# EFFECTS OF HCI ON THE PERFORMANCE OF Mn-BASED SORBENTS AT HIGH TEMPERATURE H<sub>2</sub>S REMOVAL PROCESS

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Abstract: The reaction between Mn-based sorbent and hydrogen sulfide was studied in the presence of coal derived fuel gases. The Mn-based sorbents were prepared using combinations of a MnCO<sub>3</sub>, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and bentonite. The mechanical strength of the Mn-based sorbent was highly sensitive to the induration temperature. The sulfidation of Mn-based sorbent was examined in a packed-bed reactor at temperatures ranging from 500 to 750°C, using simulated coal gas containing 1% of H<sub>2</sub>S and HCl concentrations of 0, 630, and 1260 ppmv. Some agglomerations of the particle were observed in the spent sorbents, but did not show any detectable difference between the morphologies of the fresh, sulfided, and regenerated sorbents. In this experimental study, all the HCl concentrations revealed no harmful effects on the capability of the Mn-based sorbent to remove H<sub>2</sub>S from the simulated fuel gas. The presence of the HCl in the simulated fuel gas to some extent enhanced the desulfurization efficiency under the sulfidation conditions employed in this study.

Key Words: Fuel gas, Hydrogen chloride, Hydrogen sulfide, Mn-based sorbent

# INTRODUCTION

Among the advanced power generation technologies utilizing coal, the integrated gasification combined cycle (IGCC) system offers increased efficiency and the greatest ability to meet the stringent environmental emission limits. This technology features complete conversion of coal to fuel gas followed by gas cleaning and a combined cycle gas turbine/steam system for power generation. In this system, particulate matter and gaseous species, mainly H<sub>2</sub>S, must be purified from coal-derived fuel gas before being

oxidized in the IGCC combustion turbine. To maximize the thermal efficiency for the overall conversion of coal to electricity, this process requires that the sulfur species must be removed at high temperature.<sup>1)</sup>

One of the crucial factors for the successful application of the high temperature desulfurization is the development of sorbents which can effectively remove sulfur compounds from fuel gases in the temperature range  $600 \sim 800^{\circ}$ C. To eliminate some of the disadvantages associated with single metal oxides, recent research has shifted from pure metal oxides to mixed metal oxides. Among the mixed metal oxides, recent high temperature desulfurization research has concentrated on zinc-based sorbents such as zinc ferrite (ZnFe<sub>2</sub>O<sub>4</sub>, mixed ZnO-Fe<sub>2</sub>O<sub>3</sub>) and zinc

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titanate(ZnO<sub>x</sub>TiO<sub>2</sub>, mixed ZnO-TiO<sub>2</sub>) because of the highly favorable thermodynamics of ZnO-H<sub>2</sub>S reaction. In multicycle tests, however, zinc ferrite shows a progressive decay of sulfidation reactivity<sup>2</sup>, loss of sorbent efficiency<sup>3</sup>, and degradation of the mechanical properties, especially in fluidized-bed reactor.<sup>4</sup> When zinc-based sorbents are used in a highly reductive atmosphere, the mixed metal oxides are reduced either into their metallic state, or to form metal carbides, by which their applications are limited. This influences the mechanical strength and the sulfur uptake capacity of the sorbents.

To overcome such problems of zinc-based sorbents, several metal oxide-based sorbents that have been investigated include oxides of iron (Fe), copper (Cu), manganese (Mn), cerium (Ce), and tin (Sn).<sup>5)</sup> Among the sorbents investigated as potentially suitable alternatives, Mn-based sorbents have received considerable attention. Manganese(II) oxide, the stable phase under the reducing atmosphere of coal gas, does not show sulfidation to an extent as much as copper oxide. However, kinetic studies have shown that the intrinsic sulfidation rate of Mn-based sorbent is approximately one order of magnitude greater than those of CaO and ZnO, and two orders of magnitude higher than that of V<sub>2</sub>O<sub>3</sub>. 6,7) Mn-based sorbent also showed desulfurization potential in the temperature range of 600~700°C where the other metal oxides currently known to be reactive with H2S are unsatisfactory.<sup>8)</sup> In 1993, Hepworth et al.<sup>9)</sup> evaluated the behavior of single and mixed-metal oxide sorbents (iron, nickel, calcium, copper, sodium, zinc, and manganese) for removing sulfur from hot fuel gases, based on thermodynamic considerations. They concluded manganese oxide as a prime candidate sorbent capable of being utilized under a wide temperature range.

