

Original Article

CO₂ capture in the form of thermally stable solid compounds using ammoniated brine

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Abstract

Capture of CO₂ in the form of thermally stable solid compounds is an interesting alternative for CO₂ sequestration and utilization. In this study, CO₂ capture using ammonia base absorbent in a bubble column reactor with various parameters (NaCl concentration, reaction temperature, CO₂ flow rate, and ammonia concentration) was investigated. The precipitated products mainly consisted of thermally unstable [ammonia salts; e.g. NH₄HCO₃, (NH₄)₂CO₃] and stable solid [NaHCO₃, Na₂CO₃] products. The results revealed that increasing NaCl concentration and/or ammonia concentration or decreasing reaction temperature and/or CO₂ flow rate increased CO₂ capture capacity and the amount of the stable solid products. Operating conditions set at 3.0 M of NaCl with 43 wt% of ammonia solution, a reaction temperature of 20 °C, and a CO₂ flow rate of 100 mL/min were found to provide the maximum NaHCO₃ and Na₂CO₃ amounts of 20.67 wt% and 39.41 wt%, respectively. The stable solid products were also characterized by SEM/EDS and XRD.

Keywords: CO₂ capture, stable solid compounds, ammoniated brine, desalination, modified Solvay process

1. Introduction

The degree of global warming effects caused by emissions of greenhouse gases has been continuously increasing. Among these gases, CO₂ has been increasingly released into the atmosphere in the past several decades due to increasing fossil fuel combustion in industrial-scale production and transportation. Indeed, petroleum exploration and production

is an industrial sector that contributes a significant share of the global CO₂ emissions. At the end of 2015, the level of CO₂ concentration was around 400 ppm (Mauna Loa Observatory, Hawaii, USA, 2015), close to the critical 450 ppm level at which irreversible changes may occur in the environment. CO₂ emissions from the combustion of coal and natural gas, especially arising from the petroleum industry, were the first and second largest sources of release into the atmosphere, respectively (EPPO, 2015).

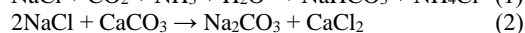
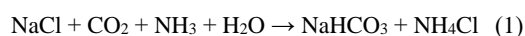
Several CO₂ capture techniques have been developed to reduce the amount of CO₂ in the atmosphere; these include membrane separation, cryogenics, physical adsorption and

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chemical absorption (Li *et al.*, 2013; Olajire, 2010; Shakerian *et al.*, 2015; Tan *et al.*, 2012). Among the available CO₂ capture techniques, chemical absorption has advantages over the others in terms of capture efficiency (which, in this case, is better than 95%), reusability, and regeneration (Peng *et al.*, 2012a). Using amine compounds, such as Monoethanolamine (MEA), Diethanolamine (DEA), or ammonia solution, is highly attractive for the capture of CO₂ released during petroleum production (Léonard *et al.*, 2015; Luis 2016; Peng *et al.*, 2012b) and this is especially true of ammonia, which has a high absorption efficiency and capacity (1.2 kg CO₂/kg NH₃) (Diao *et al.*, 2004; Shakerian *et al.*, 2015; Yu & Wang, 2015). Indeed, ammonia solution is believed to be the most suitable amine compound because it i) is viable, ii) is inexpensive, iii) is stable under high CO₂ concentrations, iv) is less toxic than MEA and DEA, v) can be regenerated, requiring low energy consumption, and vi) can tolerate the NO_x and SO_x that normally contaminate the gases released from petroleum wells (Chen *et al.*, 2012; Qin *et al.*, 2011; Sutter *et al.*, 2015).

The use of ammonia solution to capture CO₂ can be greatly beneficial when applied to sectors of the petroleum industry that are located in an ocean, because the seawater serves as an unlimited source of alkaline and alkaline earth ions, especially Na⁺ and Ca²⁺, which are important in the capture of CO₂ (El-Naas *et al.*, 2010; Huang *et al.*, 2001; Jibril & Ibrahim, 2001; Nikulshina *et al.*, 2008). In the presence of Na⁺, ammonia, and CO₂, seawater can undergo reactions to form carbonate or bicarbonate compounds, following pathways similar to those widely known from the Solvay process, shown in equations (1)–(3):



