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Simultaneous Experiments of Sulfidation and Regeneration in Two Pressurized Fluidized-bed Reactors for Hot Gas Desulfurization of IGCC

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Abstract−Hot Gas Desulfurizarion for IGCC is a new method to efficiently remove H_2S in fuel gas with regenerable sorbents at high temperature and high-pressure conditions. The Korea Institute of Energy Research did operation of sulfidation in a desulfurizer and regeneration in a regenerator simultaneously at high pressure and high temperature conditions. The H_2S concentration at exit was maintained continuously below 50 ppmv at 11,000 ppmv of inlet H_2S concentration. The sorbent had little effect on the reducing power in the inlet gas in the range from 11% to 33% of H_2. As inlet H_2S concentration was increased, H_2S concentration in the product gas was also increased linearly. The sorbent was maintained at low sulfur level by the continuous regeneration and the continuous solid circulation at the rate of 1.58×10^{-3} kg/s with little mean particle size change.

Key words: Hot Gas Desulfurization, Hydrogen Sulfide, Sorbent, Fluidized Bed Reactor, IGCC

INTRODUCTION

A Hot Gas Desulfurization (HGD) technique is one of elemental technologies in the IGCC (Integrated Gasification Combined Cycle) having both high thermal efficiency and very low emissions [Gangwal et al., 1989; Woods et al., 1990; Choi et al., 2001]. The existing conventional wet-type H_2S desulfurization processes require cooling and reheating of the gas stream, resulting in significant reduction in thermal efficiency of the system as well as costly wastewater treatment. Hot gas desulfurization is a new method to efficiently remove H_2S, COS in fuel gas with regenerable sorbent at high temperature and high-pressure condition.

The HGD process consists of a sulfidation reactor, a regeneration reactor and solid circulation loops connecting both reactors. The key for successful process development is how well the solid circulation and transport system between two reactors operate. Especially, it is difficult to run the system continuously and stably because it is operated at high pressure and high temperature.

Most of the researches of hot gas desulfurization sorbent development have been performed in batch cyclic test or TGA to see how much sorbents absorb sulfur of H_2S and COS in reducing gas [Li and Flytzani-Stephanopoulos, 1997; Gasper-Galvin et al., 1998; Jothimurugesan and Gangwal, 1998; Abbasian and Slimane, 1998; Alonso et al., 2000; Lee et al., 1995, 1997; Lim et al., 2000; Song et al., 2000]. However, it is not enough to see the real performance of the sorbent in a batch cyclic test because a real hot gas desulfurization plant is operated at the continuous mode of sulfidation and regeneration in which the sulfur loading of the sorbent in the desulfurizer is maintained at low % level rather than at the level of maximum sulfur loading. Therefore, a study of the continuous operation is needed to confirm the real performance of sorbent at the last stage of the sorbent development. The Korea Institute of Energy Research (KIER) has been developing a hot-gas desulfurization process that has two fluidized bed reactors consisting of a desulfurizer and a regenerator [Yi et al., 1999a]. Previous researches have shown the effects of various parameters on voidages and pressure balance curves in the solid circulation system [Yi et al., 1999b, 2001], the control structures for the stable solid circulation between two reactors [Yi and Luyben, 1999].

The purposes of this work are to show the real performance of the developed sorbent in continuous mode, to prove the feasibility of HGD process by long-term operation of the proposed process, and to obtain data for the scale-up.

EXPERIMENTS

Fig. 1 shows the schematic of the bench scale unit of KIER hot gas desulfurization process. The general features of the system include a fluidized regenerator, a fluidized desulfurizer, a riser, a multicyclone, and a loopseal. A fluidized regenerator is a 1,200 mm tall bed of 97.5 mm I.D. It has a perforated type distributor and a small cyclone. A fluidized dusulfurizer is also the same size as a regenerator. An underflow standpipe and a slidevalve are located below each reactor to control the reactor bed level by maintaining the solid circulation rate. The underflow standpipe of 25 mm I.D. is located at middle section of the distributor. The bed height is calculated continuously by the data from two differential pressure transducers at the reactor wall. The slide valve is closed automatically when the calculated bed height is smaller than the desired low limit of the bed height, and it is open when the bed height is larger than the high limit. The bed height is controlled within the range of low and high limit because it is an inventory control. The sorbent from a desulfurizer is passed through a horizontal pipe and a riser and is collected in the multi-cyclone. The collected sorbent goes into a regenerator passing through a loopseal to prevent the gas and sorbents from flowing backward. Solid circulation rate is calculated indirectly by measuring of the bed height change in the reactor after closing one

