Project Title: **BENCH-SCALE DEVELOPMENT OF A HOT CARBONATE ABSORPTION PROCESS WITH CRYSTALLIZATION-ENABLED HIGH PRESSURE STRIPPING FOR POST-COMBUSTION CO₂ CAPTURE**

ICCI Project Number: 11/US-6  
Principal Investigator: Yongqi Lu, Illinois State Geological Survey – University of Illinois at Urbana-Champaign (ISGS-UIUC)  
Other Investigators: Manoranjan Sahu, Xinhuai Ye, Qing Ye, Massoud Rostam-Abadi, David Ruhter, Ivan Sugiyono (ISGS-UIUC)  
Kevin O’Brien, Scott Chen (Carbon Capture Scientific)  
Project Manager: Joseph Hirschi, ICCI

**ABSTRACT**

The University of Illinois at Urbana-Champaign (UIUC) and Carbon Capture Scientific (CCS), LLC are developing and evaluating a Hot Carbonate Absorption Process with Crystallization-Enabled High Pressure Stripping (Hot-CAP) to overcome the energy use disadvantage of conventional monoethanolamine (MEA)-based processes. Project objectives include performing a proof-of-concept study aimed at generating process engineering and scale-up data to help advance the Hot-CAP technology to pilot-scale demonstration level within three years. The project has two phases to achieve these objectives. This report presents a summary of the work performed during Phase I.

The Hot-CAP employs a potassium carbonate (PC) aqueous solution as a solvent. Three inorganic catalysts and ten organic promoters were investigated to accelerate the rate of CO₂ absorption into PC solutions. Rates into 40wt% PC solution promoted by three amine promoters at 70°C were higher than or comparable to those into 5M MEA at 50°C. A crystallization kinetic study was performed to investigate crystallization of potassium bicarbonate from CO₂-rich PC solutions under different cooling conditions. Results revealed that KHCO₃ was the only component in crystal particles – selected promoters added to the PC solution were not present. Mean particle size reached ~370µm with uniform size distribution during a linear cooling process (70 to 30°C in ~40 minutes). High-pressure vapor-liquid equilibrium data were measured for 40-60wt% PC slurry with different carbonate-to-bicarbonate (CTB) conversion levels at 140-200°C. High pressures (~400 psia) could be attained over PC slurry under equilibrium conditions, indicating that high-pressure CO₂ stripping for PC slurry is feasible with the Hot-CAP. Risk mitigation studies were conducted for two major technical risks in the design: the heat exchanger and the crystallizer. Vendor discussions and literature reviews were performed to address these two risks and a revised flowchart for the process was developed.
EXECUTIVE SUMMARY

The University of Illinois at Urbana-Champaign (UIUC) and Carbon Capture Scientific (CCS), LLC are developing and evaluating a Hot Carbonate Absorption Process with Crystallization-Enabled High Pressure Stripping (Hot-CAP) for post-combustion CO₂ capture. The Hot-CAP uses a carbonate salt (e.g., K₂CO₃) as a solvent and integrates warm temperature (60-80°C) CO₂ absorption, crystallization of bicarbonate from a CO₂-rich solution, bicarbonate slurry-based high-pressure (10-40 bar) CO₂ stripping, and combined SO₂ removal with CO₂ capture. A preliminary techno-economic analysis shows that the energy use of the Hot-CAP is about 0.21 kWh/kg CO₂ capture, about 40% less than that of its MEA counterpart.

Objectives of the project include performing a proof-of-concept study aimed at generating process engineering and scale-up data to help advance the Hot-CAP technology to pilot-scale demonstration level within three years. The project is being performed in two phases: Phase I from January 1, 2011 to June 30, 2012 and Phase II from July 1, 2012 to December 31, 2013. This report is a summary of the work completed during Phase I.

CO₂ absorption into a carbonate solution without a promoter or catalyst tends to be slower than that into an amine. Parametric tests of CO₂ absorption were performed using a batch stirred tank reactor. Rate constants of the absorption reaction in 40wt% potassium carbonate (PC) solution with carbonate-to-bicarbonate (CTB) conversion levels between 20 and 40% at 60, 70, and 80°C were determined. Rates into the 40wt% PC with 20% CTB conversion (PC40-20) at 80°C were 13-32 times lower than those into the 3M MEA loaded with 0.2 mol/mol CO₂ (MEA3-40) at 50°C.

Three Lewis-base inorganic salts (CAT1, CAT2, and CAT3) were investigated as catalysts for absorption. Adding 4wt% CAT1 or CAT2 into PC40-20 raised CO₂ absorption rates by twice at 60-80°C. Increasing catalyst (CAT2) dosage from 4 to 6wt% further increased rates by up to 23% depending on the temperature.

Five amino acid salts (K-glycine, K-sacrosine, K-proline, K-taurine, and K-alanine) and five amines (diethanolamine (DEA), 2-amino-2-methyl-1-propanol (AMP), piperazine (PZ), hexamethylene diamine (HDA), and hexylamine (HA)) were selected as organic promoters for CO₂ absorption. K-sacrosine and K-glycine improved absorption rates more significantly than other amino acid salts; however, even promoted rates at 70°C were still several times lower than those into MEA3-40 at 50°C.

Among the five amine promoters, rates promoted with PZ and AMP were the highest, followed by HDA. Rates into PC40-20 promoted with 1M PZ, 1M AMP, and 1M HDA at 70°C were higher than or comparable to those into 5M MEA loaded with 0.2 mol/mol CO₂ (MEA5-40) at 50°C. Results indicated that amine promoters are promising for significantly accelerating CO₂ absorption into PC solutions.
Crystallization of KHCO₃ formed during CO₂ absorption from CO₂-rich PC solutions is an important step in the Hot-CAP. Crystallization kinetic studies were performed at different cooling pathways and rates using an automated calorimetric reactor system. The 40wt% PC solution with 40% CTB conversion (PC40-40) at 70°C was employed to simulate the CO₂-rich solution exiting the Hot-CAP absorber. In all examined cooling processes, a temperature break point at 54±3°C was observed, below which massive crystallization occurred and continued. SEM analysis showed that the mean size of crystal particles increased with decreasing temperature during cooling. For the linear cooling process, mean particle size was ~370μm, and the mode occurred at 350-400μm when the temperature was cooled down to 30°C. The particle size was uniform, about 92wt% within 250-520μm. The size of crystal particles from the convex cooling process tended to be slightly larger than those from linear and concave cooling processes.

XRD analysis showed that AMP, PZ, and their organic derivatives were not present in crystal products from PC40-40. Crystal particles from PC40-40+1M AMP consisted solely of HKCO₃. Crystal particles from the PC40-40+0.2M PZ consisted of HKCO₃ and a small amount of K₂H₂(CO₃)₃·1.5H₂O. Crystal particles from PC40-40+K₂SO₄ contained only a small quantity of K₂SO₄. Vapor-liquid equilibrium (VLE) data are essential for design and scale up of the stripping column in the Hot-CAP. VLE data for 40, 50, and 60wt% PC slurry with different CTB conversion levels at 140-200°C were measured using a high pressure autoclave reactor. The partial pressure of CO₂ increased significantly with increasing temperature and CTB conversion level, whereas that of water vapor increased with increasing temperature but slightly decreased with increasing CTB conversion level. Results showed that high pressure could be attained over PC slurry under equilibrium conditions. For example, partial pressure of CO₂ over 50wt% PC at 200°C was greater than 300 psia, and total pressure was greater than 380 psia when the CTB conversion level was at ~80%. Thus, high-pressure CO₂ stripping using PC slurry was shown to be feasible for the Hot-CAP process.

Risk mitigation studies were conducted with a focus on the two major technical risks in the design: the heat exchanger and the crystallizer. Vendor discussions and literature reviews were performed to address these two risks. A revised flowchart for the process with multiple crystallizer units was developed to meet the need of heat recovery from inflow CO₂-rich solution to mother liquid.

