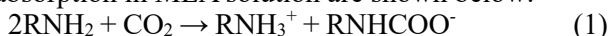


CO₂ desorption using ultrasound at low temperature from CO₂-loaded amine solution under pressure conditions

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1. Introduction

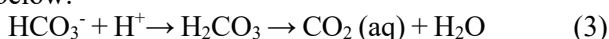
As the main greenhouse gas, carbon dioxide (CO₂) in the atmosphere would rise the global temperature, causing extreme weather and disasters. To reduce the concentration of atmospheric CO₂ and achieve the “carbon-neutral” goal, CCS (carbon dioxide capture and storage) technology which could recover pure CO₂ selectively from the exhaust gas of power plants and store it underground was gathering more attention. The chemical absorption method using amine solution as CO₂ absorbent is mainly applied for CO₂ recovery from exhaust gas in CCS process for low cost. Conventional chemical absorption method chose monoethanolamine (MEA) as the absorbent¹⁾. Reaction formulas of CO₂ absorption in MEA solution are shown below:



(R: C₂H₅O, RNH₂: MEA)

CO₂ is absorbed as both carbamate ion (RNHCOO⁻) and bicarbonate ion (HCO₃⁻). The CO₂ absorption rate and capacity are high for MEA, however, high temperature (> 110 °C) is necessary for desorbing the absorbed CO₂ from 4.9 M of MEA solution²⁾, which resulted in approximately 70-80 % of the operating cost for a CCS process³⁾, and more CO₂ generation for producing the extra heat energy. Therefore, a new method that could desorb CO₂ from CO₂-absorbed amine solution at low temperature must be developed.

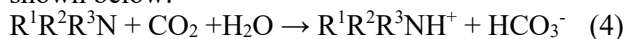
In this research, desorbing CO₂ from CO₂-absorbed amine solution by ultrasound at low temperature (20-25 °C) was studied. Ultrasound can desorb CO₂ (aq) as CO₂ (g) from amine solution from our previous studies⁴⁾. Thus, increasing the CO₂ (aq) state in CO₂-absorbed amine solution can enhance the CO₂ desorption efficiency of ultrasound. The equilibrium equation of CO₂ in solution is shown below:



HCO₃⁻ can transform to CO₂ (aq) easily by changing the solution pH, and when pH < 8.2, CO₂ (aq) would be the main species of CO₂ in solution⁵⁾. Thus, increasing the bicarbonate ion concentration and reducing the solution pH was effective for

increasing CO₂ (aq) in solution, and then CO₂ (g) can be desorbed continuously under ultrasound.

Tertiary amine, which only forms bicarbonate ion during CO₂ absorption, was chosen as the candidate sorbent in this research. The CO₂ absorption reaction formula of tertiary amine is shown below:



To decrease solution pH for increasing the state of CO₂ (aq) after CO₂ absorption, a tertiary amine, triethanolamine (TEA), which has low pK_a (7.85) was chosen. Moreover, CO₂ absorption under CO₂ pressure conditions of 0.1 and 0.5 MPa was applied to increase the CO₂ absorption amount to reduce the solution pH after absorption. And then, the CO₂ desorption ability of both MEA and TEA solution under low temperatures by ultrasound or stirring was evaluated and compared. To decide the best conditions for ultrasound CO₂ desorption, the relationships between ultrasound output power and CO₂ desorption amount were investigated. The desorption results were investigated when reached ultrasound power was 17 W in amine solution measured by calorimetric method here, and more detailed information will be shown in the presentation.

2. Experimental

TEA (Wako, 98 wt. %), MEA (Wako, 99 wt. %), and ion-exchange water were used to prepare the amine solution. 200 mL CO₂-absorbed TEA and MEA solution were prepared in a pressure vessel under 0.1 and 0.5 MPa CO₂ gas injection (99.99 %, Japan liquid carbon) for 18 hours with stirring at 750 rpm. The CO₂ absorption amount in the solution was determined from the weight change before and after the absorption. The change of solution pH value was detected by a pH meter (HM-30P, TOA DKK). All the absorption experiments were held at 20-25 °C.

