Korean J. Chem. Eng., **24**(3), 457-460 (2007)

Effect of water pretreatment on CO_2 capture using a potassium-based solid sorbent in a bubbling fluidized bed reactor

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(*Received 21 August 2006 • accepted 1 November 2006*)

Abstract−A bubbling fluidized bed reactor was used to study CO_2 capture from flue gas by using a potassium-based solid sorbent, sorbKX35 which was manufactured by the Korea Electric Power Research Institute. A dry sorbent, sorbKX35, consists of K_2CO_3 for absorption and supporters for mechanical strength. To increase initial CO_2 removal, some amount of H_2O was absorbed in the sorbent before injecting simulated flue gas. It was possible to achieve 100% CO_2 removal for more than 10 minutes at 60 °C and a residence time of 2 s with H_2O pretreatment. When H_2O pretreatment time was long enough to convert K_2CO_3 of sorbKX35 into $K_2CO_3 \cdot 1.5H_2O$, CO_2 removal was excellent. The results obtained in this study can be used as basic data for designing and operating a large scale CO_2 capture process with two fluidized bed reactors.

Key words: Solid Sorbent, Fluidized Bed Reactor, CO_2, H_2O Pretreatment

INTRODUCTION

The concentration of CO_2, a green house gas, in the earth's atmosphere is increased by combusting fossil fuels to generate electricity. Since Russia ratified the Kyoto Protocol in 2004, research in CO_2 recovery and sequestration has attracted public attention across a variety of industrial fields. Several methods have been suggested for CO_2 recovery, including wet absorption, adsorption, membrane separation, and cryogenic separation. However, these methods need to overcome the limits of cost and energy required to treat the massive flue gas streams from fossil fuel-fired power plants. Recently, CO_2 capture using dry sorbents has been studied as an innovative concept for CO_2 recovery [1-5]. CO_2 is efficiently removed from a flue gas stream by reaction 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. Because solid sorbents are made of cheap alkali metals and carbonated sorbents can be regenerated with heat only from the flue gas stream, the solid sorbent process for CO_2 capture is thought to be cost-effective and energy-efficient. In the solid sorbent process, heat control is important to avoid hot spots generated during the highly exothermic carbonation reaction, and high superficial velocity is necessary to reduce reactor size. To meet these requirements a fluidized bed reactor could be the best candidate for the CO_2 capture process using dry sorbents. The fluidized bed reactor can give high heat and mass transfer rates between gas and particles, remove heat produced during exothermic reaction, maintain isothermal conditions through the reactor due to rapid mixing and, accordingly, is suitable for large-scale operations [6].

The present work attempts to study the CO_2 capture characteristics and performance of a potassium-based solid sorbent in a bubbling fluidized bed reactor before designing and operating a large scale CO_2 capture process with two fluidized bed reactors. The effect of H_2O pretreatment on CO_2 removal was closely examined to understand CO_2 capture characteristics of solid sorbent.

EXPERIMENTAL

1. Material and Apparatus

Fig. 1 shows a schematic diagram of the experimental apparatus, including a bubbling fluidized bed reactor. 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. Reactor temperature was controlled by a furnace and a temperature

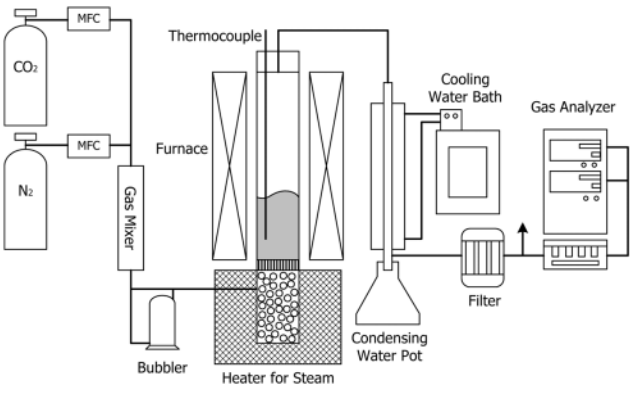

Fig. 1. Schematic diagram of experimental apparatus used in this study.

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‡This work was presented at the 6th Korea-China Workshop on Clean Energy Technology held at Busan, Korea, July 4-7, 2006.

controller and measured by thermocouples fitted in the reactor. To prevent an abrupt rise in temperature and to keep the temperature constant, cold air was blown to the reactor during the carbonation reaction. Each gas flow was quantitatively controlled with a mass flow controller (Brooks, Japan) and then provided to the reactor. Reactor product gases first flowed through a condenser to remove H_2O, then passed through a filter to remove dust, and finally, to a gas analyzer (ABB, USA) that can exclusively analyze CO_2 every 10 seconds.

