

## Characteristics of absorption and regeneration of carbon dioxide in aqueous 2-amino-2-methyl-1-propanol/ammonia solutions

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**Abstract**—In this study, the removal efficiency, absorption amount, and loading value of CO<sub>2</sub> into aqueous blended 2-amino-2-methyl-1-propanol (AMP)/ammonia (NH<sub>3</sub>) solutions were measured by using the absorption and regeneration continual process. The effect of adding NH<sub>3</sub> to enhance absorption characteristics of AMP was investigated. The performance was evaluated under various operating conditions. As a result, the method of blending AMP and NH<sub>3</sub> was not adequate because of a problem with scale formation. Consequently, NH<sub>3</sub> of 1, 3, 5, and 7 wt% was added to 30 wt% AMP. Of these additions, 5 wt% NH<sub>3</sub> was the optimum concentration because the CO<sub>2</sub> removal efficiency and absorption amount were almost 100% and 2.17 kg CO<sub>2</sub>/kg absorbent, respectively. Also, the scale problem was almost absent. As the regenerator temperature varied from 80-110 °C, the loading of rich amine was almost constant, but the loading of lean amine was decreased as the regenerator temperature increased. Thus, the optimum regenerator temperature was 110 °C in this experiment.

Key words: Carbon Dioxide, 2-Amino-2-methyl-1-propanol, Ammonia, Absorption, Regeneration

### INTRODUCTION

The large increase in greenhouse gases due to the development of technology and the spread of industrialization has greatly contributed to global warming, which accounts for a considerable part of global environmental destruction [1]. In particular, CO<sub>2</sub> is the largest component of greenhouse gases. The importance of carbon dioxide sequestration is gradually being addressed all over the world.

Several technologies are being used to separate CO<sub>2</sub> from the flue gas of conventional fossil fuel-fired power plants. Some representative technologies are chemical absorption, physical absorption, cryogenic methods, and membrane separation [2]. Chemical absorption is generally recognized as the most effective technology at present [3]. Industrially important chemical absorbents are monoethanolamine (MEA), diethanolamine (DEA), and AMP. The sterically hindered amines, such as AMP, are a different class of chemical absorbents and have been used as commercially useful CO<sub>2</sub> absorbent because of their advantages in absorption capacity, degradation resistance, and regeneration energy [4,5]. NH<sub>3</sub> seems to be an alternative solvent for removing CO<sub>2</sub> from flue gas. Although NH<sub>3</sub> solvent has scale formation problems, it has both a high absorption capacity and absorption rate, no absorbent degradation problem, and a low corrosion problem [6-8].

Recently, the use of blends of alkanolamines, a solution of two or more amines in varying concentration, has been shown to produce absorbents with excellent absorption characteristics as well as reductions in energy requirements. A number of research studies related to the absorption of CO<sub>2</sub> into aqueous AMP solutions have

been reported in the literature [9-17].

Unlike previous studies of CO<sub>2</sub> solubilities and the kinetics of aqueous amine solutions, this study investigated the CO<sub>2</sub> removal efficiency and the absorption amount and loading value of CO<sub>2</sub> into aqueous blended AMP/NH<sub>3</sub> solutions using the absorption and regeneration continual process. The added effect of NH<sub>3</sub> to enhance absorption characteristics of AMP was studied. The performance was evaluated under several operating conditions.

### THEORY

In aqueous solutions of primary (MEA) and secondary (DEA) alkanolamines the following reactions with CO<sub>2</sub> occur [18].



Where R is alkyl and R' is H for primary amines and alkyl for secondary amines.

The zwitterion mechanism originally proposed by Caplow [19] and reintroduced by Danckwerts [18] is generally accepted as the reaction mechanism for Eq. (1).



If the carbamate is unstable, as in the case of a hindered amine carbamate, it undergoes a carbamate reversion reaction as follows [4]:



Eq. (3) means that for the hindered amines one mole of CO<sub>2</sub> is absorbed per mole of amine. However, a certain amount of carbamate hydrolysis occurs with all amines so that even with MEA and DEA the CO<sub>2</sub> loading may exceed 0.5, particularly at high pressures.

