Screening of Spray-Dried K₂CO₃-Based Solid Sorbents using Various Support Materials for CO₂ Capture

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Abstract

K₂CO₃-based dry regenerable sorbents were prepared by spray-drying techniques to improve mass produced K₂CO₃-Al₂O₃ sorbents (KEP-CO2P, hereafter), and then tested for their CO₂ sorption capacity by a 2,000 Nm³/h (0.5 MWe) CO₂ capture pilot plant built for Unit 3 of the Hadong thermal power station in 2010. Each of the sample sorbents contained 35 wt.% K₂CO₃ as the active materials with various support materials such as TiO₂, MgO, Zeolite 13X, Al₂O₃, SiO₂ and hydrotalcite (HTC). Their physical properties and reactivity were tested to evaluate their applicability to a fluidized-bed or fast transport-bed CO₂ capture process. The CO₂ sorption capacity and percentage utilization of K₂CO₃-MgO based sorbent, Sorb-KM2, was 8.6 g-CO₂/100 g-sorbents and 90%, respectively, along with good mechanical strength for fluidized-bed application. Sorbs-KM2 and KT were almost completely regenerated at 140°C. No degradation of Sorb-KM by SO₂ added as a pollutant in flue gas was observed during a cycle test.

Keywords: CO2capture, Dry regenerable solid sorbent, Flue gas, Fluidized-bed reactor
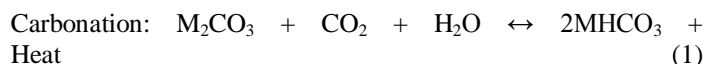
I. INTRODUCTION

Carbon capture and storage (CCS) from large point sources such as thermal power plants is one option to reduce anthropogenic carbon dioxide emissions. Fossil power plants are the main source of CO₂ emissions throughout the world, contributing approximately 40% of total global emissions. Coal-fired power plants alone contribute approximately 70% of the emissions from fossil power plants [1].

The Intergovernmental Panel on Climate Change (IPCC) predicts that anthropogenic CO₂ emissions could be reduced by 80~90% for a conventional fossil fuel-fired power plant installed with CCS technologies [2].

CCS technologies applicable to the power generation sector can be categorized as post-combustion capture (mainly CO₂ separation from N₂), pre-combustion capture (CO₂/H₂) and oxy combustion including chemical looping combustion (CLC), based on the power system. Considerable attention has been focused on cost-effective and energy-efficient CCS techniques such as wet scrubbing using amine solution, cryogenic and membrane, etc. One of the advanced concepts for CO₂ capture is a chemical absorption process with dry regenerable solid sorbents [3]. This technology was proposed to overcome the wet scrubbing process.

The CO₂ capture process using alkali metal carbonate based solid sorbents consists of two reactors of carbonation and regeneration. This process can be used to treat large volume of flue gases from fossil power plants. This process has several advantages over other processes: better gas contact with smaller sorbent particles, ease of sorbent make-up and removal, easy control of the exothermic carbonation reaction temperature, and continuously steady operation.

The following reaction proceeds in each reactor [4][5]:

Carbonation: $M_2CO_3 + CO_2 + H_2O \leftrightarrow 2MHCO_3 + Heat$ (1)

Regeneration: $2MHCO_3 \leftrightarrow M_2CO_3 + CO_2 + H_2O$ (2)

Here, M denotes Na or K, and the reaction enthalpy of Eq. (1) for Na and K is -132.60 and -141.17 kJ/mole respectively.

Lee, et. al. [6]-[10] reported alkali metal-based sorbents using Al₂O₃, activated carbon, TiO₂, MgO, ZrO₂ and SiO₂, etc. as supporters with various preparation methods. The supporter has the important role of carbonation and regeneration.

