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Effect of bed height on the carbon dioxide capture by carbonation/regeneration cyclic operations using dry potassium-based sorbents

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Abstract−The effect of bed height on CO_2 capture was investigated by carbonation/regeneration cyclic operations using a bubbling fluidized bed reactor. We used a potassium-based solid sorbent, SorbKX35T5 which was manufactured by the Korea Electric Power Research Institute. The sorbent consists of 35% K_2CO_3 for absorption and 65% supporters for mechanical strength. We used a fluidized bed reactor with an inner diameter of 0.05 m and a height of 0.8 m which was made of quartz and placed inside of a furnace. The operating temperatures were fixed at 70 °C and 150 °C for carbonation and regeneration, respectively. The carbonation/regeneration cyclic operations were performed three times at four different L/D (length vs diameter) ratios such as one, two, three, and four. The amount of CO_2 captured was the most when L/D ratio was one, while the period of maintaining 100% CO_2 removal was the longest as 6 minutes when L/D ratio was three. At each cycle, CO_2 sorption capacity (g CO_2/g sorbent) was decreased as L/D ratio was increased. The results obtained in this study can be applied to design and operate a large scale CO_2 capture process composed of two fluidized bed reactors.

Key words: Solid Sorbent, Fluidized Bed Reactor, CO_2 Capture, Carbonation/Regeneration, Bed Height

INTRODUCTION

The concentration of CO_2 in the earth's atmosphere has been increased by combusting fossil fuels to generate electricity in power plants. In order to reduce net CO_2 emissions into the atmosphere, several options have been suggested, which are reducing energy consumption by increasing the efficiency of energy conversion, switching to less carbon intense fuels, and using renewable energies. These options, however, may not be enough to mitigate global warming in the future, so the technology of CO_2 capture and storage has been recently considered as an imminent and important option for mitigating global warming [1].

Several methods have been developed for CO_2 capture such as wet absorption, adsorption, membrane separation, and cryogenic separation. However, these methods have been faced on the limits of cost and energy required to treat the massive flue gas streams from fossil fuel-fired power plants. Recently, CO_2 chemical absorption using dry regenerable solid sorbents has been studied as an innovative concept for CO_2 recovery [2-15]. CO_2 is efficiently removed from the flue gas stream by reacting with solid sorbents while regeneration produces an off-gas containing only CO_2 and H_2O. The condensation of an off-gas generates highly pure CO_2, which is suitable for chemical feed stock or sequestration. CO_2 capture with a solid sorbent is cost-effective since solid sorbents are made of cheap alkali metals.

The CO_2 capture process with a solid sorbent generally consists of two reactors such as carbonation reactor and regeneration reactor. Using sodium-based solid sorbent, several researches have been executed to reveal both carbonation and regeneration reaction kinetics [6,12], to investigate effects of operating variables on CO_2 removal [3,11,13], and to test solid performance by continuous operation [7,8]. Among several alkali and alkali earth metals for CO_2 absorption, Lee et al. [3] reported that the potassium carbonate showed higher total CO_2 capture capacity than the sodium carbonate at the same operating conditions. And several researches have been performed using potassium-based solid sorbent to find out optimal compositions of the sorbent [4], effects of operating variables on CO_2 removal [10], and the performance of the sorbent by continuous operation [14,15]. However, the reaction characteristics of the potassium-based solid sorbent were not completely identified for some operating variables such as regeneration temperature, gas residence time, etc.

The present work attempts to study the CO_2 capture characteristics and performance of a potassium-based solid sorbent, SorbKX35T5, in a bubbling fluidized bed reactor before designing and operating a large scale CO_2 capture process with two interconnected fluidized bed reactors. The effect of both H_2O pretreatment of solid sorbent and temperature control in the fluidized bed reactor on CO_2 removal was investigated in our previous paper [10]. The present study attempts to examine the effect of bed height on the CO_2 capture characteristics and performance of a potassium-based solid sorbent, SorbKX35T5, in a bubbling fluidized bed reactor.

