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Simultaneous removal of H_2S and COS using Zn-based solid sorbents in the bench-scale continuous hot gas desulfurization system integrated with a coal gasifier

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Abstract−A bench-scale continuous hot gas desulfurization system using Zn-based solid sorbents was developed to remove H_2S and COS simultaneously in a 110 Nm^3/h of real coal-gasified syngas. The bench-scale unit, which consisted of a fast fluidized-bed type desulfurizer and a bubbling fluidized-bed type regenerator, was integrated with a 3 ton/day-scale coal gasifier installed at the Institute for Advanced Engineering. The solid sorbents, which consisted of 50 wt% of ZnO for sulfides sorption and 50 wt% of supporters for mechanical strength, were manufactured by a spray drying method and supplied by Korea Electric Power Corporation Research Institute. The bench-scale unit was designed to operate at the high temperature of above 500 °C and the high pressure of 19 kg_f/cm^2 gauge. Integration of the bench-scale unit with a coal gasifier was first performed to investigate the operation stability of the integrated system. And the long-term continuous operation above 30 h was performed to analyze the desulfurization performance of the bench-scale unit. The concentration of both H_2S and COS in the syngas was measured by a continuous UV gas analyzer and an online gas chromatograph and that of both H_2S and COS after desulfurization was measured by an online gas chromatograph. Through the above 30-h continuous operation, the sulfur removal reached up to 99.9%.

Key words: Hot Gas Desulfurization, Solid Sorbents, Bench-scale Unit, Integration with a Coal Gasifier, IGCC

INTRODUCTION

The Integrated Coal Gasification Combined Cycle (IGCC) system mainly consists of a gasification block, a gas clean-up block, and a power block. An IGCC plant tends to include a highly efficient hot gas desulfurization (HGD) system to remove both H_2S and COS in the syngas. The HGD technique is one of the elemental technologies having both high thermal efficiency and very low emissions [1]. The existing conventional wet-type desulfurization processes, such as Selexol™ and Rectisol®, require cooling and reheating of the gas stream, which results in significant reduction in thermal efficiency of the system. The HGD system has been recognized as a new method to efficiently remove H_2S and COS simultaneously in fuel gas with regenerable sorbent at the high temperature and high pressure condition [2].

Research Triangle Institute (RTI) International and Eastman Chemical Company had reported successful demonstration of a dual loop transport reactor-based desulfurization technology with regenerable sorbent [3]. It is also reported that RTI has developed 50 MWe-scale warm gas cleanup process at Tampa Electric power company and the work will be completed by September 2015 [4]. Yi et al. [5] reported 100-h continuous operation results using two bubbling-beds for desulfurization and regeneration and a riser for the solid transportation system. Jo et al. [6] and Park et al. [7] reported the experimental results of a bubbling reactor-based compact two-bed HGD system. Jo et al. [8] also reported cold-mode and hot-mode tests of a small-scale (5 Nm^3/h of gas treatment) HGD system which consists of a fast fluidized-bed desulfurizer and a bubbling fluidized-bed regenerator. Yi et al. [9] recently reported experimental results of KIER fluidized hot-gas desulfurization processes with two different modes such as a bubbling-bubbling mode and transport-bubbling mode.

In this study, a bench-scale unit (BSU, 110 Nm^3/h of gas treatment) which consists of a fast fluidized-bed desulfurizer and a bubbling fluidized-bed regenerator has been developed. The BSU was designed to operate at the high temperature of above 500 °C and the high pressure of above 19 kg_f/cm^2 gauge conditions. The BSU was integrated with a 3 ton/day-scale coal gasifier located at the Institute for Advanced Engineering (IAE) in Suwon, Korea. First, the solid circulation rate and voidage in the desulfurizer were obtained by cold-mode tests, and long-term continuous operation of above 30 h was performed using Zn-based dry sorbents to check feasibility of stable operation using real syngas at high pressure conditions.

