

Study on Carbon Dioxide Removal from Flue Gas by Absorption of Aqueous Ammonia

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Introduction

It has been known for more than 100 years that carbon dioxide (CO₂) is a greenhouse gas and the release of CO₂ from fossil fuel may affect the climate of the earth.¹ The growing awareness of the risks of climate changes has generated public concerns and, since 1989, the interests of researchers in sequestering CO₂. As the world population increases and energy demand rises, increased burning of fossil fuels will continue to drive atmospheric CO₂ levels upward. The Inter-government Panel on Climate Change (IPCC) predicts that atmospheric CO₂ concentrations will be increased by approximately twice from the pre-industrial concentration of 270 ppm to a concentration of 530 ppm in 2050 and could potentially exceed 700 ppm by 2100.² This increase will significantly affect the global weather and the physiological basis of plant production unless major changes are made. According to the United Nations Framework Convention on Climate Change (UNFCCC) at Kyoto,³ a commitment to reduce CO₂ emissions by 6% below the 1990's level was made by several countries. President Bush also announced the Global Climate Change Initiative (GCCII) with the goal of significantly reducing the U.S. greenhouse gas intensity by 18% by 2012⁴.

Power generation contributes one-third of the CO₂ released from fossil fuel combustion worldwide,⁵ which cause future generation of CO₂ through combustion will be substantial. The goal of reducing CO₂ concentrations in the atmosphere can be met either by decreasing the rate at which CO₂ is emitted into the atmosphere or by increasing the rate at which it is removed from it.⁶ A lot of research has been focused on determining a fast and inexpensive method to sequester carbon nowadays.

There are two typical strategies to reduce CO₂ emission from power plant combustion, one is to concentrate the CO₂ in-situ during the fuel conversion process, and the other one is to extract the CO₂ from the combustion flue gas followed by sequestration process. Since the fuel conversion process is usually very complex and difficult to control, the former technique is still highly investigative using.⁷ Several possibilities for the latter method have been proposed and developed, such as chemical solvents, physical absorption, cryogenic methods, membrane systems, biological fixation, and so on.⁸⁻¹⁰ Physical solvents are favored by high pressures and low concentrations of inert gases. CO₂ can be physically absorbed in a nonreactive solvent according to Henry's law and then regenerated using pressure reduction or heat. Chemical solvents are preferred for cases with low concentrations or amounts of CO₂ in the combustion gases and do not gain significant advantage by operating at elevated pressure. The chemical solvent methods are generally recognized as the most effective technologies at present. However, the cost for separation of CO₂ is high, typically in the range \$40-200 /ton of carbon.¹¹ In addition, the chemical solvent method also has several major problems including a slow absorption rate, small solvent capacity, and special equipment requirements. To reduce the cost of capturing CO₂, a low cost solvent that can minimize the operation cost, the equipment size, and equipment corrosion is desirable.

Among a lot of absorbents, amines have been considered as typical CO₂ absorbents. Chosen for principal commercial efforts in CO₂ capture and regeneration, they include monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA). In addition to aqueous solutions of alkanolamines, proprietary formulations comprising mixtures of the amines with various additives are also widely used. The MEA process has been thought as one of the most successful amine CO₂ absorption methods. In the MEA process, the MEA aqueous solution absorbs CO₂ at 100°F or slightly higher, and when the CO₂-rich MEA solution is heated to approximately 250°F, the CO₂ gas is released in

high purity. The MEA process is termed “regenerable” because the CO₂ is absorbed at low temperature and then released at a higher temperature. The regenerated, high purity CO₂ gas stream could be sequestered by a variety of technologies, and the regenerated MEA solution that remains is in a CO₂-lean condition, which can be reused for CO₂ capture. Thus, the MEA process has been widely used for CO₂ regeneration. However, it is an expensive option with the cost of CO₂ separation in the range from \$40 to \$70/ton of CO₂ removed due to its low loading capability, slow absorption rate and so on. It is not a best way to control large amount of CO₂ emission from utility flue gas.

