

Capture and separation of CO₂ from flue gas by coupling free and immobilized amines

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Abstract: A novel system was proposed for the capture and separation of CO₂ from flue gas. In this method, a resin was employed to regenerate the amine capturing CO₂ from flue gas at room temperature. The feasibility for the resin to regenerate amines such as MEA, MAE, TEA, and ammonia was demonstrated. It was also discovered that the resin could be regenerated by hot water.

Keywords: separation; CO₂; flue gas; amine

Introduction

The emission of greenhouse gases into atmosphere causes the earth's mean temperature to rise. This is called global warming, or greenhouse effect. Among those greenhouse gases, CO₂ is the main contributor (Houghton, 1990). Thus, many research groups have studied how to control CO₂ emission into atmosphere. Before CO₂ can be sequestered from power plants or industrial sources, it must be captured as a relatively pure gas. CO₂ is routinely separated and captured as a by-product from industrial processes such as synthetic ammonia production, hydrogen production, and limestone calcination. However, existing capture technologies are not cost-effective when considered in the context of CO₂ sequestration.

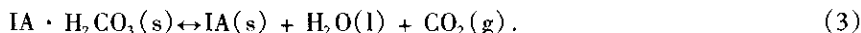
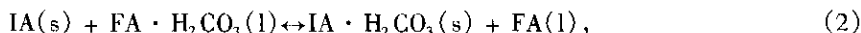
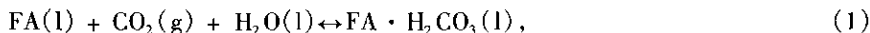
Chemical solvent scrubbing techniques to capture separate CO₂ from fossil-fuel power plants involve two steps. The first step employs one or more basic chemical scrubbers to capture CO₂ from flue gas. In the second step, the captured CO₂ is stripped by steam at high temperatures. The stripping of the CO₂ is energy intensive. Energy is required not only to heat the compounds of CO₂ with chemical solvents, but also to heat about 80% of water in the solutions during the regeneration of the chemical solvents. Along with the intensive energy requirement for the regeneration of the absorbents, there are also problems of reagent loss and corrosion due to the reagent degradation and the formation of heat stable salts in the presence of SO₂, NO_x and O₂ in flue gas. To circumvent these drawbacks, several new options were proposed.

Mimura, T. *et al.* have developed a KS-2 process on the basis of sterically hindered amines. This process was addressed to require about 20% less energy than the conventional MEA process. Also a much slower corrosion rate was achieved (Mimura, 1997). Bai, H. *et al.* have suggested that ammonia be a scrubber for CO₂ (Bai, 1997). In addition to the attempts to explore new absorbents, much effort has also been spent to develop membrane techniques with various chemical solvents to facilitate the capture of CO₂. Through combining gas absorption and membrane separation, Feron, P. H. M. *et al.* successfully developed a process for the production of CO₂ from flue gas. The process offers the advantages of equipment compactness, excellent selectivity, and energy savings (Feron, 1997). Chakma, A. used a polyethyleneglycol(PEG-400) membrane in series with a diethanolamine/PEG-400 membrane to separate CO₂ and SO₂ from flue gas (Chakma, 1995).

In this study, a new approach for the capture of CO₂ from flue gas is proposed. For this approach, dual amines are employed. One of them, free amine (FA, in liquid form) is used to capture CO₂ from flue

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gas, while another, immobilized amine (IA, in solid form) regenerates the FA. The CO₂ is then transferred from liquid FA onto the solid IA. The resultant IA can be recycled by heating it in hot water or by using steam, and the emitted CO₂ is collected, ready for disposal. The reactions involved could be expressed as follows.



This report addresses the experimental results on the feasibility of regeneration of various chemical absorbents, including MEA, MAE, TEA and ammonia by using free base immobilized onto resin. The possibility to regenerate resin by using hot water was also examined. Additionally, several cycles were run to test the sustainability of the resin.