In Phase II, CO₂ absorption testing will continue by using a bench-scale, packed-bed absorber fabricated in Phase I. A high-pressure stripping column will be designed and fabricated, and experiments will be performed to evaluate the slurry-based stripping performance under continuous mode. A feasibility study will be conducted to prove a process concept for combined SO₂ removal and CO₂ capture. Finally, experimental results will be used as a basis for performing risk analysis, process simulation, and techno-economic studies to evaluate the overall performance of the Hot-CAP as a post-combustion CO₂ capture process for coal-fired power plants.
OBJECTIVES

The Hot Carbonate Absorption Process with Crystallization-Enabled High Pressure Stripping (Hot-CAP) is being developed as a post-combustion CO₂ capture technology to overcome the energy use disadvantage of conventional monoethanolamine (MEA)-based processes. Objectives of this proof-of-concept study are to generate process engineering and scale-up data for advancing Hot-CAP technology to the pilot-scale demonstration level within three years. The project employs lab- and bench-scale test facilities to measure thermodynamics and reaction engineering data for evaluating technical feasibility and cost-effectiveness, performance and scale up, and commercial competitiveness in two 18-month phases. The following work activities were involved in Phase I:

1 – Testing of CO₂ Absorption into Carbonate Solution: CO₂ absorption into 40wt% potassium carbonate (PC) solutions at 60-80°C was measured using a stirred tank reactor, and classic absorption theory was applied to determine kinetic parameters. Three inorganic catalysts, five amine promoters, and five amino acid salt promoters, were tested for their ability to accelerate rates of CO₂ absorption into PC solutions with results compared to absorption rates of MEA solutions. Effects of major impurities, such as a sulfate salt, on CO₂ absorption were also investigated. A bench-scale, packed-bed column of 10-cm diameter and 2-m height was designed and fabricated for these studies.

2 – Testing of Potassium Bicarbonate Crystallization from PC Solution: An automated calorimetric reactor system was used to study the crystallization of potassium bicarbonate from the 40wt% PC solution. Parametric tests were conducted to investigate the crystallization performance of potassium bicarbonate under different cooling rates, residence times, cooling profiles, end temperatures, and presence of absorption promoters and/or potassium sulfate salt. Dynamic changes in morphology and structure of crystal samples were characterized by XRD, particle size distribution, and SEM analyses.

3 – Measurement of Vapor Liquid Equilibrium (VLE) for Potassium Bicarbonate/Carbonate Slurry: A high-pressure stirred cell reactor setup was assembled for VLE measurements. An experimental procedure, including gas and liquid sampling and analysis, was developed and verified by comparing experimental data with data available in the literature. VLE measurements were performed for K₂CO₃/KHCO₃ slurry at different K₂CO₃-equivalent weight concentrations (≥ 40wt%), carbonate-to-bicarbonate (CTB) conversion levels (≥ 50%), and temperatures (140-200°C). The presence of potassium sulfate salt and its effect on VLE behavior were also investigated.

4 – Risk Mitigation and Techno-economic Analysis: Major technical risks associated with the development of the Hot-CAP were identified and a risk mitigation study was performed focusing on the two technical risks in the design: the heat exchanger and the crystallizer. After a literature review and discussions with vendors, a new crystallization process flowchart was proposed to facilitate heat recovery and to prevent fouling of potassium bicarbonate on the surface of the heat exchanger and crystallizer. Risk mitigation and techno-economic modeling work will continue in Phase II.
INTRODUCTION AND BACKGROUND

CO₂ capture from coal-fired power plant flue gas is the most expensive step in an integrated CO₂ capture, sequestration, and storage (CCS) process. According to a recent review of capture technologies, commercially available conventional mono-ethanol-amine (MEA) absorption processes typically cost 50 to 70 $/tonne CO₂ avoided.[1] The major cost contributor, amounting to about 60%, is due to energy use for CO₂ stripping and compression that results in a significant de-rating (about 30%) of the power plant.[2,3] Reducing energy consumption of the MEA process is the key to lowering total CO₂ capture cost.

In the stripper of an absorption-based CO₂ capture process (see Figure 1), steam supplies the energy required by the three components of heat: heat of reaction (heat of absorption and crystallization), sensible heat, and stripping heat (per unit mass or mole CO₂):

\[ Q_{\text{Total}} = Q_{\text{Sensible}} + Q_{\text{Reaction}} + Q_{\text{Stripping}} \]  

(1)

In addition, work is required for compressing CO₂ from the operating pressure of a stripper (e.g., about 25 psia in the MEA process) to a sequestration-ready pressure of 2,000 psia, which strongly depends on operating pressure and steam usage in the stripper.

For a baseline MEA process, \( Q_{\text{Sensible}} \), \( Q_{\text{Reaction}} \), and \( Q_{\text{Stripping}} \) are roughly 450, 825, and 275 Btu/lb CO₂, respectively (a total of about 1,550 Btu/lb CO₂).[4] This large energy requirement for the MEA process lies mainly in the following four factors: 1) a high \( Q_{\text{Reaction}} \), 2) a high solvent recirculation rate which increases \( Q_{\text{Sensible}} \) and power used by the circulation pump, 3) a stripper operating at near atmospheric pressures resulting in higher compression work, and 4) a high \( Q_{\text{Stripping}} \) per unit of CO₂ regeneration because

![Figure 1: Schematic of three heat components required in CO₂ stripper column.](image)
water vapor pressure in the gas stream leaving the stripper being operated at a low pressure accounts for a large portion of the total pressure at the top of the stripper.

To overcome the disadvantage of this intense energy use incurred by a conventional MEA process, the Hot Carbonate Absorption Process with Crystallization-Enabled High Pressure Stripping (Hot-CAP) was proposed and is evaluated in this project.

In the Hot-CAP, diagrammed in Figure 2, hot flue gas (at 150°C) exiting the electrostatic precipitator (ESP) or baghouse of a power plant is directly introduced into an absorption column operating at 70-80°C and atmospheric pressure where CO₂, SO₂, and other acid gases are absorbed into a carbonate (K₂CO₃ or Na₂CO₃) solution. The CO₂-rich carbonate solution exiting the absorption column is cooled in a heat exchanger by the CO₂-lean carbonate solution circulating to the column prior to entering a crystallization reactor. In the crystallizer, bicarbonate crystals are formed due to the low solubility of bicarbonate at low temperature (25-35°C). These crystals are filtered and the resulting slurry is heated using the warmer regenerated lean carbonate solution from the stripper before entering a high pressure stripper, which operates at up to 40-atm and 140-200°C. The CO₂-rich gas stream released in the stripper contains a relatively small amount of water vapor. Upon exiting the stripper, it is further cooled, dehydrated, and compressed to a sequestration-ready pressure. The CO₂-lean solution exiting the stripper returns to the crystallization reactor after exchanging heat with the feed slurry. It should be noted that because of the crystallizer in the Hot-CAP, the stripping process is decoupled from and thus independent of the absorption process.

![Figure 2: Schematic diagram of proposed Hot-CAP process.](image_url)

For sulfate removal, a small slipstream of the carbonate solution is extracted from the crystallization tank and fed to a declaimer unit where hydrated lime is added to convert SO₄²⁻ in the solution to CaSO₄ (gypsum) crystals, which are separated from the solution by a filtration unit. The pH of the solution in the sulfate declaimer is adjusted using small
amounts of high-pressure CO\(_2\). The reclaimed solution passes through a flash unit (not shown in Figure 2) and then returns to the crystallization tank after CO\(_2\) is separated.

