

CO₂ ABSORPTION INTO CONCENTRATED CARBONATE SOLUTIONS WITH
PROMOTERS AT ELEVATED TEMPERATURES

BY

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THESIS

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ABSTRACT

As atmospheric carbon dioxide (CO₂) emissions continue to increase, it becomes important to develop methods to capture CO₂ from large emission sources such as power plants. The Hot Carbonate Absorption Process with Crystallization Enabled High Pressure Stripping (Hot-CAP), which employs a concentrated potassium carbonate/bicarbonate (PCB) aqueous solution as a solvent and a potassium carbonate/bicarbonate slurry for CO₂ stripping, is a novel method to capture this CO₂ more efficiently than conventional technologies. We focused on addressing the issue associated with a slow rate of CO₂ absorption into a potassium carbonate/bicarbonate solution by using amine and amino acid promoters. We will conduct an initial screening study using a lab scale stirred tank reactor. Promoters which showed the most potential were tested on a bench scale, packed bed column to simulate real process conditions.

Five different primary/secondary amines and three amino acid salts were evaluated as promoters for a concentrated 40 wt% potassium carbonate/bicarbonate solution using a batch stirred tank reactor. Using amino acids, absorption rate was improved compared to the unpromoted 40 wt% potassium carbonate/bicarbonate but was not sufficiently high for the practical purpose. Amine promoters increased absorption rates into potassium carbonate/bicarbonate solution at 70°C by 3.5 to 50 times, with piperazine (PZ) and aminomethyl propanol (AMP) showing the highest promotion rate. Compared to the 5 M monoethanolamine (MEA) solution at 50°C (typical absorption temperature in benchmark MEA process), the absorption rates into the potassium carbonate/bicarbonate solution promoted with 1 M PZ and 1 M AMP at 70°C (typical absorption temperature in Hot-CAP) were higher or comparable either at CO₂ lean or rich conditions.

As determined by testing of CO₂ absorption in a bench scale, packed bed column, use of selected rate promoters increased the rate of CO₂ removal into potassium carbonate/bicarbonate solution. The 40 wt% potassium carbonate/bicarbonate solution promoted with 0.5 M PZ, DEA or AMP tested at 70°C performed 1 to 3 times better than 5 M MEA at 50°C at their respective lean loading levels and 3 to 5 times better at rich CO₂ loading levels, when other conditions were the same.

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Chapter 1

Introduction

1.1 Need for carbon capture and sequestration

As global warming becomes an important issue, many countries are looking to limit their emissions of greenhouse gases, with carbon dioxide (CO₂) being the main focus. As a result of this, CO₂ capture and sequestration is considered an important option to mitigate CO₂ emissions in recent years. While many emerging technologies are being investigated, they are expensive and not economically feasible. Eventually government regulations and economics will be the driving force behind finding and implementing an efficient treatment for CO₂ containing waste gases.

CO₂ emissions broken down by sector are shown in Figure 1.1. In 2012, over 25% of CO₂ emissions were the result of electricity generation. This is the most by any sector and because of the nature of electricity generation at large scales, represents an easier target for lowering CO₂ emissions in the short term than other sectors, such as transportation.

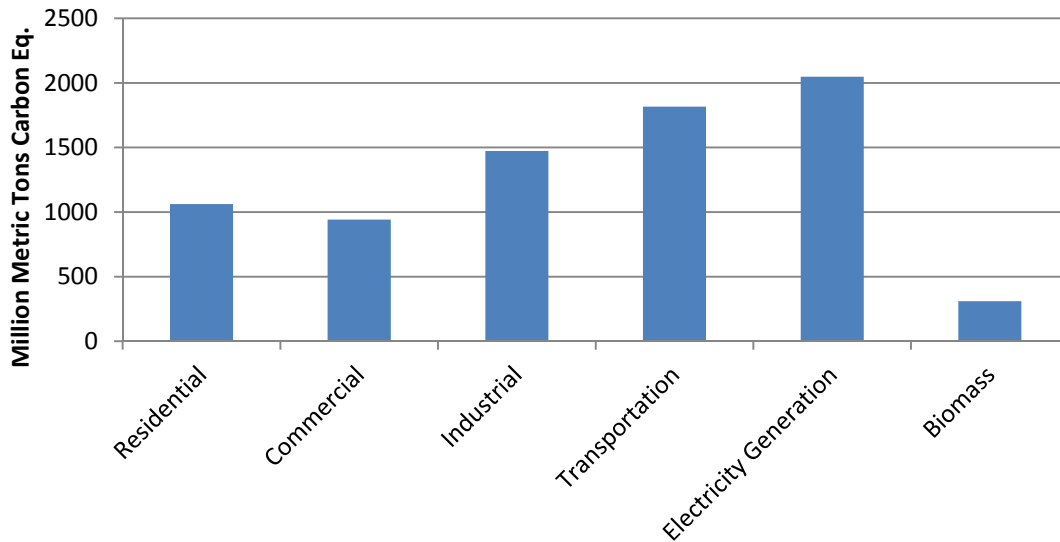


Figure 1.1. 2012 Carbon Dioxide Emissions by Sector (U.S. Energy Information Administration, 2013).

The breakdown of CO₂ emissions from electricity generation by source is depicted in Figure 1.2. Coal makes up 75% of CO₂ emissions from electricity generation, which means that with the development of effective postcombustion CO₂ capture technologies there could be a noticeable reduction in overall U.S. emissions.

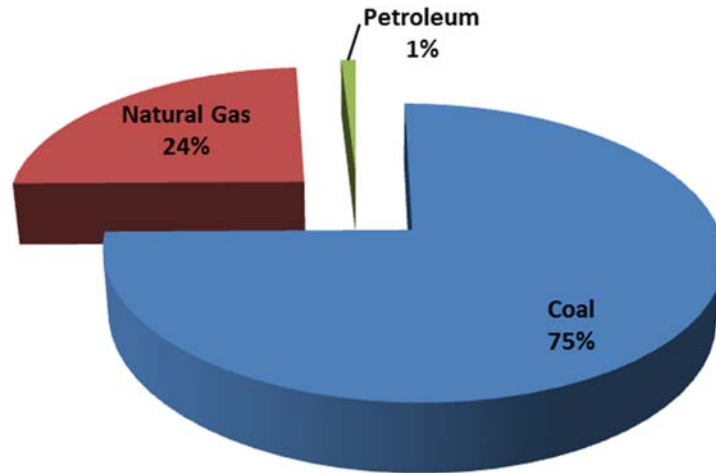


Figure 1.2. Resulting Carbon Dioxide Emissions from Electricity Generation by Fuel Type in 2012 (U.S. Energy Information Administration, 2013).

The reason coal emits more CO₂ than natural gas is because of the high carbon intensity and thus the high flue gas concentration. Flue gases from coal fired power plants contain 10% to 15% CO₂ while gas fired turbines produce flue gas containing only 2% to 3% CO₂. There is no indication that coal utilization for electricity generation will decrease in the near future, therefore, there is a need to develop technologies that will allow the use of fossil fuels, particularly coal, in a cleaner way.

1.2 CO₂ capture methods

CO₂ can be captured from fuel combustion flue gas (postcombustion capture), fuel gasification syngas (precombustion capture), or by oxyfuel combustion (Figueroa et al., 2008). Postcombustion technologies available for CO₂ removal include membranes, adsorption, chemical absorption, physical absorption and cryogenic processes. Some of these technologies

are well established and used commercially, while others are in need of additional process improvements to be feasible.

1.2.1 Membranes

Selective membranes can be used to separate gases by exploiting differences in physical or chemical interactions between gases and the membrane. Currently, membranes are used to remove CO₂ from natural gas streams which have a high pressure and a high concentration of CO₂. Advantages for the use of membranes in natural gas industry include no regeneration energy, no moving parts and the membrane can be replaced depending on process conditions. Some drawbacks for using membranes are their performance at high temperatures, where selectivity and permeability still need to be improved for postcombustion CO₂ capture application (Kenarsari et al., 2013).

1.2.2 Adsorption

Adsorption involves the use of certain solids with a high surface area to separate CO₂ from a gas mixture. These adsorbents are desorbed through a regeneration process. Examples of solid adsorbents include zeolites, activated carbon, polymers and molecular sieves. In general, a two bed system is used, where one bed is adsorbing CO₂ while the other is being regenerated using pressure, temperature or electrical swings. This technology has not proven to be cost effective for a low value, high volume product like CO₂ in power plant flue gas (Boot-Handford et al., 2014).

1.2.3 Chemical absorption

Chemical absorption systems have been in use since the 1930's for acid gas treating, although until recently have not been looked at for large scale applications such as removing CO₂ from power plant flue gas. The system consists of an absorber and a desorber as well as a cross exchanger. In this process, CO₂ in the untreated flue gas will react counter currently with a lean solvent solution in the absorption column. The CO₂ rich solution is sent to the stripping column where it is heated by steam from the reboiler and CO₂ is stripped off from the hot solution. The lean solvent is sent back to the absorption column while the product CO₂ is sent on for further dehydration and pressurization. The main energy penalties in this process occur from

the heat (steam) use needed to regenerate the solvent as well as the energy needed to further compress the CO₂ so it can be stored and transported (Boot-Handford et al., 2014).

1.2.4 Physical absorption

During physical absorption, the untreated flue gas is fed counter-currently with the solvent in an absorption column. The CO₂ is absorbed by the solvent, and then the rich solution passes through a series of flash drums at varied pressures. The CO₂ is released as a result of this depressurization. The optimal temperature for physical absorption processes is 40°C and the feed gas must be at high pressure with concentrated CO₂. Based on these parameters physical absorption is much more effective in pre-combustion processes such as extracting the CO₂ from natural gas or coal syngas.

1.2.5 Cryogenic processes

Using cryogenic technology to separate CO₂ from other components is most feasible in oxyfuel combustion and precombustion processes because of the high CO₂ partial pressure (pCO₂). In this process compression, cooling, condensation and distillation steps are used to produce liquid CO₂. Applying this method to a postcombustion scenario, where a hot flue gas is present with a relatively low CO₂ partial pressure would result in a large energy penalty and a low efficiency process.

While many of these acid gas removal processes show potential for CO₂ absorption, the use of chemical solvents are the most well developed and the most effective technique to remove large quantities of CO₂ at postcombustion conditions.

1.3 Chemical solvents for CO₂ adsorption and absorption

Many chemical solvents have been studied to determine if they have the potential to remove CO₂ from flue gas at a commercial scale. This includes monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), diisopropanolamine (DIPA), diglycolamine (DGA) and potassium carbonate (K₂CO₃). In general, most solvents are either primary or secondary amines, with tertiary amines occasionally used. Besides being used in single component solutions, many of these amines are combined into multicomponent mixtures

in an attempt to enhance their CO₂ capture potential. Currently, the solvent investigated the most is MEA, which is the industry standard, while potassium carbonate as a less expensive, inorganic solvent is of increasing research interest. Their chemical structures are shown in Figure 1.3.

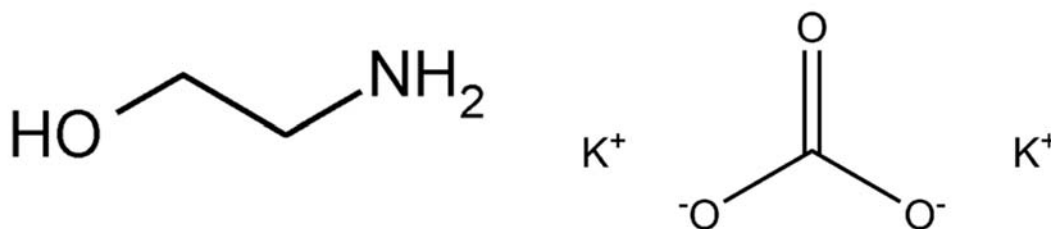


Figure 1.3. Structure of Chemical Solvents - Right Potassium Carbonate, Left Monoethanolamine (Royal Society of Chemistry, 2014).

1.3.1 Amine based solvents

Amines have long been the solvent of choice for CO₂ removal because of their fast reaction rates and high capacity for absorbing CO₂. The current industry standard is an aqueous MEA solution of 15% to 30% by weight. MEA is one of the few solvents that can be used on flue gas because of its effectiveness at low partial pressures of CO₂. The major drawbacks for MEA and amines in general, are their high heats of absorption coupled with the fact they are inclined to undergo thermal and oxidative degradation. Another issue with amine systems is corrosion. Existing processes need to add a corrosion inhibitor to the aqueous MEA solution. Even with this inhibitor, solution concentrations can be raised only to 30% MEA by weight, mainly for corrosion concerns (Cullinane, 2005).

1.3.2 Potassium carbonate

An emerging class of solvents used in treating flue gases are aqueous potassium carbonate based solutions. Currently, depending on individual processes, the preferred configuration is a 20% to 40% by weight solution of K₂CO₃. The main benefits of using potassium carbonate as a solvent include its low heat of absorption which results in a lower energy penalty in the stripping column, low solvent cost, no degradation problem and little corrosion concern. However, a major downside for this system configuration is the reaction rate with CO₂, which is slower than aqueous amines. This limits the use of potassium carbonate

solutions in applications where a high percentage of the CO₂ must be removed because the height of the absorption column needed would be unrealistic (Kothandaraman et al., 2009).

1.3.3 Ideal solvent properties

In creating a CO₂ capture system that will be cost effective enough to be feasible economically, improvements to the current processes must occur. The most important of these advances will be the development of more effective solvents. Important solvent properties include fast CO₂ absorption rate, high CO₂ capacity, low regeneration energy requirements, low degradation rates, low solvent costs and low corrosivity. Solvents with a fast reaction rate will result in a smaller absorber, less packing and reduced pressure drop. The absorber could be operated closer to equilibrium, which would result in a CO₂ richer solution and thus a more efficient stripper and lower regeneration costs. High capacity solvents result in a lower circulation rate and a lower energy requirement for regeneration. A low corrosivity solvent can be used with equipment made of carbon steel, instead of stainless steel, which will reduce capital costs. There will be a tradeoff between solvent cost and benefits derived from its use, making the utilization of an inexpensive bulk material important (Cullinane, 2002).

1.4 Carbonate based technology

Based on the ideal solvent properties laid out in the previous section, potassium carbonate solutions are a good fit for large scale CO₂ capture, except for their slow absorption rate of CO₂. If these reaction rates can be improved to levels of standard amine solvents, these carbonate solutions can achieve efficiency improvements in other parts of the capture process.

1.4.1 Promoters studies

To achieve a chemical solvent with as many of the desired characteristics outlined in the previous section as possible, it is likely there will need to be a mixture of at least two components. While some experimental solutions have used mixtures of amines, many utilize a potassium carbonate based solution with a small dosage of an amine. This is in an effort to capture the fast reaction rate of the amine, while taking advantage of the lower heat of absorption and thus more energy efficient regeneration potential of potassium carbonate. Using potassium carbonate as the bulk solution, Tseng et al. (1988) investigated CO₂ absorption into promoted

solutions using DEA. For carbonate conversions below 30%, the reaction rate was controlled by the rate of formation of zwitterion intermediate, while at carbonate conversions above 30% the rate was controlled by abstraction rate of proton from the zwitterion intermediate.

Cullinane (2005) experimented with the thermodynamics and kinetics of a different promoter, piperazine (PZ), with a potassium carbonate bulk solution. Carbamate intermediates were only minor components of the solution. Most of the absorption resulted in protonation of PZ. Capacity of the 0 to 3.1 m (mol/kg water) concentrated potassium carbonate and 0.45 to 3.6 m PZ solutions were comparable or better than MEA over a range of different $p\text{CO}_2$. Absorption rates in the solutions were 2 to 3 times faster than 5 M MEA at a constant $p\text{CO}_2$. The only limitation found was the fact the solvent's components were solids at room temperature. As a result the absorption needs to be run at an elevated temperature, or the concentrations of the potassium carbonate and PZ decreased.

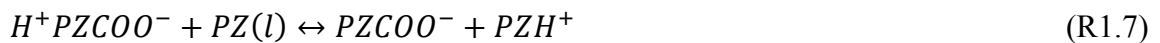
Chen (2007) continued the work of Cullinane by expanding testing from lab scale to a pilot plant. A 5 m concentrated potassium carbonate and 2.5 m PZ solution was found to be 2 times faster reacting than a 7 M MEA solution. However, in measuring the heat duty for desorption of CO_2 from the stripper, the energy required was higher than MEA. Even though these indicators of performance were found to be equal or better than MEA, on this large scale there were a lot of problems with the solubility of the solution. These resulted in periodic interruptions in instrumentation from solids being present, as well as complete shutdown of the plant on several occasions. Thee et al. (2009) studied CO_2 capture by a potassium carbonate solution promoted with MEA. Using a lab scale setup they found the addition of MEA accelerated the apparent pseudo first order rate constant of unpromoted potassium carbonate, and therefore, the overall absorption of CO_2 into potassium carbonate solutions was improved.

1.4.2 Reaction mechanism of piperazine promoted potassium carbonate

Promoting the reaction rate of PCB with PZ has advantages over using traditional amine promoters. These advantages include PZ being able to react with two moles of CO_2 per mole of amine, because PZ is a diamine. It also has a higher capacity for CO_2 absorption than other amines. Another positive attribute is the high pK_a which is close in value to MEA; a high pK_a usually leads to a fast rate of absorption. Lastly, since there is a large amount of PCB in the

solution, it acts as a buffer and reduces the protonation of the amine, leaving more free amine to react with CO₂ (Cullinane, 2005).

The following system has been proposed for the mechanism of which CO₂ absorbs into an aqueous PCB/PZ system according to Hillard (2005):



The different structures of piperazine in this reaction are depicted in Fig. 1.4.

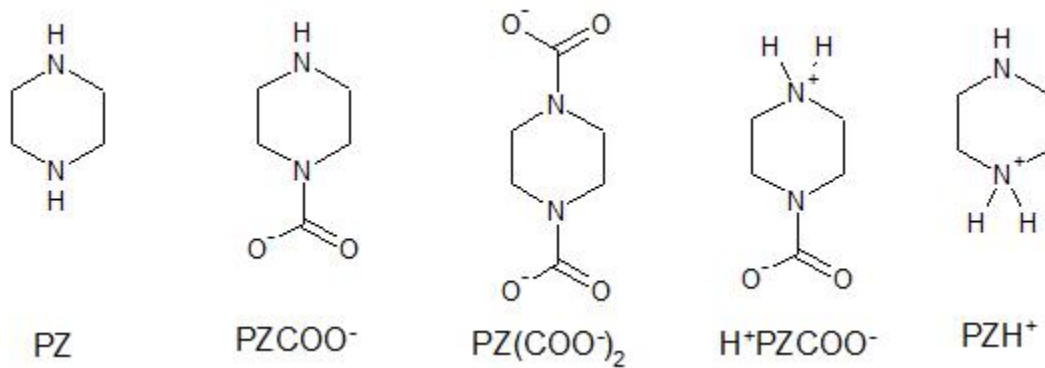


Figure 1.4. Structures of piperazine in the presence of CO₂

1.4.3 Other processes under development

One carbonate process under development is by Shell, with special attention paid to the precipitation aspect. After the absorption column, a crystallizer is used along with a hydrocyclone to better concentrate the carbonate solution sent to the regenerator. An accelerator is used to enhance mass transfer of CO₂ to the liquid phase. This process has the potential for low energy consumption, options for heat integration to dissolve solids and if a nonvolatile

accelerator is used, a water wash may not be required and there will be no amine emissions to the atmosphere. A pilot plant investigation has been completed; there was a potential of a total reboiler energy requirement of 2.2 to 2.5 MJ/kg CO₂ (Moene et al., 2013).

An Australian group has been working on a process using precipitating potassium carbonate. The benefits over traditional amines include low regeneration energy (2 to 2.5 GJ/tonne CO₂), savings of over \$20/tonne CO₂ than competing amines, and low volatility and environmental impact. They also are focusing on better heat integration throughout the process. A pilot plant has been set up (Anderson et al., 2013).

Akermin is investigating a carbonate based technology which is catalyzed with enzymes which increase the rate of CO₂ hydration to bicarbonate. A key part of this technology is the biocatalyst delivery system. The enzyme is formulated and suspended directly on the structured packing material that is placed in the absorption column. Currently a carbonic anhydrase enzyme developed by Novozymes is yielding the best results because its properties fit well with the process conditions. Using this enzyme, the height of the absorption column can be reduced by up to 90% when a 20 wt% K₂CO₃ is used over uncatalyzed K₂CO₃ (Black et al., 2012).

1.5 Other emerging absorption technologies

1.5.1 Advanced amines

Amine solvents have long been used for CO₂ absorption; however, marked improvements are being made in both the formulation of new solvents, and modifications to the process to increase efficiency. One example is the use of an 8 M piperazine (PZ) solution, which has twice the rate of CO₂ absorption and 1.8 times the intrinsic working capacity of traditional 30 wt% MEA. Since 2001 the reboiler heat duty for amine scrubbing has improved from 5.5 MJ/tonne CO₂ to as low as 2.6 MJ/tonne CO₂ in 2012 (Boot-Handford et al., 2014). Many companies use proprietary solvents as well as advanced heat integration techniques to further decrease their parasitic energy loss.

1.5.2 Amino acid salts

Another class of solvents for CO₂ capture application is amino acid salts. They are being investigated because of their fast reaction kinetics, high achievable cyclic loadings, good stability

towards oxygen and favorable CO₂ binding energy. One advantage of using these salts is for high CO₂ loading, precipitation will occur. Either bicarbonate salt or the neutral amino acid can precipitate out, resulting in increased absorption capacity. The majority of the testing done is on the laboratory scale and performance has been dependent on individual amino acid salts tested.

