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Shaping Technology of Coal Gas Sorbents by Using a Spray Dryer

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Abstract−The goal of this study was to develop HTHP sorbents for adaptation in fluidized bed desulfurizers or Transport Reactors. For this purpose, we shaped zinc-based sorbents (ZAC series) by using a spray dryer with a pressurized nozzle atomizer. To prepare the slurry for spraying, raw materials in submicron units and organic additives were used. We characterized the sorbents by SEM, XRD, Mean Particle Size Analysis, BET Surface Area and Attrition Ratio. The mean particle size was about 112 μm, the attrition resistance was very good and the TGA sulfur capacity of the fresh sample was calculated at about 23-24 wt%.

Key words: IGCC, Sorbent, Desulfurization, Spray Dryer, Hot Gas Clean-up

INTRODUCTION

Hot Gas Desulfurization (HGD) technology, which is predicted for use in Clean Coal Technologies (IGCC, PFBC & MCFC), is a technique for removing sulfur compounds (H_2S, COS) from fuel gas or coal gas by using regenerable metal oxide sorbents at a high temperature (350-650 °C) and high pressure (20-30 bar) [Song et al., 2000]. HGD technology is a key element in the optimal development of the integrated gasification combined cycle (IGCC) process, and many researchers [Lee et al., 1997; Ryu et al., 1998] have paid attention because of the potential for high thermal efficiency and low environmental impact. HGD processes are classified into such types as the fixed bed, the moving bed, the fluidized bed and the transport reactor process [Park et al., 1993].

Fluidized bed and transport reactor processes have merits such as excellent thermal translation effect and lower pressure drop in comparison with other processes [Ryu et al., 1999]. To complete the HGD technology, development of regenerable metal oxide sorbents is essential.

Sorbents used in the HGD process are kinds of metal oxides such as iron oxide (FeO, Fe_2O_3, Fe_3O_4), calcium oxide (CaO), zinc oxide (ZnO) and complex oxidants (e.g., zinc ferrite, zinc titanate) [Gangwal, 1991] and the basic reaction of sulfidation is expressed by the following equation:

$$\text{MO (metal oxide)}+H_2S \leftrightarrow \text{MS (metal sulfide)}+H_2O \qquad (1)$$

Durable sorbents must be regenerated several times and have the ability to preserve an initial sulfur capture capacity through the sulfidation/regeneration cycles. Generally, regeneration is undertaken by using an oxidant such as oxygen or air and air/steam, and the reaction is expressed by the following equation:

$$\text{MS (metal sulfide)}+3/2\ O_2 \leftrightarrow \text{MO (metal oxide)}+SO_2 \qquad (2)$$

To date, zinc oxide-based sorbents including zinc titanate are considered as the leading regenerable sorbents for HGD [Gupta et al., 1998; Lee et al., 1997].

In the HGD process, sorbents are reused through the recirculation of sulfidation/regeneration. Sulfur dioxide produced during the regeneration process is recovered as elemental sulfur or sulfuric acid through a sulfur recovery process and they can be used for other purposes.

Suitable sorbents in the fluidized bed have to possess characteristics such as semi spherical shape, particle size of 50-300 μm and high attrition resistance [Gupta et al., 1996; Abbasian et al., 1997]. To prepare these sorbents, a spray dryer is suitable. Spray dryers are widely used in the organic and inorganic industries and in the fine ceramics industry because of their merits, such as rendering homogeneous shape of products, multiple production ability, and economics. Feed slurry must be sprayed into a flow of uniform heating air without pulsing and with continuous velocity. Viscosity and surface tension of the liquid determine the spraying capacity. Spray dryers are classified by the structure of the atomizer such as the pressure nozzle, the two-fluid nozzle, and the rotary wheel atomizer [Masters, 1985]. In powder processing, decision factors for the product's particle size are known as size, size distribution, shape, and surface electric charge of raw materials. And the decision factors for the slurry's dispersion capability are known as the viscosity and the pH.

In this research, we prepared ZAC series sorbents, which were types of zinc-based sorbents, by using a spray dryer. We then surveyed the characterizations of shaping and reactions. The primary objective of this study was to establish the basic technique for optimal sorbent preparation.

EXPERIMENTAL SECTIONS

In this study we used reagents such as ZnO powder as an active material, celite as a support, alumina sol as an inorganic binder and some organic additives as a dispersion agent and a defoamer. We shaped the ZAC series sorbents 14th times using a nozzle type spray dryer, which had been set to optimal operating conditions in the shakedown test. After pre-drying, the sorbents were calcined in the muffle furnace with air conditioning for 2-3 hours. Since the TGA

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reactions of ZAC-4 and ZAC-9 were excellent, we produced ZAC-4N and ZAC-9N impregnated 7.5 wt% nickels (Nickel Nitrate). Otherwise, ZAC-11(N)~ZAC-14(N) were shaped with the directly impregnated Ni slurry by using a spray dryer. To confirm the operating condition of the spray dryer, we shaped the zinc titanate series sorbents, called as the NZT series. After calcination, optical microscope and SEM analyses were carried out to observe the surface shape, the internal structure and the distribution of raw materials.

We modified an attrition tester of ASTM D 5757-95. This facility was used to evaluate the attrition resistance of sorbents. A 50 g sample (upper 40 μm) of the ZAC series sorbents was charged in the fluidizing region of the attrition tester, then the nitrogen gas was used for 1 hour through a 3-hole nozzle air-jet plate with a flow rate of 10 *l*/h. After 1 hour, a fresh collection thimble replaced the used collection thimble, and the weight of collected fines was measured. Under the same conditions, the sample was tested for 4 hours by fluidization. After that, the weight of total collected fines was measured and attrition resistance was calculated.

Several analyses were carried out such as BET surface area, XRD and Bulk density of the ZAC series sorbents.

A TGA test of the ZAC series sorbents was undertaken by using the Rheometrics STA (Simultaneous Thermal Analyzer) 1500. The used gas compositions, in sulfidation, were H_2-10.38 vol%, CO-16.8 vol%, CO_2-6.1 vol%, N_2-66 vol%, H_2O-10 vol% and H_2S-3 vol%. Air was used as a regeneration gas. The sample amount was about 10 mg, and the size distribution range was 40-160 μm. The sulfidation/regeneration experiments were done at 500 °C, 540 °C and 650 °C.