The solid sorbent, sorbKX35, 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. SorbKX35 has a 1.06 g/cm^3 of bulk density, 92.0 μm of mean particle diameter, and 34.9 m^2/g of BET surface area. Highly pure N_2 and CO_2 were supplied by the Special Gas Company (Korea).

2. Procedure

Taking the real operation conditions in a large scale fluidized bed reactor into account, 125 g of the sorbent was put into the reactor to maintain a residence time of gas mixture of 2 s and a superficial velocity of 0.03 m/s. 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, which was confirmed by measuring the relative humidity. H_2O pretreatment--meaning that only N_2 was passed through a gas bubbler and as a result, the sorbent contains certain amount of H_2O before carbonation--was performed with a total flow rate of 2.9 L/min including H_2O to enhance the initial reaction rate. Regeneration was carried out at over 200 °C in N_2. At each carbonation, new sorbent calcined at 400 °C was used.

RESULTS AND DISCUSSION

The reaction involved in the CO_2 capture using dry sorbents is

$$K_2CO_3 \cdot 1.5H_2O + CO_2 \leftrightarrow 2KHCO_3 + 0.5\ H_2O \quad (1)$$

The reaction is reversible and highly exothermic, so heat control will be an important factor in a commercial system. Therefore, a fluidized bed reactor which has the advantage of heat dissipation can be a good solution for this process.

To increase reactivity of the sorbent during carbonation, H_2O pretreatment was carried out. As can be seen in Fig. 2, H_2O content of the sorbent, expressed as g-H_2O/g-sorbent (wt%), was linearly increased with increasing pretreatment time. Theoretical H_2O content to convert all of K_2CO_3 of sorbKX35 to $K_2CO_3 \cdot 1.5H_2O$ is 6.8%. When 125 g of sorbKX35, which gave residence time of 2 s in the reactor, was used, H_2O pretreatment time of about 60 min was needed to achieve H_2O content of 6.8%. However, because feed gas contains H_2O of 12.2% at the bubbler temperature of 50 °C, H_2O pretreatment of 60 min can give excessive H_2O during carbonation reaction, which can cause agglomeration of the sorbent due to high deliquescence of K_2CO_3.

Fig. 3 shows CO_2 concentration (dry basis) changes during carbonation and regeneration reactions using sorbKX35 in a bubbling fluidized bed reactor. Carbonation was carried out at 60 °C in 10% CO_2, 77.8% N_2 and 12.2% H_2O, while regeneration occurred at 200 °C in N_2. The left part of the figure represents the carbonation reaction and the right part the regeneration reaction. An initial CO_2 concentration of 0%, corresponding to 100% CO_2 removal, was continued for about 10 min before increasing abruptly to about 5% and then increased slowly during the rest of carbonation reaction. 100% CO_2 removal for initial 10 min suggests that sorbKX35 can perform well in a large scale CO_2 capture process with two fluidized bed reactors.

Fig. 4 represents the effect of H_2O pretreatment time on CO_2 removal. Without H_2O pretreatment, CO_2 removal decreased abruptly

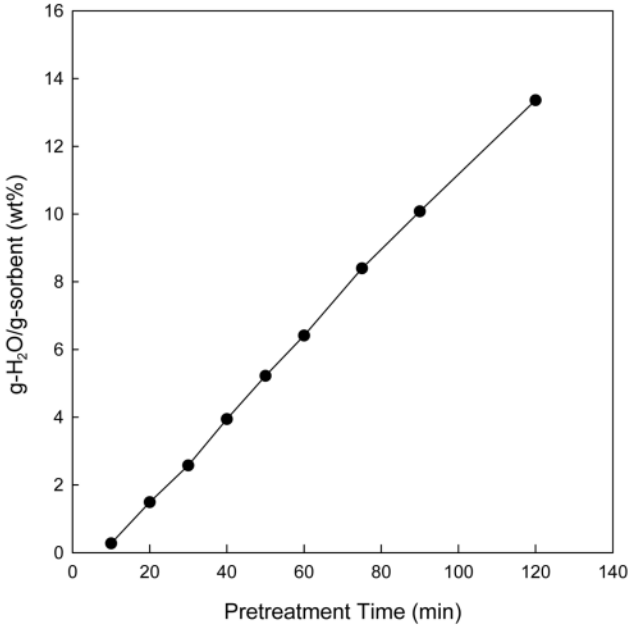

Fig. 2. H_2O content of sorbKX35 according to H_2O pretreatment time (bubbler at 50 °C)

