

Effect of water pretreatment on CO₂ capture using a potassium-based solid sorbent in a bubbling fluidized bed reactor

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Abstract—A bubbling fluidized bed reactor was used to study CO₂ 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 K₂CO₃ for absorption and supporters for mechanical strength. To increase initial CO₂ removal, some amount of H₂O was absorbed in the sorbent before injecting simulated flue gas. It was possible to achieve 100% CO₂ removal for more than 10 minutes at 60 °C and a residence time of 2 s with H₂O pretreatment. When H₂O pretreatment time was long enough to convert K₂CO₃ of sorbKX35 into K₂CO₃·1.5H₂O, CO₂ removal was excellent. The results obtained in this study can be used as basic data for designing and operating a large scale CO₂ capture process with two fluidized bed reactors.

Key words: Solid Sorbent, Fluidized Bed Reactor, CO₂, H₂O Pretreatment

INTRODUCTION

The concentration of CO₂, 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 CO₂ recovery and sequestration has attracted public attention across a variety of industrial fields. Several methods have been suggested for CO₂ 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, CO₂ capture using dry sorbents has been studied as an innovative concept for CO₂ recovery [1-5]. CO₂ is efficiently removed from a flue gas stream by reaction with solid sorbents while regeneration produces an off-gas containing only CO₂ and H₂O. The condensation of an off-gas generates highly pure CO₂, 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 CO₂ 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 CO₂ 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 CO₂ capture characteristics and performance of a potassium-based solid sorbent in a bubbling fluidized bed reactor before designing and operating a large scale CO₂ capture process with two fluidized bed reactors. The effect of H₂O pretreatment on CO₂ removal was closely examined to understand CO₂ 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

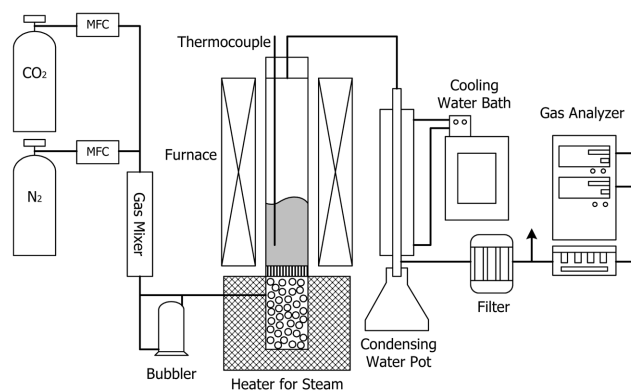


Fig. 1. Schematic diagram of experimental apparatus used in this study.

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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 H₂O, then passed through a filter to remove dust, and finally, to a gas analyzer (ABB, USA) that can exclusively analyze CO₂ 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% K₂CO₃ for absorption and 65% supporters for mechanical strength. SorbKX35 has a 1.06 g/cm³ of bulk density, 92.0 μm of mean particle diameter, and 34.9 m²/g of BET surface area. Highly pure N₂ and CO₂ 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 CO₂ 10%, N₂ 77.8% and H₂O 12.2% was provided. The H₂O needed for carbonation was fed by passing the CO₂ and N₂ through a temperature-controlled gas bubbler, and the feed line was heated to avoid H₂O condensation. The bubbler product was assumed to be saturated with H₂O, which was confirmed by measuring the relative humidity. H₂O pretreatment—meaning that only N₂ was passed through a gas bubbler and as a result, the sorbent contains certain amount of H₂O before carbonation—was performed with a total flow rate of 2.9 L/min including H₂O to enhance the initial reaction rate. Regeneration was carried out at over 200 °C in N₂. At each carbonation, new sorbent calcined at 400 °C was used.

RESULTS AND DISCUSSION

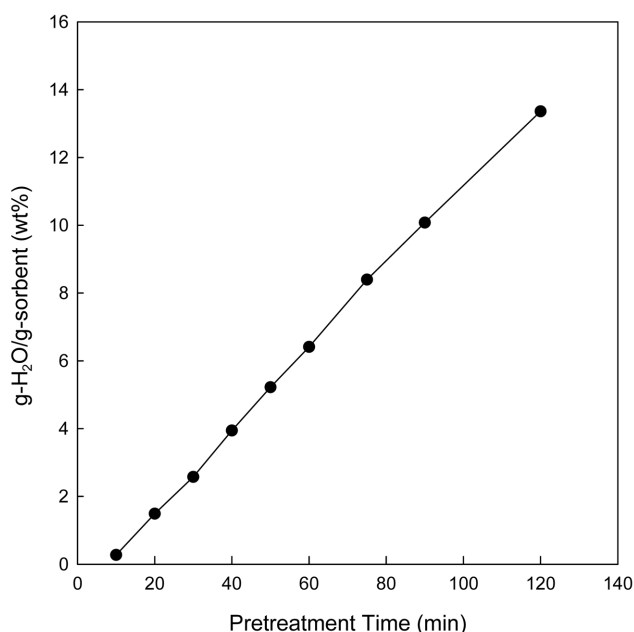
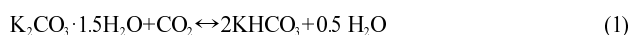