KEPCO Research Institute (KEPRI) is developing regenerable sorbents using K₂CO₃ with a spray dryer method applicable to post-combustion CO₂ capture, with the process developer, Korea Institute of Energy Research (KIER). In 2006 and 2007, KIER's 2 Nm³/h and 100 Nm³/h (0.6 ton CO₂/d) circulating fluidized process using the developed K-based solid sorbent called KEP-CO2P, supplied from KEPRI, continuously achieved 80% CO₂ removal from simulated flue gas and 85% removal from flue gas, respectively. In 2010, the 2,000 Nm³/h (0.5 MW) capture process was installed into the slip stream of the flue gas of a coal-fired power plant of Korea Southern Power Co., Ltd. (KOSPO) located in Hadong, Korea, and has been evaluated for various operation conditions and sorbents.

KEPRI has tried to develop a K₂CO₃-based solid sorbent able to maintain initial performance, chemical durability, and good physical properties. This work presents the CO₂ sorption capacity and regenerability as well as the physical properties of seven K₂CO₃-based solid sorbents. The sorbents were prepared using a spray-dryer, with a focus on their application to a fast fluidized-bed reactor process and the reactivity was tested by thermogravimetery analysis (TGA).

II. EXPERIMENTAL

A. Sorbent Preparation

The sorbent was produced using a spray-drying method which is easily scalable to commercial quantities in batches of approximately 6 kg. The preparation process consists of several steps: 1) mixing the raw materials in water with dispersants, 2) comminution of the raw materials and colloidal slurry preparation with a high-energy bead mill, 3) spray drying to form a spherical-shaped green body, followed by pre-drying and calcinations steps. Among these process the slurry preparation is the most important step for obtaining spherically-shaped sorbent without defects, such as doughnut, hollow, or dimple shapes.

The raw materials used included commercial grade K_2CO_3 (Dongyang Chemical Co., Korea) as an active material, and various materials such as Al_2O_3, TiO_2, MgO, Zeolite 13X, hydrotalcite (HTC) and SiO_2 used as support materials. Seven formulations contained approximately 35 wt.% of the solid active material. All of the solid materials were mixed in a batch with water as solvent by a mechanical mixer, and then each formulation was comminuted with a ball mill. The solid concentration, viscosity and pH of these colloidal slurries were controlled by the addition of organic additives such as dispersants or water, to maintain them in the form of a homogeneous, dispersed and stable fluid, in this comminution step. The comminuted slurries were spray-dried to form the spherical solid sorbent and then the sorbents were calcined in a muffle furnace at 500~650°C under an air atmosphere. These sorbents were designated the Sorb-K series with each support material.

B. Physical Characterization

The physical properties for each seven sorbents were characterized through standard test methods. A packing volume/tap density device (Single Autotap, Quantachrome), ASTM D 4164-88, and sieve shaker (Meinzer II), ASTM E-11, were used to determine bulk density, size distribution and average particle size, respectively.

The attrition resistance for the circulating fluidized-bed process was evaluated using a modified three-hole air jet attrition tester based on the ASTM D 5757-95. The attrition index (AI) was determined to be 10 slpm (standard l/min) over 5 h periods, as described in the ASTM method. The attrition index is the percentage fines generated over 5 h:

AI (5) = total fines collected for 5 h/amount of the initial sample (50 g) × 100   (3)

The corrected attrition index (CAI) is the percent of fines generated over 4 h using the following equation:

CAI (5) = (total fines collected for 5 h - fines collected for first 1 h)/(amount of initial sample - fines collected for first 1 h) × 100
    (4)

The AI (CAI) of fresh Akzo and Davison FCC catalysts, which were used as references, were 22.5(18.0)% and 18.4 (13.1)%, respectively, under the same conditions. In a circulating fluidized-bed CO_2 capture process, materials with an

