

The Removal of Hydrogen Sulfide with Manganic Sorbent in a High-Temperature Fluidized-Bed Reactor

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Abstract—The removal of hydrogen sulfide (H₂S) from simulated gas was carried out in a batch type fluidized-bed reactor using natural manganese ore (NMO), which consists of several metal oxides (MnO_x: 51.85%, FeO_y: 3.86%, CaO: 0.11%). The H₂S breakthrough curves were obtained by changing temperature, gas velocity, initial H₂S concentration, and aspect ratio. Moreover, the effects of the particle size and the particle-mixing fraction on H₂S removal were investigated in a binary system of different particle size. From this study, H₂S removal efficiency increased with increasing temperature but decreased with increasing excess gas velocity. The breakthrough time for H₂S decreased as the gas velocity increased, which leads to reducing gas-solid contacting due to gas bypassing in a fluidized bed reactor. Improvement of H₂S removal efficiency in continuous process can be expected from the results of the binary particle system with different size in a batch experiment. The NMO could be considered as a potential sorbent in H₂S removal.

Key words: Hydrogen Sulfide, Manganic Sorbent, Binary Particle System, Fluidized-Bed Reactor

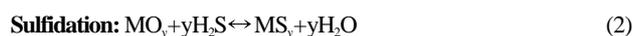
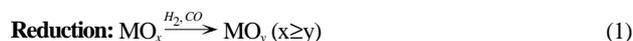
INTRODUCTION

The integrated gasification combined cycle (IGCC) system is one of the most promising power systems for producing electrical energy from coal due to the noticeable improvement in thermal efficiency [Gangwal et al., 1989; Woods et al., 1990; Choi et al., 2001; Yi et al., 2001]. The IGCC process gasifies coal under reducing conditions with essentially all the sulfur existing in the form of H₂S in the product fuel gas. The need to remove H₂S from coal-derived fuel gases is a significant concern which stems from stringent government regulations and also from a technical point of view: the need to protect turbines from corrosion. Westmoreland et al. [1976] carried out comparative studies on several proposed sorbent systems that consisted almost entirely of metal oxides. Metal oxides have been proposed because they tend to be more reactive at high temperature where desulfurization is desirable to conserve the sensible heat in gasifier fuel gas.

Westmoreland et al. [1977] screened the high temperature desulfurization potential of 28 solids, primarily metal oxides, based upon thermodynamic considerations alone. This earlier work, which was subsequently followed by kinetic studies, predicted manganese oxide stability and a high degree of desulfurization to temperatures in excess of 1,000 °C. In addition, manganese showed desulfurization potential in the range of 600-700 °C at which traditional metal oxides are known to be less reactive with H₂S. These kinetic studies determined the initial rates for the reaction between H₂S and MnO, CaO, ZnO, and V₂O₃ over a temperature range of 300-800 °C. The relative magnitude of reaction rates decreased in the order: MnO >

CaO ≈ ZnO > V₂O₃. They concluded that MnO possessed favorable properties for a high temperature desulfurization process and highly recommended that further studies be carried out. And many researchers have studied manganese oxides as a promising sorbent of H₂S [Wakker and Gerritsen, 1990; Wakker et al., 1993].

The chemistry of a complete sulfidation reaction may be represented by the overall reactions,



where M is Mn, Fe, Ca, etc. Also, natural manganese ore contains oxides of metals such as MnO₂, Fe₂O₃ and CaO, which can be considered to be potential sorbents for H₂S. The main object of this study is to explore the possibility of using natural manganese ore for H₂S sorption in a fluidized bed reactor. Also, fluidized bed reactors offer several potential advantages over fixed bed reactor for high-temperature desulfurization of coal-gas. They provide excellent gas-solid contact via vigorous agitation of small particles and thereby also minimize diffusional resistances, give faster overall kinetics, and allow pneumatic transport. Fluidized beds prevent solids segregation at high temperature, offer the capability of continuous adding or removing sorbent, and allow control of highly exothermic sorbent regeneration reactions.

In the present work, the removal of H₂S was closely examined in a fluidized-bed reactor as a function of temperature, initial H₂S concentration, gas velocity, aspect ratio, and particle size and particle mixing fraction in a binary system of different particle size.