Fig. 2. H₂O content of sorbKX35 according to H₂O pretreatment time (bubbler at 50 °C)

The reaction involved in the CO₂ capture using dry sorbents is



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, H₂O pretreatment was carried out. As can be seen in Fig. 2, H₂O content of the sorbent, expressed as g-H₂O/g-sorbent (wt%), was linearly increased with increasing pretreatment time. Theoretical H₂O content to convert all of K₂CO₃ of sorbKX35 to K₂CO₃·1.5H₂O is 6.8%. When 125 g of sorbKX35, which gave residence time of 2 s in the reactor, was used, H₂O pretreatment time of about 60 min was needed to achieve H₂O content of 6.8%. However, because feed gas contains H₂O of 12.2% at the bubbler temperature of 50 °C, H₂O pretreatment of 60 min can give excessive H₂O during carbonation reaction, which can cause agglomeration of the sorbent due to high deliquescence of K₂CO₃.

Fig. 3 shows CO₂ 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% CO₂, 77.8% N₂ and 12.2% H₂O, while regeneration occurred at 200 °C in N₂. The left part of the figure represents the carbonation reaction and the right part the regeneration reaction. An initial CO₂ concentration of 0%, corresponding to 100% CO₂ removal, was continued for about 10 min before increasing abruptly to about 5% and then increased slowly during the rest of carbonation reaction. 100% CO₂ removal for initial 10 min suggests that sorbKX35 can perform well in a large scale CO₂ capture process with two fluidized bed reactors.

Fig. 4 represents the effect of H₂O pretreatment time on CO₂ removal. Without H₂O pretreatment, CO₂ removal decreased abruptly

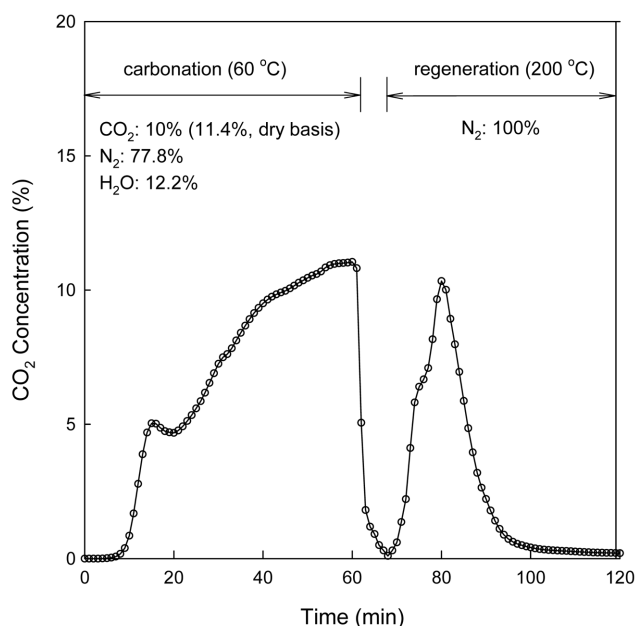


Fig. 3. CO₂ concentration during carbonation-regeneration cycle (H₂O pretreatment for 20 min before carbonation, bubbler at 50 °C).

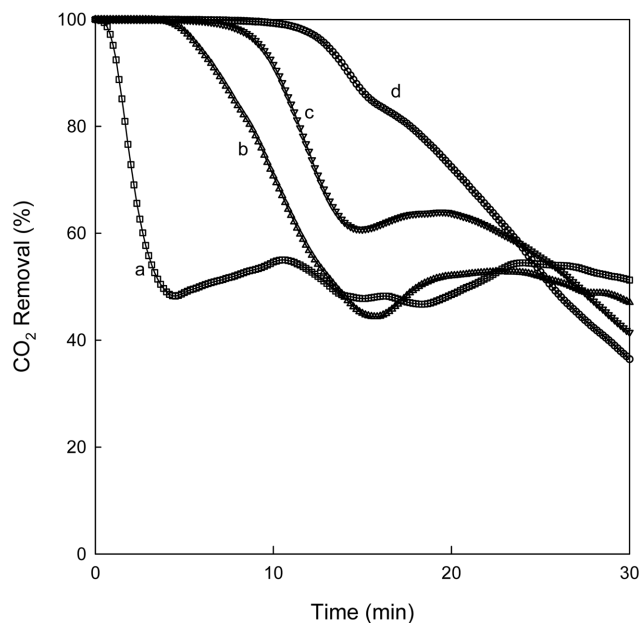


Fig. 4. Effect of H₂O pretreatment time on CO₂ removal (bubbler at 50 °C, reactor at 60 °C). a: 0 min; b: 10 min; c: 20 min; d: 30 min.