EXPERIMENTAL

1. Material and Apparatus

Fig. 1 shows the schematic diagram of the experimental apparatus including a bubbling fluidized bed reactor [10]. The apparatus consists of a gas injection part, reactor, gas post-treatment part, and gas analyzer. A reactor with an inner diameter of 0.05 m and a height of 0.8 m was made of quartz and placed inside of a furnace. The

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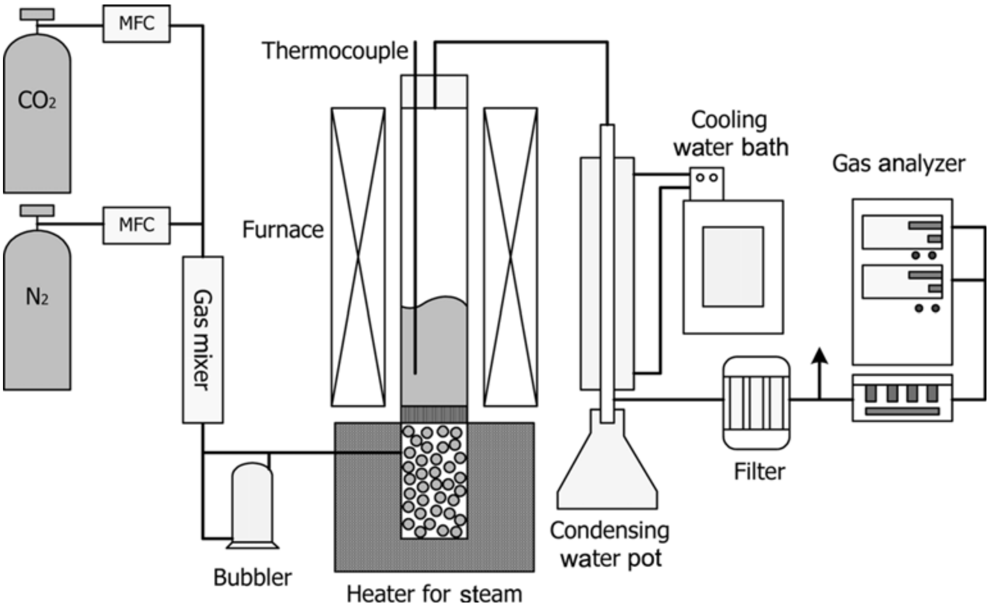

Fig. 1. Schematic diagram of experimental apparatus used in this study.

reactor temperature was controlled by a furnace and a temperature controller and was measured by thermocouples fitted in the reactor. Each gas flow was quantitatively controlled with a mass flow controller (Brooks, Japan) and then provided to the reactor. Product gases of the reactor were analyzed by a gas analyzer (ABB, USA) every 10 s.

The solid sorbent, SorbKX35T5, used in this study was provided by the Korea Electric Power Research Institute (KEPRI). It consists of 35% K_2CO_3 for absorption and 65% supporters for mechanical strength. SorbKX35T5 has a 0.31 cm^3/g of pore volume, 215 Å of pore diameter, 0.91 g/cm^3 of bulk density, 0.21% of porosity, and 38.48 m^2/g of BET surface area. Highly pure N_2 and CO_2 were supplied by the Special Gas Company (Republic of Korea).

2. Procedure

To simulate real flue gas composition, a gas mixture of CO_2 10%, N_2 77.8%, and H_2O 12.2% was provided. The H_2O needed for carbonation was fed by passing the CO_2 and N_2 through a temperature controlled gas bubbler, and the feed line was heated to avoid H_2O condensation. The bubbler product was assumed to be saturated with H_2O, and this was confirmed by measuring the relative humidity. Regeneration was carried out at 150 °C in N_2. For both carbonation and regeneration, gas velocity was set to 0.03 m/s. To examine the effect of bed height on CO_2 removal, we varied the mass of the sorbents in the reactor like 89.3 g, 178.6 g, 267.9 g, and 357.1 g in order to set L/D (Length vs. Diameter) ratio becomes 1, 2, 3, and 4, corresponding to gas residence time of 1.7, 3.3, 5, and, 6.7 s, respectively.

