A kinetic study of the sulfidation-regeneration of zinc oxide sorbent

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A kinetic study of the sulfidation-regeneration of zinc oxide sorbent

by

Oreoluwa Abimbola Sofekun

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in partial fulfillment of the requirements for the degree of

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For the Graduate College
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Experimental studies on the sulfidation/regeneration of zinc oxide have been conducted to obtain precise data on the kinetics and structural changes involved, and to formulate appropriate rate expressions. The regeneration of zinc oxide (oxidation of zinc sulfide) particles conducted in a thermogravimetric analyzer (TGA) was found to be fast and complete between 548 and 630°C, with zinc oxide being the only product formed. However, under the influence of external mass transfer, an oxysulfate intermediate which decomposes upon completion of the reaction was observed for the first time (by XRD). The intrinsic kinetic parameters for the oxidation reaction were determined and the surface reaction model \(-r = kK_A [O_2] / (1 + K_A [O_2])\) with no dissociation of oxygen was found to depict the initial rate data very well up to 609°C. Simple power law models were found to be inadequate.

Variations in surface area, pore volume, and pore size distributions caused by sintering with and without reaction were determined for the regeneration of zinc oxide between 575 and 640°C. In the absence of reaction, sintering resulted in a reduction of the sorbent surface area and an increase in average pore size. The reaction of zinc sulfide to zinc oxide in the absence of sintering resulted in an increase in surface area, while under reaction/sintering conditions the surface area increased up to a conversion of 0.75 and then decreased sharply. However, the surface area of the product was still greater than that of the reactant at all temperatures investigated.
A detailed analysis of the sulfidation of zinc oxide conducted in a TGA in the temperature range 541 to 747°C revealed that a simple power law model with reaction order $n = 1.18$ and not $n = 1.0$ fitted the reaction data very well up to 697°C. At 747°C, it was observed that conversions obtained were significantly lower than those obtained at 697°C. This was found to be a result of changes in the structural parameters of the sorbent due to sintering.
CHAPTER 1. GENERAL INTRODUCTION

Projections made by the U. S. Department of Energy (DOE) indicate that the demand for electricity in the next millennium would be greater than what can be supplied by natural gas and oil burning. This has led to renewed interest in electric power generation from coal. The conventional coal gasification processes are known to have a very negative impact on the environment due to the high levels of particulates emitted and formation of $SO_x$ and $NO_x$. This has led to the development of two new processes: the Integrated Gasification Combined Cycle (IGCC) and the Gasifier/Molten Carbonate Fuel Cells (MCFC) which are both virtually emission-free.

A schematic diagram of IGCC is shown in Fig. 1. The Gasifier/MCFC process is identical to this, except that the gas turbine is replaced by a MCFC.

Fig. 1 Integrated Gasification Combined Cycle (Gangwal et al., 1989a)
Since both systems utilize CO and H\textsubscript{2} as fuel, coal gas would be an ideal choice if the sulfur levels could be reduced. Fuel gas obtained from gasifiers normally contains ~500 ppm of sulfur however the gas turbine in the IGCC cannot tolerate more than 100 ppm, and MCFCs require sulfur levels to be less 1 ppm. The requirement of temperature and pressure matching of system components in both the IGCC and MCFC imposes an additional constraint on the desulfurization since the present commercial processes of H\textsubscript{2}S involve wet-scrubbing with an alkali at 250°F. Therefore the economic viability of these systems is dependent on the development of a high temperature sorbent.

Commercialization of a particular sorbent depends on factors such as operating temperature, amount of reduction tolerated, sulfur loading achieved at breakthrough, regeneration characteristics, and sorbent strength over several cycles.

With these requirements in mind, a number of studies have been conducted and the literature is extensive. A thermodynamic analysis conducted by Westmoreland and Harrison (1976) identified oxides of Zn, Mn, Mo, V, Ba, Sr, Fe, Co, Cu, Ca and W as potential sorbents for H\textsubscript{2}S removal between 400 and 1500°C. Sorbents and processes based on oxides of copper (Tamhankar et al., 1986), cerium (Kay and Wilson, 1978), manganese (Wakker and Gerritsen, 1990), cobalt (Anderson et al., 1985), tin (Karpuk, 1993; Nielsen and Siguidardottir, 1993), iron (Joshi and Levenberger, 1977; Sugitani, 1989), and zinc (Gupta et al., 1992; Gupta and Gangwal, 1992) have been studied singly and in combination. Some of these studies were conducted on metal oxides dispersed on silica, alumina, titania and chromia which were meant to act as supports for strengthening
mechanical structure, as stabilizers against reduction of the metal oxide, and/or as chemical modifiers to promote the formation of elemental sulfur during regeneration (Gangwal et al., 1995). Further details can be found in reviews that have been conducted by Gangwal, 1991; Thambimuthu, 1993; Gangwal et al., 1993; Jalan, 1985; and Christoforou et al., 1995a.

These reviews all indicate that zinc oxide and zinc oxide based mixed oxides appear to be the most promising. In particular, zinc titanate (Zn$_2$TiO$_4$ or ZnTiO$_3$) which is made by reaction between zinc oxide and titanium oxide, and Z-Sorb III, a zinc oxide-nickel oxide-based sorbent developed by Phillips Petroleum, are presently undergoing extensive testing (Gangwal et al., 1992; Khare et al., 1995). However, pure zinc oxide is yet to be matched in its sulfur removal capacity by any other oxide.

The chemical changes that are believed to occur in the sorbent during the desulfurization process are summarized in the following equations:

\[
\text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2\text{O}, \quad \text{sulfidation}
\]

\[
\text{ZnS} + \frac{3}{2} \text{O}_2 \rightarrow \text{ZnO} + \text{SO}_2, \quad \text{regeneration}
\]

The SO$_2$ produced during regeneration can be treated by conversion to elemental sulfur which can be sold, used in the production of sulfuric acid, or converted to a disposable sodium or calcium sulfate.

Two drawbacks have inhibited the commercialization of ZnO as a desulfurization sorbent: reduction/volatility in the reducing coal gas at temperatures above 600°C, and the formation of ZnSO$_4$. Zinc sulfate being a compound with a larger molar volume than either
ZnO or ZnS, tends to block the pores in the sorbent thus leading to low sorbent utilization at breakthrough. Thermodynamic analysis predicts that ZnSO₄ is a stable phase when regeneration is carried out at low temperatures or at high oxygen concentrations, but there has been no direct evidence to support this prediction. Indirect evidence such as the high levels of SO₂ in the reactor when regenerated ZnO is sulfided has been used to indicate its formation.

Although this regeneration process has received considerable attention, the kinetic parameters reported in the literature were obtained under different rate-controlling regimes. Even data obtained in the same regime differ by as much as an order of magnitude. This type of disparity brings to question the validity of the studies reported. With regard to the sulfidation of ZnO, most researchers have conducted a kinetic analysis of its reaction with H₂S using a reactive gas mixture in which H₂S is just one of the components. While this has been done to simulate the actual process streams, it does not present a clear picture of the reactivity of ZnO with H₂S. Thus it is essential to investigate the true kinetics of the sulfidation of ZnO. This will lead to a better understanding of the effect of these other gases on the sorbent.

**Objectives**

In view of the above, the present research was undertaken with the following objectives:

1. To determine the true intrinsic kinetics of the regeneration process, i.e. the oxidation of ZnS.
2. To determine under what conditions, if any, sulfates are formed during this process.

3. To determine the changes that occur in the sorbent structural parameters during the oxidation of zinc sulfide.

4. To study the sulfidation kinetics of ZnO.

**Dissertation Organization**

This dissertation is written as a collection of papers published or prepared for publication in technical journals. Chapter 1 provides a general introduction to the subject matter, while in Chapter 2 a review of the literature on desulfurization is presented along with some background information on the effect of sintering on high temperature reactions and the measurement of surface area and pore volume. Chapter 3 contains an extensive account of the kinetics of zinc sulfide oxidation including a detailed analysis of the regimes of the reaction and development of a rate equation to represent the true kinetics of the reaction. This kinetic study is preceded by a review of the literature on zinc sulfide oxidation in which the existing gaps are pointed out.

Chapter 4 continues the experimental study reported in Chapter 3 with emphasis on changes in structural parameters during oxidation. Chapter 5 continues the study with a detailed experimental study of the kinetics of sulfidation. The experimental data presented in Chapters 3 and 5 provide the basic information needed to model the complete oxidation/regeneration cycle.

Chapter 6 completes the dissertation with a statement of conclusions of the present study and recommendations for future work. The Appendices provide supplemental
information on the three papers included in this thesis and references are listed in each paper. References for Chapters 1 and 2 are listed in the References chapter of the dissertation.
CHAPTER 2. LITERATURE REVIEW

In the first section of this review, the literature on the sulfidation of both single and mixed oxides is presented. The second section reviews the impact of sintering on high temperature reaction kinetics while the last two sections cover background information on methods used for sorbent surface area and pore volume measurements.

High Temperature Desulfurization

Single Oxides

The reactivity of certain metal oxides with H$_2$S has long been known. The Appleby-Frodingham process (Bureau et al. 1967) utilized ferric oxide at 400°C for coke oven gas desulfurization while ZnO was used to desulfurize hydrocarbon feedstock for ammonia synthesis (Phillipson, 1970) without regeneration. With environmental regulations becoming increasingly stringent, and tolerance for sulfur in process gases becoming lower and lower, it is now essential to develop more efficient methods for desulfurization.

Thermodynamic Screening. Westmoreland et al. (1976) conducted a study in which 28 oxides were thermodynamically screened for hydrogen sulfide removal potential from low BTU coal gas using the method of free energy minimization. Taking 95% equilibrium desulfurization and solid compound stability at temperatures between 360 and 1560°C as the minimum criteria, they found that the oxides of eleven metals (Zn, V, Ca, Ba, Mo, Cu, Fe, Sr, Co, W and Mn) were good candidates for this task.
Iron oxide was found to satisfy the criteria below 700°C where the stable form of the excess iron is Fe$_3$O$_4$ but at 700°C it is reduced to inert FeO. Zinc oxide also satisfied the criteria between 360 and 1160°C however, above 700°C zinc vapor is formed. Barium carbonate was found to be a potential sorbent between 950 and 1200°C, while calcium carbonate delivers 95% desulfurization only between 800 and 880°C. On the other hand, the maximum operating temperature for cobalt oxide would be 600°C but with cobalt metal present above 300°C. Similarly, copper metal would be present over the entire temperature range if copper oxide were to be used at 900°C, which is its 95% equilibrium desulfurization temperature. Manganese could operate up to 1060°C, but there would be a transition at 400°C from MnCO$_3$ to MnO accompanied by a progressive decrease in desulfurization capacity. Molybdenum could also operate up to 800°C while tungsten could operate up to 1000°C. Vanadium sulfide has a melting point of 650°C, thus it is very limited but strontium could be effective between 800 and 1100°C.

**Kinetic Studies.** Based on the results of this study, Westmoreland et al. (1977) conducted a kinetic study on desulfurization by MnO, CaO, ZnO, and V$_2$O$_3$ powders in a simulated gasifier effluent atmosphere over a temperature range of 300 to 800°C in a thermobalance. Linearity of the plots of initial rate versus hydrogen sulfide concentration obtained for all the oxides led to the assumption of first order kinetics. However, the intrinsic reaction rate of H$_2$S with MnS was approximately one order of magnitude greater than the rate of reaction of either CaO or ZnO sulfidation and two orders of magnitude greater than the reaction rate of V$_2$O$_3$. They also discovered that below 900°C CaO tended
to preferentially form CaCO$_3$ over CaS due to CO$_2$ in the gasifier effluent, while at 700°C ZnO formed metallic zinc vapor and its regeneration has proven to be unfeasible. Manganese oxide, on the other hand, exhibited none of these limitations.

Yumura and Furimsky (1985) conducted a study to investigate the potential of CaO, ZnO and Fe$_2$O$_3$ pellets made with 2% stearic acid binder as high temperature adsorbents of hydrogen sulfide between 600 and 800°C in a vycilor glass vertical reactor with upward flow of 10% H$_2$S in N$_2$. It was found that temperature increase from 600 to 800°C had little or no effect on the H$_2$S adsorption by ZnO and Fe$_2$O$_3$ but an increase was seen for CaO. These results are consistent with the thermodynamic analysis conducted by Westmoreland and Harrison (1976). The observed adsorption capacity of the sorbents in descending order based on sorbent weight was Fe$_2$O$_3$ > CaO > ZnO while the rate of adsorption based on surface area was ZnO > Fe$_2$O$_3$ > CaO. The fact that adsorption when normalized by surface area changes the adsorption capacities of the sorbents indicated that the surface structure of oxides is an important parameter influencing their adsorption capacities.

In addition, for both CaO and ZnO, SO$_2$ was present in the exiting gas in trace quantities, while in the presence of Fe$_2$O$_3$ relatively large quantities were recorded indicating the decomposition of sulfates. In all cases the hydrogen concentration was higher than in the blank run and it increased as temperature increased suggesting some catalytic effect of the sulfided solids on H$_2$S decomposition.

**Modeling.** Gibson and Harrison (1980) reacted spherical pellets of zinc oxide suspended in a thermobalance under mass transfer and diffusion limitations. Gas
concentrations were varied from 1 - 6 mole % H₂S, (H₂:H₂S = 5:1), and temperatures ranged from 350 to 800°C.

Using kinetic parameters extracted from the study by Westmoreland et. al. (1977), the grain model (Szekely, 1976) was used to analyze the experimental data. The value of the grain diffusion coefficient $D_A$ was chosen to provide a good fit to the data for cases in which a zero value was inadequate. The results of the experiments reflected distinct differences in three separate temperature regions: 350 - 500°C, 600 - 700°C, and above 800°C.

Between 375 and 500°C, reaction ceased long before total conversion was reached, and this cutoff was a function of temperature. By varying $D_A$ the fit of the grain model was only slightly better therefore, they concluded that a variable property model incorporating structural changes due to reaction and/or sintering may be required to provide further improvement in the fit.

In the 600 - 700°C range, reaction was rapid and essentially complete. Agreement was obtained between experiment and the model in which $D_A$ was assumed negligible up to 30% conversion. Above this, the reaction was often predicted to occur more rapidly than experimentally observed, indicating that internal diffusion is the most important resistance. Electron microprobe scan for sulfur showed that the concentration of sulfur increased from zero at the center of the pellet to a significant amount at the outer radius. In addition, the sulfur profile corresponded closely to the radial profile obtained from the grain model and the shrinking core model under conditions of diffusion limitations.
Above 800°C, the reaction rate became highly unpredictable and the reaction tended to die-off at low but unpredictable conversion. This was ascribed to the reaction between vapor phase zinc and hydrogen sulfide which tended to block the pores.