EXPERIMENTAL

1. Fluidized-Bed Reactor

The experimental system, which consists mainly of a fluidized

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[†]This paper is dedicated to Professor Dong Sup Doh on the occasion of his retirement from Korea University.

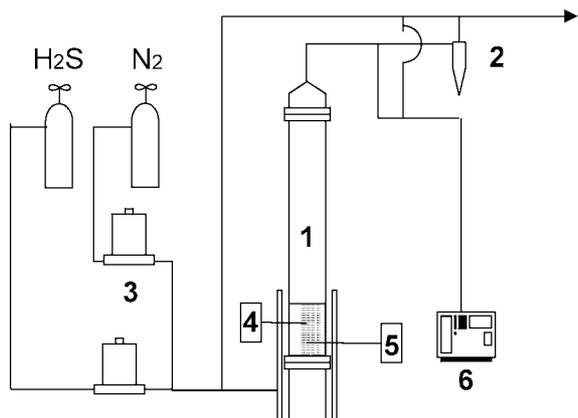


Fig. 1. Schematic diagram of the fluidized bed reactor.

- | | |
|-------------------------|----------------------------|
| 1. Fluidized bed | 4. Pressure transducer |
| 2. Cyclone | 5. Temperature controller |
| 3. Mass flow controller | 6. Wet gas analysis system |

bed reactor, gas handling and metering equipment, and a gas analyzer is shown schematically in Fig. 1. The fluidized bed reactor was a stainless steel pipe of 4 cm inside diameter and 80 cm length. It was fitted with a sintered metal (sus 316) gas distributor. The reactor was heated electrically to the height of 10 cm above the distributor by means of heating wire. Gas supplied to the reactor passed through a preheater that was also electrically heated. Temperature of reactor and preheater was maintained by PID controllers. The exterior of whole reactor unit was insulated heavily with ceramic wool to minimize heat loss.

2. Procedure

The reactor was operated in a batchwise manner with a single charge of NMO particles. Their chemical and physical properties are summarized in Table 1. Reactions were carried out with N_2 containing up to 2 vol% H_2S ; throughout a run gas samples were taken from the reactor inlet and outlet streams and analyzed with a wet

Table 1. Chemical and physical properties of NMO

(a) Chemical analysis (wt%)

Component	Mn	SiO ₂	Al ₂ O ₃	Fe	CaO	MgO	Balance O ₂ of Mn and Fe
wt%	51.9	3.13	2.51	3.86	0.11	0.25	36.33

(b) Physical properties

Density (kg/m ³)	3,980
Pore volume (cm ³ /g)	0.0392 (5-3000 Å)
Surface area (m ² /g)	20

Table 2. Experimental conditions

Operating variables	Operating conditions
Aspect ratio (L/D)	0.5, 1, 2, 3
Gas velocity (m/sec)	0.150, 0.250, 0.350, 0.450
H ₂ S concentration (ppm)	2,500, 5,000, 5,500, 7,100, 10,000, 16,600, 20,000
Particle size (mm)	0.194, 0.230, 0.274, 0.359, 0.505
Bed temperature (°C)	400, 500, 600, 700

analysis method (ASTM D2725 Test Method). The flow rate of gas was set to the desired value, and after steady-state temperature was reached, H_2S was introduced at such a rate as to give an inlet H_2S concentration. A run was continued until the outlet concentration of H_2S became greater than about 90% of its inlet value. The N_2 - H_2S stream was then turned off, and the reactor was purged with N_2 . The experimental conditions are in Table 2.

RESULTS AND DISCUSSION

The results obtained with the fluidized bed reactor are shown in Figs. 2-8. They are plotted in the form of "breakthrough curves" and indicate the effect of the main process variables on the changing rate of H_2S concentration in the outlet gas. All are seen to be more or less sigmoid in shape. The experimental data in terms of H_2S breakthrough curves for the sorbent examined at various temperatures are given Fig. 2. This figure shows that the breakthrough curves shift to the right with increasing temperature, which indicates a higher rate of sorption and sorption capacities of sorbents for H_2S . Moreover, the slope of the breakthrough curves decreases

