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Performance analysis of K-based KEP-CO2P1 solid sorbents in a bench-scale continuous dry-sorbent CO_2 capture process

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Abstract–Korea Institute of Energy Research (KIER) and Korea Electric Power Corporation Research Institute (KEPCO-RI) have been developing a CO_2 capture technology using dry sorbents. In this study, KEP-CO2P1, a potassium-based dry sorbent manufactured by a spray-drying method, was used. We employed a bench-scale dry-sorbent CO_2 capture fluidized-bed process capable of capturing 0.5 ton CO_2/day at most. We investigated the sorbent performance in continuous operation mode with solid circulation between a fast fluidized-bed-type carbonator and a bubbling fluidized-bed-type regenerator. We used a slip stream of a real flue gas from 2 MWe coal-fired circulating fluidized-bed (CFB) power facilities installed at KIER. Throughout more than 50 hours of continuous operation, the temperature of the carbonator was maintained around 70-80 °C using a jacket-type heat exchanger, while that of the regenerator was kept above 180 °C using an electric furnace. The differential pressure of both the carbonator and regenerator was maintained at a stable level. The maximum CO_2 removal was greater than 90%, and the average CO_2 removal was about 83% during 50 hours of continuous operation.

Keywords: CO_2 Capture, Dry Sorbents, Fluidized-bed Process, Bench-scale Unit, Continuous Operation

INTRODUCTION

During the past few decades, various CO_2 capture and storage (CCS) technologies have been developed to mitigate global warming. CCS is expected to play a major role in global greenhouse gas emission reduction; in fact, the International Energy Agency (IEA) has estimated that it will account for as much as one-fifth of the total reductions by 2050 [1]. To date, several CO_2 capture technologies using wet solutions have been demonstrated at real sites, such as the Technology Centre Mongstad (TCM), the National Carbon Capture Center (NCCC), and Southern Company [2-5]. In Korea, 10 MWe-scale CO_2 capture plants using wet solutions and dry sorbents have been tested at the Boryeong and Hadong coal-fired power plants, respectively [6,7].

Dry-sorbent CO_2 capture technology was developed by KIER and KEPCO-RI starting in 2002 as part of the 21st Century Frontier Programs funded by the Ministry of Science, ICT and Future Planning. KIER developed a dry-sorbent CO_2 capture process using fluidized-bed reactors [8-11], and KEPCO-RI developed dry sorbents consisting of Na_2CO_3 or K_2CO_3 for the CO_2 sorption and supporters for the mechanical strength [12-14]. CO_2 in the flue gas is efficiently captured by reaction with the dry sorbents in the carbonation reactor, and the captured CO_2 is released in the regeneration reactor. The reactions are as follows:

Carbonation reaction

$$M_2CO_3(s)+CO_2(g)+H_2O(g)\rightarrow 2MHCO_3(s),\ \text{exothermic} \qquad (1)$$

Regeneration reaction

$$2MHCO_3(s)\rightarrow M_2CO_3(s)+CO_2(g)+H_2O(g),\ \text{endothermic} \qquad (2)$$

where M represents Na or K, s is the solid phase, and g is the gas phase.

We used a bench-scale continuous dry-sorbent CO_2 capture process to analyze the performance of the K-based dry sorbents, KEP-CO2P1. From the 2 MWe coal-fired CFB power facilities installed at KIER, a slip stream of real flue gas was used. The performance was analyzed for more than 50 hours of continuous operation. The CO_2 removal efficiency and regenerability, the dynamic sorption capacity, and the physical properties of the dry sorbents were evaluated using the experimental data. The results were applied to design a pilot-scale dry-sorbent CO_2 capture process.