During the gasification of coal the chlorine is converted to hydrogen chloride (HCl) in the coal gas product.<sup>10)</sup> The HCl must be removed to protect power generation equipment such as gas turbines, and to minimize deterioration of desul-

furization sorbents. The concentration of HCl in a coal gas stream is dependent on the chlorine content of the coal, the gasification temperature, and the type of gasifier, but it has not been estimated precisely. Recently, the concentration of HCl vapors was found to be about 300 ppmv in the gas stream from a fixed-bed gasifier using a coal containing 0.24 wt% Cl. Baker and Perkins noted that the concentration of HCl in gasified coal gas is likely to be about five times greater than that in coal-fired flue gas because of the lower gas volumes of the coal gas stream.

Gangwal et al. 13) pointed out that the presence of HCl in the feed gas significantly decreased the H<sub>2</sub>S absorbing capacity of the zinc ferrite sorbent after the second regeneration cycle. In 1991, Jain et al. 14) found that the presence of HCl in syngas had little deleterious short-term effect on the desulfurization performance of zinc ferrite and zinc titanate sorbents. But, recently, Gupta and O'Brien<sup>10)</sup> studied the effect of HCl vapors on the zinc titanate sorbent in a bench scale atmospheric fluidized-bed reactor at temperatures ranging from 538 to 750°C, concluding that the presence of HCl vapor in simulated fuel gas had no harmful effect on the performance of the zinc titanate sorbent at temperatures below 550°C. In fact, the results indicate that the presence of the HCl actually enhances the H<sub>2</sub>S removal capability of the sorbent.10)

In this study, we report on the studies of sulfidation/regeneration processes and physico-chemical properties of Mn-based sorbents, including the effect of HCl vapors on the H<sub>2</sub>S absorption of Mn-based sorbents. The objective of this study was to evaluate the performance of Mn-based sorbents, to identify possible deleterious changes in the sorbent caused by the HCl vapors, and to investigate the behavior of the chloride species in a packed bed reactor.

## **EXPERIMENTAL**

Sorbent Preparation and Characterization

Mn-based sorbents were prepared combinations of a MnCO<sub>3</sub>, TiO<sub>2</sub> (substrate), Fe<sub>2</sub>O<sub>3</sub>, and bentonite (inorganic binder), based on desired compositions determined on a weight percent basis. Briefly, the preparation of Mn-based sorbents was as follows: after each component is mixed in the desired weight ratio, an appropriate amount of deionized water is added into a mixed powder under continuous stirring at room temperature. The final mixtures were dried in a drying oven at 110°C for 24 hrs and then calcined in a muffle furnace at 400°C for 5 hrs, followed by induration (2 hrs) at 950 ~1,100°C. After induration, the solid was crushed and sieved to the desired size (-20 to +30 mesh).

The fresh, sulfided, and regenerated sorbents were characterized by several analytical techniques. To study the chemical compositions and the distribution of the elements in the sorbents, a scanning electron microscope (SEM) JSM-5600 coupled to a Si/Li detector Kevex and a Sun SparcStation 5 for energy dispersive X-ray (EDX) analysis were used. X-ray diffraction (XRD) test for the identification of crystalline phases in the mixed oxide sorbents was performed in a D/MAX 2200 + Ultima (Japan) instrument using a Ni-filtered CuKa radiation. Also, the attrition resistance of the developed sorbent was determined in accordance with the ASTM D5757-95 method. 15)

## Suifidation/Regeneration Test

The cyclic desulfurization tests were conducted in a bench-scale reactor designed for operation up to 1,000°C. The schematic diagram of this bench-scale experimental system is shown in Fig. 1. The reactor consists of a quartz tube of 10 mm i.d. and 100 cm length, which was mounted vertically inside an electric furnace equipped with a temperature controller. The preheat zone was maintained about at 200°C. As shown in Fig. 1, the dry sulfidation and regeneration gases were introduced into the reactor from a cylinder. And then, the HCl was supplied to the reactor from a dilute HCl

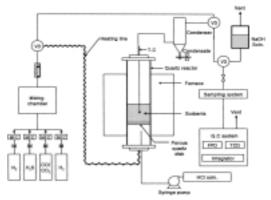


Figure 1. Schematic diagram of the packed-bed experimental apparatus.

solution, metered by a syringe pump. A porous quartz plate at the middle section of the reactor bed was used as the distributor for the simulated HCl containing coal gas. The sorbents bed, approximately 4 cm in height, consisted of 425~ 850  $\mu$  m particles supported on a fritted quartz. The reaction temperature was monitored using a K-type thermocouple positioned above the sorbent bed.