RESULTS AND DISCUSSION

The reaction using potassium-based solid sorbents for the CO_2 capture is as follows:

$$K_2CO_3+CO_2+H_2O \leftrightarrow 2KHCO_3. \quad (1)$$

The reaction is reversible and the forward reaction is highly exothermic, so heat control will be an important factor in the real commercial process. Thus, a fluidized-bed reactor can be a good solution for this process [16].

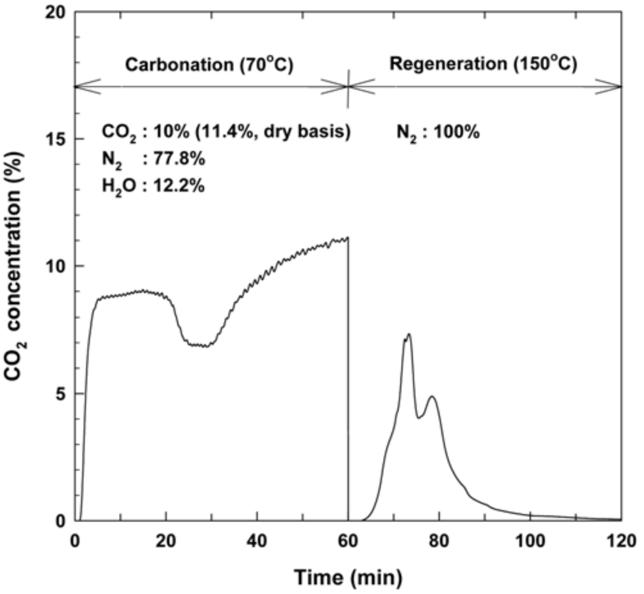

Fig. 2. CO_2 concentration during carbonation/regeneration cycle (L/D ratio of 1).

Fig. 2 shows CO_2 concentration (dry basis) changes during carbonation and regeneration reactions using SorbKX35T5 with L/D ratio of 1 in a bubbling fluidized bed reactor. Carbonation was carried out at 70 °C in 10% CO_2, 77.8% N_2, and 12.2% H_2O, while regeneration was carried out at 150 °C in N_2. An initial CO_2 concentration of 0%, corresponding to 100% CO_2 removal, was maintained for about 1 min and then increased abruptly to about 9% and maintained for about 20 min. After 20 min from the beginning of carbonation, the CO_2 concentration decreased suddenly to about 7%

and maintained for about 10 min and then increased slowly during the rest of carbonation reaction. The sudden decrease of the CO_2 concentration at 20 min from the beginning of carbonation was caused by the amount of H_2O content of the sorbent. When 125 g of sorbent was put into the reactor, 20 min H_2O pretreatment was sufficient for reactivity and CO_2 removal in the initial stage [10]. It is verified that H_2O in the gas which does not involve in the reaction increased H_2O content of the sorbent during 20 min in the initial stage.

Fig. 3 shows CO_2 removal in the carbonation reaction at the 1st cycle according to each L/D ratio. As L/D ratio increased, 100%

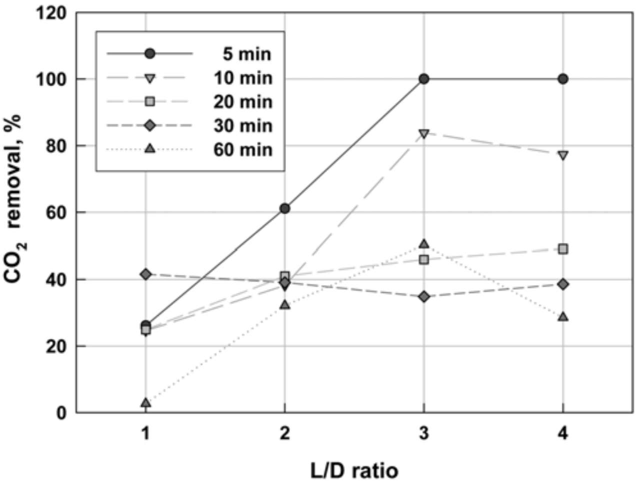

Fig. 3. CO_2 removal in the carbonation reaction at the 1st cycle according to each L/D ratio.