EXPERIMENTS

1. Sorbent Preparation and Characterization

The desulfurization sorbent used for the test in syngas cleanup process was prepared by spray-drying method. Raw materials for the preparation of the desulfurization sorbent were composed of 50 wt% ZnO as an active material, 50 wt% matrices containing multi

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binders, and a Ni-based promoter additionally added at 7.5 wt%. Commercially available powder type raw materials were well mixed in pure water. The mixed slurry was spray-dried after comminution by ball mill in a 10 kg batch scale. The spray-dried green body was calcined at 650 °C in a muffle oven for 5 h after pre-drying at 120 °C overnight to enhance mechanical strength with burning out the organic additives which were added during slurry preparation.

The physical properties of the calcined sorbent were characterized in the terms of shape, particle size, tapped density, surface area, pore volume, and attrition resistance. Attrition resistance of the calcined oxygen carrier was measured with an attrition tester based on the ASTM D 5757-95. The attrition resistance was determined at 10 standard liters per minute (slpm) over 5 h as described in the ASTM method. The attrition index (AI) is the percent fines generated over 5 h. A lower AI indicates a better attrition resistance of the bulk particles. The AIs of fresh Akzo fluid catalytic cracking (FCC) catalyst, which was used as a reference for comparison, was 22.5%, under the same measurement condition. The measured physical properties are summarized in Table 1. The prepared desulfurization sorbent had physical properties suitable for fluidized-bed applications. Most of the sorbent had dimple shape. It should be improved to spherical shape to reduce the amount of attrition loss.

Table 1. Physical properties of the desulfurization sorbents calcined at 650 °C

	Fresh
Shape	Dimple
Avg. particle size/μm	169
Size distribution/μm	68-303
Bulk density/(g/cm^3)	0.93
BET/(m^2/g)	61.1
Hg porosity/%	60.7
Hg pore volume/(cm^3/g)	0.453
Attrition index (AI)/%	7.6

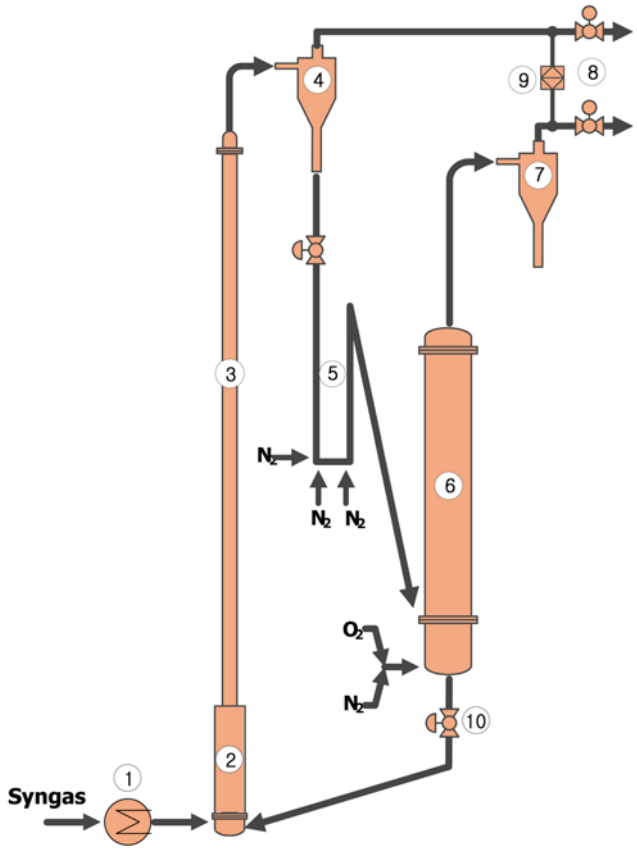


Fig. 1. Schematic diagram of the BSU.
① 2 Pre-heaters
② Desulfurizer mixing zone
③ Desulfurizer riser
④ Desulfurizer cyclone
⑤ Loop-seal
⑥ Regenerator
⑦ Regenerator cyclone
⑧ Pressure control valve
⑨ Differential pressure gauge
⑩ Slide valve