1.5.3 Ionic Liquids

Ionic liquids (ILs) are a recent introduction to the CO₂ capture conversation, as a potential replacement for traditional amines. A major issue that has been associated with CO₂ removal by amine circulation has been solvent degradation and the various problems it presents. Degradation can cause solvent loss, corrosion, fouling and foaming. ILs have negligible vapor pressure, tunable chemical properties, low regeneration energy and a wide liquid temperature range. They function with limited water, which decreases energy requirements. Certain ILs comprised of amine or carboxylate functional groups are preferential for CO₂ capture under low pressure, such as postcombustion capture. The main drawback to ILs is they are highly viscous, expensive, tend to not be stable to water vapor and flue gas impurities and have low CO₂ absorption capacity per unit of mass (Kenarsari et al., 2013).

1.5.4 CO₂ binding organic liquids

This new class of solvent is a mixture of alcohols and organic bases which reversibly react with CO₂. In amine based CO₂ capture, the efficiency is tied to the amount of water in the process. Binding organic liquids (BOLs) can be used in the presence of water without adverse effects, but do not require large amounts. CO₂ BOLs have 2 to 3 times higher capacity than aqueous alkanolamines. The difference in chemistry is the CO₂ is bound as an alkylcarbonate salt instead of a carbamate based salt. Early CO₂ BOLs had potential, but the vapor pressure was too high. Second generation BOLs are nonvolatile single component systems that react reversibly with CO₂. This resulted in a lower cost and decreased solvent regeneration energy; the stripping of CO₂ from these liquids consumes low energy. CO₂ BOLs have potential, but further investigation is needed to explore the potential of these solvents for real CO₂ capture applications (Kumar et al., 2014).

1.6 Project background

Currently, a Hot Carbonate Absorption Process with Crystallization Enabled High Pressure Stripping (Hot-CAP) is under development at the University of Illinois at Urbana-Champaign (Fig. 1.5). Flue gas CO_2 is absorbed into a potassium carbonate/bicarbonate ($\text{K}_2\text{CO}_3/\text{K}_2\text{CO}_3$ or PCB) solution at 70°C and atmospheric pressure. After the CO_2 rich PCB solution exiting the absorption column is cooled, KHCO_3 crystals are formed at 35°C . Solid crystals are filtered which produces a bicarbonate slurry that is fed to the stripper after it is preheated by the hot regenerated lean solution coming from the stripper. The slurry has higher CO_2 loading than a traditional CO_2 rich solution, thus enabling high pressure CO_2 stripping (≥ 10 atm) at temperatures ranging from 140°C to 200°C .

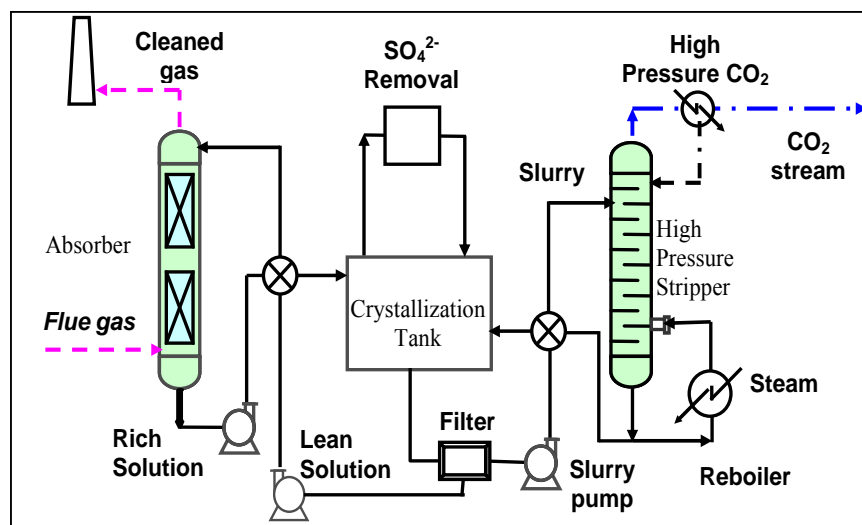


Figure 1.5. Simplified schematic diagram of Hot-CAP process.

The chemistry involved in the Hot-CAP employing an organic promoter/catalyst for CO_2 absorption followed by regeneration of the promoter/catalyst from the CO_2 rich solution, together with crystallization of bicarbonate and CO_2 stripping, is shown in Figure 1.6. During the absorption process, CO_2 absorbed by the organic promoter and the carbonate provides the capacity for CO_2 absorption (Fig. 1.6, Rx(A)). CO_2 absorption rate into the combined solution is dominated by the fast CO_2 promoter reaction instead of the direct CO_2 carbonate reaction. Depending on specific organic promoters selected, the reaction products carbamate (R_2NCOO^-) and/or bicarbonate ions (HCO_3^-) can be formed. For example, primary and secondary amines result in more stable carbamate products; whereas, in case of sterically hindered amines (or

amino acid salts), hydrolysis of the carbamate products further proceeds to form bicarbonate ions. Therefore, bicarbonate ions (HCO_3^-) are dominant in the products compared to the carbamates for hindered amines.

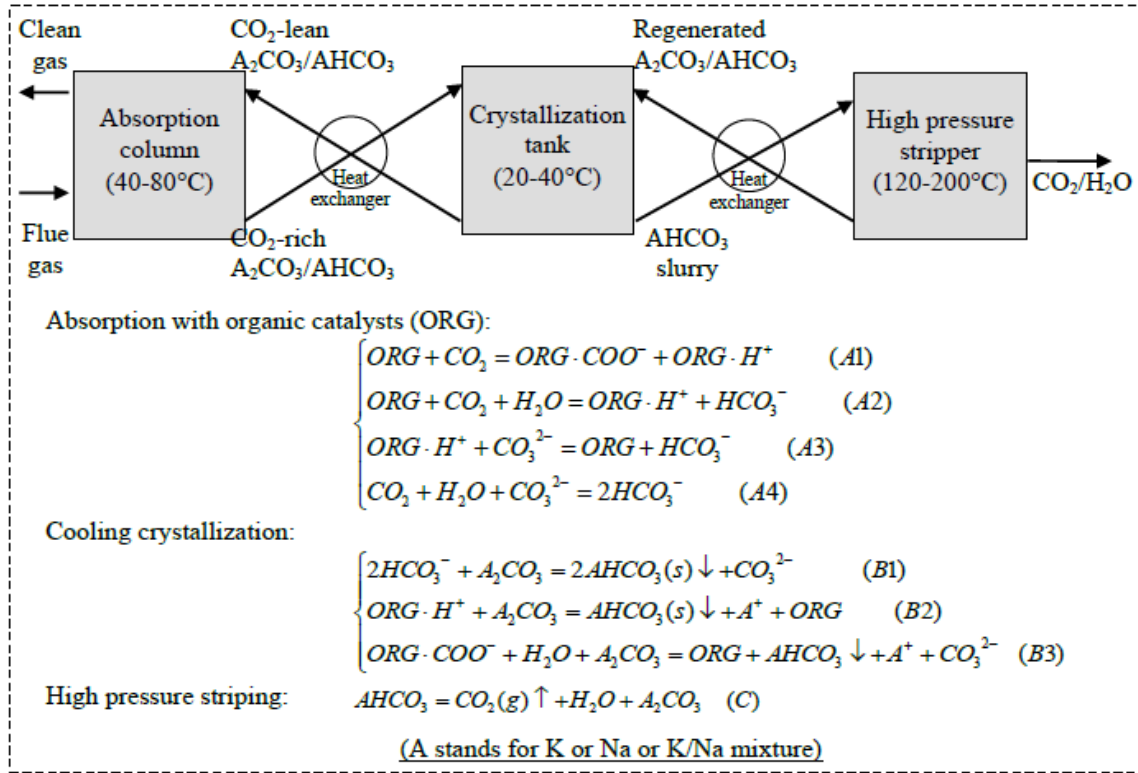


Figure 1.6. Conceptual schematic for chemical reactions involved in CO₂ absorption promoted with organic catalysts/promoters followed with crystallization of bicarbonate and CO₂ stripping.

In the cooling crystallization process, absorbed CO₂ in the rich solution from the absorber is removed in form of bicarbonate crystal particles. At the same time, the protonated amine and carbamate product in the CO₂ rich solution can be regenerated by the reactions with a potassium (or sodium) carbonate (Fig. 1.6, Rx(B)). Within the loop of absorption and crystallization, the organic promoter is not consumed and the overall CO₂ absorption reaction is:



The proposed process employing an amine, amino acid salt or a similar type of promoter in the carbonate solution is different from conventional approaches employing an amine as an absorption solvent or as a promoter mixed with a prime solvent. In conventional processes, the CO₂ rich amine solution exiting the absorption column passes directly to the stripper for

regenerating the amine. In our process the organic solvent in the CO₂ rich solution is used as a promoter or CO₂ carrier during the absorption and also can be regenerated during crystallization of the bicarbonate product. The amine promoter is circulated within the loop of absorption and crystallization without entering the stripping column. The bicarbonate salt (in the form of slurry derived from bicarbonate crystal particles formed in the cooling crystallization process) rather than the CO₂ laden promoter carbonate/bicarbonate solution is present in the stripper for CO₂ stripping and solvent regeneration (Fig. 1.6, Rx(C)).

The Hot-CAP process has advantages over the traditional MEA process and conventional PCB processes. The benchmark MEA process is energy intensive due to a high heat of reaction, low working capacity and low stripping pressure. In the Hot-CAP process, we remedy each of these shortcomings of the MEA process to increase the energy efficiency of CO₂ capture. Both absorption and stripping take place at higher temperatures than the MEA process, while stripping is performed at an increased pressure (8 to 40 atm), resulting in reductions in stripping heat associated with water vaporization in the stripper and CO₂ compression work prior to transportation. PCB is used at a concentration of 40 wt% while MEA uses only 30 wt% (5 M). The Hot-CAP process also solves the problems of solvent degradation and corrosion, in addition to eliminating a unit operation by not needing flue gas desulfurization (FGD) prior to CO₂ absorption.

Experimental studies are being conducted to investigate kinetic and thermodynamic performances of the major unit operations, (CO₂ absorption, KHCO₃ precipitation, CO₂ stripping, combined SO₂ removal and CO₂ capture) under the typical conditions of the Hot-CAP process. This work is focused on addressing the issue associated with a slow rate of CO₂ absorption into a carbonate solution compared to that of an amine solution.

1.6.1 Objectives and importance of research

The main objective of this research was to find an appropriate promoter for a concentrated carbonate solution that increased the rate of CO₂ absorption to a level equal to or above that of the benchmark MEA solvents. The new ideas included performing the absorption at elevated temperatures (~70°C), using a highly concentrated PCB solution (~40 wt%), and

testing various combinations of PCB and promoters. The effect of precipitates on the absorption also was investigated.

1.6.2 Scope of work

Our work focused on the development of rate promoters for a concentrated potassium carbonate system to be used in the Hot-CAP process. Initial tests of many amine promoters and amino acid salts were performed using a stirred tank reactor, to evaluate levels of promotion compared to unpromoted PCB as well as benchmark MEA solvents. The amine promoters with the highest absorption rates were tested more vigorously on a bench scale, packed bed column simulating real process conditions. Effects of different variables were tested to measure their impact on CO₂ absorption rate. Other carbonate salt systems with promoters, including a sodium carbonate-bicarbonate system (SCB) and a PCB/SCB mixture solution, were tested. Results of the promoted carbonate bench scale tests were compared to a typical amine solvent to evaluate their feasibility.

Chapter 2

Screening of Promoters to Accelerate CO₂ Absorption into K₂CO₃/KHCO₃ Solutions

2.1 Introduction

Five primary and secondary amine promoters were investigated under conditions typical of the Hot-CAP process. Rates of absorption into concentrated K₂CO₃/KHCO₃ (PCB) solutions promoted with these promoters at elevated temperatures were investigated and compared to unpromoted PCB solutions and 5 M monoethanolamine (MEA) solvents. Amino acids were tested at the same conditions, both as stand alone absorbents and rate promoters for PCB solutions.

2.2 Experimental methods

2.2.1 Experimental Equipment

The experimental setup consisted of a stirred tank reactor (STR), a gas supply/control unit and data acquisition instruments. The reactor was a Plexiglas vessel with a 4 inch I.D. and 7 inches in height. Four symmetrical baffles, each 0.5 inches wide, were 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 provided mixing for the liquid phase at the desired speed. A stirrer driven by an external motor (Caframo, model BCD2002) via a magnetic coupling (MMC magnetics, FCM-1) provides mixing for the gas phase up to 3,000 rpm. Temperature control of the reactor was achieved by water circulation through a stainless steel coil (0.6 cm I.D.) inside the reactor. The water temperature was controlled by a thermostatic water bath (VWR Scientific, model 1140A). The pressure of the gas stream into the reactor was controlled/ measured by a pressure transducer (Alicat Scientific, PC- 30PSIA-D/5P). The temperature inside the reactor was measured by a thermocouple (Omega, Type K, model KMQSS-125-G-6). A vacuum pump (Dekker, RVL002H-01) was used to achieve the required initial vacuum level for the system. The pressure and temperature readings were monitored and recorded by a computer through a National Instrument Digital Data Acquisition Systems (NI USB 6009). A schematic diagram and picture of the system are shown in Fig. 2.1.

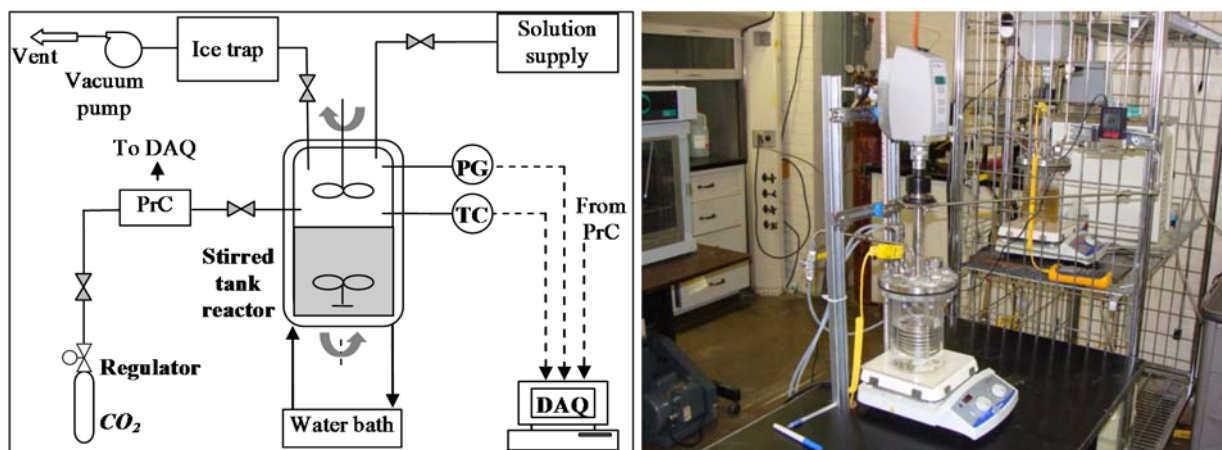


Figure 2.1. Schematic and photograph of STR experimental system.

2.2.2 Experimental Procedure and Conditions

When conducting an experiment in the STR, the system operated under batch mode. First, the system was evacuated by the vacuum pump. A gas stream of pure CO₂ was introduced, in a short burst, into the reactor to a desired pressure. The change in total gas pressure with respect to time was recorded, from which the pCO₂ was obtained by subtracting the water vapor pressure. Since pure CO₂ was used under vacuum conditions, the mass transfer resistance in the gas phase was minimal and neglected during kinetic calculations.

Using this testing procedure, different parameters were investigated to determine their effect on the rate of CO₂ absorption into the PCB solution. First, baseline tests were performed with a high concentration PCB (40 wt%, K₂CO₃ equivalent) at elevated temperatures (60° to 80°C) because these conditions were representative of the Hot-CAP absorption process. The total PCB concentration was varied, as well as the CTB (carbonate to bicarbonate) conversion of the solution to evaluate their effects on CO₂ absorption. The full test matrix can be seen in Table 2.1.

After the baseline absorption removal rates of the unpromoted PCB solutions were established, different amine rate promoters were added to determine their effect on CO₂ absorption. Five primary and secondary amines, including diethanolamine (DEA), aminomethyl propanol (AMP), piperazine (PZ), hexamethylene diamine (HDA) and hexylamine (HA), were tested in varying dosages. The majority of the tests were performed using the lean PCB solution (PCB40-20, 40 wt% PCB (K₂CO₃ equivalent), 20% CTB conversion) and selected promoters were tested in the CO₂ rich solution (PCB40-40) to determine if there was any change in

promotion performance as CO₂ loading increased. All tests were conducted at 70°C. Along with the promoted PCB solutions, 5 M MEA solutions at varying levels of CO₂ loading were tested at 50°C for comparison as an accepted industry standard. The full test matrix can be seen in Table 2.2.

Using the same setup, amino acids were tested both as rate promoters for the PCB solution as well as standalone absorbents. To absorb CO₂, amino acids need to be activated in water by adding an equimolar quantity of base. The salt form of amino acid provided the stability to the solvent at high temperature and pressure condition and reduced the volatility. In these experiments, the potassium salts of amino acids were prepared by neutralizing the dissolved amino acids with equimolar quantities of potassium hydroxide in solution. Absorption capacity was evaluated initially by using a 3 M solution and then the three amino acid salts with the highest absorption were tested further as promoters to the PCB solution. PCB40 was used for these tests and the CTB conversion was varied between 20% and 40%. The full test matrix for amino acid screening can be seen in Table 2.3.

Table 2.1. Test matrix for CO₂ absorption into PCB solutions.

Test Number	Solution	Temperature (°C)
1	PCB 40-20	60
2	PCB 40-20	70
3	PCB 40-20	80
4	PCB 40-40	80
5	PCB 20-20	60
6	PCB 20-20	60

Table 2.2 Test matrix for CO₂ absorption into promoted PCB and MEA solutions.

Test Number	Solution	Temperature (°C)
1	PCB 40-20+ 0.6M DEA	70
2	PCB 40-20+ 1.2M DEA	70
3	PCB 40-20+ 0.5M AMP	70
4	PCB 40-20+ 1M AMP	70
5	PCB 40-20+ 0.5M PZ	70
6	PCB 40-20+ 1M PZ	70
7	PCB 40-20+ 0.5M HDA	70
8	PCB 40-20+ 1M HDA	70
9	PCB 40-20+ 1M HA	70
10	PCB 40-40+ 1M HDA	70
11	PCB 40-40+ 1M PZ	70
12	PCB 40-40+ 1M AMP	70
13	5M MEA, CO ₂ loading: 0 mol CO ₂ /mol MEA	50
14	5M MEA, CO ₂ loading: 0.1 mol CO ₂ /mol MEA	50
15	5M MEA, CO ₂ loading: 0.2 mol CO ₂ /mol MEA	50

Table 2.3. Test matrix for CO₂ absorption into K-Amino Acid salt solutions and amino acid salt-promoted PCB solutions.

Test Number	Solution	Temperature (°C)
1	3M K-Glycine	70
2	3M K-Sacrosine	70
3	3M K-Proline	70
4	3M K-Taurine	70
5	3M K-Alanine	70
6	PCB 40-20+1M K-Glycine	70
7	PCB 40-20+1M K-Sacrosine	70
8	PCB 40-20+1M K-Proline	70
9	PCB 40-40+1M K-Glycine	70
10	PCB 40-40+1M K-Sacrosine	70

2.2.3 Determination of CO₂ Absorption Rate

When gas absorption takes place in a stirred cell reactor, Equation 2.1 can be derived based on the conservation of mass, the ideal gas law, and Henry's law. The mass transfer resistance in the gas phase is minimal and can be neglected. The instantaneous rate of CO₂ absorption into the liquid phase can be calculated from the change of CO₂ partial pressure over time (Kucka et al., 2003):

$$R = - \frac{V_G}{A \cdot R_{gas} \cdot T} \frac{dP_i}{dt} \quad (2.1)$$

where R is the absorption flux of CO₂; V_G is the volume of the gas phase; A is the gas liquid interfacial area; R_{gas} is the universal gas constant; T is the temperature; P_i is the CO₂ partial pressure and t is time. This absorption rate is used to compare the performance of different solutions.

2.3 Results and discussion

2.3.1 CO₂ absorption into reference PCB solutions

2.3.1.1 Reaction mechanism for un-promoted PCB

CO₂ is absorbed into the PCB solution based on the following overall reaction:



The following elementary steps make up this overall reaction (Augugliaro & Rizzuti, 1987; Cents et al., 2001; Cents et al., 2005; Ghosh et al., 2009; Pohorecki & Moniuk, 1988; Vázquez et al., 1997):



Under certain conditions, the overall reaction can be modeled as pseudo first order with respect to CO₂. This rate is a linear function of the hydroxide ion concentration; therefore, R2.2 and R2.4 are the most important rate determining steps (Alper & Deckwer, 1980; Cents et al., 2001; Danckwerts, 1968; Vázquez et al., 1997).

2.3.1.2 Results of CO₂ absorption into unpromoted PCB solutions

The effect of the temperature on the rate of CO₂ absorption into the PCB40-20 solution is shown in Fig. 2.2. Henry's constant, which indicates CO₂ solubility, and reaction kinetics both strongly depend on the temperature. As the temperature increases, the CO₂ solubility decreases, while the rate constant of the absorption reaction increases. The net effect of the temperature on the CO₂ absorption rate depends on which property undergoes a greater change. Increasing the reaction temperature from 60°C to 80°C improved the CO₂ absorption rates, which indicated an increase in temperature was beneficial for promoting the CO₂ absorption rates into the 40 wt% PCB solution.