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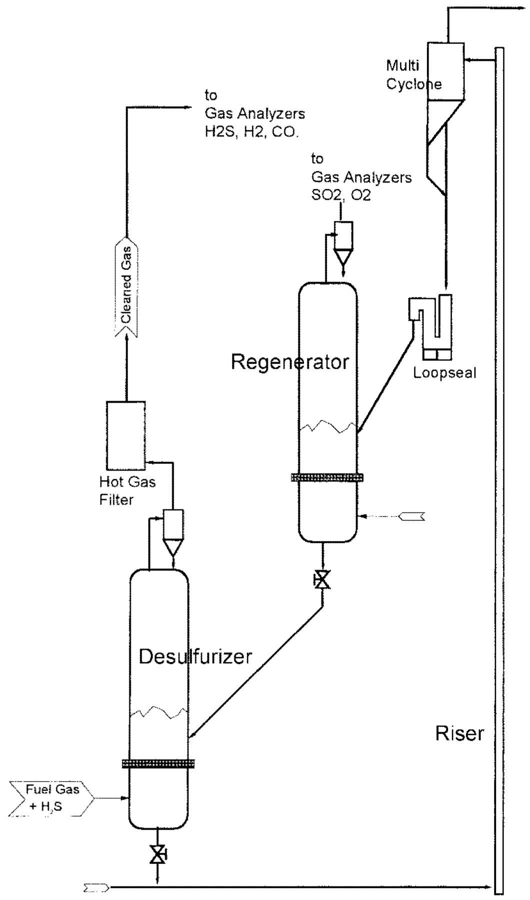

Fig. 1. Schematic of the bench scale unit of KIER hot gas desulfurization process.

of the slide valves. The pressure at each reactor should be controlled precisely by pressure control valves because the sorbent circulation occurs in high pressure. The temperature in the reactor is maintained by heaters on the outside of the reactor. Filters were installed in the outlets of a multi-cyclone and two reactors.

Table 1. Inlet gases concentrations and reaction conditions of these experiments

	Sulfidation		Regeneration	
Test No.	No. 1	No. 2	No. 1	No. 2
Test hours	72	47	72	47
H_2, %	11.7; 22; 33	11.7	-	-
CO, %	19	19	-	-
CO_2, %	6.8	6.8	-	-
N_2, %	Bal.	51.2	Bal.	Bal.
H_2S, %	0.4; 1.0; 2.0	1.3	-	-
H_2O, %	10	10	-	-
O_2, %	-	-	6.6	2.5; 5
Total, %	100	100	100	100
H_e, m	.2-.4	.2-.4	.2-.4	.2-.4
U_o, m/s	.05	.05	.05	.05
T, °C	600	600	700	700
P, kPa	445.7	445.7	445.7	445.7

Table 1 shows the inlet gases concentrations and the conditions of sulfidation and regeneration reactions used in these experiments. The gas concentrations of H_2, CO, H_2O, CO_2, H_2S, N_2 for sulfidation reaction are the same as the condition of the air-blown gasifier and the O_2 concentration for regeneration reaction is from 2.5 to 6.6%. The fluidizing superficial gas velocity of both reactors is 0.05 m/s because the minimum fluidizing velocity of the used particles is 0.01 m/s. The temperature in the desulfurizer is 600 °C, and the temperature in the regenerator is 700 °C, and the pressures of both reactors are 4.457×10^5 Pa. Initial sorbent inventory is 8.2 kg.

The used sorbent, named EZ4, was formed by a spray drying method by Korea Electric Power Research Institute (KEPRI) and Korea Institute of Energy Research (KIER). The average particle size of sorbent is 0.085 mm. The skeletal, particle, and bulk densities of the sorbent are 3,100, 1,600, and 1,100 kg/m^3, respectively. The porosity is 0.50, and the BET surface area is 3,500 m^2/kg. Mercury pore volume, median pore diameter based on volume, average pore diameter based on (4V/A) is 2.97×10^{-5} m^3/kg, 2.7×10^{-7} m, 3.38×10^{-7} m respectively. The attrition loss based on ASTM-D 5757-95 is 5 hours loss (AI), 36.2%, 4 hours loss between 1 hr and 5 hr (CAI), 11.2%, that shows the larger initial attrition characteristics compared with AI, 11% and CAI, 8.8% of the calcined Akzo FCC.

