

Removal of CO₂ Greenhouse Gas by Ammonia Scrubbing

Hsunling Bai* and An Chin Yeh

*Institute of Environmental Engineering, National Chiao Tung University,
Hsinchu, 30039 Taiwan, Republic of China*

This paper provides preliminary results on the novel study of ammonia scrubbing for the removal of carbon dioxide from flue gas. Experimental results indicated the potential of CO₂ reduction by NH₃ scrubbing is very promising. The overall CO₂ removal efficiencies could be above 95% under proper operation conditions. The absorption capacity of NH₃ was around 0.9 kg of CO₂/kg of NH₃ reagent being used. This should be higher than that by a MEA solution. The reaction products were analyzed and determined by X-ray diffraction analysis, SEM picture, and pH measurements. All the measurements indicated that an ammonium bicarbonate solution and its crystalline solids are the major products of reaction.

Introduction

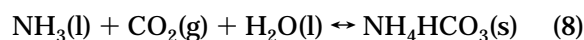
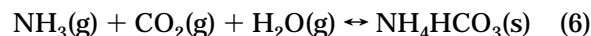
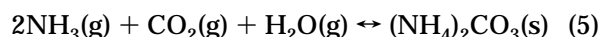
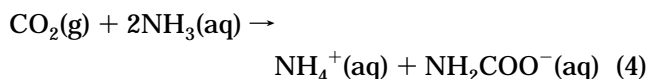
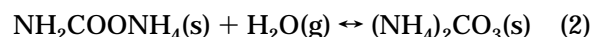
Carbon dioxide is the major greenhouse gas of which emissions need to be reduced. Although CO₂ emission from electric utilities is not currently regulated in many countries including the United States, however, due to deterioration of the greenhouse effect, it is promised that CO₂ emissions in 2000 will be held to the level of emissions in 1990 via the "Convention on Climate Change". Therefore, CO₂ reduction from utility boilers will be necessary in the near future. There are various technologies used to separate CO₂ from flue gas streams. These include chemical solvent methods, physical absorption methods, cryogenic methods, membrane systems, biological fixation, and the O₂/CO₂ combustion process (Wolsky et al. (1994), Nishikawa et al. (1995), Kimura et al. (1995)). The chemical solvent methods are generally recognized as the most effective technologies at present (Chakma (1995)). Among the conventional CO₂ chemical removal processes, the monoethanolamine (MEA) process has been comprehensively studied and successfully used in chemical plants for CO₂ recovery.

Although the MEA process is a promising system for the control of CO₂ emissions from massive discharging plants, it is an expensive option since the cost of CO₂ separation may range from US\$40 to 70/ton of CO₂ removed (Chakma (1995)). In addition, it has several major problems including a slow absorption rate, a small solvent capacity, etc. (Molburg et al. (1994)). In order to improve the above defects, Wolsky et al. (1994) suggested the need of new solvent to be discovered in the future research. Such a solvent should be environmentally safe and should have a high absorption capacity at moderate temperatures and pressures. An absorption capacity of about 1 kg of CO₂/kg of solvent is a reasonable target.

Theory of NH₃–CO₂ Reactions

A novel approach that may provide another route of reducing CO₂ emissions from power plants is separation by an ammonia reagent. Injection of NH₃ gas or aqueous NH₃ for removing NO_x from flue gas is a common process in power plants (e.g., selective catalytic reduction or thermal De-NO_x). Therefore, it may be economical to use NH₃ for the removal of CO₂ since less

space and equipment will be required. Possible reactions between ammonia and CO₂ are as follows (Brooks and Audrieth (1946), Brooks (1953), Hatch and Pigford (1962), Shale et al. (1971), Koutinas et al. (1983)):



The above reactions proceed at various temperatures and operation conditions. Ammonium carbamate (NH₂COONH₄) is formed by the reaction of carbon dioxide and ammonia in the dry condition under room temperature and a pressure of 1 atm. It is very soluble in water; therefore, under moist air the hydration product of ammonium carbonate ((NH₄)₂CO₃) is produced under room temperature (Brooks and Audrieth (1946)). While under high pressure and with temperatures greater than 140 °C, the CO₂–NH₃ reaction is directed to the formation of urea (CO(NH₂)₂) (Kucheryavii and Gorlovskii (1970)).

