

## A STUDY OF SULFATE FORMATION DURING REGENERATION OF ZINC FERRITE SORBENTS

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### INTRODUCTION

Zinc ferrite ( $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$ ) is a promising regenerable sorbent for the high temperature (800 - 925 K) removal of hydrogen sulfide from coal gas to be fed to molten carbonate fuel cells<sup>1</sup>. For the desulfurization process to be economically attractive, the spent sorbent needs to be regenerated and reused. During the coal gas desulfurization step the zinc and iron oxides are converted into the corresponding sulfides. Regeneration back to the oxides is accomplished by the use of oxidizing gases such as oxygen (or air) and steam at elevated temperatures. Ideally, the regeneration should be carried out at sufficiently high temperatures to eliminate or minimize side reactions such as formation of sulfates. However, severe sintering may occur at such elevated temperatures leading to decreased sorbent desulfurization capacity. Thus, to minimize sintering it is necessary to regenerate at lower temperatures where a significant degree of sulfate formation can occur.

The presence of sulfates is detrimental to the subsequent coal gas desulfurization performance of the sorbent. It not only reduces the sulfur capacity of the sorbent, but also leads to the introduction of secondary contaminants, such as  $\text{SO}_2$ , into the hot coal gas stream. These sulfur species<sup>2</sup> are just as undesirable as  $\text{H}_2\text{S}$ . Hence for zinc ferrite to be useful as a hot coal gas desulfurization sorbent it is essential that during regeneration sulfate formation should be minimized. An experimental and theoretical study was undertaken to define conditions where sulfate formation would occur during regeneration of spent zinc ferrite sorbents.

### METHODS, APPARATUS AND PROCEDURES

Thermodynamic calculations were performed to define equilibrium conditions favorable for sulfate formation during regeneration and to predict the reaction products resulting from the interaction of zinc sulfate with hot coal gas. The regions of stabilities of oxides, sulfides and sulfates of both zinc and iron as functions of partial pressures of  $\text{O}_2$  and  $\text{SO}_2$  were determined. Gibbs energy minimization methods were used to calculate the equilibrium compositions of gases and solids under desulfurization and regeneration conditions. Fifty gaseous species and seventeen solid phases were included in these calculations.

The formation of zinc and iron oxides from corresponding sulfides results in a decrease of the mass of the specimen, whereas the formation of sulfates leads to an increase of the mass. Hence a thermogravimetric system incorporating a Cahn RG electrobalance and a programmable electronic temperature controller was used to monitor the mass of the specimen as the specimen was heated in a mixture of air and steam.

A laboratory-scale fixed-bed reactor system was used to determine the extent of sulfate formation as a function of process variables. The effluent gases from the reactor were analyzed for  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ , and residual  $\text{O}_2$  using gas chromatography. At the end of a reaction period the specimen was rapidly quenched to preserve its chemical composition that existed at the reaction temperature.

The zinc ferrite used in this study was manufactured by United Catalysts Inc. in the form of extruded pellets. For our experiments it was crushed and sieved to a particle size range of 300 - 500  $\mu\text{m}$ . To provide a uniform starting material for the regeneration experiments, the zinc ferrite sorbent was sulfided at 873 K using a simulated coal gas of the following composition: 15%  $\text{H}_2$ , 15%  $\text{CO}$ , 11%  $\text{CO}_2$ , 24%  $\text{H}_2\text{O}$ , 3%  $\text{H}_2\text{S}$ , 32%  $\text{N}_2$ . After sulfidation the sorbent had a composition (wt%) of 40.7% Zn, 24% Fe, and 35% S. The crystalline phases were  $\alpha$  and  $\beta$  ZnS and  $\text{Fe}_{0.88}\text{S}$  (pyrrhotite).

## RESULTS AND DISCUSSION

### Equilibrium Calculations

The equilibrium conditions necessary for the various solid phases to be stable in the Zn-Fe-O-S system can be conveniently expressed in the form of a stability diagram. A calculated stability diagram for a temperature of 873 K is shown in Figure 1. It illustrates that the oxides are stable at high partial pressures of  $O_2$  and low partial pressures of  $SO_2$ . For sulfates to be stable partial pressures of both  $O_2$  and  $SO_2$  need to be high. The stability diagrams for other temperatures indicated that as the temperature is increased higher partial pressures of  $O_2$  and  $SO_2$  are necessary for the stabilization of zinc and iron sulfates.