The Hot-CAP reduces all three heat components (\(Q\)\(_{reaction}\), \(Q\)\(_{sensible}\) and \(Q\)\(_{stripping}\) in the CO\(_2\) stripper unit and the CO\(_2\) compression work. The carbonate solution has a smaller heat of absorption (7kcal/mol CO\(_2\)) than the MEA. Even with inclusion of the heat of crystallization, the overall heat of reaction, \(Q\)\(_{reaction}\) (absorption + crystallization), ranges between 7 and 17kcal/mol CO\(_2\) depending on the desired bicarbonate slurry concentration. In comparison, the heat of absorption for the MEA solution amounts to 21kcal/mol CO\(_2\).

Because bicarbonate slurry is used for CO\(_2\) stripping, the CO\(_2\) working capacity of the solvent can be significantly increased. For example, for 50wt% bicarbonate slurry, the working capacity of the solvent in the stripper is 1.5-3 times higher than that of the MEA process. Furthermore, the working capacity can be adjusted according to process requirements because the concentration of the slurry can be controlled. A higher working capacity reduces the energy required to heat the slurry, i.e., results in a lower sensible heat, \(Q\)\(_{sensible}\).

Additionally, carbonate salt (K\(_2\)CO\(_3\) or Na\(_2\)CO\(_3\)) does not degrade at high regeneration temperatures. As a result, the stripper in the Hot-CAP can be operated at higher pressures. A higher stripping pressure, mostly contributed by the CO\(_2\) partial pressure, not only reduces stripping heat, \(Q\)\(_{stripping}\), but also compression work. In theory, if stripping pressure is sufficiently high, compression work may be eliminated. A preliminary techno-economic analysis shows that energy use of the Hot-CAP is about 0.21 kWh/kg CO\(_2\) capture, about 40% less than that of its MEA counterpart.

EXPERIMENTAL PROCEDURES

Testing CO\(_2\) Absorption

A stirred tank reactor (STR) experimental system was fabricated and assembled to measure rates of CO\(_2\) absorption into potassium carbonate aqueous solutions with and without promoters/catalysts at conditions typical of the Hot-CAP process. The setup, shown in Figure 3, consists of three major parts: a stirred tank reactor (STR), a gas supply/control unit, and data acquisition instrumentation. The reactor is a 4-inch internal diameter (ID), 7-inch high Plexiglas vessel with four symmetrical baffles, each 0.5-inch in width, attached inside the vessel to prevent vortex formation in the liquid phase. A magnetic stirrer (VWR Scientific, Series 400 HPS) with a 2-inch Teflon stir bar provides mixing at controllable speeds for the liquid phase. A second stirrer driven by an external motor (Caframo, Model BCD2002) via magnetic coupling (MMC Maganetics, FCM-1) provides mixing up to 3,000 rpm for the gas-phase. Reactor temperature is controlled by water circulation through a 0.6-cm outside diameter (OD) stainless steel coil inside the reactor and a temperature controlled thermostatic water bath (VWR Scientific, Model 1140A) outside the reactor, and is measured by a thermocouple (Omega, Type K, Model KMQSS-125-G-6). Pressure of the gas stream into the reactor is controlled/measured by a pressure transducer (Alicat Scientific, PC-30PSIA-D/5P). A vacuum pump (Dekker,
RVL002H-01) is equipped to provide the required initial vacuum level for the system. Pressures and temperatures are monitored and recorded by a computer through a National Instrument Digital Data Acquisition System (NI USB 6009).

![Schematic and photograph of STR experimental system.](image)

Figure 3: Schematic and photograph of STR experimental system.

The experiment operates under batch mode and pure CO\(_2\) is used. In a typical experiment, about 800 ml of solution with the desired composition is fed into the reactor. The system is evacuated to strip off air residue and other gas components and is then allowed to stabilize. After water vapor pressure over the solution is measured, a pure CO\(_2\) gas stream is introduced into the reactor in a short (<3 sec) time period to a predetermined pressure, and both stirrers (liquid phase at 450 rpm, gas phase at 300 rpm) are immediately turned on. Change in total gas pressure with time is recorded, from which CO\(_2\) partial pressure is obtained by deduction of the \(P_w\) term. Since pure CO\(_2\) is used under vacuum conditions, mass transfer resistance in the gas phase is negligible in kinetic measurements.

The instantaneous rate of CO\(_2\) absorption into the liquid phase can be calculated from the change of CO\(_2\) partial pressure over time using the following equation:

\[
J_i = -\frac{V_G}{AT} \frac{dp_i}{dt}
\]  

(2)

where \(J_i\) is the absorption flux of CO\(_2\); \(V_G\) is the volume of the gas phase; \(A\) is the gas-liquid interfacial area; \(R\) is the universal gas constant; \(T\) is the temperature; \(p_i\) is the CO\(_2\) partial pressure; and \(t\) is time.

**Testing Potassium Bicarbonate Crystallization**

An automated calorimetric reactor system (Atlas Potassium Automated Synthesis Calorimeter Reactor, Syrris Inc.) was purchased and assembled for the crystallization study (see Figure 4). The 1,000-ml reaction vessel is double-jacketed with the inner oil
jacket for temperature control and the outer vacuum jacket for thermal insulation from the environment. The system can operate at temperatures between -10 and 150°C. A turbidity probe (Atlas, Syrris Inc.) is attached to the reactor to detect the inception of crystallization and to measure the *in situ* turbidity change during the crystallization process. Operation of the system and data logging are controlled by a computer using Atlas software.

![Figure 4: Photographs of automated calorimetric reactor setup for crystallization study.](image)

In a typical experiment, the reaction vessel was charged with a 500-ml solution of 40wt% PC with 40% carbonate-to-bicarbonate conversion level (PC40-40), either with or without a salt additive or absorption promoter, at 70.0°C. The desired cooling rate and cooling pathway (i.e., linear, concave, and convex) are programmed to cool the solution to an end temperature ranging from 25 to 35°C. During the cooling crystallization process, solution in the reactor is sampled (5 ml per sample) at desired temperatures to investigate the dynamic change in crystal morphology and structure. Suspension samples are immediately vacuum-filtered through 0.2 μm membranes (Whatman). Collected crystal solids are characterized using a scanning electron microscope (SEM, S-6000, Hitachi), x-ray diffraction (XRD, Bruker D5000, Siemens), and a particle size distribution analyzer (Partica LA-950, Horiba Scientific).

When K₂SO₄ is added to PC40-40, a wet chemistry method consisting of the following steps is applied to detect its presence in the crystal product: (1) dissolving a known amount of crystal sample in deionized water, (2) adding several drops of 12M HCl solution to thoroughly neutralize CO₃²⁻, (3) mixing with an excessive amount of 0.4M BaCl₂ solution, and (4) filtering the suspension to obtain BaSO₄ solids. By measuring the weight of dried solids, the content of K₂SO₄ in the original sample can be determined.

**Measuring Vapor Liquid Equilibrium (VLE)**

A high pressure autoclave reactor system (Parr Instrument Company, Model 4531) was assembled to measure VLE data of K₂CO₃/KHCO₃ slurry with K₂CO₃-equivalent
concentrations greater than 40wt% at temperatures ranging between 140 and 200°C. The experimental setup, shown in Figure 5, consists of a high pressure stirred cell reactor, a gas supply/control unit, data acquisition instrumentation, and a gas chromatograph (GC) for measuring gas composition.

The high pressure Parr reactor is a 1-liter cylinder with 4.0-inch ID and 5.4-inch depth furnished with a self-sealing, FFKM O-ring closure for bearing working temperatures up to 275°C and pressure up to 1,900 psia (131 bar). The reactor is equipped with a DC variable speed magnetic stirrer with maximum torque of 16 inch-pounds supplied with and controlled through a Parr Series 4840 controller to provide stirring speeds for both gas and liquid phases from 0 to 600 rpm. Valves and gauges include gas inlet valve, gas release valve, liquid sampling valve, pressure gauge, and safety rupture disc for emergency ventilation, all of which are built into the reactor. An external furnace is used to heat the reactor with temperature controlled through a separate Parr Series 4840 Temperature Controller. A continuous flow of cold water with adjustable flow rates through the coil in a serpentine configuration optionally installed inside the reactor can be used to control temperature, particularly when desired operating temperatures are below 150°C.