At room temperature and atmospheric pressure, reaction equations (4)–(8) also possibly occur. The formation of ammonium (NH₄⁺) and carbamate (NH₂COO⁻) ions is very fast, and reaction equation (4) is irreversible (Hatch and Pigford (1962)). On the other hand, reaction equations (5)–(8) are reversible, with ammonium carbonate ((NH₄)₂CO₃) or bicarbonate (NH₄HCO₃) as the products (Brooks (1953), Shale et al. (1971)). The forward reactions are dominant at room temperature (Pelkie et al. (1992), Koubsky and Hladky (1976)). The backward reactions occur at temperatures of around 38–60 °C (Shale et al. (1971), Grayson (1978)). The solid ammonium carbonate and bicarbonate can either be dry powders or exist in an aqueous solution as crystalline solids.

* Author to whom correspondence should be addressed.
Phone: 011-886-3-5727834. Fax: 011-886-3-5725958. E-mail: hlbai@green.ev.nctu.edu.tw.

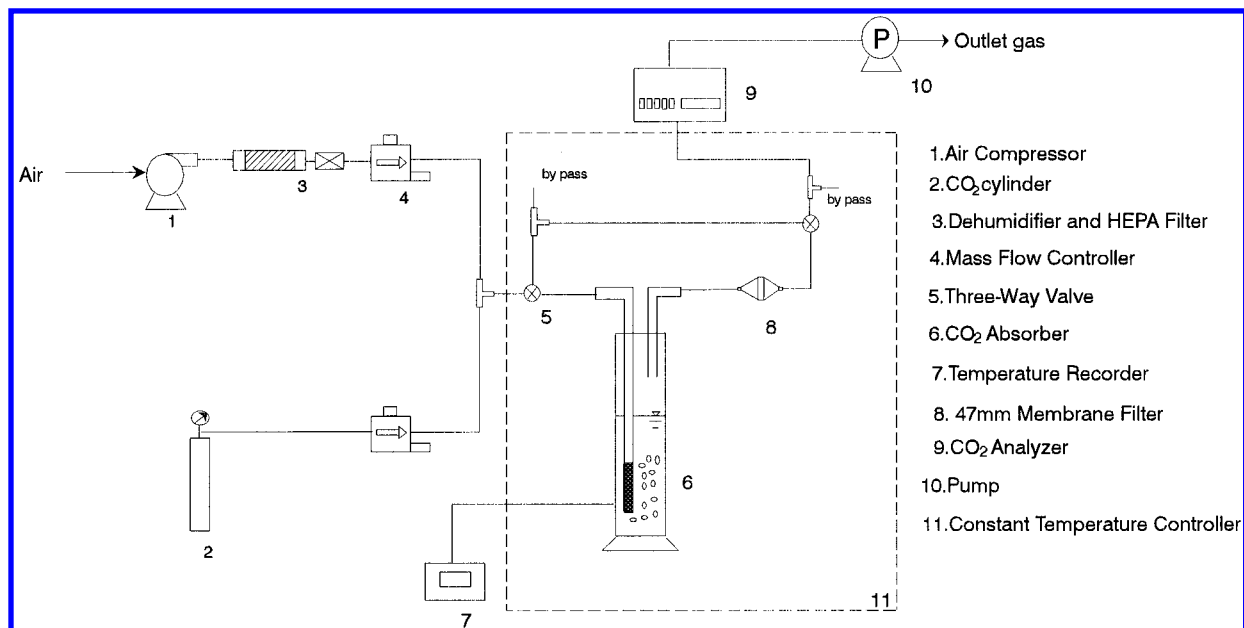


Figure 1. Schematic diagram of carbon dioxide scrubbing by an ammonia solution.