The stability diagram can be used to predict the composition of solid phases under equilibrium regeneration conditions. For example, the dotted line in Figure 1 represents a locus of points of total pressure of 0.01 atm of a mixture of  $O_2$  and  $SO_2$  (corresponding to a feed gas of 5% air - 95% steam). Initially in a fully sulfided sorbent, the equilibrium solid phases will be  $Fe_{0.88}S$  and  $ZnS$  (upper left portion of the diagram). At the start of the regeneration the  $p(O_2)$  will be less than  $10^{-18}$  atm and  $p(SO_2)$  will be about 0.01 atm. As the regeneration proceeds  $p(O_2)$  will begin to increase (going from left to right on the abscissa). Initially  $Fe_{0.88}S$  will be converted to  $Fe_3O_4$ . As the  $p(O_2)$  increases above  $2 \times 10^{-16}$  atm both  $ZnS$  and  $Fe_3O_4$  will be oxidized to form zinc ferrite. With further increase in  $p(O_2)$  ( $> 6 \times 10^{-14}$  atm)  $ZnO \cdot 2ZnSO_4$  is formed. As  $p(O_2)$  approaches feedstock level  $ZnO \cdot 2ZnSO_4$  and  $Fe_2(SO_4)_3$  become the equilibrium phases. At the end of conversion of sulfides  $p(SO_2)$  decreases and the sulfates decompose to the oxides.

The equilibrium composition of the solid phases as a function of the extent of regeneration was also calculated using a Gibbs energy minimization method. In this calculation, 1 mole of  $ZnS \cdot 2.3 Fe_{0.88}S$  was equilibrated with different quantities of a regeneration gas (air-steam- $SO_2$  mixtures). The reaction extent was defined as unity when the quantity of oxygen present in the feed gas was sufficient for the stoichiometric conversion of sulfides to oxides ( $ZnO, Fe_2O_3$ ). An example of this calculation for the case when regeneration is carried out at 873 K using 90% air - 10%  $SO_2$  at 20 atm total pressure is shown in Figure 2.

These computations, which included a large number of chemical species in addition to  $O_2$  and  $SO_2$ , confirm the general sequence of chemical reactions inferred from the stability diagrams. Initially,  $Fe_{0.88}S$  is oxidized to  $Fe_3O_4$ . At the end of oxidation of this phase  $ZnFe_2O_4$  is formed by the oxidation of  $ZnS$  to  $ZnO$  and  $Fe_3O_4$  to  $Fe_2O_3$ . At greater than stoichiometric levels of the regeneration gas,  $FeSO_4$  and  $ZnO \cdot 2ZnSO_4$  are formed. Finally, when the regeneration is complete the sulfates have decomposed to the oxides.

### Thermogravimetric Experiments

The results of TGA experiments with different gas mixtures are shown in Figure 3. On heating from ambient to 625 K at 5 K/min the specimens gained mass. At higher temperatures the mass of the specimens decreased up to a temperature of about 650 K. Above 650 K, depending on the oxygen content of the feed gas the specimens either gained or lost mass. The second mass gain peak, when present, reached a maximum in a temperature range of 825 - 925 K. Above 925 K a decrease in mass was observed with all gas compositions.

The chemical reactions associated with the various mass changes were deduced from X-ray diffraction analyses of the solid remnant quenched from various temperatures. Table 1 shows these chemical reactions. The initial mass gain is due to the oxidation of  $Fe_{0.88}S$  to  $FeS_2$  and  $Fe_2O_3$ . At temperatures above 625 K,  $FeS_2$  is also oxidized to  $Fe_2O_3$  resulting in a mass loss. The observed mass increase above 650 K is due to the oxidation of  $ZnS$  to  $ZnSO_4$ . The extent of  $ZnSO_4$  formation is a function of the oxygen content of the feed gas. Higher amounts of sulfates are formed when  $p(O_2)$  is high. Above 925 K  $ZnSO_4$  decomposes to  $ZnO$  and any residual  $ZnS$  is also oxidized resulting in a mass loss.