The chemical species in the mixture can be categorized into three groups: carbonate ions (CO₃²⁻), bicarbonate ions (HCO₃⁻), and carbamate ions (NH₂COO⁻) (Chen *et al.*, 2012; Peng *et al.*, 2012a; Qin *et al.*, 2010). These intermediate species that are present in the liquid phase can react with other positive ions (e.g. Na⁺, NH₄⁺) to generate various carbonate or bi-carbonate compounds through various pathways. Some thermally stable solid products can simultaneously precipitate out from the mixture, such as NaHCO₃ and Na₂CO₃. Besides, other solid products, such as NH₄HCO₃, NH₄(CO₃)₂, NH₂COONH₄, and NH₄Cl, are also present in the solid phase (Chen *et al.*, 2012; Darde *et al.*, 2011; Diao *et al.*, 2004; Li *et al.*, 2003; Liu *et al.*, 2009; Sutter *et al.*, 2015). However, these compounds degrade readily to CO₂, ammonia, and water, or are in equilibrium with their ions in the liquid phase.

Previously, various techniques and parameters based on the Solvay process for the sequestration of CO₂ have been intensively investigated, for example, in terms of types of alkalis (De Vito *et al.*, 2011; El-Naas *et al.*, 2017; Huang *et al.*, 2001; Peng *et al.*, 2012a; Spigarelli, 2013; Spigarelli & Kawatra, 2013), optimal conditions for CO₂ capture efficiency (Mohammad *et al.*, 2016), and precipitation of NaHCO₃ (El-Naas *et al.*, 2010; Forster, 2012; Huang *et al.*, 2001; Jibril & Ibrahim, 2001). However, no full investigation into the generation of thermally stable solid products, specifically of NaHCO₃ and Na₂CO₃, has yet been performed. In essence, the thermally stable solid products are the only compounds that permanently

capture the CO₂, which is a practical method for CO₂ sequestration if applied to the relevant sectors of the petroleum industry. This research was therefore conducted to assess a variety of operating parameters that affect the solid product formation and the CO₂ capture efficiency. The parameters studied consist of concentrations of NaCl and NH₃, flow rate of CO₂, reaction temperature, and recyclability of the ammoniated brine for multiple cycles of CO₂ capture.

2. Materials and Methods

2.1 CO₂ capture using ammoniated brine

A schematic diagram of the experimental setup for CO₂ capture in the form of thermally stable solid compounds is shown in Figure 1. A 1 L bubble column reactor (9 cm in inside diameter and 22 cm in height) made of clear acrylic was used for CO₂ capture under atmospheric conditions and was operated semi-batch wise. For a typical operation, 0.8 L of synthetic brine made of NaCl (99.0%, Carlo Erba Reagents) was charged into the reactor and then ammoniated with NH₃ gas (95.5%, Poontaweporn Ltd.) to a pH of about 13, at which saturation is reached. Then the CO₂ gas (99.98%, Lab Gas Co., Ltd.) was bubbled through the liquid column while the reaction temperature was maintained constant at 20 or 38 °C using an ice bath. The outlet CO₂ concentration in the effluent gas was monitored by a CO₂ analyzer (COZIA-WR; CO2METER, Inc.) and recorded every 15 min to determine the absorption performance. NaCl concentrations of 0.6, 1.0 and 3.0 M were studied, ranging from the equivalent of natural seawater concentration to a typical desalination wastewater concentration. The effects of NH₃ concentration (30 and 43% w/v) and CO₂ flow rate (100, 300, and 500 mL/min) as controlled by mass flow controllers (AALBORG-TIO model: GFC17) on the CO₂ capture efficiency and solid formation were also investigated. After completed reactions, the solid products were separated by filtration, dried in an oven at 110 °C for 3 h, and characterized. The recyclability of the filtrate for multiple cycles of CO₂ capture was further studied only at the optimal conditions (3M of NaCl, 20 °C, 43% w/v of NH₃, and 100 mL/min of CO₂ flow rate), providing the maximum amount of thermally stable solids. After completion of the first cycle of CO₂ capture and the removal by filtering of solids from the suspension, the filtrate

