

the Science of the Total Environment

An International Journal for Scientific Research into the Environment and its Relationship with M

The Science of the Total Environment 228 (1999) 121-133

Comparison of ammonia and monoethanolamine solvents to reduce CO₂ greenhouse gas emissions

An Chin Yeh, Hsunling Bai*

Institute of Environmental Engineering, National Chiao Tung University, 75, Po-Ai Street, Hsinchu 30039, Taiwan

Received 9 September 1998; accepted 4 January 1999

Abstract

This paper presents experimental results on the evaluation of two reagents, ammonia (NH $_3$) and monoethanolamine (MEA) solvents, for scrubbing carbon dioxide (CO $_2$) greenhouse gas emissions. The scrubbing of CO $_2$ by NH $_3$ solvent is a novel study developed by the authors, and the MEA process is a traditional process for gas purification of removing CO $_2$. The performance of these two solvents are compared in terms of CO $_2$ removal efficiency and absorption capacity. Test results show that both the CO $_2$ removal efficiency and absorption capacity of NH $_3$ solvent are better than those of MEA solvent under the operating conditions conducted in this study. The maximum CO $_2$ removal efficiency by NH $_3$ solvent can achieve 99% and the CO $_2$ absorption capacity can approach 1.20 kg CO $_2$ /kg NH $_3$. On the other hand, the maximum CO $_2$ removal efficiency and absorption capacity by MEA solvent are 94% and 0.40 kg CO $_2$ /kg MEA, respectively, under the same operating conditions tested by NH $_3$ solvent. Besides, the temperature increases due to exothermal reactions in the NH $_3$ scrubbing process are lower than those in the MEA scrubbing process. This indicates that the energy requirement for the regeneration of NH $_3$ reagent should be less than that for the regeneration of MEA reagent. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Carbon dioxide; Ammonia solvent; Monoethanolamine; Greenhouse effect; Absorption capacity

1. Introduction

The Inter-governmental Panel on Climate Change (IPCC) (IPCC, 1990) has published a report concluding that human activities result in the production of four gases (carbon dioxide, methane, chlorofluorocarbon and nitrous oxide)

which significantly contribute to global warming, and that the global warming caused by increasing emissions of these gases is one of the most serious environmental problems. Among these gases, CO₂ has the greatest adverse impact on the observed greenhouse effect causing approximately 55% of the observed global warming (IPCC, 1990). Hence, the reduction of CO₂ emissions from the fossil fuel energy systems is considered to be the most urgent to slow down the global warming trend.

^{*}Corresponding author. Tel.: +886-3-5727834; fax: +886-3-5725958; e-mail: hlbai@green.ev.nctu.edu.tw

Several alternative strategies have been proposed to reduce the emission of CO₂ into the atmosphere. These strategies include fuel alternative, energy conservation and improving power generation efficiencies (Blok et al., 1993; Huang, 1993; Bai and Wei, 1996). However, their implementation may have a limited impact on the emission reduction of CO₂. Therefore, various end-of-pipe technologies have also been tested to remove and recover CO2 from flue gas streams. These include chemical solvent absorption, physical adsorption, cryogenic separation, membrane separation, biological fixation as well as the O_2/CO_2 combustion process (Wolsky et al., 1994; Kimura et al., 1995; Nishikawa et al., 1995). Among these techniques, chemical solvent absorption methods have been extensively studied and are considered as a reliable and relatively low cost method for reducing CO₂ emission from fossil fuel power plants (Chakma, 1995).

The MEA scrubbing is so far the most acceptable chemical solvent method to react with CO₂. The chemical reaction has been described by Kohl and Riesenfeld (1985) and Hendriks et al. (1989):

$$C_2H_4OHNH_{2(1)} + CO_{2(g)} + H_2O_{(1)}$$

 $\Leftrightarrow C_2H_4OHNH_{3(aq)}^+ + HCO_{3(aq)}^-$ (1)

The MEA scrubbing is widely used in the chemical engineering process of gas purification. However, current practices of applying MEA solvent to remove CO2 from flue gas have found their limitations (Xu et al., 1991; Molburg et al., 1994): (1) MEA solvent has a low absorption capacity for CO₂; and (2) the CO₂ absorption capacity of MEA solvent is easily degraded by the presence of SO₂ and O₂ in the flue gas. Oxygen is capable of oxidizing MEA solvent, and SO₂ may react with MEA solvent to form irreversible byproducts thus reducing the reaction rate of the absorption process as well as the MEA solvent CO₂ absorption capacity. Besides, it also makes the solvent more difficult to be recovered. Wolsky et al. (1994) has addressed the problems associated with MEA solvent and suggested that future

research efforts should be directed toward developing better solvents for removal of CO₂. An ideal solvent should have at least two desirable characteristics: (1) it has an ideal capacity of one unit weight of CO₂ absorbed per unit weight of solvent; and (2) it can be recovered at a relatively lower temperature to reduce the energy requirement.

