

A long-term test of a new CO₂ sorbent (KEP-CO2P2) in a 0.5 MW_e CO₂ capture test bed

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Abstract—The performance of a new dry CO₂ sorbent KEP-CO2P2 was tested for an extended period of time of 650 hours in a 0.5 MW_e CO₂ capture test bed at Hadong coal-fired power plant. The mass-produced CO₂ dry sorbent, KEP-CO2P2 was tested for CO₂ sorption and regeneration capacity. With modification of the process as well as the use of KEP-CO2P2 sorbent in a 0.5 MW_e CO₂ capture test bed, 85% (81-90%) CO₂ removal rate was achieved in continuous operation of 650 hours. Samples were collected and analyzed using particle size analyzer (PSA), ion chromatograph (IC), inductively coupled plasma (ICP), field emission-scanning electron Microscope (FE-SEM), electron probe X-ray micro-analyzer (EPMA) and X-ray diffractometer (XRD). The analysis showed that KEP-CO2P2 was not affected by SO_x, and there were no side reactions to consume K₂CO₃. However, the regeneration of the sorbent was not complete to need future investigation.

Keywords: CO₂ Capture, K₂CO₃-based CO₂ Sorbent, 0.5 MW_e CO₂ Capture Test Bed, SO_x, K₂CO₃·1.5H₂O

INTRODUCTION

According to the 2010 IEA (International Energy Agency) publications, CCS (carbon capture and storage) is the only and the most cost-effective technology to reduce CO₂ produced by massive use of fossil fuel and can reduce the worldwide CO₂ emission by 19%. In addition, IEA puts a strong emphasis on reduction of the emission in power generation sector along with the sectors such as building, transportation, industry, and transformation. Such importance of CCS led to the agreement, in 2009 G8 meeting, to start 20 large-scale demonstration projects in 2010 to supply CCS by 2020. In Korea, CCS research was spurred by plans to construct two plants in power generation sector by 2020 [1,2].

The research on CO₂ capture technology can be divided into the development of sorbents and processes. Our focus was on the development of sorbents for commercial scale CCS plants. Various dry alkali metal-based sorbents have been developed: K₂CO₃ and Na₂CO₃ as active materials, and Al₂O₃, calcium silicate, and ZrO₂ as supports, promoters or binders [3-12]. KEPSCO RI (Korea Electric Power Corporation Research Institute) has been working on the development of K₂CO₃-based sorbents. The first mass-produced sorbent was named KEP-CO2P1 as a serial form, tested in a 2,000 Nm³/h (0.5 MW_e) CO₂ capture test bed [13]. Although KEP-CO2P1 showed excellent physical durability within a certain period of time, several disadvantages were observed as the recirculation number was increased.

First, the sorbents were not regenerated completely due to the formation of complex compound of potassium dawsonite [potassium aluminum carbonate hydroxide, KAlCO₃(OH)₂], which could be produced by the reaction of K₂CO₃ with Al₂O₃.

Second, as the concentration of SO_x in the flue gas was not kept constant and very high intermittently, SO_x in flue gas reacted with K₂CO₃ and K₂SO₄ was formed. The formed K₂SO₄ was quite stable at 180-550 °C, i.e., the sorbent reacted with SO_x irreversibly and consumed. Consequently, if the sorbent had been used for a long period, more K₂SO₄ would have accumulated in the reactor, and so CO₂ sorption capacity of sorbent was deteriorated [13,14].

Finally, while the absorption reaction of KEP-CO2P1 was completed in a few seconds, its regeneration reaction did not proceed well. This phenomenon could be explained as that the incomplete regeneration might be caused by alumina, which was used to enhance the durability of the sorbent, an important physical property.

To address the above problems, a new durable and completely regenerable sorbent with the minimal amount of alumina, called KEP-CO2P2 was designed and manufactured. This new sorbent was investigated in this paper. The new sorbent was tested in CO₂ capture test bed comprised of a fast fluidized-bed reactor for CO₂ sorption and a bubbling fluidized-bed reactor for sorbent regeneration, one of which had 2 Nm³/h reactors and the other had 100 Nm³/h reactors, prior to the long-term test in a 2,000 Nm³/h (0.5 MW_e) CO₂ capture test bed which had been built in Unit 3 of Hadong coal-fired power plant in 2010 [15-23].