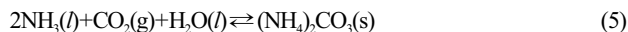
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Another alternative mechanism for the bicarbonate formation was proposed by Chakraborty et al. [20].



The chemical reactions between  $\text{CO}_2$  and  $\text{NH}_3$  can be expressed by the following reaction [7,21]:



The wet method of ammonia scrubbing into flue gas to capture  $\text{CO}_2$  produces ammonium carbonate  $((\text{NH}_4)_2\text{CO}_3)$  and ammonium bicarbonate  $(\text{NH}_4\text{HCO}_3)$  [6,8].

## EXPERIMENTAL

### 1. Apparatus

A schematic diagram of the experimental system for studying  $\text{CO}_2$  absorption and regeneration is shown in Fig. 1. The experimental apparatus consisted of a gas injector, absorber, regenerator, and gas analyzer. The absorber and regenerator, which were made of 316 stainless steel with an internal diameter of 50.8 mm, have a height of 900 mm and 800 mm, respectively. Packing material (1/4 inch Raschig rings) was placed inside to enhance the reaction of liquid and gas. The temperature of the absorber and regenerator was measured by a K-type thermocouple with an accuracy of  $\pm 0.1$  K. Compressed air was sent to the filter to remove particulates and then dehumidified by passing it through a silica gel air dryer. The clean air

served as diluting gas and it was mixed with pure  $\text{CO}_2$  gas. The flow rates of the gases were controlled by mass flow controllers (5850E, Brooks Instruments, USA). The  $\text{CO}_2$  gas analyzer, a ZRF model (Fuji Electric, JPN, 0-20 vol%), was used to measure  $\text{CO}_2$  outlet gas concentrations in the absorber. The condenser was connected to the top of the regenerator to prevent loss of absorbent.

### 2. Procedure

Analytical grade AMP and  $\text{NH}_3$  solution with purity of 99% and 28% were supplied by Acros Organics (USA) and Junsei Chemical (JPN), respectively. Aqueous solutions were prepared with distilled water. The  $\text{CO}_2$  gas was a commercial grade with a purity of 99.9%. The absorber and regenerator were heated to the desired temperature, and then an absorbent of 250 mL was injected into a storage tank. A pump (AX1-12-PEC-Z, Cheonsei Co. Ltd., KOR) was used to circulate the absorbent which reacted with the  $\text{CO}_2$  gas. The outlet  $\text{CO}_2$  concentration from the absorber was continually measured by a ZRF model  $\text{CO}_2$  gas analyzer. The experimental conditions were as follows: an absorber temperature of  $40^\circ\text{C}$ , regenerator temperature of  $80$ – $110^\circ\text{C}$ , a gas flow rate of  $7.5$  L/min, a  $\text{CO}_2$  inlet concentration of 12 vol%, and a liquid circulation rate of 110 mL/min. The experimental data were taken at steady state.

Rich amine and lean amine were extracted from the absorber and regenerator, respectively, to determine the characteristics of  $\text{CO}_2$  absorption and regeneration, and then they were analyzed by titrimetric method. First, 100 mL of distilled water was injected into a 250 mL beaker. The beaker was stirred with magnetic stirrer. The pH of the distilled water was raised to 11.4–11.6 by carefully adding a 0.5 N-NaOH solution. Either a rich or lean amine solution was