Ammonia seems to be an alternative solvent for removing CO₂ from flue gas. This is partly due to that ammonia reagent which has already been used in the De-NO_x process (such as selective catalytic reduction and selective non-catalytic reduction) in the flue gas systems. The ammonia gas or solvent is also an excellent reagent for removing SO₂ and HCl from waste gas streams (Bai et al., 1994; Bai and Chu, 1997). Therefore, it may be possible using the ammonia reagent to scrub all acid pollutants including the CO₂ greenhouse gas. However, NH₃ scrubbing is a new process for removing CO₂ emissions from flue gas in the environmental engineering field and limited information on its technical as well as economical effectiveness is available. A review of the NH₃-CO₂ reactions is referred to Bai and Yeh (1997), who conducted a preliminary study of CO₂ removal by NH₃ scrubbing. The results showed that possible reactions between CO₂ and NH₃ solvent in the CO₂ scrubber were:

$$2NH_{3(1)} + CO_{2(g)} + H_2O_{(1)} \leftrightarrow (NH_4)_2CO_{3(s)}$$
 (2)

$$NH_{3(1)} + CO_{2(g)} + H_2O_{(1)} \leftrightarrow NH_4HCO_{3(s)}$$
 (3)

It was also found that the crystalline products formed in the CO₂ scrubber should be primarily composed of white NH₄HCO₃ crystals.

This paper is an extensive study of Bai and Yeh (1997). A semi-continuous flow reactor is used to study the removal of CO₂ using the NH₃ solvent. The CO₂ removal efficiency as well as the CO₂ absorption capacity of NH₃ solvent is evaluated under various operating conditions. A similar study is also performed using the MEA solvent under the same operating conditions. The removal efficiency of CO₂ and the CO₂ absorption capacity of the two solvents are then compared.

2. Experimental method

The schematic diagram of the experimental system for studying the reaction between CO₂ and NH₃ solvent is shown in Fig. 1. The CO₂ absorber was a semi-continuous flow reactor with CO₂ gas continuously fed into the absorber, but the absorbent in the absorber was not circulated during each test. Compressed air was passed through a HEPA filter (Gelman Science, Ann Arbor, MI) to remove particulates and then dehumidified by passing it through a silica gel air dryer. The clean air was then served as diluting gas and it was mixed with pure CO₂ gas before entering the absorber via a fritted sparger. The CO₂ gas was obtained from a pure CO₂ cylinder (99.9%). The CO₂ absorber was a 60-mm i.d. glass bottle containing 200 ml of NH₃ or MEA solvent. The scrubber was approximately 21 cm long. It was installed in a constant temperature controller. Stock solutions of NH₃ (FISON, 35% (w/w)) and MEA (R.D.H., 99% (w/w)) were diluted using Milli-Q water (Millipore Corp., Bedford, MA) to obtain the desired solvent concentrations. Bai and Yeh (1997) reported that NH₃ solvent reacted with CO₂ and resulted in the formation of white ammonium bicarbonate solid particles. Since the solid particles would escape and plug the pipe line, a 0.45 μ m glass fiber filter (Gelman Sciences, Ann Arbor, MI) was placed after the scrubber to capture the escaping particles.

Concentrations of the gases were controlled using mass flow controllers (MKS Instruments, Inc., Andover, MA). The ZRH model infrared gas analyzer (California Analytical Instruments, Inc., Orange, CA) was used for measuring the CO₂ inlet and outlet gas concentrations. The analyzer was capable of detecting CO₂ with a concentration range of 0.00-40.00% (v/v). Although the absorber was placed in a constant temperature controller, temperature variations during the reaction were unavoidable due to endothermalexothermal reactions occurring in the absorber. Hence a temperature sensor was placed at 4 cm above the bottom of the scrubber and the temperatures were continuously recorded during the reactions.

Several operating parameters such as CO_2 inlet concentration, total gas flow rate, solvent concentration and operating temperature were systematically varied in order to investigate their influences on the CO_2 removal efficiency and absorption capacity of the two solvents. The inlet concentrations of CO_2 were from 8.00 to 16.00% (v/v). The total gas flow rates of CO_2 and clean air were kept at 2–10 l/min. The solvent concentrations were in the range of 7–35% (w/w). The

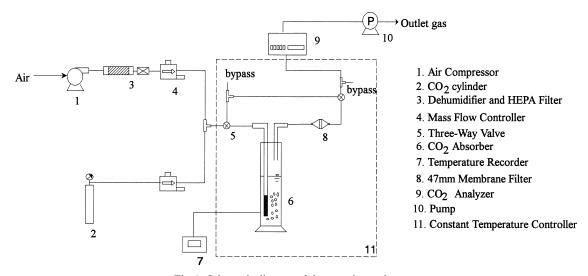


Fig. 1. Schematic diagram of the experimental setup.