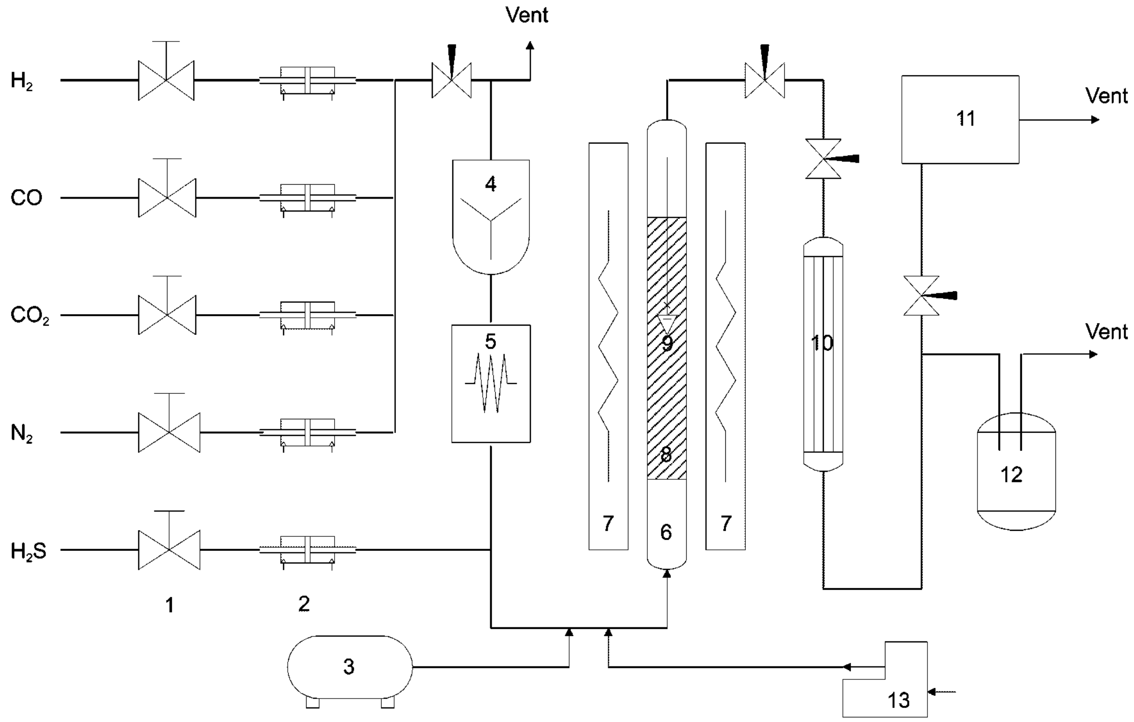


Fig. 1. Apparatus for sulfidation and regeneration.

1. Solenoid valve
2. Mass flow controller
3. Air compressor
4. Mixer
5. Pre-heater
6. Reactor
7. Electric heater
8. Fluidized bed
9. Thermocouple
10. Condenser
11. Gas chromatography
12. NaOH solution
13. Steam generator

Table 1. Sulfidation/Regeneration conditions of the HTHP reactor

Composition	Mole fraction (%)		Reaction condition		
	Sulfidation	Regeneration			
H_2	10	Dry air	Condition	Sulfidation	Regeneration
CO	20				
CO_2	7		Temp. (°C)	500	540
CH_4	0.4				
H_2S	0.4		Pressure (kgf/cm^2)	7	7
N_2	52.2				
Steam	10		Space velocity (h−1)	1800	1800
Total	100				

The 10-cycle test of ZAC-4N was performed in the test facility, which can be operated at high temperature and high pressure (HTHP) and is shown in Fig. 1. Operating conditions were as follows: temperature was 500 °C, the pressure was 7 kg/cm^2, and space velocity was 1,800 hr^{-1}. Steam (10 vol%) was used to simulate the coal gas and the size distribution of sorbents was 75-125 μm and the sorbents were packed at a weight of approximating 100 g in the reactor. Simulated gas flow was controlled quantitatively by an MFC, preheated at about 300 °C in the mixer and supplied to the reactor. Then, H_2S (about 4,000 ppm) gas and steam were supplied directly in the front of mixer. When the sulfidation reaction ended at the breakthrough point, the supply of H_2S and simulated mixed gases was stopped. Then, nitrogen gas was used to purge the HTHP reactor for about 1 hour. After purging, regeneration of sorbents was carried out at 500 °C by using dry air. Typical test conditions maintained during experiments on the HTHP reactor are presented in Table 1.

During experiments, a reactor effluent slipstream was analyzed continuously by a Finnigan 9001 gas chromatograph (GC) for H_2S, COS and SO_2. These analyses were continued until reaching the breakthrough point of H_2S, 200 ppm, then the sulfur capture capacity was calculated from these data.

At the end of the multiple cycles, typically 10 cycles of absorption and regeneration, the reactor was opened and the sorbent was removed from the reactor for a scanning electron microscope (SEM).