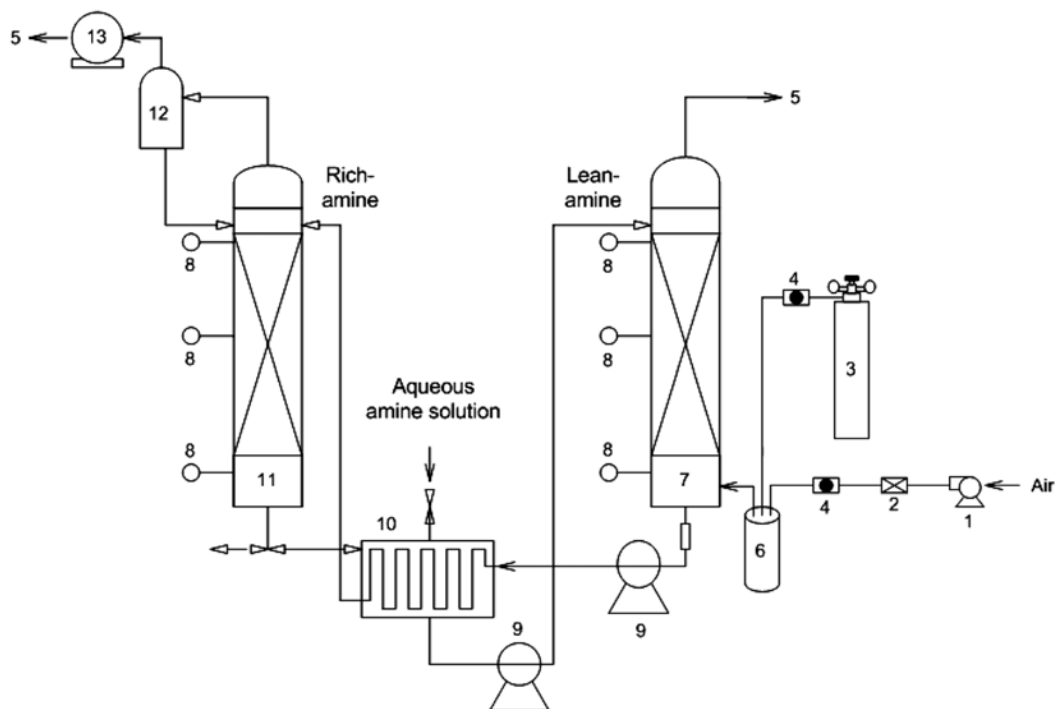


Fig. 1. Schematic of experimental apparatus.

- |                           |                           |                                     |               |
|---------------------------|---------------------------|-------------------------------------|---------------|
| 1. Air compressor         | 5. $\text{CO}_2$ analyzer | 9. Liquid pump                      | 13. Gas meter |
| 2. Filter                 | 6. Mixing chamber         | 10. Heat exchanger and storage tank |               |
| 3. $\text{CO}_2$ cylinder | 7. Absorber               | 11. Regenerator                     |               |
| 4. Mass flow controller   | 8. Thermocouple           | 12. Condenser                       |               |

added to the beaker by a 10 mL pipette for the rich amine solution or a 25 mL pipette for the lean. And then 0.5 N-NaOH was added to the amine solution by the titrimetric method until its pH reached 11.5.

## RESULTS AND DISCUSSION

### 1. Effect of AMP/NH<sub>3</sub> Blends

The CO<sub>2</sub> outlet concentrations were investigated by using the absorption and regeneration continual process for blended AMP/NH<sub>3</sub> absorbents. The conditions of the experiment consisted of the regenerator temperatures of 80-110 °C and a gas flow rate of 7.5 L/

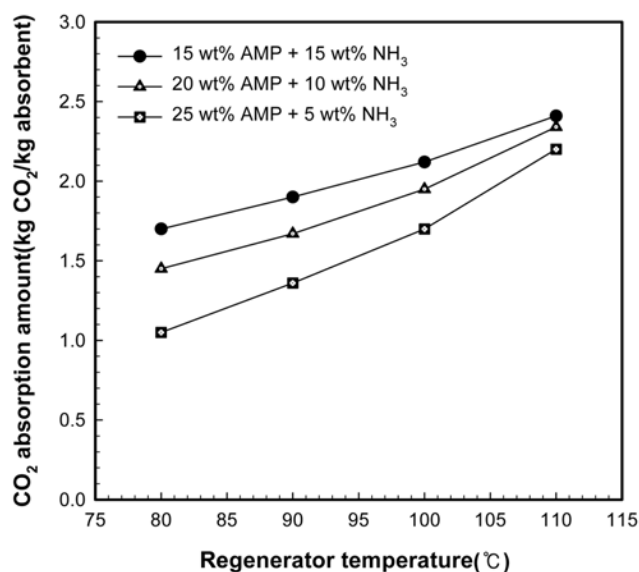


Fig. 2. Effect of CO<sub>2</sub> absorption amount as a function of regenerator temperatures in blended absorbents (wt% AMP/wt% NH<sub>3</sub>).