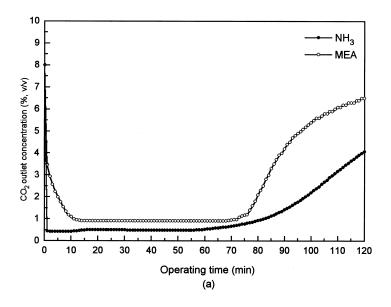
experiments were conducted under operating temperature range from 10 to 40°C.

3. Results and discussion

3.1. Effect of operating time

Fig. 2a shows the change of CO₂ outlet concen-

trations as a function of operating time by the NH_3 and MEA scrubbings. The absorber was operated at an operating temperature of 25°C, a CO_2 inlet concentration of 8.00% (v/v), a gas flow rate of 2 l/min and solvent concentration of 28% (w/w) for both the NH_3 and MEA solvents. It is seen that the operating time required to



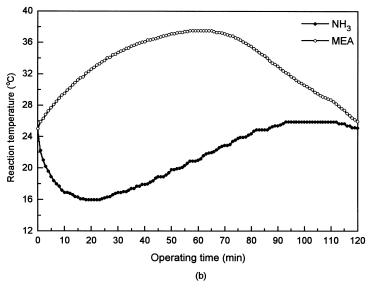


Fig. 2. The effect of operating time on (a) CO_2 outlet concentration and (b) reaction temperature using NH_3 and MEA solvents. The operating conditions were at CO_2 inlet concentration of 16.00% (v/v), gas flow rate of 2 l/min, solvent concentration of 28% (w/w), and operating temperature of 25°C.

reach a stable and maximum CO₂ removal rate is approximately 1 min for the NH₃ solvent. The CO_2 outlet concentration is 0.46% (v/v) which corresponds to 94% CO₂ removal, and the high CO₂ removal efficiency can be maintained over 70 min. However, the CO₂ removal efficiency does not reach its maximum value until after 10 min of operation using the MEA solvent. This indicates that the reaction rate of the NH₃ solvent with CO₂ is faster than that of the MEA solvent. Furthermore, the high CO₂ removal efficiency by the NH₃ scrubbing is maintained longer than that by the MEA scrubbing. Therefore, using the NH₃ solvent for scrubbing CO₂ from the flue gas provides a wider operating range than by using the MEA solvent.

Although the operating temperature was kept constant, temperature variations in the absorber were unavoidable due to endothermal-exothermal reactions between CO₂ and the absorbents. The temperature variations in the absorber were plotted in Fig. 2b as a function of operating time. The operating conditions were the same as those for Fig. 2a. As can be seen, the temperature variations of NH₃ scrubbing in the absorber decrease initially, and the minimum reaction temperature is 16°C. It then gradually increases to its maximum temperature of 26°C and decreases until it reaches 25°C of its original reaction temperature. However, the temperature variation of MEA scrubbing in the absorber gradually increases to its maximum temperature of 38°C, and then decreases to its original controlled temperature of 25°C. The results indicate that the CO₂-NH₃ reactions are a series of endothermal-exothermal reactions. On the other hand, the CO₂-MEA reaction is typically an exothermal reaction process.

The comparison of CO₂ scrubbing by NH₃ and MEA reagents is further studied in terms of solvent concentration, total gas flow rate, operation temperature, and CO₂ inlet concentration. Because the variations of CO₂ removal in the absorber with respect to operating time for other tests are similar to those shown in Fig. 2a, the following discussion on the CO₂ removal efficiency is focused on the comparison of maximum efficiencies of both solvents.

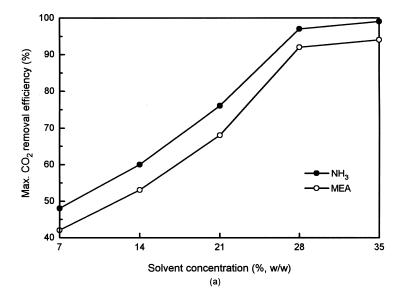
3.2. Effect of solvent concentration

In order to compare the performance of the two solvents, the maximum CO₂ removal efficiencies using the NH₃ and MEA solvents are shown in Fig. 3a. The operating conditions were at a gas flow rate of 2 1/min, a CO₂ inlet concentration of 16.00% (v/v) and an operating temperature of 25°C. It is seen that the maximum CO₂ removal efficiencies using the NH₃ solvent are approximately 6-7% higher than that using the MEA solvent. The maximum CO₂ removal efficiencies using the NH₃ solvent increase from 48% to 99% for NH₃ solvent concentrations, increase from 7% (w/w) to 35% (w/w). The maximum CO₂ removal efficiencies are from 42% to 92% for MEA solvent concentrations range from 7% (w/w) to 35% (w/w).