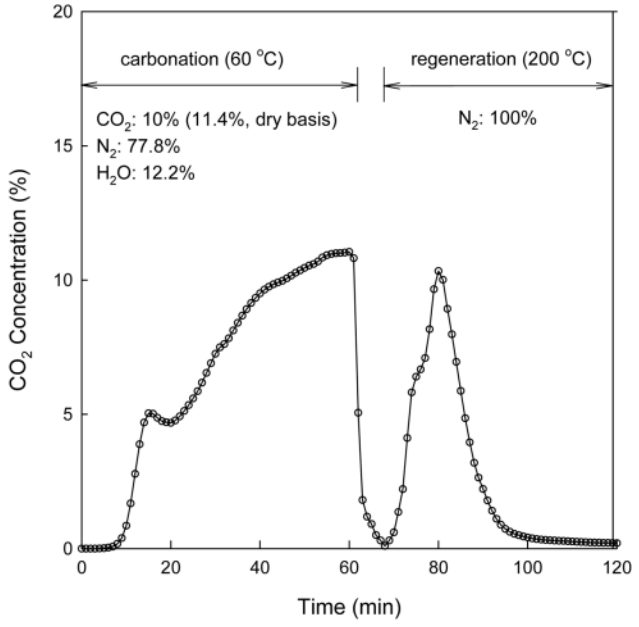

Fig. 3. CO_2 concentration during carbonation-regeneration cycle (H_2O pretreatment for 20 min before carbonation, bubbler at 50 °C).

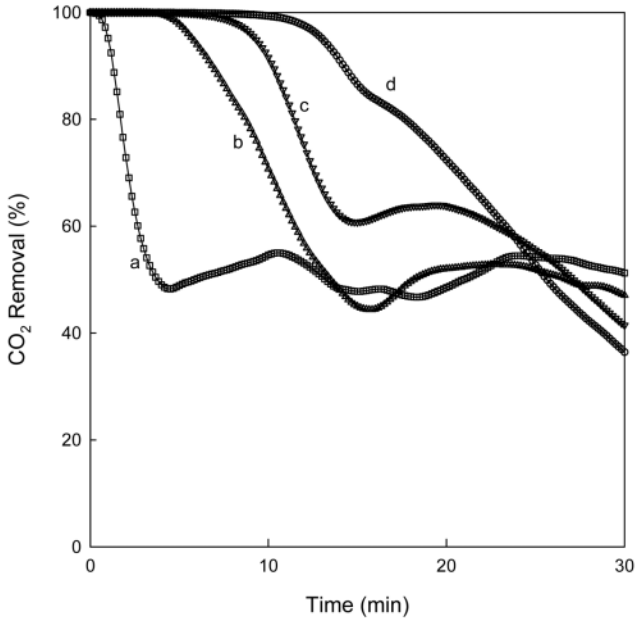

Fig. 4. Effect of H_2O pretreatment time on CO_2 removal (bubbler at 50 °C, reactor at 60 °C). a: 0 min; b: 10 min; c: 20 min; d: 30 min.

from the beginning, whereas with H_2O pretreatment, 100% CO_2 removal was maintained for about 10 min before monotonic decrease. When feed gas was injected into the reactor without H_2O pretreatment, a residence time of 2 s in the reactor seemed to be insufficient for CO_2 and H_2O in the feed gas to react with the K_2CO_3 of sorbKX35 to form $K_2CO_3 \cdot 1.5H_2O$ and further to form $KHCO_3$ through carbonation. However, when K_2CO_3 of sorbKX35 was converted into $K_2CO_3 \cdot 1.5H_2O$ in advance with H_2O pretreatment, the sorbent showed its full performance at such a short residence time. SorbKX35 was manufactured by controlling surface area and pore volume to enhance the capability of water sorption and the reactivity.