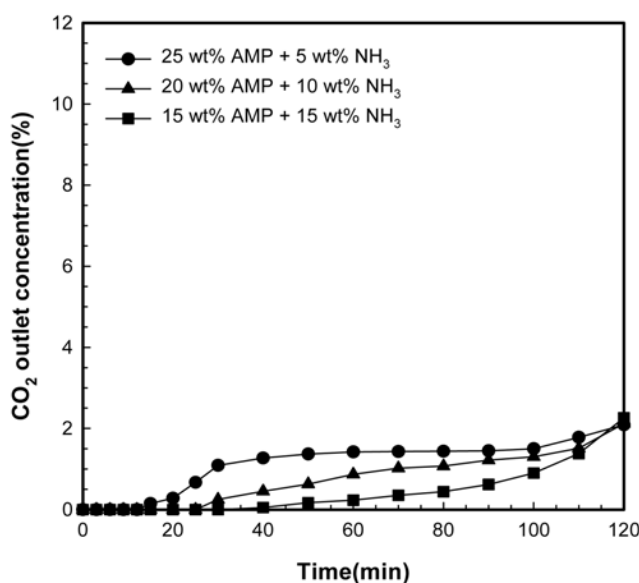


Fig. 3. Effect of operating time on CO<sub>2</sub> removal efficiencies of blended absorbents (wt% AMP/wt% NH<sub>3</sub>).

min.

Fig. 2 shows the effect of the mixture ratio and regenerator temperatures on the CO<sub>2</sub> absorption amount in the blended absorbents (wt% AMP/wt% NH<sub>3</sub>). At each regenerator temperature, the amount of CO<sub>2</sub> absorption with AMP/NH<sub>3</sub> ratio (25/5, 20/10, and 15/15) was 1.05-2.20, 1.45-2.34, 1.70-2.41 kg CO<sub>2</sub>/kg absorbent. As the concentration of NH<sub>3</sub> increased, the absorption amount increased.

This trend could be caused by the higher CO<sub>2</sub> absorption rate of NH<sub>3</sub> than that of AMP. Also, reactivity and CO<sub>2</sub> absorption capacity improved based on reaction (2) and additional reaction (5), (6). As the regenerator temperature varies so does the CO<sub>2</sub> absorption amount because the removal efficiency of AMP is greatly dependent on regenerator temperature.

As can be seen from Fig. 3, although CO<sub>2</sub> absorption amount (kg CO<sub>2</sub>/kg absorbent) increased as the mixing ratio of NH<sub>3</sub> increased, CO<sub>2</sub> removal efficiency decreased faster by time. This result is due to the increase of ammonium carbamate and ammonium bicarbonate. The generation of these products is demonstrated by the reaction of CO<sub>2</sub> and NH<sub>3</sub> in the existing studies [6,8]. Therefore, this method of blending AMP and NH<sub>3</sub> used in this experiment seems inadequate, but the gradual addition of NH<sub>3</sub> can be expected to be a better method.

### 2. Effect of the Additive Ratio of NH<sub>3</sub> to AMP

To determine the effect of concentrating NH<sub>3</sub> by 1, 3, 5, 7 wt%, the absorption and regeneration continual process was studied blending NH<sub>3</sub> with 30 wt% AMP. The experimental conditions were as follows: absorber temperature of 40 °C, regenerator temperature of 110 °C, and gas flow rate of 7.5 L/min.

As seen from Fig. 4, the CO<sub>2</sub> outlet concentration with NH<sub>3</sub> concentrations in 30 wt% AMP is presented by time. The initial CO<sub>2</sub> removal efficiency increased by the addition of NH<sub>3</sub>. With an increase of 2 wt% NH<sub>3</sub>, the time which CO<sub>2</sub> concentration maintained 0% was increased approximately 5 minutes.