1 Material and methods

1.1 Materials

Monoethanolamine (MEA, minimum 98%), methylaminoethanol (MAE, minimum 98%), triethanolamine (TEA, 99.7%), CO₂ (8.5%, with N₂ as balance), ammonia (NH₄OH, 28% – 30%), resin (A-830, weakly basic anion exchange, Purolite Co.).

1.2 Absorption of CO₂

A CO₂ (8.5%) feed gas was passed through a bubbling absorption reactor (45 mm in diameter) with a sinter bottom at a flow rate in the range of 200 and 500 ml/min. The reactor contained 50, 100, or 200 ml of absorbent (MEA, MAE, TEA, NH₄OH) at various concentrations. The experimental temperature was 25 °C. A cold trap with ice was employed to eliminate moisture in the CO₂ gas stream coming out of the reactor. The change in the concentration of CO₂ with time was monitored by a FT-IR spectrometer (Model 1605, Perkin-Elmer Co.) with a 10-cm light pass gas cell and the amount of CO₂ absorbed was calculated using a concentration vs. time curve.

1.3 Regeneration of absorbent

After the absorption of CO₂ reached its equilibrium, the absorbent became a CO₂-rich solution. To regenerate the absorbent, the CO₂-rich solution was transferred into a 250 ml Erlenmeyer flask, and then a resin, A-830, ranging from 20 to 100 grams was added to the flask. The mixture was stirred for 2 hours at 400 or 800 r/min and room temperature (25 °C). The regenerated absorbent solution was separated from the resin by filtration under vacuum. Some experiments were conducted by pumping the CO₂-rich solution through a sintered-bottom glass tube containing resin.

1.4 Recovery of resin and CO₂

To reuse the resin, which adsorbed carbonic acid in the regeneration of the CO₂-bearing absorbent, hot de-ionized water (60, 80 or 100 °C) was employed. The resin and de-ionized water were mixed in a 250 ml Erlenmeyer flask at ratios of water volume to resin weight between 50/50, 100/100 and 200/50 ml/g and the mixture was stirred at a speed of 400 r/min. A condenser was connected to the flask to prevent the water evaporating from the mixture and to separate gaseous CO₂ from moisture.

In some experiments, water in a 250 ml Erlenmeyer flask was passed through a chromatography column by a peristaltic pump. The water was heated before entering the column by a thermostat. The resin to be regenerated was packed into the column, which was also heated by the thermostat up to a set temperature. The water coming out of the column was returned to the flask for reuse to regenerate the resin. Also, a condenser was connected to the flask to prevent the water evaporating from the mixture and to separate gaseous CO₂ from moisture.

The released CO₂ was passed under a vacuum through a container with NaOH(0.1 mol/L) solution to convert the CO₂ into carbonate for the determination of total CO₂. The total CO₂ was determined by an indirect ion chromatography method. In this method, CaCl₂ (20 mmol/L) reacts with carbonate to form CaCO₃ precipitate, resulting in a reduction of calcium ion concentration in the solution. The total CO₂, which corresponds to the amount of carbonate, was calculated based on the relationship of carbonate concentration and the decrease in calcium ion concentration. To determine calcium ion concentration by ion chromatography (Model 2010i, Dinex Co.), a cation separation column CS12 (Dionex Co.) was employed with a suppressor of CMMS (Dionex Co.). Nine mmol/L of HCl was used as an eluent, while 10 mmol/L of TBAOH was used as a regenerant. The flow rates of the eluent and the regenerant were 0.6 and 6.5 ml/min, respectively.