One can also observe that as the NH_3 and MEA solvent concentrations are greater than 28% (w/w), the increasing rate of CO_2 removal efficiency decreases. This is because the CO_2 removal efficiencies are already very high. Therefore, it is practical to use 28% (w/w) of solvents concentration for obtaining a high CO_2 removal efficiency.

The curves shown in Fig. 2a are similar to the breakthrough curve as obtained in many sorption tests. The point at which the CO_2 outlet concentration equals to the inlet concentration was selected as the 'breakthrough point' for the CO_2 absorption process. When the breakthrough point was reached, the experiment was terminated. The time to reach the breakthrough point for each experiment was different depending on the operating conditions. It varied from 20 min to 3 h. The total quantities of CO_2 removal were calculated via the breakthrough curves, and the CO_2 absorption capacity expressed in kg $\mathrm{CO}_2/\mathrm{kg}$ solvent was obtained.

The comparison of CO₂ absorption capacity as functions of NH₃ and MEA solvent concentrations is shown in Fig. 3b. It is seen that the influence of solvent concentration on the CO₂ absorption capacity using the NH₃ solvent is more than that using the MEA solvent. The CO₂ absorption capacity of NH₃ solvent decreases with increasing the NH₃ solvent concentration. It is



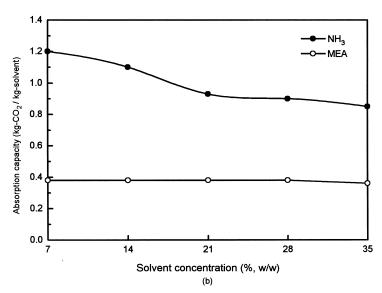


Fig. 3. The effects of solvent concentration on (a) CO_2 removal efficiency and (b) solvent absorption capacity. The operating conditions were at CO_2 inlet concentration of 16.00% (v/v), total gas flow rate of 2 l/min, and operating temperature of 25°C.

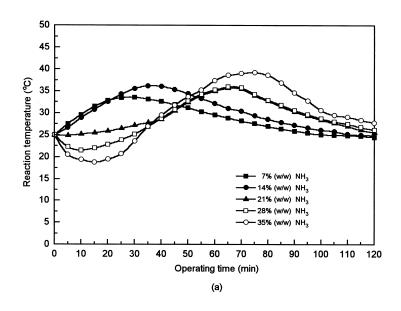
1.20 kg CO₂/kg NH₃ for the NH₃ solvent concentration of 7% (w/w). And for the NH₃ solvent concentration of 35% (w/w) the measured CO₂ absorption capacity is 0.85 kg CO₂/kg NH₃. The CO₂ absorption capacity of NH₃ solvent is close to or even exceeds that of an ideal solvent as proposed by Wolsky et al. (1994). On the contrary, the CO₂ absorption capacity of MEA sol-

vent is almost not affected by the solvent concentration. They are approximately $0.38-0.36~kg~CO_2/kg~MEA$ for MEA solvent concentrations range from 7% to 35% (w/w). These values are similar to those measured by Jou et al. (1995) and Shen and Li (1992), who obtained the CO_2 absorption capacity of $0.36~kg~CO_2/kg~MEA$. Based on the results obtained in this study, the mass

basis CO₂ absorption capacity of NH₃ solvent was 2.4–3.2 times of that of the MEA solvent. The purchase price for industrial grade NH₃ solvent is approximately one-sixth of that for the MEA solvent at the same weight basis in the world market (Kohl and Riesenfeld, 1985; Handbook of Fine Chemicals, 1996). On the other hand, the MEA solvent is the most economical

reagent among all alkanolamines from the cost of reagent. Therefore, it is economical using the NH₃ solvent as a scrubbing reagent.

