Korean J. Chem. Eng., 14(6), 513-518 (1997)

A STUDY ON REGENERATION OF ZINC TITANATE SORBENTS FOR H_2S REMOVAL

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(Received 22 September 1997 • accepted 17 November 1997)

Abstract – In this study the regeneration of used zinc titanate sorbents for high temperature desulfurization of fuel gases was investigated. Zinc titanate sorbents with Zn/Ti molar ratio of 1.5 were prepared and the regeneration was carried out in quartz fixed-bed reactor of 1 cm diameter. Regeneration of zinc titanate sorbents at high temperature is exothermic reaction that brings about deterioration of sorbents. So far experimental parameters such as reaction temperature, concentration of oxygen, flow rate and steam content have been considered to obtain suitable regeneration conditions. H_2S and SO_2 breakthrough curves were obtained during desulfurization-regeneration. Also, properties of the sorbents before and after regeneration were analyzed using SEM, XRD, Hg-porpsimetry and BET method. From such results, we obtained the most suitable regeneration conditions including 650 °C of regenerating temperature, 5 % of oxygen content and 10 % of steam in the gas stream.

Key words: Zinc Titanate, Desulfurization, Regeneration, Deterioration, Sulfur Capacity

INTRODUCTION

Use of coal for producing electric power has been expected to increase more than 30 % in 5 years due to the low price and large amount of coal deposits. But the removal of high levels of contaminants in coal such as particulates, sulfur and nitrogen oxides has been remained as a key problem to be solved. Among them, sulfur has received more attention than any other coal contaminants because it is a main precursor to acid rain and causes severe corrosion problems in most systems using coal gasification such as power plants (gas turbine combined cycle, fuel cell) and synthesis gas conversion plants (methanol, ammonia).

High temperature desulfurization of coal-derived fuel gas from the coal gasification unit is considered as one of the most promising advanced technologies to remove sulfur compounds from coal so that environmental considerations are eliminated from the choice of using coal versus oil or natural gas as a fuel feedstocks. In addition, the method offers potential improvements on the thermal efficiency of the systems using coal gasification like integrated coal gasification combined cycle (IGCC) [Kim et al., 1996] for producing electrical power, which is consisted of coal gasification, gas purification and power producing unit.

So far several sorbents have been proposed and investigated for the regenerative removal of the sulfur compound like H_2S from the flue gas of coal gasification unit at high temperatures. From the results of the extensive works on the sorbents by many authors [Lee et al., 1996; Gupta and Gangwal, 1992; Ayala, 1992; Gangwal et al., 1995], zinc titanate is presently the leading candidate sorbent. It has a high sulfur removal capacity and good physical property and also it is easily regenerated with air. During the repeated cycles of desulfurization and regeneration, it is well known that the deterioration of the sorbent due to the sintering and evaporative loss of zinc compound occurs because of higher operating temperatures than 600 °C [Gupta and Gangwal, 1992, 1993; Gupta et al., 1993; Gangwal and Gupta, 1993]. Especially the temperature of the sorbent is increased rapidly by exothermic sulfur oxidation reaction when it is regenerated with air [Gupta and Gangwal, 1993]. So the control of operating temperatures and the optimization of regenerating conditions are very important in this desulfurization process.

In the case of zinc titanate sorbent, the desulfurization process is consisted of desulfurization and regeneration step as follows [Ayala et al., 1993]:

- **possible desulfurization reactions**

$$ZnTiO_3+H_2S \rightarrow ZnS+TiO_2+H_2O \quad (1)$$

$$Zn_2TiO_4+2H_2S \rightarrow 2ZnS+TiO_2+2H_2O \quad (2)$$

$$Zn_2Ti_3O_8+2H_2S \rightarrow 2ZnS+3TiO_2+2H_2O \quad (3)$$

- **possible regeneration reactions**

$$ZnS+TiO_2+3/2O_2 \rightarrow ZnTiO_3+SO_2 \quad (4)$$

$$2ZnS+TiO_2+3O_2 \rightarrow Zn_2TiO_4+2SO_2 \quad (5)$$

$$2ZnS+3TiO_2+3O_2 \rightarrow Zn_2Ti_3O_8+2SO_2 \quad (6)$$

$$ZnS+2O_2 \rightarrow ZnSO_4 \quad (7)$$

$$ZnO+H_2 \text{ (or CO)} \rightarrow Zn+H_2O \text{ (or } CO_2) \quad (8)$$

Among the reactions proposed, main reactions in our case

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are (2) and (5). In addition to the sintering at high temperature, deterioration of the sorbents resulted from the side reactions depending on the reaction conditions like sulfation reaction and zinc evaporation reaction presented in (7) and (8), respectively.