Tamhankar et al. (1981) studied 45 wt % iron oxide–55 wt % silica particles dispersed in a porous silica matrix in a TGA. However, iron oxide was observed to react with the CO and H₂ present in the gasifier faster than it reacted with H₂S, and this led to the formation of metallic iron. It was also observed that the reaction rate for the sulfidation of unreduced iron oxide was much slower than that of the reduced iron oxide. Furthermore, analysis of the reaction products by Mossbauer spectroscopy revealed the formation of a nonstoichiometric oxide, FeS_{(1+\alpha)}, where \( \alpha \) may range from 0 to 0.2 and in this case \( \alpha \) was 0.1. Using the data on the smallest particles to obtain the rate constant, \( k \), and the data for the large pellets to calculate the effective diffusivity, \( D_e \), a theoretical fit to the reduction and sulfidation profiles were made using the grain model.

**Sorbent performance.** Studies on the ZnO–H₂S reaction carried out on commercial pellets by Giner (1981) and Grindley and Steinfeld (1981) had shown very low sorbent conversions and high breakthrough H₂S levels due to the drastic reduction in pore volume and surface area upon sulfidation. However, Tamhankar et al., (1986) obtained conversions at breakthrough above 0.85 at 538°C and above 0.8 at 650°C for highly porous zinc oxide. The corresponding outlet H₂S concentrations were 1.2 and 6.8 ppm which are below their respective equilibrium values of 4.2 and 16 ppm. They suggested that these subequilibrium levels were due to formation of a chemisorbed surface sulfide layer with substantially lower
free energy than the bulk sulfide while Lew et al. (1989) proposed that the low levels resulted from reaction between H₂S and Zn vapor. They also observed zinc deposits on the quartz wall downstream of the bed which was an indication of zinc loss by reduction and subsequent evaporation. Furthermore, sulfidation decreased as the number of cycles increased indicating incomplete regeneration or the effect of zinc losses.

**Mixed Oxides**

*Comparative Studies.* In view of the problems associated with single oxides, mixed oxides were sought as potential sorbents. In 1986, Tamhankar et al. studied several highly porous mixed oxides: ZnO–Fe₂O₃, CuO–Fe₂O₃, CuO–Al₂O₃ and CuO–Fe₂O₃–Al₂O₃, and ZnO with the aim of explaining sorbent performance in terms of changes in phase composition and surface area during successive sulfidation–regeneration cycles in a quartz reactor.

Zinc ferrite, ZnFe₂O₄, was formed by heating powders of ZnO and Fe₂O₃ at 815°C, with the objective of combining their theoretical sulfur capacities of 415 g S per kg Fe₃O₄ and 393 g S per kg of ZnO. The porous zinc ferrite powders in this study yielded a conversion of 0.75 and 0.35 - 0.40 in pelleted form and H₂S was reduced to less than 1 ppm. In an earlier study using commercial sorbents, Grindley and Steinfeld (1981) had observed high H₂S breakthrough levels of 2 - 10 ppm at a sorbent conversion of 0.2.

During regeneration, formation of zinc ferrite from the oxides was incomplete and similar to zinc oxide sulfidation. The sulfidation of zinc ferrite resulted in the deposition of zinc on the reactor walls since ZnFe₂O₄ is reduced to ZnO and Fe₃O₄ in the reducing gas.
The rate of zinc loss was found to be 8% /1000 h at a space velocity of 2100. In multicycle testing, breakthrough conversion declined from 0.95 in the first cycle (c-1) to 0.7 in c-4 while H₂S levels in the exit gas remained at 2-3 ppm, which is less than the equilibrium level for the sulfidation of ZnO.

The copper ferrite study was undertaken with the hope of avoiding the two difficulties that arose with zinc sorbents: loss of metallic zinc at temperatures above 600°C and the high temperatures required for decomposition of zinc sulfate formed during regeneration. However, the H₂S levels in the exit gas remained below 2 ppm only until a conversion of 0.5 while at 0.78, these levels had risen to 10 ppm for the reaction at 538°C. At 650°C and 80% conversion, breakthrough sulfide was 85 - 90 ppm, close to the metallic copper equilibrium level and as in the case of zinc ferrite, copper ferrite was not completely regenerable.

Based on bench scale experiments by Flytzani-Stephanopoulos (1986c), Gangwal et al. (1989) selected the following mixed oxides for further testing: (CuO)₃-Al₂O₃-Fe₂O₃, (C₃)FA; (ZnO)₀.₈₆-(CuO)₀.₁₄-Fe₂O₃, (ZC)F; CuO-Al₂O₃, CA; and (ZnO)₀.₆-TiO₂-, (0.8Z)T. Pellets of each oxide were prepared with 2% inorganic binder (bentonite) to achieve the desired crush strength and with varying amounts of an organic binder (methyl cellulose) to provide a trade off between porosity and strength.

Multicycle single pellet studies were conducted in a TGA with reduction preceding the sulfidation runs. A reduction corresponding to 30 - 50% of the theoretical value for the of CuO to Cu and Fe₂O₃ to Fe₃O₄ was observed during the reduction of (ZC)F sorbents,
while in the following sulfidation cycle the observed weight gain corresponded closely to complete formation of ZnS, FeS, and CuS. However, regeneration at 650°C was incomplete due to the formation of either ZnSO₄ or CuSO₄ which were easily decomposed during the following reductive regeneration cycle. It was also noted that the sample formed without the organic binder maintained a second sulfidation cycle very much like the first while the other pellets showed less reactivity.

The effect of binder content appeared insignificant on the performance of CA sorbents but this could have been a direct consequence of its very high surface area and small crystallite sizes. The reduction was quite rapid and corresponded to nearly complete CuO reduction to Cu and the sulfidation was also very rapid. In the oxidative regeneration at 550°C, formation of the oxysulfate which later decomposed to the sulfide was observed however its presence was not confirmed by XRD.

For the (C3)FA sorbent, reduction was also rapid and almost complete reduction of CuO to Cu and Fe₂O₃ to Fe₃O₄ was obtained. The oxidative regeneration at 650°C showed a weight loss followed by a weight gain which indicated competing reactions. The sorbent with 5% organic binder performed much better during the second sulfidation cycle than the sorbent without the binder. This indicated structural changes in the sorbent without the binder after the first cycle. This was also evidenced by the differences in their crush strengths.

On the other hand, the (08.Z)T sorbent lost only 0.13% of its weight during reduction, and there was also a much lower amount of sulfate formed during regeneration.
This appeared to confirm the findings of Lercher et al. (1984) in which they established that since the amount of Zn$^{2+}$ cations on the surface of the ZnO-TiO$_2$ mixtures decreases as the amount of TiO$_2$ increases, TiO$_2$ would stabilize ZnO against reduction. The crush strengths of the pellet both before and after regeneration were quite “respectable” and the reduction in the pore volume of the sorbents appeared to correlate with the extent of conversion.

**Zinc Ferrite**

The literature presented in the previous section seem to indicate that zinc ferrites and zinc titanates perform quite respectably as desulfurization sorbents. For this reason, this section is devoted to presenting detailed information on the desulfurization behavior of zinc ferrites and the next section to zinc titanates.

**Kinetics.** Focht et al. (1988) further examined the characteristics of the ZnFe$_2$O$_4$-H$_2$S reaction in the laboratory by exposing single cylindrical pellets to a simulated oxygen-blown water quenched fluidized bed gasifier effluent in a thermobalance between 300 and 700°C. The pellets were initially exposed to H$_2$S-free reducing gas at the temperature of interest in order to simulate what occurs in a fixed bed reactor.

Reduction occurred very rapidly and after 10 minutes was essentially complete and only at that time was H$_2$S introduced into the system. Below 400°C, ZnFe$_2$O$_4$ was stable in the reducing atmosphere but at higher temperatures, it was reduced to ZnO and Fe$_2$O$_3$ which was progressively reduced to FeO via Fe$_3$O$_4$.

Reaction at 550°C in 3% H$_2$S resulted in final values of conversion in excess of 1 due to the formation of nonstoichiometric iron oxide FeS$_{1+y}$. Tamhankar (1981) had
reported a value of 0.2, while in this study a value of 0.05 was obtained. The temperature sensitivity of the global reaction rate in the range 300-700°C was quite low. This low temperature sensitivity was taken as a first indication of the influence of transport resistances on the global kinetics.

Scanning Electron Micrographs, SEM, of a pellet partially sulfided above 500°C showed a sharp interface between the unreacted core and product layer. As the temperature was lowered to 400°C, the reaction became more diffuse and at 300°C, a homogeneous reaction was evident. This confirmed the kinetic results since a sharp interface is characteristic of a reaction in which the global reaction rate is governed by transport resistance. Such behavior is likely to occur at higher temperatures while at lower temperatures surface kinetics may be the dominant effect. In contrast, the lack of radial sulfur dependence is consistent with a system where surface chemistry/solid state diffusion through a nonporous product layer surrounding individual grains offers the controlling resistance. Obviously, a reaction zone of finite thickness would occur when all the resistances are important, a phenomenon expected at intermediate temperatures.

**Modeling.** The unreacted core model assuming mass transfer control led to under prediction at low conversions and over prediction at high conversions. The reverse was the case when pore diffusion control was assumed. The mass transfer coefficient $k_{m,A}$ used was obtained from the Frossling equation (Hughmark, 1967) and effective diffusivity $D_c$ from the random pore model (Wakao and Smith, 1962). Using both of these constants and assuming mixed control led to under prediction over the entire conversion range. Only by
mathematically fitting these constants was the model a good fit to the data. These fitted values were 80% and 60% greater than the values predicted for $k_{m,A}$ and $D_c$ respectively.

**Structural Parameters.** Sintering studies conducted by Sa et al. (1989) showed that ZnFe$_2$O$_4$ produced at 815°C did not sinter until the temperature was raised above 700°C. At this point, the specific surface area was found to decrease by 20% to 6 m$^2$/g and the pore volume by 5% to 0.34 cm$^3$/g but there was still no significant change in the average pore volume. However reduction studies showed that reduction of the oxide to Fe$_3$O$_4$ occurred rapidly in the 500–600°C range. This was accompanied by a decrease in surface area and pore volume and an increase in average pore size. Above 700°C, FeO was produced leading to a 50% reduction in both surface area and pore volume while the average pore size increased. This loss of pore structure is believed to be the major cause of the poor sulfidation characteristics of over reduced pellets since at 700°C sulfidation was accompanied by a 20% volume reduction, a 13% increase in mass due to sulfidation, and a 40% increase in the pellet density. The fact that reduction temperature and conversion are most important in determining the final surface area was confirmed by a plot of surface areas with conversion in which pellets reduced at different temperatures had different initial surface areas but parallel loss of surface vs. conversion profiles.

**Regeneration.** Focht et al. (1986) showed that significant amounts of ZnSO$_4$ were formed during regeneration at 550°C but that this sulfate could be decomposed at this same temperature by switching to a reducing atmosphere. At 550 and 650°C complete regeneration was possible but at 850°C, reaction stopped well before complete regeneration.
The macroscopic pellet volume was found to decrease by 3% at 500°C while at 850°C it decreased by 40%. However, a 70% reduction in the original surface area and a 20% reduction in the pore volume were observed at 750°C, partial restoration of the surface area is seen at 650°C while at 550°C after removal of the sulfate formed, almost complete restoration was observed. Increasing the oxygen concentration to 6% in the regeneration gas resulted in a slightly lower restoration of the original surface area which could be due to the exothermic temperature effects at the higher oxygen concentrations.

In a continuation of the earlier study, Focht et al. (1989) studied the regeneration kinetics and multicycle behavior of zinc ferrite as a function of gas composition and temperature. Regeneration was complete at both 650 and 750°C and the global rates were not much different. However, in the second sulfidation cycle, the sorbent regenerated at 750°C had a much lower performance than the one regenerated at 650°C. At both 550 and 850°C the global rate was slower and complete regeneration was not attained, while at 850°C severe structural property changes prevented complete regeneration. SEM revealed that the pellet regenerated with oxygen (2.1 %) had a sharp interface separating the unreacted core from the product layer. This sharp reaction front is indicative of a system in which the intrinsic rate is quite fast and the global rate is controlled by transport resistances. However, with 30% steam, there was no sharp reaction front which indicates that the reaction is intrinsically slow so that the reaction occurs in a zone within the pellet.

By assuming that the excess mass present after the pellet had attained a steady weight in the oxidizing medium was due to the formation of sulfates, they deduced that
15 - 25% and 1 - 10%, of the initial sulfide was converted to sulfates at 550 and 650°C respectively. This was further buttressed by the fact that addition of SO₂ to the reactant gas resulted in even higher weight gains. However, no spectroscopic method was used to identify this phase.

**Multicycle Testing.** Focht et al. (1986) showed that at 550°C, the ratio of the conversion obtained at the same reaction time for the second and first cycles, \(X_2 / X_1 > 1\) for the first 70 minutes while at 650°C \(X_2 / X_1 \approx 1\) and at 750 °C, \(X_2 / X_1 < 1\). The sulfidation reaction at 550°C is known to be diffusion controlled (Focht et al. 1988). Hence pore volume and pore size should be more important than the surface area in determining the global reaction rate. The relatively small decrease in pore volume coupled with the increased average pore size following regeneration at 550 and 650°C are believed to be responsible for the favorable second cycle sulfidation reactivity following regeneration at 750°C.

In a subsequent study, (Focht et al., 1989) regeneration at 650°C, resulted in a significant reactivity increase between cycles 1 and 2 while the 3rd cycle reactivity was slightly lower but the 4th was exactly like the 1st. In a modified eight cycle run in which 10 minutes were allowed for standard reduction, and 60 minutes for regeneration at 550°C, a gradual decrease in reactivity was observed with only two-thirds of the initial reactivity maintained after eight cycles.
Zinc Titanates

**Reduction.** In a hydrogen environment, ZnO was reduced 3-10 times faster than Zn-Ti-O in the temperature range of 600 to 900°C (Lew et al., 1989; Lew, 1990; Lew et al., 1992a). For Zn-Ti-O, reduction became faster than sulfidation at 942°C while for ZnO the same was observed at 848°C. Thus the desulfurization temperature could be 94°C higher and this should compensate for the lower sulfidation rate.

**Kinetics and First Cycle Performance.** Based on positive results obtained by Flytzani-Stephanopoulos (1986), Lew et al. (1989) conducted a study on several mixed oxides containing different ratios of zinc to titanium dioxide. The zinc titanate, Zn$_2$TiO$_4$, was found to have H$_2$S removal efficiency similar to ZnO but it only reached 65% conversion at breakthrough. Even lower breakthrough conversion (50%) was observed with a sorbent comprised of a 3:1 ratio of Zn to TiO$_2$. The only mixed sorbent which reacted completely even after several cycles had the composition 0.4 Zn : 1 Ti (Z2T-C1) and was made from a titanium chloride precursor rather than titanium isopropoxide. Conversions based on ZnS formation of between 100% and 135% were observed and it was hypothesized that this was due to the incorporation of sulfur into the Zn-Ti-O lattice which might have been distorted by residual chloride ions. However there were no chloride species in the XRD results and wide angle XRD showed no oxide solutions.