A compact and efficient auxiliary FGD (flue gas desulfurization) facility was added to the 0.5 MW_e CO₂ capture test bed to lower and to keep constant the concentration of SO_x in flue gas. The auxiliary FGD facility was designed to have minimum size in order to

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minimize its size in a planned large-scale demonstration facility. With modification of the process as well as the use of KEP-CO2P2 sorbent in a 0.5 MW_e CO₂ capture test bed, 85% (81-90%) CO₂ removal rate was achieved in continuous operation of 650 hours. The purity of CO₂ was 90-92 vol% and the removed amount can be converted to 11 ton CO₂/day.

The performance and characteristics of KEP-CO2P2 sorbent in the long-term test were investigated in this paper.

MATERIAL AND METHODS

1. Preparation of Sorbent

The spray-dry fabrication of the sorbents in this study takes two steps: making slurry by mixing and pulverizing the raw materials, and spray-drying the slurry. In step 1, highly uniform slurry was obtained by high energy ball milling (FrymaKoruma, MS-2) of a mixture of K₂CO₃, several supports such as alumina, inorganic binders, and promoters in distilled water. The uniformity of the slurry was carefully controlled by adding dispersant. The spheroidization of the sorbent, which is desirable for high fluidity, is largely dependent on the homogeneity of the distribution of the K₂CO₃ and binders. In addition, other properties such as viscosity (~6,540/cP) and pH (11.9) of the slurry were kept at proper values such that the slurry had good characteristics for spray-drying. The slurry was then sieved through 40-65 µm sieve. In step 2, the slurry was transformed to spherical solids in a certain range of sizes by a pilot plant-size spray-dryer at room temperature, and then dried at 105 °C in a convection oven for 24 hours and calcinated at 550 °C in a muffle furnace. More information about the sorbent preparation was reported in previous papers [6,13].

Fig. 1 shows the sampling positions, and Table 1 shows the sam-

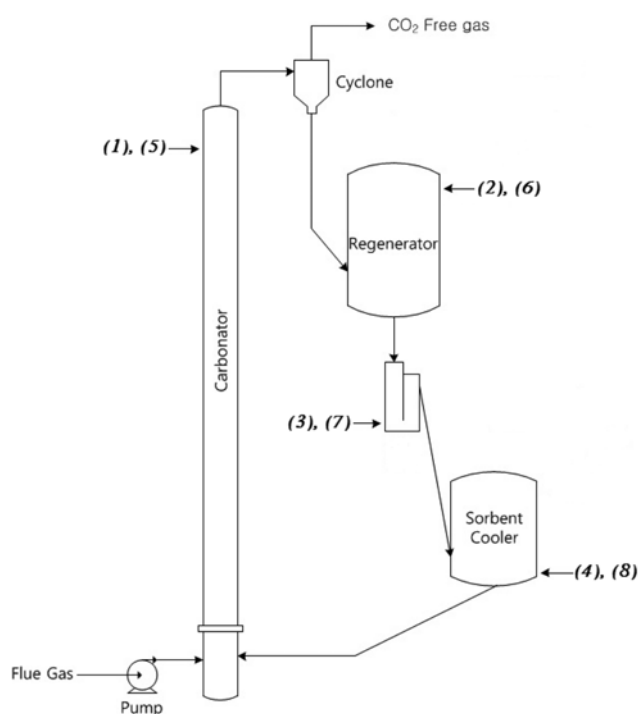


Fig. 1. Sampling positions.

Table 1. Nomenclature of samples

Sampling position	Sampling date	
	After 550 hours	After 650 hours
Carbonator	Sample (1)	Sample (5)
Regenerator (top)	Sample (2)	Sample (6)
Regenerator (bottom)	Sample (3)	Sample (7)
Sorbent cooler	Sample (4)	Sample (8)
Unused	Sample (0)	

Table 2. Concentration of flue gas on Tele-monitoring system (TMS)

Items\Concentration	Maximum	Average	Minimum
SO _x (ppm)	57.16	27.92	10.21
NO _x (ppm)	73.66	52.02	38.08

ple names according to sampling dates and positions. The unused, fresh sample was named Sample(0).

The typical concentrations of SO_x and NO_x observed on TMS (tele-monitoring system) of Hadong power plant are summarized in Table 2. Some more information of Hadong power plant including clean-up systems can be found in our recent paper [13]. As presented in Table 2, the concentration of SO_x varied drastically such that the maximum concentration was five-times higher than the minimum concentration. Thus, a compact and efficient auxiliary FGD facility was installed in the 0.5 MW_e CO₂ capture test bed to maintain the concentration of SO_x in the input flue gas at a constant low level.

