Utilization of tertiary amine solutions and ultrasound irradiation for CO₂ desorption at low temperature in a process of CCS

CCSにおける二酸化炭素の低温脱離を目的とした第三級アミン溶液と超音波照射の利用

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1. Introduction

CCS (carbon dioxide capture and storage) is a technology of recovering carbon dioxide (CO₂) from exhaust gas of fired power plant and storing it in underground. Monoethanolamine (MEA) is mainly used as a chemical absorbent in CCS technology. MEA has several advantages compared to other alkanolamines such as high CO₂ absorption amount per unit weight and high CO₂ absorption rate [1]. MEA reacts with CO₂ and carbamate ion (RNHCOO⁻) is generated according to Eq. (1). And HCO₃⁻ is also generated according to Eq. (2).

2RNH₂ + CO₂ → RNH₃⁺ + RNHCOO⁻    (1)

RNH₂ + CO₂ + H₂O → RNH₃⁺ + HCO₃⁻    (2)

(R: C₂H₅O, RNH₂: MEA)

After the CO₂ absorption from exhaust gas using MEA, CO₂ is recovered from the MEA solution as pure CO₂ gas which is stored in underground.

However, the drawback of MEA utilization is high cost because desorption of CO₂ from MEA solution (4.9M) requires high temperature of >110°C [2]. Therefore, it is necessary to find out new method to desorb CO₂ from amine solution at low temperature.

We have been focussed on ultrasound to desorb CO₂ from CO₂ adsorbed MEA solution at low temperature. We clarified that deaerating action of ultrasound is available for desorption of CO₂(g) from CO₂(aq) in low concentration, 0.2M, of MEA solution at 25°C [3]. We also clarified that CO₂ desorption by ultrasound works at pH <8.2 because only CO₂(aq), the main species of CO₂ at these pH vaues, can be desorbed by ultrasound (Fig. 1).

In this study, we tried to use tertiary amine solution instead of primary amine, MEA, in the presence of ultrasound. Normally, tertiary amine solution is lower CO₂ absorption rate than MEA solution. However, CO₂ absorption capacity, CO₂ mole per one mole of amine, of tertiary amine is higher than that of primary amine.

CO₂ absorption reaction using tertiary amine solution is shown as Eq. (3).

R⁴⁺R²R³⁻N + CO₂ + H₂O → R⁴⁺R²R³NH⁺ + HCO₃⁻    (3)

Ultrasound can desorb CO₂(aq) as CO₂(g) from amine solution. However, direct desorption of CO₂ from CO₃²⁻, HCO₃⁻, and RNHCOO⁻ is difficult for ultrasound. We consider that CO₂(g) can be desorbed continuously by the shift in the equilibrium of CO₂ toward the CO₂(aq) (HCO₃⁻ + H⁺ → H₂CO₃ → CO₂(aq) + H₂O). Therefore, we consider that dissociation constant (pKa) of tertiary amine solution regulates CO₂(g) desorption amount by ultrasound irradiation. Thus, we investigated the influence of pKa of tertiary amine on CO₂ desorption using ultrasound irradiation at low temperature. In this study, we used two tertiary amine solutions, triethanolamine (TEA) and N-Methyldiethanolamine (MDEA), which are different value of pKa, 7.85 (TEA) and 8.65 (MDEA) [4].

2. Experiment

CO₂-absorbed TEA solution (TEA-CO₂) and CO₂-absorbed MDEA solution (MDEA-CO₂) were prepared in a pressure vessel with 5.0 M tertiary amine solution (TEA or MDEA) under the condition of 0.5 MPa CO₂ gas for 12 h with stirring at 750 rpm. The absorption amount of CO₂ in the amine solution was determined from the change in the weight of amine solution before and after CO₂ absorption. The desorption of CO₂ from the CO₂ absorbed amine solution was performed by ultrasound irradiation using an ultrasound generator (Kaijo, TA-4021) and a submersible transducer (28 kHz). A submersible transducer was placed at the bottom of a water-filled tank, and the flat-bottom flask containing TEA-CO₂ solution or MDEA-CO₂ solution (100 mL) was placed directly above the transducer. These solutions were irradiated by ultrasound for 15min at 20-25°C. The reached power from transducer to the solution in the flask was 12W by calorimetrically method. The

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desorption ratio (%) of CO₂ gas was determined from the weight loss of the solution after the desorption experiment.

3. Results and discussion

Fig.2 shows CO₂ absorption amount of TEA and MDEA solution and the value was 154 g/L and 207 g/L, respectively. MDEA, which is higher pKa value, showed higher CO₂ absorption amount than TEA. Fig.3 shows changes of CO₂ desorption amount by irradiation time of ultrasound. CO₂ desorption amount from TEA and MDEA solution was 71g/L and 36g/L, respectively. TEA, which is lower pKa value, shows lower CO₂ absorption amount but shows higher CO₂ desorption amount. CO₂ desorption ratio was calculated by following formula.

\[
\text{CO₂ desorption ratio (\%) = \left( \frac{\text{CO₂ desorption amount}}{\text{CO₂ absorption amount}} \right) × 100.}
\]

CO₂ desorption ratio of TEA and MDEA is 46% and 17%, respectively. TEA can desorb almost half amount of CO₂ absorbed. From this result, the ultrasound can desorb CO₂ gas from TEA solution more efficiently than from MDEA solution. The difference of CO₂ desorption amount of TEA and MDEA solution may come from the difference of pH value of each solution. Fig.4 shows changes of pH value of each solution at CO₂ desorption process using ultrasound irradiation for 15 min. Before the ultrasound irradiation (0 min), TEA, which is lower pKa value, shows lower pH value than MDEA. The lower pH increases molar ratio of CO₂(aq) (Fig.1). Ultrasound can desorb CO₂(aq) as CO₂(g) from amine solution. Therefore, CO₂ desorption amount increased even at low temperature using lower pKa tertiary amine solution and ultrasound irradiation.

Conclusion

The tertiary amine solution, which has lower pKa value, is more effective on CO₂ desorption combined with ultrasound irradiation. TEA shows high CO₂ desorption ratio of 46% for 15 min irradiation even at low temperature.

References