EXPERIMENTS

1. The Bench-scale Unit

Fig. 1 shows a schematic diagram of the bench-scale dry-sorbent CO_2 capture process which could capture 0.5 ton CO_2/day at most. It consists of a fast fluidized-bed-type carbonator (①) for CO_2 sorption, a bubbling fluidized-bed-type regenerator (②) for sorbent regeneration, two cyclones (③), a loop-seal (④), and a standpipe. The lower part of the carbonator is a mixing zone with an inner diameter of 100 mm and a height of 2,700 mm, and the upper part of the carbonator is a fast zone with an inner diameter of 75 mm and a height of 10,800 mm. The regenerator is a 2,000 mm-tall bed with an inner diameter of 250 mm, and it has a perforated distributor.

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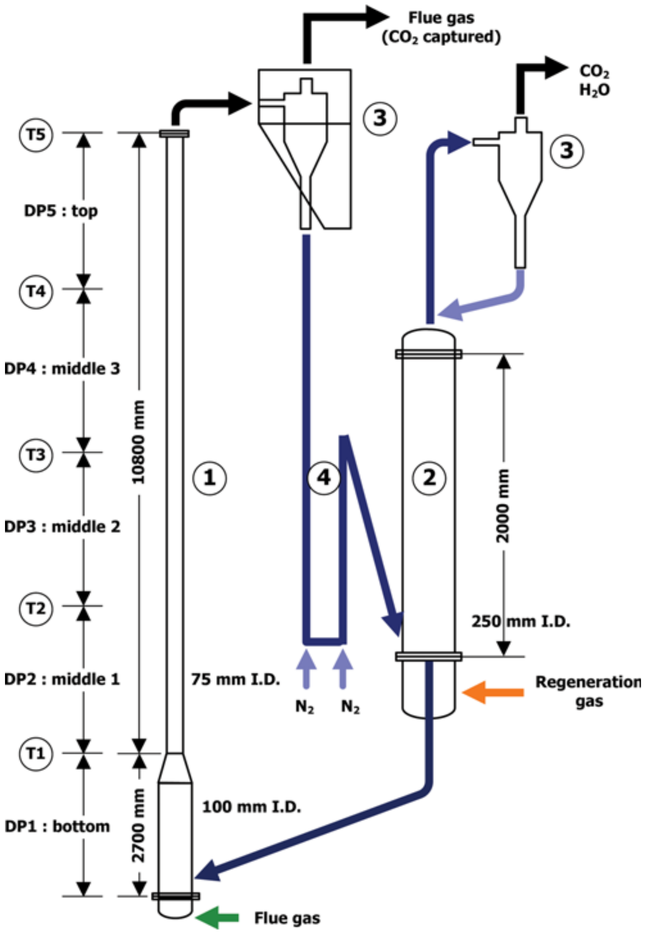

Fig. 1. Schematic diagram of bench-scale dry-sorbent CO_2 capture.

The bench-scale unit includes the flue gas pre-treatment system, which comprises a pre-heater for increasing the flue gas temperature, a boost fan for supplying the flue gas to the carbonator, a bubbler [15] for moisturizing the flue gas to make the carbonation reaction occurs, and a sorbent cooler for cooling down the sorbents to the carbonation temperature from the regenerator. It also includes a filter system to capture fine particles, condensers to remove the condensate of the gas stream, and online gas analyzer to measure the CO_2 concentration of the gas stream after each reactor.

Table 1. Experimental conditions

	Carbonation	Regeneration
Reactor type	Fast fluidized-bed	Bubbling fluidized-bed
Feed gas	Coal-fired flue gas - CO_2 7-9% (dry basis) - H_2O 12-19%	N_2
Residence time	2.5-5.5 sec (gas)	10-20 min (solid)
Temperature	70-80 °C	>180 °C
Pressure	1 atm	
Continuous operation	>50 hours	
Inventory	KEP-CO2P1 Sorbents, 120 kg	