To determine the role of iron oxides in the formation of  $ZnSO_4$ , TGA experiments were conducted with a sulfided  $ZnO$  sorbent ( $ZnS$ ). During heating of the  $ZnS$  in an

atmosphere of 50% air - 48% N<sub>2</sub> and 2% steam no mass change was observed below 925 K, but a mass loss was observed above this temperature. This indicates that ZnSO<sub>4</sub> formation is significantly reduced in the absence of Fe<sub>2</sub>O<sub>3</sub>. The presence of Fe<sub>2</sub>O<sub>3</sub> has been reported to accelerate the formation of ZnSO<sub>4</sub> by catalyzing the formation<sup>3,4</sup> of SO<sub>3</sub>.

#### Fixed Bed Reactor Experiments

In these experiments, about 2 g samples of sulfided zinc ferrite sorbents were regenerated isothermally using gas mixtures with various air-steam ratios. Gas chromatographic analysis of the reactor effluent gases indicated oxygen was completely consumed initially and during a major portion of the regeneration period. During regeneration with air - steam mixtures small amounts of H<sub>2</sub>S (0.2 vol%) and elemental sulfur were produced, but the major gaseous species was SO<sub>2</sub>. The formation of H<sub>2</sub>S and elemental sulfur is due to the reaction of iron sulfides with steam.

Table 2 lists the weight percentages of sulfides and sulfates of specimens regenerated for various periods of time. It indicates that the sulfide content of the specimen is progressively reduced as the duration of regeneration increases. In contrast, the amount of sulfate remaining in the sorbent initially increases, reaches a maximum when about 99% of the sulfide is converted and then decreases. The occurrence of such a maximum in sulfate content was predicted by the thermodynamic calculations.

Table 3 lists the weight percentages of sulfate remaining in the sorbents regenerated at various temperatures. The regeneration was carried out until the concentration of SO<sub>2</sub> in the reactor effluent decreased below 0.5 vol%. This condition occurred typically when the total amount of feed gas supplied was about 150% of that required for stoichiometric conversion of the sulfides to oxides. The results of these experiments (Table 3) indicate that sulfate formation is favored by lower temperatures and higher partial pressures of O<sub>2</sub>.

Other parameters in the regeneration process exhibit a minor influence on the extent of sulfate formation. Increasing the space velocity appeared to decrease the amount of sulfate formed. This may be due to either an increase in the surface temperature of the sorbent during the exothermic oxidation or to a decrease in the contact time between SO<sub>2</sub> and the sorbent. Particle size of the sorbent over the range 0.5 to 5 mm had no observable effect on the amount of sulfate remaining in the sorbents. Furthermore, replacing steam with nitrogen as a diluent in the regeneration feed gas had no effect on the residual sulfate level. However, the presence of SO<sub>2</sub>, even in the amount of 0.5 vol%, significantly increases sulfate formation below 975 K. Above 975 K, SO<sub>2</sub> in the feed gas had only a small effect on the amount of residual sulfate in the sorbent. Other conditions being equal, cycling between sulfidation and regeneration did not significantly change the amount of sulfate formed during regeneration. Finally, sulfided zinc oxide sorbents regenerated in air - steam mixtures contained a significantly lower amount of sulfate than zinc ferrite sorbents regenerated under similar conditions.

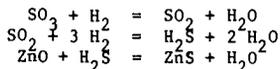
#### Behavior of Sulfates in Hot Coal Gas Atmosphere

The zinc sulfate present in the regenerated sorbent decomposes under the reducing conditions of hot coal gas releasing SO<sub>2</sub> and SO<sub>3</sub>. Figure 4 illustrates the concentration of SO<sub>2</sub> observed in the reactor effluent when a regenerated sorbent containing zinc sulfate is exposed to a simulated coal gas. The SO<sub>2</sub> content is initially high but it declines with time in an approximately exponential manner. At higher temperatures the SO<sub>2</sub> level generally is high because of more rapid decomposition of the sulfate. Gas chromatography was incapable of measuring the SO<sub>3</sub> released. However, high temperature Knudsen cell mass spectrometric experiments indicated that the SO<sub>3</sub>/SO<sub>2</sub> ratio is about 0.2.

The SO<sub>2</sub> and SO<sub>3</sub> released into the hot coal gas can be reduced and removed by another bed of fresh zinc ferrite sorbent provided sufficient concentration of hydrogen is available in the hot coal gas stream. In the initial stages of desulfurization, the hydrogen present in the coal gas is consumed in converting the Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub>.