from the beginning, whereas with H₂O pretreatment, 100% CO₂ removal was maintained for about 10 min before monotonic decrease. When feed gas was injected into the reactor without H₂O pretreatment, a residence time of 2 s in the reactor seemed to be insufficient for CO₂ and H₂O in the feed gas to react with the K₂CO₃ of sorbKX35 to form K₂CO₃·1.5H₂O and further to form KHCO₃ through carbonation. However, when K₂CO₃ of sorbKX35 was converted into K₂CO₃·1.5H₂O in advance with H₂O pretreatment, the sorbent showed its full performance at such a short residence time.

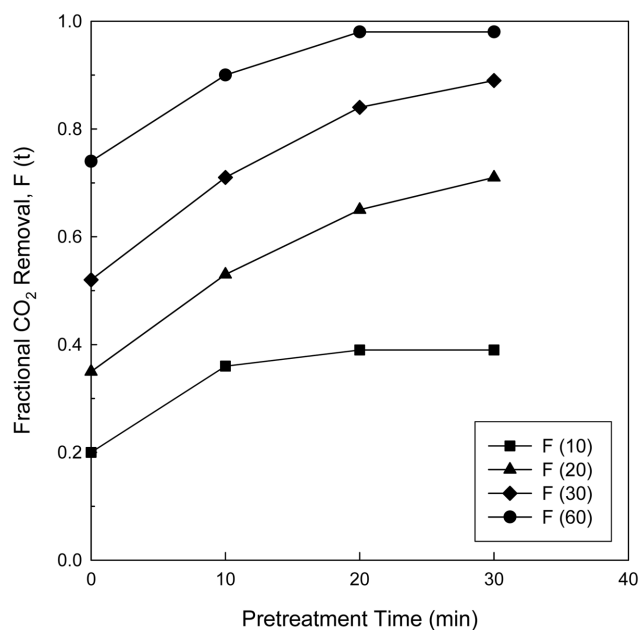


Fig. 5. Fractional CO₂ removal, F(t), according to H₂O pretreatment time (bubbler at 50 °C, reactor at 60 °C).

SorbKX35 was manufactured by controlling surface area and pore volume to enhance the capability of water sorption and the reactivity.

To understand more detailed CO₂ removal performance with H₂O pretreatment, the results were presented as fractional CO₂ removal, F(t), which is defined as follows:

$$F(t) = \frac{\text{captured CO}_2 \text{ amount for reaction time, } t \text{ [min]}}{\text{theoretical CO}_2 \text{ capture capacity}} \quad (2)$$

From Fig. 5, as H₂O pretreatment time increases, fractional CO₂ removal generally increases. However, 20 min H₂O pretreatment appears to be sufficient for reactivity and CO₂ removal in the initial stage. H₂O pretreatment for a much longer period of time can hinder fluidization of sorbKX35 in a fluidized bed reactor due to agglomeration, so that appropriate H₂O 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 H₂O to the reactor sufficiently and effectively.

In Fig. 6, the effect of bubbler temperature on CO₂ removal was investigated. Without H₂O pretreatment, the amount of H₂O 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% H₂O in the feed gas, respectively. As bubbler temperature increased, CO₂ removal was generally increased. From Fig. 6, supplying more H₂O during carbonation seems to be favorable for CO₂ removal. However, from Fig. 4-6, it should be noted that in the reactor of such a short residence time of 2 s, H₂O pretreatment before carbonation is more effective and important than H₂O supply during carbonation to achieve higher CO₂ removal and to operate the system stably.