2 Results and discussion

2.1 Regeneration of amines and ammonia

After capturing CO₂ from flue gas, the absorbent, an amine or ammonia, was converted into carbamate or/and bicarbonate. To reuse the absorbent, a regeneration step is required to release the absorbent from its carbamate or bicarbonate. It has been found that a resin with free base functional group is able to regenerate the amines and ammonia. The reaction likely involves the decomposition of the carbamate or bicarbonate followed by combination of CO₂ by the free base in the resin, as shown in Equation (2). To demonstrate the ability of a resin, A-830, to regenerate MEA from its carbamate and/or carbonate after it absorbs CO₂, CO₂ absorption curves using the fresh MEA and regenerated MEA solutions were traced by FT-IR spectrometer, as shown in Fig. 1. One hundred milliliters of fresh MEA (7.5%) absorbed 91.4 mmoles of CO₂. The resultant solution was regenerated by 20g of A-830 at room temperature. After regeneration, the solution was reused to absorb CO₂. The absorbed CO₂ was 26.4 mmoles, indicating that 28.8% of MEA's CO₂ capture capacity was regenerated by the resin or 1.3 mmoles of CO₂ can be absorbed by the MEA regenerated by one gram of the resin. The low regeneration percentage of MEA's CO₂-capture capacity by A-830 is ascribed to an insufficient amount of resin. When the concentration of MEA was decreased down to 1%, the regeneration efficiency of MEA capacity by A-830 was increased to 58%. As shown in Fig. 2, fresh MEA absorbed 14.4 mmoles of CO₂ and the regenerated MEA absorbed 8.4 mmoles of CO₂. Although the MEA regeneration efficiency increased, the amount of CO₂ absorbed by the regenerated MEA by one gram of resin decreased dramatically down to 0.42 mmoles. Thus, in practice, higher concentration of MEA will be better to make full use of the resin.

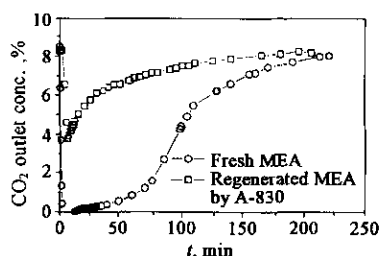


Fig. 1 CO₂ absorption using fresh MEA and regenerated MEA by A-830

(absorption: MEA: 7.5%, 100 ml; CO₂ inlet: 8.5%, 220 ml/min; temp.: 25°C; MEA regeneration: A-830: 20 g; stirring speed: 800 r/min; time: 2h; temp.: 25°C)

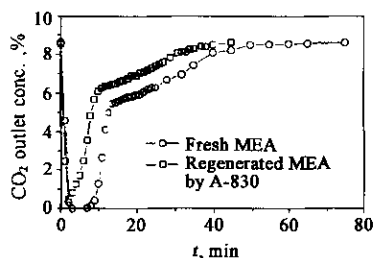


Fig. 2 CO₂ absorption using fresh MEA and regenerated MEA by A-830

(absorption: MEA: 1%, 100 ml; CO₂ inlet: 8.5%, 220 ml/min; temp.: 25°C; MEA regeneration: A-830: 20 g; stirring speed: 800 r/min; time: 2h; temp.: 25°C)

To simulate the real working condition, a 50 ml of 20% of MEA was employed for the capture of CO_2 , the absorption curve is illustrated in Fig. 3. To regenerate the MEA saturated by CO_2 , 50g of resin was used. Only 44 ml of solution, liquid 1, remained after regeneration and filtration. This is probably due to the adherence of MEA to the resin. To wash off the MEA on the resin, 50 ml of water was utilized, and another 44 ml of filtrate, liquid 2, was obtained. Both solutions were reused to absorb CO_2 , and the absorption curves are also shown in Fig. 3. It was estimated that the CO_2 absorbed by the regenerated MEA in liquid 1 and 2 were 37.6% and 14.7% of that absorbed using the fresh MEA, respectively. Totally, 52.3% of MEA's CO_2 absorption capacity was regenerated. This result indicates that A-830 is able to effectively regenerate MEA.