RESULTS AND DISCUSSION

1. Sulfidation Characteristics in Desulfurizer

In the HGD system the concentration of H_2S in the product gas leaving the desulfurizer should maintained below the environmental regulation. Both temperature and pressure must be controlled in both the desulfurizer and the regenerator.

The reaction in the desulfurizer is as follows:

$MeO+H_2S=MeS+H_2O$

Fig. 2 shows the H_2S concentration in the exit of the desulfurizer and the bed height for 72 hours during test no. 1. Inlet H_2S concentration in simulated gas is 11,000 ppmv. The H_2S concentration in the exit is maintained below 40 ppmv when the system is operated stably. Bed height in the desulfurizer of Fig. 2 is calculated from two differential pressures data in the fluidized bed. The bed height is maintained within the range from 0.2 to 0.4 m though it is not

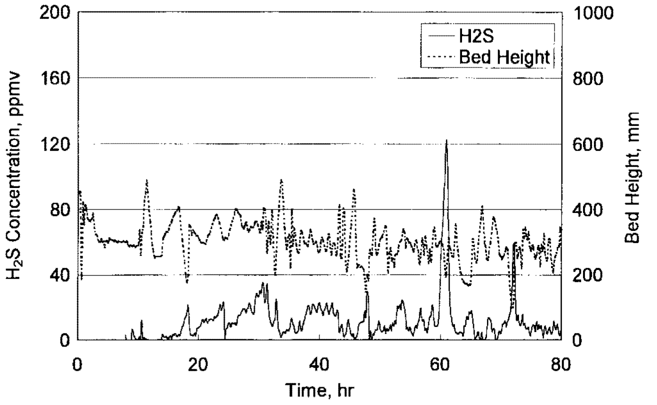

Fig. 2. H_2S concentrations in the exit of the desulfurizer and the bed height changes for 80 hours (test No. 1).

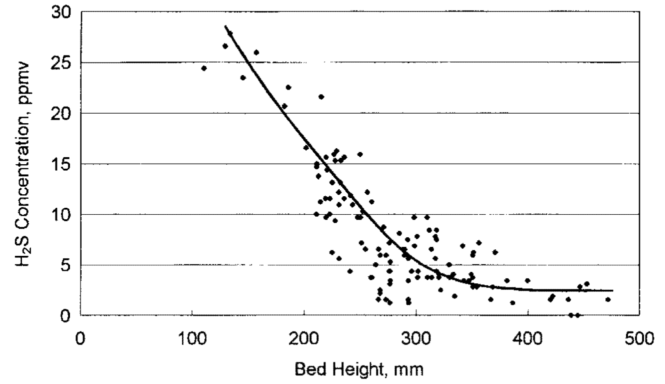

Fig. 3. Effects of bed height on exit H_2S concentration (test No. 1).

controlled tightly. When the time axis is around 60 hours in the Fig. 2, H_2S concentration increases to 120 ppmv suddenly. The steam (H_2O) was injected about 40% by mistake. H_2S capture efficiency dropped because the steam disturbed good fluidization state in the reactor. In the HGD system the concentration of H_2S in the product gas leaving the desulfurizer is maintained far below the environmental regulation. Both temperatures are controlled both in the desulfurizer, 600 °C and in the regenerator, 700 °C at high pressure of 4.457×10^5 Pa.

Fig. 2 also shows the effects of bed height indirectly. The data from Fig. 2 are collected in Fig. 3 to see the effects of bed height on the exit H_2S concentration. As the bed height is changed from 0.15 to 0.45 m, the H_2S concentration is decreased from 30 ppmv at 0.15 m, 15 ppmv at 0.2 m, 10 ppmv at 0.3 m and leveled off at around 10 ppmv at the height larger than 0.3 m. It may be the maximum performance of used sorbent even though it has enough residence time, or it can be due to the lower detection limit of the used analyzer. It is important to know the effects of bed height on outlet H_2S concentration, that are closely related with the performance of the process and the needed residence time to get enough reaction. The absolute value of the exit H_2S concentration is more important than the conversion because it is required that the limit of the emission standard for regulation be satisfied.