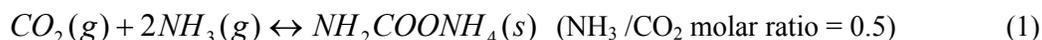
A current commercial approach in fertilizer industry which may provide an inexpensive and effective route of reducing CO₂ emissions from power plants is extracting CO₂ by an ammonia (NH₃) reagent in a wet scrubber. A wet pressurized scrubber is used to produce NH₄HCO₃ currently. How to de-pressurize is a challenge to us. Injection of NH₃ gas or aqueous NH₃ for removing NO_x (selective catalytic reduction) from flue gas is a common process in power plants. Unlike the Monoethanolamine (MEA) process, the aqueous ammonia process does not have absorbent degradation problems, which are caused by sulfur dioxide and oxygen in the flue gas and does not cause equipment corrosion, as in the case of MEA¹². In the work by Bai and Yeh,¹³ based on breakthrough curves, the NH₃ scrubbing capacity was calculated to be around 0.35 mol of CO₂/mol of NH₃ on a molar basis, or 0.9 -1.2 kg of CO₂/kg of NH₃ on a mass basis. The removal efficiency is approximate 99%. Yeh And Bai¹⁴ concluded that the maximum CO₂ removal efficiency by NH₃ absorbent can reach 99% and the CO₂ loading capacity can approach 1.20 Kg CO₂/Kg NH₃. However, the maximum CO₂ removal efficiency and loading capacity by MEA absorbent were 94% and 0.40 Kg CO₂/Kg MEA, respectively. In the work by Smouse,¹⁵ a multi-pollution control concept with spraying aqueous ammonia into actual flue gas to capture CO₂, SO₂ and NO_x emissions was proposed and developed. The capture efficiency of CO₂ in absorber was in the range from 76.4% to 91.7% at 35 °C.

The products in the aqueous ammonia scrubber could include ammonium bicarbonate, ammonium carbonate, and ammonium carbamate (all in crystalline or aqueous solution forms), plus reagent CO₂, NH₃, and NH₄OH. Of these by-products, ammonium bicarbonate has been utilized by certain developing countries as a crop fertilizer for over 30 years with proven results. A process using coal char to produce ammonium bicarbonate for fertilizer has been developed and used commercially over 50 years. As an alternative to use ammonium bicarbonate as fertilizer, the ammonia (NH₃) in ammonium bicarbonate can be regenerated. Ammonium bicarbonate decomposes at the relatively low temperature of 60°C, compared to a 120°C regeneration temperature for MEA solutions. The preliminary experiment of Bai and Yeh results led to a conceptual solvent regenerable process where the crystalline NH₄HCO₃ product is heated to regenerate the NH₃.¹³ With its lower costs, higher loading capacity and higher CO₂ absorption efficiency, lower decomposition temperatures, less corrosive environment for absorber material and good performance of fertilizer, the ammonium scrubbing technique presents many advantages for the capture of CO₂ over the conventional MEA process.

Theory of NH₃-CO₂-H₂O reaction

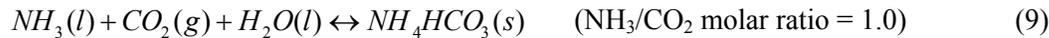
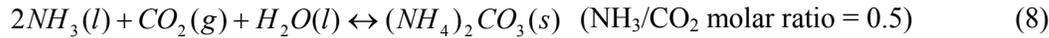
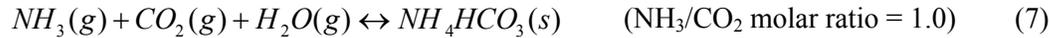
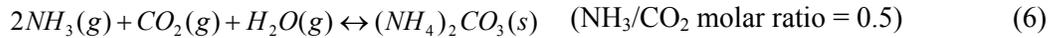
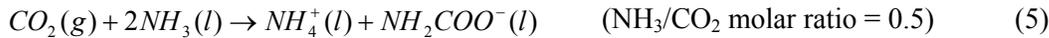
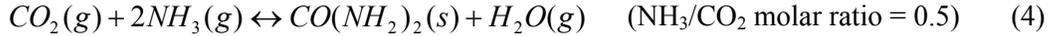
Although the aqua ammonia scrubbing process is an attractive way to capture low concentration CO₂ from flue gas, chemistry reaction among CO₂, ammonium and H₂O is very complex and poorly understood – many species co-exist in the solution in an unstable transition. These species could include, but not limited to, ammonium bicarbonate, ammonium carbonate, and ammonium carbamate (all in crystal and aqueous solution forms), plus CO₂, NH₃, and NH₄OH. To meet the need for a CO₂ capture process, the reactions must be investigated in detail, along with the composition of flue gas, the reaction rate, CO₂ partial pressure and solubility, product separation, and so on.