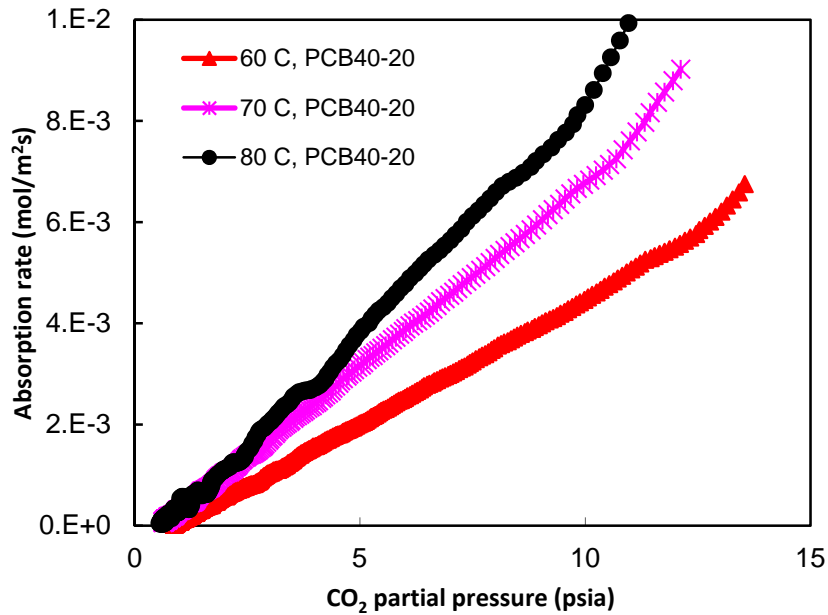


Figure 2.2. Absorption of CO₂ into PCB40-20 solution at varying temperatures.

The absorption of CO₂ into PCB40-20 and PCB40-40 at 80°C, and PCB20-20 and PCB20-40 at 60°C is depicted in Fig. 2.3. The higher the CTB conversion level, the lower the CO₂ absorption rate for the PCB solution with the same concentration and temperature. This tendency was greater for the 40 wt% PCB solution tested at 80°C.

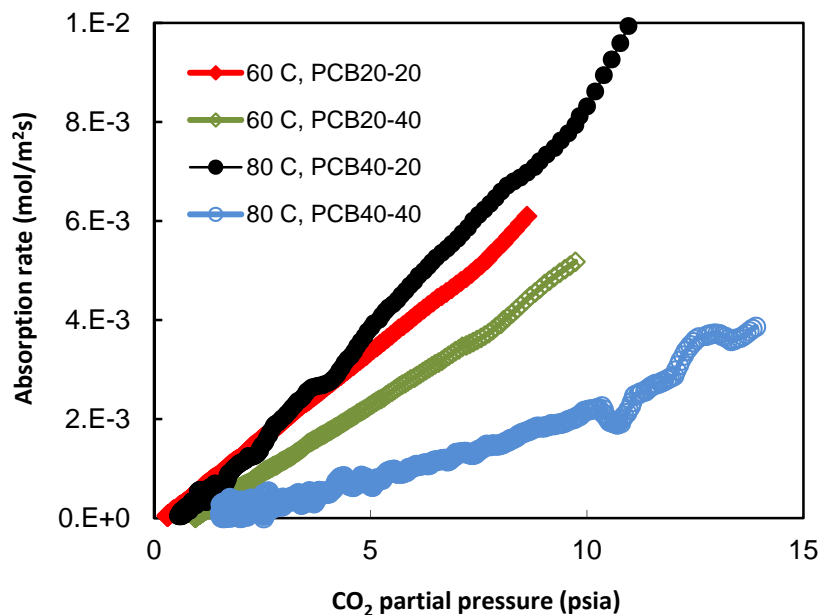


Figure 2.3. Absorption of CO₂ into PCB solutions at varying PCB concentrations and CTB conversion levels at 60 and 80°C.

The rate of CO₂ absorption into PCB40-40 at 80°C was the slowest among the solutions tested. The explanation could be that the equilibrium pressure of CO₂ over PCB40-40 at 80°C was higher than those over the PCB40-20 solution at the same temperature and the 20 wt% PCB solutions (PCB20-20 and PCB20-40) at 60°C. As a result, at the same CO₂ partial pressure, the driving force for CO₂ absorption into PCB40-40 is reduced compared to the other solutions.

Increasing the PCB concentration increased the ionic strength and viscosity, and lowered the CO₂ solubility of the solution. These factors are important to CO₂ reaction kinetics, physical mixing, and mass transfer in the liquid phase during the absorption process. The rates of CO₂ absorption into the PCB solution with higher concentration are adversely impacted at the concentration range between 20 wt% and 40 wt% (Comstock & Dodge, 1937). However, there is potential for the reduced absorption rate into a high concentration PCB solution (40 wt% vs. 20 wt%) to be overcome by increasing the reaction temperature as shown above, where the PCB40-20 at 80°C has a comparable absorption rate to PCB20-20 at 60°C.

2.3.2 Screening of amine promoters

2.3.2.1 Reaction mechanism for PCB promoted with amines

Addition of amines or similar types of promoters (such as amino acid salts) into the PCB solution can enhance the absorption rate by a “shuttle mechanism” (Bosch et al., 1989). When a primary or secondary amine promoter is added to the carbonate solution, the reactions consist of a sequence of elementary steps as follows.



Where B is a base, R_2NH is an amine and R_2NCOO^- is a carbamate intermediate.

In the promoted absorption, fast CO_2 absorption reactions occur with amines near the interface (R2.6), followed by regeneration of reaction products (reverse R2.6, R2.7 and R2.8) by the carbonate in the bulk of the solution. The slow reaction in the bulk carbonate solution (R2.9, R2.10) 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 carbonate solution without a promoter, R2.9 and R2.10 are the most important and R2.10 is slow under low alkaline conditions.

2.3.2.2 Results of amine promoter screening

Rates of CO_2 absorption into unpromoted and promoted PCB40-20 solutions at a temperature typical of Hot-CAP absorption ($70^\circ C$) are depicted in Fig. 2.4. In preliminary studies, all five amine promoters, depending on the type and dosage of amines, enhanced the rate of absorption to various extents. Absorption rates were promoted by 3.5 to 50 times compared to the unpromoted PCB solution when the pCO_2 was between 1 and 5 psia. Among the five amines, at the same dosage (1 or 0.5 M), PZ and AMP had the highest potential rate of promotion, followed by HDA.

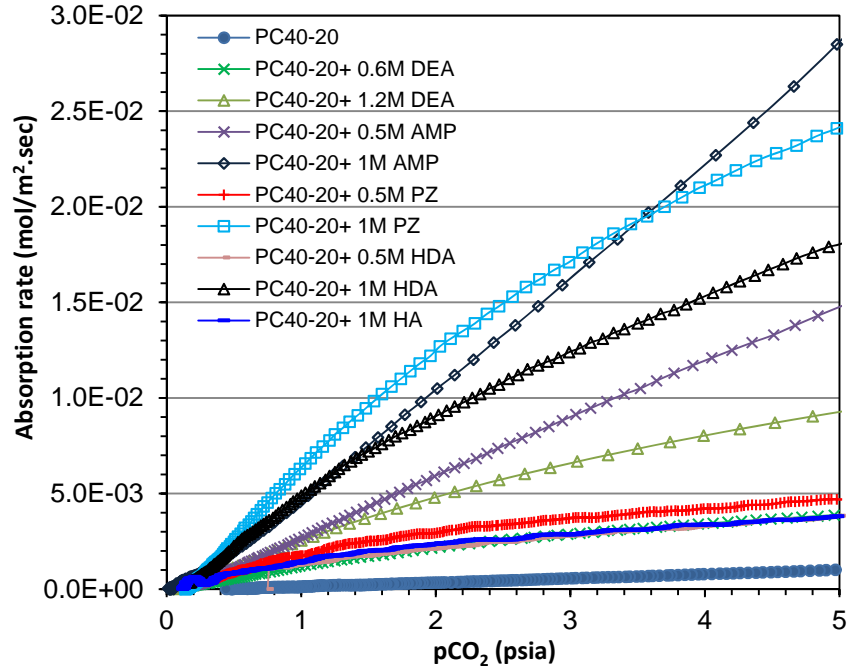


Figure 2.4. Rates of CO₂ absorption into promoted PCB40-20 at 70°C.

When applied to an absorption column setup, the PCB solution travels down the height of the column and the constant CO₂ absorption causes an increase in CO₂ loading. Depending on the amount of CO₂ absorbed, or the CO₂ loading, the absorption rate will decrease down the column because of a decrease in driving force. Thus, it is essential to measure the absorption rate into the solution with different CO₂ loading levels to study how absorption rate varies along the absorption column. PCB40-20 was employed to simulate the CO₂ lean solution at the top of the absorption column and PC40-40 for the CO₂ rich solution at the lower part of the column. Over the duration of a test in the STR, the change in CTB of the solution was negligible. In these experiments, 1 M PZ, AMP or HDA promoter was added to the PCB solutions. These promoters were selected based on their potential for promoting the CO₂ absorption rate. Results of these tests are shown in Fig. 2.5.

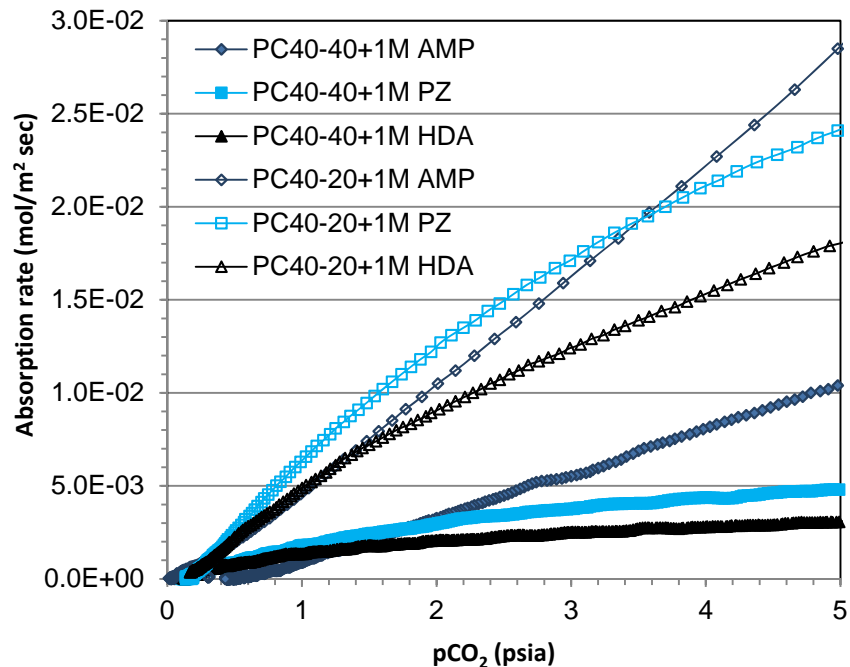


Figure 2.5. CO₂ absorption rates into promoted PCB40-20 and PCB40-40 solutions at 70°C.

The CO₂ absorption rate into the PCB40-40 with the addition of 1 M AMP was 2 to 3 times lower than that of the PCB40-20 with the same promoter; however, for 1 M PZ and HDA promoters in the PCB40-40 and PCB40-20 solutions, the difference between absorption rates was 5 to 6 times lower under the same conditions. The decrease in absorption rate as the CTB increased from 20% to 40% was expected because the driving force of CO₂ absorption into PCB40-40 was smaller.

2.3.2.3 Comparison between promoted PCB solution and MEA solution

In Fig. 2.6, CO₂ absorption rates into PCB40-20 with additions of 1 or 1.2 M of amine promoters were compared with those into 5 M MEA solutions. Fresh 5 M MEA solution and solutions loaded with 0.1 or 0.2 mol CO₂/mol MEA, were selected for the comparison. Compared to the MEA solution with 0.2 mol/mol CO₂ loading at 50°C (a lean condition typical of MEA processes), absorption rates into the PCB40-20 (a lean condition typical of Hot-CAP) promoted with 1 M PZ, 1 M AMP or 1 M HDA at 70°C were higher at CO₂ partial pressures greater than 2 psia and comparable at lower partial pressures.

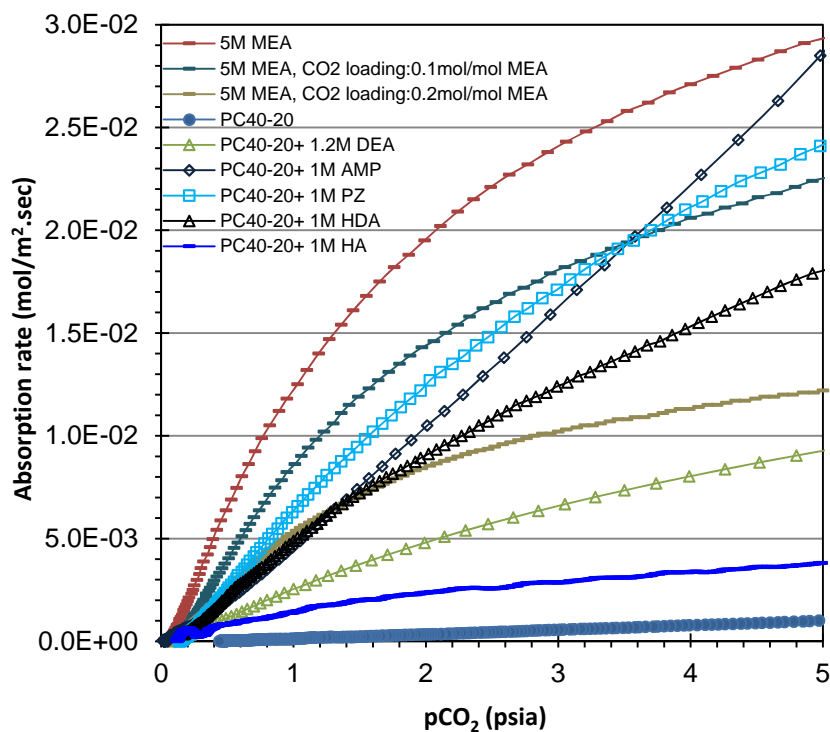


Figure 2.6. CO₂ absorption rates into promoted PCB40-20 solutions at 70°C and 5 M MEA solutions at 50°C.

Also shown in Fig. 2.6, the MEA solutions exhibited a similar trend with respect to the impact of CO₂ loading on the absorption rate. For example, compared to the fresh MEA, absorption rates into the 5 M MEA loaded with 0.1 or 0.2 mol CO₂/mol MEA decreased by 25% and 60%, respectively. In a typical MEA process, the CO₂ rich solution can contain more than 0.4 mol CO₂/mol MEA. With the use of amine promoters, CO₂ absorption rate into a PCB solution can be enhanced to levels above or equal to that of 5 M MEA.

2.3.3 Screening of Amino Acid Salt Promoters

2.3.3.1 Absorption into amino acid salt solution

Absorption rates into five different 3 M amino acid salt solutions are shown in Fig. 2.7. The K-Glycine solution had the highest absorption rate, followed by K-Sarcosine and K-Proline. 3 M K-Glycine, K-Sarcosine and K-Proline salt solutions at 70°C exhibited absorption rates higher than or comparable to those into the 5 M MEA solution at 50°C.

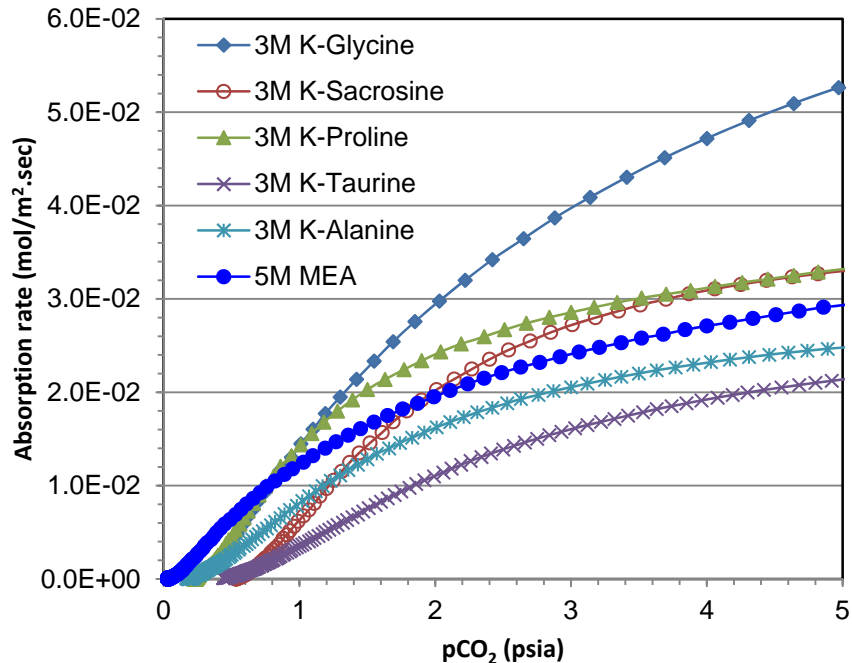


Figure 2.7. CO₂ absorption rates into amino acid salt solutions at 70°C

The differences in absorption rates into these amino acid salt solutions were caused by different molecular structures and locations of amino groups. Glycine is similar in structure to primary amines; whereas, proline and sacrosine are secondary amine group acids. Even though sacrosine is a non-standard amino acid, it has been shown to have potential in regard to CO₂ capture. The K-taurine and K-alanine salt solutions had the lowest rates for CO₂ absorption. The reaction mechanism of CO₂ with amino acid salts can be described by the formation of carbamates, followed by the hydrolysis of carbamates to produce bicarbonate ions, which is similar to that for alkanolamines (Kumar et al., 2014).

2.3.3.2 Absorption into amino acid salt promoted PCB solution

The three best performing amino acids, K-glycine, K-sacrosine and K-proline, were selected as promoters for CO₂ absorption into PCB. CO₂ absorption rates into the PCB40-20 solution with and without amino acid salt promoters were compared with those into 5 M MEA with CO₂ loading of 0.2 mol CO₂ /mol MEA (40% amine conversion, MEA5-40) at 50°C (Fig. 2.8). A promoter concentration of 1 M was used.

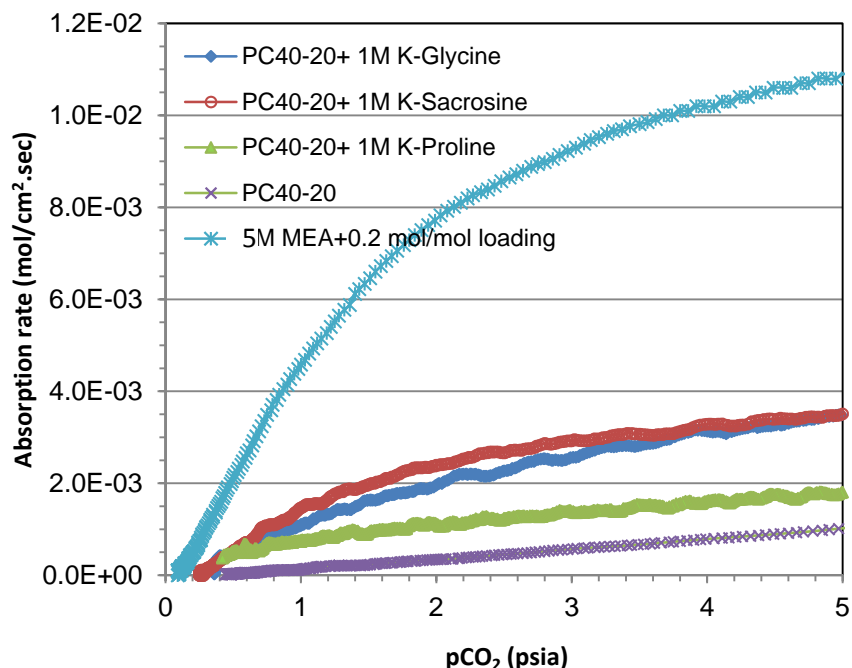


Figure 2.8. Comparison of CO₂ absorption rates into amino acid salt promoted PCB40-20 at 70°C and into MEA at 50°C.

The absorption rate into the MEA5-40 solution at 50°C was 10 to 35 times greater than the rate into the baseline PCB40-20 without a promoter at 70°C for pCO₂ between 1 and 5 psia. Adding 1 M amino acid salt promoters improved the absorption rates in the PCB40-20. The addition of K-glycine and K-sacrosine increased absorption rates by 3 to 11 times for the CO₂ partial pressure range tested. However, these promoted rates were lower than those into the MEA solution. The equilibrium vapor pressures over the amino acid salt solutions were higher than those over the MEA, which could reduce the driving force for the CO₂ absorption.

The rates of CO₂ absorption promoted by K-glycine and K-sacrosine in the PCB solutions with different CTB conversion levels are shown in Fig. 2.9. Absorption rates into the promoted PCB40-40 were lower than those into the PCB40-20 by the same promoters. The addition of 1 M K-sacrosine in the PCB40-20 and PCB40-40 was more effective for accelerating the CO₂ absorption compared to 1 M K-glycine in the same solutions. The differences in absorption levels from PCB40-20+1 M K-glycine compared to PCB40-40+1 M K-glycine were minimal considering the large change in CTB conversion. In the MEA solution when the loading was increased by just 0.1 mol CO₂/mol MEA, the absorption rate decreased (Fig. 2.6). The rates into PCB40-40 promoted by K-glycine could be close to those into the 5M MEA with a CO₂ loading higher than 0.2 mol CO₂/mol MEA.

