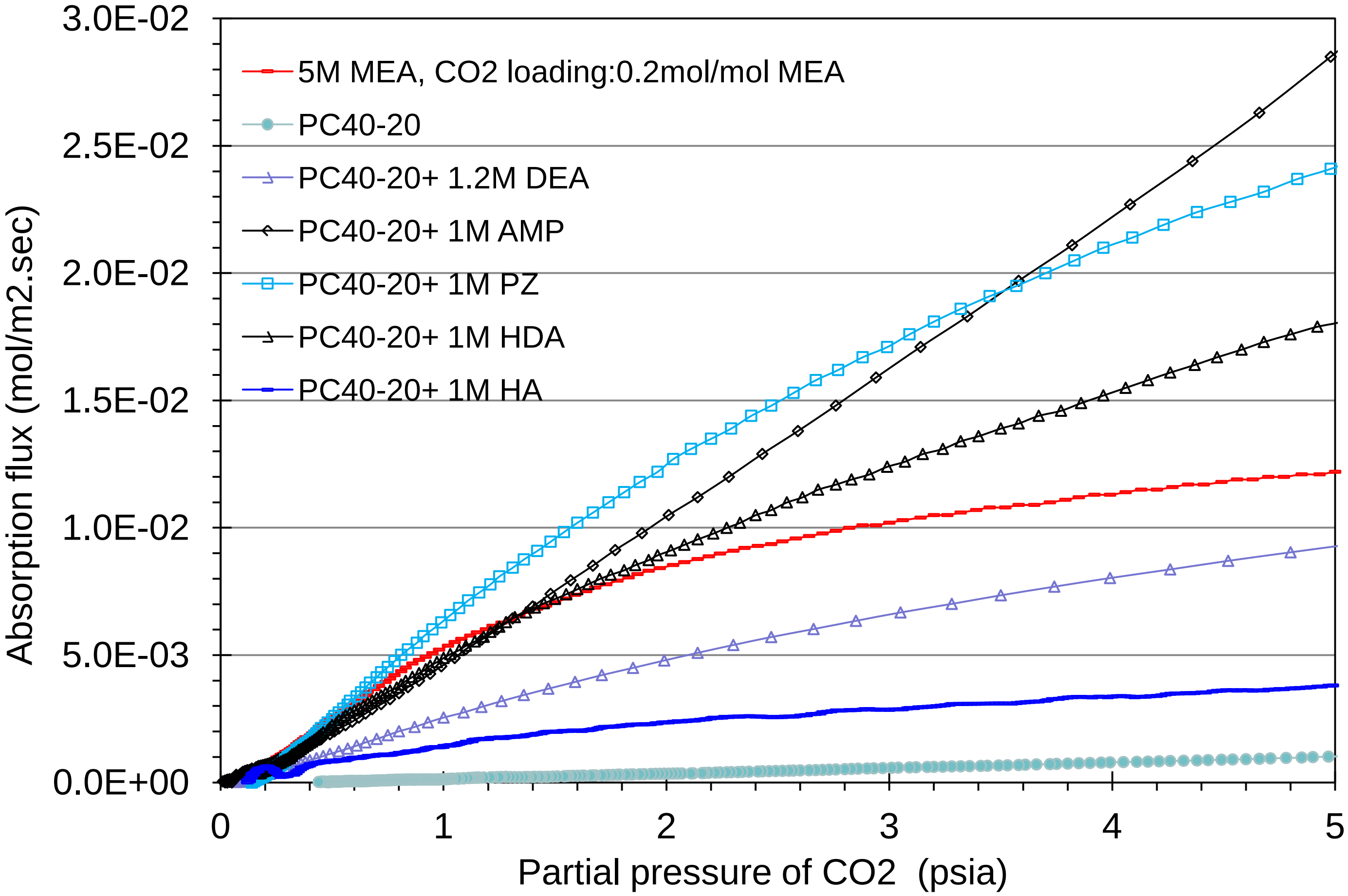




- ❑ Rates promoted by amines 3.5-30 times compared to reference PC
- ❑ Rates promoted by amino acid salts by 3-11 times
- ❑ Rates most effectively promoted with 1M PZ, 1M AMP and 1M HDA

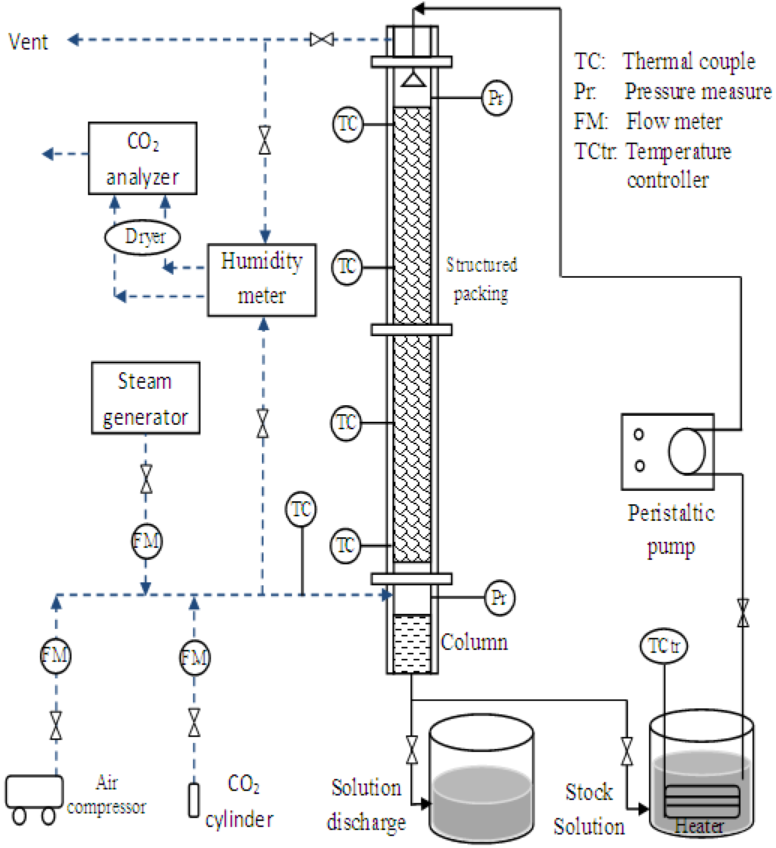
DEA: diethanolamine; AMP: 2-amino-2-methyl-1-propanol; PZ: piperazine; HDA: hexamethylene diamine; HA: hexylamine