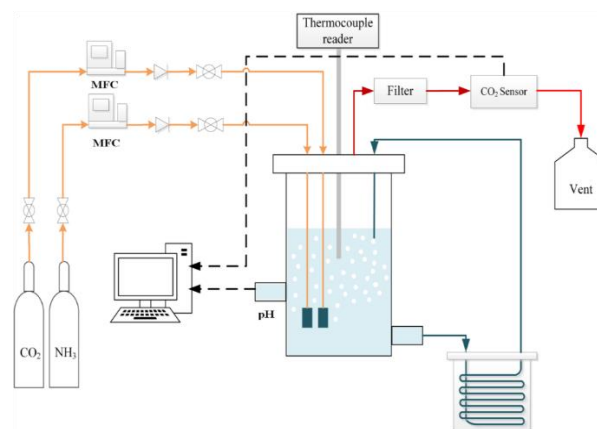


Figure 1. Schematic diagram of CO₂ capture process using ammoniated brine.

was then reused in a 2nd cycle of CO₂ capture without making up either the NaCl or the NH₃ concentration. Similarly, the filtrate obtained after completion of the 2nd cycle of CO₂ capture was then reused in the 3rd cycle of CO₂ capture. In each cycle, the CO₂ capture efficiency was determined and the filtered solids from each cycle were further analyzed for their compositions.

2.2 Characterization of the solid products

The carbonated products from the CO₂ capture process, including the by-products from the reactions, were separated into two parts: liquids and solids. These products were analyzed qualitatively and quantitatively to identify the species and carbon distribution in different phases and compounds. To identify the carbon captured in the forms of carbonate and bicarbonate, the solid products were analyzed using a double titration method using phenolphthalein and methyl orange indicators, respectively (standard methods 2320 for the examination of waste and wastewater). The thermal stability of the solid products was studied by drying them in an oven at 110°C for 3 h, and the remaining solids were further investigated to identify the crystalline phases using X-ray diffractometer (XRD: Philips X³Pert, 2Theta = 10-80, step size 0.02). A scanning electron microscope and energy dispersive X-ray spectrometer (FE-SEM/EDS:JOEL JSM-7600F) were used to analyze morphology and elemental composition.

3. Results and Discussion

3.1 Effects of NaCl concentration on CO₂ capture performance and product distribution

The outlet CO₂ concentrations were close to zero during the first 45 min of CO₂ capture and began to increase after that, as the formation of solid products started. The lowest CO₂ outlet concentration, indicating the highest CO₂ capture rate, was found when the mixture had the highest NaCl concentration tested (3.0 M). It can be seen from Figure 2 that CO₂ capture capacity was related to the NaCl concentration and

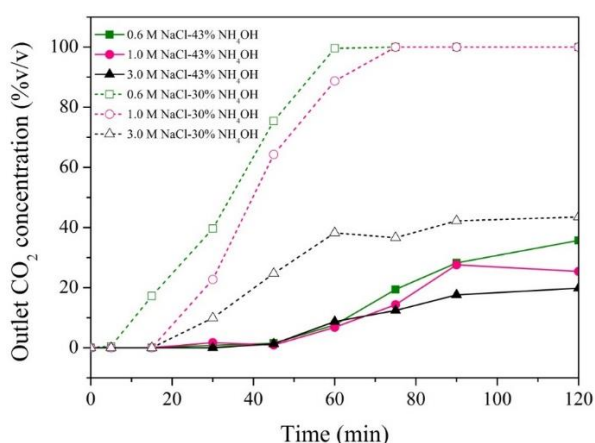


Figure 2. Variation of outlet CO₂ concentration with time on stream for different ammonia concentrations and NaCl concentrations at 20 °C, on using 1 L/min CO₂ flow rate.

increased with NaCl concentration. This is due to the fact that Na⁺ ions reacted with carbamate-ion intermediates to form NaHCO₃ and Na₂CO₃ solids, which were precipitated out of the suspension by the widely known salting-out effect (Sanchez-Fernandez *et al.*, 2013). Then the chemical equilibrium for the reaction between NH₄⁺ (formed by NH₃ reacting with H₂O) and CO₂ in the mixture was shifted towards forming more carbamate ions, resulting in more CO₂ capture. The 0.6 M NaCl case, representing ammoniated seawater, could essentially capture nearly 100% of the CO₂ for the first 45 min. After that, the CO₂ capture capacity constantly decreased until it reached 60% at 120 min.