2. Effects of H_2 Concentration

H_2 concentration in the inlet-simulated gas is changed to see the effect of reducing power on desulfurizing ability of the sorbent in the desulfurizer. The inlet H_2 concentration is increased from 11.7% to 33%, and N_2 is decreased for the balance. Fig. 4 shows the effects of H_2 concentration on outlet H_2S concentration in the desulfurizer. The bed height was controlled more tightly within ±5 cm range for 50 minutes for each test. The outlet H_2S concentration is maintained below 20 ppmv though the H_2 concentration is changed from 11.7%, 22% to 33%, when the bed height is 0.3 m and solid circulation rate is 1.58×10^{-3} kg/s. It is shown that the sorbent has little effect on the reducing power in the inlet gas.

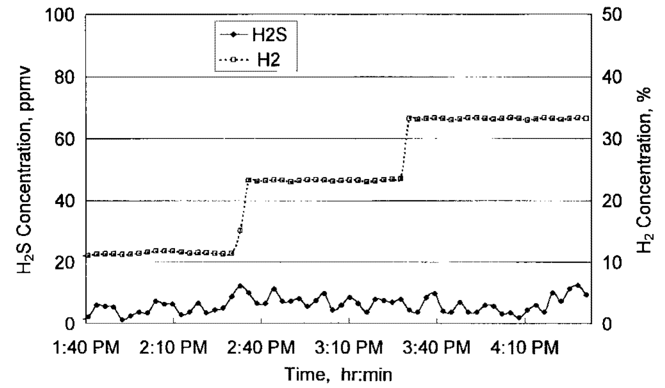

Fig. 4. Effects of H_2 concentration on H_2S exit concentration in the desulfurizer (test No. 1).

3. Effects of H_2S Inlet Concentration

The H_2S inlet concentration depends on the sulfur content in the solid fuel. It is meaningful to see the sorbent reactivity at the high H_2S concentration gas. Fig. 5 shows the effects of H_2S inlet concentration on desulfurizing ability. Inlet H_2S concentration in the simulated gas is changed from 20,000 ppmv to 4,000 ppmv. As inlet H_2S concentration is increased, H_2S concentration in the product gas is also increased linearly. As a matter of fact, because the detection limit of the used on-line gas analyzer is about 5 ppmv, the other technique or analyzer is needed to measure the lower concentration range of H_2S.

4. Regeneration Characteristics

The reaction in the regenerator is as follows:

$$MeS+3/2\ O_2=MeO+SO_2$$

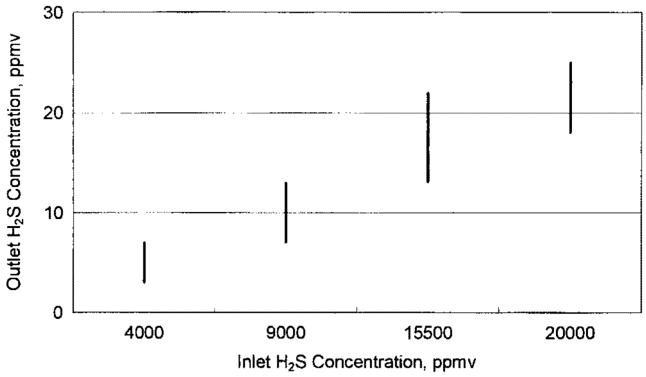

Fig. 5. Effects of inlet H_2S concentration on outlet H_2S concentration (test No. 1).

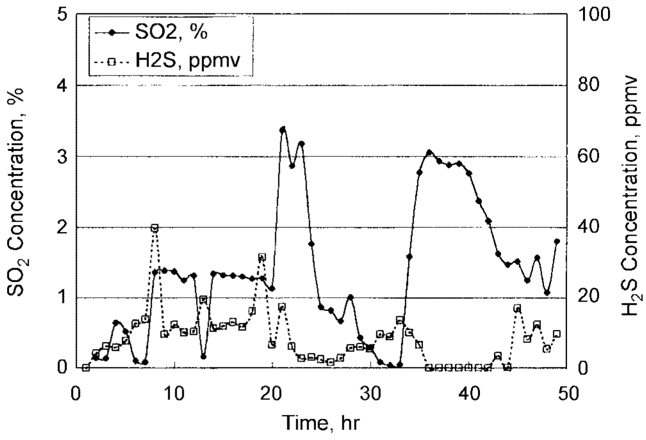

Fig. 6. Outlet SO_2 concentration from the regenerator and the outlet H_2S concentration from the desulfurizer measured at every hour (test No. 2).