# Rates of $CO_2$ Absorption: Promoted PC vs. Amines

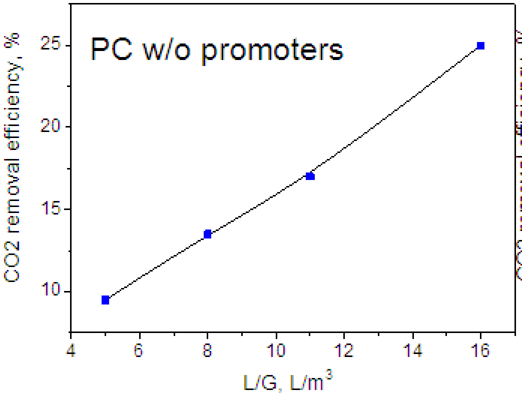


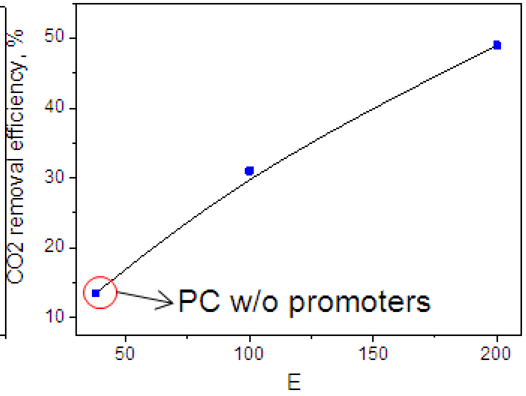
- ❑ Rates into 5M MEA with 0.2 mol $CO_2$/mol at 50°C were 10-35 times > reference PC40-20 at 50°C
- ❑ Rates into PC40-20 with 1M PZ, 1M AMP, or 1M HAD at 70°C comparable to or higher than 5M MEA at 50°C

# Absorption Column Test in Progress

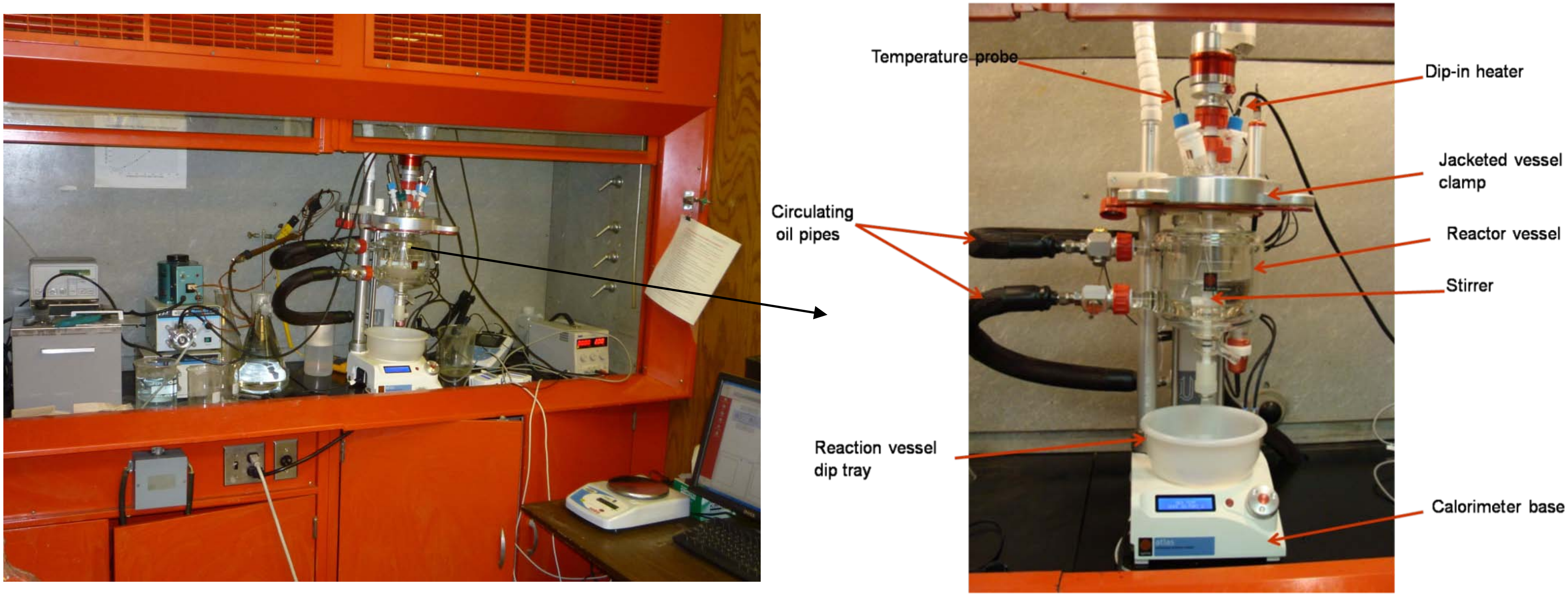


| | Specification |
|---|---|
| Column height | 3.0 |
| Packed bed height, m | 2.0 |
| Absorber diameter, cm | 10 |
| Height of packing element, cm | 10 |
| Diameter of packing element, cm | 10 |
| Specific surface area (a), $m^2/m^3$ | 800 |
| Void fraction (ε) | 0.66 |