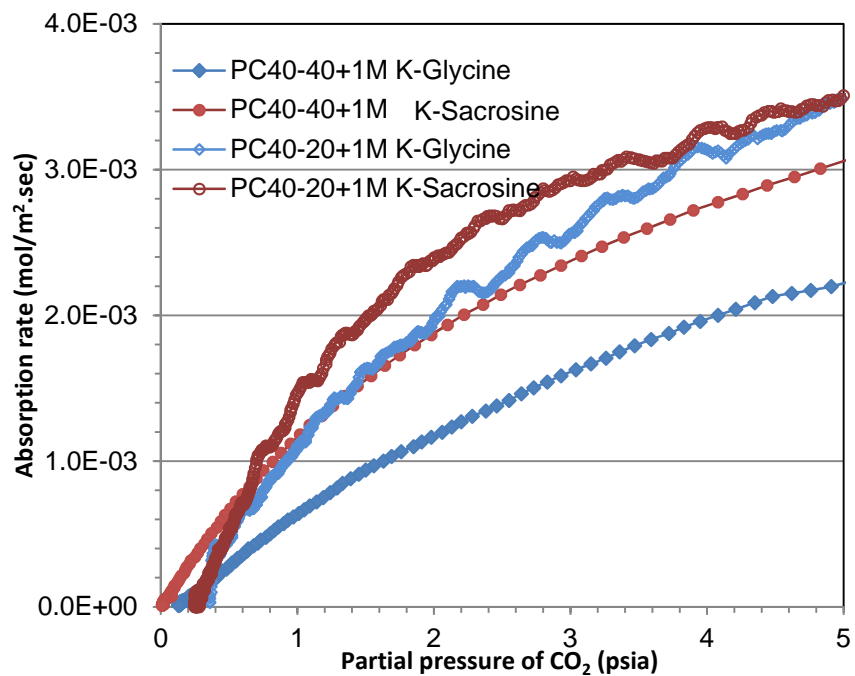


Figure 2.9. CO₂ absorption rates into PCB40-40 and PCB40-20 at 70°C promoted by amino acid salts.

Chapter 3

Kinetic Study of CO₂ Absorption into a Concentrated K₂CO₃/KHCO₃ Solution in a Packed Bed Column

3.1 Introduction

After screening and selecting promoters with the greatest potential of boosting rates of CO₂ absorption in concentrated K₂CO₃/KHCO₃ (PCB) solution, a bench scale, packed bed column was fabricated to test the performance of CO₂ absorption into the PCB solution with the selected promoters.

3.2 Experimental methods

3.2.1 Packed bed column system

A bench scale, packed bed absorption column, designed and fabricated for the CO₂ absorption study, was built of cast acrylic so flow through the column could be observed. The acrylic material was tested by immersing it into a 40 wt% PCB solution for a month, after which no signs of corrosion or degradation were seen. The column was constructed to be 3 m tall and have a 10 cm I.D. and packed with a corrugated stainless steel packing material (Hai-Yan New Century Petrochemical Device Co., Ltd, Model 500) of 2 m height. The structured packing had a specific surface area of 800 m²/m³ (Table 3.1).

Table 3.1. Geometric specifications of the structured packing material.

Specification	
Height of packing element, mm	100
Diameter of packing element, mm	100
Specific surface area (a), m ² /m ³	800
Angle of inclined corrugation to the horizontal(θ), degree	45
Corrugation crimp height, mm	5
Side dimension of corrugation, mm	10
Void fraction (ϵ)	0.66

The gas stream was a simulated flue gas mixture consisting of air, CO₂ and water vapor. Air was supplied from an air compressor and CO₂ from a compressed gas cylinder; flows were

monitored by two mass flow meters (Dwyer, GFM) controlled by needle valves. Steam from a steam generator (Chromalox/CMB-3) was mixed with the CO₂ air gas to provide the required gas inlet temperature and humidity. The PCB feed solution was pumped from a 10 gal stirred tank using a peristaltic pump (MasterFlex). The liquid flow rate was controlled by setting the speed (RPM) of the pump. An electric heater with temperature control was mounted inside the tank to maintain the desired temperature. The inlet and outlet CO₂ concentrations were measured by a CO₂ analyzer (Quantek Instruments, Model 906) after any moisture was removed from the gas streams by a diffusion dryer. A schematic of the packed bed column setup is shown in Figure 3.1.

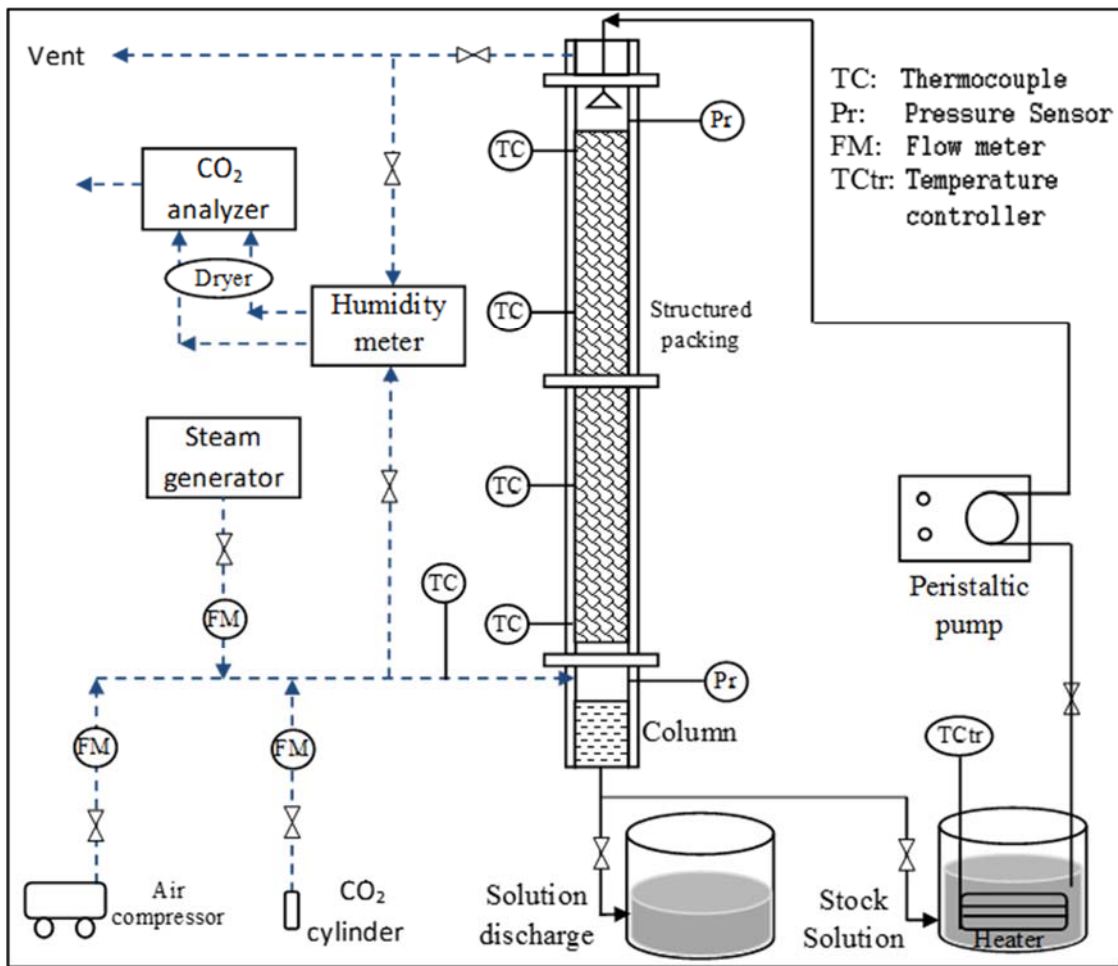


Figure 3.1. Schematic of bench scale, packed bed column.



Figure 3.2. Photographs of the bench scale, packed bed absorption column setup: (a) the packed column; (b) a packing unit (10 cm diameter by 10 cm high) (c) Chromalox steam generator.

3.2.2 Methods of CO₂ absorption experiments

Flow meters and control valves to regulate CO₂, steam and air flows were calibrated. The liquid flow rate was calibrated for both water and hot PCB solution. Five thermocouples were attached along the height of the column to measure the temperature profile in the column, three in the packing, one on the top and one on the bottom of the column. The pressure drop across the column was measured using a U-tube. A humidity analyzer (VAISALA) measured the moisture contents of the inlet and outlet gas streams. The absorption operated counter currently, meaning the liquid was pumped to the top of the column and flowed downward while the gas flowed upward from the bottom. The CO₂ rich solution exiting the column returned to the tank and was recycled in the system for continuous use. Since the volume of feed solution in the tank was large, and the amount of CO₂ absorbed during each cycle was small, feed solution composition did not change in a short period of time (e.g., 10 min). This was verified by testing CO₂ loading at short time intervals and allowed for a pseudo steady operation under a preset condition as well as enough time for liquid sampling and CO₂ concentration measurements during the continuous test.

Based on CO₂ concentrations in the dried inlet and outlet streams, CO₂ removal efficiency of the solution at a given CTB conversion level was given by the following:

$$CO_2 \text{ Removal Efficiency} = \frac{CO_2 \text{ Inlet Volume \%} - CO_2 \text{ Outlet Volume \%}}{CO_2 \text{ Inlet Volume \%}} \quad (3.1)$$

This removal efficiency was used for comparison or used to identify the molar flow rate or other variables that depended on the rate at which CO₂ was absorbed.

Using this setup, tests were carried out in three stages. First, unpromoted PCB was tested at various conditions to establish baseline removal rates to compare to promoted solutions. The concentration of PCB was varied from 20 wt% to 40 wt% and a range from lean to rich CO₂ loading, of CTB conversions was tested. Since a PCB concentration of 40 wt% was considered to be the standard, multiple liquid to gas ratios (L/G), measured in L/m³, were tested. The baseline temperature was 70°C but tests also were performed at 80°C to evaluate the effect of temperature on CO₂ absorption. The full test matrix for these solutions can be seen in Table 3.2.

Once a baseline removal was established for PCB at the desired concentrations and CTB conversions, testing was done to evaluate the effectiveness of various rate promoters. This involved testing multiple amine promoters with differing dosages, as well as evaluating the effect of L/G ratio and CO₂ inlet concentration on CO₂ removal effectiveness. The test matrix was set so only one variable was changed at a time from the predetermined baseline conditions. These tests were performed at 70°C. For a reference, 5 M MEA was tested, with the temperature set point at 50°C. The full test matrix for these solutions can be seen in Table 3.3.

After these tests were completed, other solvents were investigated for their absorption potential including sodium carbonate/bicarbonate solution (Na₂CO₃/NaHCO₃, SCB) and PCB/SCB mixture solutions. These solutions were investigated in a similar fashion to PCB where only one variable at a time was changed to see the effect of different variables such as promoters, L/G ratios, SCB and PCB/SCB concentrations and CO₂ inlet concentrations. The full test matrix can be seen in Table 3.4.

Table 3.2. Unpromoted potassium carbonate test matrix.

Test No.	Initial absorbent*	Temp (°C)	L/G @0.56 LPM liquid flow rate (L/m ³ @ actual condition)	CO ₂ inlet concentration, vol%
1	PCB40-20	70	2, 4, 8, 12	14
2	PCB40-30	70	2, 4, 8, 12	14
3	PCB40-40	70	2, 4, 8, 12	14
4	PCB20-20	70	4	14
5	PCB20-30	70	4	14
6	PCB20-40	70	4	14
7	PCB30-20	70	4	14
8	PCB30-30	70	4	14
9	PCB30-40	70	4	14

* PCB40-20: 40 wt% (K₂CO₃-equivalent) PCB solution with 20% CTB conversion.

Table 3.3. Promoted potassium carbonate and monoethanolamine test matrix.

Test No.	Initial absorbent	Temp (°C)	L/G @0.56 LPM liquid flow rate (L/m ³ @ actual condition)	CO ₂ inlet concentration, vol%
1	PCB40-20+1 M DEA	70	4	14
2	PCB40-20+0.5 M DEA	70	2, 4, 8	14
3	PCB40-20+0.5 M DEA	70	4	8
4	PCB40-20+1 M AMP	70	4	14
5	PCB40-20+0.5 M AMP	70	2, 4, 8	14
6	PCB40-20+0.5 M AMP	70	4	8
7	PCB40-20+0.75 M PZ	70	4	14
8	PCB40-20+0.5 M PZ	70	2, 4, 8	14
9	PCB40-20+0.5 M PZ	70	4	8
10	PCB30-20+0.5 M PZ	70	4	14
11	PCB20-20+0.5 M PZ	70	4	14
12	5 M MEA	50	4	14

Table 3.4. Sodium carbonate and potassium/sodium carbonate mixture tests.

Test No.	Initial absorbent *	Temp (°C)	L/G @0.56 LPM liquid flow rate (L/m ³ @ actual condition)	CO ₂ inlet concentration, vol%
1	SCB15-15	70	4, 12	14
2	SCB15-15+0.5 M PZ	70	4, 12	14
3	PCB25/SCB10-20+0.5 M PZ	70	4, 8, 12	14
4	PCB25/SCB10-20+0.5 M PZ	70	4	8
5	PCB25/SCB10-20+1 M DEA	70	4	14
6	PCB20/SCB15-20+0.5 M PZ	70	4	14
7	PCB12.5/SCB5-20+0.5 M PZ	70	4	14

* SCB15-15: 15 wt% (Na₂CO₃-equivalent) SCB solution with 15% CTB conversion; PCB25/SCB10-20: 25 wt% (K₂CO₃-equivalent) PCB and 10 wt% SCB mixture solution with 20% CTB conversion.

3.2.3 Method of CO₂ loading analysis

The CO₂ loading of the PCB solution is a very important measure in comparing CO₂ removal rates of different solutions to each other. As the solution flows down the column, it absorbs CO₂ in the form of KHCO₃. Near the bottom, increasing amounts of carbonate are converted to bicarbonate, therefore, CTB conversion increases and the driving force for absorption decreases because the concentration of CO₂ in the solution is closer to equilibrium. This has a major effect on the CO₂ absorption rate; therefore, a reliable way to measure CTB conversion was needed.

Liquid PCB samples, with or without an amine promoter, were taken at predetermined time intervals during each test and analyzed using the Chittick apparatus. A schematic of the apparatus is shown in Fig. 3.3. During analysis, the CO₂ laden sample was placed in a flask and rested on a magnetic stirrer. The flask was connected to an adjustable graduated tube and a fluid reservoir, which contained a 2 M HCl solution. When an excess of acid was added to the sample, CO₂ in the solution was released by the following reactions:



(RNH_3^+ : protonated amine; $RNHCOO^-$: carbamate; R: hydrocarbon substitutes in an amine promoter)



Figure 3.3. A photograph of a chittick apparatus used for CO₂ loading measurement.

As CO₂ was released from the PCB sample, the liquid in the graduated tube was displaced. CO₂ loading in the sample was calculated from the displaced volume of liquid which was equal to the volume of released CO₂. This technique was used for measuring the loading of MEA solutions as well.

While using the Chittick apparatus was accurate, it proved to be time consuming. Therefore, a different approach was adopted as an alternative. During a test, CO₂ loading in the solution increased over time as the CO₂ absorption continued. Using the initial CTB conversion (eg., 20%), CO₂ loading was estimated from the CO₂ removal efficiency and the gas and liquid flow rates based on a mass balance principle. As any CO₂ that was lost in the gas stream had to be absorbed into the liquid solution, with known reactions, the CTB conversion level could be estimated at a given time and related to a CO₂ absorption rate.

3.2.4 Method of mass transfer coefficient measurement

To determine the impact of mass transfer in the overall rate of CO₂ absorption, it was important to quantify the gas and liquid phase mass transfer coefficients of the bench scale absorption column. These coefficients were related directly to the mass transfer resistance in the column and were an important parameter in evaluating CO₂ absorption performance. Literature data are available for similar absorption columns, but because a small difference in the setup can cause a great variance in these correlations, a study on measuring mass transfer in the current column was essential (Kim & Deshusses, 2008; Onda et al., 1968; Rocha et al., 1996; Wang et al., 2005).

To determine the liquid phase mass transfer coefficient of the packed bed column, the physical absorption of oxygen from air into water was studied by measuring the amount of oxygen dissolved into water throughout the column. The solubility of oxygen into water was low, and used as a sparingly soluble gas in the absorption. In this scenario the overall mass transfer is dominated by the liquid phase, making it possible to calculate the liquid side mass transfer coefficient (Kim & Deshusses, 2008). This was done by introducing air from a cylinder into the bottom of the absorption column. The air flow rate was measured by the same calibrated mass flow meter used in the CO₂ absorption tests. The water used in the experiment was DI water swasparged with nitrogen to minimize initial dissolved oxygen. The N₂ treated water was pumped to the top of the column and flowed down through the column for O₂ absorption. Unlike the CO₂ absorption tests, the spent water exiting the column was not recirculated in the system. The flow rate of water was varied along with the flow of air to cover the full operating range of the column. When the column reached steady state at each preset condition, as indicated by a stable temperature profile along the column as well as a stable O₂ concentration in the liquid outlet, liquid samples were taken at the inlet and outlet. Samples were analyzed for dissolved oxygen concentration using a dissolved oxygen (DO) meter (Hach, Model HQ30d).

As the main resistance to mass transfer during the absorption of oxygen into water was localized in the liquid phase, the individual liquid mass transfer coefficient was approximated as the overall liquid phase coefficient:

$$\frac{1}{K_L a_e} = \frac{1}{k_L a_e} \quad (3.2)$$

where $K_L a_e$ (s^{-1}) is the overall liquid phase mass transfer coefficient, $k_L a_e$ (s^{-1}) is the individual liquid phase mass transfer coefficient and a_e (m^2/m^3) is the effective surface area of the packing material. The following equation can thus be derived to calculate the individual liquid mass transfer coefficient based on the measurement of dissolved O_2 in water during the absorption.

$$k_L a_e = \frac{u_L}{Z} \times \ln \left(\frac{C^* - C_{L,in}}{C^* - C_{L,out}} \right) \quad (3.3)$$

where C^* (mg/L) is the physical solubility of oxygen at the interface, $C_{L,in}$ and $C_{L,out}$ (mg/L) are the inlet and outlet concentrations of dissolved oxygen in the water, u_L (m/s) is the specific liquid flow rate and Z (m) is the height of the packing in the column. The value of C^* , estimated based on the Henry's law, was approximated as a constant because the change of O_2 concentration in air (21 vol%) during the absorption was negligible.

To measure the gas phase mass transfer coefficient, the absorption of CO_2 into a 1.0 M NaOH solution was measured. The overall rate of CO_2 absorption was found to be contributed by both the liquid and gas phase mass transfer although the reaction of CO_2 and NaOH in the liquid phase was fast. In the measurement, the column operated counter currently. The inlet gas contained 4% CO_2 and the experiment was run at ambient temperature ($\sim 20^\circ C$). When a stable outlet CO_2 concentration as well as a stable temperature profile were seen in the column, the inlet and outlet gas compositions were measured by the CO_2 analyzer. The NaOH solution was not recirculated through the column to ensure that the column was running at steady state, and there was no change in the pH of the inlet solution. Conditions tested on the packed bed column are shown in Table 3.5.

Table 3.5. Test matrix for mass transfer coefficient measurement of the packed bed column.

Test #	Solvent Used	Superficial Gas Velocity (m/s)	Superficial liquid velocity (cm/s)		
1	1M NaOH	0.23	0.12	0.3	0.5
		0.34	0.12	0.3	0.5
		0.47	0.12	0.3	0.5
2	DI Water	0.23	0.12	0.3	0.5
		0.34	0.12	0.3	0.5
		0.47	0.12	0.3	0.5

The overall gas phase mass transfer coefficient (K_{Ga_e}) is measured by the absorption of CO_2 into the NaOH solution at ambient temperature according to the following equation:

$$K_G a_e = \frac{u_G}{Z} \times \ln \left(\frac{[CO_2]_{in}}{[CO_2]_{out}} \right) \quad (3.4)$$

where K_{Ga_e} (s^{-1}) is the overall liquid phase mass transfer coefficient, u_G (m/s) is the gas velocity, and $[CO_2]_{in}$ and $[CO_2]_{out}$ (mol/L) are CO_2 concentrations at the gas inlet and outlet, respectively.

The relationship between the overall gas phase mass transfer coefficient and individual liquid and gas mass transfer coefficients is shown in the following equation:

$$\frac{1}{K_G a_e} = \frac{1}{k_L a_e E H} + \frac{1}{k_G a_e} \quad (3.5)$$

where k_{Ga_e} (s^{-1}) is the individual gas phase mass transfer coefficient, E is the enhancement factor due to the chemical reaction and H is the dimensionless Henry's constant. The value of E can be calculated as follows (Cents et al., 2005; Liao & Li, 2002):

$$E \approx Ha = \frac{\sqrt{D_{CO_2} k_{OH^-} [OH^-]}}{k_L} \quad (3.6)$$

where D_{CO_2} (m^2/s) is the diffusivity of CO_2 into the NaOH solution, k_{OH^-} (L/mol*s) is the kinetic rate constant and $[OH^-]$ (mol/L) is the OH^- concentration in the bulk solution. To use equation (3.6) the value of the Hatta number (Ha) must be greater than 3, and the absorption of CO_2 into the NaOH solution is considered pseudo first order (Cents et al., 2005; Liao & Li, 2002).