2. The Bench-scale Unit

Fig. 1 shows a schematic diagram of the bench-scale unit (BSU), which consists of a fast fluidized-bed desulfurizer, a bubbling fluidized-bed regenerator, a multi-cyclone, and a loop-seal. The lower part of the fast fluidized-bed desulfurizer is a 0.6 m tall pipe of 0.06 m I.D. The upper part of the desulfurizer is a 5.4 m tall pipe of 0.05 m I.D. A bubbling fluidized-bed regenerator is a 1.5 m tall bed of 0.1 m I.D. It has a perforated type distributor and a small cyclone. There are two electric pre-heaters to increase the syngas temperature up to 500 °C, which is the desirable to maintain the desulfurizer temperature. Two pressure control valves control the reactor pressure separately. The differential pressure between two reactors has been maintained stably by manipulating two pressure control valves.

3. Experimental Procedure

3-1. The Cold-mode Test

To perform a cold-mode test, we introduced N_2 in the desulfurizer instead of a real syngas. The minimum fluidization velocity (U_{mf}) of the sorbents is measured as 0.7 cm/s and the gas flow rate for loop-seal and regenerator was set to 3 U_{mf}. At first, the sorbents were introduced to the loop-seal and regenerator and then the solid circulation was started by opening the slide valve, which is located between the regenerator and the desulfurizer. From the cold-mode test, the solid circulation rate was measured by the opening area of the slide gate.

3-2. The Hot-mode Test

Fig. 2 shows the schematic of the integration system with coal gasifier. To perform a hot-mode test using real syngas, the temperature of the HGD system was set to the desired temperature using N_2 as the fluidization gas at the desired pressure conditions. And the HGD system inlet and outlet valve (①, ②) were first open and the syngas flow rate of the HGD system was controlled by the HGD system by-pass valve (③). The operating pressure of the integrated system was controlled by the main control valve (④). When the syngas flow rate was adjusted to the set value of 110 Nm^3/h, the

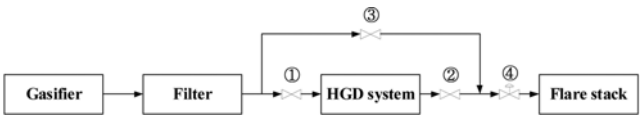


Fig. 2. Schematic of the integration system with a coal gasifier.
① HGD system inlet valve
② HGD system outlet valve
③ HGD system by-pass valve
④ Main pressure control valve

Table 2. The experimental conditions of the hot-mode test

	1st Pre-heater	2nd Pre-heater	Desulfurizer	Loop-seal	Regenerator
Pressure (kg_f/cm^2 gauge)			19		
Temperature (°C)	350	500	550	500	650
Gas flow rate (Nm^3/h)	110 (syngas)	110 (syngas)	110 (syngas)	2.0 (N_2)	8.5 (N_2+O_2)

solid circulation was started and the needed oxygen in the regenerator was introduced. The concentration of both H_2S and COS in the syngas was measured by a continuous UV gas analyzer and an online gas chromatograph and that of both H_2S and COS after desulfurization was measured by an online gas chromatograph. The experimental conditions of the hot-mode test are summarized in Table 2.

RESULTS AND DISCUSSION

Fig. 3(a) shows the differential pressure profiles of the loop-seal and the regenerator, and Fig. 3(b) shows the differential pressure profiles of the desulfurizer. To circulate the solid between the desulfurizer and the regenerator, the slide valve should be opened above around 25%. The desulfurizer, loop-seal and regenerator showed the stable differential pressure profiles so that the solid circulation was maintained at a stable manner. To measure the solid circulation rate, we stopped the injection of gas flow in the loop-seal and measured the difference of differential pressure in the regenerator in a given time. Using a bulk density of the sorbents, the solid circulation rate was calculated. We increased the slide valve opening areas as 25%, 30% and 35%, which resulted in the increase of the differential pressures of the desulfurizer. Based on the mass balance, the desired solid circulation rate based on the desulfurizer diameter was 7-8 kg/m^2s when the inlet sulfur content was assumed to be around 5,000 ppmv. Table 3 shows the solid circulation rate according to the valve opening area. Between 30% and 35% of the slide valve opening area, the desired solid circulation rate could be acquired.