2. Methods

The long-term test lasted continuously 650 hours and sorbents were sampled from four different positions after 550 hours and 650 hours of continuous operation. The samples were compared with fresh sorbents. Various analyses were performed, such as IC (ion chromatograph) analysis to investigate the effects of SO_x, NO_x and Cl in flue gas on the sorbent, ICP (inductively coupled plasma) analysis to investigate the content of Al, Zr, K etc. in the sorbent, surface analysis with SEM (scanning electron microscope) and EPMA (electron probe X-ray micro-analyzer) to observe the surface phenomena, and XRD (X-ray diffractometer) analysis to elucidate the possibilities of side product formation such as K₂SO₄ and potassium dawsonite.

Bulk density and AI (attrition index) were measured according to ASTM D 4188 and ASTM D 5757-95, respectively. Average particle size and size distribution were analyzed by a particle size analyzer. BET (Brunauer-Emmett-Teller) was measured by Autosorb-2000 (Quantachrome). The chemical reactivity of the sorbents was assessed using a simultaneous thermal analyzer (Rheometrics Scientific STA 1500), which has the dual functions of TGA (thermo gravimetric analysis) and DSC (differential scanning calorimetry). The composition of the simulated flue gas as reaction gas was 14.4 vol% CO₂, 5.4 vol% O₂, and 10 vol% H₂O with the remainder being N₂. Pore distribution and porosity were analyzed by a porosimeter (AutoPore IV, 9500 Hg porosity meter, Micromeritics®).

Anion concentration was analyzed by IC (ion chromatograph, ICS-1600, Dionex) with a commercial eluent of Eluent Mpak A

Supp 5 Eluent. The sample was prepared by extraction with a distilled water (sample: water=1:10, mass ratio) after 1 hour stirring, and then filtration.

Cation concentration was analyzed using ICP-OES (inductively coupled plasma-atomic emission spectroscopy, Optima 7300DV, Perkin Elmer). The sample was prepared by high pressure acid digestion using about 0.02 g sample and mixed acid (H₂SO₄ 3 mL+H₃PO₄ 1 mL) in a muffle furnace at 270 °C for 65 hours.

The surface of samples was examined with UHR FE-SEM (ultra-high resolution field emission-scanning electron microscope, S-5500, Hitachi, Japan). The specimen was prepared to have 5-6 nm thickness and coated with OsO₄.

The EPMA (electron probe X-ray micro-analyzer, Shimadzu Corp., Japan) used in this study has 0.2-30 kV accelerating voltage and 0.5-1,000 nA in beam current.

The crystal structure of specimen was analyzed using an XRD (D/MAX 2200, Rigaku International) with Cu K α at 40 kV and 30 mA in 3°-80° of 2 θ .

RESULTS AND DISCUSSION

To compare the fresh sorbent with the used ones and to understand the phenomena occurring in the carbonation reactor (carbonator), the regeneration reactor (regenerator) and the sorbent cooler, sorbents were sampled at two different operating dates and analyzed with various instruments.

1. Physical Properties and Sorption Capacity

For comparison, the key physical properties and sorption capacity of the fresh sorbents of KEP-CO2P1 and KEP-CO2P2 are shown in Table 3. Both sorbents were fabricated well to have spherical shape. Most of physical properties of the sorbents were almost identical even though BET of KEP-CO2P2 was a little low. However, the durability and CO₂ sorption capacity, the most important key parameters, were improved in KEP-CO2P2.

Table 3. Physical properties and CO₂ sorption capacity of mass-produced sorbents

Properties\Sample	KEP-CO2P1	KEP-CO2P2
Shape	Spherical	Spherical
Average particle size (mm)	105-110	106-127
Particle distribution (mm)	43-270	41-268
Bulk density (g/cm ³)	0.87-0.90	1.02-1.15
BET (m ² /g)	40.7	8.27
Attrition Index (AI, %)	<12	<10
CO ₂ sorption capacity (wt%)	~8	~10

2. Porosity

Table 4 shows the porosity and pore size distribution of the sorbent. After measuring porosity, we tried to classify porosity with several ranges, and found that the sorbent could be described best by dividing the pore distribution below and over 1 μ m. As can be seen in the table, the porosity below 1 μ m was increasing from the carbonator to the sorbent cooler through the regenerator, and also from top to bottom in the regenerator while the porosity over 1 μ m remained relatively unchanged. Based on the porosity change, it can be concluded that absorption and regeneration steps proceeded smoothly.