CO₂ desorption experiments using ultrasound were performed using an ultrasound generator (Kaijo, TA-4021) and a submersible transducer (Kaijo, 28 kHz). The submersible transducer was placed at the bottom of a water-filled tank, and a flat-bottom flask containing 100 mL of CO₂-absorbed amine solution was set directly above the transducer at 4.8 cm. The irradiation time was 60 minutes, and the temperature was kept at 20-25 °C. CO₂ desorption using stirring

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was performed using a magnetic stirrer at 1500 rpm for 60 min under 20-25 °C using the same flask and solution for comparison. The weight change of the solution after the desorption was recorded. The desorption ratio (%) of CO₂ was calculated by the following formula:

$$\text{CO}_2 \text{ desorption ratio} = (w_b - w_a) / w_b \times 100 \% \quad (5)$$

w_b: solution weight before desorption

w_a: solution weight after desorption

3. Results and discussion

Figure 1 shows the CO₂ absorption amount of TEA and MEA solution under different CO₂ pressures. Increasing pressure promoted CO₂ absorption for both amine solution. Especially, the CO₂ absorption amount of TEA at 0.5 MPa increased significantly by 2.3 times than 0.1 MPa. Also, the absorption under pressure conditions successfully reduces the initial pH of each amine solution (TEA: 11.5, MEA: 12.2) to below 8.5, which is favorable for CO₂ (aq) state formation.

Desorption results of the CO₂-absorbed amine solution are shown in Fig. 2. For both TEA and MEA solution, the CO₂ desorption amount increased as CO₂ absorption pressure increased. When applying ultrasound to desorb CO₂ in CO₂-absorbed TEA solution, the CO₂ desorption ratio was 6.8 and 2.3 times higher than stirring for the solution absorbing CO₂ under 0.1 and 0.5 MPa relatively. Especially, the desorption ratio reached over 60 % when applied ultrasound for the solution absorbing CO₂ under 0.5 MPa. It is suggested that CO₂ (aq) was the main species in CO₂-absorbed TEA solution, and only ultrasound can significantly promote the desorption of CO₂ (aq) as CO₂ (g) in TEA solution under low temperature. On the other hand, the CO₂ desorption ratio of all the CO₂-absorbed MEA solution was under 20 %, which suggested that CO₂ was absorbed as RNHCOO⁻ in MEA solution, which was difficult for CO₂ desorption by stirring or ultrasound. Furthermore, when applied ultrasound for CO₂ desorption, the desorption ratio of TEA solution was 2.2 and 3.4 times higher than MEA solution for solution absorbing CO₂ under 0.1 and 0.5 MPa relatively. Thus, ultrasound was considered more favorable to desorb CO₂ for tertiary amine than primary amine at low temperature.

4. Conclusion

The CO₂ desorption ratio of TEA and MEA solution after 0.1 and 0.5 MPa CO₂ absorption was investigated in this research. Higher pressure resulted in higher absorption amount and lower pH for both amine solution. CO₂-absorbed TEA solution showed a significantly higher CO₂ desorption ratio by ultrasound (61 % for CO₂ absorbed TEA solution under 0.5 MPa) than stirring while CO₂-absorbed MEA solution showed a relative low desorption ratio

(less than 20 %) by either stirring or ultrasound. Thus, the utilization of ultrasound could efficiently promote CO₂ desorption for tertiary amine solution at low temperature when CO₂ was absorbed under pressure conditions.

Acknowledgment

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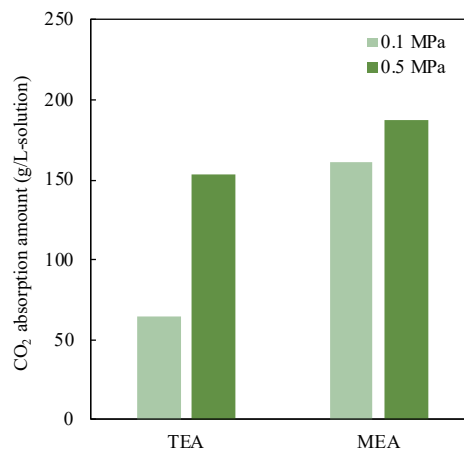


Fig. 1 CO₂ absorption amount of MEA and TEA solution under 0.1 and 0.5MPa at 20-25 °C

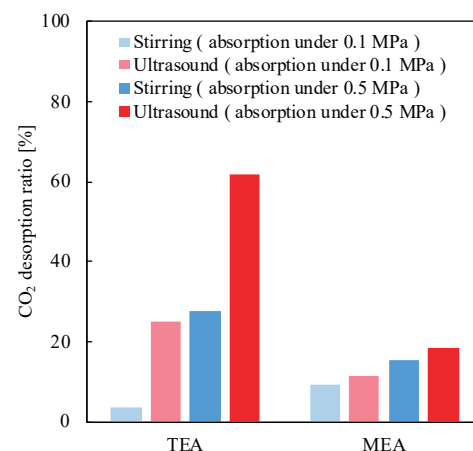


Fig. 2 CO₂ desorption ratio of CO₂-absorbed amine solution at each CO₂ absorption condition by stirring or ultrasound at 20-25 °C