CO₂ can be removed by ammonium scrubbing through chemical absorption at various temperatures and operating conditions. As illustrated by equation (1), ammonium carbamate (NH₂COONH₄) is the main product in dry conditions (without moisture) under ambient conditions. However, ammonium carbamate, is very soluble in water. Under moist air, the hydration product of ammonium carbonate, (NH₄)₂CO₃, is produced at room temperature, as illustrated in equation (2).¹³

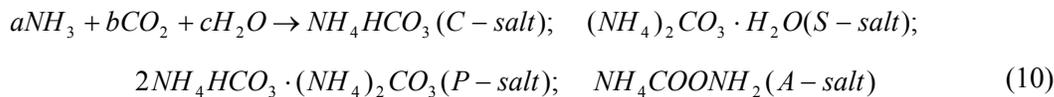




The gas-liquid chemical reactions between NH_3 and CO_2 in the wet scrubber can be illustrated by the following equations:¹³



At room temperature and atmospheric pressure, reactions (4)-(9) would occur. These reactions are very temperature sensitive. Due to the different concentrations of reactants and reaction conditions (temperature and pressure), different carbon-ammonium composites (i.e., different ammonium salts), can be obtained, as illustrated by equation (10):



Equation (11) indicated that ammonium bicarbonate and ammonium carbonate could be converted to each other at certain condition,



All the products are white solids and may be a single salt or mixed salts. Reaction (8) and (9) are the most probable in this study for CO_2 removal by NH_3 scrubbing. In view of achieving a maximum of NH_3 utilization in the capture of CO_2 (minimum inventory required for CO_2 sequestration), reaction (9) will be ideal. Theoretically, a maximum 2.59 kg of CO_2 /kg of NH_3 can be reached if only reaction (9) occurs in the wet scrubber.

In commercial processes, the reaction follows the following two steps: gaseous CO_2 dissolves in solution and reacts with aqueous ammonia. Based on previous studies, the reaction process is diffusion controlled – dissolution of gaseous CO_2 in solution. Therefore, increasing CO_2 dissolubility in water (solution) could enhance the reaction rate.

Experimental Study

The schematic diagram of the experimental system for studying on removing CO_2 gas by ammonium scrubbing is shown in Figure 1. The CO_2 scrubber was a glass container (I.D. 50mm) filling with 150 ml of 15% ammonium solution. The CO_2 gas was fed from a simulated flue gas cylinder with CO_2 concentration 14.7%. A mass flow controller is used to control the inlet CO_2 flow rate. A filter was placed after the scrubber to capture the escaped particles. Photoacoustic multi-gas analyzer (INNOVA 1312) was used for monitoring the outlet CO_2 and ammonium concentration. An magnet stirring system is used to help the reactant vertically mixed well. Experiments were conducted at room temperature condition ($25 \pm 1^\circ C$). Flow rate of flue gas was kept as 3 L/min. The ammonium solution was obtained from a standard ammonium solution (Fisher Science, 29.7% (w/w)), which was diluted using DI water (in some case spent-solution was used as the thinner). In order to investigate the influence of additional MEA on CO_2 's ammonium scrubbing, a few milliliter of MEA solution was additionally used with ammonium solution together. Some experiments were also used spent solution from previous experiments as the thinner to dilute the standard ammonium solution instead of DI water, or dissolving ammonium bicarbonate into the ammonium solution to make the initial ammonium solution in a certain carbonate degree. The influence of such additives on reaction efficiency was discussed in this paper. Results from seven experiments have been presented in this paper. Six of them were run at the stirring system under

different operating condition. One experiment was operated without stirring. The operation conditions for all seven experiments are listed in the Table 1.