Once the overall gas phase mass transfer was determined based on the CO_2 absorption measurement (Eq. (3.4)) and the individual liquid phase mass transfer coefficient was determined by the O_2 absorption measurement (Eq. (3.3)), the individual gas phase mass transfer coefficient of the column was calculated from the Eq. (3.5). Different from the CO_2 absorption tests, half of the structured packing (1 m high) in the packed bed column described above was removed in the measurements of mass transfer coefficients. This was done because both absorption processes took place at an increased rate and especially during the liquid phase mass transfer coefficient measurement the water reached a maximum oxygen absorption by the time it traveled through 2 m of packing regardless of the conditions. Results of mass transfer measurements were believed

to be valid because either the absorption of oxygen into water or the absorption of CO₂ into NaOH was not completed through the 1 m packing.

These measurements were also done using the same methods on a 3 m tall, 5 cm I.D. column packed with 1 m of stainless steel Pall rings that had a specific surface area of 500 m²/m³. This was done to validate the above methods since literature data with this packing were more available. For example, the correlations proposed by Onda et al. (1968) have been accepted for such columns (Kelly et al., 1984; Sanyal et al., 1988; Tontiwachwuthikul et al., 1992).

3.3 Results and discussion

3.3.1 Determination of mass transfer coefficients

3.3.1.1 Liquid phase mass transfer coefficient

The measured individual liquid phase mass transfer coefficients ($k_{L a_e}$) for the random Pall ring packings are shown in Figure 3.4. The experimental values are close to those predicted by Onda's correlation, for each condition tested (Onda et al., 1968). In both the predicted and experimental values, the value of $k_{L a_e}$ was independent of changes in gas velocity. In comparison, changes in liquid velocity did have an effect on mass transfer. As liquid flow rate was increased, rate of liquid phase mass transfer also increased, which was most likely due to an increase in the effective area for gas liquid absorption caused by greater wetting of the packing. Since these results for the Pall ring packing were consistent with the literature data, the measurement methods were considered to be validated (Kim & Deshusses, 2008; Piché et al., 2001).

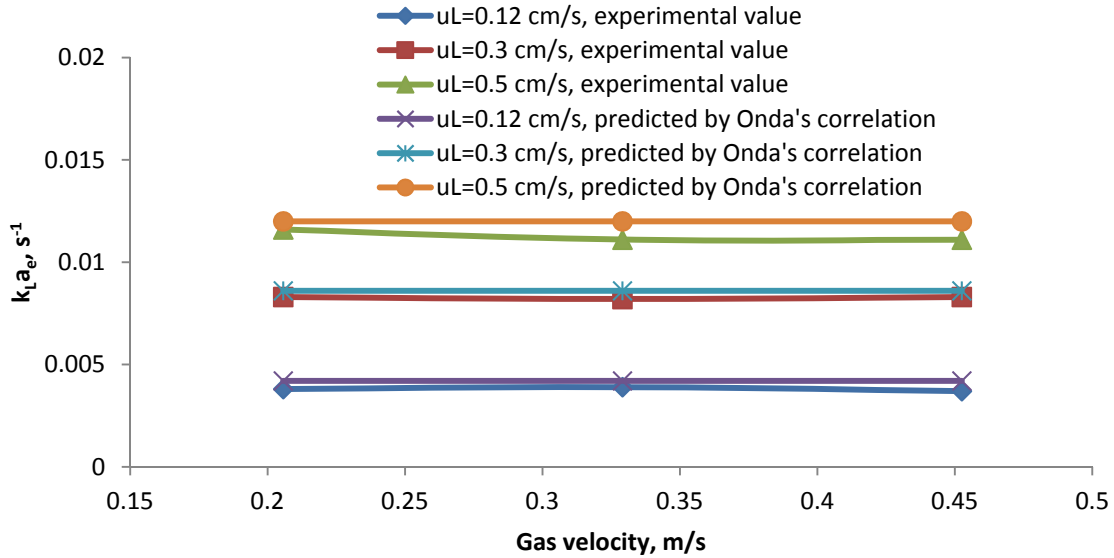


Figure 3.4. Liquid phase mass transfer coefficients in packed bed columns with random Pall ring packing at varying gas flow rates.

The measured $k_L a_e$ values for the structured packing are shown in Figure 3.5. At the same liquid flow rates, the $k_L a_e$ values for the structured packing were 30% higher than the random packing. This was expected as the structured packing was designed to have better mass transfer properties, such as a higher specific surface area, than the random packing.

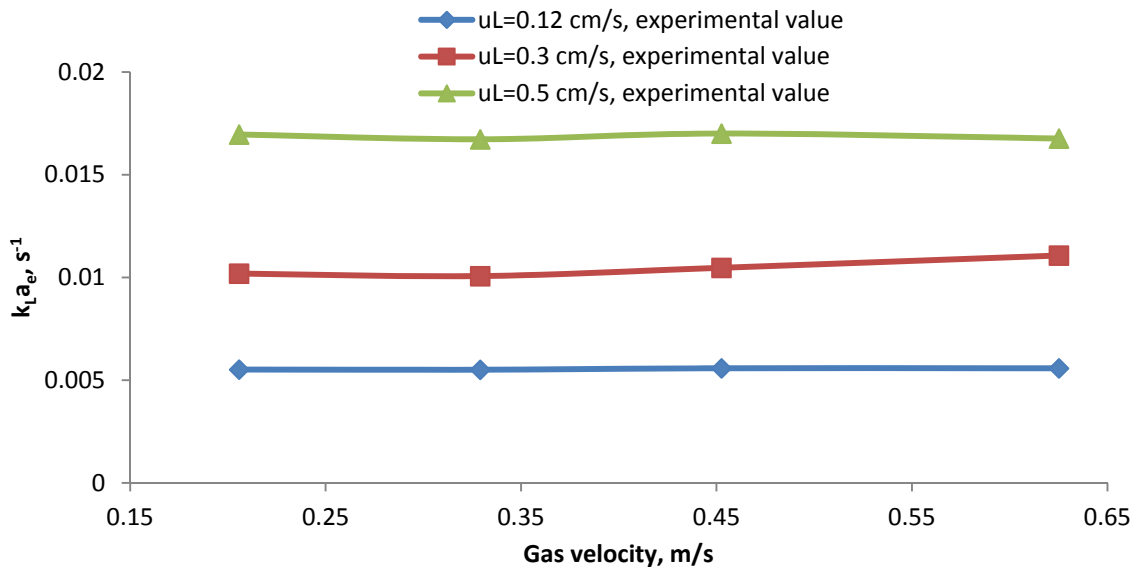


Figure 3.5. Liquid phase mass transfer coefficients in packed bed column with structured packing at varying gas flow rates.

3.3.1.2 Gas phase mass transfer coefficient

Values for the overall gas phase mass transfer coefficients (K_{Gae}) for the random Pall ring packing tests are shown in Figure 3.6. It was apparent the K_{Gae} was independent of gas velocity, indicating the liquid phase mass transfer was dominant under the test conditions. Comparisons between the predicted and experimental values were in good agreement with each other.

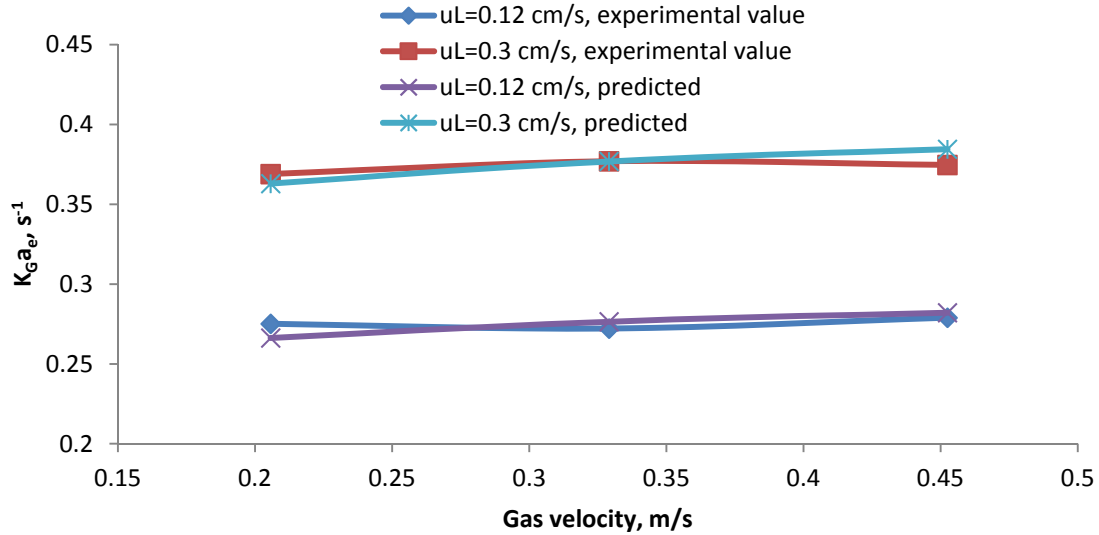


Figure 3.6. Overall gas phase mass transfer coefficients in packed bed column with random packing at varying gas flow rates.

K_{Gae} values increased as liquid flow rate increased. This may be because a higher liquid velocity leads to a larger individual liquid mass transfer coefficient as well as a greater effective surface area from the improved liquid wetting. Based on the previous theory, the individual liquid phase mass transfer coefficient was found using O_2 absorption and calculated with Equation 3.3. Using that k_L value and Equation 3.6 the enhancement factor was found. These variables were used, along with the known Henry's constant, to calculate the k_L term in Equation 3.5. Since the values of the calculated k_{Lae} term and the measured K_G term were equal, the k_G was negligible and did not need to be determined.

Measured K_{Gae} values for the random packing matched well with values calculated using Equation 3.5 when the experimental k_{Lae} values shown in Figure 3.4 were used. Based on these correlations, K_{Gae} values for the structured packing were calculated using k_L and Equation 3.5

(Fig. 3.7).

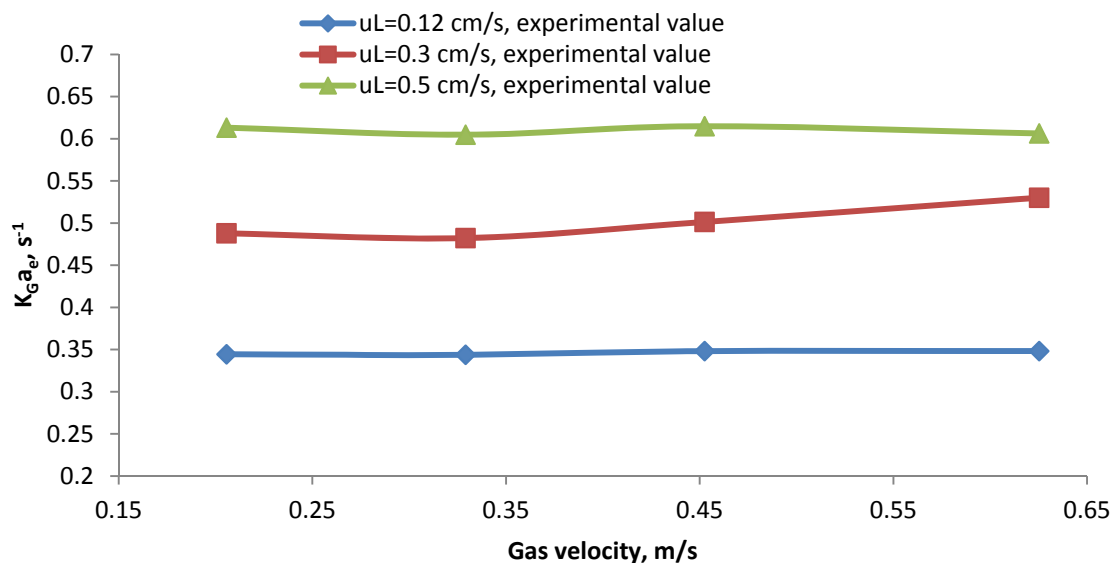


Figure 3.7. Gas phase mass transfer coefficients in packed bed column with structured packing at varying gas flow rates.

3.3.2 CO₂ Absorption into PCB solution without a promoter

To establish a baseline absorption rate for PCB before a promoter was added, tests were done to see the effect of different process variables on CO₂ removal efficiency. This included testing the L/G ratio, CO₂ loading of the solution, concentration of PCB in the solution and absorption column temperature. The baseline process conditions are shown in Table 3.6.

Table 3.6. Baseline conditions for un-promoted PCB solutions in packed bed column testing.

Concentration of PCB solution (wt%, K ₂ CO ₃ -equivalent)	40
Temperature (°C)	70
Initial CTB conversion ratio	20
Liquid to gas ratio (L/m ³)	4
Liquid flow (LPM)	0.56
Gas flow (LPM)	110
CO ₂ inlet concentration (vol%)	14

3.3.2.1 Effect of liquid to gas ratio on CO₂ absorption

In an absorption column, liquid to gas ratio (L/G) is an important parameter. Depending on the liquid removal efficiency, the L/G can be minimized, leading to a higher throughput of flue gas with minimal liquid flow. This not only reduces the amount of chemical used, but also pumping and heating costs associated with solvent circulation. To investigate the effect of L/G

ratio, tests were run on the base case solution which was 40 wt% PCB; at CTB conversion of 20%, 30% and 40%, which were typical CO₂ loading values during the absorption process. The temperature in the column was kept constant at 70±5°C. Liquid flow was held constant at 0.56 LPM and gas flow was varied from 47 to 280 LPM (at actual conditions). This led to a range of L/G ratio from 2 to 12 L/m³. These values were chosen based on the minimum L/G which was calculated using the vapor-liquid equilibrium (VLE) data for a PCB system. Based on this curve, in order to achieve 90% CO₂ removal (2 psia to 0.2 psia pCO₂) the L/G at equilibrium must be at least 4 L/m³ for PCB40. This minimum value was used as a basis to determine a range of values to test (Fig. 3.8).

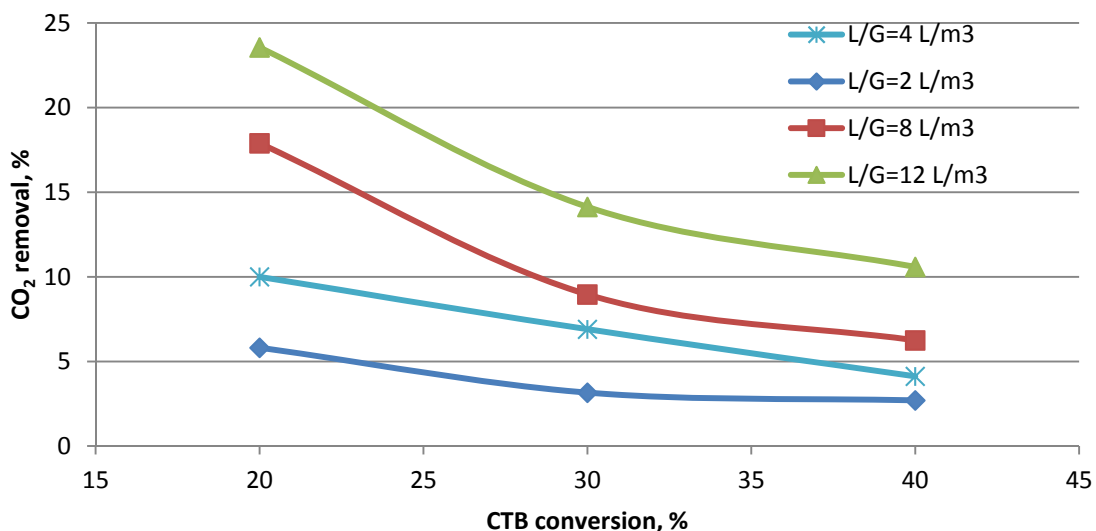


Figure 3.8. Effect of L/G ratio and CTB conversion on CO₂ removal efficiency of unpromoted PCB40 solution.

As the L/G ratio was increased, higher CO₂ removal was observed. This was expected because with the same liquid flow, gas residence time in the column was longer, allowing for more CO₂ to be absorbed into the solution from one pass through the column. The highest removal rate measured was 23.5%, in the PCB40-20 at an L/G of 12, and the removal at an L/G of 4, the typical operating condition, was 10%. The main purpose of these tests was to explore the effects of changing different variables on the performance of CO₂ absorption, not to achieve 90% CO₂ removal efficiency. In practice, the height of a packed bed column would have to be more than 10 times higher than the current column setup to achieve 90% CO₂ removal.

3.3.2.2 Effect of CO₂ loading on CO₂ absorption

The effect of CO₂ loading in the solution on the CO₂ removal rate is important. In practice, the lean solution (with low CO₂ loading) would come in to the column from the top at a CTB conversion level of 20%. The solution would flow through the column and exit at a rich CTB conversion level of 40% to 45%. The counter current flow is important to maximize driving force here. The lean solution at the top will be in contact with flue gas that has had CO₂ removed out of it. The rich solution, which has a much higher CO₂ content, is in contact with the fresh flue gas containing a higher CO₂ concentration (~14%). In the column setup for this experiment, the change in CTB conversion from top to bottom in the solution could be minimal as a high level of CO₂ removal (eg., 90%) was not intended. To measure the removal efficiency of lean and rich solutions and all points in between, the solution was recycled back through the column while the CO₂ inlet concentration stayed the same, and the CO₂ loading of the inlet solution and removal efficiencies were measured at predetermined intervals. This gave a simulation of the complete working height of a full size absorption column.

The trend for each L/G is the same; as the CTB conversion (CO₂ loading) increased, the CO₂ removal efficiency decreased (Fig. 3.8). This was due to the change in driving force as a result of an increased CO₂ concentration in the liquid. The inlet CO₂ concentration was held constant and, as the CTB conversion increased in the solution, it became closer to equilibrium with the gas. This directly decreased the driving force for the absorption of CO₂ into the solution, causing the removal rate to decrease.

3.3.2.3 Effect of concentration of PCB solution on CO₂ absorption

As a part of this novel process, the use of a highly concentrated PCB solution was important. This would allow for the use of less liquid flow which leads to a reduced size of equipment and large energy savings associated with less power use for pumping liquid and less energy use in the solvent regeneration process. A PCB40 solution was adopted as a baseline. For the comparison purpose, PCB solutions of lower concentrations were tested. However, since these solutions contained less PCB, their CTB conversion changes through an absorption column would have to be larger to have a comparable capacity to PCB40 (Fig. 3.9).

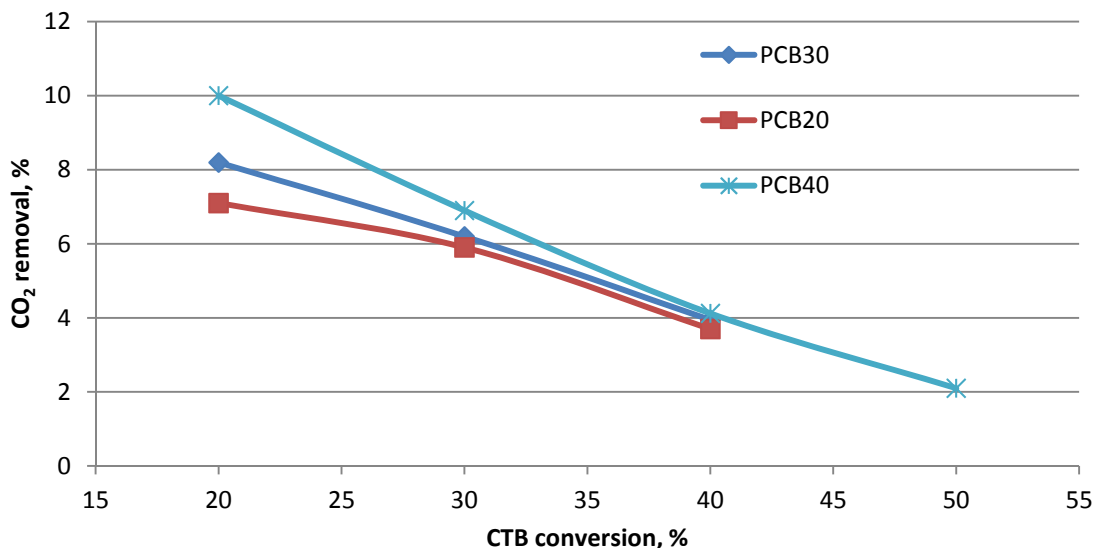


Figure 3.9. Effect of concentration variation of PCB solution on CO₂ removal efficiency.

The higher concentration of PCB resulted in higher absorption of CO₂, especially initially. However, such a difference was not great and as the CO₂ loading increased, the differences caused by the different PCB concentrations was negligible. It was expected there would not be much change in the removal efficiency because it was thought to be limited by a slow reaction rate, not a lack of capacity in the PCB solution, which was being varied in the tests. These data give us a reference for varying total PCB concentrations in solution, which will later be compared with the promoted PCB solutions as well as 5 M MEA.

3.3.2.4 Summary of unpromoted PCB testing

After setting up and verifying the performance of the absorption column, unpromoted PCB solutions were tested for CO₂ absorption to give a baseline for comparisons with amine promoted PCB solutions. CO₂ removal rates were low, but there was enough deviation the changes of certain key variables could be investigated to evaluate their impacts on CO₂ absorption. The efficiency of CO₂ removal using PCB solutions without a promoter varied between 5 and 25%, depending on L/G ratio, CTB conversion in inlet solution and total PCB concentration. Removal efficiency increased with increasing L/G ratio and PCB concentration. As CO₂ loading in the inlet solution increased, removal efficiency decreased.