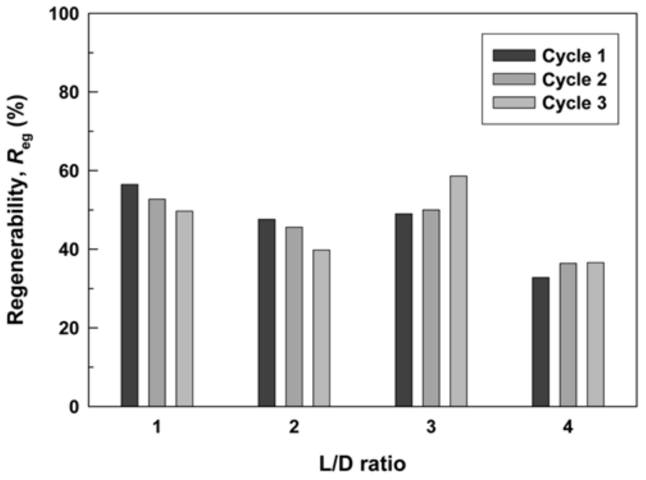

Fig. 4. Regenerability of each cycle according to L/D ratio.

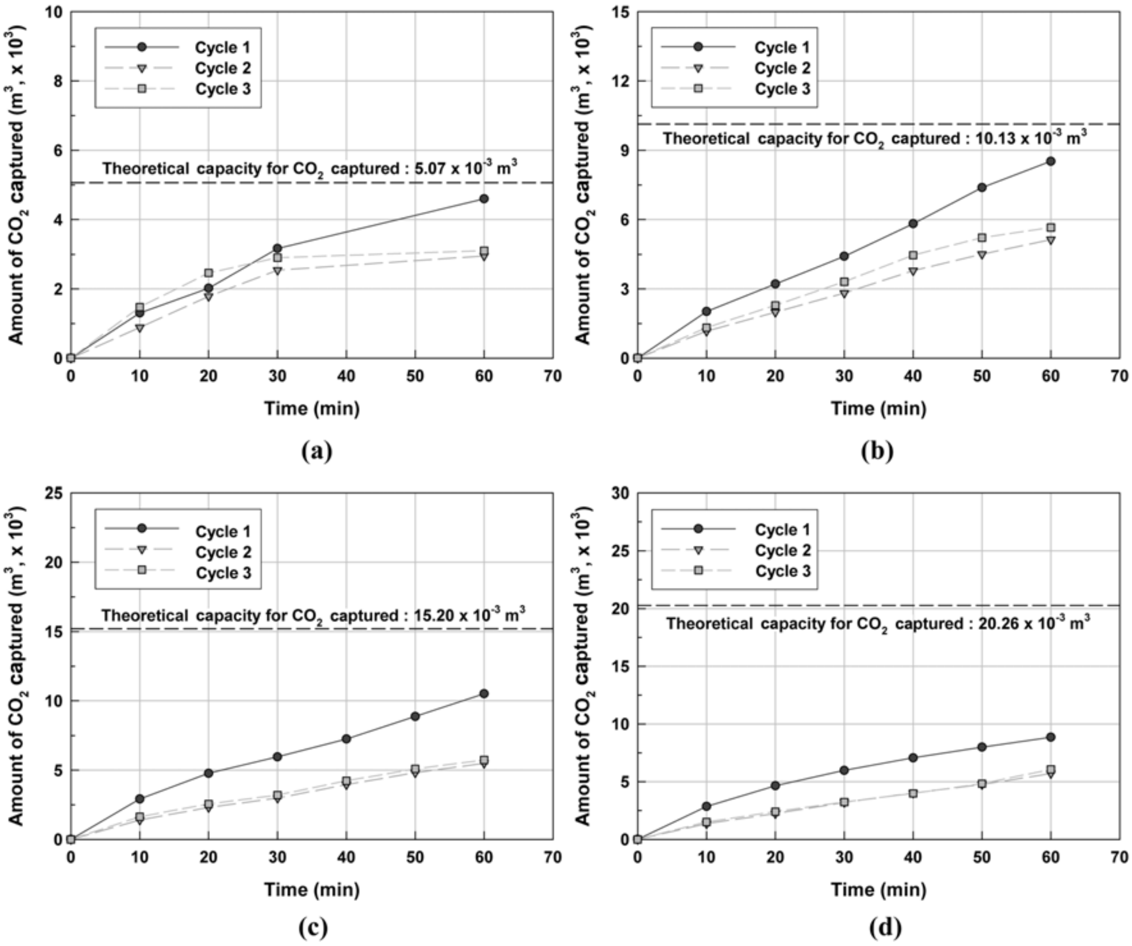

Fig. 5. Total amount of CO_2 captured for each cycle (a: L/D ratio of 1, b: L/D ratio of 2, c: L/D ratio of 3, d: L/D ratio of 4).

CO_2 removal period in the beginning of the reaction also increased. For L/D ratio of 3 and 4, initial CO_2 removal of 100% was maintained for more than 5 min. Also, L/D ratio of 3 showed the highest CO_2 removal during 1 hour among other L/D ratios. In Fig. 4, the regenerability, R_{rg} (%), of each cycle according to L/D ratio was shown, which is expressed as follows:

$$R_{rg}(\%) = \frac{\text{The amount of } CO_2 \text{ regenerated}}{\text{The amount of } CO_2 \text{ captured}} \times 100. \qquad (2)$$

The regeneration at each cycle for every L/D ratio was performed at 150 °C and R_{rg} was less than 60% for all cases. Lee et al. [4] reported $KHCO_3$ could be completely regenerated into K_2CO_3 at over 150 °C from fixed bed experimental results. However, R_{rg} of SorbKX35T5 at 150 °C in N_2 for 1 hour was not complete in a bubbling fluidized bed reactor in this study.

Fig. 5 shows the amount of CO_2 captured for each cycle at L/D ratio of 1, 2, 3, and 4. For every L/D ratio, the amount of CO_2 captured decreased as the number of cycle increased because of the incomplete regeneration of the sorbent as mentioned above. For L/D ratio of 1, the amount of CO_2 captured converged