Fig. 4a,b demonstrates plots of temperature variations in the absorber with respect to operating time using the NH₃ and MEA solvents, respectively. As can be seen in Fig. 4a, if the NH₃ solvent concentration is lower than 21% (w/w),



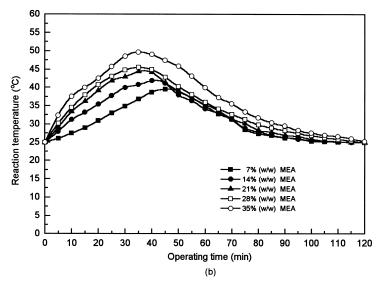


Fig. 4. The effects of solvent concentration on (a) NH_3 and (b) MEA temperature variations. The operating conditions were at CO_2 inlet concentration of 16.00% (v/v), total gas flow rate of 2 l/min, and operating temperature of 25°C .

the CO₂-NH₃ reactions in the absorber appear to be an exothermal reaction process. However, if the NH₃ solvent concentration is greater than 28% (w/w), the CO₂-NH₃ reactions are a series of endothermal-exothermal reactions. And the maximum temperatures using the NH₃ solvent increase with increasing solvent concentrations. The reason for the effect of NH₃ solvent concentration on the endothermal-exothermal reaction is not well understood at the present time. On the other hand, it is seen from Fig. 4b that the CO₂-MEA reaction occurring in the absorber is clearly an exothermal reaction. The maximum temperatures using the MEA solvent increase with increasing the solvent concentration. One can also observe that the maximum temperatures for MEA solvent are higher than those for NH₃ solvent. For example, the maximum temperature using 35% (w/w) MEA solvent is approximately 50°C, while it is less than 40 using 35% (w/w) NH₃ solvent. The high temperature indicates that the heat released in the MEA scrubbing process will require more heat during regeneration. As a result, the energy requirement for the whole scrubbing-regeneration process should be higher for the MEA process as compared to the NH3 process.

3.3. Effect of total gas flow rate

Fig. 5a shows the effect of total gas flow rate on the CO_2 removal efficiency. The gas flow rates evaluated in this study were in the range of 2–10 l/min, corresponding to gas residence times of 6.0–1.2 s. The definition of gas residence time is the solvent volume divided by the gas flow rate. The CO_2 inlet concentration was 16.00% (v/v), the operating temperature was 25°C and the solvent concentration was 28% (w/w). It was observed that the maximum CO_2 removal efficiencies using the NH $_3$ solvent decrease from 97% to 72% for gas flow rates increase from 2 to 10 l/min. And the maximum CO_2 removal efficiencies decrease from 92% to 62% using the MEA solvent.

Fig. 5b shows the effect of the gas flow rate on the CO₂ absorption capacity of NH₃ and MEA solvents. It was also observed that the gas flow rate has a slight influence on the CO₂ absorption capacities of $\mathrm{NH_3}$ and MEA solvents. The $\mathrm{CO_2}$ absorption capacity of either the $\mathrm{NH_3}$ or the MEA solvent decreases with increasing the gas flow rate. The absorption capacities for the $\mathrm{NH_3}$ and MEA solvents are 0.90–0.76 kg $\mathrm{CO_2/kg}$ NH $_3$ and 0.38–0.26 kg $\mathrm{CO_2/kg}$ MEA, respectively, for gas flow rates from 2 to 10 l/min. The difference between the observed absorption capacities for the $\mathrm{NH_3}$ and MEA solvents can be as high as 2.9 times under the same gas flow rate.

The effects of gas flow rate on the temperature variations in the absorber with respect to the operating time for the CO₂-NH₃ and CO₂-MEA reactions were similar to Fig. 4a,b. The CO₂-NH₃ reactions are also a series of endothermal-exothermal reactions, while the CO₂-MEA reactions are exothermal reactions. The maximum temperatures for both the NH₃ and MEA scrubbings increase as the total gas flow rate increases.

3.4. Effect of operating temperature

Fig. 6a shows the comparison of maximum CO₂ removal efficiencies using the NH₃ and MEA solvents under different operating temperatures. The inlet CO₂ gas as well as the original reagent solvents were kept at the operating temperature. However, the temperature in the reactor was changed due to exothermal-endothermal reactions. The CO₂ inlet concentration was 16.00% (v/v), the solvent concentration was 28% (w/w)and the gas flow rate was 2 1/min. As can be seen, increasing the operating temperature tends to increase the CO₂ removal efficiency. The CO₂ removal efficiencies using the NH₃ solvent are 92–99% for operating temperatures of 10–40°C. And the CO₂ removal efficiencies using MEA solvent are 88-94% for operating temperatures of 10-40°C.