Furthermore, kinetic experiments conducted in a thermobalance in the absence of gas film diffusion with -115 to +170 mesh particles revealed that the initial sulfidation rates of the mixed oxides were comparable to ZnO, but as time progressed, the higher the
titanium content, the slower the reaction became. However, the rate of sulfidation for Z2T-
Cl was higher at later times than for ZnO thus indicating faster diffusion which can only be
due to a more open structure (Cl species).

Another sorbent (1.5 ZnO:TiO₂, L-3140) was selected by Woods et al. (1990) as the
best compromise between sulfur capacity and zinc losses due to reduction and vaporization.
They found that between 425 and 540°C, sulfidation was fast and strongly influenced by
temperature. However, between 650 and 760°C, sulfidation kinetics exhibited no
temperature.

In a subsequent study, Lew et al. (1992b) observed that the initial rates of sulfidation
for ZnO at 600 and 700°C were approximately 1.5 - 2 times higher than for all ZnTiO
sorbents containing greater than 25 mol% TiO₂ while initial sulfidation rates were similar
for the different zinc titanate phases. The activation energies obtained from the Arrhenius
plots of ZnO and ZnTiO were about the same but the frequency factor for ZnO was three
times greater than that of ZnTiO. This was ascribed to the presence of titanium blocking
some reaction sites in the titanates. The sulfidation rates were also found to be temperature
dependent contrary to the results obtained by Woods (1990). This difference could be
because his reaction conditions were not free from mass transfer and pore diffusion
limitations.

Regeneration. Regeneration appeared to be largely successful in restoring the
original Zn-Ti-O sorbent’s structural properties. The x-ray diffraction patterns were
essentially identical confirming that crystalline phase changes associated with sulfidation

were also reversible. Using steam for regeneration resulted in slower kinetics of L-3140. Focht et al. (1989) had shown that zinc ferrite, ZnFe$_2$O$_4$, reactivity generally decreased during multicycle operation, especially at high temperatures; however, L-3140 showed no such behavior. On the other hand, Lew et al., (1992) reported that in the second regeneration cycle both oxides were only regenerable up to 95%.

**Structural Parameters.** Woods et al. (1990) measured the dimensions of the pellet before and after reaction and concluded that the volume remained essentially constant throughout. This is contrary to the conclusions reached by Sa et al. (1989) on the volume reduction following sulfidation of L-1442 zinc ferrite pellets at 700°C. However, since L-1442 had a methocel binder and L-3140 a bentonite binder, it is not clear if this difference was due to the effect of the binder or was an inherent property of L-3140.

In addition, in the temperature range of interest, no reduction of the sorbent occurred and the structural properties of the fresh and reduced sorbents were essentially equal. Sulfidation, however, resulted in increased surface area between 650 and 760°C, constant area at 815°C, and a decreased area at 870°C. This was also contrary to Sa et al.'s results but similar to Gangwal et al.'s 1989 findings on 0.8 ZnO: TiO$_2$ which had both types of binder. Zn–Ti–O particles reacted by Lew et al. (1992) showed an increase in surface area (in agreement with Flytzani-Stephanopoulos et al., 1987) whereas ZnO showed a decrease after sulfiding. This, however contradicts their 1989 work which indicated the opposite trend.
Flytzani-Stephanopoulos et al. (1987) had also reported surface area increases upon sulfidation of the sorbents, indicating that increases or decreases may be specific to individual systems. Since surface area is inversely related to pore diameter, these data suggest that sulfidation produces a roughening of the interior surface which causes the increased surface area and decreased pore size. Sintering becomes significant above 800°C, and generally has the effect of smoothening roughened surfaces, thus reducing the surface area and increasing the average pore size.

**Sintering**

While a wide range of porous solids have an internal surface area greater by several orders of magnitude than the external surfaces, some very fine powders have a large external surface and a small or even negligible internal surface. When aggregation of such particles occurs, e.g. through sintering then part of the external surface becomes converted into an internal surface and a pore system is developed.

A study conducted by White (1967) identified three stages in the sintering process. In the first stage the areas of contact between adjacent particles form and grow, while in the second stage the growing necks merge and the large number of small particles is replaced by a smaller number of large particles. In the last stage the pore space becomes broken up with isolated closed pores remaining which shrink in size as densification proceeds. Thus it can be seen that the first stage of sintering could lead to a reduction in pore size while the second stage could produce interparticle porosity whose surface may be inaccessible both to reacting gas during a gas-solution reaction and to nitrogen used to measure the solid surface area.
area (Caillet and Harrison, 1982). Sintering thus reduces surface area by reducing both the internal and external surface available for adsorption and reaction.

**Determination of Surface Area**

The amount of reaction which occurs in a gas-solid noncatalytic reaction is dependent on contact between the reacting gas and solid. This invariably depends on the surface area of the solid. Many methods are available for measurements of the surface area of a solid such as direct observation by an optical or electron microscope. Apart from this being very tedious, if the solid is porous as in the case of most solids used in gas-solid reactions, the surface area measured would be that attributed to only the external surface of the solids. The interior surface area, which for highly porous materials could be twice the external surface area, could not be measured. Thus an indirect method, the adsorption of gases, is used for estimation of surface areas of porous solids. The best known and most commonly used of this class of methods is the Brunauer-Emmett-Teller, BET, method (1938).

The BET method is based on adsorption of a particular gas with known molecular area onto a solid surface. By establishing the conditions under which a monolayer of gas is adsorbed onto the solid surface, the total surface area of the solid can be determined. The relationship between the volume of gas adsorbed and the relative pressure is given by (Satterfield, 1970)

\[
\frac{P}{V(P_0 - P)} = \frac{1}{V_mC} + \frac{(C - 1)P}{V_mC P_0}
\]  

(1)
where $V =$ volume of gas adsorbed at pressure $P$

$V_m =$ volume of gas adsorbed in monolayer

$P_o =$ saturation pressure of adsorbate gas at the experimental temperature

$C =$ a constant related exponentially to the heats of adsorption and liquefaction of the gas

$$C = \exp(q_1 - q_L) / RT$$ (2)

where $q_1 =$ heat of adsorption on the first layer

$q_L =$ heat of liquefaction of adsorbed gas on all other layers.

The values of $V_m$ and $C$ can be easily obtained from the above equation.

The specific surface area of the solid ($m^2/g$) is then given by

$$S = \frac{X_m}{M} N A_m \times 10^{-20}$$ (3)

where $X_m =$ monolayer capacity of adsorbate ($g$ adsorbate / g solid)

$M =$ molecular weight of adsorbate

$A_m =$ area occupied per molecule of adsorbate ($\AA^2$)

The BET equation is valid over $0.05 \leq \frac{P}{P_o} < 0.3$.

The larger the value of $C$, the more the isotherm approaches the type II (or IV) form and the more accurately the surface area can be determined. In particular, low $C$ values (25-30) may lead to erroneous surface area values when krypton is the adsorbate.

Adsorption of nitrogen at 77 K is the most commonly used technique when the total surface area of the sample of solid being measured is above $1 \ m^2$. However, when the
amount of sample available is limited such that that total surface area is ≤ 5 m², an
adsorbate with a low saturation pressure is desired in order to minimize errors arising from
measurement of the dead space volume.

Thus krypton which has a very low saturation pressure ($P_o = 1.76$ Torr @ -196°C) is
used. However unlike nitrogen which is generally accepted to have a molecular cross-
sectional area of 16.2 nm, there is no consensus for the cross sectional area of krypton.
Thus, whenever possible, the surface area should be measured by nitrogen and then the
value of $A_m$ for krypton adjusted to match the nitrogen values. This technique was used in
this study.

**Determination of Pore Size Distribution and Pore Volume**

The proportion of the surface area of a solid reached by reactant molecules is
dependent on the ease of transport of molecules from the exterior of the grains to the
various pores of the internal surface of the solid, and therefore upon the pore size
distribution (Gregg and Sing, 1967).

Two different methods may be used to determine the pore size distribution: physical
adsorption of a gas (applicable to pores < 60 nm in diameter) and mercury porosimetry (for
pores > 3.5 nm). Since the true pore structure is very complex, there is an abundance of
literature on interpretation, in terms of pore shapes, of hysteresis loops from physical
adsorption data. Therefore the reported pore-size distribution is totally dependent on the
model assumed for interpretation. In this study, the amount of nitrogen desorbed as a
function of reduced pressure is used to determine the pore size distribution based on the assumption of cylindrical pores.

When the relative pressure of a system is reduced to a critical value, the liquid condensed within any given pore begins to evaporate from a meniscus which stretches across the pore. The value of the radius of this meniscus which is given by the Kelvin equation:

\[
\ln\left(\frac{P}{P_0}\right) = -\frac{2\gamma}{rRT}V_m\cos\phi
\]  

(4)

where \(P_0\) = the saturated vapor pressure at temperature \(T\) (°K)

\(\gamma\) = surface tension

\(V_m\) = molar volume of the adsorbate in liquid form

\(R\) = gas constant per mole

\(\phi\) = angle of contact between the liquid and the wall of the pore (assumed to be zero).

However, in this step only the liquid core evaporates — an adsorbed layer of gas remains on the wall of the pore and this layer is stripped off bit by bit as the system pressure is reduced. The thickness of this layer is given by the Halsey equation (Halsey, 1948)

\[
t = \sigma \left[\frac{5}{\ln(P/P_0)}\right]^{1/3}
\]  

(5)

The value of \(\sigma\), the average thickness of a single layer of adsorbed molecules (which is not necessarily the same as the molecular diameter of the molecules), is dependent on the mode of stacking assumed for successive molecular layers in the adsorbed film. For nitrogen with
a hexagonal packing $\sigma = 3.54 \text{ Å}$ (Lippens et al., 1964) and for close packing $\sigma = 4.3 \text{ Å}$ (Shull, 1948). The value of the pore radius at a given pressure $p_1$ is therefore given by

$$r_{p_1} = r_{k_1} + t_1 \quad (6)$$

Details on the estimation of the pore size distribution from these equations can be found in the literature (Gregg and Sing, 1967; Satterfield, 1970; Dollimore and Heal, 1964). Although this procedure can also be used to calculate the cumulative pore area, $S_{\text{cum}}$, the value obtained is usually less accurate than the surface area obtained by the BET method. It should also be noted that the Kelvin equation is not applicable to pores below 1.5 nm in diameter.
CHAPTER 3. HIGH TEMPERATURE OXIDATION OF ZINC SULFIDE: KINETIC MODELING UNDER CONDITIONS OF STRICT KINETIC CONTROL

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Abstract

A detailed analysis of the oxidation of zinc sulfide particles was conducted in a thermobalance between 548 and 630°C with different oxygen concentrations. It was found that in the presence of external mass transfer effects, an oxysulfate intermediate was formed. However, when the flow rate was chosen such that this effect was eliminated, no sulfates were formed. Analysis of the controlling regimes indicated that even the use of small particles (<200 mesh) did not eliminate internal diffusional resistance. Thus using only the initial rate data, the surface reaction model \(-r = k \frac{[O_2]}{1 + K_A [O_2]}\) with no dissociation of oxygen was found to depict the data very well up to 609°C. Simple power law models were found to be wholly inadequate to represent the data.

Introduction

General

Many industrial processes are accompanied by the formation of H2S in admixture with H2, CO, CO2, steam, CH4, and higher hydrocarbons, e.g. pyrolysis, cracking, hydrocracking, hydrorefining, and gasification. The removal of sulfur from these fluid streams is necessary for several reasons. If the stream is to be released as a waste, then
environmental regulations dictate that the sulfur levels be between 10 and 500 ppm, depending on location. If the fluid is to be burnt as fuel, sulfur must be removed to much lower levels to prevent the poisoning of sulfur-sensitive catalysts or to satisfy process requirements.

Two of the processes requiring the most stringent permissible levels of sulfur are the Integrated Gasification Combined cycle (IGCC) and the Gasifier/Molten Carbonate Fuel Cells (MCFC) which could be used to generate electricity. Fuel gas obtained from gasifiers normally contains 500-2000 ppm of sulfur, but the gas turbine in the IGCC cannot tolerate more than 100 ppm. MCFCs require sulfur levels to be less than 1 ppm, a level which the present commercial wet-scrubbing process cannot attain. Furthermore, temperature and pressure matching of system components is essential to the economic viability of these IGCC and MCFC power systems.

Attempts to commercialize the combined cycle have renewed interest in the search for high temperature solid adsorbents for H₂S. Based on the thermodynamic analysis of Westmoreland and Harrison (1976), several oxides have generated great interest as possible sorbents. Single oxides such as ZnO, Fe₂O₃, and CaO as well as mixtures of zinc, iron, and titanium oxides have all been tested with varying degrees of success, but there is yet much uncertainty about the behavior of these oxides as H₂S sorbents.

Zinc oxide has received considerable attention as a possible high temperature desulfurization sorbent due to its ability to reduce H₂S to very low levels (<5 ppm). The
chemical changes that are believed to occur in the sorbent during this sulfidation are given by

$$\text{ZnO} (s) + \text{H}_2\text{S} (g) \rightarrow \text{ZnS} (s) + \text{H}_2\text{O} (g)$$

Studies by Gibson and Harrison (1980), Westmoreland et al. (1977), Yumura et al. (1985), Tamhankar et al. (1981), and Grindley and Steinfeld (1981) show that ZnO has a very high H$_2$S absorption rate. However, at temperatures above 800°C, vaporization of ZnO occurs due to reduction by the H$_2$/CO in the fuel gas. This results in cessation of the reaction with H$_2$S. In addition, the regeneration of ZnO at high temperatures and oxygen concentrations leads to the formation of zinc sulfate. These problems led to the study of mixed oxides with the aim of combining the positive aspects of each of the individual oxides. Thus oxides of ZnO-Fe$_2$O$_3$, CuO-Fe$_2$O$_3$, CuO-Al$_2$O$_3$, CuO-Fe$_2$O$_3$-Al$_2$O$_3$, ZnO-TiO$_2$, to name a few, have been studied (Tamhankar et al., 1981; Lew et al., 1989; Focht et al., 1988; Sa et al., 1989, Woods et al., 1990). ZnFe$_2$O$_4$ was found to decompose to ZnO and Fe$_3$O$_4$ in a reducing atmosphere (Focht, 1988), thus it is just as limited as its constituent single oxides. Copper ferrite was found to reduce H$_2$S to 2 ppm but very low sorbent utilization was observed (Grindley and Steinfeld, 1981).