Further quantitative analysis of the composition of the solid products obtained at the end of the CO₂ capture process was performed. As previously stated, the solid products consisted of both thermally unstable solid products (i.e., ammonia salts) and thermally stable solid products (i.e., Na₂CO₃, NaHCO₃, NH₄Cl, and NaCl) (Nikulshina *et al.*, 2008). Thus, the quantitative analysis was firstly carried out via air oven drying at 110°C for 3 h, used as a thermal decomposition process, to determine the amount of unstable solid products containing NH₄HCO₃ and (NH₄)₂CO₃ (Chen *et al.*, 2012; Yeh *et al.*, 2005). The products from this thermal decomposition were NH₃, H₂O, and CO₂. Secondly, a double titration was used following the thermal decomposition to quantify the amount of Na₂CO₃ and NaHCO₃ (Millero *et al.*, 1993).

Table 1 shows the weight losses during oven drying, which correspond to the weights of ammonium salts and residual water in wet cake samples of different brine concentrations. The amounts of ammonium salts and residual water obtained were in the range of ca. 58–70 wt% and tended to decrease with increasing brine concentration. It should be noted that this range of weight loss already includes the weights of residual water (10–12 wt% in all samples), as determined by a Karl Fischer titration. Furthermore, the quantities of C-containing compounds from CO₂ capture that were thermally stable could be determined by the double titration method. First, HCl

Table 1. Carbon distribution in the solid products for various NaCl concentrations after 2 h of CO₂ absorption at 20 °C, using a CO₂ flow rate of 1 L/min, and with a NH₃ concentration of 30% w/v.

NaCl (M)	Composition of solid (wt%)			
	Ammonium salts + residual water*	Na ₂ CO ₃ **	NaHCO ₃ **	Others***
0.6	69.7	8.8	16.5	5.0
1.0	66.4	10.9	15.3	7.4
3.0	58.6	13.2	17.3	10.9

*Determined from weight losses by thermal decomposition at 110°C for 3 h. These weight losses included residual water content of 10–12 wt%, determined using Karl Fischer titration, and the rest were the weights of ammonium salts (NH₄HCO₃ and (NH₄)₂CO₃).

**Thermally stable solids were determined by a double titration method.

***Calculated from 100 - (Ammonium salts + residual water + NaHCO₃ + Na₂CO₃).

was used as a titrant with phenolphthalein as indicator, and the color of the solution changed from light pink to clear liquid when CO_3^{2-} reacted with H^+ to form HCO_3^- . Then, a further titration was done with HCl, but the indicator was changed to methyl orange, allowing a change in color from yellow to orange when HCO_3^- reacted with H^+ to form H_2CO_3 . Data from these first and second titrations could be used to calculate the amounts of Na_2CO_3 and NaHCO_3 , respectively, as shown in Table 1. It can be seen from Table 1 that the amount of Na_2CO_3 clearly increased with brine concentration. Similarly, the total amount of Na_2CO_3 and NaHCO_3 increased with concentration of NaCl. This can be explained by the fact that, as the brine concentration increases, so does the amount of Na^+ , shifting the equilibrium between NH_4^+ and the ammonium salts (i.e., $\text{NH}_4\text{HCO}_3/(\text{NH}_4)_2\text{CO}_3$) toward the active NH_4^+ side. Thus, increasing the amount of NH_4^+ resulted in greater capture of CO_2 , producing in turn a higher amount of the carbamate $[\text{NH}_2\text{COO}^-]$ ions, which subsequently transformed to bi-carbonate ions, and then carbonate ions, finally producing thermally stable products, especially Na_2CO_3 (Jilvero *et al.*, 2014; Niu *et al.*, 2012; Wang *et al.*, 2011; Xiang *et al.*, 2012). In addition to the formations of ammonium salts, Na_2CO_3 , and NaHCO_3 , other products such as chloride compounds (i.e., NH_4Cl and NaCl) also appeared.