The purpose of the paper is to fix out the optimum regeneration conditions to minimise the physical and chemical deterioration of the zinc titanate sorbent.

EXPERIMENTAL

1. Preparation of Zinc Titanate Desulfurization Sorbents

Several reactor types such as fixed bed, moving bed and fluidized bed are suggested for high temperature desulfurization process in the IGCC [Park et al., 1993; Khare et al., 1996; Swisher and Gupta, 1996; Copeland et al., 1996; Rutkowski et al., 1996]. In the preparation of the sorbents, attention is forcused on the hardness and shaping property of the sorbent for their application to the fluidized bed reactor because of its advantages in control of the operating temperature.

ZnO and TiO_2 powder mixtures with particle sizes less than 50 μm were prepared by pulverizing original oxide particles (TiO_2 from Hankook titanium, Co. and ZnO from Sambo Co., Korea) using a ball mill. The mole ratio of ZnO to TiO_2 was fixed to 1.5. The ratio was known as an optimum for the desulfurization sorbent in our previous work [Lee et al., 1996]. After adding 2-5 wt% of inorganic binder and proper amount of organic binders, the paste of the powder mixtures were made. After injection molding, drying at 120 °C for 24 hours, calcination at 900 °C for 5 hours and pulverizing, zinc titanate sorbents in the particle size range from 100 to 300 μm were prepared for to use in the fixed bed and/or fluidized bed.

The properties of zinc tatanate sorbents prepared were characterized by means of various instruments such as BET surface analyzer (Micromeritics Gemini 2375), Hg-porosimetry (Micromeritics AutoPore III), ICP (Inductively-Coupled Plasma, Jobin-Yvon, Jobin-Yvon 38 plus), EDX (Energy Dispersive X-ray, FISONS, KEVEX Superdry), XRD (X-ray Diffractometer, RIGAKU, D/Max-2500). The experimental results by instrumental analysis are shown in Table 1. From the results of XRD shows that Zn_2TiO_4 phase, known as the most active form of zinc titanate, is formed by the preparation method used in our laboratory.

2. Experimental Apparatus and Procedure

Vertical fixed bed quartz-microreactors with 3 cm and 1 cm diameters were used to prevent corrosion by H_2S gas. The temperatures of sorbents were measured by chromel-alumel thermocouple fixed in the center of the sorbent bed. The H_2S gas balanced with N_2 was added to the mixed gas, containing H_2, CO, CO_2 and N_2, to make a reactant gas input with

Table 1. Properties of prepared zinc titanate sorbents

Zn/Ti mole ratio	BET (m^2/g)	Hg-pore area (m^2/g)	Bulk density (g/ml)	ICP analysis	XRD phase
1.5	2.48	2.309	1.2293	Zn: 65.9 %	Zn_2TiO_4

Table 2. Nominal test conditions

	Sulfidation	Regeneration
Temperature (°C)	650	600-750
Pressure (atm)	1	1
Flow rate (ml/min)	250-500	250-500
Gas composition (vol.%)	H_2S 1.0 H_2 11.7 CO 19.0 CO_2 6.8 H_2O 5.0 N_2 balance	O_2 2-10 H_2O 10-20 N_2 balance

a similar composition to the real flue gas from the gasifier. This mixed gas was introduced from the bottom of the reactor and the flow rate was controlled by mass flow controller. For the introduction of steam, syringe pump (0.001-30.0 ml/min) was used. The water from the syringe pump was evaporated in the pyrex preheating mixer packed with glass beads. The preheater was installed before the main quartz reactor and had a 4 cm diameter. 300 °C of preheating was needed to control the fluctuation of the reactor temperature by cold feed input. All the temperatures of the stainless line including input and output from the reactor were maintained at 150 °C to prevent condensation of reactant and product gases. GC (Gas Chromatograph, Shimadzu GC 8A) equipped with TCD (Thermal Conductivity Detector) and Hysep Q-Porapac T packed column was used to analyze the product stream.