In addition to regenerating MEA, the resin has also been found to be able to regenerate MAE, TEA and NH_4OH . Fig. 4 depicts the CO_2 absorption using the fresh MAE and regenerated MAE by A-830. It is obvious that the regenerated MAE solution can be reused to absorb CO_2 , and the regeneration efficiency of MAE's CO_2 absorption capacity is 37.3%. Fig. 5 shows the CO_2 absorption curves using the fresh TEA and regenerated TEA by A-830. The regeneration efficiency of TEA's CO_2 absorption capacity is found to be as high as 69.1%. The CO_2 absorption using the fresh ammonia and regenerated ammonia by the resin is also demonstrated in Fig. 6. The regeneration efficiency of NH_4OH 's CO_2 absorption capacity is found to be 18.7%. Although the regeneration efficiency is comparatively low because of the high molar concentration of NH_4OH , the amount of CO_2 absorbed by the regenerated NH_4OH by one gram of resin is high, up to 1.4 mmoles.

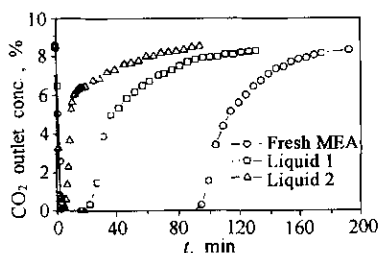


Fig. 3 CO_2 absorption using fresh MEA and regenerated MEA by A-830

(absorption: MEA: 20%, 50 ml; CO_2 inlet: 8.5%, 200 ml/min; temp.: 25°C; MEA regeneration: A-830, 50 g; stirring speed: 800 r/min; time: 2h; temp.: 25°C)

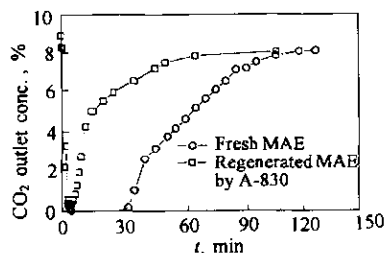


Fig. 4 CO_2 absorption using fresh MAE and regenerated MAE by A-830

(absorption: MAE: 7.5%, 100 ml; CO_2 inlet: 8.5%, 220 ml/min; temp.: 25°C; MAE regeneration: A-830: 20 g; stirring speed: 800 r/min; time: 2h; temp.: 25°C)

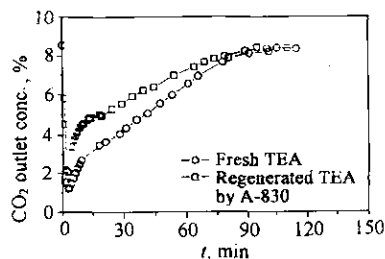


Fig. 5 CO_2 absorption using fresh TEA and regenerated TEA by A-830

(absorption: TEA: 7.5%, 100 ml; CO_2 inlet: 8.5%, 220 ml/min; temp.: 25°C; TEA regeneration: A-830: 20 g; stirring speed: 800 r/min; time: 2h; temp.: 25°C)

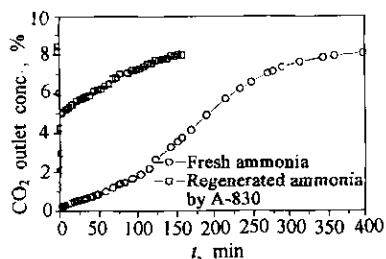


Fig. 6 CO_2 absorption using fresh NH_4OH and regenerated NH_4OH by A-830

(absorption: NH_4OH : 7.5%, 100 ml; CO_2 inlet: 8.5%, 220 ml/min; temp.: 25°C; NH_4OH regeneration: A-830: 20 g; stirring speed: 800 r/min; time: 2h; temp.: 25°C)

Finally, the CO₂ absorption capacity and the regeneration efficiency by A-830 resin for the above four types of absorbents is listed in Table 1.