A vacuum pump (Dekker, RVL002H-01) is used to remove residual air, inert gas, or other undesirable gases, if any, from the experimental system. Reactor pressure is measured by a pressure transducer (Omega, PX409-1.0KAUSB) and monitored/recorded by a computer. A GC (Shimadzu GC-2014) equipped with a TCD and a RT®-Q-Bond column is used to measure gas compositions. Gas samples are obtained using a 100 µl syringe (Cat.#20162, Restek Corporation) through a 10 mm septa fit into a ¼” tee tubing gas sampling port.

VLE measurements for the K₂CO₃/KHCO₃ aqueous system are performed under batch mode. In a typical experiment, 1,000 g K₂CO₃/KHCO₃ slurry of a desired composition is
fed into the Parr reactor. After careful assembling and leakage checking, the system is evacuated to a required level at room temperature. Stirrers for both gas and liquid phases are turned on (both at 250 rpm) while the furnace heater heats up the reactor to the desired temperature with the system approaching an equilibrium state in about two hours when pressure change is negligible over time. A pure N₂ gas stream is then introduced into the reactor to a predetermined pressure. After stabilization, the N₂ gas partial pressure in the reactor is determined and recorded by the difference between total pressures prior to and after N₂ gas injection. The gas sample for GC analysis is extracted using the syringe from the gas stream released from the reactor through a needle valve.

The VLE measurement is based on a desorption method. The K₂CO₃/KHCO₃ aqueous system is exposed for desorption under desired conditions. When desorption reaches an equilibrium state, a pure N₂ gas stream is introduced into the Parr reactor to a predetermined pressure. CO₂ partial pressure (Pᵢ) is determined from the CO₂:N₂ concentration ratio determined by the GC and the known N₂ gas partial pressure in the reactor. Consequently, water vapor partial pressure can be obtained by the following equation:

\[
P_{\text{H₂O}} = P_T - P_i - P_{N₂}
\]

where \(P_T\) is the total pressure of the system recorded by the pressure transducer.

The equilibrium liquid composition can be obtained from the predetermined composition of the initial K₂CO₃/KHCO₃ slurry and the mass balance of CO₂ in liquid and gas phases. Because a much larger amount of solution is used and the volume of the gas phase is small, the change in liquid composition is usually negligible and may be compensated, if necessary, from the CO₂ desorption.

RESULTS AND DISCUSSION

**Kinetics of CO₂ Absorption into PC Solution**

**CO₂ Absorption Rates without Promoters:** The effect of temperature on the rate of CO₂ absorption into 40wt% PC with 20% CTB conversion (PC40-20) is shown in Figure 6. Henry’s constant (CO₂ solubility) and reaction kinetics, both of which affect CO₂ absorption rates, are a strong function of temperature. As temperature increases, CO₂ solubility decreases, while the rate constant of the absorption reaction (\(\text{OH}^- + \text{CO}_2 = \text{HCO}_3^-\)) increases. The net effect of temperature on CO₂ absorption rate depends on which term is more significant. Results reveal that increasing reaction temperature from 60 to 80°C remarkably improved CO₂ absorption rates.
Figure 6: CO\textsubscript{2} absorption into PC40-20 and PC40-40 at 60, 70, and 80°C.

When absorption of CO\textsubscript{2} into PC40-20 at 80°C was compared to that into PC40-40, it can be seen in Figure 6 that the higher the CTB conversion rate, the lower the CO\textsubscript{2} absorption rate for PC solutions with the same concentration. The equilibrium pressure of CO\textsubscript{2} over PC40-40 at 80°C is much higher than that over PC40-20. As a result, under the same operating CO\textsubscript{2} partial pressure, the driving force for CO\textsubscript{2} absorption into PC40-40 was significantly reduced.

**Determination of Rate Constants:** For absorption of CO\textsubscript{2} into PC solution, the major reactions are:

\[
CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \quad (R1)
\]

\[
CO_2 + OH^- \rightleftharpoons HCO_3^- \quad (R2)
\]

Under certain conditions, absorption reactions can be pseudo-first-order with respect to CO\textsubscript{2}, whose rates are a linear function of the hydroxide ion concentration: \[5,6,7,8\]

\[
r = -d[CO_2]/dt = k_{ov} \times [CO_2] \quad (4)
\]

\[
k_{ov} = k_{H_2O} + k_{OH}[OH^-] \quad (5)
\]

where \(k_{ov} (s^{-1})\) is the overall first-order rate constant, and \(k_{H_2O} (s^{-1})\) and \(k_{OH} (m^3 kmol^{-1} s^{-1})\) are kinetic rate constants for reactions (R1) and (R2), respectively. The value of \(k_{H_2O}\) is small (between 0.02 and 0.0375 \(s^{-1}\) at 25-50°C)[8-10] and thus negligible compared to the value of \(k_{OH}\), which varies from 6×10\textsuperscript{3} to 3×10\textsuperscript{7} \(m^3 kmol^{-1} s^{-1}\) depending on temperature and ionic type and strength in the PC solution.[8,11,12]

Experiments were performed to ensure that the absorption reaction satisfied the pseudo-first-order assumption defined by the following equations, which can be derived based on the mass conservation principle, the ideal gas law, and Henry’s law:[13]
\[
J_i = - \frac{V_G}{AR T} \frac{dP_i}{d t} = k_L \sqrt{\left( 1 + \frac{Dk_{ov}}{k_L^2} \right)} \times (C^* - C^b)
\]  
(6)

\[
C^* = \frac{P_i}{He_i}
\]  
(7)

where \(k_L\) is the physical mass transfer coefficient in liquid phase, \(D\) is the diffusivity of \(CO_2\), \(C^*\) and \(C^b\) are the physical solubility of \(CO_2\) at the pressure prevailing at the interface and the concentration of free molecular \(CO_2\) in liquid phase, respectively, and \(He_i\) is the Henry’s law constant.

The value of \(C^b\) is negligible compared to \(C^*\) in an alkaline solution. Therefore, by combining Equations (6) and (7) and integrating, the following equation is obtained:

\[
Ln\left( \frac{P_{i,0}}{P_i} \right) = \sqrt{k_L^2 + Dk_{ov}} \frac{RTA}{V_G He_i} \Delta t
\]  
(8)

where \(P_{i,0}\) is the initial partial pressure of \(CO_2\). Values of related kinetic rate constants, \(k_{ov}\) and \(k_{OH}\), are determined from the slope of the straight line obtained by plotting \(Ln(P_{i,0}/P_i)\) vs. \(RTA\Delta t/(V_G He_i)\).