The solid products after drying were analyzed to determine the phase and crystallinity by using XRD: see Figure 3. As expected, it was found that the remaining products or the thermally stable solid products consisted of NaHCO_3 (JCPDS file no. 01-072-1663), Na_2CO_3 (JCPDS file no.00-018-1208), and NaCl (JCPDS file no.01-088-2300). The dried solid products from using different brine concentrations were investigated for their particle sizes, morphologies, compositions, and elemental distributions using SEM/EDS, and were compared to those of commercial Na_2CO_3 dried at the same conditions. The SEM/EDS images obtained from a solution with 3.0 M NaCl, as shown in Figure 4, represent typical size and morphology of the dried solid products. The particle sizes were found to be in a range 90-140 nm and the morphologies were irregular shaped agglomerated particles similar to those in commercial Na_2CO_3 , for every brine concentration. It was found that the solid product contained C, O, Na, N, and Cl elements in the amounts of 14.18, 45.33, 37.34, 1.18, and 1.97 %, respectively. The presences of C, O, Na, and Cl were in a good agreement with what was found via XRD, confirming the presences of NaHCO_3 , Na_2CO_3 , and NaCl in the solid products. A trace of the N element was also detectable, but it was only slight; this could be due to some N-containing products derived from reaction with ammonia. Figure 4 shows uniform distributions of C, O, and Na elements, while those of N and Cl were found to be scattered, confirming that N-containing and Cl-containing products were only present in traces. These products could potentially be NH_4Cl and unreacted NaCl (Jibril & Ibrahim, 2001).

3.2 Effects of ammonia concentration on CO_2 capture performance and product distribution

The concentration of ammonia in the solution is a factor affecting the chemical absorption and the absorption efficiency of CO_2 . Generally, if the concentration of ammonia in the solution is increased, the forward reaction kinetics in the

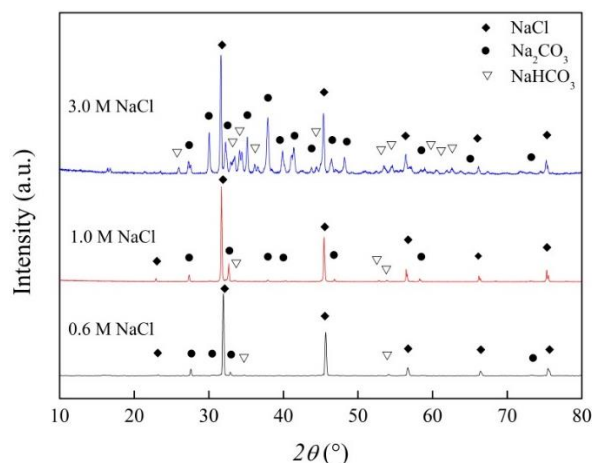


Figure 3. XRD patterns of thermally stable solids from runs with 0.6, 1.0, and 3.0 M NaCl.

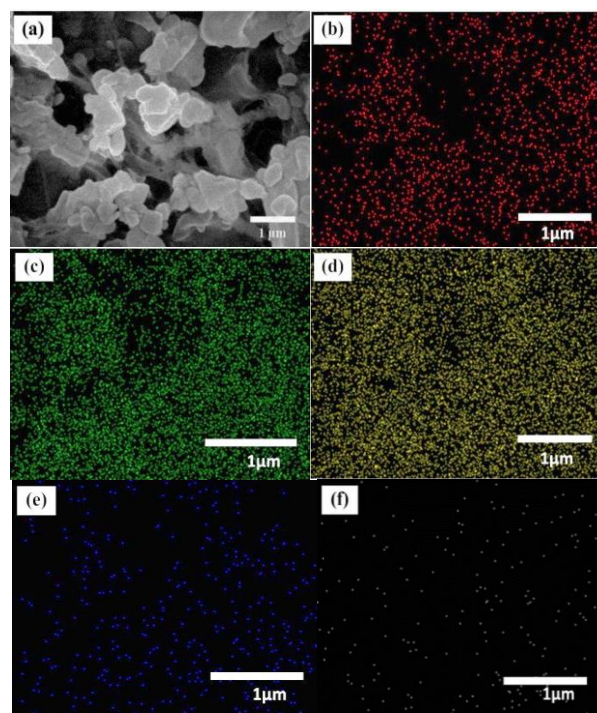


Figure 4. SEM/EDS images of the solids after thermal drying, obtained using 3.0 M NaCl: a) SEM image, and images of element distributions of b) C, c) O, d) Na, e) N, and f) Cl.