Comparative results of the influence of operating temperature on the CO₂ absorption capacities of NH₃ and MEA solvents are shown in Fig. 6b. It is observed that the operating temperature has a slight influence on the CO₂ absorption capacity of MEA solvent. The absorption capacities of MEA solvent are approximately 0.35–0.40 kg CO₂/kg MEA for operating temperatures range from 10 to 40°C. However, the CO₂ absorp-

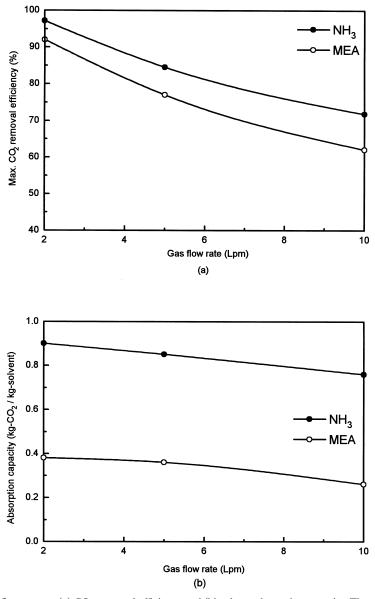
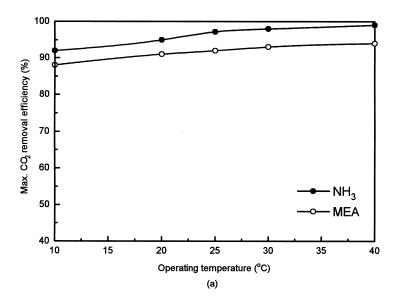


Fig. 5. The effects of gas flow rate on (a) CO_2 removal efficiency and (b) solvent absorption capacity. The operating conditions were at CO_2 inlet concentration of 16.00% (v/v), solvent concentration of 28% (w/w), and operating temperature of 25°C.

tion capacity for $\mathrm{NH_3}$ scrubbing is observed to decrease with increasing the operating temperature. It is 1.10 kg $\mathrm{CO_2/kg}$ $\mathrm{NH_3}$ at an operating temperature of 10°C, and is 0.82 kg $\mathrm{CO_2/kg}$ $\mathrm{NH_3}$ at an operating temperature of 40°C. The $\mathrm{CO_2}$ absorption capacity of the $\mathrm{NH_3}$ solvent is 2.3 times that of the MEA solvent at an operating temperature of 40°C.

The effects of operating temperature on the temperature variations in the absorber with respect to operating time using the NH₃ and MEA solvents were similar to Fig. 4a,b. The CO₂-NH₃ reaction at 10°C of operating temperature is an exothermal reaction. However, the CO₂-NH₃ reactions at 20-40°C of operating temperatures are endothermal-exothermal reactions. And the



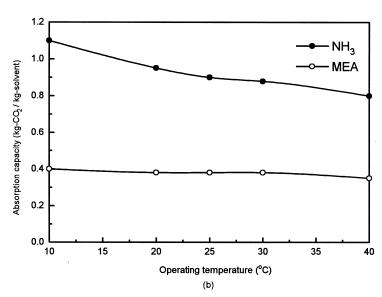


Fig. 6. The effects of operating temperature on (a) CO_2 removal efficiency and (b) solvent absorption capacity. The operating conditions were at CO_2 inlet concentration of 16.00% (v/v), solvent concentration of 28% (w/w), and total gas flow rate of 2 l/min.

CO₂-MEA reactions at 10-40°C of operating temperatures are exothermal reactions.

3.5. Effect of CO_2 inlet concentration

The effect of CO₂ inlet concentration was also studied. However, the effects of CO₂ inlet con-

centration on the CO_2 removal efficiency as well as the CO_2 absorption capacity were not significant, so the results were not shown in this study. The maximum CO_2 removal efficiencies by the NH $_3$ scrubbing are 94–97%. While by the MEA scrubbing the maximum CO_2 removal efficiencies are 88–92% for the CO_2 concentration ranges

from 8.00 to 16.00% (v/v). The $\rm CO_2$ absorption capacities of $\rm NH_3$ and MEA solvents are relatively constants and they are approximately 0.90 kg $\rm CO_2/kg$ $\rm NH_3$ and 0.38 kg $\rm CO_2/kg$ MEA, respectively, for $\rm CO_2$ inlet concentrations of 8.00–16.00% (v/v). The calculated $\rm CO_2$ absorption capacity of $\rm NH_3$ solvent is about 2.4 times that of the MEA solvent.

3.6. Environmental impact of NH₄HCO₃ byproduct

A massive reaction product may be produced by the NH₃ process. This can be resolved by an installation of a regeneration system. In addition, since a large amount of NH₃ is required for the NH₃ scrubbing process to reduce CO₂ emission, decomposition of the reaction product to regenerate NH₃ and CO₂ gas is desired. A proper design of the regeneration system can separate the NH₃ and CO₂ gases. The regenerated NH₃ gas (or liquid) can be used again in the NH₃ scrubber and as a reagent for the selective catalytic reduction process for removing the NO_x air pollutant. The regenerated CO₂ gas is in a pure state and can be used in many chemical plants.