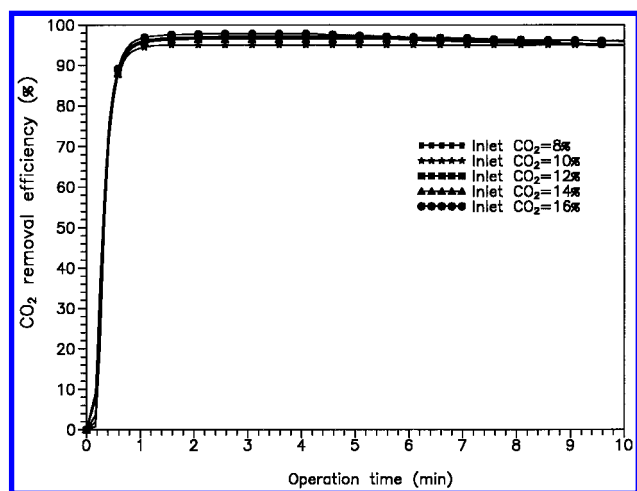


Figure 2. CO₂ removal efficiency as a function of the reaction time for various inlet CO₂ concentrations.

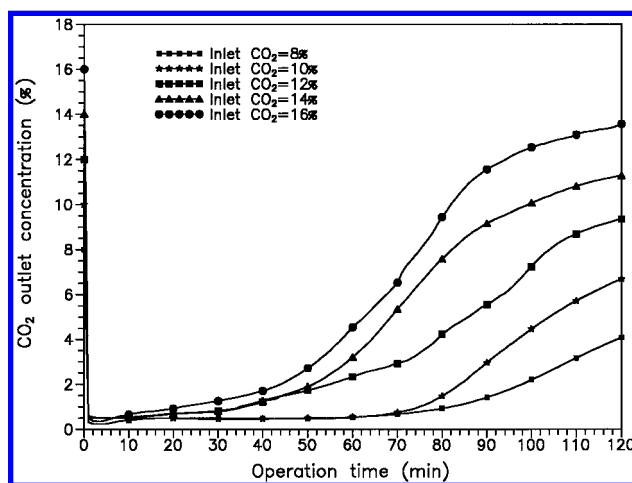


Figure 3. Breakthrough curves of CO₂ removal by ammonia absorption.

Although reaction equation (1) may also be applied to the reduction of CO₂ emission from flue gas since the concentration of CO₂ in flue gas is high, which could be up to 16% (v/v), a large amount of NH₃ gas would be required to effectively reduce the CO₂ emission. This may lead to concern over an explosive problem with the dry NH₃-CO₂ reaction if the process is designed improperly. The explosive limit for NH₃ gas is 15–28% (v/v) (Merck (1996)). Therefore, for the sake of safety and simplicity, the wet method (i.e., using ammonia scrubbing instead of ammonia injection) is employed in this study. Reaction equations (7) and (8) are the most probable in this study for CO₂ removal by NH₃ scrubbing.

Experimental Section

The schematic diagram of the experimental system for studying the reaction between CO₂ and an ammonia solution is shown in Figure 1. The CO₂ scrubber was a 60 mm i.d. glass bottle containing 200 mL of a 28% (w/w) ammonia solution. The CO₂ gas was obtained from a pure CO₂ cylinder. Clean air serving as the diluting gas was introduced and mixed with pure CO₂ gas before entering the scrubber via a fritted sparger. Concentra-

tions of the gases were controlled by 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 inlet and outlet CO₂ gas concentrations. Experiments were conducted under room temperature conditions (25 ± 1 °C) in this study. The inlet concentrations of CO₂ were 8, 10, 12, 14, and 16% (v/v), respectively. The total flow rates of CO₂ and clean air were kept at 2 L/min. The ammonia solution was obtained from a standard ammonia solution (FISONS, 35% (w/w)) which was diluted using Milli-Q water (Millipore Corp., Bedford, MA). The solid products in the aqueous solution were collected and dried at 40 °C. In addition, due to the fact that some products may escape from the solution, a filter was also placed after the scrubber to capture the escaped particles. The pH value of the product solution was determined by a digital pH meter (SUNTEX sp-701). The reaction products were also analyzed by X-ray diffraction (XRD; MAC Science MXP3) and scanned at 20 kV by a scanning electron microscope (SEM; Hitachi, S570). The dry powders of ammonium carbonate (Merck, 99%+), ammonium carbamate (Merck, 99%+), and ammonium bicarbonate