3.3.3 CO₂ absorption into PCB solution with a promoter

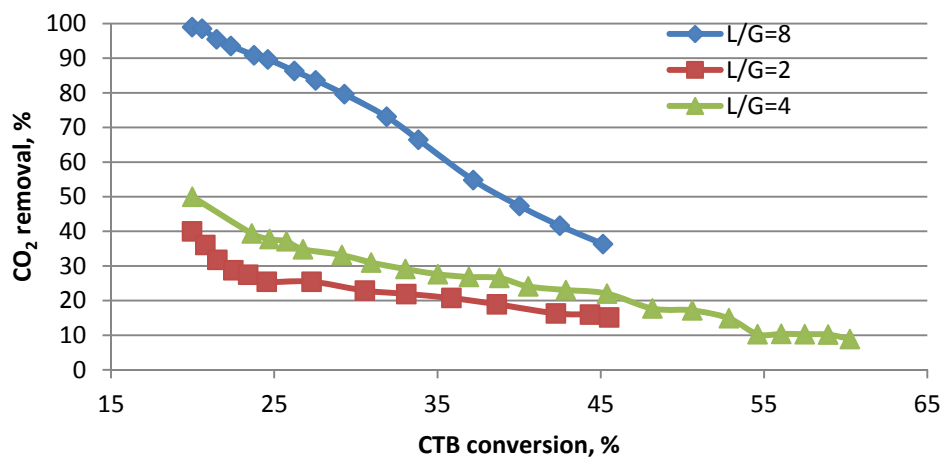
After establishing baseline CO₂ removal of the unpromoted PCB solution, amine promoted PCB solutions were investigated. From the screening process described in the previous chapter, DEA, AMP and PZ were chosen as promoters. Parametric tests with respect to different variables including L/G ratio, inlet CO₂ concentration, promoter dosage, total PCB concentration and CO₂ loading were conducted. Base case conditions are depicted in Table 3.7. For each additional test, a variable was changed and its effect was measured.

Table 3.7. Baseline conditions for promoted PCB solutions in packed bed column testing.

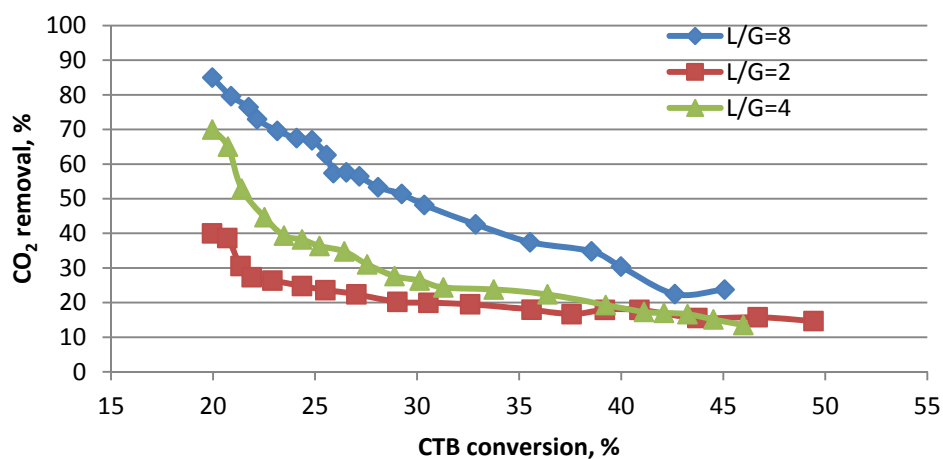
Concentration of PCB solution (wt%)	40
Temperature (°C)	70
Initial CTB conversion ratio	20
Liquid to gas ratio (L/m ³)	4
Liquid flow (LPM)	0.56
Gas flow (LPM)	110
CO ₂ inlet concentration (vol%)	14
Promoter	PZ, DEA, AMP
Promoter dosage (mol/L)	0.5

3.3.3.1 Effect of liquid to gas ratio and CO₂ loading on CO₂ absorption

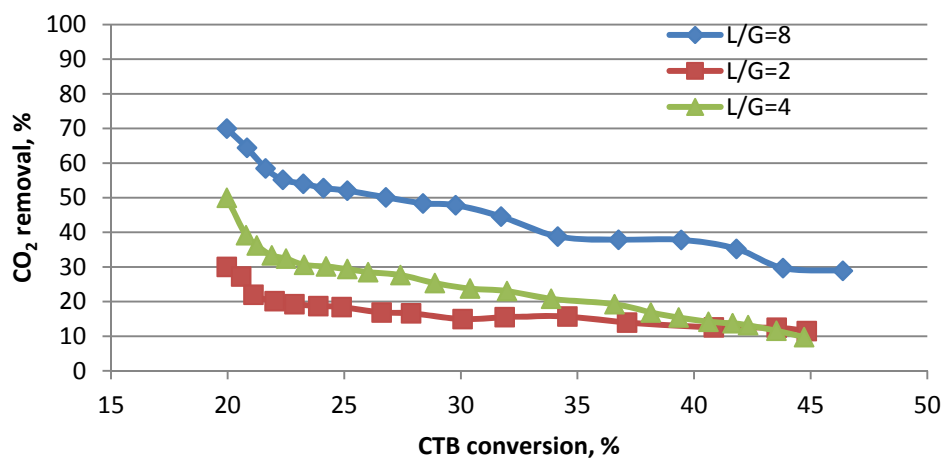
Tests were conducted on PCB40 with the addition of 0.5 M promoter to investigate the effects of L/G ratio and CO₂ loading on CO₂ removal efficiency. All other variables were kept the same as the base case. L/G ratio was varied at 2, 4 and 8 L/m³, equivalent to 0.50, 1 and 2 times, respectively, the theoretical minimum L/G for PCB40. Desired L/G ratios were achieved using the same procedure as in the unpromoted solution, by varying the gas rate while keeping the liquid flow rate constant. The results for PCB40 with each of the promoters are presented in Fig. 3.10 (a)-(c).



(a)



(b)



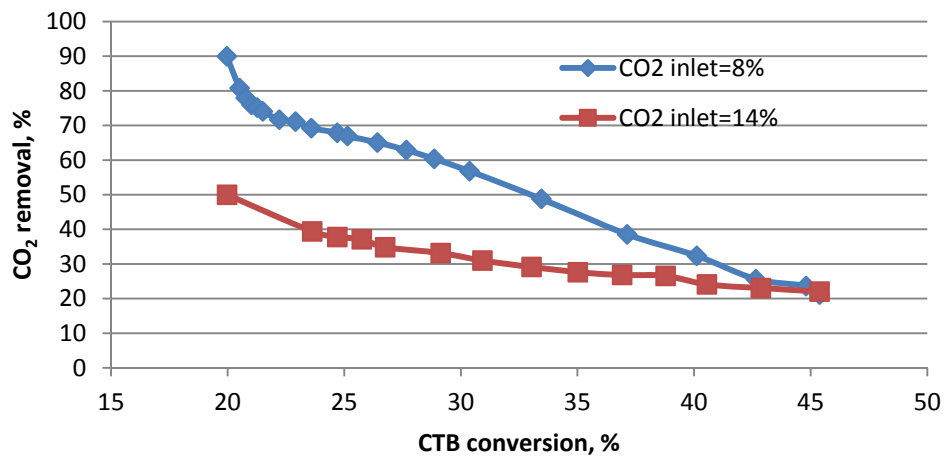
(c)

Figure 3.10. Effect of L/G ratio on CO₂ removal in PCB40 in the presence of (a) 0.5 M PZ, (b) 0.5 M AMP and (c) 0.5 M DEA.

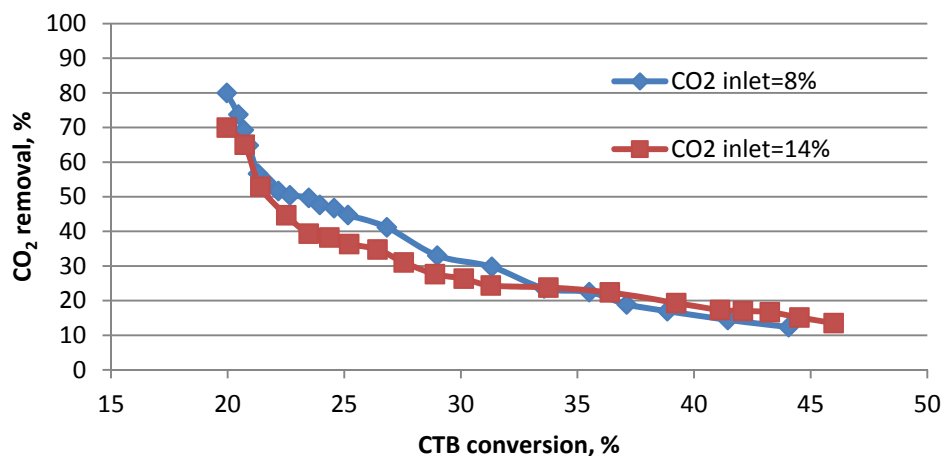
The trend for L/G ratio was the same as seen in the unpromoted PCB solution. In the PCB40+0.5 M PZ solution, increasing L/G from 2 to 4 increased CO₂ removal efficiency by 20% to 30%, depending on the CO₂ loading. The performance at a higher L/G was increased because of the enhanced gas liquid contact and an increased gas residence time. CO₂ removal efficiency decreased with increasing CO₂ loading, mirroring the results in the unpromoted solution. For PCB40+0.5 M DEA, CO₂ removal efficiency decreased from 50% to 15% at an L/G of 4 when the CTB conversion at the inlet increased from 20% to 40%. This was caused by the reduced mass transfer driving force for CO₂ absorption as the CO₂ loading increased. All three promoters had similar behavior; when the L/G was set to 8, removal rate was higher than the L/G of 2 or 4. For DEA and AMP, the difference between the L/G of 2 and 4 decreased as CO₂ loading increased and, under the inlet CTB conversion above 40%, CO₂ removal rates were nearly the same. Addition of 0.5 M PZ promoted CO₂ absorption into PCB40. For example at an L/G of 8, removal efficiency was above 90% when the CTB conversion in the inlet solution was in the 20% to 25% range.

3.3.3.2 Effect of inlet CO₂ concentration on CO₂ Absorption

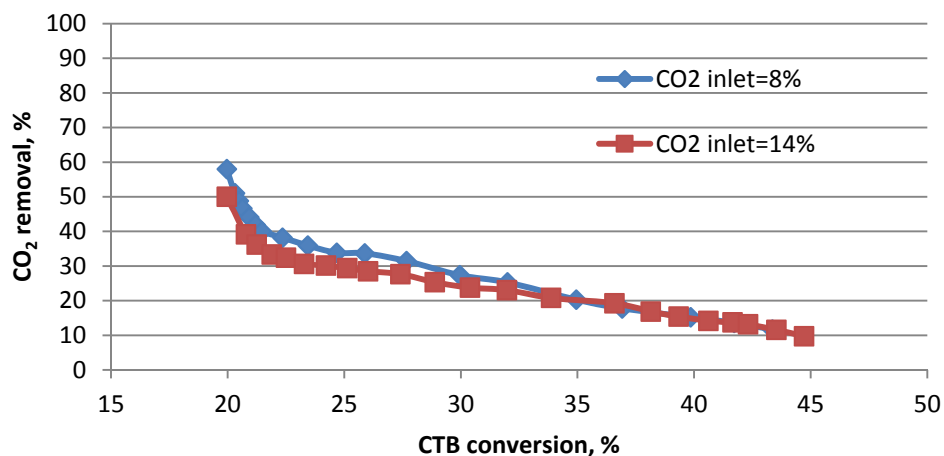
Inlet CO₂ concentration was varied from 14 vol% to 8 vol% to investigate its effect on the CO₂ removal efficiency. Results from the tests at the two CO₂ inlet concentrations are shown in Figure 3.11 (a)-(c), for each of the three promoters.



(a)



(b)



(c)

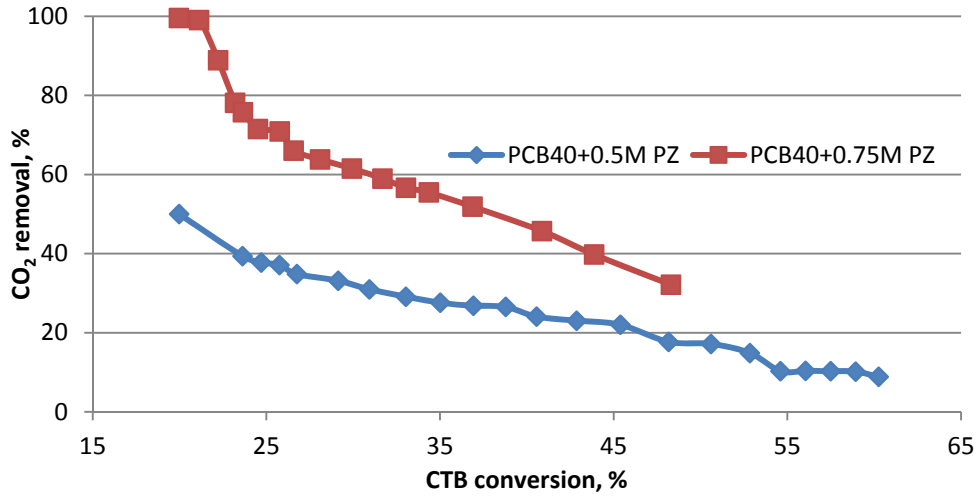
Figure 3.11. Effect of inlet CO₂ concentration on CO₂ removal in PCB40 in the presence of (a) 0.5 M PZ, (b) 0.5 M AMP and (c) 0.5 M DEA.

A higher inlet CO₂ concentration resulted in lower CO₂ removal efficiency under the same conditions. At a higher inlet CO₂ concentration, a larger amount of CO₂ needed be removed to achieve the same removal efficiency. But at the same time, a higher inlet CO₂ concentration lead to a larger driving force for CO₂ absorption. A reduction in CO₂ removal efficiency at a higher inlet CO₂ concentration indicated the increase in CO₂ removal rate was less than the increase in the rate of CO₂ inflow. Among the three solutions, the effect of inlet CO₂ concentration was more for the PCB+PZ than the PCB+AMP or PCB+DEA. When AMP and DEA were used as promoters, results were similar as initial removal efficiencies at low CTB conversion were similar for the inlet CO₂ concentration of 8% and as the CTB conversion increased past 35%, the removal efficiencies were identical.

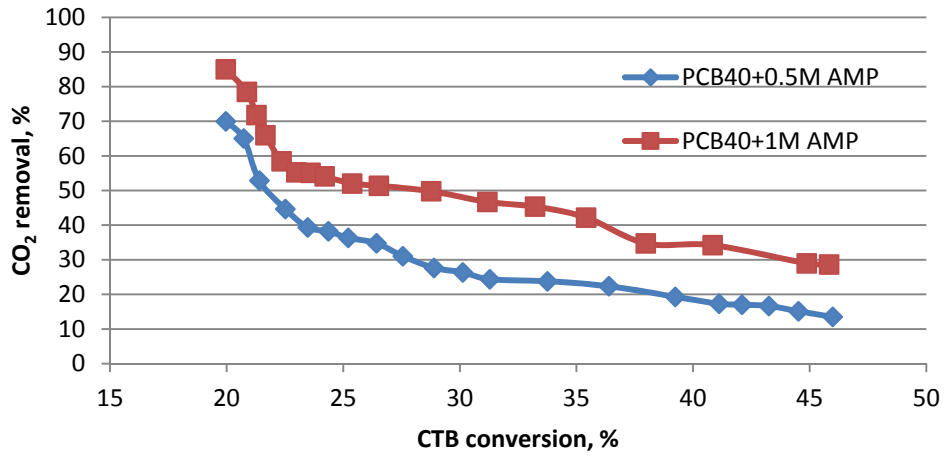
However, the PZ promoted solution behaved differently. Initially, at a CTB conversion level of 20%, removal of CO₂ from the gas stream containing 8% CO₂ at the inlet was 50% greater than the 14% inlet. Removal efficiency for the gas stream with the lower inlet CO₂ concentration decreased quickly as CO₂ loading increased. Until 42% CTB conversion, both the high and low inlet CO₂ concentrations resulted in the same removal efficiency.

3.3.3.3 Effect of promoter dosage on CO₂ absorption

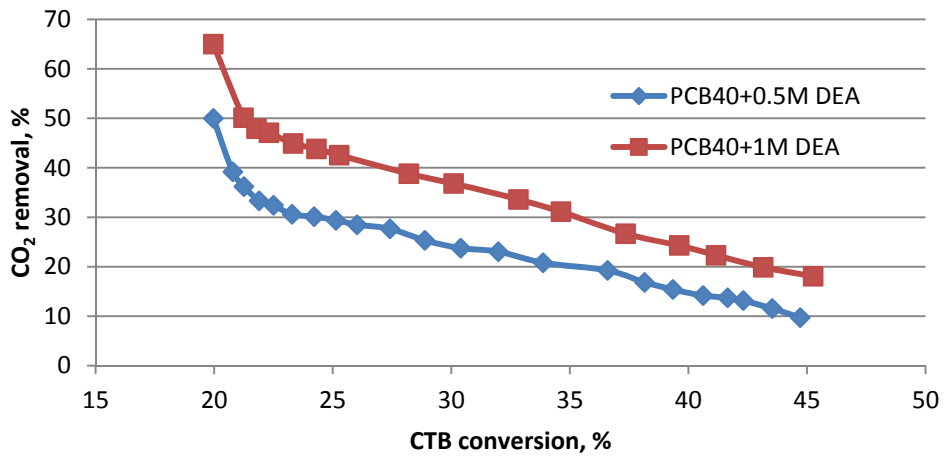
The dosage of the promoters in the PCB40 solution was increased to 1 M for DEA or AMP and 0.75 M for PZ to investigate its effect on the CO₂ removal efficiency. The higher PZ dosage of 0.75 M was selected because of solubility and precipitation concerns about PCB+PZ solutions. Results shown in Fig. 3.12 (a)-(c) compare this higher dosage to the baseline dosage of 0.5 M.



(a)



(b)



(c)

Figure 3.12. Effect of promoter dosage on CO₂ removal in PCB40 in the presence of (a) 0.5 M PZ, (b) 0.5 M AMP and (c) 0.5 M DEA

For all three promoters, CO₂ removal efficiency increased with increasing promoter dosage when the other test conditions remained the same. This increase in removal was due mainly to faster CO₂ absorption reactions in the presence of a larger amount of amine promoter according to a “shuttle” mechanism (Hook, 1997). The PCB40 solution promoted with 0.75 M PZ compared to 0.5 M PZ had the largest increase in removal efficiency. As a result of the solubility issue with the PCB40+0.75 M PZ solution, there was precipitation in the column from the beginning of the test; the longer the solution was circulated, the more precipitation accumulated on the packing. Since some of the promoter or KHCO₃ was immobilized in the packing during this test, it was difficult to compare it to other tests because of the hydrodynamic performance of the packing column. When the 1 M dosage of AMP was used, it improved the removal rate by 18% at lean loading (20% CTB conversion) and by 48% at rich loading (45% CTB conversion) over the 0.5 M dosage in PCB40. Similar behavior was seen with the addition of 1 M DEA in PCB40; at lean loading the removal efficiency was 23% better and at rich loading the efficiency was 50% better than the addition of 0.5 M dosage. CO₂ removal efficiency can be increased by increasing promoter dosage in the concentrated PCB solution (40 wt%).

3.3.3.4 Effect of PCB concentration on CO₂ absorption

For the reasons described above, a concentrated PCB solution is preferred by the Hot-CAP. The elevated temperature of the absorption process allows for the use of 40 wt% PCB solution, which would not be possible at traditional absorption temperatures because of solubility limitations. Even though this is a key part of the process, lower PCB concentrations were tested to measure the effect it would have on CO₂ removal rate. For lower concentrations of PCB, the operating lean/rich range of CTB conversion would have to be higher to achieve the same amount of CO₂ removal. The results of tests varying PCB concentration are shown in Fig. 3.13. All solutions used were promoted with 0.5 M PZ.

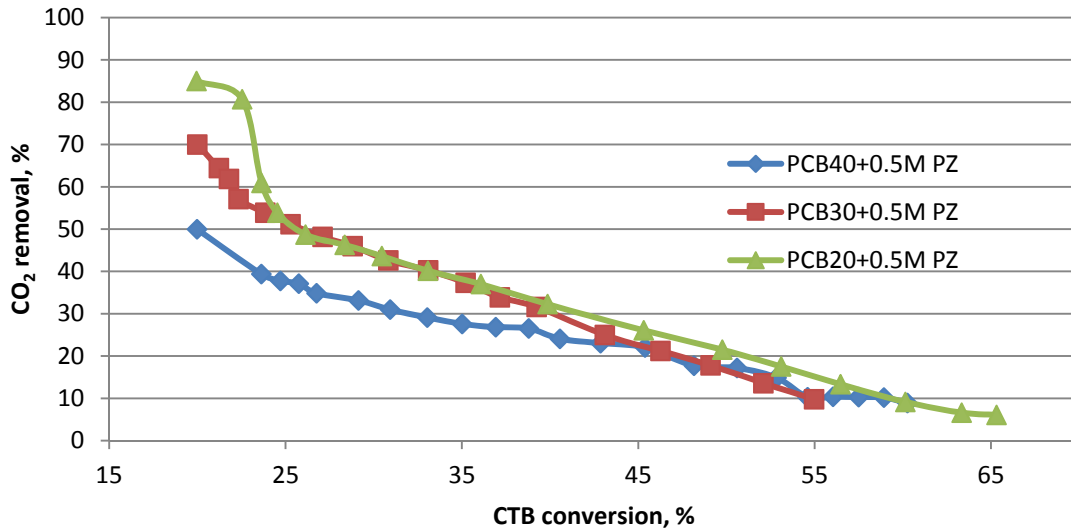


Figure 3.13. Effect of PCB concentration on CO₂ removal, promoted with 0.5 M PZ at L/G=4.