RESULTS AND DISCUSSION

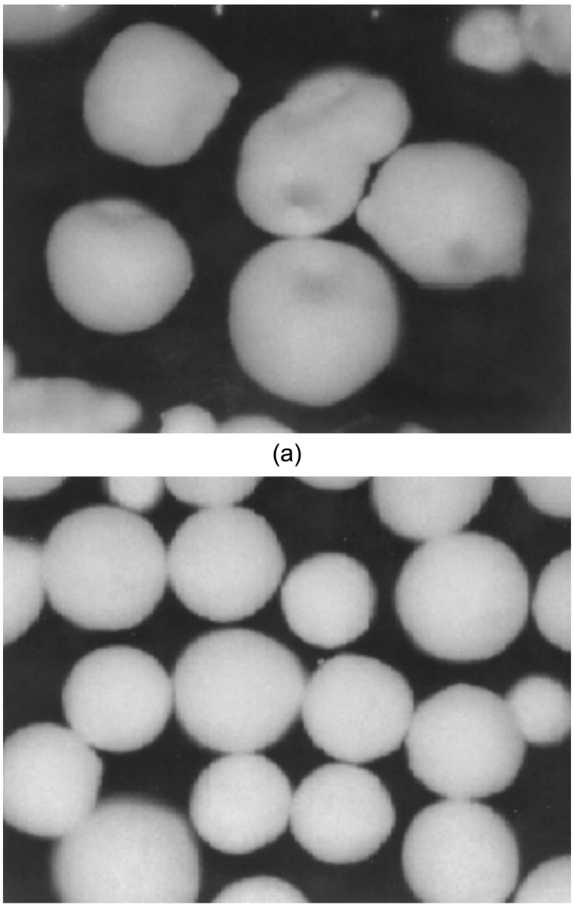
1. Preparation of a Slurry and Operation of a Spray Dryer

A key element to produce sorbents possessing good particle size distribution and shape depends on how well the slurry is sprayed. In order to shape sorbent by using a spray dryer, operating conditions of a spray dryer and spraying conditions of the slurry must be balanced with each other. The operating conditions of a spray dryer were as follows: particle size distribution range=40-300 μm, nozzle diameter=0.51 mm, slurry feeding pressure=8-10 Kg/cm^2, inlet air temperature=280-300 °C, outlet air temperature=90-130 °C. The uniformity, the concentration and the viscosity of the slurry in a viewpoint of spraying conditions were then inspected.

The uniformity of the slurry can be determined depending on how similar the raw materials sizes are to one another. And it was necessary to prepare the uniform slurry to achieve the desired particle size (about 100 μm). So we prepared about 1 μm ZnO and celite as raw materials and alumina sol as an inorganic binder. With these reagents, we prepared the spraying slurry by using a shear mixer and a mechanical mixer through controlling the slurry concentration, pH and viscosity. When the average particle size of celite was 30-40 μm, ZAC-3 sorbents were shaped and the average particle size was 177 μm, the shape was a nonspherical type, a doughnut form, and attrition resistance was lower than any other sorbents. Other main factors that affected the slurry spraying were slurry concentration and viscosity. In each experiment, we were convinced that the suitable slurry concentration was about 40-45% in the case of the ZAC series sorbents; and further, we could not prepare the slurry that had a 50% upper concentration. Actually, the slurry with a 50% upper concentration had not been mixed at all because of the slurry becoming paste. In addition to the slurry concentration, viscosity is another main factor. In this study, we were convinced that suitable viscosity was 300-600 cps from the shakedown test results of the spray dryer, and for the ZAC series, suitable viscosity was 350-450 cps.

The pH of ZAC-1~ZAC-10 slurry was measured at about 8.6, and agglomeration of the slurry did not occur in mixing raw materials and preparing slurry; therefore, the pH was not controlled. But in the case of ZAC-11(N)~ZAC13(N), the basic slurry had been prepared the same as for the components of ZAC-9, and 7.5 wt% nickel was impregnated directly into the basic slurry. In order to impregnate nickel, we made nickel citrate. Because the nickel citrate solution was a very strong acid (pH: 1.2), the pH control was necessary to prevent agglomeration of the slurry. So, we controlled the pH of the nickel citrate solution to about 8.6 and prepared the spraying slurry. To prevent slurry contamination by any small quantity of inorganic salt contained in the agent, ethanolamine was used as the pH control agent. The basic slurry of ZAC-14 (N) was prepared by using dissolved solid 7.5 wt% nickel.

Through these experimental results, we were convinced that the inlet air temperatures, the drying conditions in the chamber, and feeding pressure were not main factors in the basic operations. When the slurry concentration or viscosity was high, it was found that damage of the feed pump stator was very severe. In case of ZAC-5~ZAC-7, the slurry concentration was slightly higher (about 48%)



(a)

(b)

Fig. 2. (a) Optical microscopes picture of ZAC 1, (b) Optical microscopes picture of ZAC 4.

than any other slurry. Thus, ZAC-5 was shaped into a very good spherical type, but most of ZAC-6 and ZAC-7 were shaped as a dimple or a non-spherical type, because of non-constant spraying pressure, which was due to mechanical damage of the stator. After spraying a high concentration slurry at about 10 *l*, we knew that the average life of the stator was at an end. Also, when the good slurry containing suitable concentration and viscosity was sprayed, the stator could no longer be used because the raw materials contained ceramic characteristics. After the slurry was sprayed at about 50-80 *l* (operation time of the spray dryer was about 10-16 hours), severe damage occurred to the stator and it could not be used in slurry spraying.

2. Optical Microscope and SEM Analysis of Sorbents

Fig. 2a and 2b show the optical microscope picture of the ZAC-1 and the ZAC-4 sorbent. The ZAC-1 surfaces were very rough and semi-spherical types. Many dimple types were observed and sometimes agglomerations were observed. But the shapes of the ZAC-4 were almost spherical types without any dimple or hollow types. The difference between the particle size before and after calcination was minimal. The ZAC-5 and other sorbents which were shaped to reproduce the ZAC-4 sorbent have been shown to be good spherical types.

Fig. 3a and 3b show SEM images of the ZAC-5 and the ZAC-3 sorbent. In Fig. 3a, some small size particles were observed, because we did not sieve the sorbents. ZAC-3's image are a result of using celite, whose average particle size was about 30-40 µm. Even if it were spherically shaped, almost all particles formed holes. The active material and the support were only mixed, not bonded, and the average size of the sorbents was about 177 µm because of the large size of support. On the other hand, the ZAC-4 and others sorbents were shaped as spherical types because the slurries were prepared uniformly and the raw materials contained even particle distribution.