Values of \(k_{ov}, [OH]\), and \(k_{OH}\) determined from these experiments are listed in Table 1. It should be noted that few reports are available for \(k_{OH}\) in PC solutions with moderate to high CTB conversion levels and high carbonate concentrations comparable to those employed in the Hot-CAP.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>PC Solution</th>
<th>(k_{ov}, (s^{-1}))</th>
<th>([OH], (mol/L))</th>
<th>(k_{OH}, (L/mol s^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>PC40-20</td>
<td>2.99×10^4</td>
<td>2.68×10^{-3}</td>
<td>1.11×10^6</td>
</tr>
<tr>
<td>70</td>
<td>PC40-20</td>
<td>6.82×10^4</td>
<td>4.33×10^{-3}</td>
<td>1.57×10^6</td>
</tr>
<tr>
<td>80</td>
<td>PC40-20</td>
<td>1.23×10^5</td>
<td>6.75×10^{-3}</td>
<td>1.82×10^6</td>
</tr>
<tr>
<td>80</td>
<td>PC40-40</td>
<td>7.83×10^4</td>
<td>2.50×10^{-3}</td>
<td>3.13×10^7</td>
</tr>
</tbody>
</table>

**MEA Comparison:** Rates of \(CO_2\) absorption into PC40-20 were compared to those into 5M MEA aqueous solution, as shown in Figure 7. Since MEA is more reactive and allows a greater conversion rate in an absorption column, a 5M MEA solution with 40% conversion rate or \(CO_2\) loading level of 0.2 mol/mol MEA (MEA5-40) was selected for comparison with PC40-20 (20% conversion). Compared to PC40-20 at 80°C, the rate of \(CO_2\) absorption into MEA at 50°C is 13-32 times greater, depending on the range of \(CO_2\) partial pressure. Promoters or catalysts are thus required to accelerate the rate of \(CO_2\) absorption into PC solutions.
Kinetics of CO₂ Absorption into PC Solution with Inorganic Catalysts: Based on a literature search, three catalysts CAT1, CAT2, and CAT3 were selected to promote CO₂ absorption into PC40-20. These three catalysts can be viewed as a Lewis base with a single, lone pair of electrons on anions which can serve to neutralize the Lewis acidity of CO₂. In order for a “base” to act as a promoter, it must possess certain required properties. A base too strong may form a very stable CO₂-base complex or simply react with water to generate more OH⁻; on the other hand, too weak a base may not efficiently interact with CO₂.

Results show that adding 4wt% CAT1 or CAT2 in PC40-20 raised CO₂ absorption rates by approximately twice. Rates into PC40-20 with 4wt% CAT2 are shown in Figure 8. In
contrast, adding 5wt% CAT3 did not present any promotion effect, but slightly reduced the rate of CO₂ absorption (data not shown in figure). That could be due to some adverse change in physical property of the solution after being mixed with CAT3. In general, PC40-20 with either CAT1 or CAT2 exhibited higher absorption activity at 60°C than PC40-20 without any catalyst at 70 or 80°C; but the difference was not significant.

The apparent enhancement factor \((E)\) is defined as a ratio of the rate of CO₂ absorption into PC solution with a catalyst to that without a catalyst. Values of \(E\) for 4wt% CAT1 and CAT2 catalysts at 60, 70, and 80°C are shown in Figure 9. It can be seen that CAT1 and CAT2 have similar promotion effects \((E=\sim2)\) on CO₂ absorption, suggesting that their anions (CAT1 and CAT2 have the same anions) might act mainly as a promoter.

CO₂ absorption rates into PC40-20 at different CAT2 dosage were further investigated and values of \(E\) for 2, 4, and 6wt% CAT2 at 60, 70, and 80°C are also shown in Figure 9. In general, the rate increased as CAT2 dosage increased. This tendency was more significant at 60 and 80°C than at 70°C. It should be noted that at 70°C, the enhancement factor reached a minimum for all three catalyst dosage levels. That can be explained by the fact that temperature affects both catalytic kinetics and CO₂ solubility. When temperature is increased, kinetics is enhanced while CO₂ solubility is reduced. The net effect of temperature on absorption rate is a combination of these two factors resulting in minimum \(E\) values at 70°C. It should also be noted that rate promotion by adding 6wt% CAT2 did not level off suggesting that additional increases in CAT2 dosage may further increase the absorption rate.

![Figure 9: Enhancement factor of CO₂ absorption into PC40-20 with addition of CAT1 and CAT2 catalysts at 60-80°C.](image)

Compared to 5M MEA at 50°C, the rate of CO₂ absorption into PC40-20 promoted with selected inorganic catalysts was still one order of magnitude lower based on STR experiments.
**Kinetics of CO$_2$ Absorption into PC Solution with Organic Promoters:** Addition of amine or similar types of promoters (such as amino acid salts) into carbonate solutions such as PC can enhance absorption rates according to a “shuttle mechanism” [14]. When a primary or secondary amine promoter is added to the carbonate solution, reactions consist of a sequence of elementary steps as follows:

$$2R_2NH + CO_2 \leftrightarrow R_2NCOO^- + R_2NH_2^+ \quad (R3)$$

$$R_2NH_2^+ + B \leftrightarrow R_2NH + BH^+ \quad (R4)$$

$$R_2NCOO^- + H_2O \leftrightarrow R_2NH + HCO_3^- \quad (R5)$$

$$CO_3^{2-} + H_2O \leftrightarrow OH^- + HCO_3^- \quad (R6)$$

$$CO_2 + OH^- \leftrightarrow HCO_3^- \quad (R7)$$

In the promoted absorption, fast CO$_2$ absorption reactions occur with amines near the interface (R3), followed by regeneration of intermediate reaction products (reverse R3, R4, and R5) by the carbonate (K$_2$CO$_3$) in the bulk solution. The slow reaction in the bulk carbonate solution (R6 and R7) serves as a sink for CO$_2$. The regeneration of amine reaction products depends on the activity of base component (B) to attract protons (in this case amine is the most important base). In comparison, in the PC solution without a promoter, reactions R6 and R7 are the most important and R7 is very slow under low alkaline conditions.

Many amine promoters for CO$_2$ absorption have been widely studied and applied in industry; however, most of these studies have been limited to low temperatures ($\leq$50°C) and low concentrations of carbonate salt solution. In this study, amine or amino acid salt promoters are used to enhance rates into more concentrated PC (40%wt K$_2$CO$_3$-equivalent) at temperatures of 60-80°C.

**Amine Promoters:** Five primary and secondary amines, including diethanolamine (DEA), aminomethyl propanol (AMP), piperazine (PZ), hexamethylene diamine (HDA), and hexylamine (HA), were tested as promoters and rates of absorption into amine-promoted 40%wt PC solutions were measured using the STR setup. Figure 10 shows rates of CO$_2$ absorption into the promoted PC40-20 at 70°C. Results indicate that all five amine promoters enhanced the rate into PC to various extents depending on type and dosage of amine. Absorption rates were promoted by 3.5 to 50 times in the pressure range between 1 and 5 psia compared to the PC without a promoter. Among the five amines, rates promoted with 1M PZ and 1M AMP were the highest, followed by 1M HDA.
AMP promoted the absorption rate mainly due to its relatively large “CO₂-carrying” capacity, since it is a hindered amine and absorbs CO₂ at a 1:1 molar ratio. The addition of PZ enhanced absorption because PZ is highly active with CO₂ (e.g., more reactive than MEA) to form carbamate and dicarbamate species.\textsuperscript{[15]} The addition of HDA may decrease the stability of carbamate in the solution, resulting in more CO₂ absorption.

CO₂ absorption rates into PC40-20 with additions of 1M or 1.2M amine promoters were compared with those into 3M and 5M MEA (see Figure 11). Two 3M MEA solutions, fresh solution and solution loaded with 0.2 mol CO₂/mol MEA (40% MEA conversion, MEA3-40), and three 5M MEA solutions, fresh solution and solutions loaded with 0.1 and 0.2 mol CO₂/mol MEA (MEA5-20 and MEA5-40, respectively), were selected for the comparison. It appeared that rates into 5M MEA were not significantly higher than those into 3M MEA counterparts at the same CO₂ loading levels. For example, the rate into MEA5-40 was only about 10% higher than that into MEA3-40. Note that CO₂ diffusion resistance in the gas phase in the presence of water vapor at 70°C might also impact the overall rate of CO₂ absorption when absorption is sufficiently fast.

The CO₂ loading level of 0.2 mol/mol MEA corresponds approximately to that of CO₂-lean MEA at the inlet of the absorption column.\textsuperscript{[3]} Compared to MEA5-40 at 50°C, absorption rates into PC40-20 promoted with 1M PZ, 1M AMP, and 1M HDA at 70°C were higher at CO₂ partial pressures greater than 2 psia and comparable at lower partial pressures. Results indicate that employing these amines as promoters is promising for significantly increasing the PC solution adsorption rate.