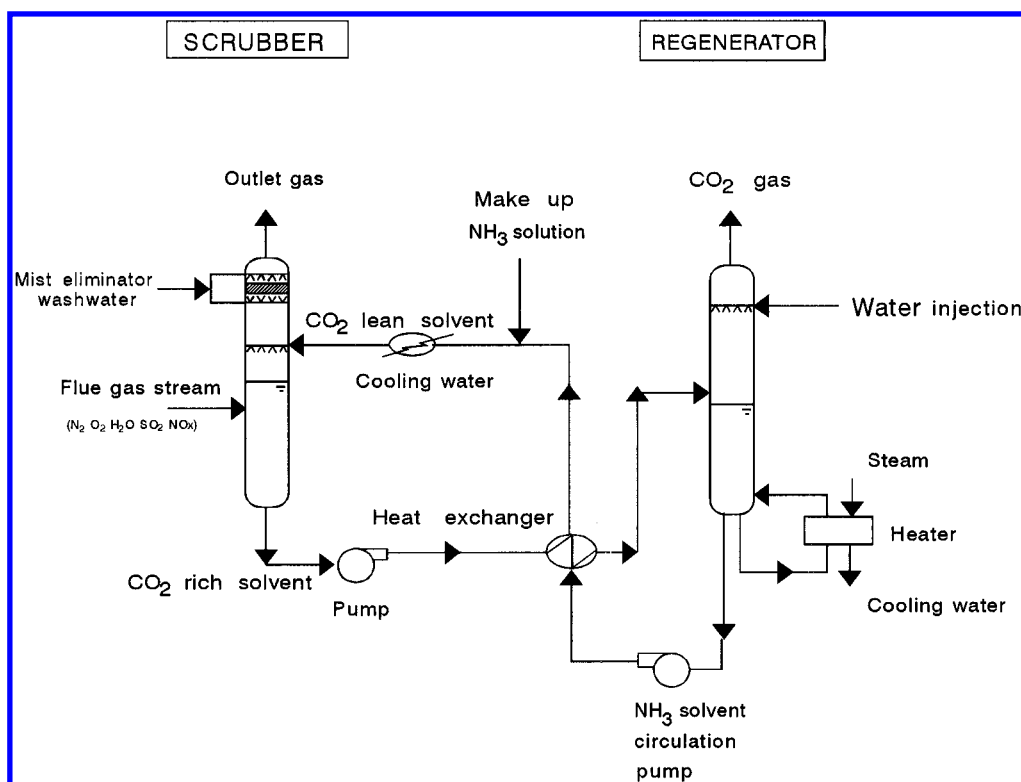


Figure 4. Conceptual design of the CO₂ scrubber and NH₃ regeneration system.

Table 1. Identification of Reaction Products

methods	standard compounds	reaction products
SEM picture	NH ₄ HCO ₃ (NH ₄) ₂ CO ₃ NH ₂ COONH ₄	small porosity medium porosity large porosity
XRD analysis	NH ₄ HCO ₃ (NH ₄) ₂ CO ₃ NH ₂ COONH ₄	2θ = 16.2, 29.7, 42.1 2θ = 29.6, 35.2, 42.0 2θ = 17.0, 32.0, 34.0
pH measurement	NH ₄ HCO ₃ (NH ₄) ₂ CO ₃ NH ₂ COONH ₄	pH = 7.8 pH = 9.1 pH = 9.2

(R.D.H., 99%+) are used as the standards for product identification.

Results and Discussion

Figure 2 is a plot of CO₂ removal efficiency as a function of operation time in the scrubber. The total operation time during the experiments was 10 min. As can be seen, the effect of inlet CO₂ concentration on its removal is minimal. The operation time required to reach a 90% CO₂ removal is around 40 s for all experiments. After 60 s the CO₂ removal efficiencies are quite stable in the range from 95 to 98%. This indicates a high potential of CO₂ scrubbing with a fast absorption rate by the NH₃ reagent. The CO₂ removal efficiency may be higher than that by the conventional MEA process (~90%) under proper operation conditions.