3. IC Analysis

To investigate the effects of SO_x, NO_x and Cl in flue gas on the sorbent, anion concentration was analyzed by IC. As shown in Table 5, the SO_x concentration of unused sorbent (Sample (0)) was 0.176 wt% and that of eight used sorbent samples ranged 0.185-0.329 wt%. We can see that SO_x concentration remained almost the same or slightly increased. When this result is compared with previous result with KEP-CO2P1 sorbent, where the SO_x concentration after use increased to 1.5 wt%, it can be concluded that the auxiliary FGD worked well [13]. And also, the concentrations of NO₃⁻ and

Table 4. Porosity of the sorbents measured by pore size analyzer (PSA)

Sample\Size	0.003-1 μ m		1-360 μ m	
	After 550 hrs	After 650 hrs	After 550 hrs	After 650 hrs
Carbonator	16.38%	16.09%	40.27%	39.93%
Regenerator (top)	19.36%	17.74%	39.16%	41.23%
Regenerator (bottom)	19.54%	18.89%	40.45%	43.16%
Sorbent cooler	19.33%	20.57%	48.38%	40.91%
Unused	21.53%		62.87%	

Table 5. Anion concentrations analyzed by Ion chromatography (IC)

Sample\Ion	Cl ⁻ (wt%)		NO ₃ ⁻ (wt%)		SO ₄ ²⁻ (wt%)	
	After 550 hrs	After 650 hrs	After 550 hrs	After 650 hrs	After 550 hrs	After 650 hrs
Carbonator	0.016	0.003	0.013	0.010	0.293	0.278
Regenerator (top)	0.016	0.002	0.029	0.011	0.296	0.275
Regenerator (bottom)	0.017	0.017	0.030	0.010	0.329	0.276
Sorbent cooler	0.015	0.014	0.011	0.008	0.220	0.185
Unused	0.015		0.009		0.176	

Cl^- of eight samples remained almost the same as those of unused sample, indicating that the NO_x and HCl in flue gas did not affect KEP-CO₂P2 sorbent.

4. ICP Analysis

The cation concentration in the sorbent was analyzed by ICP to investigate the variation during absorption and regeneration. Because of Al, Si, etc. in the sorbent, it was not easy to dissolve the sorbent completely. After some trial-and-error, the sorbent samples were dissolved completely and clearly by high pressure acid digestion. As shown in Table 6, the concentrations of Al and Ca,

which came from binder, support or promoter, changed slightly or insignificantly. But the concentration of K was reduced 1-1.5 wt% after continuous operation for ~650 hours. It is equivalent to about 2.45 wt% of K_2CO_3 , and the reduction rate was a little high considering the expected lifespan of the sorbent. However, in our experience most of the reduction usually occurred in the initial stage of the sorbent test, and as the CO_2 capture test bed stabilized and the operation period was extended, the reduction rate was decreased. The reduction of K could also come from gradual wearing-out of the sorbent by friction. To confirm the abrasion of the sorbents,

Table 6. Cation concentrations analyzed by ICP

Sample\Ion	K (wt%)		Al (wt%)		Ca (wt%)	
	After 550 hrs	After 650 hrs	After 550 hrs	After 650 hrs	After 550 hrs	After 650 hrs
Carbonator	18.23	19.38	23.19	23.00	3.57	3.67
Regenerator (top)	18.98	18.87	22.45	23.55	3.11	3.53
Regenerator (bottom)	19.00	19.26	23.21	23.59	2.95	3.70
Sorbent cooler	19.42	18.81	25.06	23.38	3.39	3.56
Average	18.91	19.08	23.48	23.38	3.26	3.62
Unused	20.46		23.98		3.32	