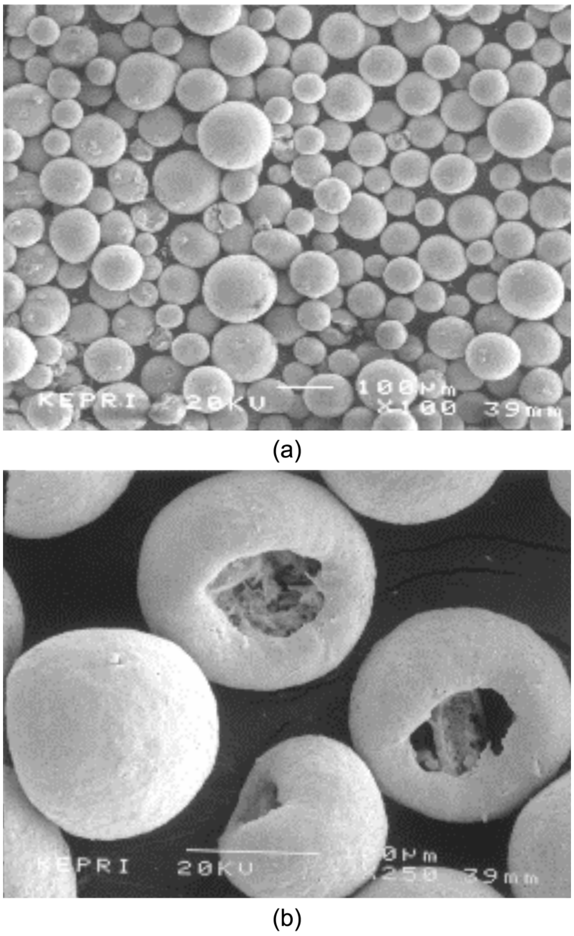


Fig. 3. (a) SEM picture of ZAC-5 (100×), (b) SEM picture of ZAC-3 (250×).

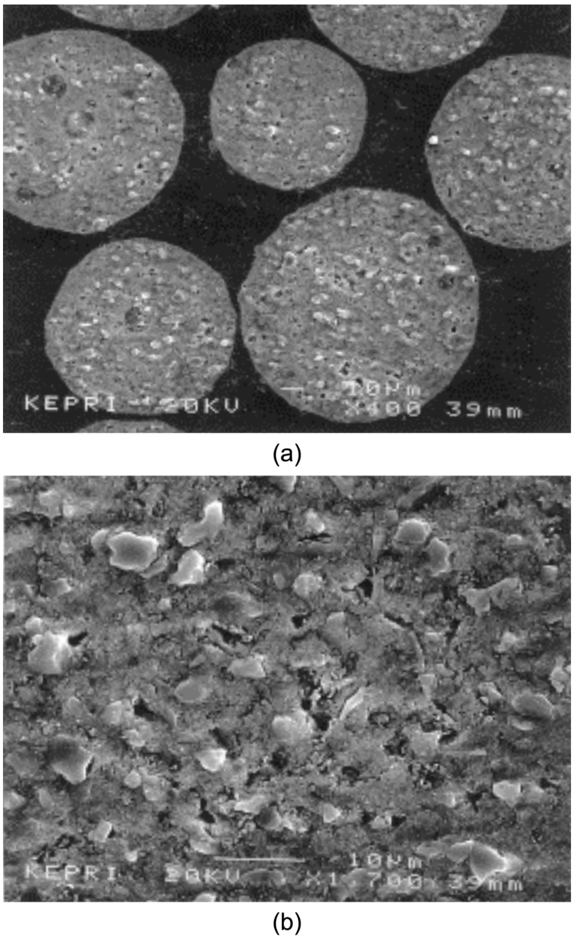
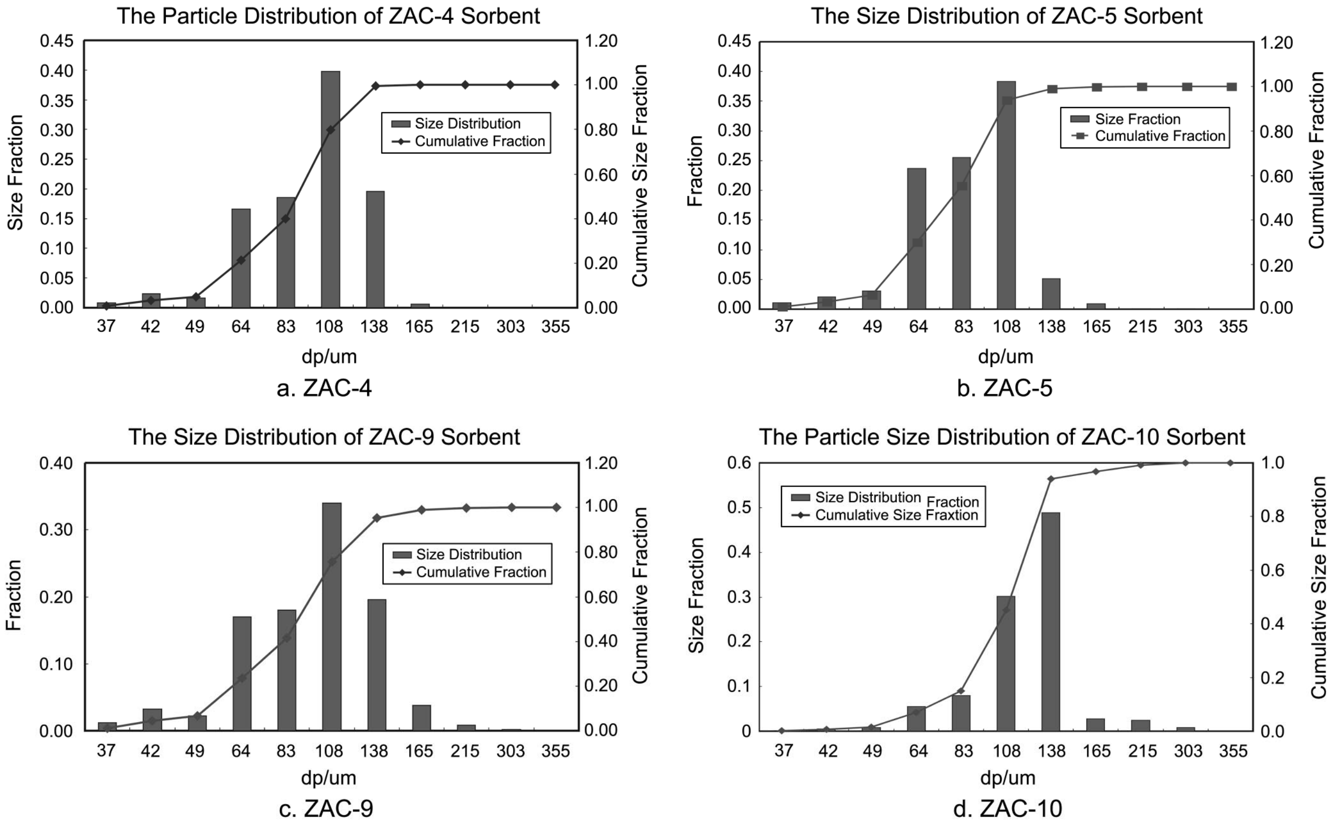