In order to evaluate the capacity of the NH₃ reagent, the operation time was increased to 2 h. Figure 3 shows the outlet CO₂ concentrations as a function of operation time. They act as "breakthrough" curves for the NH₃ reagent. For an operation time of less than around 30 min, the outlet concentrations of CO₂ are quite low for inlet CO₂ concentrations. For a longer operation time the outlet CO₂ concentrations increase, which indicates a gradual deterioration of the NH₃ scrubbing capacity. Besides, increasing the inlet CO₂ concentration results

in a decrease in the operation time available for efficient control of CO₂ gas. For example, the outlet CO₂ concentration after 2 h of operation time is 4% for 8% (v/v) inlet CO₂ concentration, which corresponds to 50% of CO₂ being removed at that instance. On the other hand, the outlet CO₂ concentration at the same operation time is 13.5% for 16% (v/v) inlet CO₂ concentration, which corresponds to only 15% of CO₂ being removed at that instance. Based on the breakthrough curves, the NH₃ scrubbing capacity can be calculated to be around 0.35 mol of CO₂/mol of NH₃ on a molar basis or 0.9 kg of CO₂/kg of NH₃ on a mass basis. According to Jou et al. (1995) and Shen and Li (1992), the maximum capacity of MEA is 0.36 kg of CO₂/kg of MEA. Therefore, the absorption capacity of the NH₃ solution should be higher than that of the MEA solution on a mass basis.

The crystalline solids in the solution were taken for SEM pictures, XRD analyses, and pH measurements. The results are summarized in Table 1. The SEM pictures reveal that the reaction product has a surface structure similar to that of standard ammonium bicarbonate (NH₄HCO₃) powders. The XRD pattern of the reaction products is also compared to standard compounds. The product is identified to be NH₄HCO₃ with peaks at 2θ = 16.2, 29.7, and 42.1. In addition, the pH values of the product solutions were around 7.9–8.0 for

various inlet CO₂ concentrations. As compared to the pH values of standard NH₄HCO₃, (NH₄)₂CO₃, and NH₂-COONH₄ solutions (7.8, 9.1, and 9.2, respectively), it is obvious that NH₄HCO₃ is the main product of the CO₂-NH₃ reaction in this study.

Based on the preliminary experimental results, a CO₂ treatment process using a NH₃ solution may be designed conceptually. A simplified diagram of the CO₂ scrubbing and regeneration system is shown in Figure 4. The large amount of ammonia required can be obtained by regeneration of the reaction product. It can be done by heating up the crystalline product since the reaction is reversible. The CO₂ and NH₃ gases are released after heating. Since NH₃ is very soluble in water while the solubility of CO₂ in water is low (Perry and Green (1984)), they are separated by proper design of the water injection system. The ammonia solution is then recycled and used as the scrubbing agent. The remaining CO₂ gas is in an almost pure state and can be used in the chemical industry or disposed of by injection into deep ocean (Rose (1993)). Once the feasibility of the regeneration system is proved, the large amount of ammonia solution required as well as the treatment of the products will not be major concerns in our proposed process.

The loss of NH₃ into the atmosphere may be another problem even with the ammonia solution scrubbing system. However, it can be minimized by the installation of a mist eliminator at the top section of the scrubber (see Figure 4). The mist eliminator is equipped with a layer of mesh and washwater at the top and bottom of the mesh. The mesh eliminates the ammonia in the droplets and the washwater washes out the ammonia in the gaseous phase. Besides, since the scrubber will be operated at near room temperature, a reheater is required after scrubbing for the flue gas to produce buoyancy.

Conclusions

Study of CO₂ removal by means of ammonia scrubbing has been performed experimentally in a semicontinuous-flow reactor under various inlet CO₂ concentrations. The overall CO₂ removal efficiencies in this study could be above 95% under proper operation conditions. The absorption capacity of NH₃ was around 0.9 kg of CO₂/kg of NH₃ reagent being used. This should be higher than that of the MEA solution. The reaction products were analyzed and determined by X-ray diffraction analyses, SEM pictures, and pH measurements. All the results indicated that an ammonium bicarbonate solution and its crystalline solids are the major products of reaction.

The preliminary results have shown that the potential for removing CO₂ via ammonia scrubbing may be very promising. Future work must be conducted to test the feasibility of ammonia scrubbing for CO₂ removal from stack gas. This is currently underway, which utilizes a continuous-flow CO₂/NH₃ reactor to simulate conditions in the actual flue gas system. In addition to the CO₂ scrubbing from flue gas systems, the process proposed in this study may also be applied to the purification of CO₂ in the chemical industry.