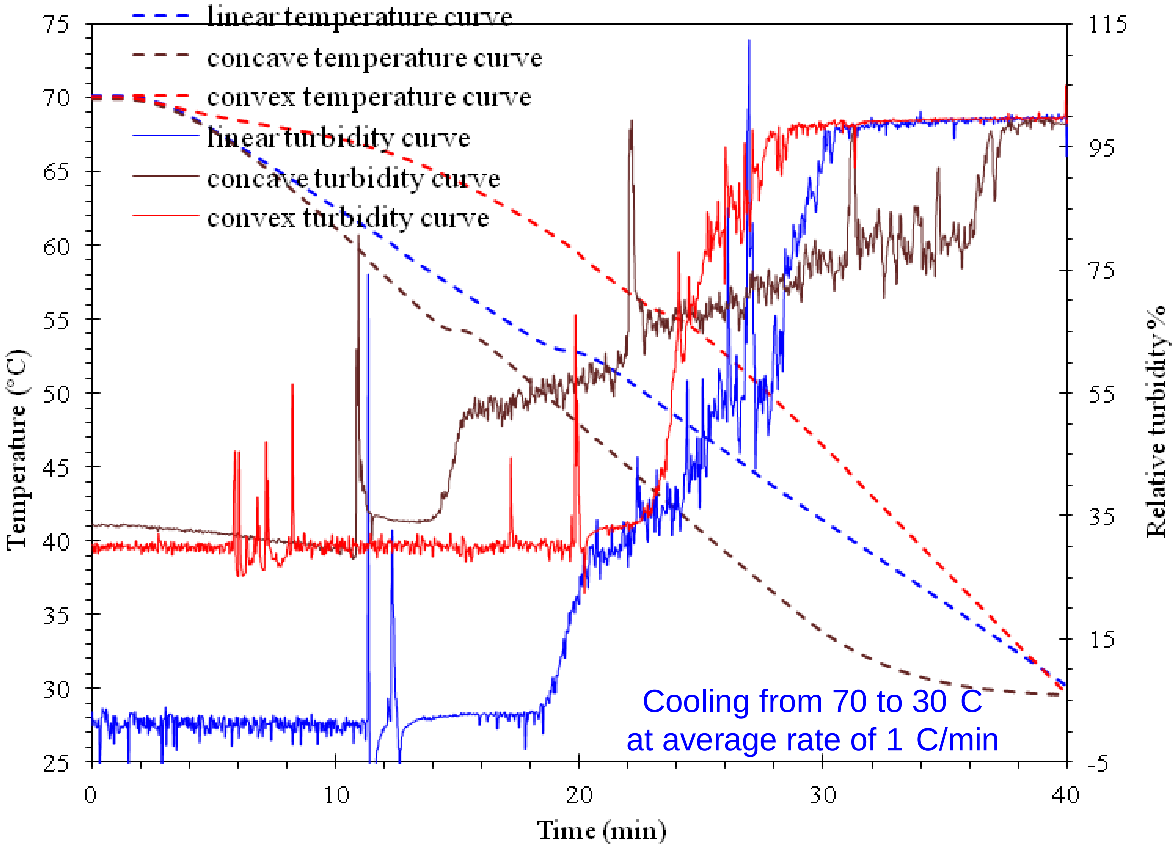
# 3.2 Studies of Bicarbonate Crystallization



An automated calorimetric reactor instrument
(Reactor double-jacked for precise T control; heat measurable during phase transition and reaction; in-line turbidity monitoring)

- ☐ $KHCO_3$ crystallization from PC solutions:
  - 40wt% PC with 40% CTB conversion (PC40-40) without and with promoters
  - Cooling PC solutions from 70 to ~30°C

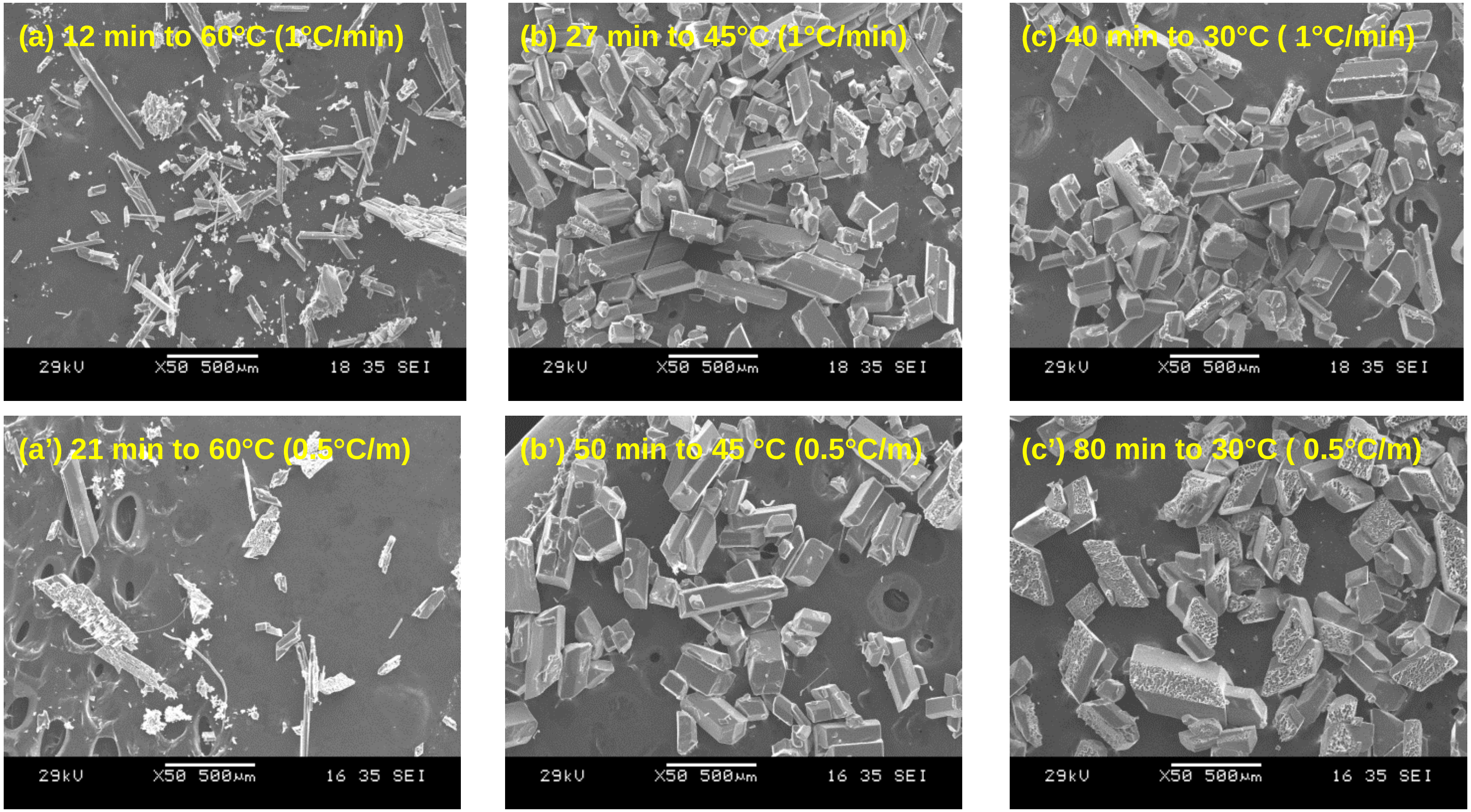
# Effect of Cooling Temperature Profile on $KHCO_3$ Crystallization