Fig. 5 shows the CO<sub>2</sub> absorption amount (kg CO<sub>2</sub>/kg absorbent) by the additive ratio of NH<sub>3</sub> to 30 wt% AMP. These experimental

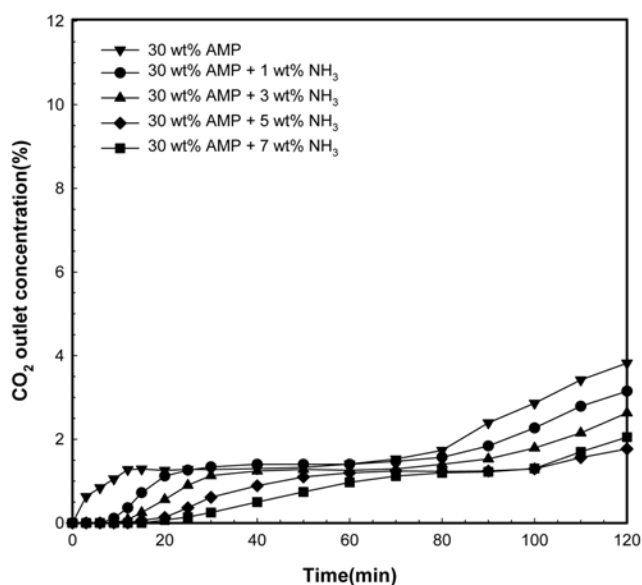


Fig. 4. Effect of operating time on CO<sub>2</sub> removal efficiencies of NH<sub>3</sub> additives in 30 wt% AMP.

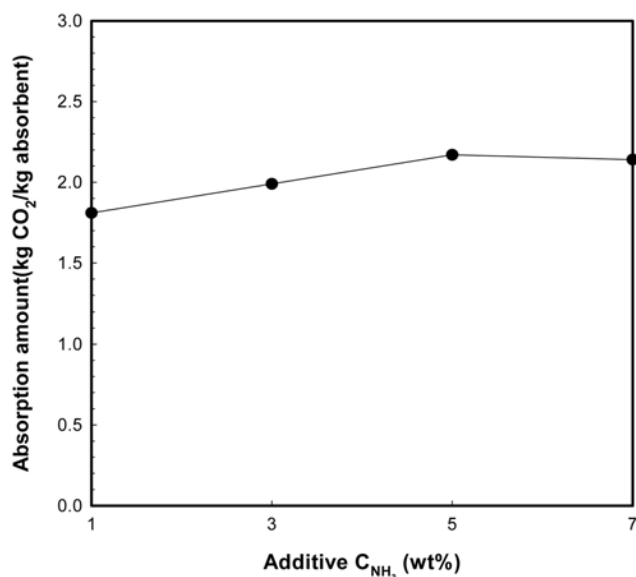


Fig. 5. Effect of CO<sub>2</sub> absorption amounts as a function of NH<sub>3</sub> additive concentrations in 30 wt% AMP.

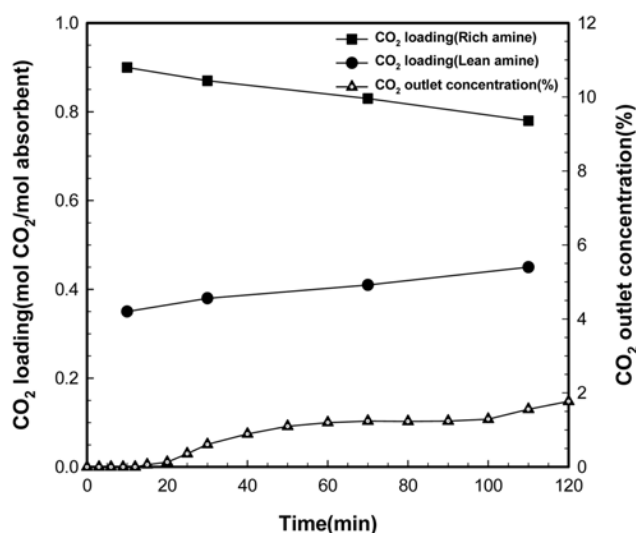


Fig. 6. Effect of operating time on CO<sub>2</sub> loading and CO<sub>2</sub> removal efficiencies of 30 wt% AMP+5 wt% NH<sub>3</sub>.

results were calculated by using the data of the breakthrough curves shown in Fig. 4. As can be seen, the CO<sub>2</sub> absorption amount by additive ratio of NH<sub>3</sub> was 1.81, 1.99, 2.17, and 2.14 kg CO<sub>2</sub>/kg absorbent. This result was caused by the improved CO<sub>2</sub> reactivity and CO<sub>2</sub> absorption capacity. The reasons for this improvement are explained in paragraph 1.