As previously mentioned, to convert all of K₂CO₃ of sorbKX35 into K₂CO₃·1.5H₂O through H₂O pretreatment, sorbent should contain H₂O content of 6.8 wt%, which can be obtained by 60 min H₂O

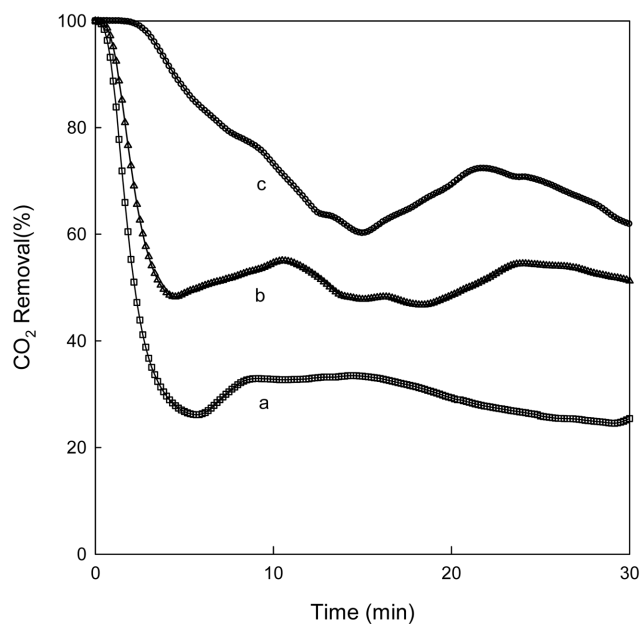


Fig. 6. Effect of bubbler temperature on CO₂ removal (reactor at 60 °C). a: 40 °C; b: 50 °C; c: 60 °C.

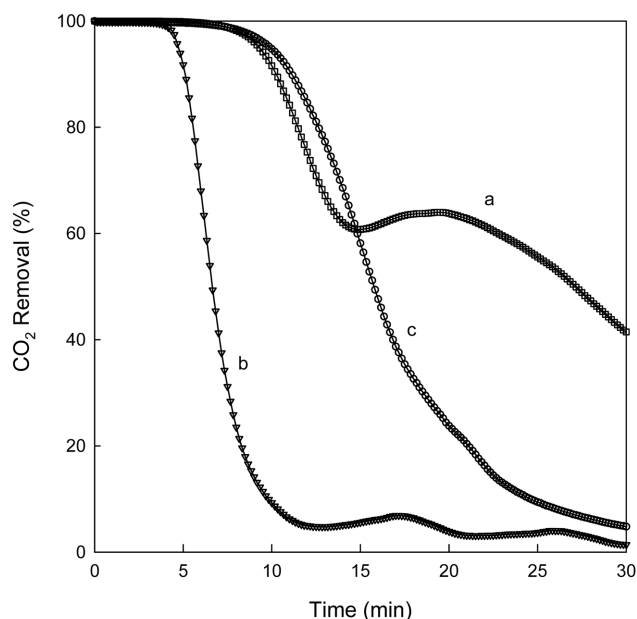


Fig. 7. Effect of H₂O pretreatment on CO₂ removal (bubbler at 50 °C, reactor at 60 °C). a: 20 min pretreatment & reaction with H₂O; b: 20 min pretreatment & rxn without H₂O; c: 60 min pretreatment & reaction without H₂O.

pretreatment. As can be seen in Fig. 7, the case of 60 min pretreatment and no H₂O supply during carbonation showed almost the same CO₂ removal for initial 15 min as that of 20 min pretreatment and H₂O supply during carbonation, while the case of 20 min pretreatment and no H₂O supply during carbonation showed lower CO₂ removal. If perfect H₂O pretreatment, meaning perfect conversion of K₂CO₃ to K₂CO₃·1.5H₂O, was guaranteed, H₂O supply during carbonation could be minimized.

Although in the present study regeneration occurred in N₂ to quantitatively analyze CO₂ from a reactor, in a commercial process regeneration should be carried out in steam for the produced pure CO₂ stream to be applied in subsequent use or sequestration. The commercial process for CO₂ 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 CO₂ and H₂O 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 H₂O 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 H₂O in the flue gas. In addition, heat from exothermic reactions should be well dissipated to keep the carbonation temperature constant. Finally, H₂O 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 CO₂ capture process of a large scale with two fluidized bed reactors.

CONCLUSIONS

CO₂ capture from flue gas by using a potassium-based solid sorbent was investigated in a bubbling fluidized bed reactor. The sorbent was pretreated with H₂O before carbonation to increase reactivity and CO₂ removal in the initial stage. Without H₂O pretreatment, CO₂ removal decreased abruptly from the beginning, whereas with H₂O pretreatment, 100% CO₂ removal was maintained for about 10 min before monotonic decrease. In the reactor of a short residence time of 2 s, H₂O pretreatment before carbonation was more effective and important than H₂O supply during carbonation to achieve higher CO₂ 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 CO₂ capture process with two fluidized bed reactors.

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