Table 1. TGA test conditions and gas compositions

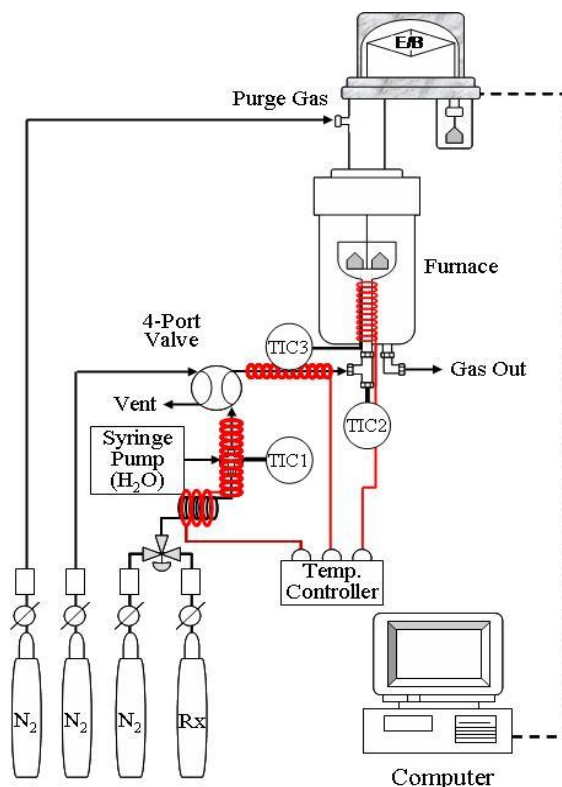| Conditions		Carbonation	Regeneration
Gas composition [vol.%]	CO_2	14.4	
	O_2	5.4	
	H_2O	10.0	
	N_2	70.2	100
Temperature [°C]		65-85	120-180
Pressure		ambient	ambient
Total gas flow rate [mL/min]		60	60

Fig. 1. The Diagram of the TGA gas supply system. TIC: temperature indicator and controller, EB: electronic balance.

AI < 20% would be acceptable for a transport reactor or a bubbling fluidized-bed reactor for use with flue gas under atmospheric pressure. A lower AI or CAI indicates a better attrition resistance of the bulk particles [5].

C. Chemical Reactivity

The chemical reactivity of the sorbents was assessed using a simultaneous thermal analyzer (Rheometrics Scientific STA 1500), which has the dual functions of thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC). Carbonation was performed from 65°C to 85 °C at every 5°C, respectively. The compositions of simulated flue gas were 14.4 vol.% CO_2, 5.4 vol.% O_2, and 10 vol.% H_2O with the remainder being N_2, as in Table 1. The total flow rate was 60 mL/min (standard) and the amount of each sample was about 10 mg. After CO_2 sorption was completed, regeneration was tested at 140°C and 180°C and the heating rate was 5°C/min. The regeneration gas was a neat N_2 gas with a flow rate of 60 mL/min (standard). The reaction test was performed to confirm the reproducibility of the results at least three times for each sorbent and it was found that each reactivity was similar in the

repeated test.

mechanical strength, particle size, and tap density and so on as

Table 2. Physical Properties of the developed K_2CO_3-based sorbents

	Sorbent						
	KEP-CO2P	Sorb-KB	Sorb-KT	Sorb-KM2	Sorb-KH	Sorb-KS	Sorb-KX
K_2CO_3 [wt.%]	35	35	35	35	35	35	35
Support material	γ-Al_2O_3	ε-Al_2O_3	TiO_2	MgO	HTC	SiO_2	13X
Solid Content [%]	32.5	30.5	31.3	32.1	19.9	29.5	
pH	11.9	11.8	10.4	13.7	10.6	12.0	11.8
Viscosity [cP]	6,540	440	2,800	104,000	6,400	280	810

Table 3. Slurry properties of the developed K_2CO_3-based sorbents

	Sorbent						
	KEP-CO2P	Sorb-KB	Sorb-KT	Sorb-KM2	Sorb-KH	Sorb-KS	Sorb-KX
Tap Density [g/cc]	0.98	0.97	1.11	0.99	1.11	1.05	0.72
Average Particle Size [μm]	103	126	118	113	111	124	148
Particle Size Distribution [μm]	37-303	49-303	42-303	19-300	16-300	19-280	57-355