The product gas was passed through condenser to condense all the water and HCl vapors. The outlet and inlet fuel gases from and to the reactor were analyzed by gas chromatography using a thermal conductivity detector (TCD) for SO<sub>2</sub> and a flame photometric detector (FPD) for H<sub>2</sub>S, respectively. The chloride content of spent sorbent samples was measured by leaching the sample in deionized water

Typical experiments consisted of the following steps. First, 4 g of the sorbent(particle size =  $425 \sim 850 \mu \text{ m}$ ) was charged to the reactor, and then the reactor was heated to the desired operating temperature with a continuous flow of N<sub>2</sub> through the sorbent bed. All the experiments were carried out at nearly atmospheric pressure.

For sulfidation experiments, fresh sorbent was exposed to a simulated fuel gas containing H<sub>2</sub> (20%), H<sub>2</sub>O (20%), H<sub>2</sub>S (1%), and N<sub>2</sub> balance at a constant temperature in the range of 500~700°C. The feed gas rate of 300 cm<sup>3</sup>/min (STP) was typically used. The sulfidation cycle step continued until the H2S concentration in the

Parameters	Sulfidation	Regeneration		
Sorbent mass	4 g	4 g		
Temperature	500~700°C	800°C		
Particle size	$425 \sim 850 \ \mu \text{m}$	$425 \sim 850 \ \mu m$		
Gas flow rate	300 cm <sup>3</sup> /min (STP)	200 cm <sup>3</sup> /min (STP)		
Pressure	1 atm	1 atm		
Gas compositions	H <sub>2</sub> 20% - H <sub>2</sub> O 20% - H <sub>2</sub> S 1% - N <sub>2</sub> balance	90% N <sub>2</sub> - 10% O <sub>2</sub>		
HCl concentration	0, 630, 1,260 ppmv			

Table 1. Conditions of fixed-bed sulfidation and regeneration experiments

reactor exit gas reached 500 ppmv, which was arbitrarily as the breakthrough value. Following the sulfidation, the reactor was changed to the regeneration step and heated in a nitrogen atmosphere to the desired regeneration temperature. Once the desired temperature was attained, the flow of regeneration gas started. The typical regeneration gas contained 90 mol% N2 and 10 mol% O2 at temperature 800°C. This regeneration reaction ended when the outlet SO<sub>2</sub> concentration dropped below 500 ppmv. The experimental conditions for sulfidation and regeneration are summarized in Table 1.

At both ends of the sulfidation and the regeneration step, samples of the sorbent particles were withdrawn and analyzed for chlorine content. The condensate and other gas stream scrubbing solutions were collected to determine the chlorine-ion material balance during both the sulfidation and regeneration steps. In this study, all the chloride concentration were analyzed by ion chromatography.16)

## **RESULTS AND DISCUSSIONS**

#### XRD and Attrition Resistance

XRD analysis of a fresh Mn-based sorbent sample indicated the presence of three major Pseudobrookite (Fe<sub>2</sub>TiO<sub>5</sub>), (FeTiO<sub>3</sub>), and Bixbyite (Mn<sub>2</sub>O<sub>3</sub>), as shown in Fig. 2(A). Fig. 2(B) is a diffraction pattern of a sulfided sample from the simulated fuel gas inlet section, where the sorbent underwent sulfidation to the highest extent prior to breakthrough. The presence of MnS and FeTiO3 as major phases is identified in the reacted sample. But, no FeS was detected for the sulfided sorbents, indicating that the iron-based materials were not used in

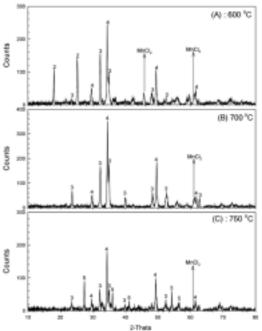


Figure 2. XRD patterns for Mn-based sorbent samples: (A) fresh, (B) sulfided at 600°C, (C) regenerated at 800°C. Phases Mn<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>TiO<sub>5</sub>, FeTiO<sub>3</sub>, MnS, and  $TiO_2$  are indicated by 1, 2, 3, 4, and 5, respectively.

the desulfurization process and/or iron was in an amorphous structure. This corresponded to other previous results.<sup>17)</sup> The pattern of the same sulfided sample following oxidative regeneration is shown in Fig. 2(C), where in addition to Mn<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>TiO<sub>5</sub>, and FeTiO<sub>3</sub> as major phases the presence of TiO2 as a minor phase is noticed.