2. Experimental Conditions

The experimental conditions are shown in Table 1. The flue gas, which was drawn from the 2 MWe CFB power facilities, was almost cooled down so that moisture, which was needed to make the carbonation reaction occur, should be added in a bubbler before being introduced to the carbonator. The moisture content in the flue gas was controlled by adjustment of the bubbler temperature [15]. The inlet concentration of CO_2 in the flue gas was maintained in the range of about 7-9 vol% (dry basis) during continuous operation. The gas residence time of the carbonator was controlled between 2.5 to 5.5 seconds by variation of the output of the booster fan, while the solid residence time of the regenerator was kept between 10 to 20 minutes by variation of the opening position of the slide valve installed between the regenerator and the carbonator. The temperatures of the carbonator and the regenerator were maintained around 70 to 80 °C and above 180 °C, respectively, at atmospheric pressure conditions. The KEP-CO2P1 sorbents, which consisted of 35 wt% of K_2CO_3 for CO_2 sorption and 65 wt% of supporters for mechanical strength, were used, and the weight of the whole inventory reaches to 120 kg.

3. Sorbent Characterization

To find the changes in sorbent before and after reaction, a cold type field emission scanning electron microscope (SEM, SEM-4800, HITACHI Ltd.) was used. BET analysis is the standard method for determining surface areas from nitrogen adsorption isotherms; thus, a surface area analyzer (BET, ASAP 2420, Micromeritics Instrument Corp.) was used to find changes in surface area of sorbent before and after reaction. Hg-porosimetry was carried out on a Demo AutoPore IV 9500 V1.07 (Micromeritics) to find changes in the bulk densities, skeletal densities, and particle densities of sorbent before and after reaction.

RESULTS AND DISCUSSION

Fig. 2 shows the temperature profiles and the differential pressure profiles of the carbonator during continuous operation. The temperature in the carbonator was controlled by manipulation of the cooling water flow rate, which was introduced to the jacket of the carbonator. The differential pressure in the carbonator indicated the solid hold-up in the measuring section. In Fig. 2(a), the temperature of each point during continuous operation was well maintained between 70 and 80 °C, which has been reported as the optimum operating temperature of K-based dry sorbents for carbonation reaction. Since the flue gas and the dry sorbents flew co-currently from the bottom of the carbonator, a considerable amount of exothermic heat was generated by reaction in the mixing zone, so the highest temperature in the carbonator was in the mixing zone. As seen in Fig. 2(b), the differential pressure of each section of the carbonator during continuous operation was well maintained at a stable level. The differential pressure of the mixing zone fluctuated because a turbulent regime formed, while the other pressures were stably maintained because a pneumatic conveying regime formed. The value of dp5, differential pressure of top section of the carbonator, was about 100 mmH_2O greater than the other differential pressures of the fast zone since the dp5 included the top region of the