Acknowledgment

Support from the National Science Council, R.O.C., through Grant No. NSC-85-2211-E-009-027 is gratefully acknowledged.

Literature Cited

- Brooks, R. Manufacture of Ammonium Bicarbonate. British Patent 742,386, 1953.
- Brooks, L. A.; Audrieth, L. F. Ammonium Carbamate. *Inorg. Synth.* **1946**, *2*, 85.
- Chakma, A. Separation of CO₂ and SO₂ from Flue Gas Streams by Liquid Membranes. *Energy Convers. Manage.* **1995**, *36*, 405.
- Grayson, M. *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed.; John Wiley & Sons: New York, 1978; Vol. 2.
- Hatch, T. F.; Pigford, R. L. Simultaneous Absorption of Carbon Dioxide and Ammonia in Water. *Ind. Eng. Chem. Fundam.* **1962**, *1*, 209.
- Jou, F.-Y.; Mather, A. E.; Otto, F. D. The Solubility of CO₂ in a Mass Percent Monoethanolamine Solution. *Can. J. Chem. Eng.* **1995**, *73*, 140-147.
- Kimura, N.; Omata, K.; Kiga, T.; Takano, S.; Shikisima, S. The Characteristics of Pulverized Coal Combustion in O₂/CO₂ Mixtures for Recovery. *Energy Convers. Manage.* **1995**, *36*, 805.
- Koubsky, P.; Hladky, V. Equilibrium Calculations in the System NH₃-CO₂-H₂O. *Int. Chem. Eng.* **1976**, *16*, 392.
- Koutinas, A. A.; Yianoulis, P.; Lycourghiods, A. Industrial Scale Modelling of the Thermochemical Energy Storage System Based on CO₂ + 2NH₃ ↔ NH₂COONH₄ Equilibrium. *Energy Convers. Manage.* **1983**, *23*, 55.
- Kucheryavii, V. I.; Gorlovskii, D. M. Densities of Coexisting Phases in the Equilibrium Gas-Liquid System NH₃-CO₂-CO-(NH₂)₂-H₂O at High Temperatures and Pressures. *Zh. Prikl. Khim.* **1970**, *43*, 1675.
- Merck, K. *Reagents-Chemicals-Diagnostics*; IRIODIN/AFFLAIR: Darmstadt, Germany, 1996.
- Molburg, J. C.; Thimmapuram, P.; Doctor, R. D. Comparison of Salient Features of Alternatives CO₂ Recovery Processes. A&WMA Annual Meeting, Cincinnati, June 1994; Paper 94-RA113.02.
- Nishikawa, N.; Hiroano, A.; Ikuta, Y.; Futuda, Y.; Kaneko, M.; Kinoshita, T.; Ogushi, Y. Photosynthetic Efficiency Improvement by Microalgae Cultivation in Tubular-Type Reactor. *Energy Convers. Manage.* **1995**, *36*, 681.
- Pelkie, J. E.; Concannon, P. J.; Manley, D. B.; Poling, B. E. Product Distributions in the CO₂-NH₃-H₂O System from Liquid Conductivity Measurements. *Ind. Eng. Chem. Res.* **1992**, *31*, 2209.
- Perry, R.; Green, D. *Perry's Chemical Engineer's Handbook*, 6th ed.; McGraw-Hill: New York, 1984.
- Rose, J. Disposing of CO₂ from Fossil-Fueled Power Plants. *Environ. Sci. Technol.* **1993**, *27*, 1282.
- Shale, C. C.; Simpson, D. G.; Lewis, P. S. Removal of Sulfur and Nitrogen Oxides from Stack Gases by Ammonia. *Chem. Eng. Prog. Symp. Ser.* **1971**, *67*, 52.
- Shen, K.-P.; Li, M.-H. Solubility of Carbon Dioxide in Aqueous Mixtures of Monoethanol-amine with Methyl-diethanolamine. *J. Chem. Eng. Data* **1992**, *37*, 96-100.
- Wolsky, A. M.; Daniels, E. J.; Jody, B. J. CO₂ Capture from the Flue Gas of Conventional Fossil-Fuel-Fired Power Plants. *Environ. Prog.* **1994**, *13*, 214.

Received for review November 26, 1996
Revised manuscript received March 4, 1997
Accepted March 4, 1997*

IE960748J