These data highlight similar properties seen in previous tests. For example, the differences in CO₂ removal efficiency were large at lean loading; as CTB conversion increased, removal rates at different PCB concentrations became comparable. The PCB20 had the highest CO₂ removal efficiency, followed by PCB30, and finally PCB40. According to the literature, absorption rates of PCB solutions increase with increasing concentration at first and then pass through a maximum. This is accounted for by the naturally increasing viscosity as the concentration increases, as well as changes in pH in the solution (Comstock & Dodge, 1937). These values are not comparable. Since a greater CTB conversion range would have to be used in PCB20, CO₂ removal rates equivalent to a 15% to 65% CTB conversion change could be compared to those of PCB40 equivalent to a 20% to 45% CTB conversion change.

3.3.3.5 Comparison of different promoters on CO₂ absorption

The effectiveness of different promoters for accelerating CO₂ absorption into PCB40 was compared on the basis of 0.5 M dosage of promoter. Test results for the comparison are displayed in Fig. 3.14.

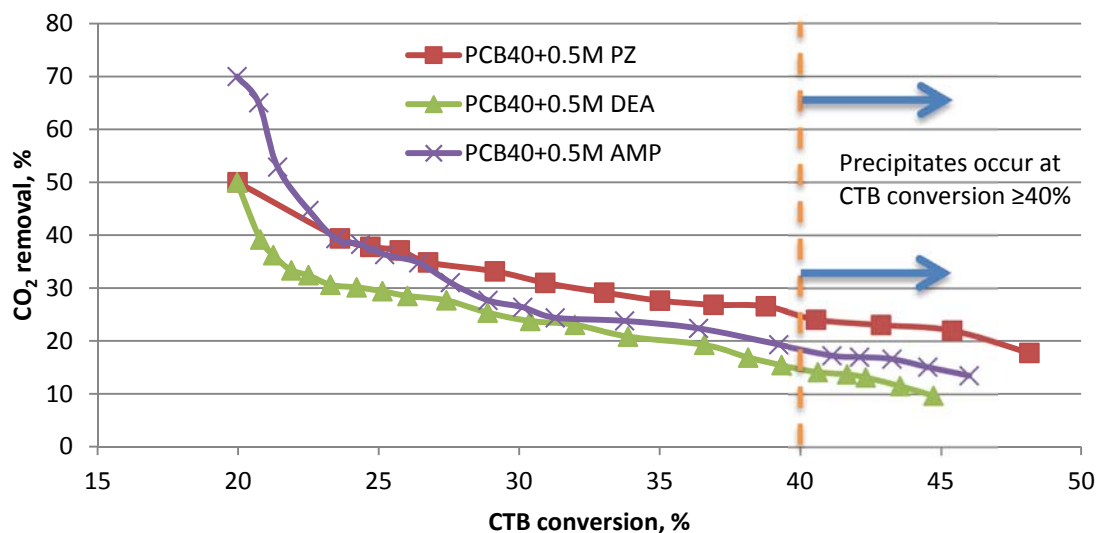


Figure 3.14. Performance of different promoters at baseline conditions.

The PCB40 solution promoted with AMP had the highest initial CO₂ removal efficiency. However, the efficiency diminished quickly as the CTB conversion increased. By 25% CTB conversion at the inlet, the PCB40 solution promoted with PZ has higher removal efficiency. The PCB solution promoted with DEA started out with the same removal as with PZ but quickly dropped off as the CO₂ loading increased. Over the entire lean to rich loading range (20% to 45% CTB conversion), the addition of PZ gave the highest CO₂ removal.

3.3.3.6 Effect of KHCO₃ precipitation on CO₂ absorption

In the previous CO₂ absorption tests shown in Fig. 3.14, precipitation occurred at a CTB conversion level of 40% in the inlet solution. To investigate the impact of KHCO₃ precipitation, the rates of CO₂ absorption into the promoted PCB40 solutions were tested for an extended period of time even after precipitates occurred. The solubility limit of KHCO₃ in the PCB40 solution was equivalent to 45% CTB conversion at 70°C (Haynes et al., 1959). This corresponded to seeing precipitation at 40% inlet CTB conversion because at a CO₂ removal efficiency of 20% taken as an example, the CTB conversion changes by approximately 6% as the solution runs through the packed column. Precipitation of KHCO₃ would result in a decrease in total PCB concentration. However, as shown in Fig. 3.14, the data for high CTB conversion levels are indicative that CO₂ removal efficiency remained stable and no sharp decline was seen after KHCO₃ precipitates were present and accumulated in the PCB solution. No plugging

associated with precipitation in the structured packing was observed during the tests. Similar results for CO₂ absorption in the presence of precipitates were seen in PCB40 promoted with PZ, AMP and DEA. Therefore, it is possible for CO₂ absorption to be operated in the presence of KHCO₃ precipitation without adversely affecting rate of absorption, provided the equipment can handle the precipitates.

3.3.4 CO₂ removal rates for unpromoted PCB, promoted PCB and benchmark 5 M MEA solutions.

Results of CO₂ removal in unpromoted and promoted PCB solutions have been described separately. Results of tests performed with unpromoted PCB40, PCB40 promoted with PZ, DEA or AMP at the baseline dosage of 0.5 M and 5 M MEA solutions for their effectiveness of CO₂ removal are shown in Fig. 3.15. Absorption temperature was 70°C for the PCB without or with a promoter and 50°C for the MEA solution, which were typical of the Hot-CAP and MEA process, respectively. Other variables were maintained at the baseline conditions. Since PCB and MEA absorb CO₂ through different chemical pathways, the method by which the CO₂ loading is reported is different. The Hot-CAP employs the PCB40 solution with the lean CO₂ loading equivalent to 15% to 20% CTB conversion and the rich CO₂ loading equivalent to 40% to 45% CTB conversion. In comparison, the MEA process operates at a CO₂ loading of about 0.2 mol CO₂/mol MEA in the lean 5 M MEA solution and 0.40 to 0.45 mol CO₂/mol MEA in the rich solution. Therefore CO₂ removal efficiencies at these corresponding lean and rich values can be compared.

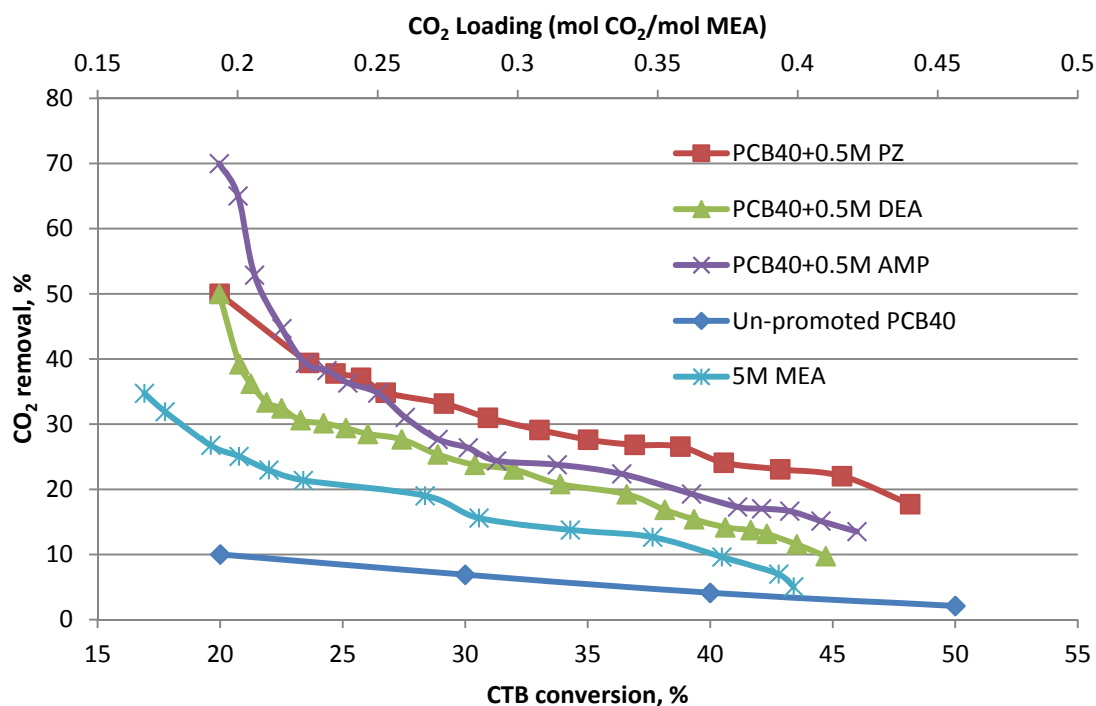


Figure 3.15. Comparison of CO₂ removal efficiency in 5 M MEA and PCB40 solutions with and without promoters at baseline conditions.

There was an increase in CO₂ removal rate for each of the promoters used over the unpromoted PCB solution. At lean CO₂ loading, CO₂ absorption was increased by 5 to 7 times with the promoters, and at rich loading (eg., CTB conversion of 45%); the rate was promoted 3 to 7 times. Both the promoted and unpromoted PCB solutions had similar trends over the CTB conversion range tested; the higher the CO₂ loading, the lower the absorption of CO₂ from the simulated flue gas into the solution. The promoters tested did increase the rate of CO₂ absorption into the concentrated PCB solution, by on average 5 times, over its unpromoted counterpart.

The promoted PCB solutions also outperformed the 5 M MEA solution, at a lean loading of 0.2 mol CO₂/mol MEA, the 5 M MEA solution had a removal efficiency of 25%, and at a rich loading of 0.4 mol/mol, only 5% of CO₂ was removed. At similar lean conditions with a CTB conversion of 20%, PCB40+0.5 M AMP had the highest removal efficiency of the three promoters at 70%, and at rich conditions with a CTB conversion of 40%, PCB40+0.5 M PZ had the highest removal efficiency at 25%. Based on trends observed in these experiments, CO₂

removal rates into the promoted lean and rich PCB solutions at 70°C were higher than their 5 M MEA counterpart solutions at 50°C. At lean loading, removal rates of CO₂ in the promoted PCB were 1 to 3 times higher than the 5 M MEA, and at rich loading, rates in the promoted PCB40 solutions were 3 to 5 times higher than the 5 M MEA.

3.3.5 CO₂ absorption into Na₂CO₃/NaHCO₃ solution

A SCB solution can be used as an alternative solvent to a PCB solution in the Hot-CAP. SCB has some advantages over PCB including the fact that sodium bicarbonate (NaHCO₃) can be precipitated more easily via cooling to form a NaHCO₃ slurry for CO₂ stripping because it has lower solubility than KHCO₃. In addition, NaHCO₃ slurry can produce a higher stripping pressure than KHCO₃ slurry since the CO₂ equilibrium pressure over SCB is higher than that over PCB.

Similar absorption tests were performed with SCB solutions (Table 3.4). Because solubility of NaHCO₃ is lower than KHCO₃, a SCB solution with a total concentration (Na₂CO₃ equivalent) of 15 wt% (SCB15) was used instead of 40 wt% for PCB. To meet the comparable goal of CO₂ removal with this lower concentration, a wider operating range of CTB conversion was required for the SCB15 if similar conditions were used for both the SCB15 and PCB40 solvents. For the PCB40 solution, a lean solution of 20% and a rich solution of 40% to 45% CTB conversion were typical of the process. To achieve the desired CO₂ removal with the SCB15 solution, the lean solution at 15% CTB conversion and the rich solution at 55% to 60% CTB conversion were preferred. The baseline process conditions for CO₂ absorption into SCB are shown in the following table.

Table 3.8. Baseline conditions for SCB solutions in packed bed column testing.

Concentration of total SCB (Na ₂ CO ₃ -equivalent, wt%)	15
Temperature (°C)	70
Initial CTB conversion ratio	15
Liquid to gas ratio (L/m ³)	4
Liquid flow (LPM)	0.56
Gas flow (LPM)	110
CO ₂ inlet %	14
Promoter	DEA, AMP, PZ
Promoter dosage (mol/L)	0.5

3.3.5.1 Effect of L/G ratio and CO₂ loading on CO₂ removal in unpromoted SCB solutions

To establish a baseline to compare the promoted SCB15 solution, unpromoted SCB15 was first tested at L/G ratios of 4 and 12 L/m³, which were equivalent to 0.55 and 1.65 times its minimum L/G, respectively (Knuutila et al., 2010). The other process conditions are given in Table 3.8. Results of the CO₂ absorption at varying L/G ratios and CTB conversion levels are shown in Fig. 3.16.

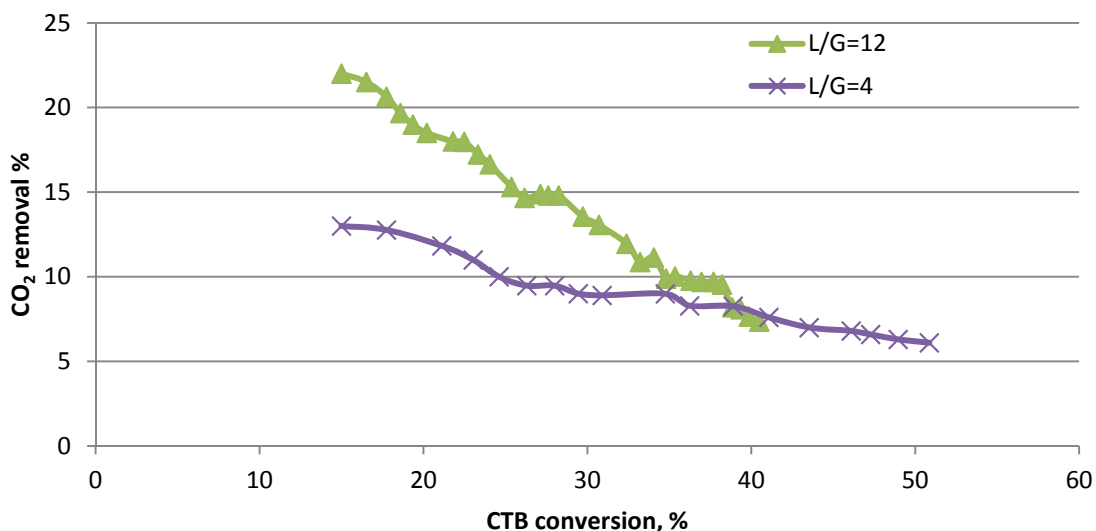


Figure 3.16. Effect of L/G ratio and CTB conversion on CO₂ removal efficiency in unpromoted SCB15 solutions.

Results of these tests were similar to the unpromoted PCB tests. The higher L/G ratio resulted in a higher CO₂ removal, especially at lean CTB conversion. This was due to the increased gas residence time in the column as afore described for PCB. CO₂ absorption rates of the unpromoted SCB15 solution were low at lean CTB but decreased even more with increasing CTB conversion. This was due to the reduced driving force as more CO₂ was loaded into the solution, causing a decrease in CO₂ absorption performance.

3.3.5.2 Effect of L/G ratio and CO₂ loading on CO₂ removal in promoted SCB solutions

Only PZ promoter was tested to accelerate the absorption rates of SCB15 solutions. In Fig. 3.17 is depicted the effect of L/G ratio on CO₂ removal by SCB15 solutions promoted by 0.5

M PZ. The L/G ratios of 4, 8, and 12 L/m³ were selected, which were equivalent to 0.55, 1.10 and 1.65 times the minimum L/G.

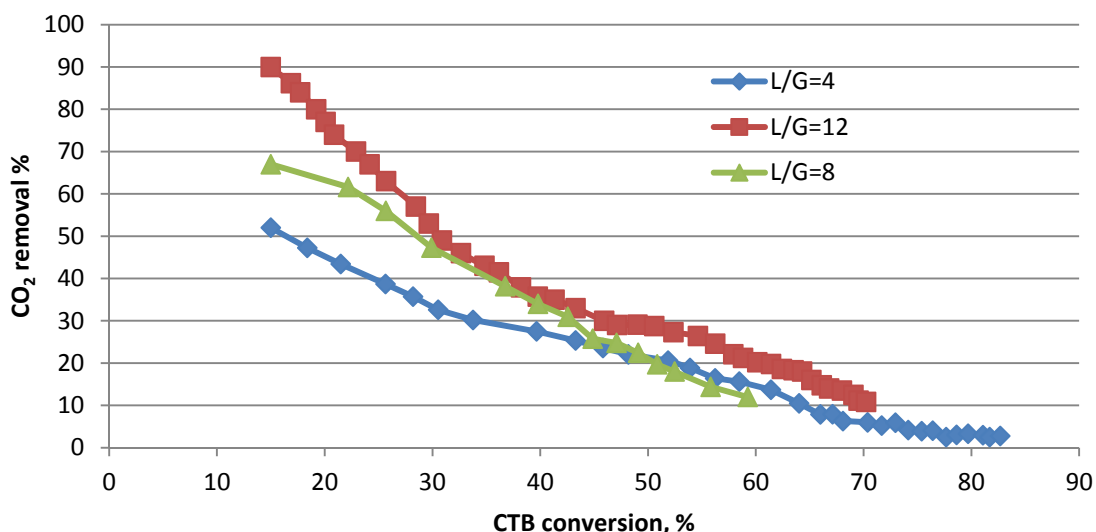


Figure 3.17. Effect of L/G ratio and CTB conversion on CO₂ removal efficiency in promoted SCB15 solutions.

At the same CTB conversion at the inlet, the rate of CO₂ absorption into the SCB15 increased with increasing L/G ratio. This tendency was the same as that for PCB solution and the unpromoted SCB solution. For the SCB15+0.5 M PZ solution at the L/G of 4 L/m³, the solution with 15% initial CTB conversion removed 50% of the CO₂ while that with 60% initial CTB conversion removed 15% of the CO₂. When the L/G ratio was increased to 12 L/m³, the removal efficiency increased, but a larger difference was seen at lower CTB conversion. At 15% initial CTB conversion, the higher L/G of 12 resulted in 90% removal of the CO₂ and at 60% initial CTB conversion, it removed 20% of the CO₂. The increase in removal efficiency was 1.8 times in the lean SCB+PZ solution but only 1.3 times in the rich solution. As described earlier, higher CO₂ removal efficiencies at higher L/G ratios can be attributed to better gas liquid contact and longer gas residence times.

3.3.5.3 Comparison of CO₂ removal efficiencies in SCB15, PCB40, and 5 M MEA

In Figure 3.18, the results of the unpromoted SCB15 and SCB15 promoted with 0.5 M PZ are compared with those of 5 M MEA, unpromoted PCB40 and PCB40 promoted with 0.5 M

PZ as previously described. All these data were from tests conducted at the same conditions, with an L/G ratio of 4 L/m³ and 70°C. The only differences in the tests were the compositions of the solutions themselves and the CO₂ loading ranges.

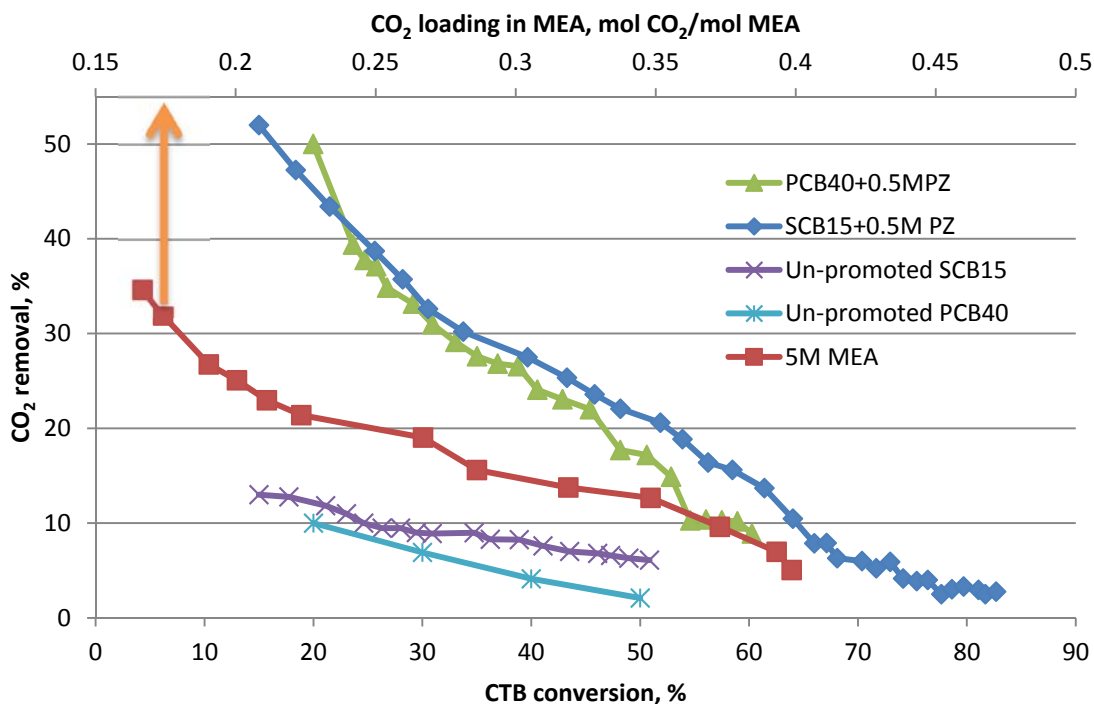


Figure 3.18. Comparison of CO₂ removal rates in unpromoted SCB15, promoted SCB15, unpromoted PCB40, promoted PCB40 and 5 M MEA.