Fig. 3 shows the XRD patterns of sulfided Mn-based sorbent at various sulfidation temperatures with 1,260 ppmv HCl. After sulfidation, the diffraction peaks of MnS and FeTiO<sub>3</sub> as major phases are identified and the MnCl<sub>2</sub> as a

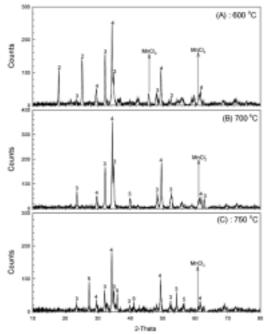


Figure 3. XRD patterns for sulfided Mn-based sorbent samples with sulfidation temperature: (A) 600°C, (B) 700°C, (C) 750°C. Phases Fe<sub>2</sub>TiO<sub>5</sub>, FeTiO<sub>3</sub>, MnS, and TiO2 are indicated by 2, 3, 4, and 5, respectively.

minor phase is indicated in all samples. As shown in Fig. 3(B and C), the diffraction peaks assigned to FeTiO3 and TiO2 were observed in the sample. It is considered that FeTiO3 and TiO<sub>2</sub> are formed by the decomposition of Fe<sub>2</sub>TiO<sub>5</sub>. The peak intensity from FeTiO<sub>3</sub> and TiO<sub>2</sub> gradually increased and that from Fe<sub>2</sub>TiO<sub>5</sub> gradually disappeared with an increase in the sulfidation temperature. Also, the intensity of MnS peak decreased after sulfided at 750°C. The decrease of peak intensity suggests that some manganese sites in MnS (mostly in the surface) were reduced during the sulfidation. From these results, it is concluded that the decomposition rate of Fe<sub>2</sub>TiO<sub>5</sub> increases as the sulfidation temperature increases.

Attrition tester was capable of providing a meaningful assessment of the mechanical properties of regenerable sorbents. The percent attrition loss after 5 hrs is defined as the Air Jet Index (AJR), and is calculated from the elu-

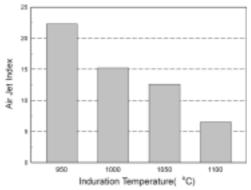


Figure 4. Attrition resistances of the fresh sorbent against induration temperature.

triated fine particles. The elutriation of sorbents significantly affected the sulfur uptake capacity. Consequently, as the sorbent elutriation increased, the sulfur uptake capacity of sorbent decreased, presumably due to the losses of active sites in the sorbent. The results obtained in the attrition unit with the Mn-based sorbents are shown in Fig. 4. A comparison between the results obtained from different induration temperatures indicates that the sorbents indurated at 1,100°C have attrition losses that are about 3.4 times less than that of the sorbent indurated at 950°C and about 1.9 times less than the sorbent indurated at 1,050°C. This suggests that the mechanical strength of the Mn-based sorbent highly depends on the induration temperature.

#### Sulfidations

Fig. 5 shows scanning electron micrographs of the various solid sorbents indurated at 1.100°C. Parts A and B of Fig. 5 show the scanning electron micrographs of the fresh and sulfided sorbents. The sulfidation was performed with 1%  $H_2S$  - 20%  $H_2$  - 20%  $H_2O$  -  $N_2$  balance gas mixtures at 700°C and SV=12,000 hr<sup>-1</sup>. SEM pictures for the regenerated sorbents are shown in Parts C and D of Fig. 5 for the 1-cycle and 8-cycle regenerated, respectively. Observation of the sorbent morphology indicates some additional agglomeration of the particle/ grains in the reacted sorbents as compared to the fresh sorbent, but basically no detectable differences in the morphologies of the fresh, sulfided, and

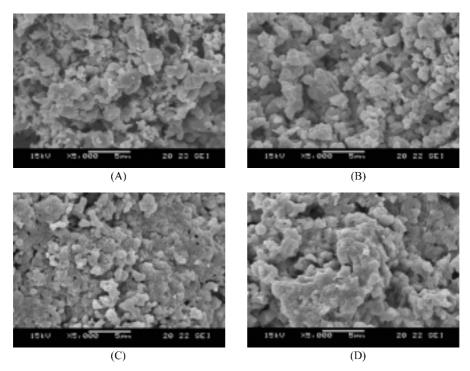


Figure 5. SEM photographs of fresh, sulfided, and regenerated sorbents indurated at 1,100°C. (A) fresh, (B) sulfided, (C) 1-cycle regenerated, and (D) 8-cycle regenerated.

regenerated sorbents were observed. However, as shown in Fig 5(D), in the SEM photograph of the 8-cycle regenerated sample, some agglomerations by sintering were observed.

For the Mn-based sorbent, the sulfidation reaction may be represented by the following equation.

$$MnO(s) + H_2S(g) \leftrightarrow MnS(s) + H_2O(g)$$
 (1)

The thermodynamic equilibrium ratio of the equation (1) was reported by Ben-Slimane et al.(1995) to be represented by the relation.<sup>18)</sup>

$$Log K = 0.204 + 2,557/T$$
 (2)

, where  $K=P_{H2O}/P_{H2S}$  and T is the absolute (Kelvin) temperature.