The desulfurization was initiated by introduction of reactant mixed gas containing 10,000 ppm of H_2S and/or COS to the fixed reactor packed with 3 g of zinc titanate sorbent. The product gas stream was analyzed to obtain breakthrough curve. After desulfurization, regeneration was carried out in the oxygen flow diluted with N_2. The effects of regeneration temperatures, oxygen contents, steam and flow rates on the sulfur removal capacities of the sorbents were observed and the fluctuations of the reactor temperatures were also recorded to fix out the optimum regeneration conditions. The optimum conditions were suggested by comparing the H_2S breakthrough curves recorded during the desulfurization after regeneration steps in various regeneration conditions. In Table 2, various regeneration conditions are represented.

RESULTS AND DISCUSSION

1. Regeneration Reactions

Because regeneration reaction is the exothermic reaction between sulfur and oxygen, the reaction temperature is increased with oxygen contents in the feed gas. The increase in reaction temperature resulted in the deterioration of the sorbents due to the loss of volatile zinc compound and severe sintering. In the paper, we estimate the effects of regeneration temperature, contents of the oxygen, flow rates on the sulfur removal capacities of sorbents to find out the optimum conditions for long-term, continuous desulfurization process.

In addition, regeneration by syngas with similar composion with flue gas from the gasifier was tried and the effects of steam on the regeneration was estimated. From the results above, regeneration conditions were fixed and the conditions proposed were used to the continuous desulfurization-regeneration cycles to apply it for the commercial use.

1-1. The Effect of Regeneration Temperature

To prevent the evaporative loss of zinc compound and severe sintering during the regeneration at high temperature, the regeneration temperature had to be controlled as low as possible. In the work, the effect of temperature was estimated in the range from 600 °C to 750 °C on fixed oxygen contents at 5 %. Fig. 1-a,b,c showed the breakthrough curves of SO_2, temperature variation curves during the regeneration, and the breakthrough curves of H_2S after regeneration, respectively, when the regeneration temperature was increased. As the temperature was increased, the sorbent was regenerated rapidly as shown in Fig. 1-a. But at higher temperatures than 650 °C, there were no differences in SO_2 concentrations as a function of regeneration time except the pattern of temperature increase due to the exothermic reaction (Fig. 1-b), indicating that the sorbents were well regenerated at temperatures higher than 650 °C. Also, the sorbent regenerated at 650 °C showed same sulfur removal capacity compared with fresh sample or the sorbents regenerated at higher temperatures than 700 °C as shown in H_2S breakthrough curves in Fig. 1-c.

From the experimental results at 600 °C, it was concluded that regeneration of zinc titanate was incomplete at 600 °C, which agreed with the results that the sulfur removal capacity was reduced due to the formation of zinc sulfate at lower temperatures than 593 °C [Moorehead and Henningsen, 1996].

1-2. The Effect of Oxygen Concentration

The effect of oxygen concentration on the regeneration was estimated in the oxygen concentration range from 2.0 to 10 % at a fixed initial bed temperature of 650 °C. As shown in the Fig. 2-a, the breakthrough curves of SO_2 shifted to the left when the oxygen concentration was increased. Although the bed temperature was increased more than 50 °C (Fig. 2-b), the sorbents were well regenerated and recovered the sulfur removal capacities at higher oxygen concentrations than 5 % (Fig. 2-a and 2-c). In the case of 2 or 3 % of oxygen concentrations were used, the temperature increase due to the exothermic reaction was less than 30 °C. But in the case the breakthrough time of H_2S was short compared to the sample regenerated at 5 % of oxygen, indicating that regeneration was incomplete and sulfur removal capacity was reduced after regeneration.

1-3. The Effect of Flow Rate

The regeneration reactions were carried out at different flow rates of introducing gas input on the fixed oxygen concentration of 5 % and fixed regeneration temperature of 650 °C. By increasing the flow rate from 250 ml/min. to 500 ml/min, the reaction temperature was increased rapidly and the fluctuation of the temperature was more than 130 °C as shown in the Fig. 3-a,b. This large temperature differences, more than 2 times compared to the samples treated with 250 ml/min of regenerating gas input, caused the severe sintering and reduction of sulfur removal capacities as shown in Fig. 3-c. Even though the relationships between flow rates and temperature increases were not verified clearly, it was one of the reasons that the fluidized bed, which released heat more easily than the fixed bed, was considered as an alternative type of reactor.