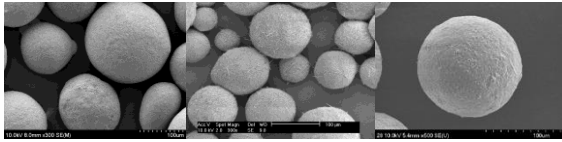Fig. 2. SEM images of the solid sorbent calcined at 550℃
(Left: KEP-CO2P, Middle: Sorb-KT, Right: Sorb-KM2)

A schematic description of the modified TGA is presented in Fig. 1. Water, quantitatively fed from a syringe pump, is contacted with the reaction gas or carrier N_2 gas. At this time, they are heated by TIC 1 to simulate flue gases at 140℃ and then the simulated gases flow to a 4-port valve. The simulated gases and regeneration gases are switched through the 4-port valve. The temperature of the simulated flue gases from the 4-port valve to the TGA inlet was controlled by TIC 2 at 100~120℃. Finally, the reaction gases were fed to the modified inlet line of the furnace which was heated with TIC3 without condensation at reaction temperature.

To obtain the net CO_2 sorption capacity from the (CO_2 + H_2O) absorption by the solid sorbents, the TGA cycle test was divided into four different sequential steps: Step I is the baseline with the neat N_2 gas. Mixture (H_2O + N_2) gas was introduced at the onset of Step II until there was no more TGA weight gain from H_2O adsorption. At the beginning of Step III, a simulated flue gas was introduced to perform the normal TGA experiment, in which the active component mainly reacts with a stoichiometric amount of CO_2 and H_2O. Finally, the sorbent was regenerated by dry N_2 while releasing CO_2 in Step IV.

The CO_2 sorption capacity, L_{CO2}, of a sorbent expressed in weight percentage was defined as:

$$L_{CO_2} = \frac{m_1 - m_0}{m_0} \times \frac{M_{CO_2}}{M_{CO_2} + M_{H_2O}} \times 100 \qquad (1)$$

where m_0 is the initial mass of a solid sorbent and m_1 is the mass measured without weight change by TGA in Step III. M is the molecular weight of CO_2 and H_2O, respectively.

III. RESULTS AND DISCUSSION

All the prepared sorbents were tested to screen a candidate applicable to the capture process for physical properties such as
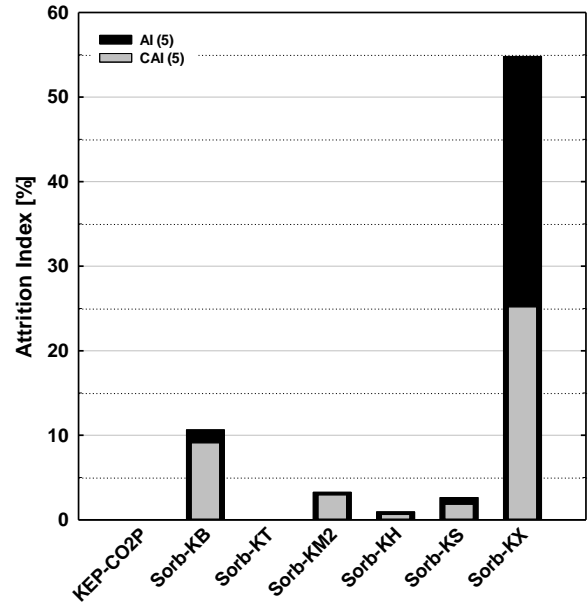

Fig. 3. The attrition index (AI) of the developed K_2CO_3-based sorbents calcined at 550℃.

well as chemical reactivity. Then, the various experiments for chemical reactivity were carried out.