to some constant value as the number of cycle increased. However, the amount of CO_2 captured still increased after 60 min at 3rd cycle for L/D ratio of 2, 3, and 4. This indicated that the amount of CO_2 captured had risen if the carbonation reaction was maintained more than 60 min. For the 1st cycle at each L/D ratio, the amount of CO_2 captured increased until L/D ratio was 3 while that of CO_2 captured rather decreased at L/D ratio of 4. This implied that the gas residence time of 5 s, corresponding to L/D ratio of 3, was sufficient to increase the total amount of CO_2 captured. In Fig. 6, the fractional CO_2 removal, F_r, was shown, which was expressed as follows:

$$F_r = \frac{\text{The amount of } CO_2 \text{ captured for reaction time}}{\text{The theoretical } CO_2 \text{ capture capacity}}. \qquad (3)$$

F_r steadily decreased as L/D ratio increased, while the total amount of CO_2 captured increased as L/D ratio increased until L/D ratio was 3. F_r also decreased as the number of cycles increased because of the incomplete regeneration of the sorbent. Even if the gas residence time increased according to the increase of L/D ratio, F_r steadily decreased since both the contact time and the contact area between gas and solid decreased as bed height increased. Clift and Grace [17] reported that mean bubble diameters in bed increased according to a distance from the distributor and mean bubble velocity increased as mean bubble diameters increased.