Fig. 4. (a) Cutting surfaces SEM picture of ZAC-4 (400×), (b) Cutting surfaces SEM picture of ZAC-4 (1700×).

Fig. 4a and 4b are the SEM images, showing how to mix raw materials uniformly by cutting and mounting surface of the ZAC-4. In these SEM Images, the white area of the cutting surface is celite of a larger size than zinc oxide. From these results, we knew that the particle size and the size distribution of active materials and a support were very important for a homogeneous mixing to prepare the spherical sorbents

3. Size Analysis and Attrition Resistance Test

After calcination of sorbents, particle size analyses were carried out by the API aerosizer, and in order to calculate the particle size distribution and average particle size, the MEINZER II sieve shaker was used additionally. Fig. 5 shows the particle size distribution of the ZAC series sorbents. The average particle size of the ZAC series was measured at about 112 µm, particle size distribution range was 38-180 µm, and size distribution was narrow and even. From these



a. ZAC-4 b. ZAC-5

c. ZAC-9 d. ZAC-10

Fig. 5. Particle size distribution of ZAC sorbents.

results, we were convinced that these sorbents were suitable in the fluidized bed process.

In the desulfurization/regeneration process of the sorbents, the active material is changed as follows: ZnO (14.34 cc/mol)→ZnS (23.85 cc/mol)→ZnO (14.34 cc/mol). At each reaction process, volume change is occurring very intensely. Especially, if a partial ZnS changes to $ZnSO_4$ (41.57 cc/mol) by a sub-reaction during the regeneration process, the volume of product is increased by about 3 times. Therefore, in order to endure the severe conditions, the sorbents composed with ceramic materials must have good durability.

Attrition Index (AI) value is the total amount of fines expressed as a weight percent (%), collected in the fine collection thimble after exactly 5.0 hours. The collection data at a time not corresponding exactly to hourly intervals was corrected either graphically or by linear regression fitting. This parameter is an indicator of short-term catalyst loss in the commercial operation. A hard catalyst is considered to have an AI of 7 or lower. Values of 12 and lower are commercially acceptable. Attrition Rate (AR) is the rate of fines generated between 1 and 5 hours expressed as weight percent per hour. This parameter is an indicator of the longer-term loss of catalyst in the commercial FCC unit resulting from attrition. Generally, values of 1.0 and less are desired. Corrected Attrition Index (CAI) is the Attrition Index minus the Initial Fines. This represents a correction for the amount of 0 to 20 micron material in the original sample as charged to the test [Joseph et al., 1998].

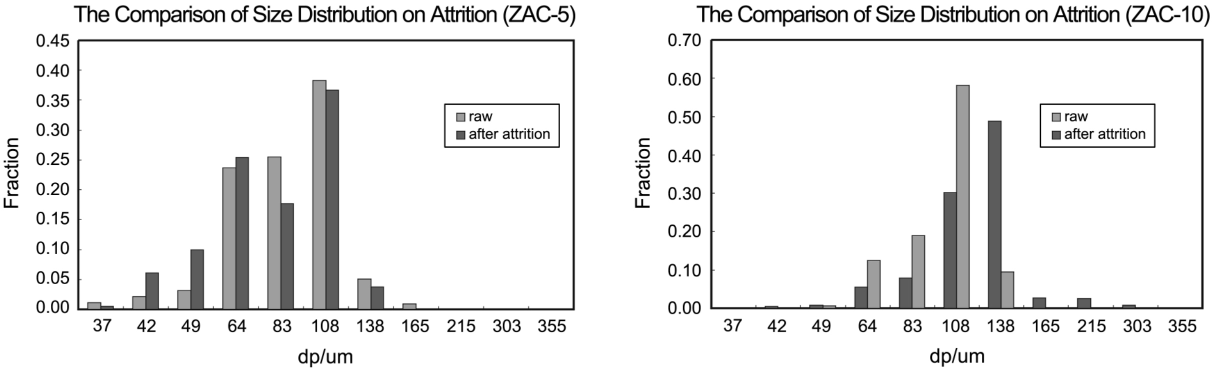
Table 2. Attrition indices and rate for ZAC sorbents and FCC catalysts

Sorbents	Attrition index		Attrition rate	
	AI(5)	CAI(5)	AR(5)	CAR(5)
AKZO	22.5	17.0	1.6	1.6
DAVISION	18.4	12.3	1.8	1.2
ZAC-4	41.0	20.5	6.1	4.5
ZAC-4N	49.0	24.0	6.1	4.4
ZAC-5	32.3	29.0	3.2	3.6
ZAC-9	32.0	29.0	3.2	3.7
ZAC-9N	40.5	22.0	5.7	4.1
ZAC-10	23.0	20.0	2.3	2.5

Table 2 shows attrition test results of ZAC series and reference catalysts (AKZO and DAVISION Co.). the attrition test was undertaken for 5 hours by the ASTM method. At the test results, the attrition resistance values of the ZAC series were not bad compared with the developing sorbents in the foreign sorbents; it satisfied the developing target value (AI<30). These results were due to using a pressure nozzle type spray dryer.