The processes that determine the global rate of gas-solid reaction(Eq. 1) are numerous and complex. In spite of the overall complexity, it is possible to describe the global rate in terms of simple mathematical methods. According to the unreacted core model, the time-conversion(rate equations) relationship for an isothermal reaction whose global rate is controlled by a combination of mass transfer and product layer diffusion resistances. 19)

Arrhenius suggested that the temperature dependence of the intrinsic rate constants, k(T), could be correlated by an equation

$$k(T) = k_0 \times \exp(-E/RT)$$
 (3)

In the above equation, ko is the frequency factor, E is the activation energy, R is the gas constant. Since the intrinsic sulfidation rates are dependent on temperature, the effect of reaction temperature on the sorbent capacity can be seen by comparing the initial reaction rate at each temperature.<sup>20)</sup>

Fig. 6 compares the H<sub>2</sub>S breakthrough curves of the Mn-based sorbent at the four different temperatures (500, 600, 650, and 700°C). The

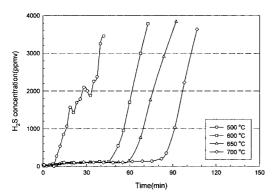


Figure 6. H<sub>2</sub>S breakthrough curves at various temperatures in simulated gas containing 1,260 ppmv HCl.

experiments were performed using 425~850 µm particles, and 1% H<sub>2</sub>S - 20% H<sub>2</sub> - 20% H<sub>2</sub>O - 1260 ppmv HCl - N<sub>2</sub> balance gas mixtures. The prebreakthrough H<sub>2</sub>S concentration at reactor exit stream was consistently below 80 ppmv. As expected from Eq. (2), the reaction temperature has strong effect on the equilibrium concentration of the sorbent. At low temperature(500°C), the drastic dearease of conversion begins to occur after 10 minutes. Thus it is considered that this reaction temperature is so low that chemical reaction or chemisorption could not occur.<sup>17)</sup> Fig. 6 clearly describes that the rate of sulfidation reaction is significantly faster at 700°C than at 500°C. As expected from Eq. (3), these results suggest that global kinetics is controlled, at least in part, by an intrinsic reaction rate between the Mn-based sorbent and H2S. This corresponded to other previous results.6,20)

Fig. 7 shows the sulfur uptakes as a function of HCl concentration at breakthrough time. Sulfur uptakes were 5.69, 6.03, and 6.29 g per 100 g of sorbent at 650°C, and the uptakes at 750°C were 6.63, 8.02, and 8.69 g per 100 g of sorbent, respectively, for the three sets of HCl concentration (0, 630, 1260 ppmv). As seen in this figure, the sulfur uptake of the sorbent is a little enhanced by the presence of the HCl in the coal gas. Possible reasons for these phenomena are as follows.

First, fixed-bed experiments with simulated

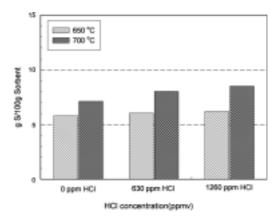


Figure 7. Sulfur uptake capacities of the sorbents up to breakthrough time in the fixed bed reactor with HCl concentration.

coal gas containing both HCl and H2S, H2S and HCl can react with MnO according to the following reactions. The  $\Delta G$  values can be calculated from the thermodynamic data at 875 K.<sup>18,21)</sup>

MnO + H<sub>2</sub>S 
$$\leftrightarrow$$
 MnS + H<sub>2</sub>O ;  $\Delta$ Gr = -52kJ/mol (1)

$$MnO + 2HC1 \leftrightarrow MnCl_2 + H_2O$$
;  $\Delta Gr = -46kJ/mol$  (4)

Because MnCl<sub>2</sub>(melting point of 650°C) in the 650~750°C temperature range is liquid, having vapor pressure, it will tend to escape a little from the sorbent[10]. Manganese chloride (MnCl<sub>2</sub>), however, has a boiling point of 1,231°C.<sup>22)</sup> The higher boiling point of MnCl<sub>2</sub> makes it much less susceptible to volatilization and loss from the sorbent.<sup>7)</sup> Because the content of H<sub>2</sub>S is higher in the fuel gas stream, the MnCl2 formed by reaction (4) reacts with H<sub>2</sub>S according to the following reaction.<sup>21)</sup>

$$MnCl_2 + H_2S \leftrightarrow MnS + 2HCl$$
;  $K_{875K} = 1.4 \times 10^{-6}$  (5)

