3Pa4-3

Desorption of carbon dioxide from monoethanolamine solution by the addition of calcium chloride under ultrasound irradiation and characteristic evaluation of generated calcium carbonate

超音波と塩化カルシウムを用いた MEA 溶液からの CO_2 脱離および生成した $CaCO_3$ の特性評価

Yuya Kitamura†, Hirokazu Okawa, Takahiro Kato, and Katsuyasu Sugawara (Akita Univ.)
北村 優弥†，大川 浩一，加藤 貴宏，菅原 勝康 (秋田大院 理工)

1. Introduction

Exhaust gas from thermal power plant is a problem because CO_2 in the exhaust gas relates to global warming. Currently, carbon dioxide and storage (CCS) techniques are expected as a global warming measure. Monoethanolamine (MEA) has been used as an absorbent for removing CO_2 because MEA offers several advantages over other alkanolamines; high CO_2 absorption amount per unit weight and high CO_2 absorption rate [1]. However, desorption of CO_2 from the MEA solution requires a high temperature of 120°C. Chemical species of CO_2 in an aqueous solution chang to dissolved CO_2 gas (CO_2(aq) and H_2CO_3), HCO_3^- and CO_3^{2-} by changing of the solution pH (Fig. 1 and Eq. (1)–(3)).

$$HCO_3^- \rightleftarrows CO_3^{2-} + H^+ \quad (Ka_1 = 4.7 \times 10^{-11},\ pKa_1 = 10.3) \tag{1}$$

$$H_2CO_3 \rightleftarrows HCO_3^- + H^+ \quad (Ka_2 = 2.8 \times 10^{-7},\ pKa_2 = 6.4) \tag{2}$$

$$CO_2(aq) + H_2O \rightleftarrows H_2CO_3 \quad (K = 1.7 \times 10^{-3}) \tag{3}$$

Fujiwara et al reported that deaerating action of ultrasound is available for desorption of CO_2(g) from CO_2(aq) in low concentration of MEA solution (0.2 M) at low temperature of 25°C [2]. However, ultrasound treatment cannot easily desorb CO_2(g) at pH >8.2. It is because the main species of CO_2 at that pH value are HCO_3^- and CO_3^{2-} (**Fig. 1**). In previous study, we successfully increased desorption amount of CO_2(g) from the MEA solution of pH 8.2 by the increase of CO_2(aq) concentration come from the decrease of pH from 8.2 using ultrasound (28 kHz) and calcium chloride ($CaCl_2$) solution [3]. Compared with the desorption amount of CO_2(g) from the MEA solution using ultrasound without the addition of $CaCl_2$, the desorption amount treated by both using ultrasound and $CaCl_2$ showed higher value. We consider that the desorption amount of CO_2(g) was increased by the shift in the equilibrium of CO_2 toward the of the increase of CO_2(aq) ($HCO_3^- + H^+ \rightarrow H_2CO_3 \rightarrow CO_2(aq) + H_2O$) owing to a decrease in pH with an increase in the H^+ concentration in the MEA solution by the synthesis reaction of calcium carbonate ($CaCO_3$) described by Eq. (4).

$$Ca^{2+} + HCO_3^- \rightarrow CaCO_3 + H^+ \tag{4}$$

The desorption amount of CO_2(g) using ultrasound and $CaCl_2$ was higher than that using stirring and $CaCl_2$. In addition, the $CaCO_3$ particles generated after the treatment for 10 min using ultrasound were smaller than using stirring. The particle size using ultrasound was <3 µm, on the other hand, the particles gained using stirring were mixture of small size of 3 µm and large size of 6 µm. The yield of $CaCO_3$ was about 90% in both cases of ultrasound and stirring. Therefore, we consider that ultrasound promotes the nuclear formation of $CaCO_3$ and it increases CO_2(g) desorption amount from MEA solution at the early stages compared with stirring. In this study, we investigated the desorption ratio of CO_2 and the changes of $CaCO_3$ yield by the elapsed time of ultrasound irradiation and stirring. Characteristic of generated $CaCO_3$ was evaluated.

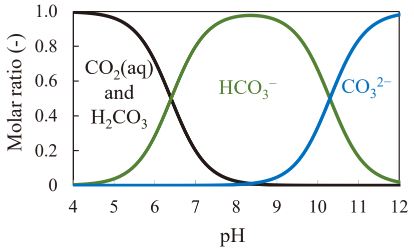

Fig. 1 Relationship between chemical speciation of CO_2 and pH in solution at 25 °C.

2. Experiment

CO_2-absorbed MEA solution (MEA-CO_2) was prepared in a pressure vessel with 0.2 M MEA solution under the condition of 0.5 MPa CO_2 gas for 20 min with stirring at 750 rpm. Then, the MEA-CO_2 solution at pH 8.2 was prepared by stirring (800 rpm) after the standing for approximately 2 h under ambient pressure. The absorption amount (mM) of CO_2 in the MEA