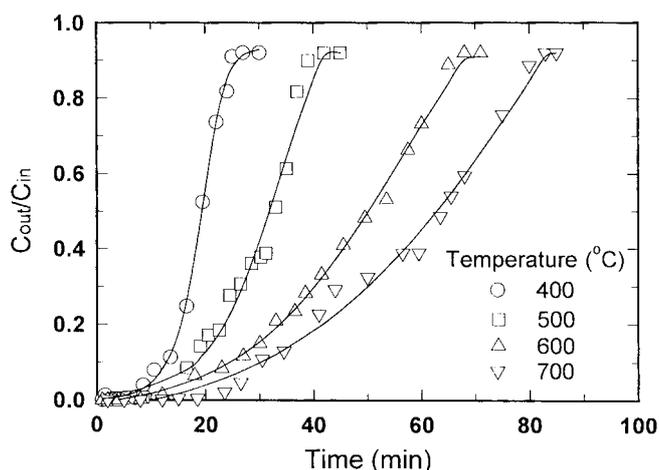


Fig. 2. The effect of temperature on H_2S removal ($L/D=1$, 0.250 m/s, $C_{in}=10,000$ ppm, $d_p=0.505$ mm).

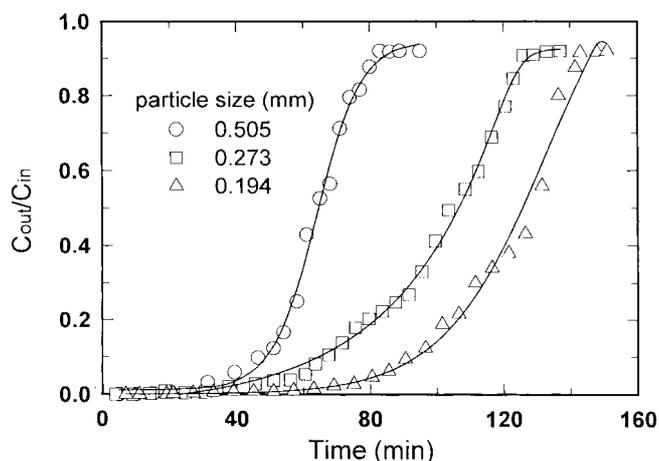


Fig. 3. The effect of particle size on H_2S removal ($L/D=1$, 0.250 m/s, $C_{in}=5,000$ ppm, 600 °C).

Table 3. The effect of bed temperature on the H₂S sorption capacity

Temp. (°C)	400	500	600	700
Capacity (H ₂ S mg/g sorbent)	52.0	82.6	138.7	156.8

with increasing temperature. This phenomenon is a fluidized characteristic due to the decrease of minimum fluidization velocity with increasing temperature [Geldart, 1972].

The main parameter determining the sorption capacity of sorbents is the particle size. The effect of particle size on the H₂S removal at 600 °C is shown in Fig. 3. As particle size decreases, the particle surface area increases. Thus, the sorption capacity is usually in inverse proportion in particle size. It means that surface area of the large-sized particle is less than that of the small-sized particle relatively; in case of the large-sized particles, solid product is easily formed in the external surface of particle and so intraparticle diffusion resistance increases [Zarkanitis and Sotirchos, 1989]. The sorption capacities of the sorbents were evaluated from experimental breakthrough curves by Eq. (3),