Cooling from 70 to 30 C at average rate of 1 C/min

- Temperature and turbidity break points occurred at 54 ± 3°C
  - Similar between linear, concave, and convex cooling processes
  - Similar between cooling rates of 1°C /min and 0.5°C /min (data not shown)
- Massive crystallization started at ~54°C and proceeded continuously
- Rate of crystallization controlled by cooling rate

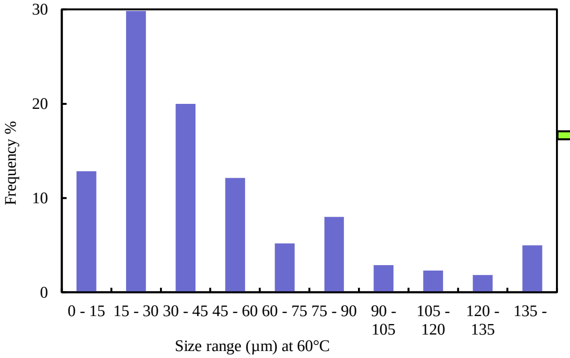
# Crystal Morphology & Structure during Crystallization

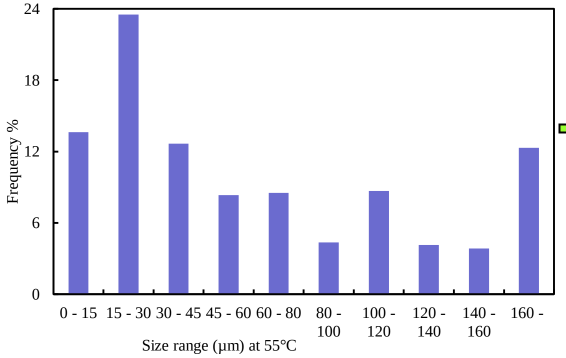


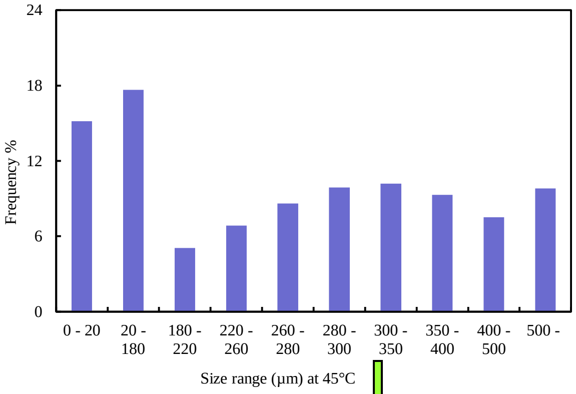
SEM images of crystal solids obtained from PC40-40 during linear cooling from 70°C

- ❑ Crystals went through a growth process
  - ➢ Crystal particles in hexagonal prism shape and grew in size during cooling
- ❑ Cooling at 0.5°C/min resulted in slightly larger particle size than 1°C /min but difference was not significant

# Crystal Particle Size Change during Crystallization

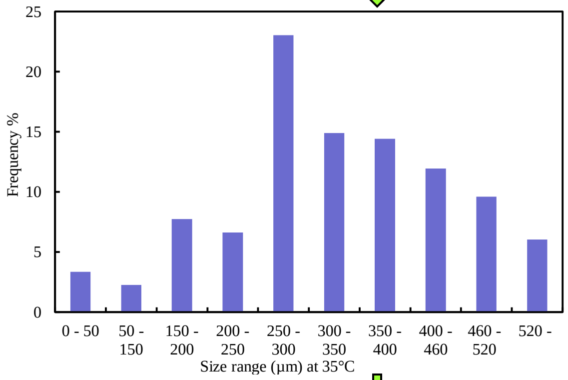


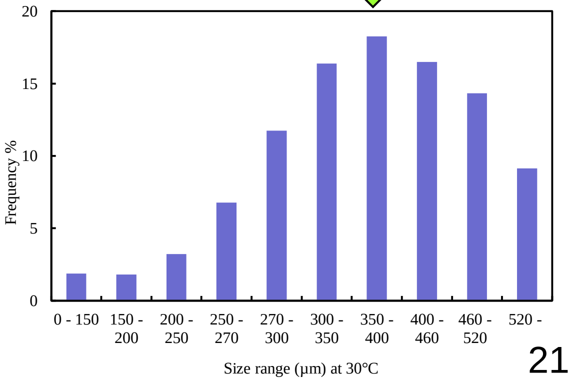




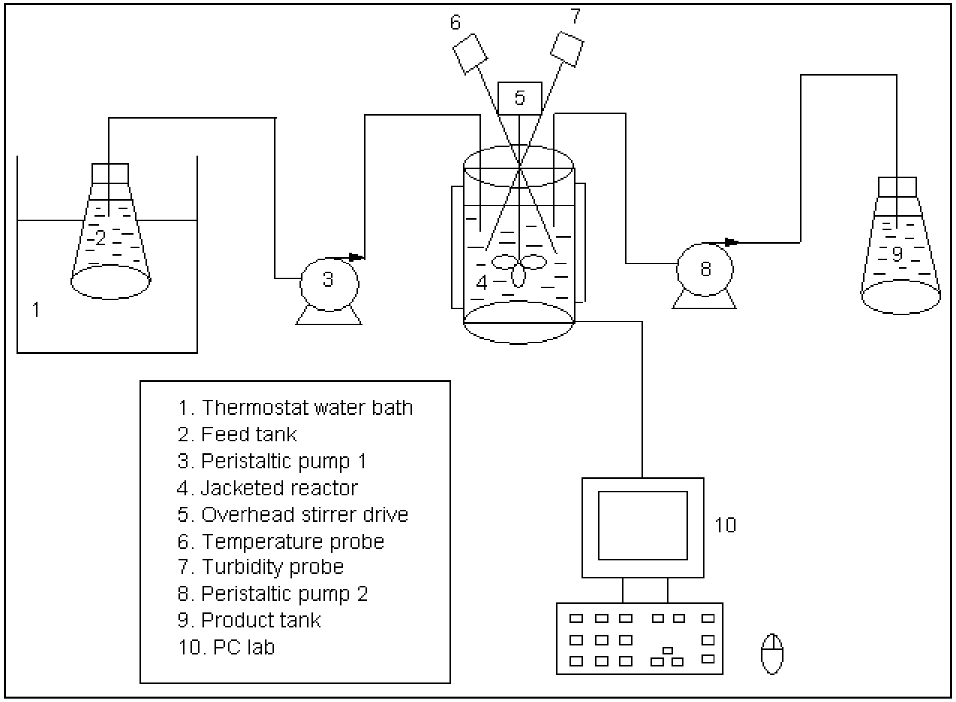
Histograms of crystal particle size distribution during linear cooling from 70 to 30°C at 1°C/min