The equilibrium constant(K) for reaction (5)increases in proportion to the rise in temperature. So, the reaction of H2S with MnCl2 at 700°C will be more favored as compared to the reaction at 600°C. MnCl<sub>2</sub> exists as a liquid phase in the temperature range between 650 to 750°C, the reaction of MnCl<sub>2</sub> with H<sub>2</sub>S is easier

than the solid phase MnO. Therefore, higher levels of HCl in the coal gas lead to higher MnCl<sub>2</sub> concentrations and hence to more rapid removal of the H<sub>2</sub>S via reaction (5). All of these reactions are more complicated because water is formed during the sulfidation. Abbasian et al.<sup>23)</sup> suggested that the enhancement of sulfidation rate (Ca-based sorbent) in the presence of HCl is caused by some surface phenomena, and that the mechanism of rate enhancement is associated with the presence of steam.

Second, an explanation for the enhancement in the breakthrough capacity in the presence of HCl may be that the presence of chloride ions affects the rate of nucleation of products or the growth of the crystallites<sup>24)</sup>, in such a way that the product layer is much more dispersed.<sup>20)</sup> Thus, easy contact to the reactant solid is maintained throughout the reaction, which improved the breakthrough capacity in the presence of HCl. However, the exact mechanism of HCl effect on sorbent capacity is not clear yet.

As can be seen in table 2, at lower temperatures, the high chloride retention by the sorbent was observed and the molten layer of MnCl<sub>2</sub> will react with H<sub>2</sub>S to form MnS and HCl via reaction (5). At higher temperature, however, a little portion of MnCl2 will leave the sorbent because of its vapor pressure, but it is not significant. This mechanism explains that the chloride content in the sorbent decreases with

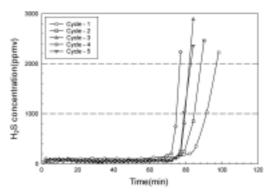


Figure 8. H<sub>2</sub>S breakthrough curves of Mn-based sorbent at 700°C and 1260 ppmv HCl.

increasing reaction temperature.

Fig. 8 shows H<sub>2</sub>S breakthrough curves of Mn-based sorbent at 700°C and 1260 ppmv HCl. The breakthrough sulfur capacity during the first cycle was slightly higher than the capacity values produced during the following four cycles. As shown in Fig. 8, the prebreakthrough time for the five sulfidation tests was from about 70 minutes to 90 minutes. Also, it should be noted that the prebreakthrough H2S concentration was consistently about 80 ppmv. These results indicate that the presence of HCl as much as 1,260 ppmv in the simulated coal gas does not appear to have significant deleterious effect on the chemical reactivity of the Mn-based sorbent as far as the sulfidation temperature is below 700°C.

Fig. 9 shows the regeneration curves and temperature profiles for Mn-based sorbent rege-

Table 2. Sorbent compositions and chlorine distribution for the Mn-based sorbents

1 \ /	HCl con. of feed (ppmv)	sorbent compositions(wt%)			(wt%)	Cl distribution(% of feed)			
		Mn	Fe	Ti	S	sorbent	condenser	NaOH soln.	- remarks
500/-	1,260	25.25	11.00	11.25	2.8	16.2	42.6	15.1	
600/-	1,260	25.83	11.32	11.57	9.60	10.5	50.2	10.4	
600/800	1,260	24.45	11.46	10.26	0.20	-	-	-	1 cycle
650/-	1,260	-	-	-	-	5.2	60.8	11.2	
650/800	1,260	24.51	12.47	10.00	0.34	-	-	-	8 cycle
700/-	1,260	25.35	12.55	12.54	15.00	4.2	60.6	8.4	
700/800	1,260	23.76	11.85	9.49	0.71	-	-	-	1 cycle
750/-	1,260	23.16	12.61	10.14	14.05	4.4	56.2	10.4	
750/800	1,260	23.62	12.72	9.75	0.45	-	-	-	8 cycle
-	-	25.23	11.00	11.24	0	-	-	-	fresh sorbent

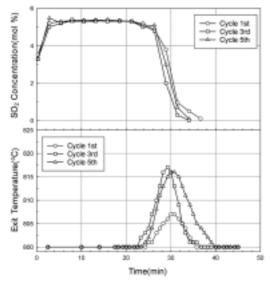


Figure 9. Regeneration curves for the Mn-based sorbent. Regeneration in  $10\%~O_2$  and  $90\%~N_2$  with a flow rate of  $200~cm^3/min$  at  $800^{\circ}C$ .

nerated in 10 mol%  $O_2$  and 90 mol%  $N_2$  at 800°C. The sorbent was regenerated completely giving the exit  $SO_2$  concentrations as high as 5.1 mol% and an regeneration time of 32 minutes. The average regeneration times were average over five cycles. Fig. 9 (the lower part) shows a temperature profile during regeneration. The regeneration was started at 800°C, and a temperature rise of  $7 \sim 17^{\circ}$ C was observed due to the exothermic character of the regeneration reaction. As can be seen in Table 2, some sulfate was formed, but it is not significant. The regeneration time is based on the time to achieve an exit  $SO_2$  concentration of less than 10% of the highest concentration achieved.