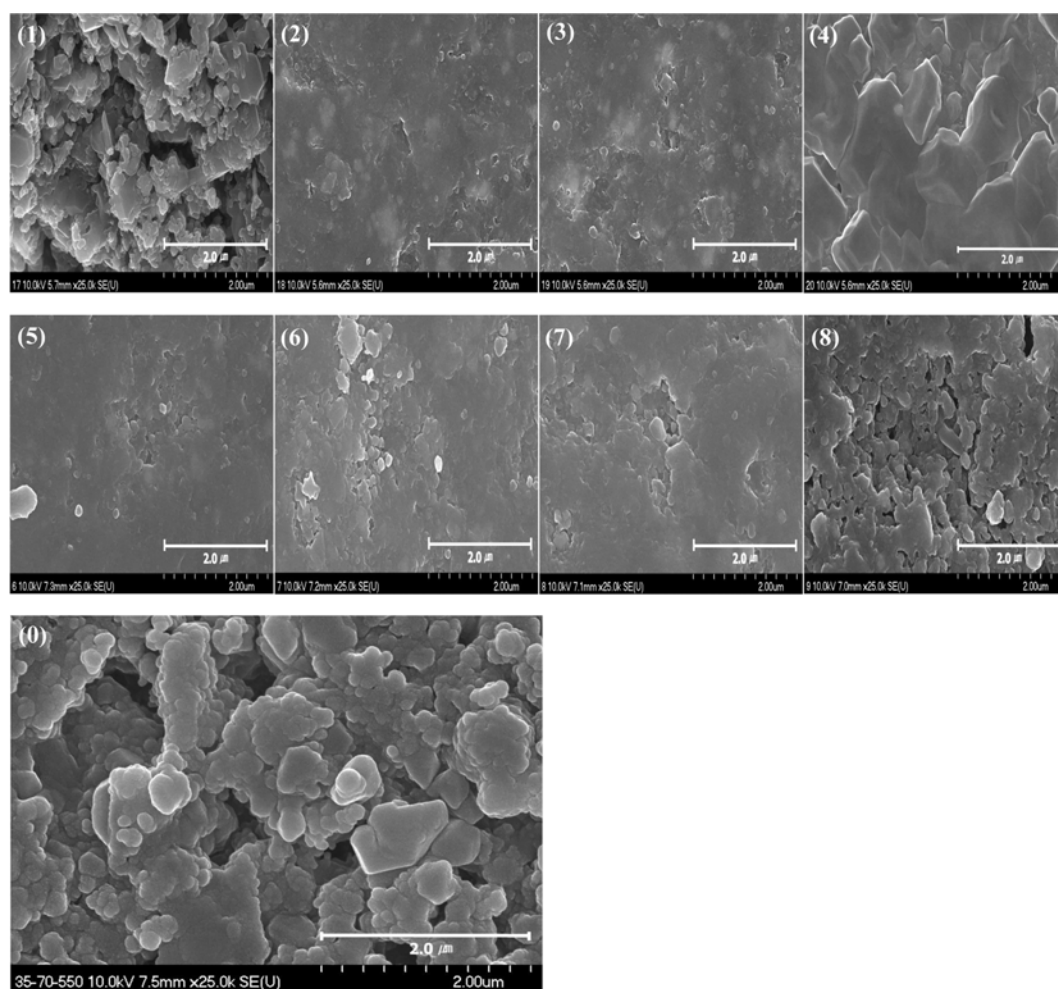


Fig. 2. SEM images of $\times 25,000$ [(1-4): after 550 hours, (5-8): after 650 hours, (9): unused].

sorbents from cyclones are planned to be analyzed in the near future.

It was very difficult to analyze accurately the content of K₂CO₃ in the sorbent, because K component could exist as K₂CO₃, KHCO₃ and K₂CO₃·1.5H₂O. Other tools such as FT-IR (Fourier transform-infrared), XPS (X-ray photoelectron spectroscopy), etc. were tried, but no improvements were made.

5. FE-SEM Analysis

FE-SEM images of the sorbent are shown in Fig. 2. Some pores were observed on the surfaces of Samples (1) and (5) sampled from the carbonator, but most of the surfaces were smooth due to the reaction with water. Compared to the surfaces of Samples (2) and (6) sampled from the top of the regenerator, the surfaces of Samples (3) and (7) sampled from the bottom of the regenerator were

less dense and more porous. Samples (4) and (8) from the sorbent cooler had considerably more pores than Samples (3) and (7) did. However their surfaces were different from that of the unused sample, Sample (0), indicating incomplete regeneration. Usually, it took one hour to regenerate the sorbents, but the results were used to optimize the regeneration conditions, including regeneration time and temperature.

6. EPMA Analysis

Some of EPMA images are shown in Fig. 3. Regardless of sampling position and time, K, Al, and Ca were observed clearly, but components from promoters or binders were indistinct or not observed. Al and Ca were distributed on entire particle of Sample (1), and had tendency to be lumped together. The images of K are