Lercher et al. (1984) had established that since the amount of Zn$^{2+}$ cations on the surface of the ZnO-TiO$_2$ mixtures decreases as the amount of TiO$_2$ increases, ZnO could potentially be stabilized against reduction. This led Lew et al. (1989) to study highly porous ZnO as well as ZnO-TiO$_2$ mixtures as potential sorbents even though thermodynamically they have sulfidation equilibria inferior to that of ZnO. They found that
the mixed oxides were reduced to metallic zinc much slower than ZnO and could be used up to 90°C higher than ZnO. The sulfidation rates of these oxides were comparable to that of ZnO but the sorbent utilization was much lower. This is in addition to the theoretical sulfur capacity being much lower than that of ZnO since TiO₂ does not react with H₂S in the temperature region of interest.

Thus it can be seen that pure zinc oxide is yet to be matched in its sulfur removal capacity by any other oxide or combination of oxides, but the problems associated with its regeneration have to be addressed. The regeneration of zinc oxide is based on the reaction

\[ \text{ZnS}_{(s)} + \text{O}_2{(g)} \rightarrow \text{ZnO}_{(s)} + \text{SO}_2{(g)} \]  
(2)

The SO₂ produced during regeneration can either be converted to elemental sulfur for sale, or be used in the production of sulfuric acid. However, sulfate formation can also take place at low regeneration temperatures or at high oxygen concentrations, and this is one of the drawbacks which has restricted commercialization. ZnSO₄ being a compound with a larger molar volume than either ZnO or ZnS tends to block the pores in the sorbent, thus reducing its availability to the reactant gas. This then leads to low sorbent utilization at breakthrough.

**Oxidation of ZnS**

The oxidation of zinc sulfide has been studied from various perspectives over the years. Earlier studies were undertaken to understand the oxidation that occurs during the smelting of zinc, while more recently it has been studied to understand the various aspects
of the regeneration of zinc oxide. The main results are presented in Table 1, some of which are discussed below.

**Reaction Kinetics.** The kinetics of the oxidation of ZnS has been studied using natural crystals, synthetic powders, and pellets. Ong et al. (1956) investigated the kinetics of naturally occurring zinc sulfide single crystals, sphalarite, between 700 and 870°C in oxygen pressures from 6 to 640 mmHg. The Langmuir–Hinshelwood-Hougen-Watson model for adsorption of reactant, no adsorption of product,

\[
-r = \frac{k K_A [O_2]}{1 + K_A [O_2]}
\]

was found to be valid up to 830°C. Another study (Canon and Denbigh, 1956) examined the reaction of (110) faces of sphalarite at temperatures between 680 and 940°C with oxygen partial pressures between 0.014 and 0.50. The reaction was found to be chemically controlled below 830°C, while above 900°C thermal instabilities arose. At much higher temperatures, vaporization of zinc resulted.

Dimitrov and Boyanov (1963) studied the oxidation of sphalarite, marmatite, and a zinc sulfide concentrate containing 2.75% Pb, 1.105 Cu, 9.37% Fe, and 4.4% SiO₂. Their results showed that impurities, structural defects, particle size variation, and degree of crystallization all combined to give rise to differences in observed reaction rates. In addition, a mixture of sulfides behaved differently from individual components. On the other hand, Dimitrov and Paulin (1965) found the same value of activation energy, 57
kcal/mole, for all powdered ZnS and its naturally occurring forms: marmatite and sphalarite.

Dimitrov et al. (1967) studied the kinetics and mechanism of the oxidation of several crystalline forms of ZnS powders between 640 and 840°C. Investigations into their reactivity carried out in a differential thermal analyzer / fluidized bed under isothermal conditions showed that ZnO was the primary oxidation product and that the reaction was topochemical as well as autocatalytic in nature.

In a study to determine the kinetics of the oxidation of ZnS as part of the sulfidation–oxidation cycle used in desulfurization, Bagajewicz (1988) conducted a thermodynamic analysis of the reaction. The analysis showed the existence of an intermediate oxysulfate, $2\text{ZnSO}_4\cdot\text{ZnO}$, as a stable and separate phase at low temperatures and high oxygen concentrations. The analysis also showed that from a thermodynamic viewpoint, the direct formation of $\text{ZnSO}_4$ is more favorable than that of the intermediate, $2\text{ZnSO}_4\cdot\text{ZnO}$, which is also more favorable than the direct oxidation to ZnO. However, no evidence of the formation of an oxysulfate was obtained when high surface area ZnO, sulfided at 550°C in a fixed bed reactor, was oxidized in a thermogravimetric analyzer (TGA) back to the oxide. They attributed the initial rise in the rate of oxidation to the increase in interfacial area between the sulfide and oxide since the oxide has a lower molar volume. By correlating the maximum rate of reaction instead of the initial rates, the experimental data were found to conform to the surface reaction controlling Langmuir–Hinshelwood–Hougen–Watson model proposed by Ong et al. (1956).
An interesting result which appears to be inconsistent with the reaction controlling kinetic models proposed by others was reported by Gerlach and Stichel (1964). They found the reaction to be controlled by adsorption of oxygen on the surface of the ZnS pellets from 640 to 750°C and obtained an activation energy of 62.4 kcal/mole. Between 750 and 830°C, the reaction was diffusion controlled and a value of 3.5 kcal/mole was obtained. It should be noted that despite the difference in controlling mechanism, the activation energies arrived at were similar to those obtained by other workers.

**Regime Analysis.** In this section, some of the studies which have analyzed changes in the reaction regime are presented. While studying the oxidation of spherical pellets of zinc sulfide between 540 and 700°C, Wada and Niwa (1957) found that the reaction was chemically controlled up to 650°C with an activation energy of 50 kcal/mole. At temperatures above 650°C, the value obtained was 5 kcal/mole which indicated diffusional limitation. However, Denbigh and Beveridge (1962) established that a region of mixed control occurs between 650°C and 750°C. Natesan and Philbrook (1969b) investigated the kinetics of the oxidation of spherical pellets of ZnS which contained 12% Fe in a TGA. Reaction was conducted between 740 and 1020°C with oxygen mole fraction varying from 0.2 to 1.0. Since the reaction rate was found to be linear with oxygen concentration up to a conversion of 0.7, it was assumed to be first order. Mathematical models were formulated to predict the reaction rate on the assumption of a single transport or interface reaction step controlling. Their analysis indicated that diffusion throughout the oxide layer was the controlling factor with an activation energy of 7.2 kcal/mole.
It should be noted that the assumption of isothermality used by most researchers for this system hinges on the results of Natesan and Philbrook (1969a). They found that although temperature differentials of as much as 39°C existed for a pellet of diameter 1.3 cm at a reaction temperature of 961°C, this differential decreased as the pellet diameter decreased. Thus they concluded that for small pellets, the assumption of isothermality was valid. In a subsequent study (Natesan and Philbrook, 1970) they found that when the reaction was carried out in a fluidized bed between 670 and 960°C, with oxygen mole fraction varying between 0.2 and 0.4, chemical reaction at the outer boundary of the unreacted sulfide core was the rate controlling step.

Prabhu et al. (1984) oxidized cylindrical pellets of ZnS (97.4% pure) having different porosities in a TGA between 480 and 600°C with oxygen fraction varying from 0.108 to 0.514. Though the reaction order varied from 0.7 to 1.25, first order was assumed in the analysis. The temperature at which shift from chemical to mixed control occurred was found to depend on the pellet porosity.

Allay and Albitzen (1984) also studied several forms of ZnS (powdered, fused, and sintered) in a TGA with temperatures ranging from 517 to 830°C. Although the temperature at which chemical control dominated the reactions depended on the initial texture of the solid, the same values (77.9 kcal/mole and $1.74 \times 10^{13}$ cm/s) were obtained for the activation energy and frequency factor, respectively. These were calculated based on a reaction order of 2/3.
**Modeling.** Many different approaches have been taken in attempts to predict the progress of a noncatalytic gas-solid reaction. One approach analyzes simultaneous reaction and diffusion in the solid by considering the solid as a single macroscopic matrix while another considers the behavior of the individual grains in the solid matrix. From the previous sections we have seen that depending on the nature of the reactant and the reaction conditions, the reaction may be chemical or diffusion controlled. Furthermore, looking at the entire reacting matrix, the reaction may be homogeneous or topochemical.

Gokarn and Doraiswamy (1971) suggested that the oxidation of spherical pellets of ZnS was kinetically controlled between 600 and 670°C, diffusion controlled between 740 and 820°C, and in the intermediate temperature range both chemical and diffusion were simultaneously operative. The shrinking core model for kinetic control provided a good fit to their experimental data in the kinetic regime, while in the diffusion regime the ash-layer model did not fit. Instead they developed a model which took into account intraparticle resistance and this was found to fit much better. The model was subsequently extended to other shapes (Gokarn and Doraiswamy, 1973).

In a similar consideration of the shrinking core model, Takamura et al. (1974) reacted 0.99-1.15 cm spheres of ZnS in the temperature range 560-970°C in a TGA. In the study, the first order power law rate equation was used to show that below 580°C the reaction proceeded homogeneously with an activation energy of 34.8 kcal/mole. The shrinking core model equation for kinetic control also seemed to fit the data but photomicrographs revealed that there was a reaction zone rather than a reaction front,
confirming the observations of Gokarn and Doraiswamy (1971). Above 690°C, deviations from linearity occurred indicating topochemical reaction and application of the shrinking core model with gas film resistance controlling provided a good fit.

The fact that some reacting systems obey the homogenous model at low temperatures and shift to the shrinking core model at high temperatures, with a transition model applicable between these two extremes, led to the proposal of a zone model by Bowen and Cheng (1969). As an extension of this model, Mantri et al. (1976) postulated that reaction occurs in three stages: (1) zone formation, (2) zone travel, and (3) zone collapse. In the first stage, zone formation begins and as reaction progresses through to the second stage, the reaction zone moves inward. At the end of the reaction a third stage is reached where the zone begins to contract, having moved inward up to the particle center. They developed an equation for zone width, based on which criteria for the homogeneous and sharp interface models were proposed.

Experimental verification of the zone model for the oxidation of zinc sulfide pellets was conducted by Prasannan and Doraiswamy (1982). They found that the sulfur profiles obtained by Auger electron spectroscopy and electron microprobe analysis for cylindrical pellets of ZnS reacted in air at 600°C are consistent with the predictions of the three stage zone model of Mantri et al. (1976).

In a similar study, Rao and Kumar (1982) reacted cylindrical pellets of different porosities between 600 and 826°C. Although surface area measurements obtained from BET, optical microscope, and electron microscope were in close agreement indicating that
the particles were nonporous, experimental conversion vs. pellet length plots indicated the existence of a reaction zone and not a sharp interface as assumed in the shrinking core model. This led to the development of a model which took into account the variations in porosity and effective diffusivity as reaction progressed.

The effect of grain size distribution was investigated by Kimura et al. (1983). Their study was conducted in a differential reactor with 99% pure ZnS in the temperature range 680-940°C. The reaction order with respect to the solid reactant was found to vary with the standard deviation of the grain size distribution in a fashion commensurate with the grain model to which a grain size distribution had been applied. The reaction order with respect to the gas was found to be 0.5 in agreement with Canon and Denbigh (1956).

**Objectives**

The regeneration of ZnO has received considerable attention and the kinetic parameters reported in the literature were obtained under different rate controlling regimes. Data thus obtained do not reflect the true kinetics and should not be used as such. Even data obtained in the same regime differ by as much as an order of magnitude. This type of disparity brings into question the validity of some of the studies reported. In the light of this observation, the present research was undertaken with the following objectives:

1. To determine the conditions, if any, under which sulfates are formed during the oxidation, since this will influence the kinetic analysis.

2. To determine the *intrinsic kinetics* of the regeneration process, i.e. the oxidation of ZnS, with unequivocal elimination of falsifying effects.
This constitutes part I of the overall program to develop a comprehensive model for this reaction which incorporates the effects of structure evolution with the progress of reaction.

**Experimental Section**

The kinetic studies were conducted using a Perkin Elmer thermogravimetric analyzer equipped with a high temperature furnace. It consists of an electrobalance which monitors any weight changes during the reaction, a platinum sample stirrup-pan assembly suspended via a platinum hangdown wire from this balance, and a glass furnace tube which is surrounded by a furnace. Sample temperature is monitored by means of an exposed junction Pt-Pt/10Rh thermocouple which is located 1 cm from the top of the sample pan and controlled by referencing it to the programmed set point. Furnace temperature is controlled by a Pt-Pt/10Rh oven thermocouple. The TGA is connected to a computer loaded with the TGA 7 series/UNIX software. Other components include a TAC 7/DX thermal analysis instrument controller, a GSA 7 gas selector accessory, and an HP graphics plotter. All these combine to provide total computerized control of the thermobalance.

A schematic diagram of the entire experimental set-up is shown in Fig. 1. All the gas flow rates were controlled using Brooks 5850E mass flow controllers. Argon and helium gases were passed through oxygen and water traps upstream of the mass flow controllers. Argon was used as the balance purge while helium or oxygen was used as the reactant purge which was fed directly into the furnace tube. BET surface area measurements were made using a Micromeritics Accusorb 2100 E instrument, X-ray diffraction (XRD) was done with Cu(kα1) radiation in a Siemens 500D diffractometer
equipped with a graphite mono-chromator, and x-ray fluorescence using the method of known addition was used in the quantification of the amounts of the phases. The reagent grade zinc sulfide used in the oxidation studies was supplied by MCB Manufacturing Chemists, Inc. X-ray diffraction showed that the material contained some barium sulfate, and by X-ray fluorescence the amount was found to be 2.6 % (weight basis). The surface area of the <200 mesh particles used in the oxidation experiments was found to be 8.459 m$^2$/g using krypton as the adsorbent.

Isothermal reactions were carried out between 548°C and 680°C and oxygen mole fraction was varied from 0.1 to 0.46. Preliminary experiments had indicated that correct temperature ramp and gas flow rate were necessary in order to ensure the integrity of the sample at the start of the oxidation. For each run, the total gas flow rate was 86 cm$^3$/min for a fixed amount of ZnS (14.4 mg) placed in the sample pan (diameter: 6 mm; thickness: 3 mm). By using this amount of material the same sample could be used for both XRD and BET surface area determination. This ensured that the surface area and phases identified were obtained under identical experimental conditions.