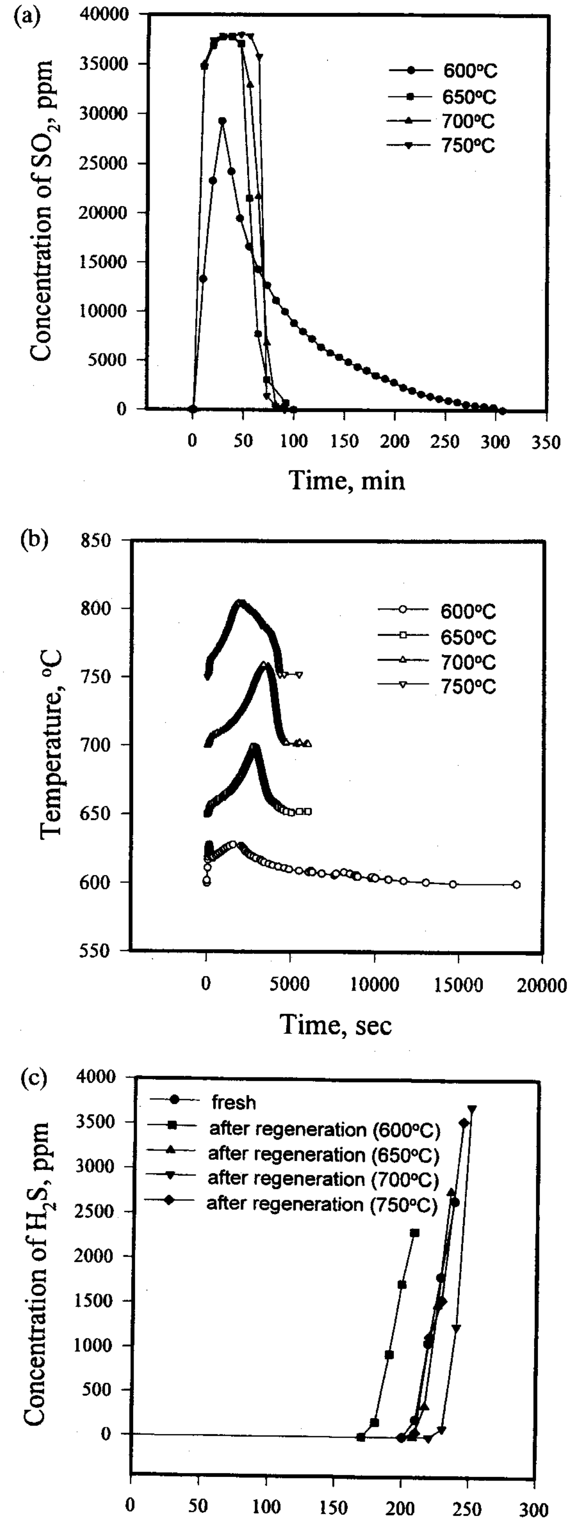

Fig. 1. (a) SO_2 breakthrough curve vs. regeneration temperature (The effect of temp.). (b) Temperature profile during regeneration (The effect of temp.). (c) H_2S breakthrough curves after regeneration (The effect of temp.).