---

okawa@mine.akita-u ac.jp (H. Okawa)

solution was determined from the change in the weight of the MEA solution before and after CO_2 absorption. The desorption of CO_2 from the MEA-CO_2 solution was performed by ultrasound irradiation using an ultrasound generator (Kaijo, TA-4021) and a submersible transducer (28 kHz) or by stirring (1500 rpm) using a magnetic stirrer. A submersible transducer was placed at the bottom of a water-filled tank, and the flat-bottom flask containing MEA-CO_2 solution (30 mL) was placed directly above the transducer. The $CaCl_2$ solution (30 mL, 5.2 mM) or ion-exchanged water (30 mL) was added to the MEA-CO_2 solution (30 mL, 110 mM CO_2). Then, ultrasound irradiation or stirring were performed for 1, 5, and 10 min. The solution temperature during irradiation maintained at 25°C. The desorption ratio (%) of CO_2 gas was determined from the weight loss of the mixed solution (60 mL) after the desorption experiment. The yield of $CaCO_3$(%) was calculated from the recovered amount (mM) of $CaCO_3$ and the added amount (mM) of Ca^{2+}. The size of generated $CaCO_3$ particles was investigated using scanning electron microscopy (SEM; Hitachi TM-1000).

3. Results and discussion

First, ion-exchanged water without $CaCl_2$ was added into the MEA-CO_2 solution followed by stirring or ultrasound irradiation for 10 min. The desorption ratio of CO_2(g) using stirring for 1, 5 and 10 min was 1.0, 1.2 and 1.2%, respectively (**Fig. 2**). And, the desorption ratio of CO_2(g) using ultrasound for 1, 5 and 10 min was 1.8, 1.9 and 2.2%, respectively. The value of desorption ratio of CO_2(g) using ultrasound for 1 min was almost twice than that using stirring. The desorption ratio of CO_2(g) using ultrasound and stirring did not change anymore after the treatment time of 1 min. Next, $CaCl_2$ solution was added into the MEA-CO_2 solution followed by stirring or ultrasound irradiation for 10 min. The desorption ratio of CO_2(g) using stirring for 1, 5, and 10 min was 5.3, 7.0, and 7.2%, respectively. And the desorption ratio of CO_2(g) using ultrasound for 1, 5, and 10 min was 8.3, 9.3 and 9.8%, respectively. The desorption ratio of CO_2(g) using ultrasound for 1 min was higher than that using stirring. Compared to the CO_2(g) desorption ratio without the $CaCl_2$ addition, the desorption ratio increased approximately 6.5% at ultrasound condition and approximately 4.3% at stirring condition. Besides, the change of CO_2 desorption ratio from 1 min to 10 min was 1.8% (5.3%→7.2%) at stirring condition and 1.5% (8.3%→9.8%) at ultrasound irradiation condition. The yield of $CaCO_3$, 89%, using ultrasound for 1 min was higher than that of 78% using stirring for 1 min. The yield of $CaCO_3$ at 10 min, ultrasound and stirring were 93% and 89%, respectively (**Fig. 3**). $CaCO_3$ particles synthesized using stirring for 1 min was observed by SEM, and the primary particles of 2–4 μm aggregated and formed secondary particles. When ultrasound used for $CaCO_3$ particles generation for 1 min, the almost primary particles were ≤1 μm. Normally, the lower ultrasound frequency such as 28 kHz has a stronger physical effect [4]. Hence, we consider that $CaCO_3$ particles were rapidly generated by the mixing of MEA and $CaCl_2$ solution using ultrasound. And H^+ concentration increased rapidly, that enhances the shifts of the CO_2 equilibrium in the direction of the CO_2(aq) increase. We can conclude that the ultrasound can desorb the CO_2 gas from the MEA solution more efficiently than stirring and the application of ultrasound makes possible to desorb CO_2 quickly.

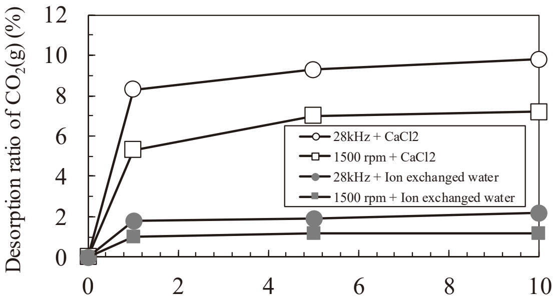

Fig. 2 Desorption ratio of CO_2 from MEA solution at pH 8.2 using ultrasound and stirring with and without the $CaCl_2$ addition.

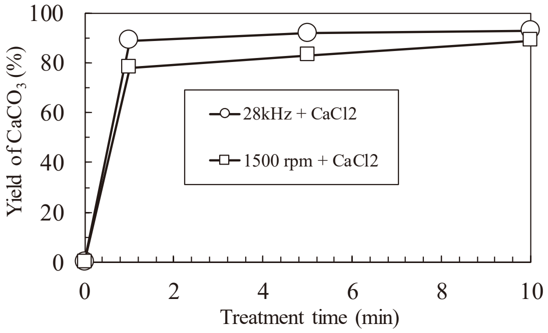

Fig. 3 Changes of $CaCO_3$ yield by elapsed time under two conditions; ultrasound+$CaCl_2$ and stirring + $CaCl_2$.

References

[1] K. Goto et al.: Int. J. Greenhouse Gas Contr., **5** (2011) 1214.
[2] T. Fujiwara and H. Okawa et al.: J. of MMIJ, **135**(1) (2019) 1.
[3] Y. Kitamura and H. Okawa et al.: Jpn. J. Appl. Phys. **59** (2020) SKKD08.
[4] T. Nakamura and H. Okawa et al., Jpn. J. Appl. Phys. **49**, 07HE11 (2010).