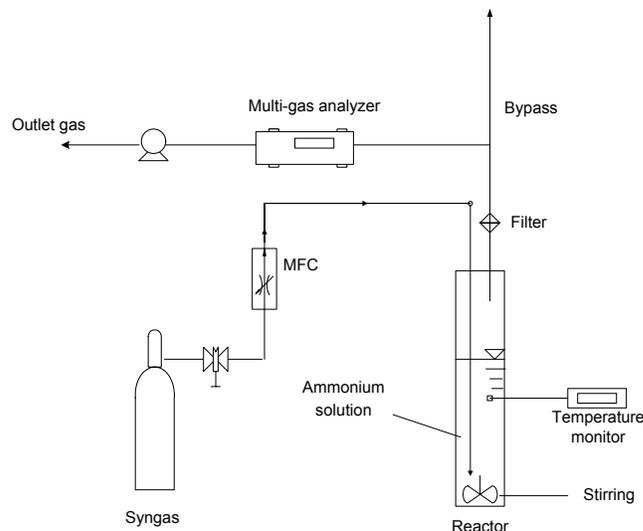


Figure 1. Schematic diagram of experiment setup

Table 1. Operation Conditions

No.	NH ₃ ·H ₂ O (%)	CO ₂ (%)	Additional MEA (ml)	Additional NH ₄ HCO ₃ (g)	Spent-solution (ml)	Stirring
Exp 1	15	14.7	0	0	0	Yes
Exp 2	15	14.7	0	0	5	Yes
Exp 3	15	14.7	1.5	0	0	Yes
Exp 4	15	14.7	0	0	30	Yes
Exp 5	15	14.7	0	6	0	Yes
Exp 6	15	14.7	0	12.7	73	Yes
Exp 7	15	14.7	0	0	0	No

Results and Discussion

Experiments 1– 6 have been conducted in a system with magnet stirring. The variation of CO₂ concentrations as a function of operation time has been shown in Figure 2. It has been found from the results, that CO₂ outlet concentration dropped into a very low level (below 1ppm) at beginning of all experiments. The outlet concentrations of CO₂ could be maintained at the low level for about 30 min. With the reaction going on, the CO₂ outlet concentrations increased gradually, and finally approached to the CO₂ inlet concentration, 14.7%. This indicates that the ammonium solution has already reached its saturated capability to absorb CO₂. In order to evaluate the capacity of the ammonium reagent, all experiments were lasted until the NH₃ scrubbing capacity became zero. The longest operation time was up to 6 hrs.

CO₂ outlet concentrations have been demonstrated in Figure 2. Those curves acted as breakthrough curves for the NH₃ reagent. The calculation and analysis from DSC and TGA showed that both ammonium bicarbonate and ammonium carbonate could appear in the solution at the final stage of the reactions. It may be explained that (NH₄)₂CO₃ was generated first at the solution (equation 8). When the CO₂ continuously bubbled into system, (NH₄)₂CO₃ might absorb CO₂ to form NH₄HCO₃, as shown in equation (11).

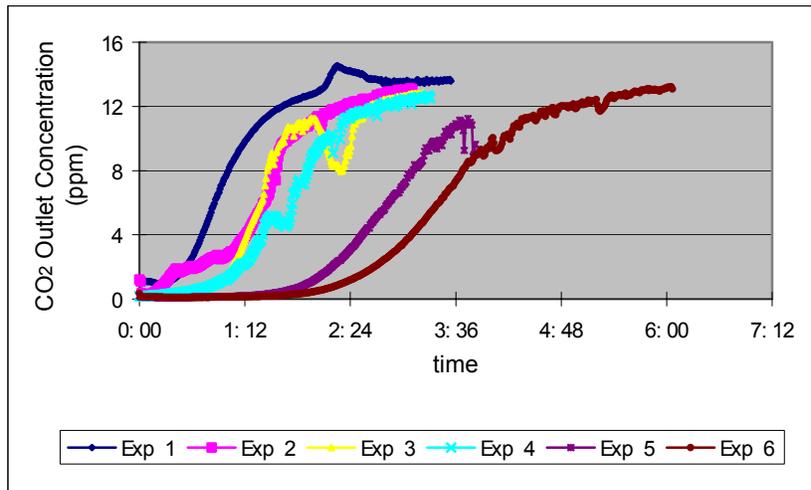


Figure 2. Variation of CO₂ outlet concentration under different operation condition