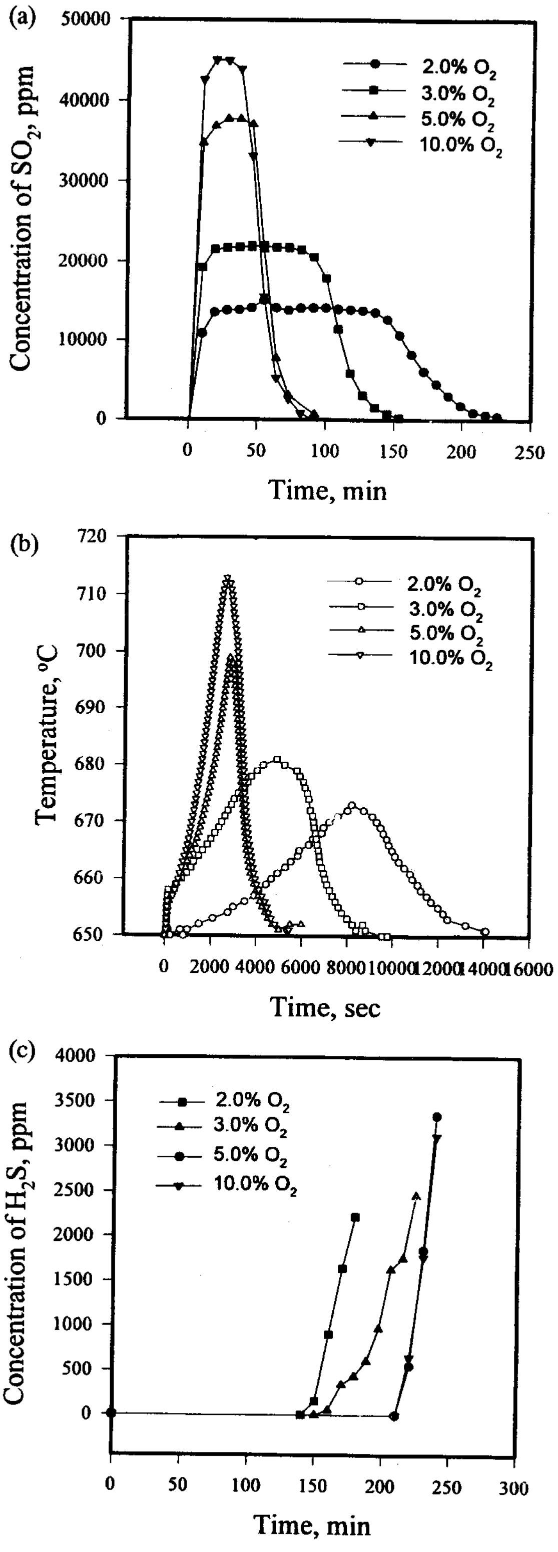

Fig. 2. (a) SO_2 breakthrough curve vs. concentration of oxygen (The effect of oxygen conc.). (b) Temperature profile during regeneration (The effect of oxygen conc.). (c) H_2S breakthrough curves after regeneration (The effect of oxygen conc.).