Figure 10: Amine-promoted CO₂ absorption rates into PC40-20 at 70°C.
Figure 11: Comparison of CO₂ absorption rates into amine-promoted PC40-20 at 70°C and MEA at 50°C.

Figure 12: Comparison of CO₂ absorption rates into amine-promoted PC40-20 and PC40-40 at 70°C.

CO₂ absorption rates into amine-promoted PC40-20 and PC40-40 were measured to investigate the effect of CO₂ loading (see Figure 12). PC40-20 and PC40-40 correspond to lean and relatively rich solutions, respectively, in the Hot-CAP. Results reveal that the
rate into PC40-40 with the addition of 1M AMP was 2-3 times lower than that of the PC40-20 with the same promoter; however, for 1M PZ and HDA promoters in PC40-40 and PC40-20 solutions, the difference between absorption rates was 5-6 times lower under similar conditions. The lower absorption rate into PC40-40 than into PC40-20 is expected because the driving force of CO₂ absorption into PC40-40 is smaller. Another factor could be due to reactions between amine promoter and bicarbonate in PC40-40, which might result in a lesser amount of free amine available for promoting absorption.

Amino acid salt promoters: Amino acids were considered to be potential promoters because they contain similar functional amino groups to amines that can undergo reactions with CO₂.[16] Five amino acids were selected and their potassium salts were prepared by reacting them with equimolar quantities of potassium hydroxide. They included potassium salts of glycine, sacrosine, proline, taurine, and alanine. 3M solutions of these amino acid salts were initially used for CO₂ absorption rate measurement. Three salts (K-glycine, K-sacrosine and K-proline) showing higher absorption rates were selected as promoters for the 40wt% PC solution. CO₂ absorption rates into PC40-20 with these acid salt promoters were compared with those into MEA3-40 (see Figure 13). In general, adding 1M amino acid salt promoters improved absorption rates with addition of K-glycine and K-sacrosine increasing absorption rates into PC40-20 by 3-11 times for CO₂ partial pressures ranging from 1 to 5 psia. Addition of 1M K-sacrosine or K-glycine promoter more effectively accelerated CO₂ absorption than addition of 1M K-proline. Overall, promoted rates were still lower than those into MEA3-40. It was observed that equilibrium CO₂ pressures over amino acid salt solutions were higher than those over MEA, which reduced the driving force for CO₂ absorption.

![Figure 13: Comparison of CO₂ absorption rates into amino acid salt-promoted PC40-20 at 70 °C and MEA at 50°C.](image-url)
**K₂SO₄ Effect on CO₂ Absorption:** SO₂ present in flue gas can also be absorbed into PC solution. To simulate this effect on CO₂ absorption, rates into PC solution with and without a promoter (AMP was used) in the presence of K₂SO₄, a product of SO₂ absorption, were investigated. K₂SO₄ concentrations used were 0.05M and 0.08M. K₂SO₄ solubility in 40wt% PC solution is about 0.2 M. Rates into PC40-20 under different conditions are shown in Figure 14. No significant differences were observed in absorption rates either with or without the AMP promoter, or in the presence or absence of K₂SO₄.

![Figure 14: Effect of K₂SO₄ on absorption rate into PC40-20 at 70ºC: (a) without a promoter; (b) with 1M AMP promoter.](image)

**Design and Fabrication of Packed-bed Absorption Column:** Based on the above lab-scale results, a bench-scale, packed-bed column was designed and fabricated, as shown in Figure 15, for scaled up absorption testing in Phase II of this study. The column consists of a 10-cm ID, 3-m high, cast acrylic tube employing corrugated stainless steel plate packing (with a specific surface area of ~800 m²/m³) to provide a 2-m high packed bed with specifications described in Table 2. The column operates in countercurrent mode with air from an air compressor, CO₂ from a compressed gas cylinder, and steam from a steam generator (Chromalox/CMB-3). Desired CO₂ concentration in the gas mixture is obtained by adjusting flow rates of CO₂ and air using valves and mass flow meters. Desired temperature (60-80ºC) is obtained by adjusting steam addition. The gas stream is fed at the bottom of the column and exits at the top for ventilation and gas analysis after CO₂ absorption. PC solution, also maintained between 60 and 80ºC by a tank thermostat, is fed to the top of the column at a controlled flow rate using a peristaltic pump. CO₂-rich solution exits at the bottom of the column and is recycled through the heated supply tank back to the top of the column under unsteady-state conditions, or is discharged to a storage tank under steady-state operation. Five thermal couples mounted
along the column measure its temperate profile. A U-shape differential pressure tube measures pressure drop in the column.

![Diagram of bench-scale, packed-bed absorption column]

Figure 15: Schematic and photograph of bench-scale, packed-bed absorption column.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height of packing element, mm</td>
<td>100</td>
</tr>
<tr>
<td>Diameter of packing element, mm</td>
<td>100</td>
</tr>
<tr>
<td>Specific surface area (a), m²/m³</td>
<td>800</td>
</tr>
<tr>
<td>Angle of inclined corrugation to the horizontal(θ), degree</td>
<td>45</td>
</tr>
<tr>
<td>Corrugation crimp height, mm</td>
<td>5</td>
</tr>
<tr>
<td>Side dimension of corrugation, mm</td>
<td>10</td>
</tr>
<tr>
<td>Void fraction (ε)</td>
<td>0.66</td>
</tr>
</tbody>
</table>

Table 2. Geometric specifications of structured packing material in bench-scale column.

Dynamics and Kinetics of Potassium Bicarbonate Crystallization

Morphology and Structure of Crystal Particles during Crystallization: Temperature and turbidity profiles for KHCO₃ crystallization under three different cooling pathways (linear, concave and convex) are shown in Figures 16(a) (1°C/min cooling rate) and 16(b) (0.5°C/min cooling rate). Both figures display a temperature break point on each temperature-time curve, which occurred upon inception of massive crystallization of the bicarbonate, as indicated by a dramatic increase in turbidity. Therefore, the steady temperature (break point) for a short period in the cooling process was maintained by a large amount of heat released from crystallization and turbidity continued to increase while temperature decreased after this point.
Temperature break points appeared earliest on concave profiles and latest on convex profiles. This can be explained in that the concave cooling process took a shorter time to reach the same temperature than the other two cooling methods; however, temperature break points were comparable (around 54±3°C) for all three cooling pathways at either cooling rate. Crystal particles were observed to form continuously over the course of cooling, but most particles were produced as temperature went below the break point. Results suggest that for PC40-40, the end temperature should be lower than the temperature break point in order to maintain an efficient crystallization process.

SEM images of crystal particles from PC40-40 during the linear cooling pathway from 70°C are shown in Figure 17. It can be seen that crystals went through a growth process.
At 60°C, no bulk crystallization was observed and crystal particles were generally small and acicular in shape (see images (a) and (a')). At 45°C (below the temperature break point), crystal particles exhibited hexagonal prism shape with particle sizes larger than those at 60°C (see images (b) and (b')). At about 30°C, crystal particle size grew further although shape did not change very much (see images (c) and (c')). Crystal particle size for samples obtained at 0.5°C/min cooling rate (see images (a')-(c')) was slightly larger and more uniform than those obtained at 1°C/min (see images (a)-(c)). In general, the difference in crystal morphology between the linear and two non-linear (images not shown) cooling processes was not significant.

Particle Size Distribution of Crystal Samples from Different Cooling Profiles: Particle size distribution (PSD) and mean size of crystal particles from samples obtained during KHCO₃ crystallization at 1°C/min cooling rate were measured. PSD histograms of five samples collected sequentially at 60, 55, 45, 35, and 30°C during the linear cooling process are shown in Figure 18a. Those of three samples collected at 45°C during linear, concave, and convex cooling processes are compared in Figure 18b.
Figure 18: Particle size distributions of crystal samples obtained during cooling-crystallization process at 1°C/min cooling rate.