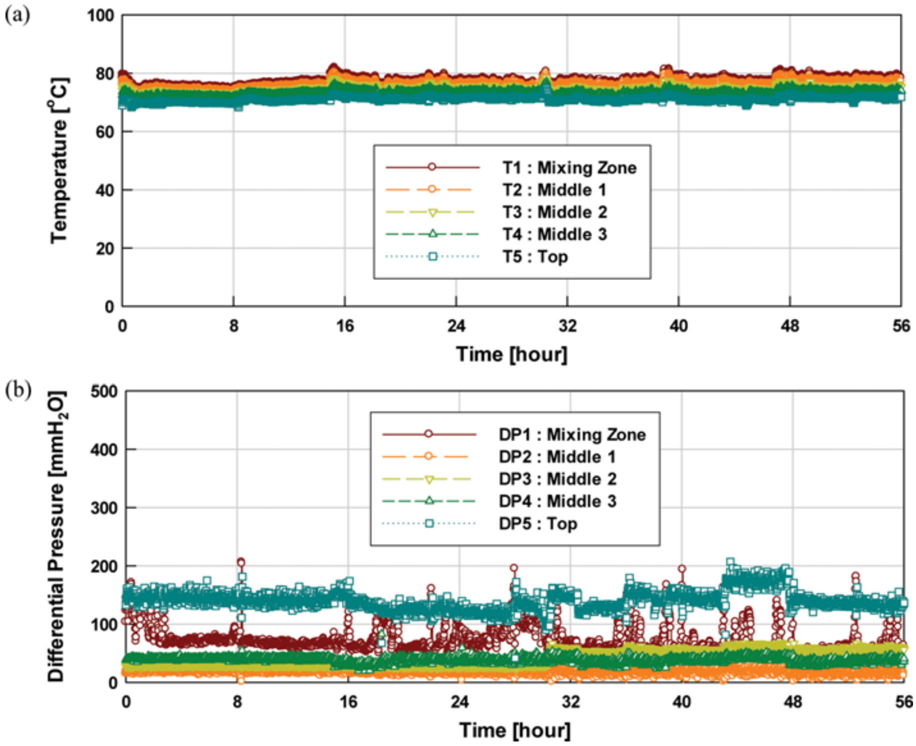

Fig. 2. Temperature profiles and differential pressure profiles of the carbonator in continuous operation.

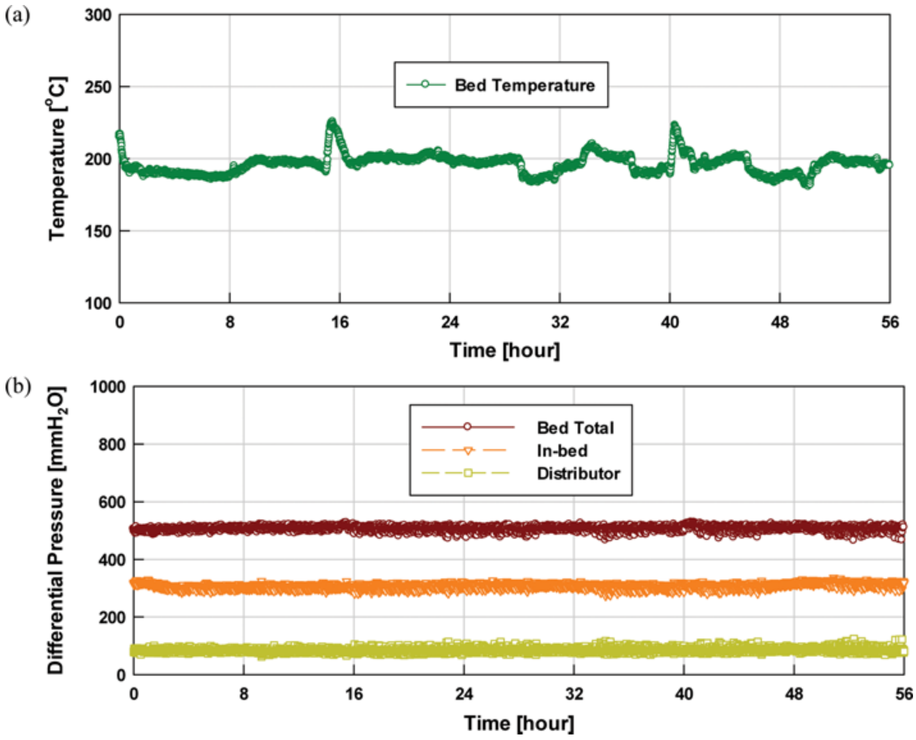

Fig. 3. Temperature profiles and differential pressure profiles of the regenerator in continuous operation.

carbonator and the cyclone.