While flowing Ar and He, the sample temperature was raised at 5°C/min to 120°C and held there for 1 hour to remove any adsorbed species. After this, the ramp was continued to the desired reaction temperature. A ten minute stabilization period was allowed before the reactant purge was automatically switched from helium to oxygen by the GSA. At the end of each run, the samples were stored in a dessicator for subsequent phase identification. Four replicates were obtained at each set of conditions.
For each temperature and at each oxygen concentration, blank runs were conducted using the same ramp conditions. The results from these runs were used as correction factors for the oxidation runs. This was necessary because of the apparent weight gain with increase in temperature which is an inherent characteristic of thermogravimetric analyzers. This weight gain usually arises from one or a combination of the following phenomena: decreased buoyancy, increased convection, and the effect of heat on the balance mechanism. Fig. 2 shows the effect of not compensating for this apparent weight gain. It can be seen that lower conversions are obtained when this buoyancy effect is not taken into consideration, and could drastically alter the reaction rates calculated, hence the kinetic parameters obtained. While this effect has been taken into account by some investigators, others have neglected it. The weight loss-time data obtained from the TGA were converted into conversion-time using the expression:

\[
X = \frac{W_0 - W_i}{0.165 \times 0.974 \times W_0}
\]  

(4)

The rate of reaction was then expressed as

\[
-r = \left( \frac{1}{M_{ZnS}} \right) \left( \frac{dX}{dt} \right), \quad \frac{\text{mol ZnS}}{g \text{ZnS} \cdot \text{min.}}
\]  

(5)

The initial rate was obtained by taking the value at zero time of a polynomial fitted to the experimental data.
Results and Discussion

Effect of Hydrodynamics

The absence of gas film diffusion can be ascertained by comparing the effect of hydrodynamics in the TGA at fixed levels of kinetic factors (Doraiswamy and Sharma, 1984). If the same ratio of sample weight to flow rate (W/F) is maintained, a plot of conversion vs. flow rate should flatten out in the region in which external mass transfer effects are negligible. A sample plot of the results of these studies at 680 °C is shown in Fig. 3. It can be seen that above 85 cm³/min, the curves are essentially flat. Thus all the reactions were conducted at W/F = 0.18 and a flow rate of 86 cc/min.

Sulfate/Oxysulfate Formation

Using the established flow rate and an oxygen mole fraction of 0.1, several runs were made at 630°C to different extents. The first was stopped after 6 min in oxygen (A), the second after 14 min (B), and the 3rd after 24 min (C). These corresponded to conversions of 0.17, 0.61, and 0.86, respectively. X-ray diffraction (Fig. 4) showed that only mixtures of ZnO, ZnS, and BaSO₄ were present. This same trend was observed at other temperatures and oxygen concentrations.

However, when the flow rate was reduced to 62 cc/min, moving the reaction to the external diffusion limited regime, ZnO, ZnS, BaSO₄, and 2ZnSO₄·ZnO (oxysulfate) were present at all temperatures. The diffractogram (low theta values) for a sample reacted for 7 min (X = 0.75) at 548 °C and oxygen mole fraction of 0.3 (Fig. 5) clearly shows the
presence of $2\text{ZnSO}_4\cdot\text{ZnO}$ ($\ddagger$) in addition to $\text{BaSO}_4$ ($\ast$). When the reaction was taken to completion, only $\text{ZnO}$ and $\text{BaSO}_4$ were present.

These results seem to indicate that under external diffusion control, the reaction progresses via an oxysulfate intermediate which then decomposes to $\text{ZnO}$ in the absence of $\text{ZnS}$. This, although thermodynamically more favorable than direct oxidation, is less favorable than the formation of $\text{ZnSO}_4$ as the intermediate (Bagajewicz, 1988).

**Autocatalysis**

The conversion-time plots obtained from the TGA are all S-shaped which is characteristic of autocatalytic reactions. Dimitrov et al. (1967) had concluded that this system was autocatalyzed by $\text{ZnO}$, but the results obtained from the present study indicate otherwise. By adding various amounts of $\text{ZnO}$ to the $\text{ZnS}$ sample at the onset of reaction, the oxidation was carried out to completion. A comparison of the conversion-time data (Fig. 6) showed that all the reactions were identical. The S-shape is, therefore, due to the dead time in getting to the full oxygen concentration when the reactant purge is switched from the helium to oxygen, and not due to autocatalysis. This dead time was deleted before the data was analyzed.

**Regime Analysis**

Rate data obtained under conditions of diffusional interference cannot be used directly to determine kinetic parameters – they would have to be suitably corrected. To avoid the need for correction using reported correlations (which are all approximate), reactions should be conducted under conditions in which these diffusional effects are...
undoubtedly absent. Although by comparing the hydrodynamic and kinetic factors, the existence of gas film diffusion resistance has been ruled out, the effects of other resistances (such as diffusion through the product or ash layer) or its combination with reaction and/or film diffusion were unknown. Knowing that single step rate determining processes are limiting cases, the shrinking core model was used to ascertain the contributions of these resistances.

Analysis showed that chemical reaction as a single step is not controlling (Fig. 7) nor is ash layer resistance. Thus the reaction is under mixed control – even the small particles (74 μm) used did not ensure the absence of ash diffusional limitations. This is an example of some of the difficulties encountered in studying this reaction. The only time when the reaction is unequivocally under chemical control is at the onset of reaction after the gas film diffusion has been eliminated, when no product layer has yet been formed. Thus this study was divided into two sections: initial rate analysis, and global rate analysis (complete modeling). Only the results of the initial rate analysis are presented in this paper. Determination of the parameters governing the global reaction rate will be included in a future communication.

Initial Rate Analysis

Initial rate data can be analyzed in two ways: by using the power law model or by Langmuir-Hinshelwood-Hougen-Watson (LHHW) models.

*Power Law Models.* The power-law model for ZnS oxidation is given by:
The order of the reaction was determined at different temperatures by plotting $\ln(r)$ against $\ln(C_{O_2})$. Plots obtained at 548 and 630°C are shown in Figs. 8 and 9. These are both linear plots but the linear regression equations obtained for the fit indicate that the slopes are significantly different; the reaction order increases from 0.63 at 548°C to 1.335 at 630°C. This brings into question the validity of simply assuming that the reaction is first order whenever the plot is linear as has been done by some workers (e.g. Westmoreland et al., 1977; Lew et al., 1992b). It also sheds more light on the reason why there is so much disparity in the reaction orders determined by several investigators.

Even if it were assumed that the reaction order was one, the Arrhenius plot of the reaction rate constant indicates two different activation energies for the temperature range studied which could be indicative of a shift in controlling mechanism of the reaction. While a postulate of just a shift in controlling mechanism may be acceptable for homogeneous reactions, for heterogeneous reactions nonreaction factors such as adsorption and desorption can profoundly influence reactivity. These effects are best considered using Langmuir-Hinshelwood-Hougen-Watson models.

*Langmuir-Hinshelwood-Hougen-Watson Models.* The power law equation assumes that the driving force for reaction is a function of the concentration of the reacting species in the fluid phase and not of the concentration of the adsorbed species on the sorbent which is more logical. By relating these surface concentrations to those existing in the bulk phase (through the use of adsorption isotherms), the reaction rate is formulated in terms of
measurable concentrations. A number of LHHW models were considered. The models based on surface reaction controlled are listed in Table 2 (Doraiswamy and Sharma, 1984). From a detailed statistical analysis of the data, it was found that the model

$$-r = \frac{kK_A [O_2]}{1 + K_A [O_2]}$$  \hspace{1cm} (7)

for reaction control, single site adsorption accurately describes the true kinetics of the reaction up to 609°C. The surface reaction rate constant $k$, and the adsorption equilibrium constant $K_A$ are given by Eqns. 8 and 9 below.

$$k = 4.089 \times 10^{20} \exp(-46110/T) \text{ mole ZnS/gZnS \cdot min.} \hspace{1cm} (8)$$

$$\ln K_A = 29300 - 23.54, \text{ cm}^3/\text{mol} \hspace{1cm} (9)$$

Fig. 10 shows a comparison of calculated and experimental rate values. The goodness of fit is established by the value of 0.986 obtained for the coefficient of determination, $R^2$.

**Conclusions**

From several considerations ZnO appears to be a very good candidate as a sorbent for H$_2$S removal from fuel gases. A survey of the literature revealed that a large number of studies have been carried out on the oxidation of ZnS to ZnO — which constitutes the regeneration step in the overall cycle for sulfur removal using ZnO. Any comprehensive modeling of each of these reactions requires an equation for the intrinsic reaction rate as well as additional data on pellet behavior during reaction to enable detailed modeling. The present study, which is restricted to a kinetic analysis of the oxidation reaction, was undertaken in view of the highly contradictory nature of the reported results.
Experimental studies show that elimination of the external mass transfer effect is essential since in its presence the course of the reaction itself changes: an oxysulfate is formed as intermediate which complicates the kinetic analysis. It was also found that the reaction is not autocatalytic as reported by some investigators. Another important observation was that it is practically impossible to run this reaction under conditions where internal ash layer diffusional effects are absent.

Thus to get the intrinsic kinetics it is essential that the rate data be obtained at gas velocities that would eliminate external mass transfer effects and at initial conditions when no ash layer would have been formed. Great care was taken to ensure that data were obtained under these very stringent conditions.

These data were then subjected to kinetic analysis using a number of possible Langmuir-Hinshelwood-Hougen-Watson models and the final rate expression obtained indicates that the reaction is surface reaction controlled with single site involvement and no dissociation between 548 and 609°C. The rate and adsorption constants can be expressed in the usual Arrhenius form.

**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F$</td>
<td>gas flow rate, cm$^3$/min</td>
</tr>
<tr>
<td>$k$</td>
<td>reaction rate constant, mol ZnS/g ZnS min</td>
</tr>
<tr>
<td>$K_A$</td>
<td>adsorption equilibrium constant, cm$^3$/mol</td>
</tr>
<tr>
<td>$M_{ZnS}$</td>
<td>molecular mass of ZnS, g/mol</td>
</tr>
<tr>
<td>$n$</td>
<td>reaction order</td>
</tr>
</tbody>
</table>
[O$_2$] concentration of oxygen, mol/cm$^3$

-r rate of reaction, mol ZnS/g ZnS min

$S_w$ surface area of ZnS, m$^2$/g

$W_0$ initial weight of sample, mg

$W_t$ weight of sample at time t, mg

$X$ conversion at time t

References


Table 1. Kinetic parameters and controlling regimes in zinc oxide oxidation

<table>
<thead>
<tr>
<th>ZnS form</th>
<th>Kinetic control model</th>
<th>E, kcal/mole</th>
<th>Diffusion/mixed control range, °C</th>
<th>E, kcal/mole</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td>crystals</td>
<td>700-870</td>
<td>LIIIW</td>
<td>60.3</td>
<td>-----</td>
<td>Ong et al. (1956)</td>
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<tr>
<td>crystals</td>
<td>680-870</td>
<td>PL, n = 0.5</td>
<td>50.4</td>
<td>830-900</td>
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<tr>
<td>pellet</td>
<td>500-650</td>
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<td>41</td>
<td>650-750 (m)</td>
<td>Denbigh and Beveridge (1962)</td>
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<tr>
<td>pellet</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>750-1250 (d)</td>
<td></td>
</tr>
<tr>
<td>pellet</td>
<td>540-650</td>
<td>----</td>
<td>50.0</td>
<td>&gt; 650</td>
<td>Wada and Niwa (1957)</td>
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<tr>
<td>pellet</td>
<td>640-750</td>
<td>LIIIW</td>
<td>62.5</td>
<td>750-830</td>
<td>Gerlach and Stichcel (1964)</td>
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<tr>
<td>pellet</td>
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<td>----</td>
<td>----</td>
<td>&gt; 675</td>
<td>Natesan and Philbrook (1969)</td>
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<tr>
<td>pellet</td>
<td>600-670</td>
<td>----</td>
<td>7.6</td>
<td>740-820</td>
<td>Gokarn and Doraiswamy (1971)</td>
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<tr>
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<td>560-690</td>
<td>PL, n = 1</td>
<td>34.8</td>
<td>600-690 (m)</td>
<td>Takamura et al. (1974)</td>
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<tr>
<td>pellet</td>
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<td>----</td>
<td>&gt; 690 (d)</td>
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<td>pellet</td>
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<td>----</td>
<td>33.1</td>
<td>----</td>
<td>Agarwal and Mohanty (1976)</td>
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<td>ZnS form</td>
<td>Kinetic control model</td>
<td>Kinetic control range, °C</td>
<td>Kinetic control E, kcal/mole</td>
<td>Diffusion/mixed control range, °C</td>
<td>Diffusion/mixed control E, kcal/mole</td>
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<td>----------</td>
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<tr>
<td>pellet</td>
<td>----</td>
<td>600-826</td>
<td>----</td>
<td>----</td>
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<tr>
<td>pellet</td>
<td>PL, n = 1</td>
<td>480-570</td>
<td>84.4</td>
<td>570-580 (m)</td>
<td>----</td>
</tr>
<tr>
<td>pellet</td>
<td>----</td>
<td>517-740</td>
<td>77.9</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>particles</td>
<td>----</td>
<td>690-960</td>
<td>PL, n = 1</td>
<td>40.3</td>
<td>----</td>
</tr>
<tr>
<td>particles</td>
<td>----</td>
<td>625-900</td>
<td>----</td>
<td>45.39</td>
<td>----</td>
</tr>
<tr>
<td>particles</td>
<td>PL, n = 0.5</td>
<td>----</td>
<td>58.3</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>particles</td>
<td>----</td>
<td>----</td>
<td>33.2</td>
<td>----</td>
<td>----</td>
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</tbody>
</table>

LIHIW: Langmuir-Hinshelwood-IIougen-Watson, PL: power law, n: reaction order, m: mixed control, d: diffusion control
Table 2. Detailed rate equations for the LHHW models

<table>
<thead>
<tr>
<th>Model</th>
<th>Rate equation</th>
<th>Linearized form</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Single site, non-dissociative adsorption reaction ZnS + O$_2$(^*$</td>
<td>(-r = \frac{kK_A[O_2]}{1 + K_A[O_2]})</td>
<td>(-\frac{1}{r} = \frac{1}{k} + \frac{1}{kK_A} \left( \frac{1}{[O_2]} \right))</td>
</tr>
<tr>
<td>2 Single site, dissociative adsorption reaction ZnS + O$^*$</td>
<td>(-r = \frac{k(K_A[O_2])^{1/2}}{1 + (K_A[O_2])^{1/2}})</td>
<td>(-\frac{1}{r} = \frac{1}{k} + \frac{1}{(kK_A)^{1/2}} \left( \frac{1}{[O_2]} \right)^{1/2})</td>
</tr>
<tr>
<td>3 Dual site, dissociative adsorption reaction ZnS + 2O$^*$</td>
<td>(-r = \frac{k(K_A[O_2])}{(1 + (K_A[O_2])^{1/2})^2})</td>
<td>(-\left( \frac{1}{r} \right)^{1/2} = \left( \frac{1}{k} \right)^{1/2} + \frac{1}{(kK_A)^{1/2}} \left( \frac{1}{[O_2]} \right)^{1/2})</td>
</tr>
</tbody>
</table>
Balance purge

P.E. 7 series

Reactant gas

OWV: One way valve

MFC: Mass flow controller

Fig. 1 Schematic Diagram of Experimental Apparatus
Fig. 2 Buoyancy Effect
Fig. 3 Conversion vs. Flow Rate for w/F = 0.18, O2 = 0.1, T = 670°C
Fig. 4  XRD at $T = 630^\circ C$, $F = 86$ cc/min.
Fig. 5 XRD at T = 548°C, F = 55 cc/min
Fig. 6 Verification of Absence of Autocatalysis

- **no ZnO added**
- **2mg ZnO added**
- **4mg ZnO added**
Fig. 7 Test for Determining Chemical Reaction Control
Fig. 8 Linearized Power Law Model at $T = 548^\circ C$
Fig. 9 Linearized Power Law Model at $T = 630^\circ C$

The equation for the model is $10.07 + 1.335^x$.
Fig. 10 Comparison of Model and Experimental Data
CHAPTER 4.  **HIGH TEMPERATURE OXIDATION OF ZINC SULFIDE: ANALYSIS OF CHANGES IN SORBENT STRUCTURAL PARAMETERS**

A paper to be submitted to Chemical Engineering Journal

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**Abstract**

Variations in surface area, pore volume and pore size distribution caused by sintering with and without reaction have been determined for the oxidation of zinc sulfide between 575 and 640°C. It has been shown that sintering reduces the surface area and increases the average pore size. In the absence of sintering, the oxidation of zinc sulfide results in a monotonic increase in surface area and decrease in pore volume, while under reaction/sintering conditions the surface area increases up to \( X = 0.75 \) and then decreases sharply. However, the surface area of the product was found to be greater than that of the reactant at all temperatures investigated. Samples reacted under different conditions but which showed the similar pore volume were found to exhibit very different pore size distributions.