When the reduction of  $Fe_2O_3$  is complete  $p(H_2)$  in the coal gas stream increases. At this stage the  $SO_2$  and  $SO_3$  will be reduced and react with zinc ferrite to form ZnS.



$SO_2$  concentrations of less than 1 ppm level were achieved by the use of a two bed system and addition of hydrogen when a regenerated sorbent containing 6 wt% sulfate was used for coal gas desulfurization.

#### CONCLUSIONS

Thermodynamic calculations and experimental studies have shown that zinc sulfate is formed during regeneration of sulfided zinc ferrite sorbents. The formation of sulfate is a dynamic process requiring the simultaneous presence of  $SO_2$  and  $O_2$ . Hence it reaches a maximum level under conditions when all the sulfides in the spent sorbent have been converted to oxides and sulfates. Sulfate formation is enhanced by lower temperatures and high oxygen partial pressures in the feed gas. The formation of the sulfate is promoted by the presence of the iron oxide component of the zinc ferrite sorbent.

During subsequent desulfurization use the zinc sulfate present in the regenerated sorbent releases  $SO_2$  and  $SO_3$  into the hot coal gas stream. These sulfur oxides can be removed by another bed of zinc ferrite provided a sufficient concentration of hydrogen is available in the coal gas stream.

#### ACKNOWLEDGEMENT

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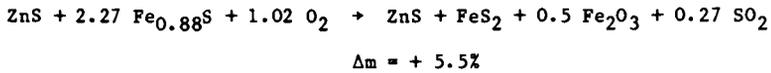
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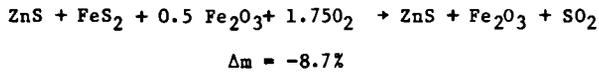
Table 1

PROGRESSION OF OXIDATION OF SULFIDED ZINC FERRITE  
DURING THERMOGRAVIMETRIC EXPERIMENTS

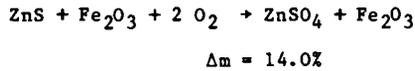
Step 1



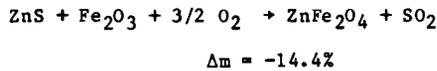
Step 2



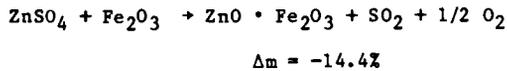
Step 3a



Step 3b



Step 4




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Note: The mass gain is based on the initial sample mass.

Table 2  
 SULFATE AND SULFIDE CONTENTS OF REGENERATED  
 SORBENTS AS A FUNCTION OF REGENERATION TIME<sup>a</sup>

| Regeneration<br>Time (min) | Fractional<br>Conversion <sup>b</sup> | Sulfate (wt%) | Sulfide (wt%) |
|----------------------------|---------------------------------------|---------------|---------------|
| 0                          | 0                                     | 0             | 35.5          |
| 30                         | 0.27                                  | 1.17          | 18.15         |
| 60                         | 0.54                                  | 1.32          | 7.82          |
| 90                         | 0.81                                  | 4.77          | 0.35          |
| 120                        | 1.1                                   | 8.31          | 0.093         |
| 145                        | 1.31                                  | 7.32          | 0.09          |

<sup>a</sup>Feed gas composition: 58% air - 42% steam; space velocity: 2420 hr<sup>-1</sup>

<sup>b</sup>Fractional conversion is unity when the amount of feed gas passed is sufficient for stoichiometric conversion of sulfides to oxides.

Table 3  
 EFFECT OF GAS COMPOSITION AND TEMPERATURE ON SULFATE FORMATION

| Temperature<br>(K) | Wt% Sulfate            |                        |                        |
|--------------------|------------------------|------------------------|------------------------|
|                    | 100% air -<br>0% steam | 58% air -<br>42% steam | 25% air -<br>75% steam |
| 823                | 13.8                   | 14.5                   | 3.5                    |
| 873                | 11.3                   | 14.9                   | 2.4                    |
| 923                | 9.3                    | 5.4                    |                        |
| 973                |                        | 4.5                    |                        |
| 1073               |                        | 2.2                    |                        |
| 1173               |                        | 0.45                   |                        |