Besides, if regeneration of the reaction product is not desirable, the NH₄HCO₃ product can be used as a source of fertilizer (Grayson and Eckroth, 1992). However, three problems may exist for NH₄HCO₃ as a fertilizer in the soil. First, according to the material safety data sheet (MSDS) (Material Safety Data Sheet, 1996), the byproduct (NH₄HCO₃) is slightly hazardous, but it does not have a significant influence on the soil. Second, the leaching of ammonia to ground water may also be possible. The ammonium bicarbonate decomposes at approximately 38-60°C (Shale et al., 1971; Grayson and Eckroth, 1992), dissociating into ammonia, carbon dioxide, and water. Rate of decomposition increases as temperature rises. However, it does not decompose at temperatures below 27°C (Grayson and Eckroth, 1992). In general, the temperature of soil is below 40°C (Tisdale et al., 1990). Therefore, there is little possibility of production of ammonia in that case if ammonium bicarbonate was used as a fertilizer in the soil. Besides, the soil has a pronounced capacity for adsorbing ammonia gas, the ability of leaching is greatly decreased (Tisdale et al., 1990).

Finally, although ammonium bicarbonate has a definite fertilizing value, it cannot compete with other ammonium compounds if it is used as a fertilizer due to nitrogen content in the product (NH₄HCO₃) being quite low (18% N) as compared with urea (45% N) (Tisdale et al., 1990; Grayson and Eckroth, 1992). Therefore, ammonium bicarbonate is not an ideal source of fertilizer from an economical point of view. However, from the view of recycling materials, ammonium bicarbonate, as a source of fertilizer should be feasible. Besides, ammonium bicarbonate can also be used as fire extinguishers, dyes, and a scale-removing compound, etc. (Grayson and Eckroth, 1992).

4. Conclusions

This study performed comparative tests on the NH₃ and MEA solvents to reduce CO₂ greenhouse gas emissions. The tests showed that the NH₃ solvent is superior to MEA solvent in its capacity to absorb and remove CO₂ from flue gas systems. The CO₂ removal efficiency for the NH₃ solvent could be as high as 99% under proper operating conditions. And the CO₂ absorption capacity of NH₃ scrubbing could be over 1.0 kg CO₂/kg NH₃. On the other hand, the maximum CO₂ removal efficiency and absorption capacity using the MEA solvent are 94% and 0.40 kg CO₂/kg MEA, respectively. Besides, the rise in temperature in the NH₃ scrubber is less than that in the MEA scrubber. This implies that if regeneration of the absorbent is desired, the regeneration heat required for the NH₃ process should be less than that for the MEA process.

Although, the experimental results have shown that the potential for removing CO₂ via NH₃ scrubbing is very promising, however, there are also potential problems for the NH₃ scrubbing process. The NH₃ and white crystalline NH₄HCO₃ may evaporate and exit into the atmosphere from the NH₃ scrubbing. Therefore, it is possible for the formation of visible plume in the flue gases. However, because the NH₃ gas

and NH₄HCO₃ are very soluble in water (Perry and Green, 1984; Grayson and Eckroth, 1992), the unreacted NH₃ which is known as NH₃ slipped and escaped the NH₄HCO₃ crystalline and in the process can be minimized by the installation of a washwater mist eliminator at the top section of the scrubber.

In addition, the NH₃ scrubbing process is most feasible near room temperature (Kohl and Riesenfeld, 1985; Bai and Yeh, 1997). Therefore, the flue gas will have to be quenched before it enters the scrubbing system, and the exit gas temperature will be too low to produce buoyancy. As a result, a reheater may be required after scrubbing. The cooling and the reheat of the flue gas can be done by a heat exchanger to reduce the energy cost.

The impurities, such as SO_x in the flue gases, degrades the absorbent function of amine. According to Steinberg (1984), MEA forms an insoluble non-regenerable salt together with SO₂. Although SO_x can also react with the ammonia solution to form (NH₄)₂SO₄ products (Bai, 1992). However, the reaction is reversible and equilibrium is reached in a very short time. A proper design of the ammonia scrubbing process can, in fact, remove all acid gases in the flue gas. This is the motivation that leads the authors to develop the ammonia scrubbing process for CO₂ control. Besides, the NH₃-SO₂ reaction product is also a source of fertilizer. The quality of $(NH_4)_2SO_4$ as a fertilizer is better than that of NH₄HCO₃ (Bai, 1992).