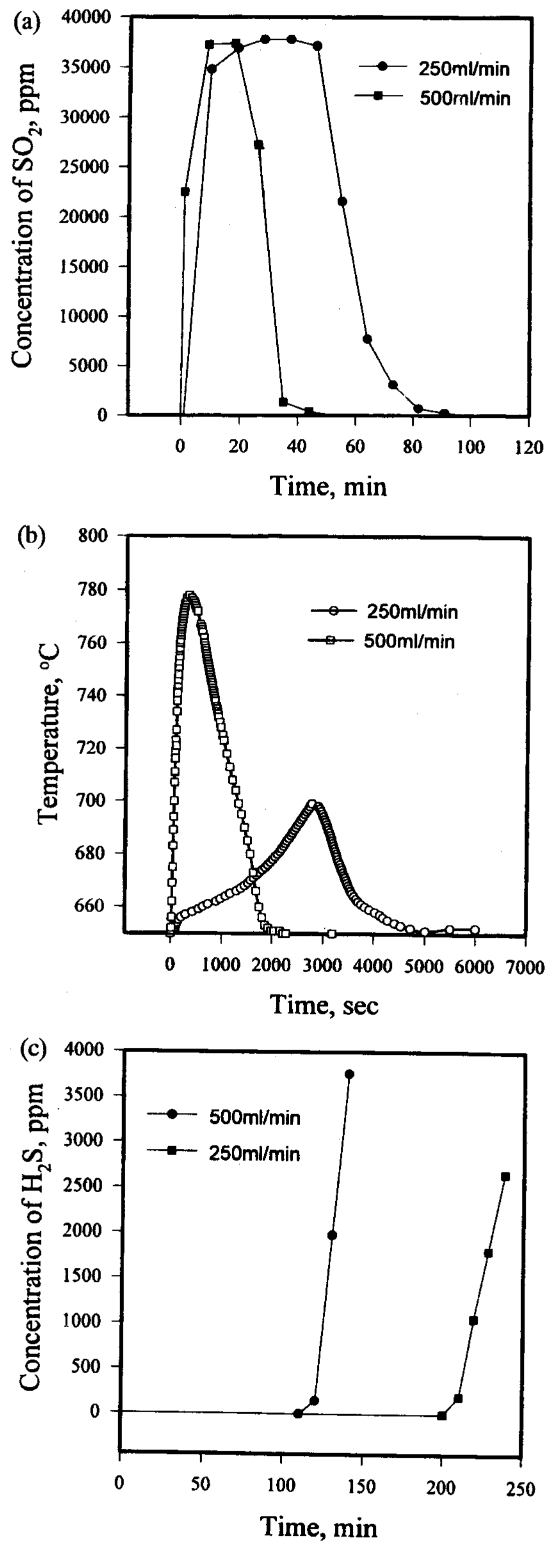

Fig. 3. (a) SO_2 breakthrough curve vs. flow rate of regeneration gases (The effect of flow rate). (b) Temperature profile during regeneration (The effect of flow rate). (c) H_2S breakthrough curves for each flow rate (The effect of flow rate).

1-4. The Effect of Steam in the Regenerating Gas Input and Usage of Flue Gas

It was reported that the increase in temperature in the regeneration step was minimized by adding steam to the regenerating gas input. But sulfur removal capacities of the sorbents were reported to be reduced by steam treatment at

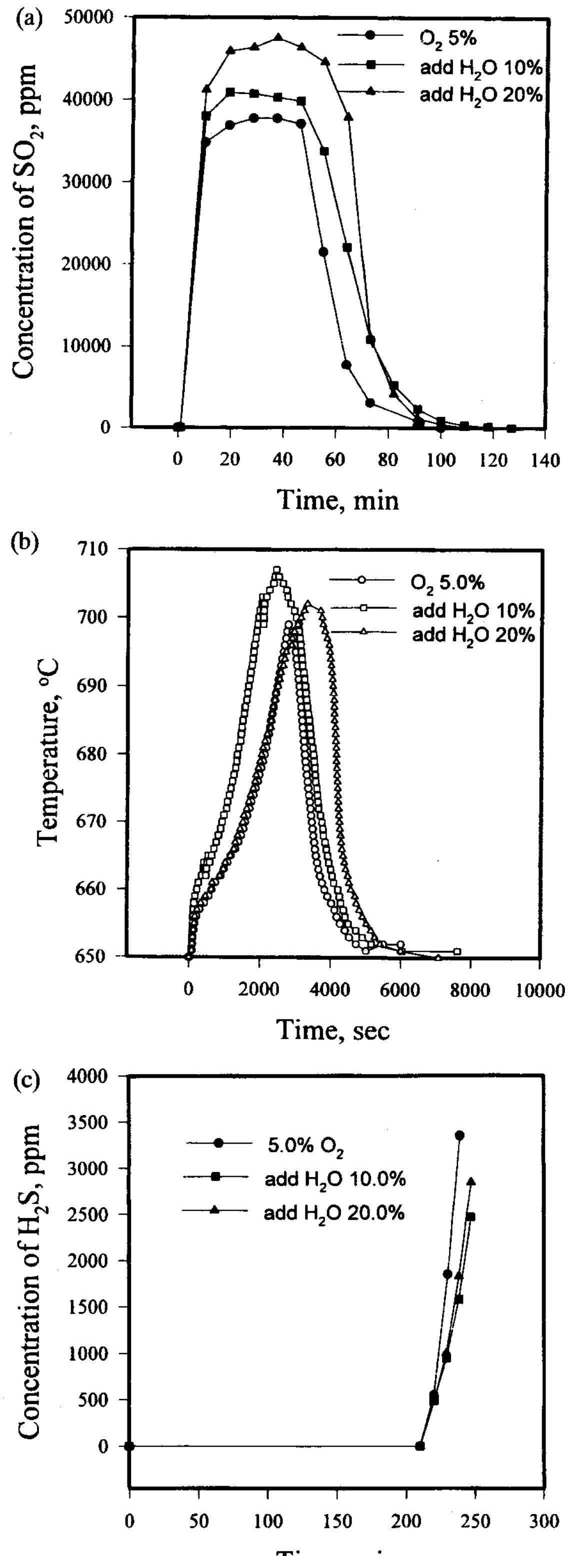

Fig. 4. (a) SO_2 breakthrough curve vs. concentration of steam (The effect of steam). (b) Temperature profile during regeneration (The effect of steam). (c) H_2S breakthrough curves after regeneration (The effect of steam).