In order to estimate the stability of the sorbents which were performed in the attrition test, we observed shape, particle size and size distribution of the ZAC-5 and ZAC-10 sorbents. They sustained their spherical shape, and the particle size distribution was decreased slightly as can be seen in Fig. 6. From these results, we are convinced that zinc-based sorbents which were shaped through the binder matrix will have good properties and we can shape sorbents possessing high density and resistance by using a spray dryer.

4. The Others' Physical Analyses



a. ZAC-5 b. ZAC-10

Fig. 6. The comparison of the size distribution on attrition of ZAC series.

Table 3. Comparison of zinc based sorbents characteristics

Properties	ZT-4	CAP-107	EX-SO3	METC-10TS	METC-10TL	ZAC-4(N)	XZ-Sorb
Size distribution (μm)	-	80-250	40-150	-	-	38-180 (40-165)	37-125
Mean particle size (μm)	~180	145-160	74-75	65	140	112	40-50
AI(CAI) (%)	(>250)	(>25)	(1.4)	4.2	1.6	6.1 (6.1)	7.66
BET (m^2/g)	3.53	1.42	119-150	20-90	20-90	20 (24)	-
Bulk density (g/cc)	-	0.55	1.6	0.9-1.07	0.9-1.07	1.05	1.0
TGA sulfur load (%)	22	16.6	10.8	22-33	22-33	23-24	22

The BET surface area of the ZAC series sorbents appeared very large in comparison with the zinc titanate sorbents. Generally, the BET surface area of zinc titanate is 2-3 m^2/g, but the ZAC series sorbents have about 20 m^2/g. From this result, we can understand that these sorbents have many more mesopores or micropores than macropores, comparatively speaking. And, it can be expected that the sulfur capture capacity will be superior to the zinc titanate sorbents in the desulfurization reaction. But if the BET surface area is larger because of many micropores, desulfurization capacity may decrease because of plugging of the micropores during the sulfidation reaction. Because of the above problem, we have focused on maintaining a suitable BET surface area and average pore size. The BET surface area of ZAC-4N increased about 4 m^2/g in comparison with ZAC-4, which is the result of new pores produced because of a twinkle surface spouting of NiO in the calcination process. But ZAC-9N was prepared by using a ball miller; therefore, twinkle surface spouting of NiO in the calcination process was prevented by raising the temperature per minute and the staying time. Therefore, the BET surface area changed a little.

The bulk density (ASTM D 4164-88 method) of ZAC-4 sorbent was 1.05 g/ml, and other ZAC series sorbents were measured at over 1.0 g/ml. The NZT sorbent series, zinc titanate based sorbents, were measured at about 1.3 g/ml.

From the XRD result of ZAC-4, 2θ angle's peaks of ZnO appeared at nearby 21.7°, 31.7°, 34.4°, and 36.2°, and the highest peak appeared at 36.2°. The highest 2θ angle's peaks of SiO_2, the main component of celite, appeared at 22.6°, and $ZnOSiO_2$ has 2θ angle's intensity peaks at 38° within 100° and 42 within 100°, and distribution is smaller than others are, but the peak intensity is higher than for the others, except for ZnO. However, 2θ angle's peaks of components, except for ZnO, are similar to others, so classification of other peaks is not actually easy.

Table 3 shows the comparable data with foreign sorbents that are under development [Gupta et al., 1998; Ranjani, 1998]. When the ZAC series sorbents were compared with the basic physical analysis results for foreign sorbents that are under development, the ZAC series sorbents were not inferior to other sorbents.

5. TGA Reaction Test of Sorbents

Chemical reactivity of sorbents was assessed with a thermogravimetric analyzer (TGA). In a TGA test, the weight of a sample hanging from the microbalance is monitored as a function of time. The weight gain is proportional to the extent of reaction in the sample. Of course, addition of inerts and binders reduces the weight gain observed at saturation, but reproducibility of the weight changes through multiple cycles of absorption and regeneration is the key parameter in sorbent development.

ZAC-4 was selected for the TGA test. The reason was that ZAC-4 was superior to any other ZAC series sorbents as detected in various physical analyses. In order for optimal temperature to be useful in test operation, sulfur absorption and regeneration tests were performed at 500 °C, 540 °C and 650 °C to compare the rate of reaction of sorbents as a function of temperature. In a typical TGA reactivity test, the samples were exposed to simulated clean coal gas (without H_2S) for the first 90 minutes at 1 atm and at 500 °C, 540 °C and 650 °C to establish a weight baseline. Then, 4,000 ppm H_2S was introduced during absorption (also called sulfidation) to check for weight changes during the reaction. Regeneration with air can follow the sulfidation when the weight should return to its base value. From experimental results, the reactivity at 500 °C and 540 °C were similar to each other but the reactivity at 650 °C was not active. Initial sulfur capacities of the ZAC-4 sorbents were 11.6% weight gain at 500 °C and 12.23% weight gain) at 540 °C. And initial sulfur capacity at 650 °C was 9% weight gain. It means that if the temperature is very high, the sulfur capacity will decrease. That was because steam and sorbent were sintered at high temperature and contact with reaction gases decreased. These initial sulfur capacities were superior to bench marking sorbents.

Dry regeneration of sorbents with diluted air produces sulfur dioxide used as a starting material for sulfuric acid production or elemental sulfur. However, sulfur species may remain in the sorbent as residual solid zinc sulfates. The presence of zinc sulfates is highly undesirable because it reduces the sulfur capacity of the sorbent in subsequent cycles and eventually cannot be removed from the sorbent even with thermal treatment. Therefore, lower zinc sulfate formation tendencies are beneficial because they minimize sorbent deterioration.

In the regeneration process with air, sorbents were not regenerated completely at 500 °C and 540 °C, but complete regeneration was achieved at 650 °C. We knew this through the TGA weight gain and the exothermic peak of DSC.