Unpromoted SCB15 had a higher removal rate than the unpromoted PCB40. This was to be expected based on the previous discussion of the effect of PCB concentration on CO₂ removal efficiency, because SCB followed a similar trend of having a maximum removal efficiency of 10 wt% to 20 wt% (Comstock & Dodge, 1937).

The addition of 0.5 M PZ promoted the rate of CO₂ absorption into the SCB15 solution: the removal was amplified by 3.8 times for the lean solution (15% initial CTB conversion) and 3.5 times for a rich solution (50% CTB conversion) over the respective unpromoted solutions. The addition of the PZ promoter into the SCB solution was as effective as into the PCB solution to promote the CO₂ absorption.

At the same L/G ratio (4 L/m³), the SCB15 solution with the addition of 0.5 M PZ had a CO₂ removal efficiency at 70°C higher than that of the 5 M MEA solution with the corresponding CO₂ loading range at 50°C (Fig. 3.18). As described before, CO₂ loading in a typical MEA absorber changes from 0.20 (lean) to 0.45 (rich) mol/mol as the solution runs through the column. For the SCB absorber, CTB conversion change from 15% at the top to 60% at the bottom is desired based on VLE behavior of SCB15. Comparing the CO₂ removal efficiencies at these values, the SCB15 solution with 0.5 M PZ would have a better performance for CO₂ absorption than the 5 M MEA solution.

3.3.6 CO₂ absorption into PCB/SCB solution mixtures

A mixture solution of PCB (25 wt%, K₂CO₃ equivalent) and SCB (10 wt%, Na₂CO₃ equivalent), symbolized as PCB25/SCB10, was tested. The composition of the solution was selected based on a crystallization study previously conducted (Lu et al., 2012). They confirmed that by cooling the CO₂ rich PCB/SCB25-10 with CO₂ loading equivalent to 40% CTB conversion from 70 to 35 °C, NaHCO₃ crystal (in form of nahcolite) was a dominant phase in a continuous mixed suspension, mixed product removal (MSMPR) reactor. Since using a mixture would be advantageous for the crystallization operation due to its lower solubility compared to a plain PCB solution while still maintaining a high solvent concentration compared to a plain SCB solution, absorption performance of the mixture solution was tested to investigate if it was comparable to the promoted PCB40 and other solutions tested. The baseline testing conditions for the PCB/SCB mixture solution are given in Table 3.9.

Table 3.9. Baseline conditions for promoted PCB/SCB solutions in packed-bed column testing.

Concentration of K ₂ CO ₃ /KHCO ₃ (K ₂ CO ₃ - equivalent, wt%)	25
Concentration of K ₂ CO ₃ /KHCO ₃ (K ₂ CO ₃ - equivalent wt%)	10
Temperature (°C)	70
Initial CTB conversion ratio	20
Liquid to gas ratio (L/m ³)	4
Liquid flow (LPM)	0.56
Gas flow (LPM)	110
CO ₂ inlet concentration (vol%)	14
Promoter	PZ, DEA, AMP
Promoter dosage (mol/L)	0.5

The L/G ratio of 4 L/m³ was chosen as the baseline for the SCB25/PCB10 solution for comparison purposes, since the vapor liquid equilibrium (VLE) data for this solution was not available. A dose of 0.5 M PZ was used as a baseline promoter for PCB/SCB solutions. The full test matrix can be found in Table 3.4.

3.3.6.1 Effect of L/G ratio and CO₂ loading on CO₂ removal in promoted PCB/SCB mixture solutions

The effects of L/G ratio and CO₂ loading on CO₂ removal were investigated in the PCB/SCB solutions in the same manner as performed previously in plain PCB or SCB solutions. The same L/G ratios of 4, 8 and 12 L/m³ were chosen. The results are presented in Figure 3.19.

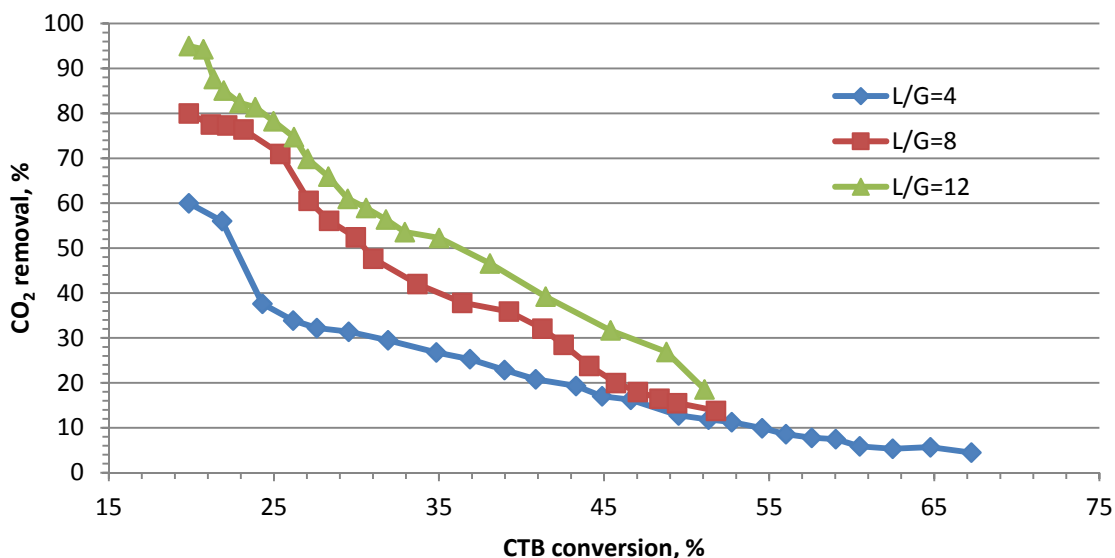


Figure 3.19. Effect of L/G ratio and CTB conversion on CO₂ removal efficiency, PCB25/SCB10+0.5 M PZ.

At the same CTB conversion, CO₂ absorption rate into the PCB/SCB solution increased with increasing L/G ratio. This trend was seen in previously tested PCB or SCB solutions. At the L/G of 4 L/m³, the PCB25/SCB10 solution with 20% initial CTB conversion removed 60% of the CO₂ while the solution with 45% initial CTB conversion removed 17% of the CO₂. When the L/G ratio was increased to 8 and 12 L/m³, removal efficiency increased, but a larger difference was seen at lower levels of CTB conversion. When increasing from an L/G of 4 to 8 L/m³, removal efficiency increased by 1.33 times in the lean solution and 1.18 times in the rich

solution. Reasons for higher efficiencies of CO₂ removal at higher L/G ratios were the same as those described for PCB or SCB.

3.3.6.2 Effect of inlet CO₂ concentration on CO₂ removal in promoted PCB/SCB mixture solutions

The inlet CO₂ concentration was varied from 14% to 8% to examine if this had any effect on removal efficiency. All other conditions remained the same and the experiment was conducted at an L/G of 4 L/m³. Results are shown in Figure 3.20.

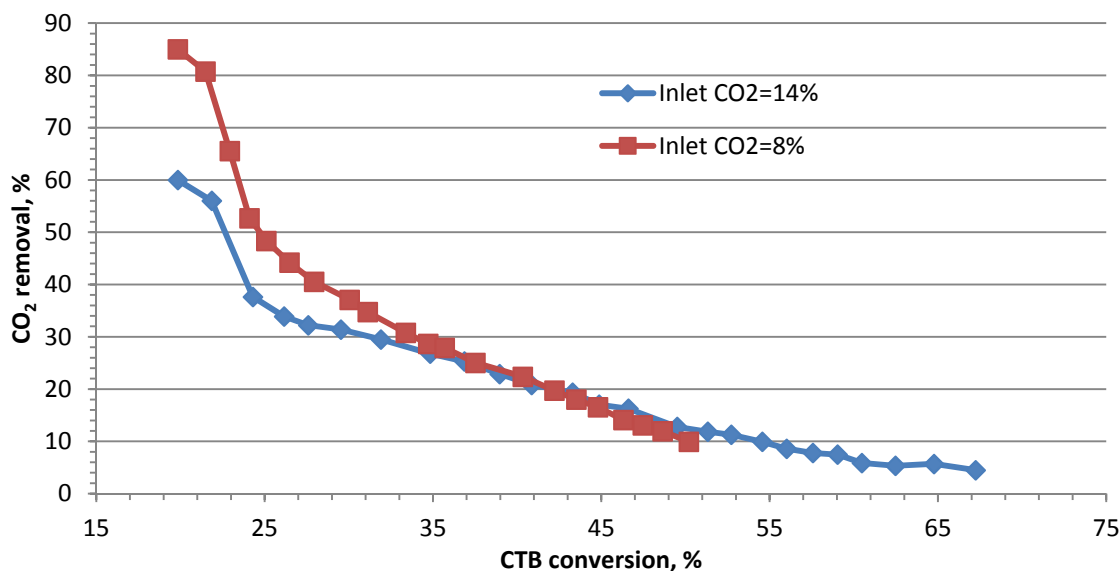


Figure 3.20. Effect of inlet CO₂ concentration on CO₂ removal, PCB25/SCB10+0.5M PZ

At a lower CO₂ inlet concentration, CO₂ removal efficiency of the lean PCB25/SCB10+0.5 M PZ solution was increased. In comparison, at the rich conditions, removal efficiency was almost identical. At a higher inlet CO₂ concentration, a larger amount of CO₂ needed to be removed to achieve the same removal efficiency while there was also a higher driving force for CO₂ absorption when inlet concentration was higher. These results can be explained by the same logic used for PCB or SCB solutions.

3.3.6.3 Effect of different promoters and varying concentrations of PCB and SCB on CO₂ removal in promoted PCB/SCB mixture solutions

As with plain PCB or SCB, it was important to see the impact of how different promoters increased CO₂ absorption rate into the PCB/SCB mixture solution. CO₂ absorption into a

PCB25/SCB10 mixture promoted with 0.5 M PZ was compared with the same mixture promoted with 1 M DEA, when all other conditions remained the same. Once the baseline conditions were established, other mixture solutions were tested including PCB20/SCB15, which had a slightly higher total SCB concentration and a lower total PCB concentration, as well as PCB12.5/SCB5, which represented both lower PCB and SCB concentrations. All other conditions besides solution compositions were kept the same, at baseline. Results are shown in Figure 3.21.

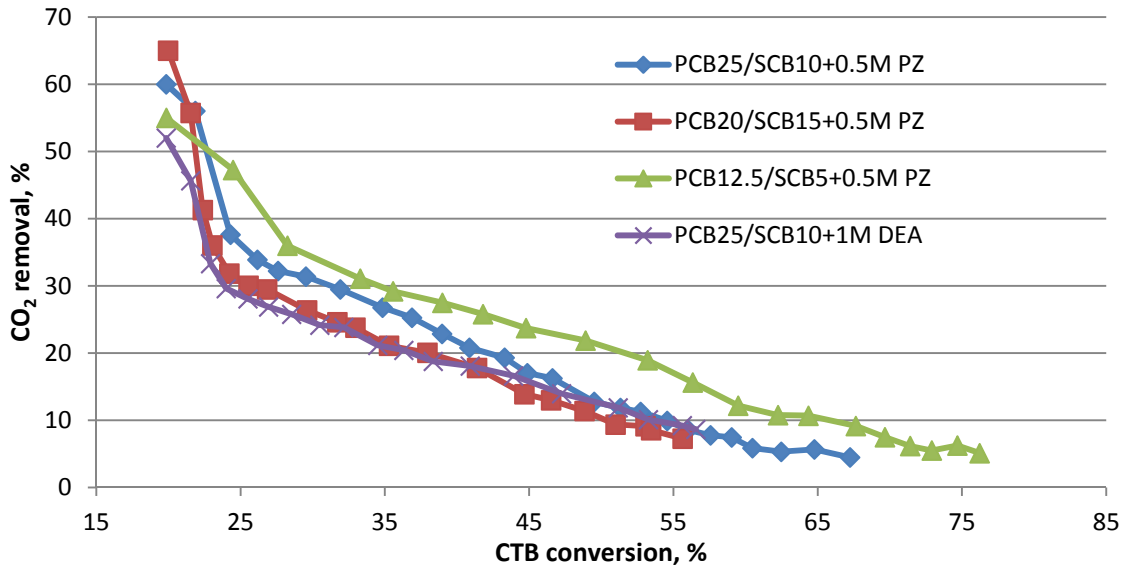


Figure 3.21. Effect of PCB and SCB concentrations and different promoters on CO₂ removal in PCB/SCB mixture.

At low CTB conversion levels, less than 50%, the PCB/SCB solution with 0.5 M PZ performed slightly better than the same solution promoted with 1 M DEA. As the CTB conversion increased to past 50%, CO₂ removal efficiencies of these solutions became comparable to each other. Throughout the entire CTB conversion range, the addition of 0.5 M PZ was more effective than 1 M DEA in promoting the rate of CO₂ absorption into the PCB/SCB solution.

PCB20/SCB15 and PCB25/SCB10 solutions promoted with 0.5 M PZ had similar concentrations of PCB and SCB. Removal efficiency was comparable at corresponding CTB conversion levels; they absorbed 60% of the CO₂ at 20% inlet CTB conversion and 20% at 40% inlet CTB conversion. PCB25/SCB10 performed better than PCB20/SCB15. The PCB12.5/SCB5 solution, which had the lowest total PCB and SCB concentration, had the highest

removal efficiency among all of the solutions. This trend was reported previously for PCB and SCB. However, a low concentration solution may not necessarily be a good option because even with a higher removal efficiency, a larger flow rate of liquid is required to achieve the same amount of CO₂ removal, or a richer CO₂ loading level, corresponding to a lower mass transfer driving force and thus kinetics, is required to increase CO₂ absorption capacity.

3.3.6.4 Comparison of promoted PCB/SCB mixture solution with promoted PCB solution and 5 M MEA

Since the baseline PCB25/SCB10+0.5 M PZ mixture had the highest removal efficiency among the mixtures tested, the absorption results were compared with previous data gathered for 5 M MEA and PCB40 promoted with 0.5 M PZ. Results of the CO₂ removal efficiency as a function of CTB conversion are shown in Fig. 3.23.

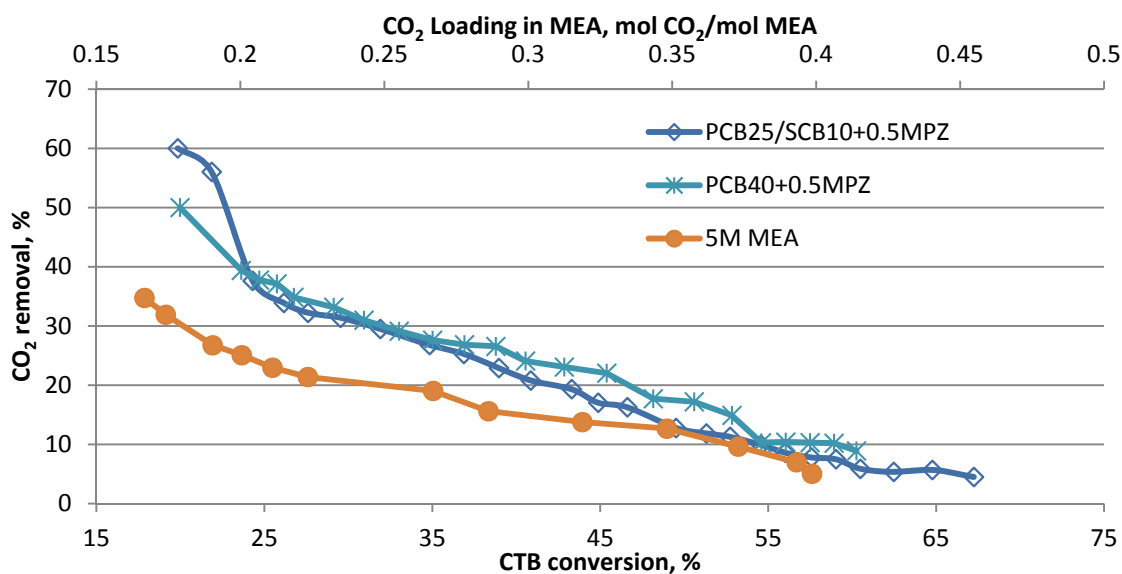


Figure 3.22. Comparison of 0.5 M PZ promoted PCB40 and PCB25/SCB10 mixture with 5 M MEA

The temperature used for the tests with the promoted PCB25/SCB10 and PCB40 solutions was 70°C and the tests with 5 M MEA solution were run at 50°C. All other conditions, such as the L/G ratio and liquid flow rate, were kept the same for comparison purposes. The horizontal axis of the figure has a scale representative of the lean and rich conditions of each solution for their practical application. At the same L/G ratio, both the PZ promoted PCB25/SCB10 and PCB40 solutions tested outperformed the 5 M MEA in terms of CO₂ removal

efficiencies at either CO₂ lean or rich conditions. The PCB25/SCB10 and PCB40 solutions with 20% inlet CTB conversion removed 60% and 50%, respectively, while 5 M MEA with 0.20 mol/mol CO₂ loading absorbed 25% of the CO₂. This continued as the CO₂ loading increased in each of the solutions.

Chapter 4

Conclusions and Recommendations

4.1. Conclusions

4.1.1 Screening of promoters to accelerate CO₂ absorption into K₂CO₃/KHCO₃ solutions

Five different primary and secondary amines were evaluated as promoters for a concentrated 40 wt% potassium carbonate/bicarbonate (PCB) solution using a batch stirred tank reactor. All amines improved the rate of CO₂ absorption into the PCB solution. These amine promoters increased the absorption rates into the PCB solution at 70°C by 3.5 to 50 times, depending on the type and dosage of the promoters, carbonate to bicarbonate (CTB) conversion and pCO₂. Among the five promoters, the rates promoted with piperazine (PZ) and aminomethyl propanol (AMP) were the highest. Compared to the monoethanolamine (MEA) solution loaded with 0.2 mol CO₂/mol MEA, a typical CO₂ lean condition in the benchmark MEA process at 50°C, the absorption rates of the PCB40-20 promoted with 1 M PZ and 1 M AMP at 70°C were greater than or equal to that of the MEA solutions. These same promoters increased absorption rate into PCB solution at higher CO₂ loading. Amine promoters are promising for accelerating CO₂ absorption into the PCB solution. The best performing promoters, PZ and AMP, and an industrial benchmark promoter, diethanolamine (DEA), were selected for further investigation in the bench scale packed bed column.

Amino acid salts also were screened as solvents for CO₂ absorption. Five amino acid salts, including K-glycine, K-sarcosine, K-proline, K-aurine, and K-alanine were tested. All of the amino acid salt aqueous solutions showed high rates of CO₂ absorption, especially 3 M K-glycine, K-sarcosine and K-proline. These solutions tested at 70°C exhibited rates higher than or comparable to those of 5 M MEA at 50°C. The three highest performing amino acid salts, K-glycine, K-sarcosine and K-proline were evaluated as promoters for CO₂ absorption into PCB40 solution at 70°C. The rates into both PCB40-20 and PCB40-40 were accelerated by these promoters. K-sarcosine and K-glycine improved the absorption rate more than K-proline. But,

compared to the rate of absorption into 5 M MEA with CO₂ loading of 0.20 mol CO₂/mol MEA, rates into the PCB40-20 promoted by these amino acid salts were lower.

4.1.2 Kinetic study of CO₂ absorption into a concentrated K₂CO₃/KHCO₃ solution in a packed bed column

Testing of CO₂ absorption in the bench scale, packed bed column revealed that the use of rate promoters increased the rate of CO₂ removal into PCB solution. The concentrated PCB40 solution promoted with 0.5 M PZ, DEA or AMP tested at 70°C performed 1 to 3 times better than 5 M MEA at 50°C at their respective lean loading levels and 3 to 5 times better at rich CO₂ loading levels, when all other conditions remained the same. In all PCB solutions tested, CO₂ removal rate increased as L/G ratio increased, as CO₂ loading decreased, or as inlet CO₂ concentration decreased. The addition of PZ into the PCB solution was the most effective among the tested promoters in accelerating the rate.

If desired, a sodium carbonate/bicarbonate (SCB) solution can be used as an alternative solvent to a PCB solution in the Hot-CAP to take advantage of certain properties. A lower concentration of SCB was tested compared to PCB because of its lower solubility. After testing SCB15 with different promoters and at different L/G ratios, results followed the same trends as the PCB solution. SCB15 promoted with 0.5 M PZ had the best performance out of the SCB solutions tested, but the overall CO₂ removal efficiency was slightly lower than the PCB40 promoted with 0.5 M PZ.

Another solvent that could be used for CO₂ absorption in Hot-CAP is a PCB/SCB mixture solution. This attempts to take advantage of the best attributes of each chemical. The results from the tests with PCB/SCB mixtures reflected the same trends of parametric effects seen in the tests with both the plain PCB and SCB solutions. The PCB25/SCB10 solution promoted with 0.5 M PZ had the highest CO₂ removal efficiency at 70°C, which was comparable to the promoted PCB40 and higher than 5 M MEA at 50°C.

4.2. Recommendations

The work presented here should be continued by investigation of the mechanism and intrinsic kinetics behind these amine promoted PCB reactions. This will help find more accurate kinetic constants that can be used to develop a model of the absorption column for the equipment design and scale up. Various chemical analysis tools can be used to identify intermediates and products of the different amine promoted reactions. Knowing the chemistry taking place will enable a better understanding of the process as a whole.

A further investigation into the effect of precipitation in the PCB solution on CO₂ absorption rate is recommended. This is an interesting phenomenon from what has been observed in the experiments thus far and is important to continue to pursue. In addition, more tests can be conducted that integrate the different unit operations of the Hot-CAP together, for example running the absorption and stripping column together in a full loop.

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