

Desorption of CO₂ from a low concentration of monoethanolamine solution using calcium chloride under ultrasound irradiation

超音波照射と塩化カルシウムを用いた低濃度モノエタノールアミン溶液からのCO₂脱離

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1. Introduction

In several alkanolamines, aqueous monoethanolamine (MEA) has been used as an absorbent in CO₂ removal processes because MEA offers several advantages over other alkanolamines; those advantages include higher reactivity or lower cost of solvent. When CO₂ is absorbed into MEA solution, carbamate ion is generated as a following reaction,



Carbamate ion is also able to react with CO₂,
 $RNHCOO^- + 2H_2O + CO_2 \rightarrow 2HCO_3^- + RNH_3^+ \quad (2)$

However, heating (regeneration process) MEA to release CO₂ consumes large amounts of energy in the conventional method.

In our previous study, we investigated whether the application of ultrasound irradiation together with N₂ gas flow could facilitate CO₂ desorption from MEA solution.¹⁾ We found that the amount of energy required to release CO₂ from a low concentration of MEA solution (0.2 mol/l) at 25 °C using ultrasound irradiation was lower than that at 49 °C using stirrer at 1,500 rpm. However, the amount of CO₂ desorption from MEA solution was 24.8% of the total CO₂ absorbed in MEA solution. Thus, it was necessary to improve the efficiency of CO₂ desorption from MEA solution under ultrasound irradiation. It has been reported that the addition of calcium chloride (CaCl₂) into MEA solution (1 mol/l) can cause a highly efficient desorption of CO₂ from MEA (more than 90%) due to CO₂ being desorbed as CaCO₃ in the solution.²⁾ In our best knowledge, it has not been tested whether the desorption of CO₂ occurs efficiently from a low concentration of MEA solution as well using CaCl₂.

Therefore in this study, we investigated the effective desorption of CO₂ from a low concentration of MEA solution using CaCl₂ under stirring or ultrasound irradiation.

2. Experiment

In this experiment, desorption of CO₂ gas from MEA solution was investigated using an ultrasound

generator and transducer (200 W/ 20 kHz). The same experiment was conducted using stirrer (stirring speed 1,500 rpm) to compare with results obtained with ultrasound irradiation.

A low concentration of MEA solution (0.2 mol/l, 50 ml) was prepared using MEA (Wako) and ion-exchange water. A simulated gas (CO₂: N₂ = 10%: 90%) was injected into MEA solution at 200 ml/min flow rate under stirring (750 rpm) at 25 °C for 30 min. Then, CaCl₂ solution was added to the absorbed MEA solution (MEA: Ca²⁺ = 2: 1), and desorption experiment was conducted under ultrasound irradiation or stirring for 5 min. After each experiment, the mass of generated CaCO₃ was measured following filtration and drying. The amount of carbon in the solution after CaCO₃ synthesis was measured using a total carbon measurement system (TC). Structural analysis of synthesized CaCO₃ was conducted using X-ray diffraction (XRD) and shapes of the CaCO₃ particles were observed using scanning electron microscope (SEM).

3. Results and Discussions

We first investigated the basic property of a low concentration of MEA solution as an absorber of CO₂. **Figure 1** shows how the amount of absorbed CO₂ and pH in the MEA solution (0.2 mol/l) changes while it is bubbled with simulated gas (200 ml/min) and stirred (750 rpm) at 25 °C for 30 min. The decrease in the pH value indicates that CO₂ was absorbed into MEA solution. In this study, the amount of recovered CO₂ from MEA solution was evaluated by the total amount of CO₂ used to CaCO₃ and CO₂ desorbed as gas. The amount of CO₂ absorption and desorption in MEA were calculated by measuring the amount of carbon in the solution using TC. The amount of CO₂ converted to CaCO₃ by the application of CaCl₂ was calculated by following formula,

$$Y_{CO_2} = (M_{CaCO_3} / A_{CO_2}) \times 100, \quad (3)$$

where Y_{CO_2} (%) is the conversion rate of CO₂

absorbed in the MEA solution to CaCO_3 , M_{CaCO_3} (g) is the mass of CO_2 precipitated as CaCO_3 , and A_{CO_2} (g) is the mass of CO_2 absorbed in the MEA solution before CO_2 recovery treatments using stirrer or ultrasound irradiation. Also, the mass of degassed CO_2 (D_{CO_2}) was calculated;

$$D_{\text{CO}_2} = A_{\text{CO}_2} - M_{\text{CaCO}_3} - M_{\text{CO}_2} \quad (4)$$

M_{CO_2} (g) is the mass of CO_2 present in the solution after treatment.