However, the amount of CO<sub>2</sub> absorption when 5 wt% NH<sub>3</sub> was added was higher than when 7 wt% was added. The reason for this result is the 7 wt% NH<sub>3</sub> caused the efficiency of removing CO<sub>2</sub> to decrease faster than 5 wt% did due to the scale formation problem. At 100 minutes, the removal efficiency of 7 wt% was lower than that of 5 wt%; consequently, it is reasonable to conclude that 7 wt% is inadequate in a continual process. Therefore, 30 wt% AMP+5 wt% NH<sub>3</sub> is the best concentration because CO<sub>2</sub> absorption capacity is

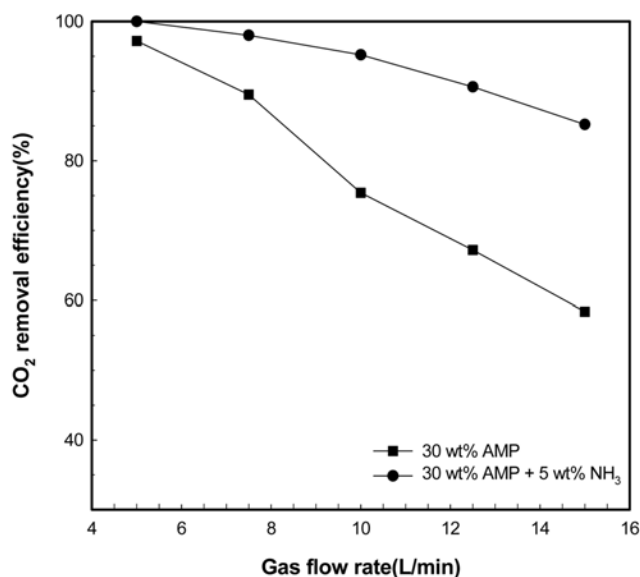


Fig. 7. Effect of gas flow rate on CO<sub>2</sub> removal efficiencies of 30 wt% AMP and 30 wt% AMP+5 wt% NH<sub>3</sub>.

improved and scale formation is almost absent.

Fig. 6 shows the changes of CO<sub>2</sub> outlet concentrations and CO<sub>2</sub> loading values by aqueous 30 wt% AMP+5 wt% NH<sub>3</sub> solution as a function of operating time. The experimental conditions were as follows: the absorbent concentration was 30 wt% AMP+5 wt% NH<sub>3</sub>, the absorber temperature was 40 °C, the regenerator temperature was 110 °C, and the gas flow rate was 7.5 L/min. The CO<sub>2</sub> loading values were calculated after they were extracted and analyzed after 10, 30, 70, and 110 minutes of operation. CO<sub>2</sub> outlet concentration increased with operating time. The CO<sub>2</sub> loading values of rich amine were analyzed by operating time decreased 0.90, 0.87, 0.83, 0.78 mol CO<sub>2</sub>/mol absorbent, because the capacity to absorb CO<sub>2</sub> decreased over time. However, the CO<sub>2</sub> loading values of lean amine increased 0.35, 0.38, 0.41, 0.45 mol CO<sub>2</sub>/mol absorbent, which could be due to the CO<sub>2</sub> regeneration efficiency decreasing, so that the CO<sub>2</sub> loading in the regenerator increased.

### 3. Effect of Gas Flow Rate

CO<sub>2</sub> efficiency was tested with gas flow rates of 5–15 L/min. As can be seen from Fig. 7, as gas flow rate increased, the efficiency of CO<sub>2</sub> removal went from 97.2% to 58.4% with an aqueous solution of 30 wt% AMP and 100% to 85.2% with the 30 wt% AMP+5 wt% NH<sub>3</sub> solution. The difference of efficiency was from 2.8 to 26.8% in two absorbents. This result was caused by addition of the higher reaction rate of NH<sub>3</sub>.