A. Physical properties

The slurry properties of the seven spray-dried sorbents are summarized in Table 2. Although the viscosity of Sorb-KM2 was approximately 104,000 cP, which was significantly higher than the normal value used in the spray-dryer process, in this work a commercial pump was used and the high viscosity slurry was successfully spray-dried.

The shape of the sorbents was spherical without dimple, doughnut, or hollow shapes, as in Fig. 2. Table 3 shows the physical properties of the seven sorbents. Most of the sorbents showed suitable physical characteristics, average particle size and particle size distribution, and tap density, for the 0.5 MW capture process. Fig. 3 shows the AI (5) and CAI (5) of each sorbent. The attrition resistance as well as the chemical reactivity is two of the critical parameters in the development of a sorbent, because any attrition of the sorbent causes the loss of active material resulting in lower product quality. Attrition can

also result in the need for additional filtration and cause plugging as well as affect the fluidization and solid circulation properties [13]. The AI (5) results of the developed K_2CO_3-
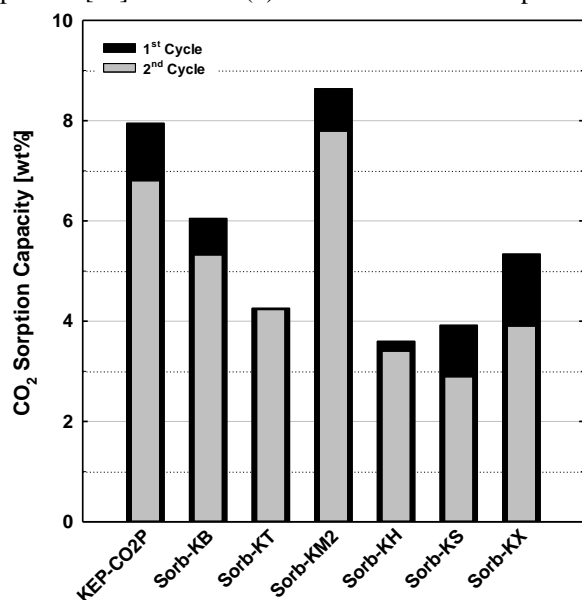

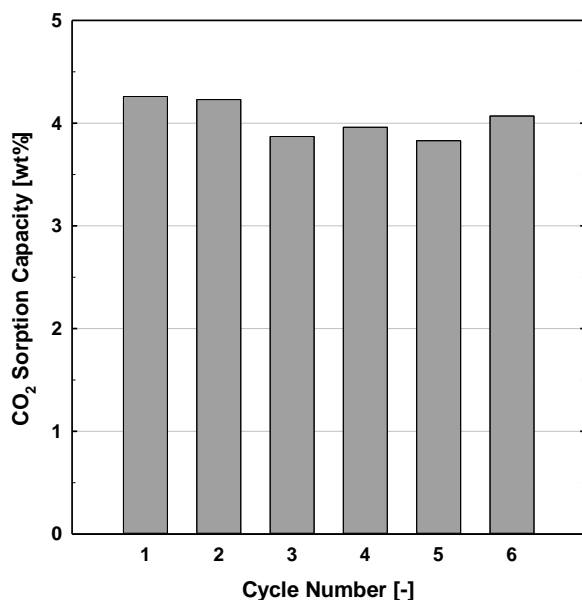Fig. 4.   The CO_2 sorption capacity of the developed K_2CO_3-based sorbents calcined at 550℃.

Fig. 5.   The CO_2 sorption capacity of Sorb-KT calcined at 550℃ during 6 cycle.

based sorbents, except Sorb-KX, were measured to be less than 11% as shown in Fig. 3. Especially, the AI (5) of sorb-KT was nearly zero like KEP-CO2P used in 0.5 MW test-bed. This means that three of the developed sorbents had suitable mechanical strength for the CO_2 capture process.