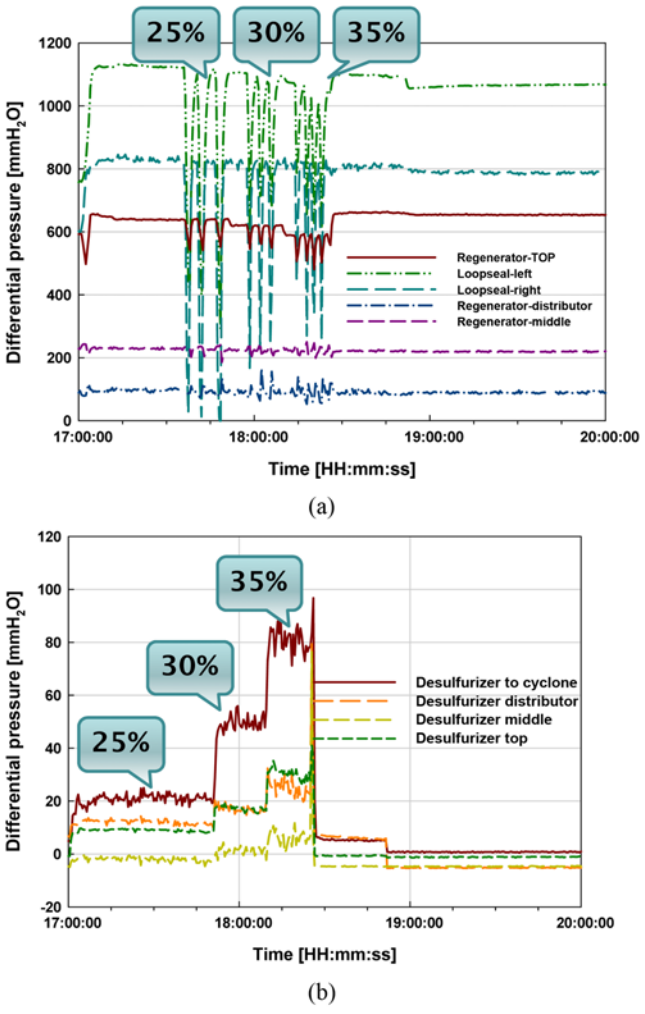


Fig. 3. The cold-mode test: (a) Differential pressure profiles of the loop-seal and the regenerator, (b) Differential pressure profiles of the desulfurizer.

Fig. 4 shows the syngas flow rate and the reactor pressure in the 30-h continuous experiments. The syngas flow rate and the system pressure have been well maintained around 110 Nm^3/h and 19 kg_f/cm^2 gauge, respectively. The control valve in the desulfurizer in the BSU was fully opened since the pressure of the syngas flow line was controlled by the control valve (④ in Fig. 2). The control valve in the regenerator was automatically controlled in order to maintain the pressure of the regenerator as close as that of the desulfurizer.