To understand more detailed CO_2 removal performance with H_2O pretreatment, the results were presented as fractional CO_2 removal, F(t), which is defined as follows:

$$F(t) = \frac{\text{captured } CO_2 \text{ amount for reaction time, t [min]}}{\text{theoretical } CO_2 \text{ capture capacity}} \quad (2)$$

From Fig. 5, as H_2O pretreatment time increases, fractional CO_2 removal generally increases. However, 20 min H_2O pretreatment appears to be sufficient for reactivity and CO_2 removal in the initial stage. H_2O pretreatment for a much longer period of time can hinder fluidization of sorbKX35 in a fluidized bed rector due to agglomeration, so that appropriate H_2O pretreatment time should be selected by considering both the reactivity of sorbent and efficiency of the operation. In a commercial system, the most important factor to increase the initial reaction rate will be the development of the method for supplying H_2O to the reactor sufficiently and effectively.

In Fig. 6, the effect of bubbler temperature on CO_2 removal was investigated. Without H_2O pretreatment, the amount of H_2O being provided to the reactor was varied by controlling the bubbler temperature. Bubbler temperatures of 40, 50, and 60 °C correspond to 7.3, 12.2, and 19.7% H_2O in the feed gas, respectively. As bubbler temperature increased, CO_2 removal was generally increased. From Fig. 6, supplying more H_2O during carbonation seems to be favorable for CO_2 removal. However, from Fig. 4-6, it should be noted that in the reactor of such a short residence time of 2 s, H_2O pretreatment before carbonation is more effective and important than H_2O supply during carbonation to achieve higher CO_2 removal and to operate the system stably.

As previously mentioned, to convert all of K_2CO_3 of sorbKX35 into $K_2CO_3 \cdot 1.5H_2O$ through H_2O pretreatment, sorbent should contain H_2O content of 6.8 wt%, which can be obtained by 60 min H_2O

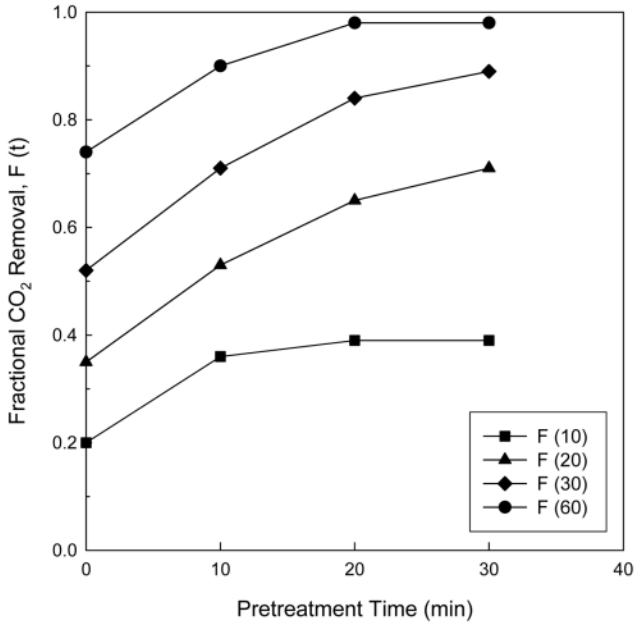

Fig. 5. Fractional CO_2 removal, F(t), according to H_2O pretreatment time (bubbler at 50 °C, reactor at 60 °C).

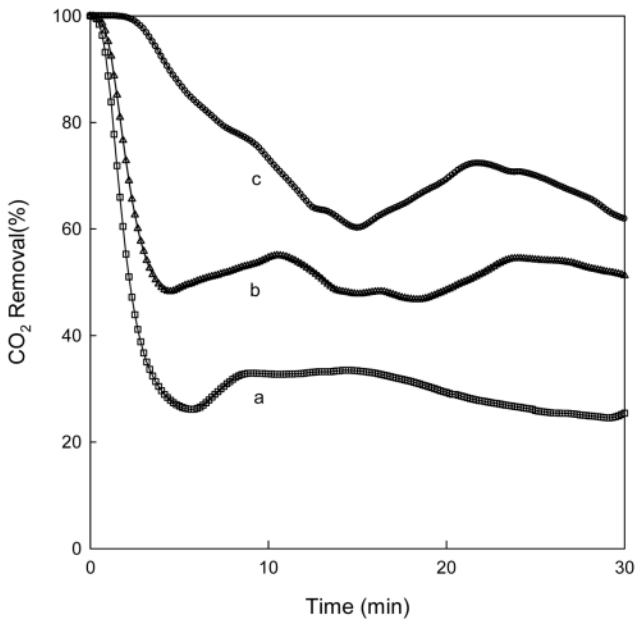

Fig. 6. Effect of bubbler temperature on CO_2 removal (reactor at 60 °C). a: 40 °C; b: 50 °C; c: 60 °C.