liquid phase, generating the solid products, are more favorable (Diao *et al.*, 2004; Liu *et al.*, 2009; Peng *et al.*, 2012a, 2012b; Yeh & Bai, 1999a; Yincheng *et al.*, 2011). Figure 2 illustrates the behaviors of the CO_2 absorption efficiency for liquid-phase ammonia concentrations of 30% and 43% w/v. It can be seen that, for all NaCl concentrations, the CO_2 absorption efficiencies after 15 min of time-on-stream test using 43% ammonia were higher than those using 30% ammonia, implying that the equilibrium of the chemical reaction has, for 43%, shifted towards the solid products. Higher concentration of NH_3 provided more NH_4^+ ions available for capturing more CO_2 to form

more carbamate-ion intermediates, resulting in higher CO₂ capture efficiency. A comparison of the product compositions for 30% and 43% ammonia, listed in Table 2, confirms that the thermally stable solid products obtained using 43% ammonia were produced in greater quantity than those obtained using 30% ammonia.

Table 2. Carbon distribution in solid products obtained using ammonia concentrations of 30 and 43% w/v after CO₂ absorption at 20 °C for 2 h using a CO₂ flow rate of 1 L/min.

NaCl (M)	Composition of solid (wt%)			
	Ammonium salts + residual water*	Na ₂ CO ₃ **	Ammonium salts + residual water*	Others***
[NH ₃] = 43% w/v				
0.6	69.7	0.6	69.7	0.6
1.0	66.4	1.0	66.4	1.0
3.0	58.6	3.0	58.6	3.0
[NH ₃] = 30% w/v				
0.6	70.4	0.6	70.4	0.6
1.0	66.3	1.0	66.3	1.0
3.0	66.1	3.0	66.1	3.0

*Determined from weight losses by thermal decomposition at 110°C for 3 h. These weight losses included residual water content of 10–12 wt%, determined using Karl Fischer titration, and the rest were the weights of ammonium salts (NH₄HCO₃ and (NH₄)₂CO₃).

**Thermally stable solids were determined by a double titration method.

***Calculated from 100 – (Ammonium salts + residual water + NaHCO₃ + Na₂CO₃).

3.3 Effects of temperature and CO₂ flow rate on CO₂ absorption

CO₂ capture using ammoniated brine typically has a high absorption efficiency, with the factors affecting the absorption efficiency including absorption temperature and CO₂ flow rate. Figure 5 shows the absorption efficiencies at two absorption temperatures (20 and 38 °C) and three CO₂ flow rates (100, 300, 500 ml/min) using a constant brine concentration of 3.0 M, in order to determine the optimal conditions for CO₂ capture in the form of thermally stable solid products. It was found that the absorption efficiency decreased with absorption temperature. This is because the highly volatile ammonia can partially evaporate at 38 °C, resulting in a lower concentration of ammonia in the solution as well as a lower CO₂ capture efficiency (Ma *et al.*, 2013). Furthermore, a lower concentration of ammonia can also result in the backward reaction from Na₂CO₃ and NaHCO₃ to their ions (Olajire, 2010; Pelkie *et al.*, 1992; Peng *et al.*, 2012a; Qin *et al.*, 2010), leading to less precipitation of the solid products. Besides, the solubility of CO₂ decreases with temperature of the liquid phase (Diao *et al.*, 2004; Niu *et al.*, 2012; Yeh & Bai, 1999), resulting in lower concentration of CO₂ in the liquid phase and even lower yield of the solid products (Zhao *et al.*, 2011). The solubilities of CO₂ and NH₃ gases in the reaction mixture can be described by

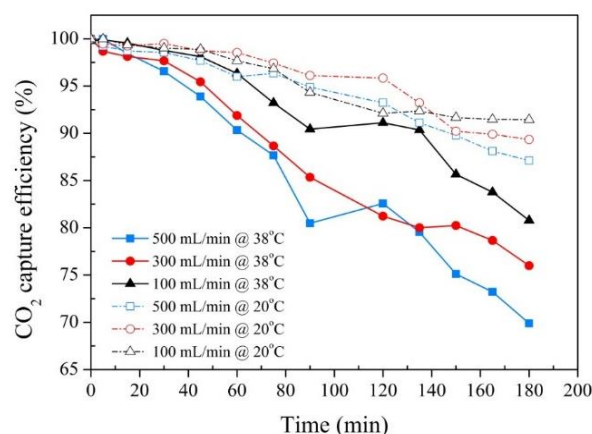


Figure 5. Effects of temperature on CO₂ capture efficiency using [NH₃] = 43% w/v, [NaCl] = 3.0 M, for CO₂ flow rates of 100, 300 and 500 mL/min, and reaction temperatures of 38 and 20 °C.