**Introduction**

The production of high temperature \( \text{H}_2\text{S} \)-free coal derived gas is a necessity for the viability of molten carbonate fuel cells (MCFC) and integrated gasification combined cycles (IGCC) — electricity generating plants of the future. The search for a suitable sorbent has been undertaken over the past three decades by numerous researchers, and zinc
oxide based sorbents have been identified as most promising — zinc oxide has the ability to reduce H₂S levels to below 5 ppm.

Gibson and Harrison (1980), Westmoreland et al. (1977), Yumura and Furimsky (1985), and Grindley and Steinfeld (1981) have shown that ZnO has a very high H₂S absorption rate. However, its regeneration has proven difficult — regeneration at low temperatures and high oxygen concentrations lead to the formation of zinc sulfate which prevents complete regeneration while high temperature regeneration causes loss of surface area due to sintering.

These difficulties led to the investigation of mixed oxides with the hope of harnessing the positive aspects of zinc oxide while minimizing the negatives. ZnO-Fe₂O₃, CuO-Fe₂O₃, CuO-Al₂O₃, CuO-Fe₂O₃-Al₂O₃, ZnO-TiO₂, to name a few, have been studied (Lew et al., 1989; Focht et al., 1988; Sa et al., 1989). Focht et al. (1988) found that in the reducing atmosphere of coal-derived gases, ZnFe₂O₄ decomposes to ZnO and Fe₃O₄, thus it is just as limited as the single oxides. On the other hand, CuO-Fe₂O₃ was found to exhibit very low sorbent utilization by Grindley and Steinfeld (1981). Lew et al. (1992b) also found that although Zn-Ti-O oxides were capable of operating at temperatures up to 94°C higher than ZnO, sorbent utilization prior to breakthrough was very low. All the other mixed oxides studied thus far performed less effectively than zinc oxide.

This has resulted in a renewed interest in investigating the sulfidation-regeneration of zinc oxide. A recent paper (Sofekun and Doraiswamy, 1996) reported the intrinsic kinetic parameters of regeneration. The present communication is concerned with the changes in
structural parameters such as surface area, pore size distribution and average pore size, which are known to play important roles in the global rate of gas-solid reactions. Pore volume and pore size distribution are particularly important since they influence the transport resistances in the sorbent. In extreme cases such as the reaction of SO$_2$ with calcium based sorbents, the severity of these structural property changes render the reacting gases incapable of penetrating the interior of the pellet, thus causing the reaction to cease before all reactant solid is consumed (Borgwardt and Harvey, 1972). It is therefore obvious that commercialization of any sorbent is dependent on its maintaining favorable structural properties over several sulfidation-regeneration cycles.

Literature Review

*Experimental.* Several experimental studies have generally been conducted with the following objectives: to provide structural information that could be used in developing new models, such as physical property variations with conversion and position in reactor, or ascertain the viability of the sorbent over several sulfidation-regeneration cycles. In general, structural changes can be attributed, in the absence of sintering, to the differences between the molar volumes of the reactant and the product. For the zinc oxide-zinc sulfide system, the molar volume of zinc sulfide is greater than that of zinc oxide. Therefore, theoretically, there should be a loss of surface area, increase in porosity, and shift towards smaller pores during sulfidation and vice-versa. However, as will be shown in subsequent paragraphs, experimental results on a number of solids have presented some interesting results.
The physical properties of unreacted and reacted commercially prepared zinc oxides were compared by Efthimiadis (1993a, b). Although the total pore volume was restored after regeneration, a significant loss in surface area persisted. This trend was also observed by Grindley (1988). In addition, there was a shift in the pore size distribution towards larger pore sizes, which was anomalous considering that ZnS being bigger than ZnO should clog the pores and shift the distribution curve towards smaller pore sizes, and the same sorbents when reacted in a fluidized bed reactor had not shown this behavior. This anomaly was attributed to reaction with water vapor in the fixed bed reactor.

In a later study, Christoforou et al. (1995b) found that ZnO supported on either α-alumina or magnesia showed insignificant changes in physical properties upon sulfidation at 600°C and regeneration at 700°C in a fluidized bed. On the other hand, Lew et al. (1992b) found that all Zn-Ti-O materials showed an increase in surface area upon sulfidation.

In 1990 Woods et al. studied the sulfidation and regeneration of zinc oxide-titanium oxide sorbents in the temperature range 650-760°C and observed little deterioration in sorbent reactivity over five cycles. This was ascribed to the complete restoration of the changes which must have occurred during the sulfidation process by the regeneration step.

All these studies have either neglected the effect of sintering which accompanies high temperature reactions (most materials usually experience loss of surface area and porosity when exposed for extended periods of time to temperatures greater than 0.4 T_m, the
Tanunan temperature, where $T_m$ is the absolute melting temperature of the material), or have been conducted on sorbents pretreated at high calcination temperatures.

Although the effect of sintering has been intensively studied for heterogeneous catalysts, very few attempts have been made to extend the studies to gas-solid noncatalytic systems. Earlier studies (Szekely and Evans, 1971a,b; Kim and Smith, 1974) had shown that the value used for pellet diffusivity, which often changes during the course of the reaction due to changes in pore structure, could determine the accuracy of the prediction of the conversion-time behavior. More recently, Sa et al. (1989) found that although cylindrical extrudates of zinc ferrite pretreated at 815°C did not exhibit further sintering when exposed to 700°C for up to 8 hr, the products of sulfidation (FeS and ZnS) did sinter between 600°C and 800°C as evidenced by the decrease in surface area and increase in average pore radius. However, there was no significant change in pore volume. Above 800°C, the pore volume decreased. Their data also showed a steady decrease in specific surface area and pore volume with fractional sulfidation; the plots were essentially parallel for all temperatures between 420 and 750°C for surface area and coincidental for pore volume. Furthermore, regeneration at temperatures below 650°C resulted in restoration of a portion of the decrease in the surface area and pore volume which accompanies sulfidation. However, above 750°C the surface area was further reduced while a bimodal pore size distribution was observed after regeneration, being most pronounced at 650°C. This shows that even calcined materials are not exempt from the effects of sintering.
While the majority of studies carried out have been on the sulfidation process, one study on the oxidation of pellets of CaS to CaO (Torres-Ordoñez et al., 1989) found that the pellet surface area increased with CaS conversion between 1400 K and 1750 K since there was no product sintering. Their data showed neither temperature nor oxygen mole fraction dependency. They also found that porosity remained unchanged up to a conversion of 50% after which it increased with conversion.

**Modeling.** Models for predicting the global rate of reaction for gas-solid reactions in general have evolved from constant structural property assumptions to variable property models. These models can be broadly classified into two categories: models that consider the solid as a collection of pores (Szekely and Evans, 1970; Bhatia and Perlmutter, 1981; Gidaspow, 1972; Hartman and Coughlin, 1976; and Ramachandran and Smith, 1977), and those that regard the pellet as a solid consisting of grains which change in size as the reaction proceeds (Calvelo and Smith, 1970, Szekely and Evans, 1970; Georgakis et al., 1979; Hartman and Coughlin, 1976). The models discussed with applicability to the sulfidation of zinc oxide, are based essentially on the general principles outlined in the models just mentioned.

Ranade and Harrison (1981) investigated the ZnO-ZnS system with the aim of verifying the modified grain model (Ranade and Harrison, 1979). A more detailed study was carried out on the MnO-MnS system by Caillet and Harrison, 1982. These two studies attempted to examine the effects of sintering alone, chemical reaction alone, and the combined effect of sintering and chemical reaction.
For pure sintering effects, Ranade and Harrison (1981) found that the following equation (Nicholson, 1965) described the sintering characteristics of the ZnO-ZnS system between 500 and 800°C:

\[
\frac{S(t) - S_e}{S_0 - S_e} = e^{-k_j t}
\]  

where \( k_j \) = the sintering rate constant defined by

\[
k_j = k_{j0} \exp (-E_j/RT)
\]

and

\( S_e = \) the equilibrium surface area defined by

\[
S_e = S_0 \exp[-d(T-623)]
\]

Caillet and Harrison (1982) tested the following sintering models:

(a) \[
\left( \frac{S_0 - S}{S_0} \right)^\alpha = K(T)t
\]

which had been shown to apply to the initial sintering stage by German and Munir (1976); and

(b) \[
\frac{dS}{dt} = -B(T)S^b
\]

for the intermediate sintering stage (German, 1978). Upon using a modification suggested by Shaffler et al. (1957), this model becomes

\[
\frac{dS}{dt} = -B_o e^{-E/RT} S_0^{1-b} S^b
\]
which also applies to the intermediate stage. They found that Eqn. 6 was a better fit for both MnO and MnS sintering data.

The effect of chemical reaction on surface area was studied by first assuming that the grain model (Szekely and Evans, 1970) was obeyed, i.e.

\[
S = \frac{S_0[1 + \bar{X}(\gamma - 1)]^{2/3}}{1 + \bar{X}\left(\gamma \frac{v_D}{v_B} - 1\right)} \tag{7}
\]

but this equation predicted an increase in surface area with conversion while their data showed the opposite. Therefore, the equation proposed by Ranade and Harrison (1981) which had predicted a decrease in surface area with increase in conversion

\[
\frac{S - S_D}{S_0 - S_D} = (1 - \bar{X})^\beta \tag{8}
\]

was expanded into a single constant equation

\[
S = \frac{S_0(1 - \bar{X}) + \bar{X}\gamma v_D S_D}{(1 - \bar{X}) + \frac{\bar{X}\gamma v_D}{v_B}} \tag{9}
\]

and was found to fit their data better.

The data used by both Ranade and Harrison (1981) and Caillet and Harrison (1982) were obtained by first reacting the sorbent at a low temperature and then subjecting it to high temperatures where the effect of sintering was studied. This, as will be shown in this paper, does not present a true picture of the structural changes which take place due to
Simultaneous sintering and reaction. In addition, the changes in pore volume and pore size distribution are also discussed.

**Experimental**

**Reaction and Sintering Studies**

The reagent grade zinc sulfide used in the oxidation studies was supplied by MCB Manufacturing Chemists, Inc. X-ray diffraction showed that the material contained some barium sulfate, and the amount was found to be 2.6 wt % by X-ray fluorescence. The oxidation of zinc sulfide was conducted in a Perkin Elmer thermogravimetric analyzer (TGA 7) equipped with a high temperature furnace. Details of the experimental set-up have been presented elsewhere (Sofekun and Doraiswamy, 1996).

The flow rates of the high purity gases (Ar, He, O₂) used in the study were controlled using Brooks 5850E mass flow controllers. For each run, the total gas flow rate was 86 cm³/min and a fixed amount of ZnS (14.4 mg) was placed in the sample pan (diameter: 6 mm; thickness: 3 mm). While flowing Ar and He, the sample temperature was raised at 5°C/min to 120°C and held constant for 1 hr to remove any adsorbed species. After this, the ramp was continued to the desired reaction temperature. A ten minute stabilization period was allowed before the reactant purge was automatically switched from helium to oxygen by the gas selector accessory.

Isothermal reactions were carried out at 575, 605, and 640°C and oxygen mole fraction was varied from 0.1 to 0.46. For each temperature and at each oxygen concentration, blank runs were conducted using the same ramp conditions. The results
from these runs were used to correct for the apparent weight gain with increase in
temperature which is an inherent characteristic of thermogravimetric analyzers. The weight
loss-time data obtained from the TGA were converted into conversion-time data using the
expression:

$$X = \frac{W_0 - W_i}{0.165 \times 0.974 \times W_0}$$  \hspace{1cm} (10)

Runs were carried out to conversions of ~ 0.25, 0.76, and 0.96. For the sintering studies, the
gas was not switched to oxygen. Instead, helium was allowed to flow for times equivalent
to those required to obtain 0.25 and 0.96 conversions at each concentration and temperature.
In addition, samples corresponding to no conversion, i.e., after 10 min at the desired
temperature, were also analyzed. At the end of each run, the samples were stored in a
dessicator for surface area and pore size distribution measurements.

**Surface Area Measurement**

Surface area and pore volume determinations were made on the same 14 mg sample.
The Micromeritics ASAP 2010 sorptometer which was used is capable of measuring the
surface area of samples as low as 0.05 m$^2$. This high level of precision makes it possible to
use the sample from a single run rather than combine samples from different runs in order
to get a batch large enough for surface area determination as has been the practice (Lew et
al., 1992, reacted 1-3 mg of sample in a TGA to obtain kinetic data while 40-60 mg were
used for surface area analysis). However, the accuracy of the measurement from the ASAP
2010 becomes highly dependent on the accuracy of the weighing balance. In this study the
balance used had an accuracy of 0.1 mg. In addition, straight-walled rather than bulb sample tubes were used in order to minimize the dead space. The samples were outgassed for 1 hr at 150°C and 10 x 10^{-6} Torr prior to analysis. The surface areas of the samples were determined using krypton as the adsorbate due to the small sample size (ca 0.1 m^2). For all the measurements made, the range of linearity was between P/P_0 = 0.05 and 0.3. The value of C, the constant in the BET equation, was greater than 50 since when krypton is used as adsorbate low values of C will lead to incorrect surface areas. A cross-sectional area of 0.24 nm^2 was used for krypton in the surface area measurements and this was determined by matching the krypton and nitrogen surface area. The surface area of the <200 mesh particles used in the oxidation experiments was found to be 8.259 m^2/g with krypton as adsorbent.