- Crystal particle size increased proportionally with decreasing temperature (or increasing time)
- At 30°C (in 40 min), mode of crystal particle size occurred at 350−400µm





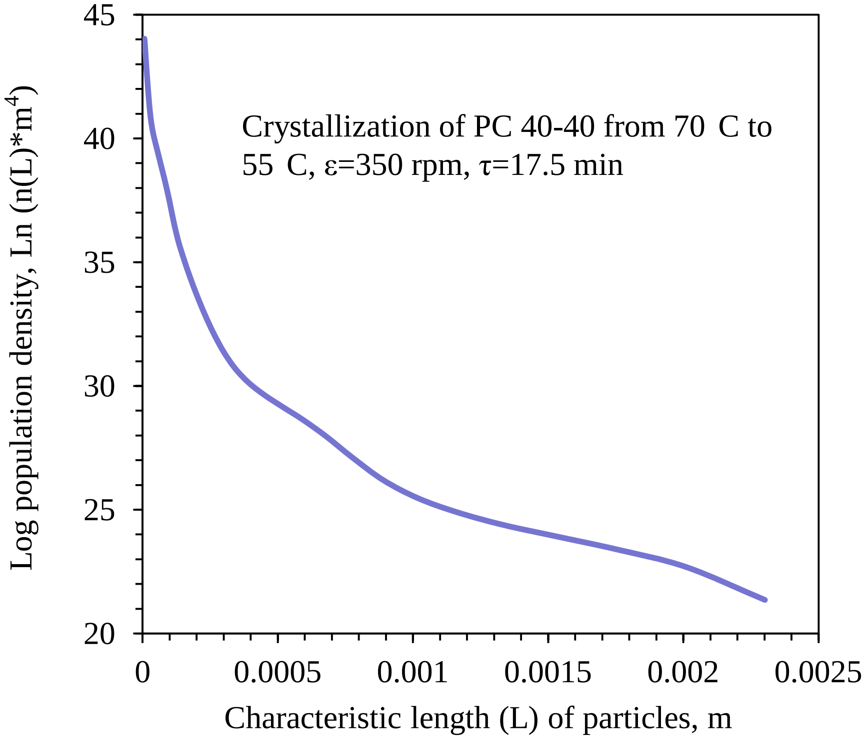
# Crystallization Kinetics Measurement under Mixed Suspension-Mixed Product Removal (MSMPR) Mode

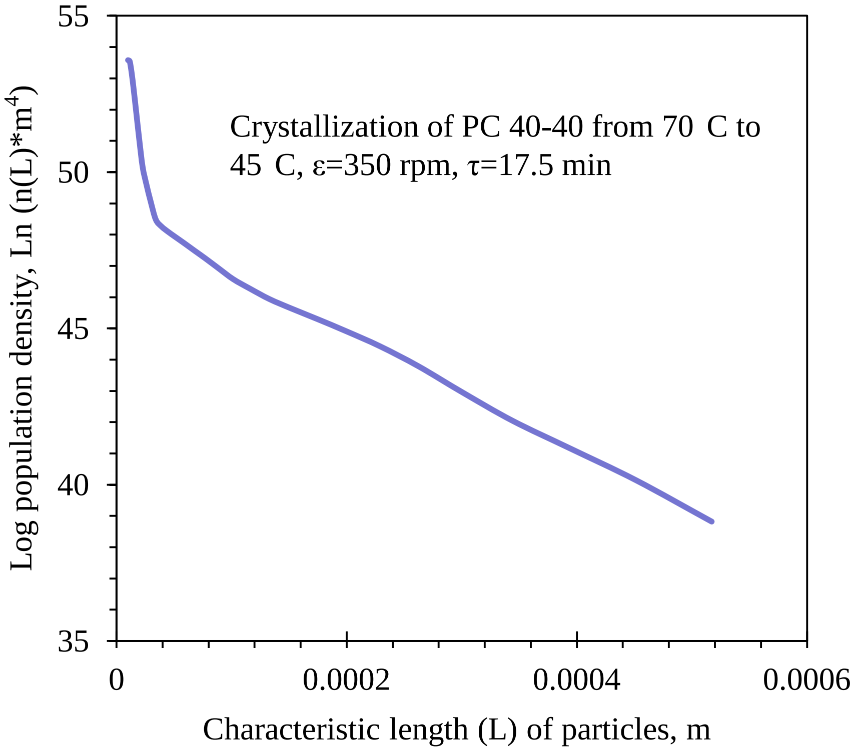


1. Thermostat water bath
2. Feed tank
3. Peristaltic pump 1
4. Jacketed reactor
5. Overhead stirrer drive
6. Temperature probe
7. Turbidity probe
8. Peristaltic pump 2
9. Product tank
10. PC lab

- MSMPR experiments to determine crystallization rate constants (nucleation and growth) from crystal particle size distribution (PSD) analysis