vapor-liquid equilibrium and Henry's law (Qi *et al.*, 2015). When temperature increases, the amounts of CO₂ absorbed in hydrate form and aqueous NH₃ decrease significantly, in contrast with increasing ammonia escape from the solution and lowering the mean mass transfer between reactants in the aqueous phase. Finally, for an exothermic reaction between the absorbed CO₂ and NH₃, increasing the temperature decreases the reaction rate. Therefore, a low reaction temperature, such as room temperature, is essential to achieving a high efficiency of CO₂ capture.

The influence of flow rate of CO₂ (100, 300, and 500 mL/min) was also investigated, as presented in Figure 5. It can be observed that, at the same reaction temperature, increasing the CO₂ flow rate slightly reduced the CO₂ capture efficiency, because the contact time for the interaction between the CO₂ and ammonia solution is shortened (Peng *et al.*, 2012; Yincheng *et al.*, 2011; Zhao *et al.*, 2013), leading to less solid products. Additionally, the contact area between CO₂ bubbles and the liquid solution is lessened with increasing flow rate, because the CO₂ bubble size becomes larger. Large bubbles decrease the specific surface area of the gas-liquid interface, thereby reducing the absorption of CO₂ into the ammoniated brine (NH₃-NaCl) mixture and lowering the rates of subsequent reactions (Yincheng *et al.*, 2011; Zhang & Guo, 2013). Therefore, the molar ratio of CO₂ and NH₃ in the liquid phase is reduced, which has a negative effect on the CO₂ capture efficiency (Zhu *et al.*, 2011). As seen in Figure 5, the CO₂ flow rate providing the highest CO₂ capture efficiency was 100 mL/min at 20 °C, and its CO₂ capture efficiency was able to remain over 91% throughout the first 3 h of the reaction.

Table 3 shows the product distributions obtained when varying reaction temperature and CO₂ flow rate. The results clearly indicate that decreasing the reaction temperature significantly promoted precipitation of NaHCO₃ and Na₂CO₃. This is because the solubility of CO₂ increases with decreasing reaction temperature, leading to more formation of carbonate and bi-carbonate ions in the solution (Choi *et al.*, 2012; Holmes *et al.*, 1998). These ions later react with the Na⁺ and thereby generate the majority of the thermally stable solid compounds (El-Naas *et al.*, 2010; Jibril & Ibrahim, 2001). On increasing CO₂ flow rate (using the same reaction temperature), the per-

Table 3. Carbon distribution in solid products at reaction temperatures of 20 and 38 °C, and CO₂ flow rates of 100, 300, and 500 mL/min. All results are for 2 h reaction time and 43% w/v NH₃.

Flow rate (mL/min) @ Temp (°C)	Composition of solid (wt%)			
	Ammonium salts + residual water*	Na ₂ CO ₃ **	NaHCO ₃ **	Others***
100 mL/min@38°C	42.75	29.09	17.93	10.23
300 mL/min@38°C	44.92	25.98	16.25	12.86
500 mL/min@38°C	45.05	23.42	17.24	14.28
100 mL/min@20°C	33.70	39.41	20.67	6.23
300 mL/min@20°C	35.69	33.03	25.30	5.99
500 mL/min@20°C	39.32	30.82	23.72	6.14

*Determined from weight losses by thermal decomposition at 110°C for 3 h. These weight losses included residual water content of 10–12 wt%, determined using Karl Fischer titration, and the rest were the weights of ammonium salts (NH₄HCO₃ and (NH₄)₂CO₃).

**Thermally stable solids were determined by a double titration method.

***Calculated from 100 – (Ammonium salts + residual water + NaHCO₃ + Na₂CO₃).

(El-Naas *et al.*, 2010; Jibril & Ibrahim, 2001). On increasing CO₂ flow rate (using the same reaction temperature), the percentage of the ammonium salts consistently increased slightly, whereas the fraction of NaHCO₃ and Na₂CO₃ jointly decreased slightly. This can be explained by the fact that, with increasing CO₂ flow rate, the contact time and the reaction time between Na⁺, NH₄⁺, HCO₃⁻ and CO₃²⁻ are reduced, resulting in a shorter time for the precipitation of the thermally stable solid products and thus the percentages of NaHCO₃ and Na₂CO₃ becoming less dominant (Zhao *et al.*, 2011; Zhu *et al.*, 2011).