**Pore Volume and Pore Size Distribution Measurement.**

The ASAP 2010 was also used for pore volume determination using nitrogen as adsorbate at 77 K. The desorption BJH method was used with the thickness of the multilayer liquid still adsorbed on the wall of the pores being given by the Halsey equation

\[
t = 3.54 \left( \frac{5}{\ln(P/P_0)} \right)^{1/3}
\]

Since the use of nitrogen to estimate the surface area of materials when the total surface area is less than 1 m^2 results in errors, the cumulative pore area estimated during this process was incorrect. This led to incorrect estimation of volume adsorbed. Therefore,
since this error applies equally to all samples, a qualitative analysis can be made of the pore volumes and pore size distributions.

Results and Discussion

The experiments in this study were designed to evaluate the trends observed by several investigators on a variety of metal oxides/metal sulfides. However, disparity between our data and previously reported data necessitated inclusion of a few experiments to investigate the effect of sintering. Thus the data obtained on sintering are by no means exhaustive and are not ideal for establishing the kinetics of sintering, but are suitable for confirming the validity of the reaction experiments.

Sintering of ZnS

Changes in Surface Area. Fourteen milligram samples were exposed to helium and argon at 585, 620, and 650°C for two different lengths of time: the first (A) corresponds to the time that the sample stays in the furnace while the system is being brought to the reaction temperature, and (B) corresponds to the time of reaction at a concentration of 10% oxygen-90% argon to reach a 95% conversion. The specific surface areas of a sample of unreacted <200 mesh zinc sulfide and of the sintered samples were then determined. The results along with 95% confidence intervals are shown in Table 1. Note that in order to standardize the table, the time at which the sample is deemed stable at the reaction temperature is called zero time but the actual time spent in the TGA (which is dependent on the ramp and equalization time as described in the experimental section) is indicated in parentheses.
The original surface area of the ZnS was $8.2594 \pm 0.0394 \text{ m}^2/\text{g}$. By the time the sample had stabilized at 640°C, the surface area had decreased to $7.45 \text{ m}^2/\text{g}$ and further decreased to $6.54 \text{ m}^2/\text{g}$ at 69 min. The same trend was recorded at 605 and 575°C. This set of data was analyzed using Eqn. 4 since $(S_o - S)/S_o < 0.5$ and this was the limit defined for the equation. The value of $\alpha$ was found to vary between 1.1 and 1.57. This value matched those obtained by German and Munir (1975b) and Caillet and Harrison (1982). Therefore, it can be safely assumed that Eqn. 4 applies to the initial stage of ZnS sintering.

**Changes in Pore Volume and Pore Size Distribution.** The pore volume of the unreacted ZnS sample was found to be $0.08 \text{ cm}^3/\text{g}$ indicating very low porosity. Figure 1 shows that the pore size varies from 2 to 110 nm with most of the contribution coming from pores in the range 12-17 nm (Fig. 2). A comparison of the pore structure of the unreacted sample (A) and samples sintered at 640°C ($t = 0$ and $t = 69.4 \text{ min}$) are shown in Figs. 3 and 4. Figure 3 shows that the pore volume is reduced by >50% by the time the sample is brought to the reaction temperature, and sintering for an additional 69 min only further reduces the pore volume from 0.0385 to 0.032 cm$^3$/g. The pore size distribution shifts from a unimodal structure to a bimodal distribution. At $t = 0$, pores in the ranges 10-12 and 30-40 nm dominate while at $t = 69.4$, the dominant pores are between 7-9 nm and 30-40 nm with a higher percent of the pore volume being due to the pores in the 30-40 nm range.

At 605°C, the same trend is seen, but then at $t = 0$ the pore volume reduced from 0.08 to 0.057. At $t = 172 \text{ min}$, the pore volume had reduced to 0.027 cm$^3$/g (Fig. 5). This reduction in pore volume is accompanied by a broadening of the pore size distribution.
Figure 5 shows that the profile is much flatter and Fig. 6 shows that there is no dominant pore size. The trends towards formation of both smaller and larger pores during the sintering seem to indicate that sintering occurs in both stage 1 and stage 3. In stage 1, the initial stage, the filling of the necks with material results in reduction of the pore size, while in stage 3 complete consolidation of the particles leads to larger inter-particle spaces.

This reasoning is buttressed by Fig. 7 which compares samples sintered at different temperatures. Sample A which was sintered at 640°C for 70 min has much higher fraction of large pore sizes when compared to either sample B (t = 605°C, 172 min) and sample C (t = 585, 279 min). However, at 575°C the pore volume decreases with increasing time up to t = 0 (0.032 cm³/g) but at t = 279, the pore volume had increased to 0.057 cm³/g. (Fig. 8) and the pore size distribution is much wider with more contribution from both smaller and larger pores (Fig. 9). However, another experiment conducted at the same temperature (Fig. 10) showed that at t = 0 most of the contribution to the pore volume comes from the pore size range 12-17 nm, same as for the original sample. However, the height of the peak was greater than for the original sample.

From analysis of the reactions at 640 and 605°C, the pore volume decreases as the sample is sintered and the average pore size increases. Sintering leads to a redistribution of the pore sizes, and for this sample both reduction and enlargement of pores is seen. The phenomenon at 575°C cannot be explained and needs to be further investigated.
Reaction with Simultaneous Sintering

Changes in Surface Area. The technique used in this study to investigate the effect of sintering on reaction is a departure from the conventional techniques used by Caillet and Harrison (1982) and Ranade and Harrison (1981). For some reason, reaction was conducted "in the absence" of sintering and the resultant samples then sintered at different temperatures. This, however, is merely a serial superimposition of sintering on reaction and not a true reaction-with-sintering study. As will be seen shortly, the results we obtained were very different from those reported in the literature. It must be pointed out that there has been no detailed analysis done on the structural changes accompanying fractional conversion for the oxidation of ZnS (i.e. regeneration of ZnO). Much of the emphasis has been on the sulfidation process. Based on this, we expected that the oxidation process would reverse the trends reported for the sulfidation process.

Samples were reacted at 575, 605, and 640°C with oxygen mole fractions varying from 0.1 to 0.45. The reactions were stopped when the weight as detected by the TGA reflected conversions of 0.25, 0.75, and 0.95. Figure 11 obtained at 605°C with an oxygen mole fraction of 0.2 shows that the surface area increases with conversion up to 0.7 and then drops sharply. The same trend was observed at all temperatures and oxygen concentrations. Data from all the runs at 605°C are shown in Table 2. This trend seems to indicate that the reaction of ZnS to ZnO leads to increase in surface area but as the product ZnO is formed, sintering of ZnO takes over and at some point (X \approx 0.70) the effect of sintering of ZnO becomes dominant. This appears to be a direct contradiction of the results
in the study by Ranade and Harrison (1981) who had indicated that the sulfided product (ZnS) was more prone to sintering. Sa et al. (1989) had indicated the same for sulfidation of zinc ferrite.

The effect of oxygen concentration on surface area is shown in Fig. 12. No significant differences can be attributed to the level of oxygen used in the oxidation process due to the random scatter in the data at each conversion. Since the sample size was very small, thus making the total surface area used in the measurement very small and susceptible to slight errors in the weighing procedure, this could account for some of the scatter seen in the data.

The effect of reaction temperature appears to be considerably more significant than that of oxygen concentration. Comparing Figs. 12 and 13 data obtained at 575 and 640°C, by disregarding the few outliers in the data it can be seen that in general, the higher the reaction temperature, the lower the surface area recorded. For the sample reacted at 640°C, the initial surface area was 7.3 m²/g, the surface area at a conversion of 70% was about 9.8 m²/g; while at 575°C the initial surface area was 7.9 m²/g, and the peak surface area centered around 11 m²/g at a conversion of 70%. This trend is as expected since the effect of sintering is more pronounced at higher temperatures.

If one only takes the initial and final surface areas into consideration, the “restoration of surface area upon regeneration” reported by several investigators (e.g. Sa et al., 1989) is evident. At all temperatures, the final surface area is higher than the initial surface area. This also shows that the higher the temperature, the lower the final area thereby shedding
more light on what other experimenters have reported as being the difficulty in surface area restoration when regeneration is undertaken at high temperatures (Sa et al., 1989).

However, as earlier paragraphs indicate, there is a lot more to the surface area variation than just the initial and final areas. The lack of fit, especially at short times, between ZnO→ZnS experimental data and the variable property model (Ranade and Harrison, 1981) may be due to their model not adequately predicting the structural changes in the pellet. Although our study was conducted with particles of ZnS, it is expected that pellets would exhibit the same characteristics. Further experiments utilizing pellets of ZnO would have to be conducted before the effect of incorporating these structural changes on the fit of the variable property grain model in comparison with the study by Ranade and Harrison can be determined.

**Changes in Pore Volume and Pore Size Distribution.** As discussed in the Introduction, it is expected that reaction would increase the surface area of the sample: this is attributed to the formation of much smaller pores which, when combined, have a larger surface area than single large pores.

At 640°C with oxygen mole fraction of 0.1 the pore volume increases with conversion up to a point and then decreases (Fig. 14). The pore size distribution (Fig. 15) shows that the sample with the highest pore volume (and highest surface area) has most of its pores in the range 10-12 nm. This is similar to the distribution for the original sample. The pore volume of 0.073 cm³/g is also close to the unsintered sample pore volume of 0.081. At X = 0.29, a dominant peak is noticed between 22 and 37 nm, but the sample had
a much broader distribution than at $X = 0.75$. By the time the reaction had reached a conversion of 0.97, there was no dominant pore size thus confirming product sintering.

Figs. 16 and 17 show the cumulative pore volume and pore size distribution curves for a reaction conducted at 640°C but with an oxygen mole fraction of 0.3. Although the pore volume range is about the same, the pore volumes recorded at equivalent conversions are different. Unlike at 10% oxygen where the pore volume at $X = 0.75$ was considerably higher than indicated in the other 3 curves, at 30% oxygen (Fig. 16) the profiles at $X = 0.75$ and 0.25 are close while those at $X = 0$ and $X = 0.97$ are also bunched together. The pore size distribution plot (Fig. 17) sheds more light on this. At $X = 0.27$ and 0.75, the most probable radius is at 12 nm while at $X = 0$ and 0.97 there is more spread in the pore sizes.

Thus although there were no significant differences in the surface areas measured (as a function of oxygen concentration), there are differences in the pore size distributions.

At 585°C, the same trend of increasing pore volume up to a point followed by a sharp decrease was observed at all oxygen concentrations. However, at 45% oxygen, the pore volume at $X = 0.85$ was 0.086, greater than even that of the unreacted ZnS. Therefore at this temperature there is a difference in the range of pore values as shown in Figs. 18 and 19. Despite this, all the samples exhibited a shift towards smaller pores as conversion increased. While all of the samples reacted at the other two temperatures showed evidence of smaller pores, only at 585 are the peaks associated with the smaller pores equal to, or in some cases greater than those associated with larger pores (Fig. 20). It is proposed that at
this temperature, sintering is still at the initial stage over the time span of the reactions. Thus the formation of smaller pores dominate.

Conclusions

The data obtained in this study have shown that oxidation of ZnS leads to an increase in surface area and pore volume in the absence of sintering or for as long as the effect of sintering is minimal. It has also shown that the occurrence of sintering simultaneously with reaction leads to a drop in this surface area, and that profiles obtained for reaction at low temperatures followed by sintering at high temperatures are not the same as reaction with simultaneous sintering.

In general, reaction at high temperatures lead to a lower pore volume due to sintering. Even samples which show similar pore volume ranges can exhibit very different pore size distributions. Furthermore, the appearance of the same surface areas does not ensure the same pore size distribution. It has been shown that redistribution of pore sizes can lead to constancy in the pore volume.

Due to the very small amounts of sample available for these structural analyses, it must be reiterated that these data are qualitative in nature. They are meant to shed some light on the evolution of structure in gas-solid reactions and not provide quantitative data that can be used in modeling. This will be addressed in a subsequent study.

Nomenclature

\[ v_B \] molar volume of reactant

\[ v_D \] molar volume of product
K(T) constant in Eqn. 4

$k_j$ sintering rate constant,

S(t) sorbent surface area, m$^2$/g

$S_e$ equilibrium surface area, m$^2$/g

$S_o$ initial surface area, m$^2$/g

$t$ time or thickness of adsorbed multilayer

$X$ conversion at time $t$

$\overline{X}$ average conversion

References


Table 1. Surface Area Variation During Sintering of ZnS

<table>
<thead>
<tr>
<th>time (min)</th>
<th>surface area (m²/g)</th>
<th>α (Eqn. 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T = 650</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>7.4157 ± 0.083</td>
<td>1.31</td>
</tr>
<tr>
<td>69.4</td>
<td>6.5425 ± 0.0503</td>
<td></td>
</tr>
<tr>
<td>T = 620</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>7.5745 ± 0.0485</td>
<td>1.18</td>
</tr>
<tr>
<td>172</td>
<td>7.0199 ± 0.0559</td>
<td></td>
</tr>
<tr>
<td>T = 585</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>7.9103 ± 0.0511</td>
<td>1.57</td>
</tr>
<tr>
<td>279</td>
<td>6.9052 ± 0.032</td>
<td></td>
</tr>
</tbody>
</table>
Table 2. Surface area variation during oxidation of ZnS at 605°C.