Fig. 3 shows the temperature and differential pressure profiles of the regenerator in continuous operation. The temperature in the regenerator was controlled by manipulation of the output of the electric furnace. The differential pressure of the bed in the regenerator indicated the solid volume in the measuring section. As seen in Fig. 3(a), the temperature of the bed during continuous operation was well maintained above 180 °C, and the average bed tem-

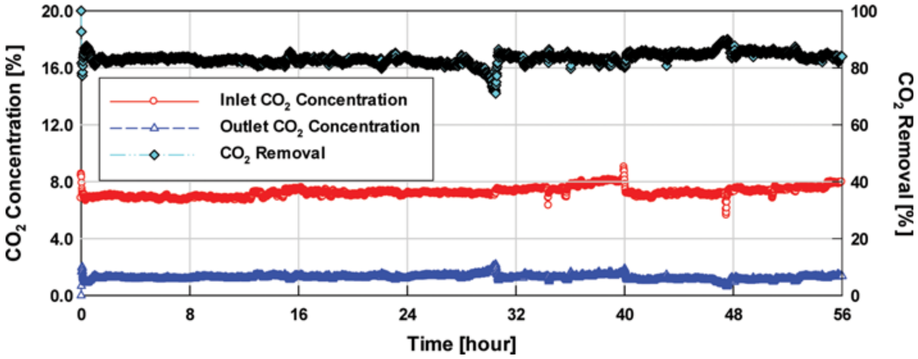

Fig. 4. Inlet and outlet CO$_2$ concentrations in the carbonator and CO$_2$ removal in continuous operation.

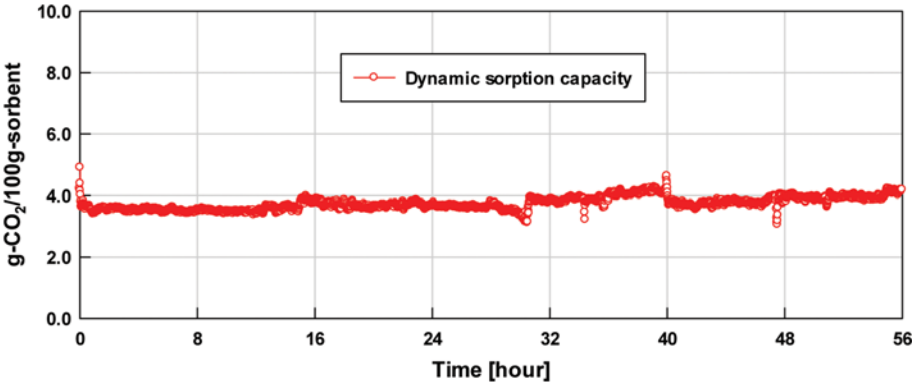

Fig. 5. Dynamic sorption capacity of the dry sorbents in continuous operation.

perature was around 195 °C. In Fig. 3(b), the differential pressures in the regenerator during continuous operation were well maintained at a stable level. The differential pressure of the bed total means the total solid volume in the regenerator, and that of the in-bed means the solid volume, which was measured from the distributor to the given in-bed height. Using the differential pressure of the in-bed and the real height, the voidage of the sorbents in the regenerator was calculated so that the total mass of the sorbents could be calculated in the regenerator. The solid residence time in the regenerator was calculated from the differential pressure of the bed and the solid circulation rate, which was controlled by the opening position of the slide valve located between the regenerator and the carbonator. The differential pressure of the distributor indicated that the fluidization gas had been well introduced to the reactor during continuous operation.

Fig. 4 shows the inlet and outlet CO$_2$ concentrations in the carbonator and the CO$_2$ removal, which was calculated by the following equation:

$$\text{CO}_2\ \text{Removal (\%)} = \frac{\text{The amount of CO}_2\ \text{captured in the carbonator}}{\text{The amount of CO}_2\ \text{introduced to the carbonator}} \times 100, \quad (3)$$

where the CO$_2$ removal was calculated using the inlet and outlet CO$_2$ concentration data at the same time. The CO$_2$ removal during continuous operation was maintained above 80%, except approximately at 30 hour after the CO$_2$ sorption reaction began. This was because the water level of the bubbler (in which moisture was needed for the carbonation reaction (1)) had fallen below the desired level to saturate the water vapor into the flue gas at the bubbler temperature. When the water level of the bubbler was recovered to the initial level, the CO$_2$ removal also rose to above 80%. The maximum CO$_2$ removal exceeded 90%, and the average CO$_2$ removal was about 83% during 50 hours of continuous operation.