B. Chemical reactivity

    Seven developed sorbents were tested for CO_2 sorption capacity. To obtain the net CO_2 sorption capacity of the solid sorbents from their absorption of CO_2 and H_2O, the TGA cycle

test was divided into four different sequential steps: Step I is the baseline with the dry N_2 gas. A mixture of H_2O and N_2 gas was
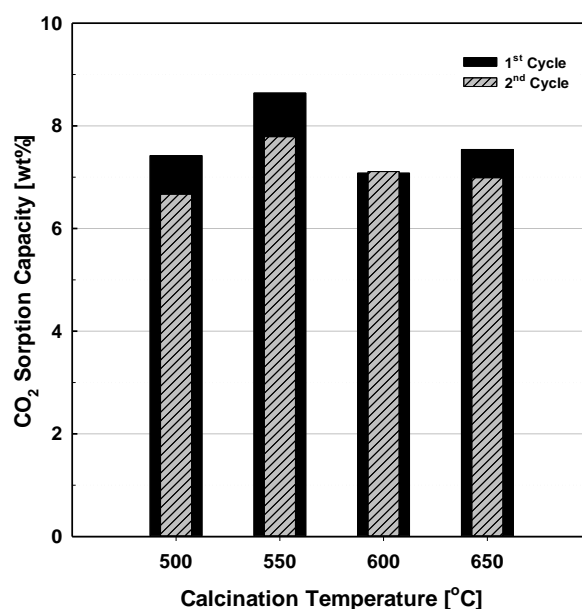

Fig. 6.   The effect of calcination temperatures on sorption capacity of Sorb-KM2.

introduced at the onset of Step II until there was no more TGA weight gain by H_2O adsorption. At the beginning of Step III, a simulated flue gas was supplied to perform the normal TGA experiment, in which the active component mainly reacts with a stoichiometric amount of CO_2 and H_2O. Finally, the sorbent was regenerated by dry N_2.

    To screen the chemical reactivity of the prepared sorbent, sorbents were dried at 180℃ and then the 2 cycle carbonation and regeneration test was carried out at 70℃ and 180℃ based on KEP-CO2P's results, respectively. Fig. 4 shows the sorption capacities of these sorbents. Especially, in the case of Sorb-KT, the sorption capacity maintained its initial value. Based on the results, 6 cycle sorption tests were carried out for Sorb-KT. There was no degradation of CO_2 sorption capacity during 6 cycles, as shown in Fig. 5.

    Sorb-KT was not selected as a candidate to apply to the 0.5 MW CO_2 capture test bed due to the lower performance than KEP-CO2P, although it showed excellent mechanical strength and no decrease in CO_2 sorption capacity. The lower CO_2 sorption capacity of Sorb-KT than KEP-CO2P was owing to drastic decreases in the active ingredient, K_2CO_3, in sorbent by new compounds such as $K_2Ti_2O_5$, $K_2Ti_6O_{13}$, and $K_2Ti_4O_9$, which were produced from K_2CO_3 and TiO_2 in the calcination process over 300℃ [6]. On the other hand, the reason why the sorbent was no degradation of performance was that K_2CO_3 in sorbent was only converted to $KHCO_3$ and the new compounds were inactive with CO_2 in simulated flue gas.