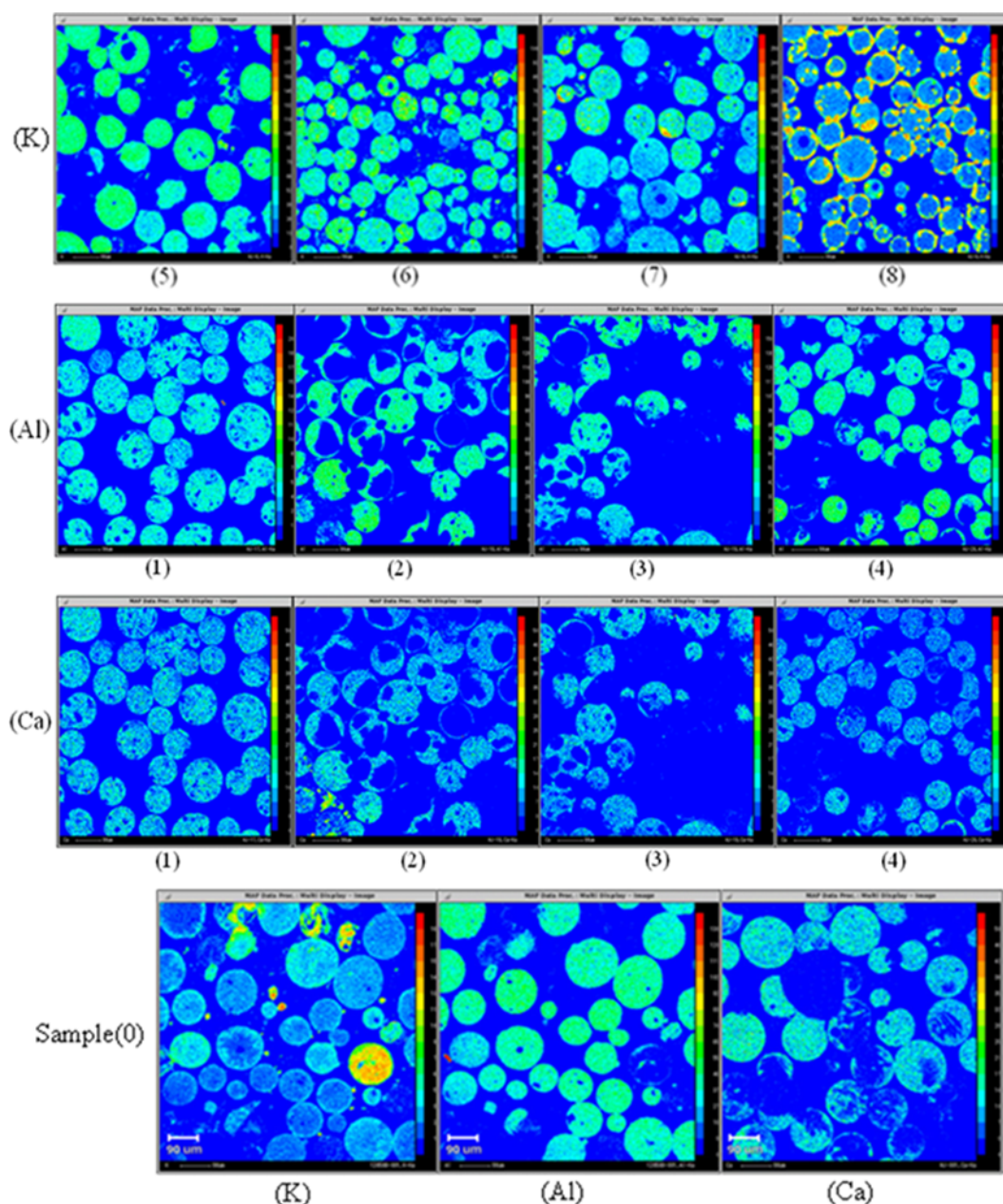


Fig. 3. EPMA spectra of K, Al, and Ca for 9 samples [(1-4): after 550 hours, (5-8): after 650 hours, (0): unused].

very similar in Samples (5), (6) and (7). However, the image of K in Sample (8) looks like K was redistributed to the surface of sorbent particles. While the distribution of Al in the used Samples (1)-(3) was less dense than that of unused Sample (0), the distribution of Ca was very similar in both the used samples and the unused one.

7. XRD Analysis

As seen in the XRD pattern of KEP-CO2P2 in Fig. 4, the peaks of K_2SO_4 produced by the reaction of K_2CO_3 with SO_x and potassium dawsonite produced by the reaction of K_2CO_3 with Al_2O_3 were

not observed. Based on the observation, addition of a compact and efficient auxiliary FGD facility was very effective to lower the concentration of SO_x in flue gas and to keep it constant. Besides, potassium dawsonite, a side product was not formed in KEP-CO2P, which resulted in a cleaner regeneration.