The regenerator is maintained at 700 °C and 4.457×10^5 Pa with the continuous solid circulation, sorbent coming from a loopseal and sorbent leaving to desulfurizer via a standpipe. Fig. 6 shows the outlet SO_2 concentration from the regenerator and the outlet H_2S concentration from the desulfurizer measured at every hour during test no. 2. The inlet O_2 concentration was maintained at 5% O_2 from 0 to 5 hour and from 18 to 47 hour, and at 2.5% O_2 between 5 and 18 hour in order to see the oxygen concentration effect. Initially, SO_2 concentration is maintained low less than 1% because most of the sorbent in the regenerator is fresh. SO_2 is 1.5% between 8 and 20 hours when the inlet O_2 concentration is at 2.5%, which shows well-matched stoichiometry. When the inlet O_2 concentration is increased to 5% from 18 hours, the outlet SO_2 concentration is also increased to 3.3% and the concentration is decreased after most of the sulfur in the sorbent is burnt. Even though there are some fluctuations in data because of the swing in bed height from 0.2 to 0.4 m, when the SO_2 concentration in the regenerator is high, the outlet H_2S concentration is lower than 10 ppmv in Fig. 6. It is because desulfurizing ability also increases in the desulfurizer when the sorbent is fully regenerated with excess oxygen. It is an indication that the sorbent is able to endure without severe deactivation in the long-term test.

4. Sulfur Analysis After Test

Table 2 shows the sulfur analysis by a sulfur determinator and by EDAX and the mean size of samples obtained at the end of the 47 hours test. As expected, the sulfur concentration in the desulfurizer, 0.193%, is higher than that of the regenerator, 0.078%. These values are low sulfur concentration, compared with the theoretical saturated sulfur concentration of the EZ4 sorbent, 11%, because the sorbent is maintained at low sulfur level by the continuous regeneration and the continuous circulation of the regenerated.

In Table 2, the sulfur in the surface of the sorbent in the desulfurizer is 2.64% and the sulfur in the inside is 1.89%, and the sulfur in the surface of the regenerator sorbent is 1.83% and that in the inside is 1.92%. It is an indirect indication that reaction occurs more on the surface than in the inside. The sulfur by EDAX shows much higher values than by sulfur determinator. It may be that the sulfur determinator cannot analyze all of the inorganic substances, such as sulfate. However, other quantitative analysis is needed to make a precise decision because EDAX data can have an error of ±1% range.

5. Particle Characteristics

Fig. 7 shows the particle size distributions of fresh sorbent, sorbent in the desulfurizer after no. 2 test, and sorbent in the regenerator after no. 2 test. Large particles of fresh sorbent become smaller by attrition, while most of the small and attrited particles are elutriated out to cyclone during fluidization. Therefore, there is little mean particle size change during 47 hours fluidization though the distribution curves show some change in size distribution. The particle mean sizes of fresh, desulfurizer, and regenerator are 0.085 mm, 0.085 mm, and 0.082 mm, respectively, that shows similar values as shown in Table 2.

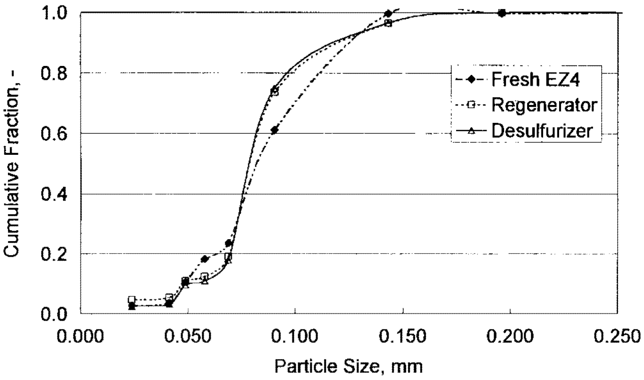

Fig. 7. Particle size distributions of fresh sorbent, sorbent in the desulfurizer, and sorbent in the regenerator (test No. 2).