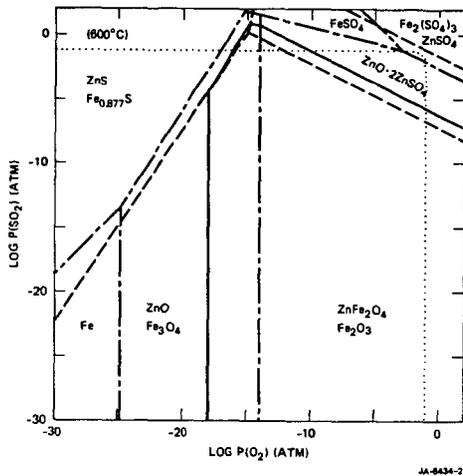


Figure 1. Stability Diagram of the Fe-Zn-O-S System at 873 K.  $ZnFe_2O_4$  Phase Field (—), Zn-O-S Phases (- - -), Fe-O-S (- · - ·).

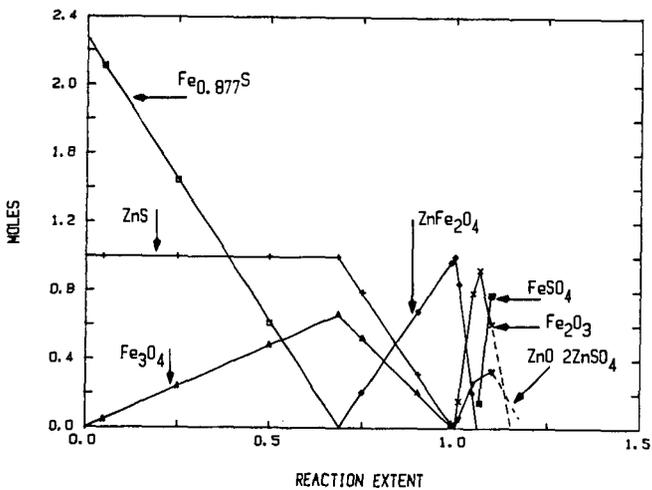


Figure 2. Equilibrium Solid Phase Products During Regeneration of Spent Zinc Ferrite Sorbents with a Gas Mixture of 90% Air - 10%  $SO_2$  at 873 K.

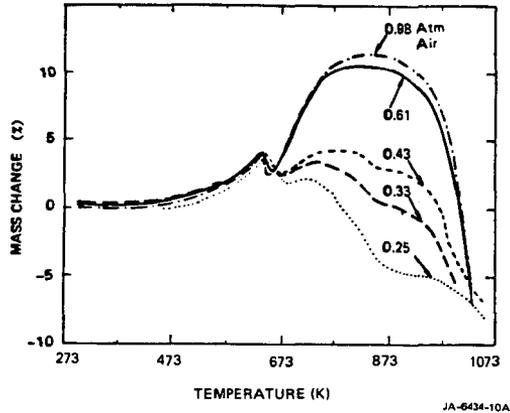


Figure 3. Temperature Programmed Thermogravimetry of Reaction of Spent Zinc Ferrite Sorbents with Various Air-N<sub>2</sub>-H<sub>2</sub>O Mixtures.  $p_{H_2O} = 0.02$  atm,  $p_{air}$  is shown and Balance  $p_{N_2}$  at 1 atm.

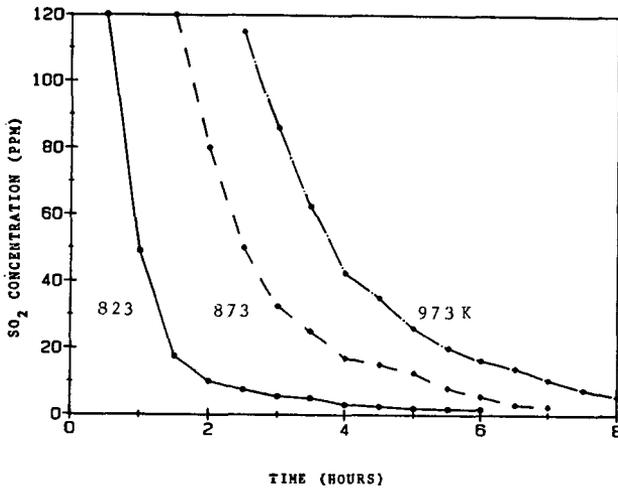


Figure 4. Release of SO<sub>2</sub> into Hot Coal Gas at 873 K by SO<sub>4</sub><sup>2-</sup> (13.5 wt%) Present in Regenerated Zinc Ferrite Sorbent.