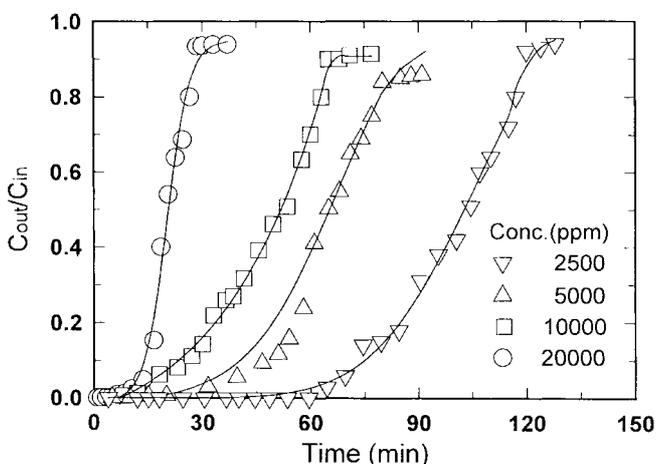
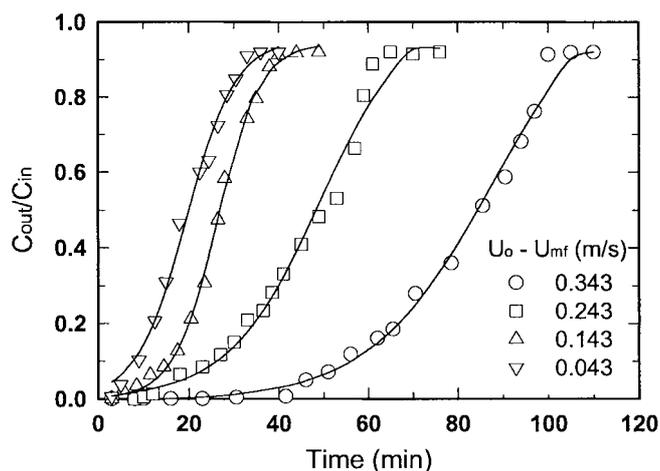
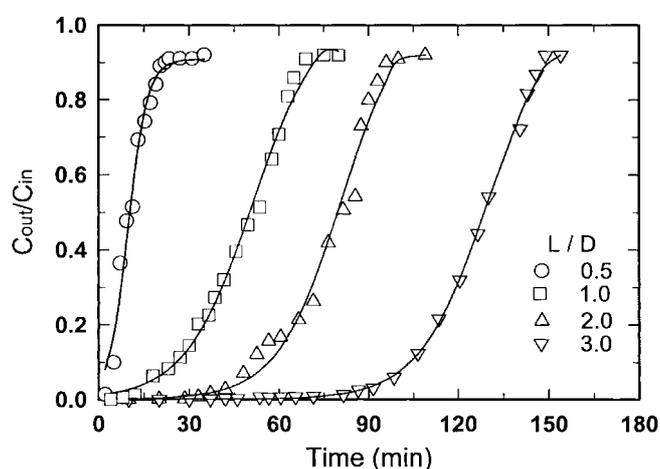
$$S = (A/W)QC_{in}M_{w,H_2S} \quad (3)$$

where A is the area above the breakthrough curve. These values are shown in Table 3.

In the meantime, the effect of the initial H₂S concentration on the H₂S removal is shown in Fig. 4, where the slope of the breakthrough curves increases with increasing initial H₂S concentration. It shows that the contact efficiency of H₂S reactant is increased and pore plugging is decreased, in case of high initial H₂S concentration.

In order to investigate the effect of gas velocity on H₂S removal, the breakthrough curves with the variation of gas velocity were examined as shown in Fig. 5. As gas velocity increases, the slope of breakthrough curves decreases. It means that gas supplied above minimum fluidization velocity passes by the bubble phase; as to the increase of gas velocity, the bubble fraction becomes higher and the flow-through velocity of bubble is fast [Geldart et al., 1981].

The effect of aspect ratio is shown in Fig. 6. As can be expected from the stoichiometry, more rapid breakthrough occurs at the lower bed heights; with a very shallow bed the breakthrough occurs al-

**Fig. 4. The effect of inlet H₂S concentration on H₂S removal (L/D=1, 0.250 m/s, d_p=0.505 mm, 600 °C).****Fig. 5. The effect of excess gas on H₂S removal (L/D=1, C_m=10,000 ppm, d_p=0.505 mm, 600 °C).****Fig. 6. The effect of aspect ratio on H₂S removal (0.250 m/s, C_m=10,000 ppm, d_p=0.505 mm, 600 °C).**

most immediately due to bypassing of the solid by the bubble gas.

Meanwhile, many researchers attempted enhancement of mixing degree and uniformity of different particles and increase of residence time for the fine particles in the bed to improve the performance of fluidized-bed [Nienow et al., 1978; Geldart et al., 1981; Jang et al., 1996]. In order to find out the method to improve the sorption capacity, the breakthrough curves with the variation of the mixing fraction of jetsam particle and the mean diameter of flotsam particle were examined as shown in Figs. 7 and 8, respectively. As can be seen in Fig. 7, the sorption capacity decreases with increasing the mixing fraction of jetsam particle since the sorption capacity of jetsam particles is lower than that of flotsam particles. Fig. 8 shows the breakthrough curves under the conditions of particle size of flotsam (70 wt%) at a fixed particle size of jetsam (30 wt%), 0.505 mm. As shown in this figure, the sorption capacity increases with decreasing the particle size of flotsam. As the particle size of flotsam is decreased, in the binary particle system, the bed density is increased and the size of bubble formed in bed is getting greater. Thus, the mixing of particles becomes superior due to the improvement of bubble mobility.