Fig. 5 shows the differential pressure of the desulfurizer, the loop-seal, and the regenerator. The desulfurizer, loop-seal and regenerator showed the stable differential pressure profiles so that the solid circulation was maintained at a stable manner. In Fig. 5(a), the differential pressure of the desulfurizer-to-cyclone was maintained between 40 and 50 mmH_2O since the opening area of the slide valve was 30%, which the solid circulation rate was around 7.0 kg/m^2s

Table 3. Solid circulation rate according to the slide valve opening area

Valve opening area [%]	Gs [kg/m^2s]
25	4.4
30	7.0
35	10.4

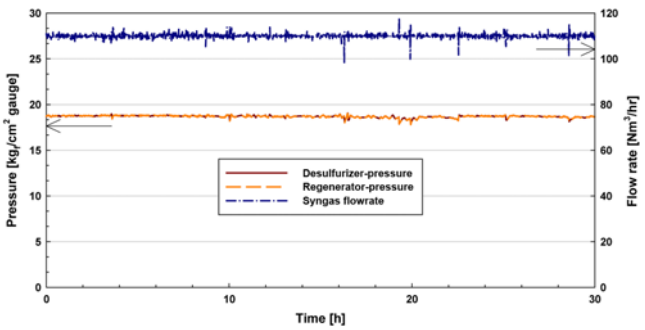


Fig. 4. The syngas flow rate and the reactor pressure in the 30-h continuous experiments.

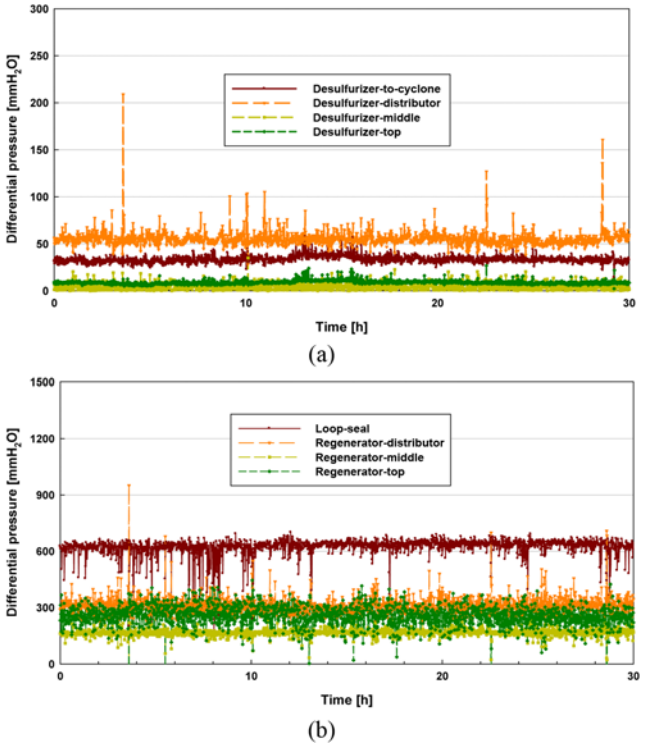


Fig. 5. The differential pressure profile in the 30-h continuous experiments: (a) desulfurizer, (b) loop-seal and regenerator.