# MSMPR Results: Examples

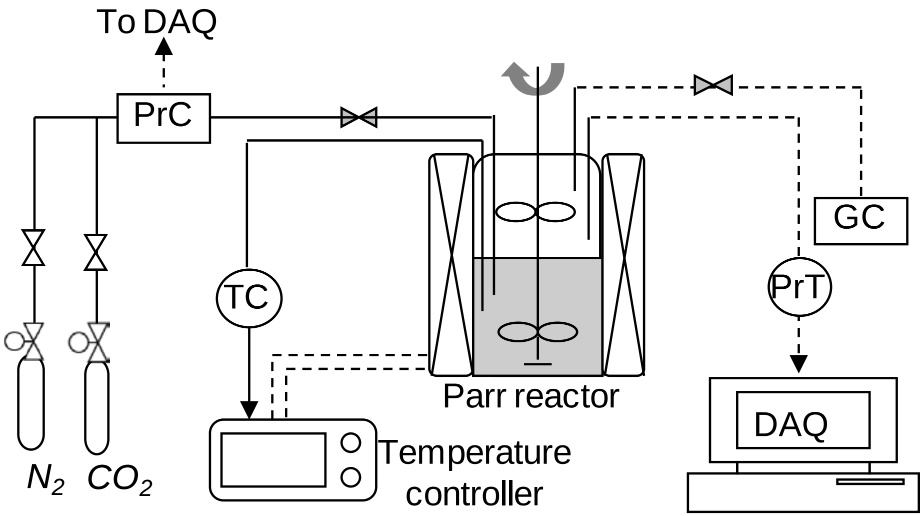


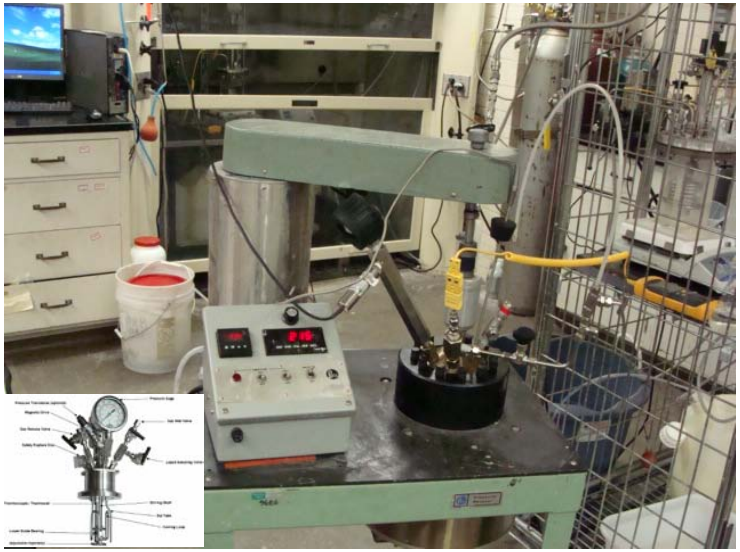


- Curves fitted to determine growth and nucleation kinetics, e.g.,
  - Average growth rate ($G_{av}$): $$G_{av} = \frac{M_T}{3\rho_s \tau k_v \int_0^\infty n(L) L^2 dL}$$
  - Total nucleation rate ($B_{TOT}$): $$B_{TOT} = \tau^{-1} \int_0^\infty n(L) dL$$

$M_T$: the suspension density,
$\rho_s$: the solid density,
$k_v$: the volume shape factor,
ε: the stirrer rpm

# 3.3 Vapor Liquid Equilibrium (VLE) Measurement of $K_2CO_3/KHCO_3$ Slurry

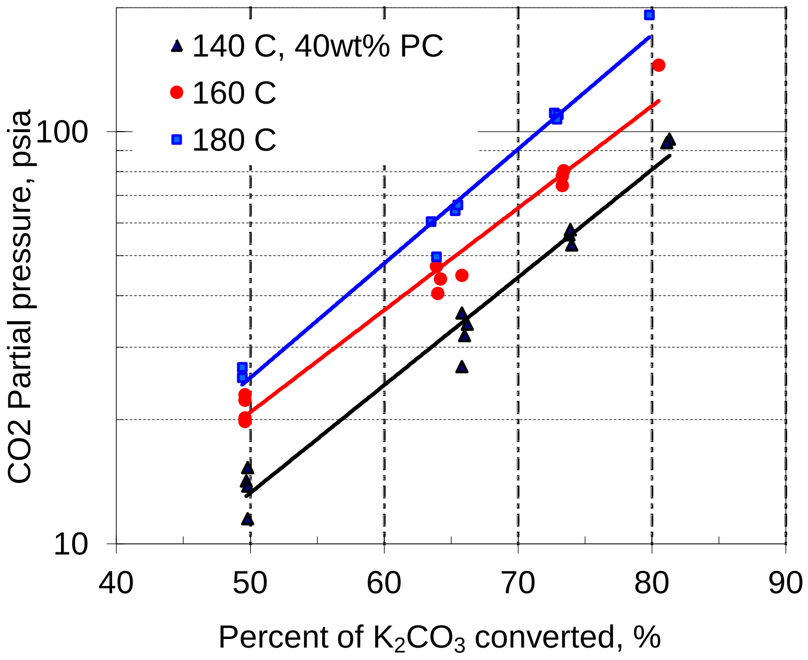


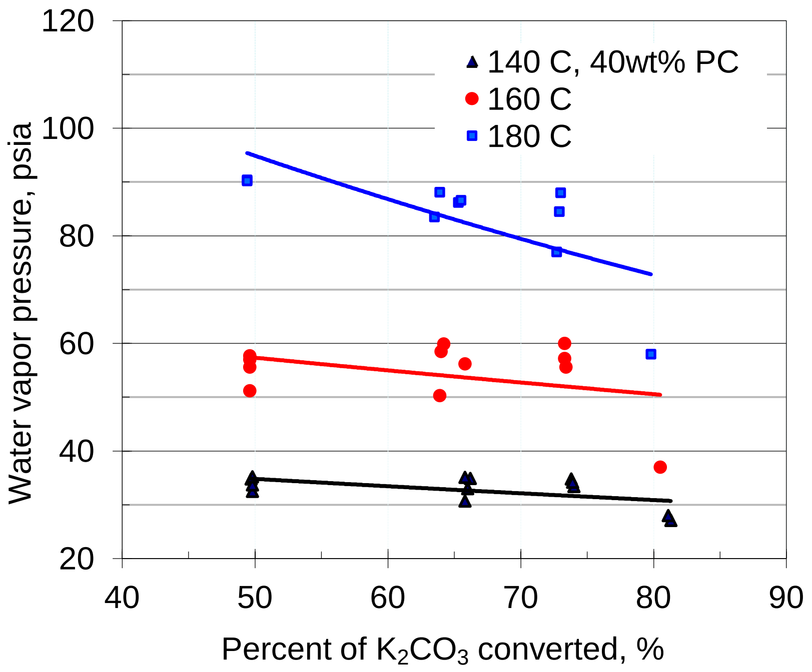


Parr Instrument Company, model 4531 (1 liter volume, maximum 1,900 psi (131 bar) at 275 C)