Efficiency decreased as the liquid-gas ratio decreased because a large amount of gas was inserted within a limited time frame. As flow rate of the mixed gas increased, the amount of CO<sub>2</sub> also increased. Therefore, by reaching relatively high CO<sub>2</sub> loading ratio, reaction and absorption capacity decreased.

When 5 wt% NH<sub>3</sub> was added to 30 wt% AMP, CO<sub>2</sub> removal efficiencies were 100% and 99% when gas flow rates were 5 and 7.5 L/min, respectively. The two conditions are highly efficient. Therefore, a gas flow rate of 7.5 L/min was determined, after the effects of corrosiveness were taken into consideration.

### 4. Characteristics of Absorption and Regeneration by NH<sub>3</sub>

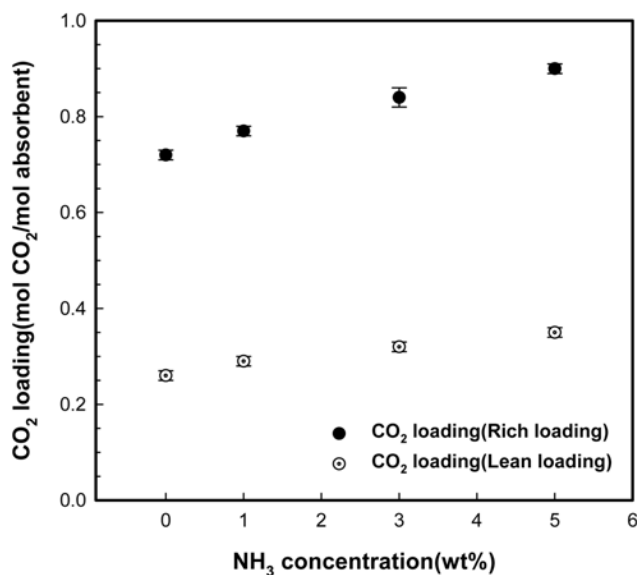


Fig. 8. Effect of CO<sub>2</sub> loading values of lean- and rich-amine as a function of NH<sub>3</sub> additives into 30 wt% AMP.

### Concentration

This experiment was conducted to determine the characteristics of CO<sub>2</sub> absorption and regeneration when 1, 3, and 5 wt% NH<sub>3</sub> was added to 30 wt% AMP by analyzing rich and lean amine from the absorber and regenerator.

Fig. 8 shows CO<sub>2</sub> loading by the amount of NH<sub>3</sub> added to 30 wt% AMP. As can be seen, CO<sub>2</sub> loading increased as the amount of NH<sub>3</sub> in both rich and lean amine increased. CO<sub>2</sub> loading was 0.72, 0.77, 0.84, and 0.90 mol CO<sub>2</sub>/mol absorbent for 0, 1, 3, and 5 wt% NH<sub>3</sub> was added to 30 wt% AMP, respectively, and for lean amine, it was 0.26, 0.29, 0.32, 0.35 mol CO<sub>2</sub>/mol absorbent, respectively. As can be seen, CO<sub>2</sub> loading increased as the amount of NH<sub>3</sub> in both rich and lean amine increased. These results need to be compared with commercially useful amine, MEA. In case of MEA, rich loading is 0.4 mol CO<sub>2</sub>/mol absorbent and lean loading is 0.15 mol CO<sub>2</sub>/mol absorbent [8]. Therefore, CO<sub>2</sub> loading of blended AMP/NH<sub>3</sub> absorbents is better than that of MEA.

This increase could have been caused by the addition of NH<sub>3</sub> as mentioned in paragraph 1. Consequently, absorbents increase their CO<sub>2</sub> capacities in the rich amine. As this rich amine entered the regenerator in the absorption and regeneration continual process, lean amine increased. The changes to the values of rich and lean amine caused by the increased concentration of NH<sub>3</sub> have clarified the characteristics of absorption and regeneration.

### 5. Characteristics of Absorption and Regeneration by Regenerator Temperature

According to previous research, CO<sub>2</sub> removal efficiency by the AMP is when using AMP is highest at the regenerator temperature is 110 °C [22]. The best regenerator temperature for NH<sub>3</sub> is about 80 °C [8]. Hence, the regenerator temperatures used in this experiment to determine the characteristics of absorption and regeneration were 80–110 °C. The concentration of absorbent was 30 wt% AMP+5 wt% NH<sub>3</sub>.