Table 7 shows the summary of peaks of $K_2CO_3 \cdot 1.5H_2O$ and $KHCO_3$. K_2CO_3 was not observed by XRD. This can be explained as that K_2CO_3 did not crystallize, or was converted to $K_2CO_3 \cdot 1.5H_2O$ by the absorption of H_2O . Fig. 4 shows the XRD patterns. In the unused Sample (0), as expected, only $K_2CO_3 \cdot 1.5H_2O$ was observed

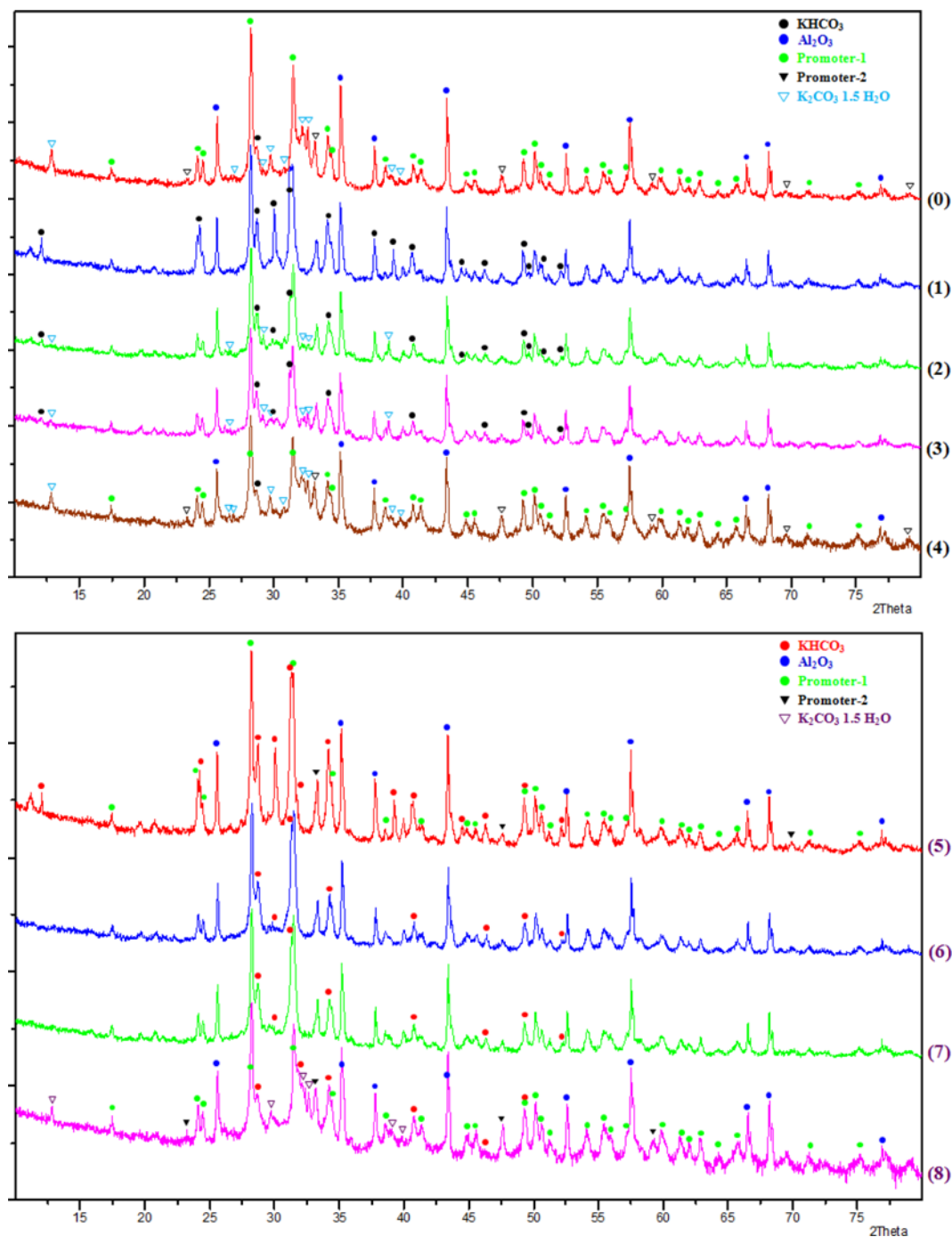


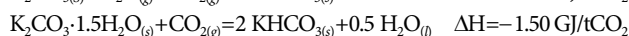
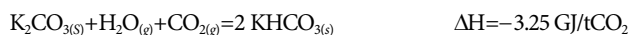
Fig. 4. XRD patterns of 9 samples [(1-4): after 550 hours, (5-8): after 650 hours, (0): unused].