3.4 Recyclability of the ammoniated brine solution

The CO₂ re-absorption ability and capture efficiency of ammoniated brine solution were examined, as demonstrated in Figure 6. Study of recyclability was performed by repeating the experiment using the optimal conditions (3M of NaCl, 20 °C, 43% w/v NH₃, and 100 mL/min of CO₂ flow rate) with the ammoniated brine solution after removing all solid particles. It can be seen that the CO₂ capture efficiencies decreased slightly with each cycle, from 92% in the first cycle to 75% in the third cycle, due to the partial loss of ammonia, which was lost with the products (Yeh *et al.*, 2005). Interestingly, the fraction of Na₂CO₃ produced decreased with each reuse, whereas the trend for NaHCO₃ was the opposite. This could be because the reaction rate of CO₃²⁻ reacting with Na⁺ to generate the Na₂CO₃ is faster than the reaction rate of the HCO₃⁻ and Na⁺ to generate NaHCO₃ (García-Abuín *et al.*, 2010; Harte *et al.*, 1933; Vasconcelos *et al.*, 2002). As a result, the accumulation of the HCO₃⁻ ions remaining in the ammoniated brine solution is

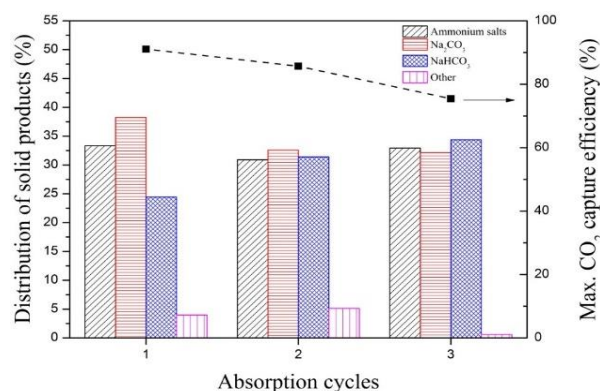


Figure 6. CO₂ absorption efficiency and product distribution through multiple absorption cycles at 20 °C using recycled solution, CO₂ flow rate of 100 mL/min, and [NH₃] of 43% w/v in the first cycle.

relatively higher than of the CO₃²⁻ ions. Therefore, as can be seen from the data in Figure 6, as the absorption was extended over more cycles, the fraction of NaHCO₃ in the product tended to increase, while that of Na₂CO₃ tended to decrease.

4. Conclusions

The capture of CO₂ into the stable solid forms NaHCO₃ and Na₂CO₃ using ammoniated brine in a bubble column reactor was studied. CO₂ gas was passed through a solution containing NH₄⁺ and Na⁺, which generated ammonium salts (unstable solid products) and insoluble carbonate salts (stable solid products), as well as NH₄Cl and NaCl as by-products. All of the parameters studied for the system, including NaCl concentration, outlet CO₂ concentration, reaction temperature, CO₂ flow rate, and ammonia concentration, influenced directly not only the efficiency of CO₂ capture, but also the distribution of components in the solid product. In experiments concerned with the variation of NaCl and ammonia concentrations, the CO₂ capture efficiency was enhanced by increasing the NaCl or ammonia concentration, owing to the larger amount of the reactants used. On the other hand, increasing the reaction temperature or the CO₂ flow rate had a negative effect on the CO₂ capture efficiency, as well as on the product yield. Although normally the rate of chemical reactions and mass transfer coefficient tend to increase with temperature (Darde *et al.*, 2011), in this case changing the reaction temperature from 20 to 38 °C significantly increased the volatilization losses of ammonia, and decreased the CO₂ capture efficiency. Mean-while, increasing the CO₂ flow rate from 100 to 500 mL/min reduced the contact time between CO₂ in bubbles with the ammoniated brine solution, and thus lowered the reaction rate, decreasing CO₂ capture efficiency. The conditions that achieved the highest amount of the stable solid compounds (39.41 wt% of NaHCO₃ and 20.67 wt% of Na₂CO₃) were 3.0 M of NaCl with 43% w/v of ammonia at a reaction temperature of 20 °C and with a CO₂ flow rate of 100 ml/min.

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