Mean size results for these samples are displayed in Figure 19. Mean particle size during the linear cooling process increased almost linearly as temperature decreased reaching about 370 µm at the end of the cooling process with the mode occurring at 350-400 µm. Particle size is uniformly distributed with about 92wt% of crystals within 250-520µm (see Figure 18). In comparing particle size for samples obtained during the three different cooling processes at the same sampling temperature (45°C), the convex cooling process
produced the largest crystal particle size, followed by linear and concave cooling processes. These results can be explained by the fact that crystal particles in the convex cooling process were allowed the longest time to grow.

Figure 19: Mean particle size of crystal samples collected at different temperatures during different cooling processes at an average 1°C/min cooling rate.

**Composition of Crystal Particles from PC Solution with Promoters and Impurities:**

XRD analysis confirmed that KHCO$_3$ is the only component in solid particles crystallized from PC40-40 without the addition of an additive (data not shown). XRD patterns of solid particles from PC40-40 in the presence of 0.05M K$_2$SO$_4$ are shown in Figure 20. Results indicated that KHCO$_3$ was again the only specie in the sample. A wet chemistry analysis revealed that about 5wt% of the original K$_2$SO$_4$ in the solution was present in the crystal product. K$_2$SO$_4$ in the crystal sample was not detected by XRD since its content was beyond the detection limit (≤ 1wt%).

XRD analysis shows that the crystal product from PC40-40 in the presence of 1M AMP consisted of only HKCO$_3$ (see Figure 21). After being washed with IPA and dried, the sample remained almost the same weight as the untreated sample and showed similar XRD patterns suggesting that any amounts of AMP and its derivatives were not appreciable in the crystal product. When 0.2M PZ was added to PC40-40, the resulting crystal product contained two phases, HKCO$_3$ and K$_4$H$_2$(CO$_3$)$_4$·1.5H$_2$O. This product was washed with IPA, after which untreated and IPA-washed samples displayed similar XRD patterns indicating that there was no appreciable organic phase present in crystal solids (see Figure 22). Thus, both AMP and PZ and their derivatives remained in the aqueous solution and did not transfer to crystal product during the crystallization process.
Figure 20: XRD patterns of crystal particles from PC40-40 mixed with 0.05M K$_2$SO$_4$.

Figure 21: XRD patterns of crystal particles from PC40-40 mixed with 1M AMP before and after washing with iso-propanol.

Figure 22: XRD patterns of crystal particles from PC40-40 mixed with 0.2M PZ before and after washing with iso-propanol.
VLE Measurement for K$_2$CO$_3$/KHCO$_3$ Slurry

**VLE Data for 40-60wt% PC Solutions at 140-200°C:** Figure 23 shows VLE data measured in this study and those reported by Tosh et al.\(^{[17]}\) for 40%wt K$_2$CO$_3$/KHCO$_3$ solution at 140°C. It can be seen that both partial pressure of CO$_2$ ($P_{CO2}$) and total pressure ($P_{CO2} + P_{H2O}$) measured in this study were generally lower, but partial pressure of water vapor ($P_{H2O}$) was higher than those reported in the literature. Pressures were measured using both a calibrated pressure transducer and a calibrated pressure gauge to crosscheck readings and temperatures from a calibrated thermal couple located near the gas-liquid interface.

Tosh et al. measured VLE data using a rocking autoclave consisting of a 3-ft long, 3-inch diameter, Schedule 40, stainless steel pipe (Type 304) jacketed by a 4-inch Schedule 40 pipe. Desired temperatures were obtained by boiling water at appropriate pressures in the jacket and heat was applied on the outside of the jacket by way of an electric winding. The rocking motion was conveyed to the autoclave by an assembly rocked through an arc of approximately 30° at a rate of 24 cycles per minute. Gas samples were drawn into a gas-sampling apparatus through a length of glass tube. To prevent water from condensing, the gas sampling assembly was heated by an electrical tape heater to the temperature at, or slightly above, equilibrium temperature.\(^{[17]}\) It is a concern that in these tests, rocking might not be sufficient to ensure thorough mixing for a uniform temperature and composition distribution in both gas and liquid phases. In addition, water condensation might occur due to insufficient or non-continuous heating of the gas sampling assembly, which would result in a lower water vapor pressure and a higher CO$_2$ pressure.

Figure 24 shows VLE data for the 40wt% K$_2$CO$_3$/KHCO$_3$ solution at different CTB conversion rates and at 140, 160, and 180°C. As expected, CO$_2$ partial pressure increased significantly as temperature and CTB conversion rate increased. When the temperature was at 180°C, CO$_2$ partial pressure could reach a value of about 180 psia at around 80% CTB conversion rate. At the three temperatures investigated, the partial pressure of water vapor generally decreased with increasing CTB conversion rate.

Figures 25 and 26 display measured values of $P_{CO2}$ and $P_{H2O}$ over 50 and 60wt% K$_2$CO$_3$/KHCO$_3$ solutions with different CTB conversion rates from about 50 to 80% at temperatures ranging from 140 to 200°C. It can be seen that the tendency for changes in $P_{CO2}$ and $P_{H2O}$ over 50 and 60wt% K$_2$CO$_3$/KHCO$_3$ solutions was similar to that over the 40wt% K$_2$CO$_3$/KHCO$_3$ solution, i.e., both $P_{CO2}$ and $P_{H2O}$ significantly increased with increasing temperature; and at the same temperature, $P_{CO2}$ significantly increased and $P_{H2O}$ slightly decreased as the CTB conversion rate of solutions increased. For the 50wt% K$_2$CO$_3$/KHCO$_3$ solution, $P_{CO2}$ could reach more than 300 psia at around 80% CTB conversion rate and 200°C, while total pressure ($P_{CO2} + P_{H2O}$) attained about 380 psia. These VLE data demonstrate the advantage of CO$_2$ stripping using a concentrated K$_2$CO$_3$/KHCO$_3$ solution with high CTB conversion at 140-200°C in that a high pressure CO$_2$ stream can be recovered in the Hot-CAP.
Figure 23: Measured and reported VLE data for 40wt% PC at 140°C: (a) CO₂ partial pressure, (b) total pressure, and (c) water vapor partial pressure.
Figure 24: VLE data for 40wt% PC at 140, 160, and 180°C: (a) CO$_2$ partial pressure and (b) water vapor partial pressure.
Figure 25: VLE data for 50wt% PC at 140, 160, 180, and 200°C: (a) CO₂ partial pressure and (b) Water vapor pressure.
Effect of PC Concentration on VLE Behavior: It is interesting to compare VLE data of K$_2$CO$_3$/KHCO$_3$ solutions of different K$_2$CO$_3$-equivalent weight concentrations. From Figures 24, 25, and 26, it can be seen that PC concentration did not significantly affect $P_{CO2}$ at the investigated concentration and temperature range. The 50wt% PC had slightly higher $P_{CO2}$ than the 40wt% PC at the same CTB conversion rates. When PC concentration increased to 60wt%, $P_{CO2}$ did not significantly increase but was comparable to that of 50wt% PC.
As expected, $P_{H_2O}$ decreased significantly as PC concentration increased from 40 to 60wt% at the same CTB conversion rates. A similar tendency in the change of $P_{H_2O}$ with CTB conversion rate was found for PC solutions of different concentrations (40, 50, and 60wt%) in that $P_{H_2O}$ decreased slightly with increasing CTB conversion rate at the investigated temperature range of 140-200°C.

Risk Mitigation and Techno-economic Analysis

One major technical risk in the Hot-CAP is associated with fouling in heat exchangers. Two cross heat exchangers, one between the absorber and crystallizer and the other between the stripper and crystallizer, involve slurry streams (see Figure 2). Fouling on heat exchanger surfaces will reduce heat transfer efficiency and create problems for continuous operation.