Table 7. Peak intensity of K₂CO₃·1.5H₂O and KHCO₃

Sample\Compound	K ₂ CO ₃ ·1.5H ₂ O	KHCO ₃
Sample (1)	N/D	High
Sample (2) & (3)	Medium	Medium
Sample (4)	High	Medium
Sample (5)	N/D	High
Sample (6) & (7)	N/D	Medium
Sample (8)	High	Medium
Sample (0)	High	N/D

N/D: non-detected

and KHCO₃ was not observed. For the set of samples consisting of Samples (1)-(4) sampled after 550 hours, only the peak of KHCO₃ was observed in sample (1) sampled from the carbonator, which shows that the absorption reaction proceeded well. However, based on the observation that the peaks of KHCO₃ still existed in Samples (2)-(3) from the regenerator, it can be inferred that the sorbent was not regenerated completely. One noteworthy observation from Samples (2)-(3) was that peaks of K₂CO₃·1.5H₂O were found in the samples. The formation of K₂CO₃·1.5H₂O instead of K₂CO₃ has a significant meaning in the regeneration process in respect of energy consumption [4,24]. The regeneration reaction equations are:



As shown, the regeneration of KHCO₃ to K₂CO₃·1.5H₂O requires less energy than the regeneration of KHCO₃ to K₂CO₃, which implies K₂CO₃·1.5H₂O is the preferred regeneration product. For another set of samples, Samples (5)-(8) sampled after 650 hours, only the peak of KHCO₃ was observed in Sample (5) similar to Sample (1). On the other hand, the peaks of K₂CO₃·1.5H₂O were not observed in Samples (6) and (7). It can be inferred that KHCO₃ was converted to K₂CO₃ instead of K₂CO₃·1.5H₂O, but due to lack of crystallinity the peak of K₂CO₃ was not observed.

When KHCO₃ formed in the carbonator was converted to K₂CO₃ or K₂CO₃·1.5H₂O in the regenerator, water content and temperature could affect the formation of these compounds; the mechanism is under investigation. Besides peaks of Al₂O₃, those of other promoters were observed to show similar intensities irrespective of sampling positions.

CONCLUSIONS

The performance of a new dry CO₂ sorbent KEP-CO2P2 was tested for an extended period of time, 650 hours, in a 0.5 MW_e CO₂ capture test bed at Hadong coal-fired power plant. With modification of the process as well as the use of KEP-CO2P2 sorbent in a 0.5 MW_e CO₂ capture test bed, 85% (81-90%) CO₂ removal rate was achieved in 650 hours continuous operation. The purity of CO₂ was 90-92 vol% and the total removed CO₂ was estimated to be 11 tons CO₂/day. The mass-produced CO₂ dry sorbent KEP-CO2P2, which was expected to have better regenerability than previous KEP-CO2P1 sorbent, was tested for CO₂ sorption and regeneration capacity. The following conclusions are made:

1) There was no peak of K₂SO₄ in XRD and SO_x concentration was low in IC analysis in all used samples. This implies no deterioration/consumption of sorbents by SO_x - a very encouraging result for KEP-CO2P2.

2) The content of K was reduced 1-1.5 wt% after continuous operation for 650 hours. The loss is equivalent to about 2.45 wt% of K₂CO₃, which is a little high. In our experience the loss rate of K₂CO₃ had been large in the beginning of tests and reduced gradually over time. Thus actual loss in commercial plant is expected to be lower than 2.45 wt% and will not be a serious problem.

3) The side products, K₂CO₃, Al₂O₃, and potassium dawsonite, were not formed during regeneration when KEP-CO2P2 was used, which implies smooth regeneration of the sorbent.

4) Even though KEP-CO2P2 is more regenerable than KEP-CO2P1, it was not completely regenerated considering the peak of KHCO₃ observed in sorbents from the sorbent cooler. We are investigating whether the problem of incomplete regeneration of very small portion of the sorbent can be solved by the change of regeneration time and temperature.

5) In the regeneration stage, either K₂CO₃ or K₂CO₃·1.5H₂O was formed. Even though K₂CO₃·1.5H₂O is a better regeneration product than K₂CO₃, the reaction mechanisms are not clearly known and under investigation in our group.

We are also working on the sorbents applied to 10 MW_e CO₂ capture pilot plant this year as well as on the process optimization, including the determination of regeneration time and temperature, and water content, etc., with the results presented in this paper.

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