2.2 Regeneration of resin and recovery of CO₂

It has been found that resin saturated with carbonic acid can be regenerated by hot water with the liberation of CO₂. The released CO₂ is recovered by using a container. The reaction can be expressed in Eq. (3). To certify the feasibility of hot water to regenerate resin, the regenerated resin by hot water was used to regenerate MEA from its carbamate and/or carbonate, and then the regenerated MEA was reused to absorb CO₂. Fig. 7 shows the capture of CO₂ using the fresh MEA, the MEA regenerated by fresh A-830, as well as the MEA regenerated by A-830 regenerated by water at 60 and 80 °C. The CO₂ absorbed using the regenerated MEA by fresh resin occupies 61.4% of that absorbed using the fresh MEA. When the resin was regenerated by water at 60 °C, the MEA regenerated by this resin was able to absorb CO₂, and the CO₂ absorbed by the regenerated MEA occupies 52.3% of that absorbed using the fresh MEA. Two more cycles were run in which the resin was regenerated by water at 80 °C. In one cycle, the CO₂ absorbed by the regenerated MEA was 40% of that absorbed using the fresh MEA. In another, the CO₂ absorbed by the regenerated MEA is 26.5% of that absorbed using the fresh MEA. These results indicated that the resin can be regenerated by hot water at 60 and 80 °C, but only part of the resin can be regenerated. However, when temperatures were increased to 100 °C, repeatable results were obtained, as shown in Fig. 8. The percentages of CO₂ absorbed by the three cycles to that absorbed using the fresh MEA are 39.3%, 40% and 40.5%, respectively. These results indicated that the resin can be repeatedly regenerated by 100 °C water. The regenerated resin's ability to regenerate MEA is approximately 66.7% of fresh resin's. The loss of 33.3% of resin's ability to regenerating MEA maybe caused by the reaction of some free functional group with CO₂. The free functional groups in the A-830 are complex amines, including primary amine. The primary amine is able to react with CO₂ to form carbamate, which is probably not decomposed in water at 100 °C. Further investigation will be needed for a more detailed interpretation.

Table 1 CO₂ absorption capacity and the regeneration efficiency by A-830 resin

| Type of absorbent | CO ₂ absorption capacity, mmol CO ₂ /100ml solution | Regeneration efficiency, % |
|--------------------|---|----------------------------|
| MEA | 91.4 | 28.8 |
| MAE | 49.6 | 37.3 |
| TEA | 28.5 | 69.1 |
| NH ₄ OH | 148.6 | 18.7 |

Note: All the absorbents in the solution have the same weight concentration

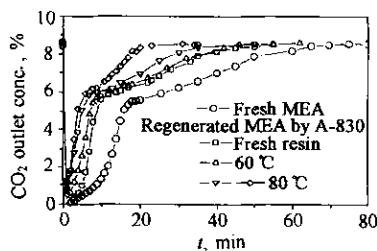


Fig.7 Capture of CO₂ by coupling MEA and A-830

(absorption: MEA: 1%, 200 ml; CO₂ inlet: 8.5%, 500 ml/min; temp.: 25 °C; MEA regeneration: A-830: 50 g; stirring speed: 400 r/min; time: 2h; resin regeneration: water: 100 ml; time: 2h)

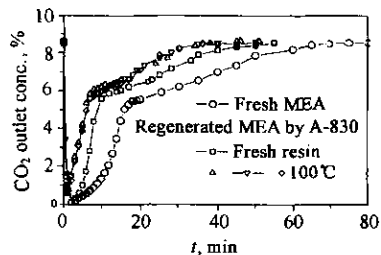


Fig.8 Sustainability of process for capture of CO₂

(absorption: MEA: 1%, 200 ml; CO₂ inlet: 8.5%, 500 ml/min; temp.: 25 °C; MEA regeneration: A-830: 50 g; stirring speed: 400 r/min; time: 2h; resin regeneration: water: 100 ml; time: 2h)

3 Conclusion

The present work shows that it is feasible to regenerate amines such as MEA, MAE, and TEA as well as ammonia after they absorb CO₂ from flue gas. A simulated MEA solution(20%) can be regenerated up to 52.3% by A-830. Also, it has been discovered that the resin can be regenerated by hot water. When the temperature is controlled at 100°C, the resin's regeneration ability will remain at 66.7% of fresh resin's regeneration ability. Future experiments will focus on seeking new resins to be regenerated by water at lower temperature.

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