lower temperature than 593 °C and steam soak was caused above 768 °C. In our case, by adding 10 % or 20 % of steam

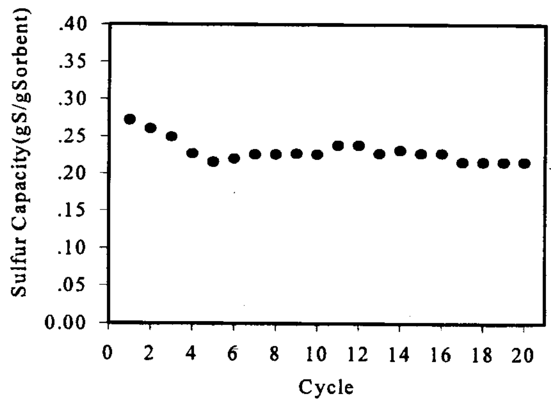

Fig. 5. Sulfur capacity of ZT-sorbent for cycles 1 to 20.

the samples were regenerated well and the increase in temperature by exothermic reaction was similar to that of the case treated with only oxygen and nitrogen stream as shown in Fig. 4-a, and b. Also it was found that sulfur removal capacity was slightly increased by adding the steam to the regenerating gas input as shown in Fig. 4-c, indicating that the sorbents could be regenerated with steam without deterioration of sorbents due to steam sock in our reaction conditions.

From the consideration of economic view point, the syngas, which had a similar composition with flue gas from the gasifier was used to regenerate the sorbents in the temperature range from 600-750 °C. But the flue gas did not regenerated the sorbents, which confirmed by no difference in XRD peaks after regeneration and no sulfur oxide compounds during regeneration. It could be concluded that the sorbents was not regenerated without oxygen in the reaction conditions.

2. Continuous Desulfurization and Regeneration Cycles

Based on the results of preliminary experiments above, optimum operating conditions for the zinc titanate sorbent were found and 20 cycles of continuous desulfurization-regeneration were carried out to for the purpose of duration test. Under 650 °C of regeneration temperature, 5.0 % of oxygen atmosphere, and 20 % of steam, the sulfur removal capacities of the sorbent after regeneration were represented in Fig. 5 as a function of number of cycle. Even though the capacity decreased slightly in initial period, it did not decrease anymore after 5 cycles up to 20 cycles. The facts meant that the optimum conditions from the preliminary test could be applied to the commercial use although more detailed researches for a long period were needed depending on the reactor types.

CONCLUSIONS

Zinc titanate sorbent, of which mole ratio of zinc to titanium was 1.5, was prepared and used to estimate the effects of regeneration temperatures, oxygen contents, flow rates, and steam on the sulfur removal capacities. Also 20 cycles of desulfurization and regeneration were carried out in the optimum condition based on the preliminary experiments. From the experiments, the conclusion were drived as follows:

1. Regeneration rate and sulfur removal capacity were in-

creased with regenerating temperature up to 650 °C. Above 650 °C, there was no difference in removal capacity after regeneration but the increase in temperature by exothermic reaction was increased with regenerating temperature.

2. The temperature of sorbent bed was increased with contents of oxygen contained in regenerating gas. Higher than 5 % of oxygen was needed to regenerate the sorbent completely and recover its original sulfur removal capacity.

3. By increasing the flow rate of regenerating gas by 2 times, the bed temperature was increased more than 2 times, indicating that detailed research for the relationship between gas input velocity and bed temperature was needed in scale-up plant.

4. Addition of the steam to the regenerating gas make the system more stable without increase in bed temperature and steam sock. The sorbent was not regenerated with the flue gas mixture from the gasifier due to the lack of oxygen contents.

5. During the 20 continuous desulfurization-regeneration cycles carried out in the conditions of 650 °C of regeneration temperature, 5.0 % oxygen and, 20.0 % steam, the sulfur removal capacity of the zinc titanate sorbent was not varied much, which showed the possibility to apply the system to the long period usage and commercial use.

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