    The CO_2 sorption capacity of Sorb-KM2, K_2CO_3-MgO based sorbent, was higher than KEP-CO2P, and its regenerability which means percentage ratio of desorption capacity by CO_2 sorption capacity was over 90%. In addition, their utilization expressed as a percentage of net CO_2 sorption capacity by TGA and theoretical CO_2 capacity, was about 90%. The reaction rate constant was analyzed to compare the
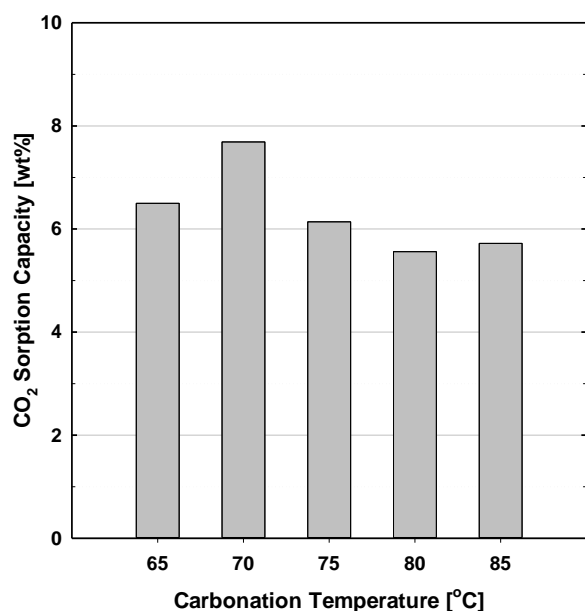
Fig. 7.   The carbonation temperature dependence of Sorb-KM2 calcined at 550℃.

developed sorbent, Sorb-KM2, with KEP-CO2P used in 0.5 MW CO_2 capture test bed for rate-based phenomenon. The reaction rate constant (k_c) of carbonation for KEP-CO2P and Sorb-KM2 was 0.216 min^{-1} and 0.356 min^{-1}, respectively.

To assess the effect of the calcination temperature, 500, 550, 600 and 650℃, on Sorb-KM2 under atmosphere, respectively, the carbonation test was examined at 70℃ under the simulated gas conditions, which in general is the amount included in the flue gas from coal fired power plant, and the sorbent was regenerated at 180℃. As shown in Fig. 6, the results indicate the highest capacity when the calcination temperature was 550℃.

The dependence of the CO_2 sorption capacity on the carbonation temperature for Sorb-KM2 calcined at 550℃ was tested at every 5℃ from 65℃ to 85℃, respectively. Simulated flue gases were supplied at 60 ml/min STP. The results are shown in Fig. 7. The maximum sorption capacity shows at 70℃ but the capacity abruptly decreased at temperatures over 75℃. It was thought that the reaction rate of CO_2 regeneration of K_2CO_3-MgO based sorbent was faster than the carbonation rate over 75℃.

The regeneration performances for Sorb-KM2 were tested at 120, 140 and 180℃ under N_2 based on the results of the KEP-CO2P used in the 0.5 MW CO_2 capture process. After 70℃ carbonation, the samples were heated at 2 ℃/min. The results are compared in Fig. 8. The regenerability of Sorb-KM2 increased at the higher temperature. Although the regeneration occurred at 140℃, the K_2CO_3-MgO based sorbent was almost completely regenerated at temperatures near 180℃. This means that the temperature of regenerator have to be maintained higher than 180℃ in order to efficiently attain CO_2 removal in the capture process. If the regeneration in the process was operated lower than 180℃, the CO_2 removal might be decreased because of the degradation of the CO_2 sorption capacity.

Deactivation by SO_2 in flue gases as well as the mechanical strength, chemical reactivity and the regeneration performance

is the one of the important factor in sorbent screening. Deactivation by pollutant, SO_2, in flue gas was tested with the simulated flue gas including 40 ppm SO_2. The test was carried out during continuous 4 cycles. First, the simulated flue gases without SO_2 as summarized in Table 1 was fed to TGA during 1 and 2 cycles and then the simulated flue gas including SO_2 was used to compare the performances in 3 and 4 cycles. The sorbents after each reaction with CO_2 were regenerated under N_2 at 180℃. In order to distinguish the differences in the performance, the results of the CO_2 sorption capacity containing the simulated gas without SO_2 and the simulated flue gas including 40 ppm SO_2 are presented in Fig. 9. The results showed that the degradation of the sorbents by SO_2 was negligible. Therefore, if this sorbent would be selected as the sorbent to operate the 0.5 MW CO_2 capture test bed, the SO_2 concentration in the flue gas should be controlled below 40 ppm to prevent the contamination by SO_2.