- ❑ Gas analysis using a GC-based method
- ❑ Liquid analysis using a back-titration method
- ❑ VLE measurement of bicarbonate slurry (40-70wt%) at 120-200°C and 1-40 bar

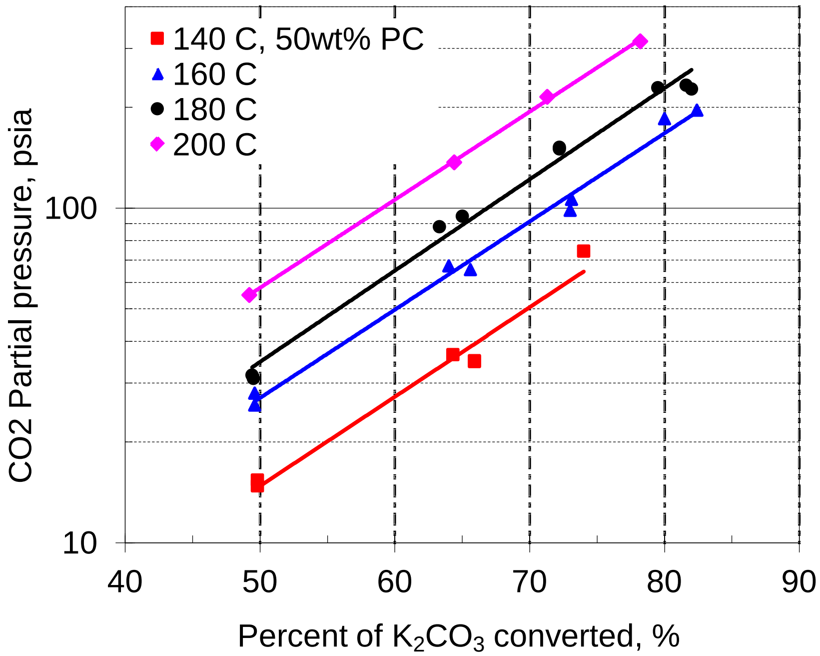
# VLE data for 40wt% $K_2CO_3$/$KHCO_3$ Solution at 140-180°C

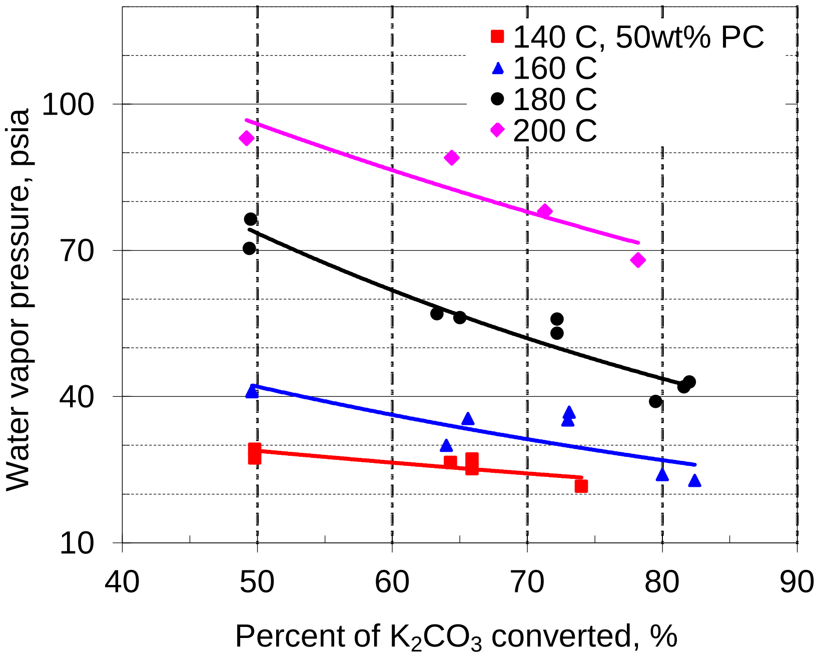




- ❑ $P_{CO2}$ increased significantly with increasing temperature and CTB conversion
- ❑ $P_{water}$ decreased with increasing CTB conversion

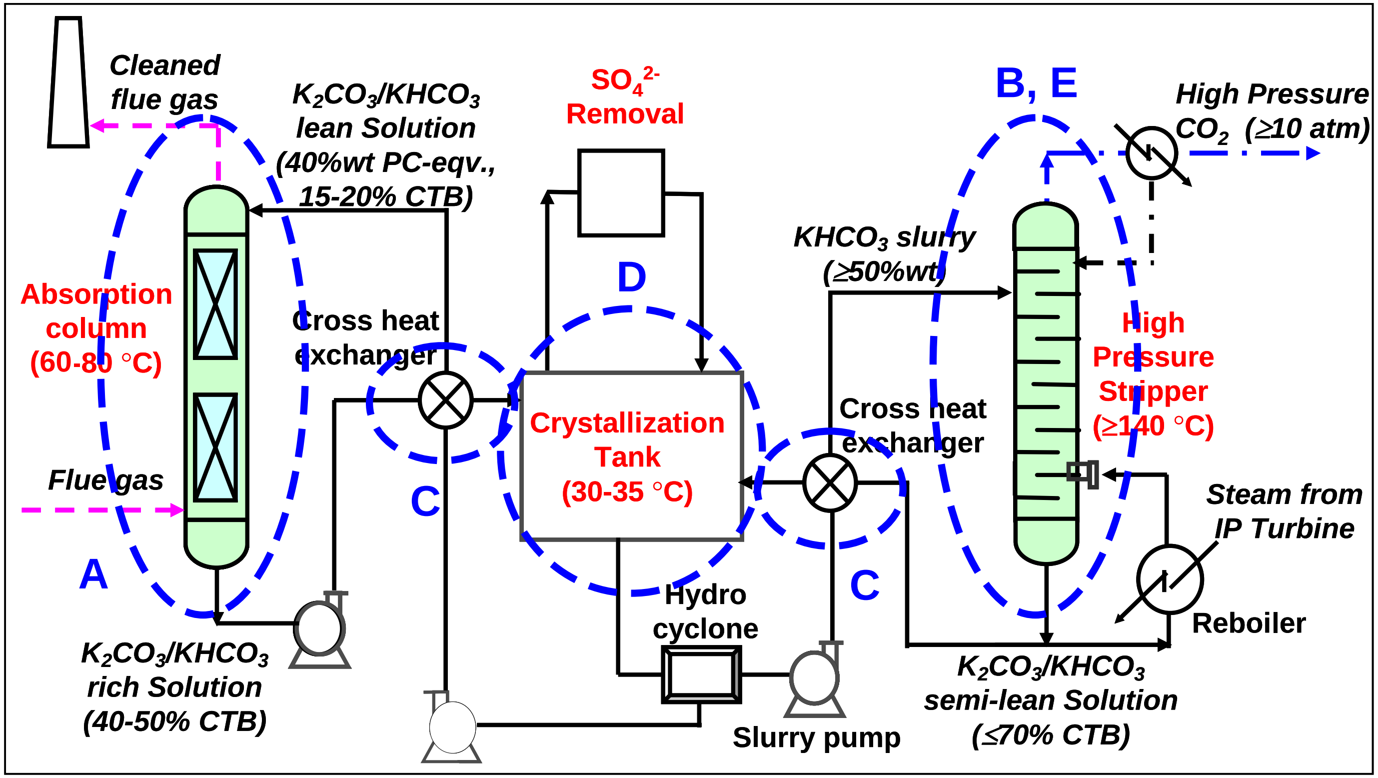
# VLE data for 50%wt $K_2CO_3$/$KHCO_3$ solution at 140-200°C