6. Particle Entrainment

For design we need to know the rate of entrainment of solids from a bed, and the size distribution of each location. One kind of valuable data in the continuous experiments is the measurement of entrainments. Particles captured in cyclones and filters of a desulfurizer and a regenerator were sampled at high pressure and high temperature and were weighed. There has been little real data from a desulfurizer and a regenerator during continuous operation in two reactors but the relative value of attrition loss from ASTM 5757-95. The conditions in the desulfurizer are 0.05 m/s, 600 °C, 4.457×10^5 Pa, and those in the regenerator are 0.05 m/s, 700 °C, 4.457×10^5 Pa. Fig. 8 shows the captured rates in cyclones and filters of a desulfurizer and a regenerator. The captured rate of cyclone of a desulfurizer shows the highest value because the volumetric flow rate in a desulfurizer is higher than in a regenerator and because the sorbents may be easily attrited due to the expansion by chemical reaction and physical adsorption of sulfur. The mean captured rates are 5.4×10^{-7} kg/s of the cyclone of a desulfurizer, 2.6×10^{-7} kg/s of the cyclone of a regenerator, 1.4×10^{-8} kg/s of the filter of a desulfurizer, 1.37×10^{-8} kg/s of the filter of a regenerator. It can be expressed by an attrition rate constant, K_a [Merrick and Highley, 1974]. The

Table 2. Sulfur analysis and particle sizes of sorbent samples after experiment of no. 2

	Sulfur determinator, %	EDAX sulfur in sorbent surface, %	EDAX sulfur in sorbent inside, %	Particle mean size, mm
Fresh EZ4	0	-	-	0.085
Desulfurizer	0.193	2.64	1.89	0.085
Regenerator	0.078	1.83	1.92	0.082
Cyclone after desulfurizer	1.163	6.70	1.52	0.035
Cyclone after regenerator	0.031	3.87	3.60	0.031
Loopseal	0.557	-	-	-
Multi-cyclone	0.456	-	-	0.067

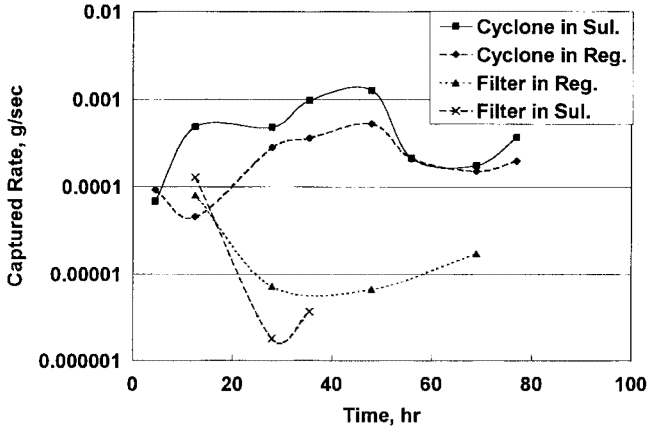

Fig. 8. Captured rates in cyclones and filters of a desulfurizer and a regenerator (test No. 2).

K_a of the desulfurizer is 4.5×10^{-6} [m^{-1}].

CONCLUSIONS

The simultaneous operation of sulfidation in a desulfurizer and regeneration in a regenerator was performed at high pressure and high temperature. The H_2S concentration at exit was maintained continuously below 50 ppmv at 11,000 ppmv of inlet H_2S concentration. The sorbent had little effect on the reducing power in the inlet gas in the range from 11% to 33% of H_2. As inlet H_2S concentration was increased, H_2S concentration in the product gas was also increased linearly. As the bed height was changed from 0.15 to 0.45 m, the H_2S concentration was decreased from 30 ppmv to 10 ppmv and leveled off at around 10 ppmv at the height larger than 0.3 m. The sorbent was maintained at low sulfur level by the continuous regeneration and the continuous solid circulation at the rate of 1.58×10^{-3} kg/s with little mean particle size change. The attrition rate constant of the desulfurizer was 4.5×10^{-6} [m^{-1}].

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NOMENCLATURE

H_e	: expanded bed height in the fluidized bed [m]
K_a	: attrition rate constant [1/m]
P	: pressure in the reactor [Pa]
T	: temperature in the reactor [°C]
U_o	: superficial gas velocity [m/s]

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