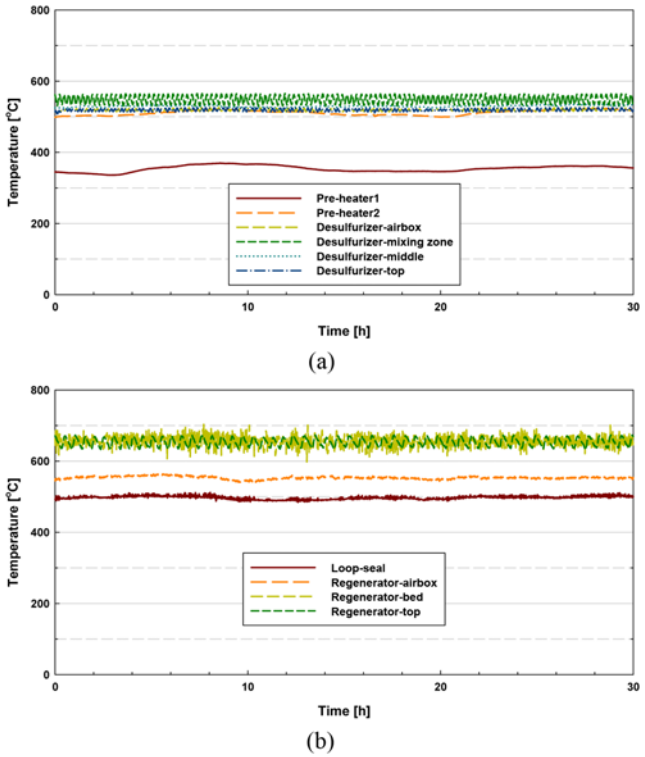


Fig. 6. The temperature profile in the 30-h continuous experiments: (a) pre-heaters and desulfurizer, (b) loop-seal and the regenerator.

based on the Fig. 3 and Table 3. The differential pressure of the loop-seal in Fig. 5(b) was maintained at a stable manner so that the pressure of the desulfurizer and the regenerator was well controlled at the same value.

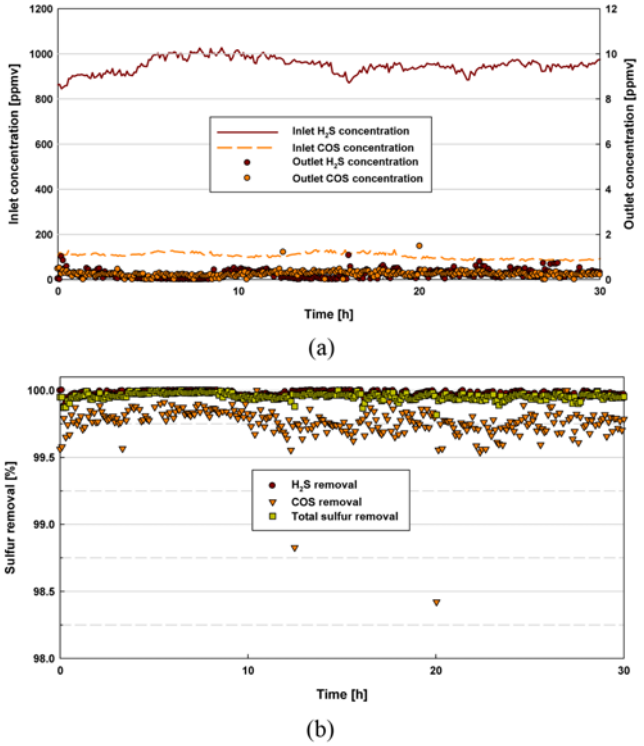


Fig. 7. The results of the 30-h continuous experiments: (a) The H_2S and COS concentration of the inlet and the outlet of the desulfurizer, (b)The H_2S, COS and total sulfur removal.

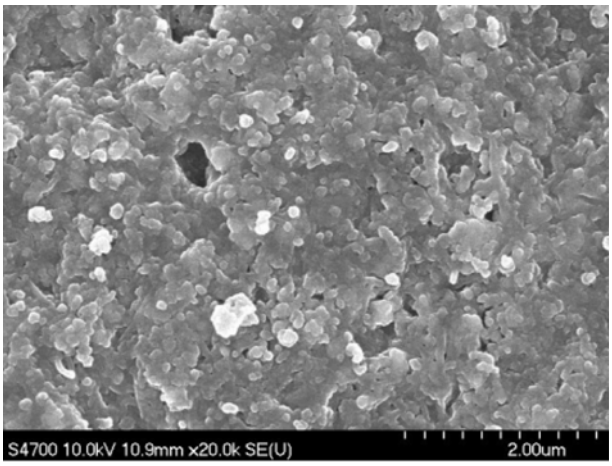
Fig. 6 shows the temperature profile of each unit. The temperature set points of the 1st pre-heater, 2nd pre-heater, desulfurizer, the loop-seal, and the regenerator were 350, 500, 550, 500, and 650 °C, respectively. The temperature of each unit was automatically controlled by the electric heater in order to maintain the set point value. In Fig. 6, the temperature of each unit was well maintained at the set point value.