Fig. 9 shows the effect of CO<sub>2</sub> loading in the absorber and regenerator. For rich amine, CO<sub>2</sub> loading remained almost constant

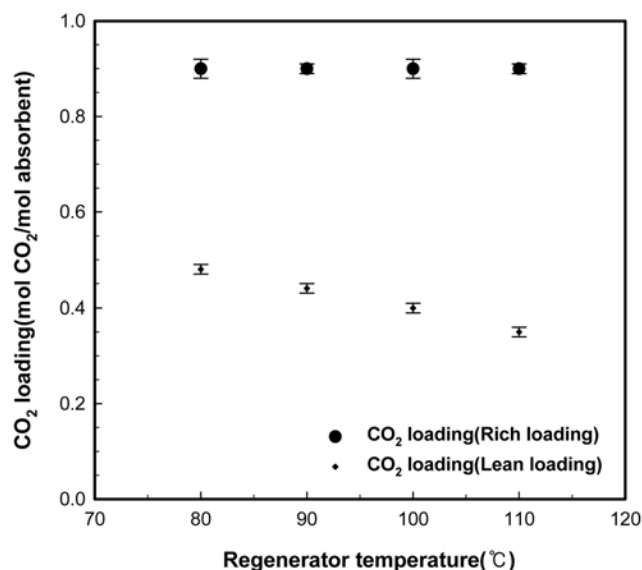


Fig. 9. Effect of CO<sub>2</sub> loading values of lean- and rich-amine as a function of regenerator temperature of 30 wt% AMP+5 wt% NH<sub>3</sub>.

of 0.90 mol CO<sub>2</sub>/mol absorbent in spite of the regenerator temperature of 80, 90, 100, 110 °C. For lean amine, it decreased 0.48, 0.44, 0.40, and 0.35 mol CO<sub>2</sub>/mol absorbent for each respective temperature.

As discussed in paragraph 1 and demonstrated in the existing study [22], regeneration efficiency of AMP differs from regenerator temperature. Lean amine loading decreased because the amount of CO<sub>2</sub>, which was discharged from the regenerator, increased as the efficiency of regeneration increased. Rich amine loading was almost constant, which was due to the constant absorber temperature.

The analysis of the rich and lean amine in this experiment revealed the amount of CO<sub>2</sub> loading in the absorber and regenerator, respectively, which clarified the characteristics of absorption/regeneration based on the effect of regenerator temperature.

### CONCLUSIONS

This experiment was designed to determine the effects of blending AMP with an increasing amount of NH<sub>3</sub>. CO<sub>2</sub> absorption amount increased as the mixing ratio of NH<sub>3</sub> increased. However, it is inadequate in CO<sub>2</sub> regeneration because of the scale formation problem. Consequently, the amount of NH<sub>3</sub> added to 30 wt% AMP was 1, 3, 5, and 7 wt%. When 5 wt% NH<sub>3</sub> was used, the amount of CO<sub>2</sub> absorption (kg CO<sub>2</sub>/kg absorbent) was the highest and the scale formation problem was almost absent. Hence, 30 wt% AMP+5 wt% NH<sub>3</sub> was the best concentration. The CO<sub>2</sub> loading of rich and lean amine was analyzed by using 1, 3, and 5 wt% of NH<sub>3</sub> by regenerator temperature. As the additive concentration of NH<sub>3</sub> increased, both rich and lean loading increased, respectively. As regenerator temperatures increased, rich loading was almost constant, but lean loading decreased. The characteristics of absorption/regeneration reaction were clarified by analyzing CO<sub>2</sub> rich and lean loading numerical values. Therefore, the optimum experimental conditions

when  $\text{NH}_3$  is added to AMP could be presented. It is expected to improve the efficiency of the process due to the improvement of the capacity of absorbent. Also, the results of this experiment could be useful for simultaneously removing and recovering  $\text{CO}_2$ .

### ACKNOWLEDGMENTS

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