- Effect of Stirring on CO₂ Removal Reaction

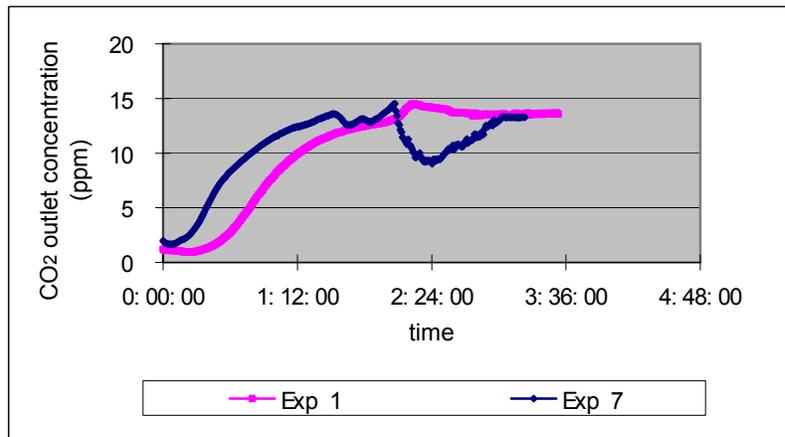


Figure 3. Effect of stirring on CO₂ removal reaction

Effect of stirring on CO₂ removal is shown in Figure 3. Result from Experiment 1 and 7 are plotted in Figure 3. Exp 7 was the system without stirring. After 2 hrs of the reaction, the CO₂ outlet concentration approached to the 14%, and NH₃ solution did deteriorate at all. However, a slightly shaking of the reactor bottle caused the CO₂ outlet concentration dropped immediately. This phenomenon was not found in the stirring system, where the CO₂ outlet concentrations were gradually approaching to the CO₂ inlet concentration and lasted at this level even the time of CO₂ supply was extended to 1 hr longer. This indicated that ammonium solution was already fully reacted with CO₂, and did not have more absorption capability. The reaction system with stirring could lead to a continuous and gradual reaction process, which is good for ammonium to play its CO₂ absorption role. A system without stirring will probably indicate a fake signal that ammonium solution is degraded, however, there are still a lot of effective ammonium available at solution. This experiment showed that it is important to have a mixing or turbulent effect on the reaction, no matter for the open experiment system or future continuous reaction system.

- Influence of additional MEA on CO₂ Removal Efficiency

The MEA has been thought as a successful CO₂ absorbent in practically industrial application except its high operating cost. It does have a good affinity to CO₂, and the reaction between MEA and CO₂ is more stable than the inorganic ammonium process to absorb CO₂. An interest was paid on the MEA-ammonium mixed reagent. As part of the reagent, 1.5ml MEA has been added into reaction system (Exp 3), where

MEA contained 1% of the reagent solution. Results from Exp 1 and Exp 3 have been compared in Figure 4. It was interesting to note that the CO₂ removal efficiency was typically higher for the MEA added system than the regular ammonium scrubbing system. At the beginning of the reaction, the CO₂ absorption efficiency could reach as high as 99%. And it did keep the higher absorption efficiency through all the reaction time. Since the CO₂ affinity ability for MEA is stronger than ammonium, the MEA is reacted with CO₂ more rapidly. Certain amount of CO₂ was absorbed by MEA, while the ammonium scrubbing was taking action afterwards. The adding of MEA did not dramatically improve the ammonium CO₂ absorption capability. It did like two absorption processes integrated together and there was a time delay between Exp 1 and Exp 3 in CO₂ outlet concentration curves. The difference of CO₂ removal efficiency in Exp 1 and Exp 3 was due to the contribution of additional MEA.