Table 2 shows the sorbent compositions and the percentage of chloride distribution by the sorbent. As expected, the percentage of CI retention decreased with an increase in temperature. When sorbent was exposed in simulated fuel gas containing 1,260 ppmv HCl, the Mn-based sorbent contained 10.5%, 5.2%, 4.2%, and 4.4% chloride at the sulfidation temperatures of 600, 650, 700, and 750°C, respectively. The sulfur content of the sulfided sorbent was increased with an increase in temperature, which is con-

sistent with the enhancement of sorbent sulfur capacity. Also, the sulfur content of the regenerated sorbent  $(0.2 \sim 0.71 \text{ }\%)$  was significantly lower than that of the sulfided sample, which means that the sorbent was easily regenerated.

## **CONCLUTIONS**

Mn-based sorbents were synthesized from calcination-induration of mixed precursors. The main crystalline phases of a fresh Mn-based sorbent were Fe<sub>2</sub>TiO<sub>5</sub>, FeTiO<sub>3</sub>, and Mn<sub>2</sub>O<sub>3</sub>. This sorbents were tested for both the sulfidation and regeneration experiments in a fixed-bed reactor.

Mechanical strength of the Mn-based sorbent was highly sensitive to the induration temperature. The Mn-based sorbents indurated at 1,100 °C have attrition losses that are about 3.4 times less than that of the sorbent indurated at 950 °C. This suggests that induration at the higher temperature gave rise to a sorbent of higher mechanical strength.

After 5 cycles sulfidation/regeneration, some agglomeration of the particle/grains was observed in the spent sorbents, but basically there were no detectable differences in the morphologies of the fresh, sulfided, and regenerated sorbents.

The breakthrough capacity of the Mn-based sorbent becomes higher when the sulfidation temperature increases from 500 to 750°C. Also, the HCl content in the simulated fuel gas did not have any deleterious effects on the Mn-based sorbents capability, its regenerability, or any other structural properties. The presence of the HCl to some extent enhanced the desulfurization capacity.

Sulfided Mn-based sorbents are fully regenerated under the regeneration conditions employed in this study. Regeneration in 10 mol%  $O_2$  and 90 mol%  $N_2$  produced  $SO_2$  concentration as high as 5.1% and a temperature rise of  $7\!\sim\!17^\circ\text{C}$  was observed.

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## REFERENCES

- 1. Grindley, T. and Steinfeld, G., Development and Testing of Regenerable Hot Coal-Gas Desulfurization Sorbent, Report, DOE/METC /16545-1125, DOE/METC, Morgantown, WV, (1981).
- 2. Sa, L. N., Foght, G. D., Ranade, P. V., and Harrison, D. P., "High-temperature desulfurization using zinc ferrite solid structural changes," Chem. Eng. Sci., 44(20), 215~224 (1989).
- 3. Ayala, R. E. and Marsh, D. W., "Characterization and Long-Range Reactivity of Zinc Ferrite in High-Temperature Desulfurization Processes," Ind. Eng. Chem. Res., 30, 55~ 60 (1991).
- 4. Gupta, R., Gangwal, S. K. and Jain, S. C., "Development of Zinc Ferrite Sorbents for Desulfurization of Hot Coal Gas in a Fluid-Bed Reactor," Energy Fuels, 6(1), 21~27 (1992).
- 5. Gangwal, S. K., "Sulfur Removal from Gas Streams at High Temperature," in Proceedings of the 3rd International Symposium and Exhibition: High-Temperature Gas Cleaning, University of Karlsruhe, Karlsruhe, Germany, pp. 489 (1996).
- 6. Westmoreland, P. R., Gibson, J. B. and Harrison, D. P., "Comparative Kinetics of High-temperature reaction between H<sub>2</sub>S and selected Metal Oxides," Environ. Sci. Technol., 11(5), 488~491 (1977).
- 7. Ben-Slimane, R. and Hepworth, M. T., "Desulfurization of Hot Coal-Derived Fuel Gases with Manganese-Based Regenerable Sorbents. 1. Loading Tests," Energy Fuels, **8**(6), 1175~1183 (1994).
- 8. Westmoreland, P. R. and Harrison, D. P., "Evaluation of Candidate solids for High-Temperature Desulfurization of Low-Btu