Fig. 5 shows the dynamic sorption capacity of the dry sorbents during continuous operation, which was calculated as:

$$\text{Dynamic sorption capacity} = \frac{\text{The captured CO}_2\ \text{flow rate in the carbonator}}{\text{The solid circulation rate}} \times 100, \quad (4)$$

where the unit of the dynamic sorption capacity is g-CO$_2$/100 g-sorbent. The average dynamic sorption capacity during continuous operation was about 4 g-CO$_2$/100 g-sorbent. The theoretical equilibrium sorption capacity of the KEP-CO2P1 sorbents was 11.14 g-CO$_2$/100 g-sorbent, based on the carbonation reaction (1). However, it decreased to around 6 g-CO$_2$/100 g-sorbent from the second cycle in the batch-type carbonation/regeneration cycle experiments at a H$_2$O content in the flue gas and a regeneration temperature similar to those of this study [16]. In view of the dynamic sorption capacity obtained by continuous operation, 4 g-CO$_2$/100 g-sorbent is reasonable compared to the batch-cycle data. The dynamic sorption capacity in continuous operation was lower than that in the batch-type cycle operation due to the following factors: i) solid residence time distribution in the regenerator, ii) gas and solid contact efficiency in the carbonator, iii) solid or gas by-passing in the

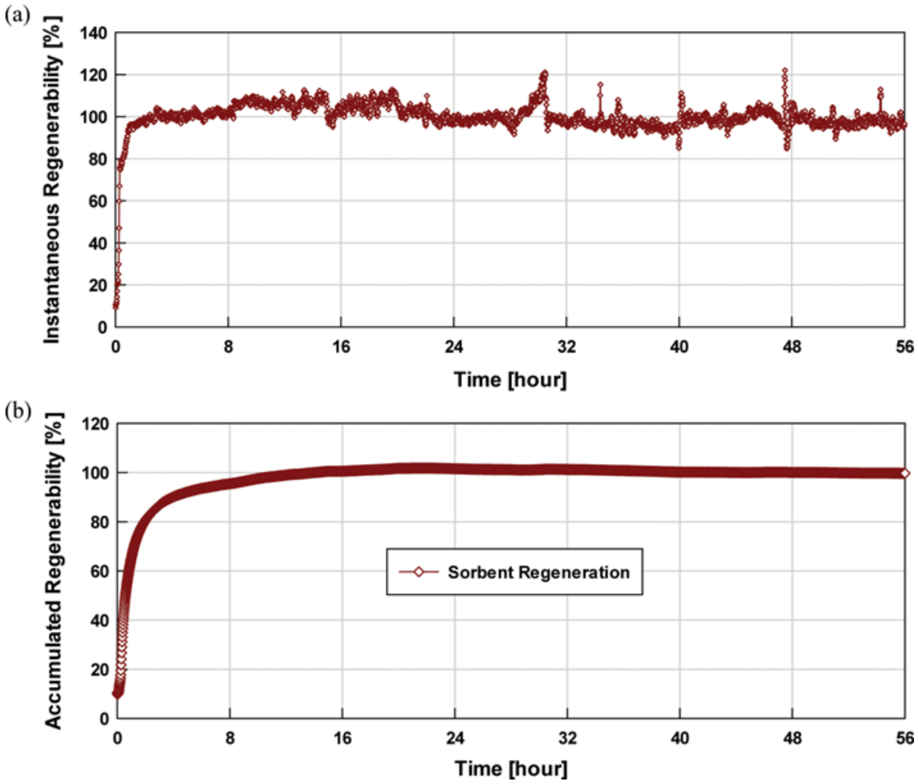

Fig. 6. Regenerability of the sorbents at the regenerator in continuous operation.

both reactors. The dynamic sorption capacity of the sorbent in continuous operation could be improved by controlling the above three factors.