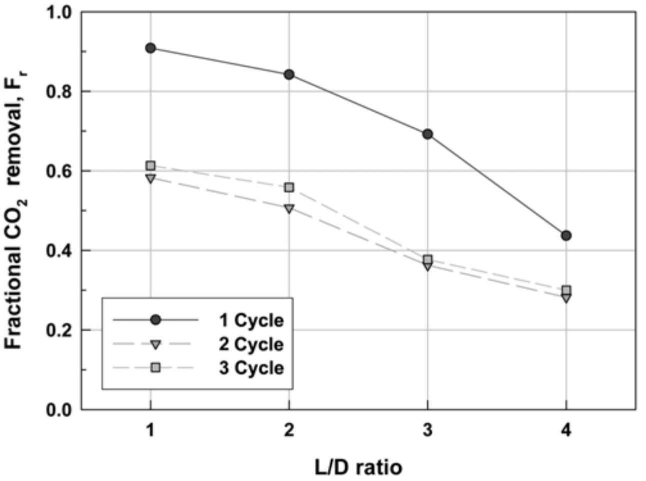

Fig. 6. Fractional CO_2 removal at each cycle according to L/D ratio.

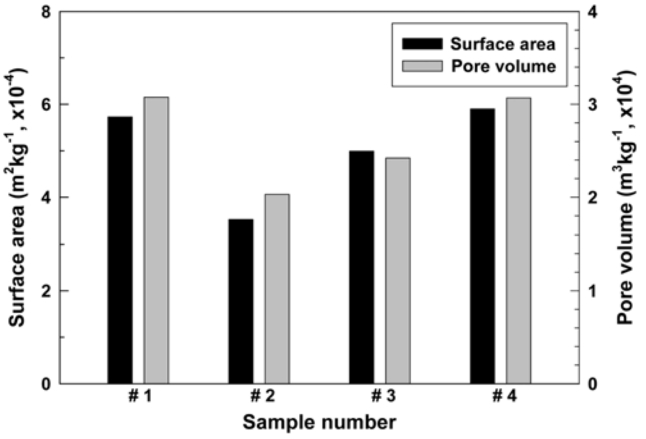

Fig. 7. Changes of surface area and pore volume after each reaction cycle (#1: fresh, #2: F_r=0.92 after carbonation, #3: regeneration at 150 °C in N_2 for 1 hour, #4: regeneration at 300 °C in N_2 for 1 hour).

SorbKX35T5 is a porous sorbent manufactured to enhance water sorption. The surface area and pore volume of fresh SorbKX35T5 are 5.73×10^4 m²/kg and 3.08×10^{-4} m³/kg, respectively, as shown in Fig. 7. When F_r was 0.92, the surface area and pore volume decreased to 3.52×10^4 m²/kg and 2.03×10^{-4} m³/kg, respectively. Regeneration at 150 °C in N_2 for 1 hour increased both surface area and pore volume to 5.0×10^4 m²/kg and 2.42×10^{-4} m²/kg, lower than the initial values, which indicates incomplete regeneration. Little change in pore size and no structural deterioration were observed in any case. The results of the BET study were consistent with those in the CO_2 removal experiment. When the regeneration was performed at 300 °C in N_2 for 1 hour, both surface area and pore volume were fully recovered to the fresh sorbent. In general, it is not necessary to fully regenerate the sorbent in a practical use, but a more detailed and systematic investigation should be carried out to fully understand the carbonation/regeneration mechanism in order to improve the CO_2 removal efficiency with potassium-based solid sorbent.

CONCLUSIONS

The effect of bed height on CO_2 capture from flue gas by carbonation/regeneration cyclic operations using a potassium-based solid sorbent was investigated in a bubbling fluidized bed reactor. As L/D ratio increased, the amount of CO_2 captured during 1 hour carbonation increased until L/D ratio was 3, corresponding to the gas residence time of 5 s. Compared with theoretical sorption capacity, L/D ratio of 1 showed the highest fractional CO_2 removal. For every L/D ratio, the amount of CO_2 captured decreased as the number of cycles increased because of the incomplete regeneration of the sorbent in N_2 for 1 hour at 150 °C. The BET analysis indicated that SorbKX35T5 sorbent could be completely regenerated over 300 °C and there was no structural deterioration at the repeated cycles. In order to improve the CO_2 removal efficiency with potassium-based solid sorbent, a more detailed investigation should be carried out to fully understand the carbonation/regeneration mechanism.

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