- Gases," Environ. Sci. Technol., 10(6), 659~ 661 (1976).
- 9. Hepworth, M. T., Ben-Slimane, R. and Zhong, S., "Thermodynamic Comparison of Several Sorbent System for Hot Coal-Derived Fuel-Gas Desulfurization," Energy Fuels, 7(6),  $602 \sim 607$  (1993).
- 10. Gupta, R. P. and O'Brien, W. S., "Desulfurization of Hot Syngas Containing Hydrogen Chloride Vapors Using Zinc Titanate Sorbents," Ind. Eng. Chem. Res., 39(3), 610~619 (2000).
- 11. Gal, E., Najewicz, A., Furman, A. H., Ayala, R. and Feitelberg, A., "Integrated Operation of a Pressurized Gasifier, Hot Gas Desulfurization System and Turbine Simulator," in Proceedings of the Coal-Fired Power Systems 94 Advances in IGCC and PFBC Review Meeting, Report No. DOE/ METC-94/1008, Morgantown Energy Technology Center, U.S. Department of Energy, WV, (1994).
- 12. Baker, W. T. and Perkins, R. A., "The Effect of Coal Bound Chlorine on Corrosion of Coal Gasification Plant," in Proceedings of International Conference on Chlorine in Coal, J. Stringer and D.D.Banerjee, Eds., Elsevier, pp. 92 (1991).
- 13. Gangwal, S. K., Harkins, S. M., Stognet, J. M., Woods, M. C. and Rogers, T. N., "Bench-Scale Testing Of Novel High-Temperature Desulfurization Sorbents," Report No. DOE/ MC/23126-2662 (DE89000935), Morgantown Energy Technology Center, U.S. Department of Energy, Morgantown, WV, (1988).
- 14. Jain, S. C., Grindley, T. and Goldsmith, H., "Effects of Chlorine on Hot-Gas Desulfurization Sorbents," in Proceedings of International Conference In Coal, Stringer, J., Nanerjee, D.D., Eds, Elservier Science, New York, USA, pp. 85 (1991).
- 15. Determination of Attrition and Abrasion of Powdered Catalysts by Air Jets. In Annual of ASTM Standards, Petroleum Products and Lubricants (III); ASTM: Philadelphia, USA, (1985).

- 16. James P. L. Jr., Methods of Air Sampling and Analysis, 3rd ed., LEWIS PUBLI-SHERS Inc, Michigan, pp. 312~315 (1988).
- 17. Lee, Y. S., Kim, H, T. and Yoo, K. O., "Effect of Ferric Oxide on the High-Temperature Removal of Hydrogen Sulfide over ZnO-Fe<sub>2</sub>O<sub>3</sub> Mixed Metal Oxide Sorbent," Ind. Eng. Chem. Res., 34(4), 1181~ 1188 (1995).
- 18. Ben-Slimane, R. and Hepworth, M. T., "Desulfurization of Hot Coal-Derived Fuel Gases with Manganese-Based Regenerable Sorbrnts. 3. Fixed-Bed Testing," Energy Fuels, 9(2),  $372 \sim 378 (1995).$
- 19. Szekely, J., Evans, J. W. and Sohn, H. T., Gas-Solid Reactions, Academic Press, New York, USA, pp. 86 (1976)
- 20. Lew, P., Jothimurugesan, K. and Flytzani-Stephanopouios, M., "High Temperature H2S Removal from Fuel Gases by Regenerable

- Zinc Oxide Titanium Dioxide Sorbents," Ind. Eng. Chem. Res., 28(5), 535~541 (1989).
- 21. Waker, J. P., Gerritsen, A. W. and Moulijn, J. A., "High Temperature H2S and COS Removal with MnO and FeO on γ (-Al<sub>2</sub>O<sub>3</sub> Acceptors," Ind. Eng. Chem. Res., 32(1),  $139 \sim 149 (1993)$ .
- 22. Handbook of Chemistry and Physics, 67th ed., CRC Press Inc., Boca Raton, FL, (1986
- 23. Abbasian, J., Wangerow, J. R. and Hill, A. H., "Effect of HCl on Sulfidation of Calcium Oxide," Chem. Eng. Sci., 48(15),  $2689 \sim 2695$  (1993).
- 24. Houte, G.V., Rodrique, L., Gernet, M. and Delmon, P., "Kinetics of the Reaction of Calcium Sulfite and Calcium Carbonate with Sulfur Dioxide and Oxygen in the presence of Calcium Chloride," Environ. Sci. Technol., **15**(3), 327~332 (1981).