IV. CONCLUSIONS

Seven K_2CO_3-based solid sorbents using various support materials were prepared by spray dryer method in 6 kg/batch, to improve the performance of KEP-CO2P. The physical properties of all sorbents, i.e. their shape, size, size distribution, bulk density, attrition resistance, etc., were characterized. All sorbents showed average particle sizes in the range of 103~148 μm and a size distribution of 16~355 μm which are appropriate for fluidized-bed application. The bulk density of the sorbents
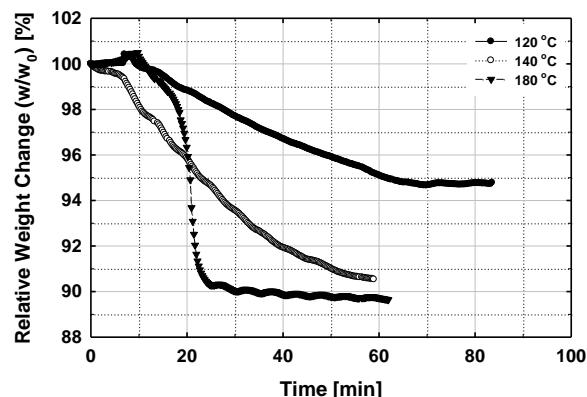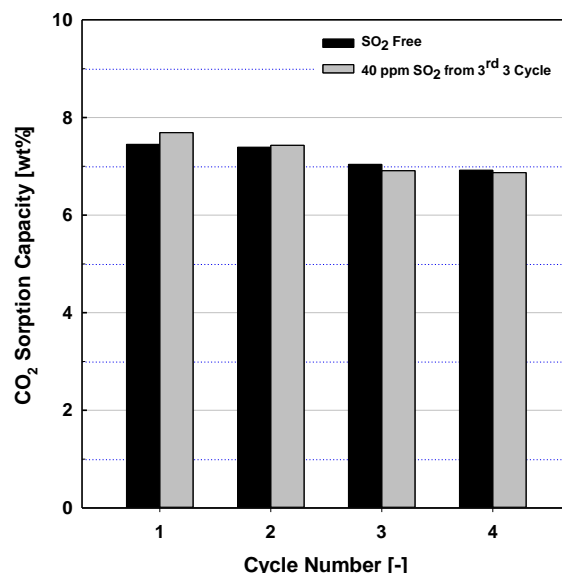

Fig. 8.   The performances of Sorb-KM2 calcined at 550℃ based on regeneration temperature under N_2.

119   Fig. 9.   The effect of SO_2 in flue gas for Sorb-KM2.

ranged from 0.72 to 1.11 g/mL. The attrition index (AI), meaning the mechanical strength of the sorbent for a fluidized-bed process was below 11%. All the physical properties of all sorbents except Sorb-KX using Zeolite 13X as a support material satisfied the requirements for the 0.5 MW dry regenerable CO_2 capture test bed. The K_2CO_3-TiO_2 based sorbent showed excellent regenerabilty without performance degradation as well as attrition resistance. However, it needs more improvement for chemical reactivity. The TGA CO_2 sorption capacity of the K_2CO_3-MgO based sorbent, Sorb-KM2, were 8.6 g-CO_2/100g-sorbents and its percentage utilization was over 90%, respectively. In the TGA runs, Sorbs-KM2 and KT were almost completely regenerated at 140°C under N_2. No degradation of Sorb-KM2 by SO_2 as a flue gas pollutant was observed during 4 cycles test. However, more detailed studies such as the regeneration performances of sorbents in the condition of high CO_2 concentration simulating real CO_2 capture process, reaction mechanism between carbonation and regeneration as well as the effect of various pollutants in the flue gas from coal fired power plant should be carried out in the future work to evaluate the cost-effectiveness and energy-efficiency of dry regenerable CO_2 sorbent technology.

ACKNOWLEDGEMENT

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