- ❑ $P_{CO2}$ reached ~300 psia at ~80% CTB conversion at 200°C
- ❑ $P_{total}$ attained ~370 psia
- ❑ Results demonstrated that producing a high pressure $CO_2$ stream is feasible in Hot-CAP

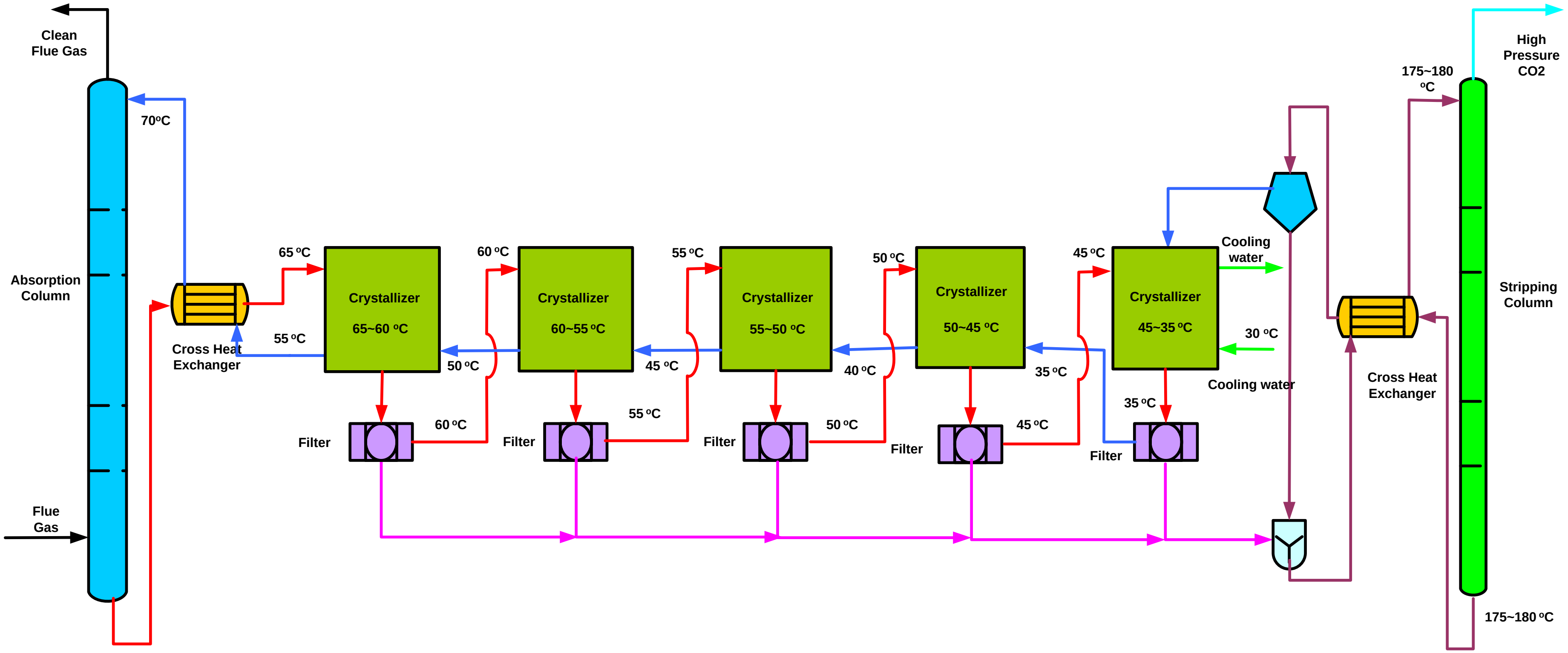
# 3.4 Technical Risks of Hot-CAP Process



Potential technical risks:

- ☐ A. Insufficient rate of $CO_2$ absorption
- ☐ B. Stripping pressure not high enough (e.g.,<10 atm)
- ☐ C. Heat exchanger and crystallizer fouling
- ☐ D. Insufficient cooling rate in crystallizer affects cost/space
- ☐ E. Stripper required to handle slurry and high pressure

# Modified Crystallizer Design Option



- ❑ Conventional single-crystallizer design requires a large ΔT between inflow and outflow, undesirable for heat recovery from inflow solution
- ❑ Multiple crystallization tanks/modules proposed with a crystallizer vendor to reduce ΔT between inflow and outflow of each crystallizer

# 4. Plans for Future Work/Development

Research Activities:

- ❑ Activity 1: Bench-scale absorption and high pressure stripping column tests
- ❑ Activity 2: Combined $SO_2$ removal and $CO_2$ capture in Hot-CAP
- ❑ Activity 3: Techno-economic studies
  - ➢ Risk mitigation of the high pressure stripper design
  - ➢ Process simulation and cost analysis

Process development:

- ❑ Continued interaction with equipment vendors to mitigate risks
- ❑ Efforts designed to assure lab/bench scale system is “compatible” with power plant environment
- ❑ Discussion of designs and results with engineering groups at utilities and other industries

# Acknowledgements

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