Fig. 7(a) shows the H_2S and COS concentration of the inlet and the outlet of the desulfurizer and Fig. 7(b) shows the H_2S, COS and total sulfur removal. The concentration of inlet H_2S and COS in the syngas was 900-1,000 ppmv and 100-150 ppmv, respectively. After the desulfurization, the concentration of both outlet H_2S and COS in the syngas was below 1 ppmv. The total sulfur removal was maintained above 99.9% during 30-h continuous operation.

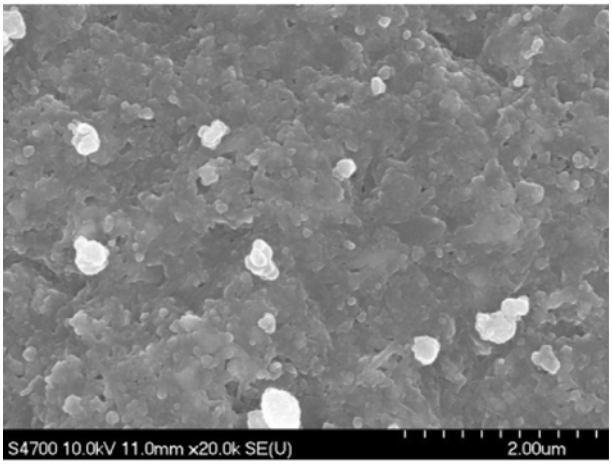
Fig. 8 shows the SEM images of the fresh sorbent, a sorbent after the sulfidation, and a sorbent after the regeneration. The surface morphology of the sorbent was changed after the sulfidation and the regeneration. Table 4 shows the Hg porosity of the fresh sorbent, a sorbent after the sulfidation and a sorbent after the regeneration. The Hg porosity of a sorbent after the sulfidation was 43.1% and that of a sorbent after the regeneration was 57.8%, which is very close to the fresh one. This indicated that the pore redeveloped after the regeneration.

CONCLUSIONS

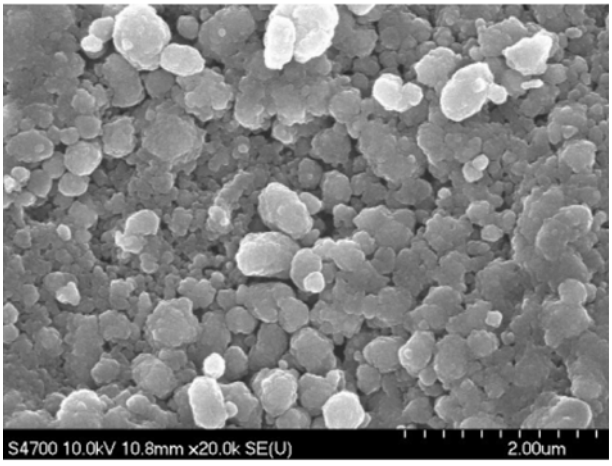
A bench-scale continuous hot gas desulfurization system using



(a)



(b)



(c)

Fig. 8. The SEM images: (a) The fresh sorbent, (b) A sorbent after the sulfidation, (c) A sorbent after the regeneration.

Table 4. Hg porosity of the fresh sorbent, a sorbent after the sulfidation and a sorbent after the regeneration

	Fresh sorbent	After sulfidation	After regeneration
Hg porosity/%	60.7	43.1	57.8

Zn-based solid sorbents, which was integrated with a coal gasifier, stably operated during 30 h for removing H_2S and COS simultaneously in a 110 Nm^3/h of real syngas at the system pressure of 19 kg_f/cm^2 gauge. During the long-term continuous operation, the concentration of both outlet H_2S and COS in the syngas was maintained below 1 ppmv so that the total sulfur removal was maintained above 99.9% when the concentration of inlet H_2S and COS in the syngas was 900-1,000 ppmv and 100-150 ppmv, respectively.

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