To address this risk, a literature review was combined with consulting several industrial crystallizer vendors to discuss potential fouling problems in a crystallization process. Vendors confirmed that scaling of crystalline on equipment surfaces would happen; however, they insured that there were methods to mitigate the scaling issue. These methods include the following specific options:

- Reducing the temperature difference in the cross heat exchanger. The smaller the temperature difference ($\Delta T$) across heat exchanger tubes, the less serious the scaling.
- Adding crystalline seeds into the crystallization solution or pre-seeding the crystallization solution will help avoid scaling on the heat exchanger surface.
- Using plate-and-frame heat exchangers, which are less expensive and easier to clean.
- Using a vacuum cooling crystallizer or a surface cooling crystallizer equipped with scrapers. In a vacuum cooling crystallizer, internal heat exchangers will not be needed. A vacuum system will be used to extract water vapor to cool the solution.
- Adding an extra heat exchanger, which will result in a cost increase; however, since multiple trains are required for a power plant-scale CO$_2$ capture system, one extra set of equipment may not significantly increase total cost.

Another technical risk in the Hot-CAP is crystallization design to recover heat from the inflow solution (saturated or unsaturated carbonate solution entering the crystallizer). Conventional crystallizers require large temperature differences between inflow and mother liquor (solution leaving the crystallizer). As a result, heat recovery from the incoming solution could be jeopardized if a single crystallizer process configuration is used. This suggests that modifications to the existing process design may be necessary.

Based on the heat recovery requirement, a modified process design, as seen in Figure 27, was proposed by vendors to facilitate heat recovery. In this design, five consecutive crystallization tanks are used instead of a single crystallizer (original design). The new configuration will reduce the temperature difference between inlet and outlet streams of each crystallizer to about 5°C, thereby facilitating heat recovery required in the Hot-CAP. For example, in the first crystallization unit, the temperature of PC will be cooled from
65 to 60°C while the mother liquor is heated from 50 to 55°C. This insures that at least 5°C of temperature driving force is available for both liquids.

![Figure 27: Modified Hot-CAP flowchart addressing heat recovery during crystallization.](image)

The original plan was for vendor engineers to further examine the feasibility of the proposed crystallization process and provide a preliminary cost estimate for continuous stirred tank reactor (CSTR) type crystallizers and their accessories. The new design with a series of multiple CSTR type crystallizers will increase costs compared to a single crystallization tank configuration; however, the increase may not be significant. Total crystallization tank volume may remain comparable if the crystallization step is the rate-limiting step. In addition, if heat transfer between mother liquor and CO$_2$-rich solution is the rate-limiting step, the increase in cost will result from total heat transfer surface area, which may not be as significant compared to the entire process since the cost of heat exchangers is usually only a small fraction of total cost for the crystallization process.

**CONCLUSIONS AND RECOMMENDATIONS**

**Conclusions**

CO$_2$ absorption rates into PC40-20 at 80°C were 13-32 times lower than those into MEA3-40 at 50°C. Adding 4wt% CAT1 or CAT2 (Lewis-base, inorganic salt catalysts) into PC40-20 raised CO$_2$ absorption rates by twice at 60-80°C. Increasing catalyst (CAT2) dosage from 4 to 6wt% increased rates by 23%. Five amino acid salts and five amines were selected as organic promoters to promote CO$_2$ absorption. Additions of K-sarcosine and K-glycine improved absorption rates more significantly than other amino acid salts; however, promoted rates at 70°C were still several times lower than those into MEA3-40 at 50°C. Among the five amine promoters, rates promoted with PZ and AMP were the highest, followed by HDA. Rates into PC40-20 promoted with 1M PZ, 1M AMP, and 1M HDA at 70°C were higher than or comparable to those into MEA5-40 at 50°C. These results indicate that amine promoters are promising for significantly accelerating CO$_2$ absorption into PC solutions. In addition, a bench-scale, packed-bed absorber was
designed and fabricated for testing CO₂ absorption. The column has a 10-cm ID and a 3-m height and is packed with two meters of structured stainless steel packing. Shakedown testing has been completed and scaled up absorption testing will continue in Phase II.

Crystallization of potassium bicarbonate from PC40-40 was studied under different cooling pathways and cooling rates. A temperature break point at 54±3°C was observed for all cooling processes, below which massive crystallization occurred and continued. SEM analysis showed that the mean size of crystal particles increased with decreasing temperature during cooling. For the linear cooling process, mean particle size was ~370μm and the mode occurred at 350-400 μm when temperature was cooled to 30°C. Particle size was uniform at about 92wt% within 250-520μm. The size of crystal particles from the convex cooling process tended to be slightly larger than those from linear and concave cooling processes. XRD analysis showed that AMP, PZ, and their organic derivatives were not transferred into crystal products from PC40-40. Crystal particles from PC40-40+1M AMP consisted solely of HKCO₃. Crystal particles from PC40-40+0.2M PZ consisted of HKCO₃ and a small amount of K₄H₂(CO₃)₃·1.5H₂O. Crystal particles from PC40-40+ K₂SO₄ contained a small amount of K₂SO₄ (~5wt% of the initial amount of K₂SO₄ in the solution).

VLE data for 40, 50, and 60wt% PC slurries with different CTB conversion rates at 140-200°C were measured using a high-pressure autoclave reactor. The partial pressure of CO₂ increased significantly with increasing temperature and CTB conversion rate while that of water vapor increased with increasing temperature but slightly decreased with increasing CTB conversion level. Results showed that high pressure could be attained over PC slurry under equilibrium conditions. For example, the partial pressure of CO₂ over 50wt% PC at 200°C was greater than 300 psia and total pressure was greater than 380 psia at ~80% CTB conversion level. High-pressure CO₂ stripping using PC slurry has proved feasible for the Hot-CAP.

Risk mitigation studies were conducted with a focus on the two major technical risks in the design: the heat exchanger and the crystallizer. Vendor discussions and literature searches were performed to address these two risks. A revised flowchart for the process with multiple crystallizer units was proposed to meet the need of heat recovery from inflow CO₂-rich solution to mother liquid.

Future Work in Phase II

In Phase II, the CO₂ absorption study will continue by using the bench-scale, packed-bed absorber fabricated in Phase I. A high-pressure stripping column will be designed and fabricated and stripping tests will be performed to evaluate slurry-based stripping performance under continuous mode. A feasibility study will be conducted to prove the concept of combined SO₂ removal and CO₂ capture. In addition, sodium carbonate as a solvent will also be investigated and compared to its potassium counterpart. Experimental results will be used as a basis to perform risk analysis, process simulations, and technical and economic studies for evaluation of the overall performance of the Hot-CAP as a post-combustion CO₂ capture technology.
REFERENCES


35
DISCLAIMER STATEMENT

This report was prepared by Yongqi Lu of the Illinois State Geological Survey at the University of Illinois at Urbana-Champaign (ISGS/UIUC), with support, in part, by grants made possible by the Illinois Department of Commerce and Economic Opportunity through the Office of Coal Development and the Illinois Clean Coal Institute. Neither Yongqi Lu, ISGS/UIUC, nor any of its subcontractors, nor the Illinois Department of Commerce and Economic Opportunity, Office of Coal Development, the Illinois Clean Coal Institute, nor any person acting on behalf of either:

(A) Makes any warranty of representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately-owned rights; or

(B) Assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method or process disclosed in this report.

Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring; nor do the views and opinions of authors expressed herein necessarily state or reflect those of the Illinois Department of Commerce and Economic Opportunity, Office of Coal Development, or the Illinois Clean Coal Institute.

Notice to Journalists and Publishers: If you borrow information from any part of this report, you must include a statement about the state of Illinois’ support of the project.