Fig. 7 presents the TGA 1.5 cycle test result at 540 °C of ZAC-4N. A baseline test was conducted for 90 minutes and a sulfidation test was carried out for about 60 minutes. In the first sulfidation reaction, weight gain was measured at 10.13% and some initial loss in capacity in the 2nd sulfidation was observed, either due to sulfate formation or structure densification. The theoretical capacity of the zinc-based sorbents is between 10% and 12% weight gain, so TGA tests show that the reactivity of the ZAC-4 and ZAC-4N is satisfactory. Differences in the total sulfur capacity between ZAC-4 and ZAC-4N sorbents are the result of differences in the zinc initial concentration in the formulation. The regeneration process of ZAC-4N at 540 °C was almost regenerated completely. The reason was that NiO, regeneration catalyst, decreased the regeneration temperature from 650 °C to nearby 540 °C. From these results, we know that the suitable reaction temperature of ZAC series sorbents was at 500-540 °C. Generally, it was reported that volatile temperature of Zn was initiated at 600 °C and volatilization progressed vividly at 650 °C [Susan et al., 1992]. The desulfurization rate of the sorbent results in a weight gain as the zinc component of the sorbent goes from the oxide form to the sulfide form. This performance suggests a window of about 600 °C below the normal operating condition, albeit being considered off-design conditions. So ZAC series sorbents were being evaluated for operation at temperature below 550 °C.

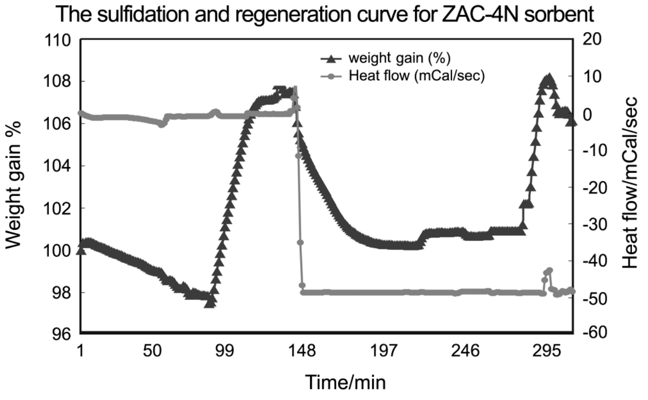


Fig. 7. 1.5 Cycle TGA reactivity for ZAC-4N sorbent at 540 °C.

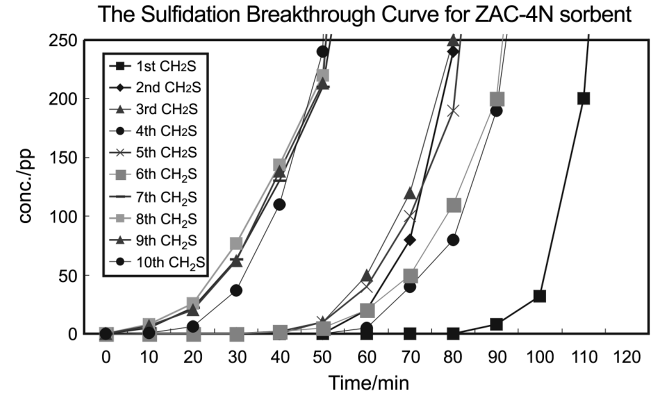


Fig. 8. Cycle sulfidation breakthrough curve for ZAC-4N sorbent.

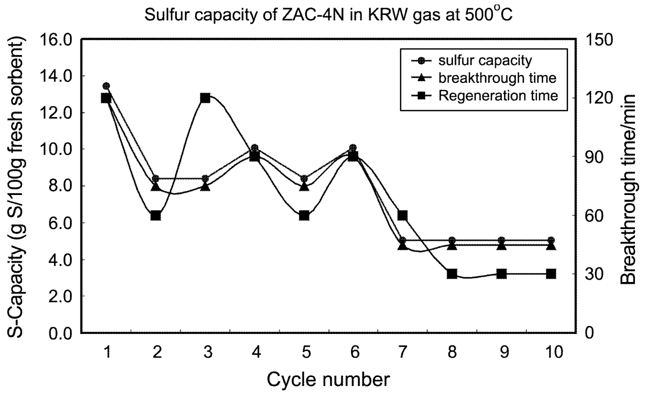


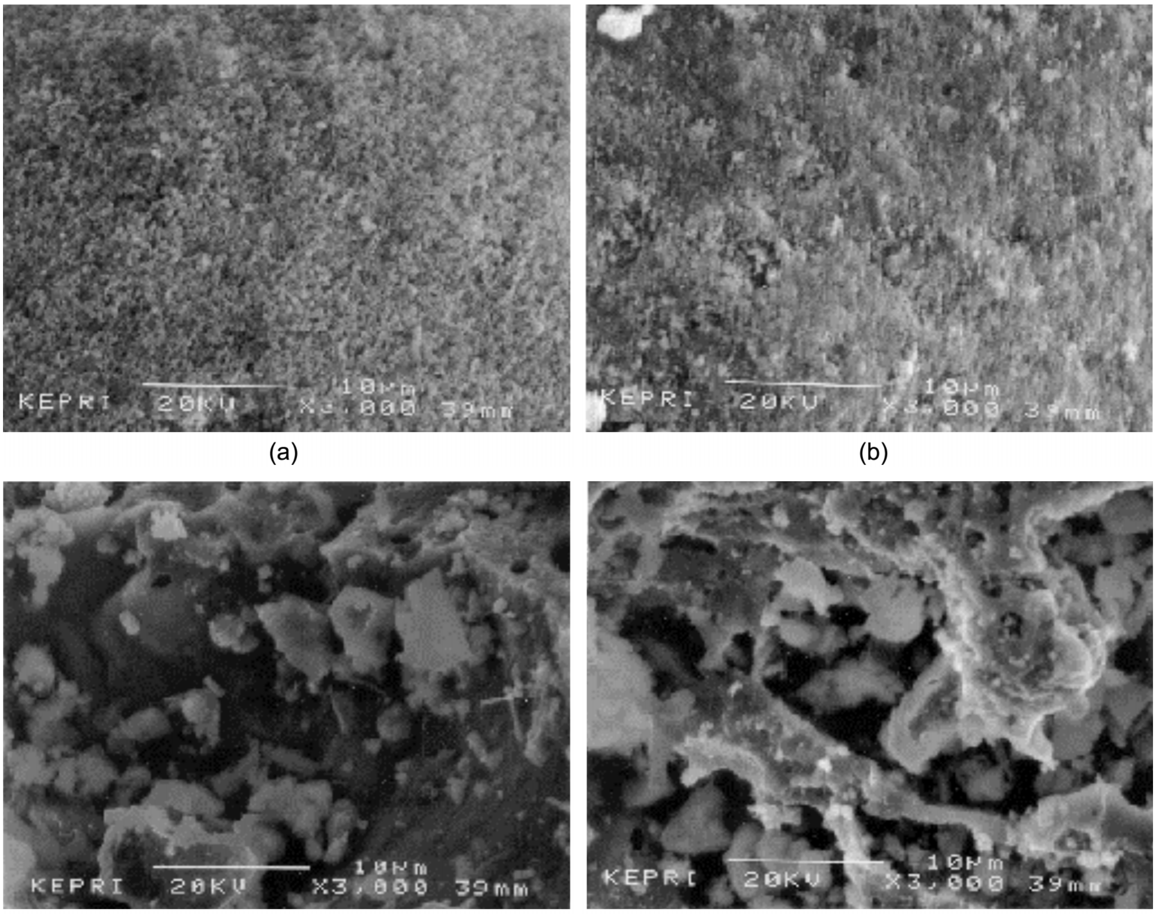
Fig. 9. Sulfur capacity, breakthrough and regeneration time of ZAC-4N.