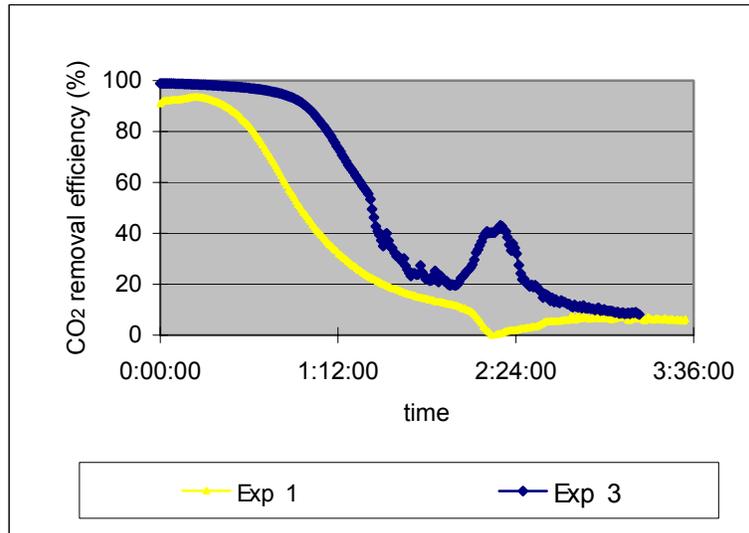


Figure 4. Influence of additional MEA on CO₂ removal process

- Influence of reuse of spent solution on CO₂ removal efficiency

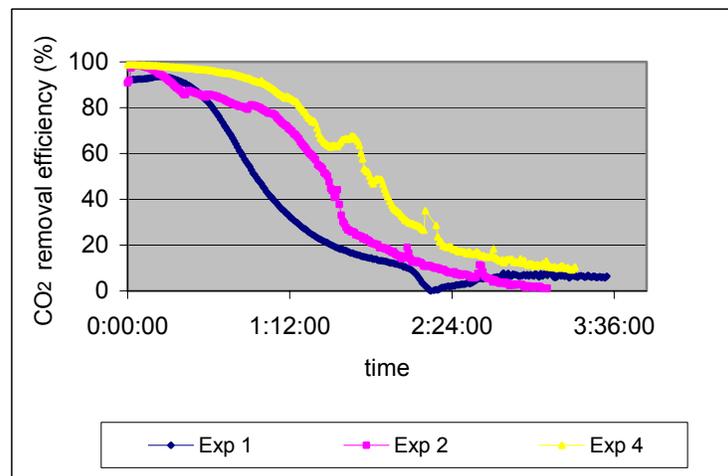


Figure 5. Influence of reuse of spent-solution on CO₂ removal efficiency

The effective ammonium concentration at solution is a critical factor to influence the CO₂ absorption rate. The higher its concentration is, the faster CO₂ absorption rate is, and greater the absorption capability. Experiment results from Exp 1, Exp 2 and Exp 4 were compared in Figure 5. CO₂ with concentration 14.7% was bubbled to 15% ammonium solution (Exp 1). 5 ml (Exp 2) and 30 ml (Exp 4) spent-solution were added into solution as part of the reagent. Figure 5 demonstrated that the CO₂ removal efficiency

was increased largely and the removal process was more stable when more spent-solution was added as reagent. The results also implied that a continuous system would have higher CO₂ removal efficiency than the incontinous system since the spent-solution was always recirculated into reactor in the continuous system.

- Influence of adding additional NH₄HCO₃ on CO₂ removal efficiency

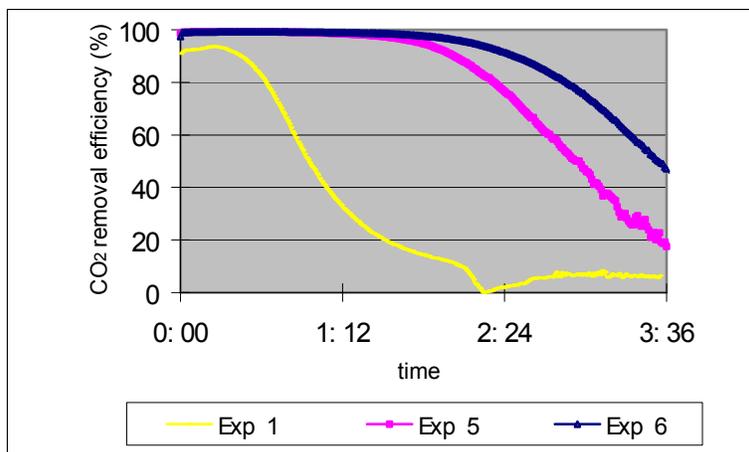


Figure 6. The variation of CO₂ removal efficiency vs. time

Similar with spent-solution, additional NH₄HCO₃ crystal dissolved into reaction solution can also help to enhance the carbonated degree of reagent solution, which will help the ammonium solution to increase its capability of CO₂ removal. Three operating conditions, Exp 1, Exp 5 and Exp 6, have been selected and discussed here. No NH₄HCO₃ was added in Exp 1, but 6 g and 17.4 g NH₄HCO₃ were added into reaction solution in Exp 5 and Exp 6, respectively. It has been shown in Figure 6 that the dissolving NH₄HCO₃ into solution could dramatically increase the system CO₂ removal capability. Instead of 20 min in Exp 1, CO₂ removal efficiency could be stabilized at 98% for more than 1 hr in Exp 5 and Exp 6. More NH₄HCO₃ is added into solution, more stable is the CO₂ removal efficiency.

Conclusions

- It is an attractive way to remove CO₂ by ammonium solution scrubbing. CO₂ removal efficiencies are quite stable in the range of 95% to 99% under proper operation conditions.
- The ammonium solution with higher carbonized degree will have better ability to absorb CO₂. Higher CO₂ removal efficiency could be lasted for much longer time. Recycle of spent-solution into reactor or adding ammonium salt into the reagent will help to maintain the carbonized degree of solution, and further enhance the ammonium solution CO₂ absorption capability.
- The addition of MEA could stabilize the CO₂ removal processes, but no significant improvement on ammonium absorption capability.

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