Fig. 6 shows the regenerability of the sorbents at the regenerator. The instantaneous regenerability was calculated as:

$$\text{Instantaneous Regenerability (\%)} = \frac{\text{The regenerated CO}_2\text{ flow rate in the regenerator}}{\text{The captured CO}_2\text{ flow rate in the carbonator}} \times 100, \quad (5)$$

and the accumulated regenerability was calculated as:

$$\text{Accumulated Regenerability (\%)} = \frac{\text{The amount of CO}_2\text{ regenerated in the regenerator}}{\text{The amount of CO}_2\text{ captured in the carbonator}} \times 100, \quad (6)$$

where instantaneous regenerability (IR) indicates the regenerability of the sorbent at a certain time, and accumulated regenerability (AR) indicates the regenerability at the cumulative time. As seen in Fig. 6(a), the IR fluctuated around the level of 100% since the data of the inlet and outlet CO_2 concentrations in the carbonator and the outlet CO_2 concentration in the regenerator were used at

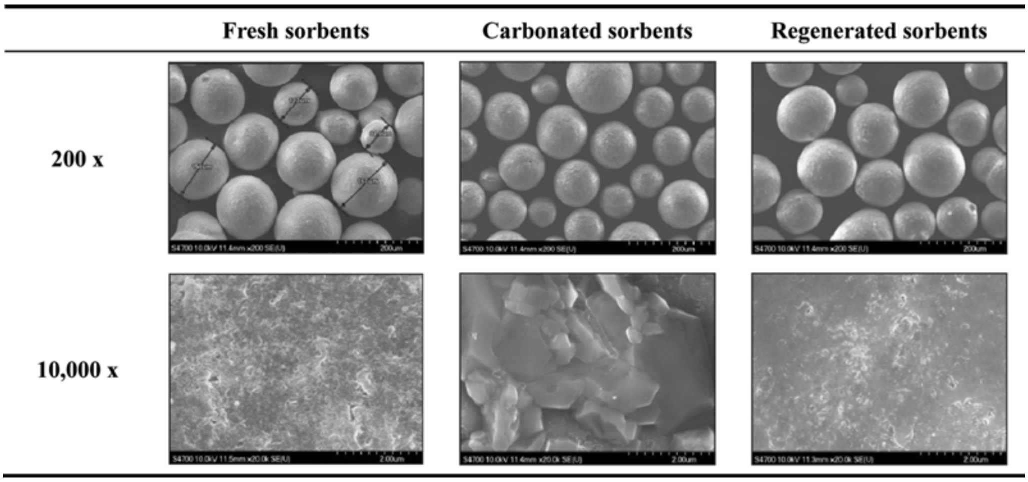

Fig. 7. SEM images of the fresh, carbonated, and regenerated sorbents.

the same time to calculate the IR in Eq. (5). The sorbents circulated between the carbonator and the regenerator during approximately one hour; thus, the CO_2 concentration data obtained at the same time had a discrepancy in time to the sorbent side. Changes in the inlet CO_2 concentration in the flue gas, fluctuations in the flue gas flow rate from the booster fan, changes in the regeneration temperature, and other factors that affect the CO_2 capture efficiency have a positive or negative influence on the IR fluctuation around the level of 100% regenerability. As seen in Fig. 6(b), the AR monotonically increased until 20 hours from start-up and converged to 100% regenerability. Based on the IR and AR, the carbonation and regeneration of the sorbents reached an equilibrium state under the same operating conditions as time went by.