Future work must be conducted to test the feasibility of NH₃ scrubbing for CO₂ removal from stack gas using a continuous flow reactor. Once the feasibility of the CO₂ removal system is proved, it will provide another route for efficient control of CO₂ emissions from utility and industrial boilers.

Acknowledgements

Support from the National Science Council, R.O.C., through grant numbers NSC 85-2211-E-009-027 and NSC 86-2211-E-009-008 is gratefully acknowledged.

References

- Bai H. Fundamental study of ammonia-sulfur dioxide reactions to form solid particles. Ph.D. Dissertation. USA: University of Cincinnati, 1992.
- Bai H, Chu C. A laboratory evaluation of NH₃ injection technology to reduce HCl emissions from incinerators. Environ Technol 1997;18:425-432.
- Bai H, Wei JH. The CO₂ mitigation options for the electric sector: A case study of Taiwan. Energy Policy 1996;24:221–228.
- Bai H, Yeh AC. Removal of CO₂ greenhouse gas by ammonia scrubbing. Ind Eng Chem Res 1997;36:2490–2493.
- Bai H, Biswas P, Keener TC. Sulfur dioxide removal by reaction with ammonia gas to form solid particles: effects of temperature and moisture content. Ind Eng Chem Res 1994;33:1231–1236.
- Blok K, Worrell E, Caelenaere R, Turkenburg W. The cost effectiveness of CO₂ emission reduction achieved by energy conservation. Energy Policy 1993;25:656–667.
- Chakma A. Separation of CO₂ and SO₂ from flue gas streams by liquid members. Energy Convers Manage 1995;36: 405–410.
- Grayson M, Eckroth D. Kirk-Othmer encyclopedia of chemical technology, vol. 2, 3rd ed. New York: John Wiley and Sons, 1992:518–519.
- Handbook of fine chemicals. Belgium: Acros Organics, 1996.
 Hendriks CA, Blok K, Turkenburg WC. In: Okken PA, Swart RJ, Zwerrer S, editors. The recovery of carbon dioxide from power plants. Dordrecht, Netherlands: Kluwer Academic Publishers, 1989:125–142.
- Huang JP. Energy substitution to reduce carbon dioxide emission in China. Energy 1993;18:281–287.
- IPCC. Policymaker's summary of the scientific assessment of climate change. Report to IPCC from working group. Branknell, UK: Meteorological Office, 1990.
- Jou F-Y, Mather AE, Otto FD. The solubility of CO₂ in a 30 mass percent monoethanolamine. Can J Chem Eng 1995; 73:140-147.
- Kimura N, Omata K, Kiga T, Takano S, Shikisma S. Characteristics of pulverized coal combustion in O₂/CO₂ mixtures for CO₂ recovery. Energy Convers Manage 1995;36: 805–808.
- Kohl AL, Riesenfeld FC. Gas purification. 4th ed. Houston: Gulf Publishing Company, 1985:29–147.
- Material Safety Data Sheet. NJ: Mallinckrodt Baker, Inc., 1996.
- Molburg JC, Thimmapuram P, Doctor RD. Comparison of salient features of alternatives CO₂ recovery processes. Cincinnati, OH, USA: 87th Annual Meeting and Exhibition of AWMA Conference, Paper 94-RA113.03, 1994.
- Nishikawa N, Hiroano A, Ikuta Y et al. Photosynthetic efficiency improvement by microalgae cultivation in tubular-type reactor. Energy Convers Manage 1995;36:681–684.
- Perry R, Green D. Perry's chemical engineer's handbook. 6th ed. New York: McGraw-Hill, 1984.

- Shale CC, Simpson DG, Lewis PS. Removal of sulfur and nitrogen oxides from stack gases by ammonia. Chem Eng Prog Symp Ser 1971;67:52–58.
- Shen KP, Li MH. Solubility of carbon dioxide in aqueous mixtures of monoethanolamine with methyldiethanolamine. J Chem Eng Data 1992;37:96–100.
- Steinberg M. Advanced technologies for the recovery, disposal, and reuse of carbon dioxide for atmospheric control. New York: Brookhaven National Laboratory, 1984.
- Tisdale SL, Nelson WL, Beaton JD. Soil fertilizer and fertilizers. 4th ed. Macmillan Publishing Company, 1990:112–188.
- Wolsky AM, Daniels EJ, Jody BJ. CO₂ capture from the flue gas of conventional fossil-fuel-fired power plants. Environ Prog 1994;13:214–219.
- Xu S, Wang YW, Otto FD, Mather AE. Rate of absorption of CO₂ in a mixed solvent. Ind Eng Chem Res 1991;30: 1212–1217.