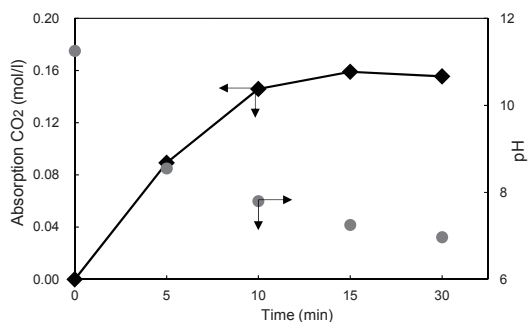


Fig. 1 Changes in the amount of absorbed CO_2 and pH in the MEA solution (0.2 mol/l) during the application of simulated gas (200 ml/min) with stirring (750 rpm) at 25 °C for 30 min.

Figure 2 shows the weight balance of CO_2 after the treatment of the MEA- CaCl_2 solution using ultrasound irradiation or stirring for 5 min at 25 °C. We considered following three forms that CO_2 in the MEA has possibly become after ultrasound or stirrer treatment; 1) CaCO_3 , 2) CO_2 gas, and 3) CO_2 stayed in MEA solutions as RNHCOO^- and HCO_3^- . We found that 63.2% of CO_2 absorbed in 0.2 mol/l MEA solution was desorbed under ultrasound irradiation and 56.8% of that was desorbed as CaCO_3 . This rate was higher than the rate of desorption under stirrer at 95 °C in the previous study.¹⁾ Likewise, in this study, 44.7% of CO_2 absorbed in 0.2 mol/l MEA solution was desorbed using stirrer and 30.2% of CO_2 absorbed was desorbed as CaCO_3 . Both percentages are lower than those with ultrasound irradiation.

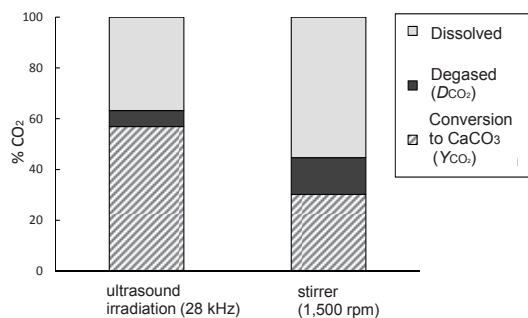


Fig. 2 The balance of CO_2 in solution after experiments with 5 min of ultrasound irradiation (28 kHz) or stirrer (1,500 rpm).

Figure 3 shows XRD patterns of CaCO_3 after ultrasound irradiation or stirring at 25 °C for 5 min. CaCO_3 recovered by ultrasound irradiation was mainly calcite whereas, CaCO_3 recovered by stirring was mainly vaterite. It is known that CaCO_3 forms vaterite at first by the reaction of Ca^{2+} with CO_3^{2-} . Further reaction changes its structure from vaterite to calcite. SEM observation showed that the particle size synthesized by ultrasound irradiation was smaller than that synthesized by stirrer. The difference in their particle sizes may reflect the difference in their structure.

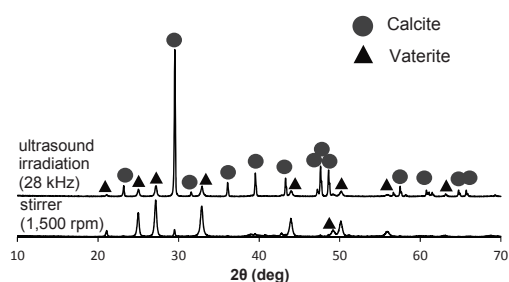


Fig. 3 XRD patterns of CaCO_3 after treating MEA solution with ultrasound or stirrer at 25 °C for 5 min.

4. Conclusion

In this experiment, CaCl_2 was added to a low concentration of MEA solution (0.2 mol/l) to increase the amount of CO_2 desorption at low temperature. The rate of CO_2 desorption from the MEA solution was compared between experiments performed with ultrasound irradiation and stirring. 56.8% of CO_2 absorbed in MEA solution was recovered as CaCO_3 under ultrasound irradiation whereas 30.2% of absorbed CO_2 was recovered as CaCO_3 under stirrer. XRD analysis revealed that the structure of recovered CaCO_3 differ between two treatment methods, indicating mainly calcite structure for ultrasound irradiation in contrast to vaterite structure for stirring. Furthermore, the particle size of CaCO_3 synthesized by ultrasound irradiation was smaller than that synthesized by stirring, likely reflecting the difference in their structure. In the future, we will deepen the understanding of the effect of ultrasound irradiation in the CO_2 desorption process by varying MEA- CaCl_2 solution conditions.

5. References

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