Fig. 7 shows the SEM images of the fresh, carbonated, and regenerated sorbents, which were taken at magnifications of 200 and 10,000. Very little difference in the surface can be observed at the magnification of 200; however, at the magnification of 10,000 the surface morphology of the carbonated sorbents has changed compared with the fresh and regenerated sorbents. This means that the surface morphology recovered after sorbent regeneration. In Fig. 8, the BET surface area, the bulk density, the skeletal density, and the particle density are shown for the fresh, carbonated, and regenerated sorbents. The BET surface area of the fresh sorbents was 39.14 g/m^2, that of the carbonated ones was 29.3 g/m^2, and that of the regenerated ones was 32.52 g/m^2. The BET surface area could be not recovered to the initial value after regeneration because of the partial regeneration at the average regeneration temperature of 195 °C and the solid residence time in the regenerator of 10 to 20 minutes in continuous operation. The bulk densities of the fresh, carbonated, and regenerated sorbents were 0.69, 0.92, and 0.73 g/cm^3, respectively; their skeletal densities were 1.53, 2.57, and 1.47 g/cm^3, respectively, and their particle densities were 1.02, 1.63, and 1.1 g/cm^3, respectively. Three types of solid density demonstrated that the carbonated sorbents had the highest values and the regenerated sorbents had almost recovered to the initial value.

CONCLUSION

We investigated the KEP-CO2P1 sorbent performance in continuous operation mode with solid circulation between a fast fluidized-bed-type carbonator and a bubbling fluidized-bed-type regenerator on a bench-scale unit. Throughout more than 50 hours of continuous operation, the temperature of the carbonator was maintained around 70-80 °C, while that of the regenerator was around 195 °C using an electric furnace, and the differential pressures of both the carbonator and regenerator were maintained at a stable level. The maximum CO_2 removal exceeded 90%, and the average CO_2 removal was about 83% during 50 hours of continuous operation. The dynamic sorption capacity and the regenerability of the sorbents were evaluated during continuous operation. Finally, we analyzed the SEM images and the physical properties of fresh, carbonated, and regenerated sorbents; the BET surface area of the regenerated sorbents was partially recovered, and the solid densities of the regenerated ones were almost recovered. In general, it is not necessary to fully regenerate sorbents in practical use, but a more detailed and systematic investigation should be carried out to enable this technology to be applied in real sites.

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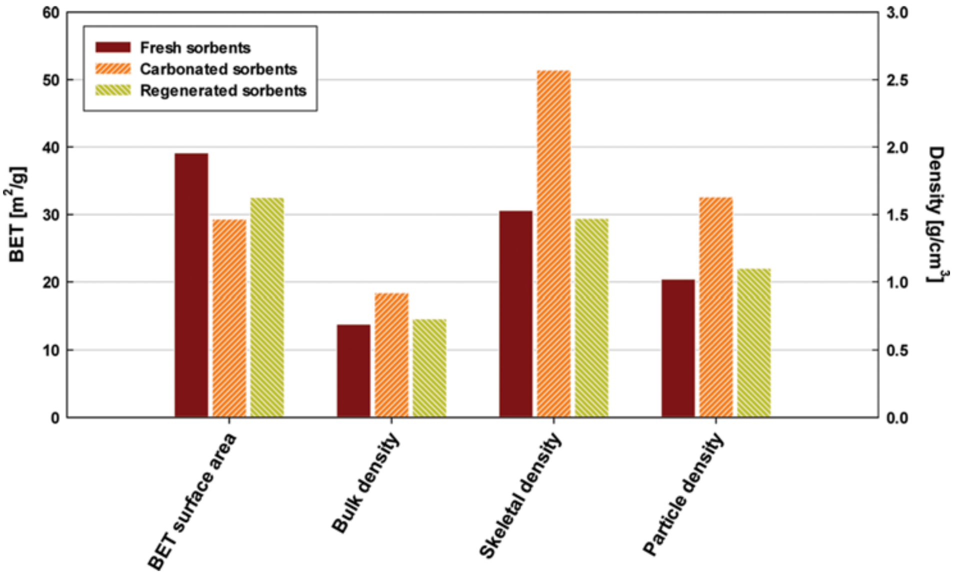

Fig. 8. BET surface area, bulk density, skeletal density, and particle density of the fresh, carbonated, and regenerated sorbents.

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