6. Sulfidation/Regeneration Characteristics of ZAC-4N in the HTHP Reactor

Sulfidation breakthrough curves for the HTHP test are plotted in Fig. 8, and breakthrough times and sulfur capacities obtained from the data and regeneration time are plotted in Fig. 9. In the first cycle, the breakthrough time was 110 minutes and concentration of H_2S and COS was about 10 ppm before the breakthrough-point (H_2S concentration 200 ppm). Regeneration time was 120 minute, then concentration of SO_2 was about 50 ppm.

As can be seen, the initial sulfur capture capacity and breakthrough time were good. But from the 2nd cycle forward, sulfur capture capacity and breakthrough time slightly decreased. Especially, in the 7th, 8th, 9th and 10th cycle, the breakthrough time decreased by 50 minutes, and also, the sulfur capture capacities decreased from about 9.0 g-sulfur/100 g-sorbent to about 5.0 g-sulfur/100 g-sorbent. Through these results, we could assume that these sorbents were sintered and reformed by steam and regeneration and deteriorated in efficiency. But the H_2S slippage was detected, as it was less than 5 ppm. The COS formation was sustained at about 20 ppm.

Reactor settings were maintained at 540 °C during the entire regeneration. Total outlet SO_2 concentration was about 10 to 15 ppm at the end of regeneration. The regeneration performance of the sorbent was very consistent during the 6th regeneration cycle. After 6th regeneration cycle, the sorbent had lower performance during the 7th to 10th regeneration as it had before 6th cycle. Average regeneration time was 1 to 2 hours. The temperature of the sorbent



(a) (b)

(c) (d)

Fig. 10. (a) SEM Picture of ZAC-4N (Fresh), (b) SEM Picture of ZAC-4N (Regeneration), (c) SEM Picture of ZAC-4N (after 5 cycle), (d) SEM Picture of ZAC-4N (after 10 cycle).

bed due to the exothermic reaction during the regeneration was about 750 °C. Regeneration time except 3rd regeneration was proportional to breakthrough time of sorbents.

Fig. 10 shows SEM images of ZAC-4N used for the sulfidation/regeneration reaction in the HTHP reactor. Fig. 10a and 10b are SEM images of a fresh and regenerated ZAC-4N sorbent. In this figure, we can see that compositions of sorbents were spread evenly and regenerated well. But we can see that regenerated sorbents are not similar to fresh sorbents because of transformation by sintering of sorbents during 10th cycle reactions. However, sorbents were regenerated nearly perfectly.

Fig. 10c and 10d are sulfidated SEM images of the ZAC-4N after 5th and 10th sulfidation. These images show that sorbents were sulfidated extremely by H_2S and sulfur compounds, and the 10th sulfidation sorbent was more sulfidated than the 5th sulfidation sorbent. This is the reason that the breakthrough time of H_2S decreased by time, although sulfidation reacted more violently.

CONCLUSIONS

Sorbents, which can remove sulfur compounds from coal gas in the HTHP desulfurization process, were prepared by using a pressurized nozzle type spray dryer, and various experiments such as physical analysis, TGA test and HTHP reactor test were performed. Our main conclusions are as follows.

From the results of the physical analysis of ZAC-4, we have determined that this sorbent is suitable for use in the fluidized bed system or in the transport reactor system for coal gas desulfurization. The main results are as follows: 1) average particle size: 112 μm 2) particle shape: spherical shape 3) Bulk density: 1.05 g/cc 4) BET surface area: 20 m^2/g 5) Attrition loss: 6.1% at 10 *l* N_2/5 hr.

From the TGA test results, we have confirmed that sulfidation temperature of ZAC series is suitable at 500 °C and regeneration temperature is good at 540 °C. Sulfur capacities were calculated at about 23% at 540 °C, about 24% at 500 °C and at 18% at 650 °C.

As the 1" HTHP reactor test results, the initial sulfidation breakthrough times were about 110 minute, but in the 7th, 8th, 9th and 10th cycle, the breakthrough time decreased by 50 minutes, and the sulfur capture capacity decreased from about 9.0 g-sulfur/100 g-sorbent to about 5.0 g-sulfur/100 g-sorbent. H_2S slippage was hardly found as it was less than 5 ppm, and the COS formation was sustained at about 20 ppm.

From the SEM figures of ZAC-4N used for sulfidation/regeneration reaction in the HTHP reactor, we observed that the regenerated SEM figure of ZAC-4N ending at 10 cycles was not similar to the fresh sorbent because of transformation by sintering sorbents during 10 cycle reactions. But sorbents were nearly perfectly regenerated.

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