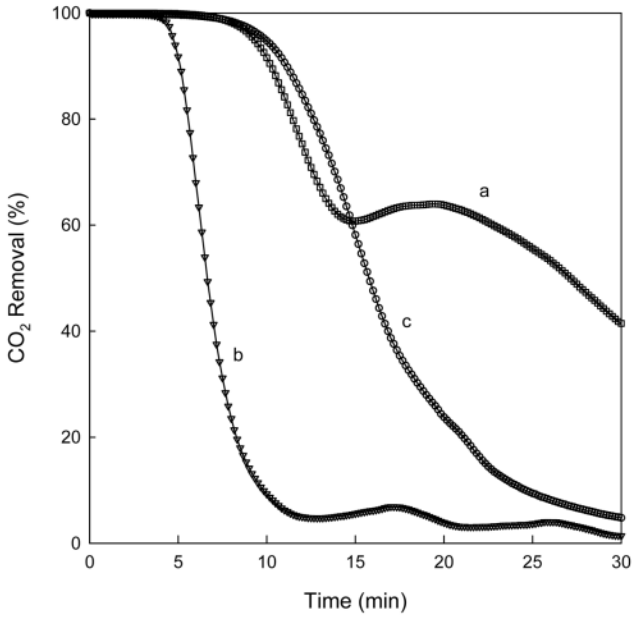

Fig. 7. Effect of H_2O pretreatment on CO_2 removal (bubbler at 50 °C, reactor at 60 °C). a: 20 min pretreatment & reaction with H_2O; b: 20 min pretreatment & rxn without H_2O; c: 60 min pretreatment & reaction without H_2O.

pretreatment. As can be seen in Fig. 7, the case of 60 min pretreatment and no H_2O supply during carbonation showed almost the same CO_2 removal for initial 15 min as that of 20 min pretreatment and H_2O supply during carbonation, while the case of 20 min pretreatment and no H_2O supply during carbonation showed lower CO_2 removal. If perfect H_2O pretreatment, meaning perfect conversion of K_2CO_3 to $K_2CO_3 \cdot 1.5H_2O$, was guaranteed, H_2O supply during carbonation could be minimized.

Although in the present study regeneration occurred in N_2 to quantitatively analyze CO_2 from a reactor, in a commercial process regeneration should be carried out in steam for the produced pure CO_2 stream to be applied in subsequent use or sequestration. The commercial process for CO_2 capture using dry sorbent consists of two fluidized bed reactors. Carbonation occurs at a transport fluidized bed reactor, while regeneration at a bubbling fluidized bed reactor. A carbonated sorbent from a transport reactor is collected in the cyclone and recycled to a bubbling reactor where CO_2 and H_2O are produced through regeneration. Before the regenerated sorbent is transferred back to the carbonator, the sorbent momentarily stays at a loop seal placed between the carbonator and the regenerator to pretreat sorbent with H_2O and to cool sorbent to the carbonation temperature for the increased reaction rate in the carbonator. There are several key factors for commercial success of this process. First, attrition-resistant and mechanically strong sorbent should be provided and it should show little or no reduction in initial reaction rate and capture capacity through repeated cycles. Second, carbonation should be carried out at as low temperature as possible without condensing H_2O in the flue gas. In addition, heat from exothermic reactions should be well dissipated to keep the carbonation temperature constant. Finally, H_2O should be effectively injected into the carbonator to increase the initial reaction rate. The results obtained in this study can be used as basic data in designing and operating a CO_2 capture process of a large scale with two fluidized bed reactors.

CONCLUSIONS

CO_2 capture from flue gas by using a potassium-based solid sorbent was investigated in a bubbling fluidized bed reactor. The sorbent was pretreated with H_2O before carbonation to increase reactivity and CO_2 removal in the initial stage. Without H_2O pretreatment, CO_2 removal decreased abruptly from the beginning, whereas with H_2O pretreatment, 100% CO_2 removal was maintained for about 10 min before monotonic decrease. In the reactor of a short residence time of 2 s, H_2O pretreatment before carbonation was more effective and important than H_2O supply during carbonation to achieve higher CO_2 removal and to operate the system stably. The results obtained in this study can be used as basic data for designing and operating a large scale CO_2 capture process with two fluidized bed reactors.

ACKNOWLEDGMENT

This research was supported by a grant (code M102KP010015-05K1601-01510) from Carbon Dioxide Reduction & Sequestration Research Center, one of 21st Century Frontier Programs funded by the Ministry of Science and Technology of Korean government.

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