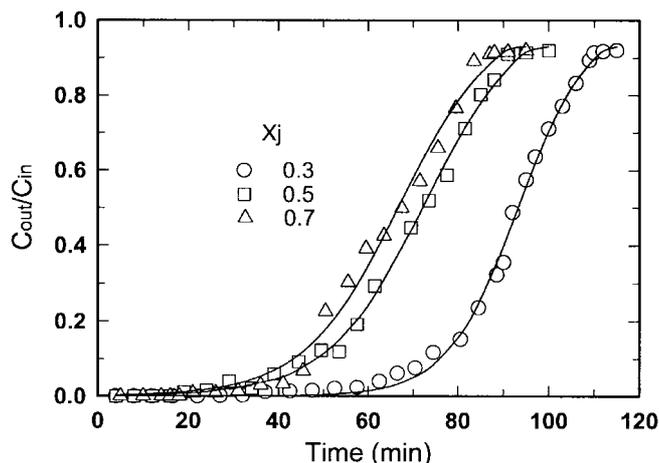


Fig. 7. The effect of flotsam particle mixing fraction on H₂S removal ($L/D=1$, 0.250 m/s, $C_{in}=5,000$ ppm, $d_{jf}=0.230$ mm, $d_{pf}=0.505$ mm, 600 °C).

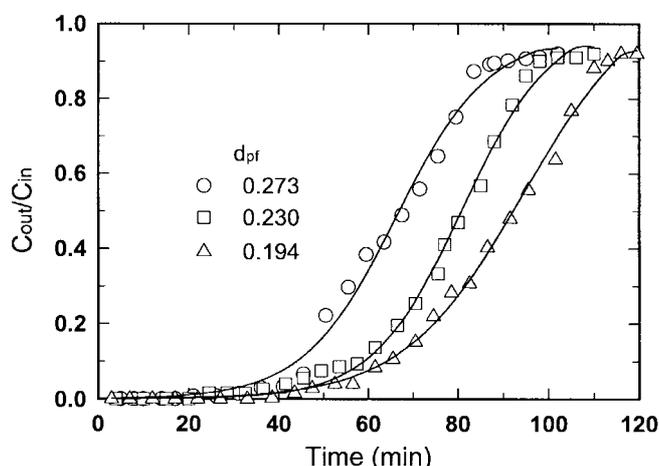


Fig. 8. The effect of flotsam particle size with jetsam rich system on H₂S removal ($L/D=1$, $C_{in}=5,000$ ppm, $d_{pf}=0.505$ mm, 600 °C).

CONCLUSIONS

Conclusions concerning the removal characteristics of H₂S from simulated gas with the natural manganese ore in a batch fluidized bed reactor are:

1. The NMO has strong mechanical strength and good H₂S removal ability in a fluidized bed reactor at temperature of 400-700 °C, which corresponds to typical gas inlet temperature to the second turbine in IGCC process.
2. The sorption capacity of H₂S increased with increasing temperature and aspect ratio, and the breakthrough time decreased as superficial gas velocity increased.
3. The slope of the breakthrough curve changes in the binary particle system with different size, which indicates that hydrodynamic characteristics of the binary particle system affect the adsorption of H₂S. And desulfurization occurred in the whole bed.

NOMENCLATURE

- A : the area above the breakthrough curve [sec]
 C_{in} : concentration of H₂S inlet gas stream [mol/m³]
 C_{out} : concentration of H₂S inlet gas stream [mol/m³]
 d_p : mean particle diameter [mm]
 d_{pf} : mean diameter of flotsam particle [mm]
 d_{pj} : mean diameter of jetsam particle [mm]
 L/D : aspect ratio [-]
 M_{w,H_2S} : molecular weight of H₂S
 Q : volumetric flow rate [m³/sec]
 S : sorption capacity [mg H₂S/g NMO]
 U_{mf} : minimum fluidization velocity [m/sec]
 U_0 : superficial gas velocity [m/sec]
 W : weight of sorbent [g]
 X_j : mixing fraction of jetsam particle in a binary particle system [-]

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