<table>
<thead>
<tr>
<th>Oxygen %</th>
<th>Conversion</th>
<th>Surface area ($m^2/g$)</th>
<th>Time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0</td>
<td>7.5414 ± 0.055</td>
<td>0 (167)</td>
</tr>
<tr>
<td>10</td>
<td>0.22</td>
<td>7.9895 ± 0.0212</td>
<td>12 (179)</td>
</tr>
<tr>
<td>10</td>
<td>0.73</td>
<td>11.7861 ± 0.0377</td>
<td>44 (211)</td>
</tr>
<tr>
<td>10</td>
<td>0.96</td>
<td>7.401 ± 0.027</td>
<td>308 (475)</td>
</tr>
<tr>
<td>20</td>
<td>0.26</td>
<td>8.6323 ± 0.06</td>
<td>8 (175)</td>
</tr>
<tr>
<td>20</td>
<td>0.82</td>
<td>10.7545 ± 0.0492</td>
<td>30 (197)</td>
</tr>
<tr>
<td>20</td>
<td>0.96</td>
<td>8.8443 ± 0.0551</td>
<td>102 (269)</td>
</tr>
<tr>
<td>30</td>
<td>0.26</td>
<td>8.1183 ± 0.0262</td>
<td>6.4 (173.4)</td>
</tr>
<tr>
<td>30</td>
<td>0.72</td>
<td>10.3652 ± 0.0579</td>
<td>21 (188)</td>
</tr>
<tr>
<td>30</td>
<td>0.97</td>
<td>9.6639 ± 0.0535</td>
<td>139 (306)</td>
</tr>
<tr>
<td>45</td>
<td>0</td>
<td>7.5745 ± 0.0485</td>
<td>0 (167)</td>
</tr>
<tr>
<td>45</td>
<td>0.23</td>
<td>8.6173 ± 0.0266</td>
<td>4.5 (171.5)</td>
</tr>
<tr>
<td>45</td>
<td>0.76</td>
<td>10.5508 ± 0.0353</td>
<td>15.5 (182.5)</td>
</tr>
<tr>
<td>45</td>
<td>0.96</td>
<td>9.0516 ± 0.0459</td>
<td>88 (255)</td>
</tr>
</tbody>
</table>
Fig. 1 Cumulative Pore Volume of Unsintered Zinc Sulfide
Fig. 2 Pore Size Distribution of Unsintered Zinc Sulfide
Fig. 3 Comparison of the Pore Volumes of Unsintered and Partially Sintered ZnS at 640°C
Fig. 4 Comparison of the Pore Size Distributions of Unsintered and Partially Sintered ZnS at 640°C
Fig. 5 Cumulative Pore Volumes of Unreacted and Sintered ZnS samples at 647°C
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Fig. 19 Pore Volumes of Partially Reacted ZnS at 575°C, O₂ = 0.2
Fig. 20 Pore Size Distributions of Partially Reacted ZnS at 575°C, O₂ = 0.2
CHAPTER 5. SULFIDATION OF ZINC OXIDE

A paper to be submitted to Industrial and Engineering Chemistry Research

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Abstract

The intrinsic kinetics of the sulfidation of zinc oxide was determined in a thermogravimetric analyzer (TGA) between 541 and 747°C. Conversion - time plots revealed that the extent of reaction observed at 747°C was lower than that at 697°C for the same length of time. This unexpected result is due to changes in the structural parameters of the sorbent brought about by sintering at the higher reaction temperature. A simple power law model with reaction order n = 1.18, and not n = 1.0 as reported by several researchers, was found to represent the reaction between 547 and 697°C.

Introduction

The need to make electric power generation by coal more competitive with natural gas burning led to the development of the integrated gasification combined cycle (IGCC) and the gasifier/molten carbonate fuel cells (MCFC) (Corman, 1986; USDOE, 1986). These two processes offer the advantages of higher efficiency thus low electricity cost, and low emission levels. The raw gas exiting a coal gasifier usually contains significant amounts of sulfur compounds, the bulk of which is present as hydrogen sulfide. The removal of H₂S is required to comply with the Federal New Source Performance Standards
(NSPS) (Gangwal et al., 1989) and more importantly to prevent corrosion of the turbine components and deactivation of the anodes in the MCFC. For the viability of these systems, removal of H₂S must be accomplished at conditions that nearly match the temperature and pressure of the gasifier and turbine.

**Literature Review**

In the U. S., research on high temperature desulfurization (HGD) has focused on the development of regenerable metal oxides capable of reducing sulfur levels in gasifier gas to less than 1 ppmv. One of the first studies in this area was a thermodynamic study conducted by Westmoreland and Harrison (1976). They found 11 metal oxides to be potential desulfurization candidates in an operating range between 360 and 1560°C. Based on this analysis, comparative evaluation of oxides of iron, manganese, copper, cobalt, calcium, copper and zinc have been made. This has revealed that iron and zinc oxides have the greatest potential as desulfurization candidates. Iron oxide has a high theoretical sulfur capacity and reduces H₂S to a few hundred ppm, but it is reduced from its active Fe₂O₃ form to FeO in the presence of H₂ or CO which are two components of gasifier gas (Yumura and Furimsky, 1985; Tamhankar, 1981). Zinc oxide, on the other hand, also has a very high theoretical sulfur capacity. It is capable of reducing H₂S to <5 ppm, and has very high reactivity towards H₂S (Gibson and Harrison, 1980; Westmoreland et al., 1977), but it is also reduced to volatile zinc metal in the reducing gas. At high temperatures it exhibits loss of surface area, and during regeneration ZnSO₄ is formed instead of ZnS.
In order to combine the positive aspects of the single oxides, mixed oxides (e.g. zinc ferrite ZnFe$_2$O$_4$; zinc titanates Zn$_2$TiO$_4$, ZnTiO$_3$, ZnTi$_2$O$_3$; CuO-Fe$_2$O$_3$; MnO-CuO; FeO-Al$_2$O$_3$; Fe$_2$O$_3$-Al$_2$O$_3$; ZnFe$_2$O$_4$-CuFe$_2$O$_4$) have been studied (Lew et al., 1989, 1992; Woods et al., 1990; Grindley and Steinfeld, 1981; Tamhankar et al., 1986). Of these mixtures, zinc titanates and zinc ferrites were considered “best.” Although zinc titanates were found to be more stable in the presence of the reducing gas, sorbent utilization was very low prior to H$_2$S breakthrough (Lew et al., 1989). Zinc ferrites were also found to decompose into their components, ZnO and Fe$_2$O$_3$, at high temperatures with Fe$_2$O$_3$ being subsequently reduced to inactive FeO.

A new sorbent Z-sorb III (zinc oxide-nickel oxide) has been developed by Phillips Petroleum and is currently undergoing extensive testing. Nickel oxide acts as a promoter which “ignites” the sulfidation reaction at a low temperature thereby preventing excessive loss of surface area seen with pure ZnO. The exact mechanism by which this works is not yet fully understood. A better understanding of the kinetics of the desulfurization reaction by ZnO would provide a few answers to these questions and this would improve the design of a sorbent that would be commercially viable.

A review of the literature on the kinetics of zinc oxide sulfidation revealed conflicting data. Gibson et al. (1980) showed that for spherical pellets of zinc oxide reacted with H$_2$S in the temperature range 350-800°C, reaction is fast and complete between 600 and 700°C. In this range, they further showed that the grain model is applicable to the global reaction rate provided the conversion is between 0.15 and 0.80. However, Yumura
and Furimsky (1985) found that increasing reaction temperature from 600 to 800°C had no effect on ZnO absorption capacity. The global reaction rate has been described by both the shrinking core model (Pineda et al., 1995; Gangwal et al., 1989) and the grain model (Gibson and Harrison, 1980). Since the assumptions in these two models are quite different, it is obvious that the sulfidation of zinc oxide has to obey one model or the other or neither. Both models cannot be equally applicable for all times.

Furthermore, experiments have been conducted with pellets and powders, using thermogravimetric analyzers (TGA), fluidized bed reactors, and packed bed reactors. It is well known that intrinsic kinetic parameters can only be obtained from reaction of small amounts of loose powders, under conditions where the effects of transport resistances are negligible. While some of the studies reported have taken care to eliminate these resistances, others have been undertaken with full knowledge of the fact that the reaction was under mass transfer limitations (Gibson and Harrison, 1980).

Experiments conducted by Westmoreland et al. (1977), Gibson and Harrison (1980) and Lew et al. (1992b) all show that the initial reaction rate is first order with respect to H₂S. While the study by Lew was carried out in the absence of external mass transfer limitations, the reactant gas used contained 2% H₂S along with 1% H₂. It has previously been shown (Lew, 1992a) that ZnO is reduced in this temperature range by hydrogen. Therefore, interaction between these two reactants could affect measurement of the intrinsic reaction rate.
It is clear from the review presented above that conclusions regarding the kinetics and modeling of the reaction are often contradictory. No precise modeling can be done unless the basic kinetic parameters used are unequivocally in the kinetic regime. The present investigation was undertaken with the objective of providing such kinetic data.

**Experimental Procedure**

The kinetic studies were conducted using a Perkin Elmer thermogravimetric analyzer equipped with a high temperature furnace. It consists of an electrobalance which monitors any weight changes during the reaction, a quartz sample stirrup-pan assembly suspended via a platinum hangdown wire from this balance, and a glass furnace tube which is surrounded by a furnace. Sample temperature is monitored by means of an exposed junction Pt-Pt/10Rh thermocouple which is located 1 cm from the top of the sample pan and controlled by referencing it to the programmed set point. Furnace temperature is controlled by a Pt-Pt/10Rh oven thermocouple. The TGA is connected to a computer loaded with the TGA 7 series/UNIX software. Other components include a TAC 7/DX thermal analysis instrument controller, and an HP graphics plotter.

All the gas flow rates were controlled using Brooks 5850E mass flow controllers. Argon and helium gases were passed through oxygen and water traps upstream of the mass flow controllers. Argon was used as the balance purge while helium or 2.1 mol % hydrogen sulfide in nitrogen was used as the reactant purge which was fed directly into the furnace tube. BET surface area measurements were made using a Micromeritics ASAP 2010 sorptometer, and X-ray diffraction (XRD) was done with Cu(kα1) radiation in a Siemens
A 500D diffractometer equipped with a graphite monochromator. The reagent grade zinc oxide (99.99% purity) used in the sulfidation studies was supplied by Fisher Scientific. The surface area of the <70 μm mesh particles used in the sulfidation experiments was found to be 2.9048 m²/g using krypton as the adsorbent.

Isothermal reactions were carried out between 541°C and 747°C and hydrogen sulfide content in the fluid stream was varied between 0.3 mol % and 0.9 mol %. For each run, the total gas flow rate was 86 cm³/min for a fixed amount of ZnO (14.4 mg) placed in the sample pan (diameter: 6 mm; thickness: 3 mm). By using this amount of material the same sample could be used for both XRD and BET surface area determinations, thus, ensuring that the surface area determination and phase identification were done under identical experimental conditions.

While flowing Ar and He, the sample temperature was raised at 10 °C/min to 140°C and held there for 15 min to remove any adsorbed species. After this, the ramp was continued at the same rate until the temperature was 100°C less than the desired reaction temperature. A 15 min stabilization period was allowed before the temperature was finally ramped at 5°C/min to the desired temperature. Fifteen minutes later, the reactant purge was then switched from He to H₂S/N₂. At the end of each run, the samples were stored in a dessicator for subsequent characterization.

For each temperature and at each hydrogen sulfide concentration, blank runs were conducted using the same ramp conditions. The results from these runs were used as correction factors for the sulfidation runs. This was necessary because of the apparent...
weight gain with increase in temperature which is an inherent characteristic of thermogravimetric analyzers. The weight loss-time data obtained from the TGA were converted into conversion-time using the expression:

\[ X = \frac{W_1 - W_0}{0.1976 \times W_0} \]  

(1)

The rate of reaction was then calculated from

\[ -r = \frac{1}{M_{\text{ZnO}}} \left( \frac{dX}{dt} \right), \quad \text{mol ZnO} \quad \text{g ZnO} \cdot \text{min.} \]  

(2)

The initial rate was obtained by taking the slope of the conversion vs. time plot at zero time.

Results and Discussion

Elimination of External Mass Transfer Resistance

The absence of gas film diffusion can be ascertained by comparing the effect of hydrodynamics in the TGA at fixed levels of kinetic factors (Doraiswamy and Sharma, 1984). If the same ratio of sample weight to flow rate (W/F) is maintained, a plot of conversion vs. flow rate should flatten out in the region in which external mass transfer effects are negligible. A sample plot of the results of these studies at 747 °C is shown in Fig. 1. It can be seen that above 85 cm³/min, the curves are essentially flat. Thus all the reactions were conducted at W/F = 0.18 and a flow rate of 86 cc/min.

Characterization of Sorbents

It has been reported in the literature that addition of hydrogen to hydrogen sulfide is required to prevent high temperature decomposition (Gibson and Harrison, 1980; Lew
et al., 1992b). It has also been reported that the decomposition of H₂S occurs very slowly below 850°C (Kirk-Othmer, 1983). Indeed, in our own experiments, a slight yellow coloration was observed in the reaction products which could indicate the presence of elemental sulfur. The diffractogram of the reactant (Fig. 2a) showed that the only compound present was ZnO (Zincite) in agreement with the manufacturer’s specifications. Samples at different stages of sulfidation were also characterized and the only compounds identified were ZnO and ZnS ( sphalarite and wurtzite). Diffractograms obtained at 747°C with 0.5% H₂S (X = 0.75) and at 747°C with 0.7% H₂S (X = 1.0) are shown in Figs. 2b and 2c. The peaks recorded correspond to those of ZnO and ZnS (Fig. 2b) and ZnS (Fig. 2c). If there was any elemental sulfur deposit, then the diffractogram would have shown additional peaks in the labeled regions of Fig. 3, which shows only the regions of Fig. 2 where the dominant sulfur peaks would have been, if they were present.

Conversion-Time Profiles

Experiments were conducted in the TGA as described in the experimental section. Varying H₂S concentration from 0.3% to 0.9% whilst keeping the temperature constant gave the expected profile — conversion increases with increase in H₂S for a given time. The profile obtained at 747°C (which is representative of all the plots obtained between 541 and 747°C) is shown in Fig. 4. After 60 min, with 0.9% H₂S, the sorbent was 99% reacted and there is no indication that it will not proceed to completion. The same trend is seen at the other concentrations and temperatures. This is similar to the results obtained by Gibson and Harrison (1980) on zinc oxide pellets.
Keeping the H$_2$S level constant while varying the temperature showed that the extent of reaction also increased as the temperature increased at 0.9%, but up to a conversion of ca. 50% there was no significant difference between the profiles obtained at 697 and 747°C. At higher conversions, the profile at 747°C was above that at 700°C (Fig. 5). At 0.7% H$_2$S (Fig. 6), the profile at 600°C was clearly above that at 500°C for the entire reaction time. However, a cross-over was seen in the plots at 747 and 697°C — higher conversions were obtained at 697°C until the sorbent was 80% reacted after which higher conversions were obtained at 747°C.

At 0.5% and 0.3% H$_2$S levels (Figs. 7 and 8), and conversions obtained at a given time at 697°C were greater than at 747°C for the entire reaction time (60 min). The maximum conversions attained were 0.82 and 0.45 at 0.5% H$_2$S and 0.3% H$_2$S, respectively, which are within the range in which the same trend was seen at 0.7% H$_2$S. This result is unexpected — if the reaction were purely kinetically controlled, then the conversion should increase with increase in temperature. Decrease in conversion with increasing temperature could occur due to a number of reasons: (1) surface diffusion/migration of adsorbed species, (2) changes in the structural properties of the solid, and (3) the possibility that increase in reactivity of the adsorbed intermediate complex with increase in temperature is more than offset by a decrease in its concentration.

Since surface diffusion effects are very seldomly recorded, we do not consider this to be a likely reason for this observation. This leaves two plausible reasons. These were addressed during the treatment of the data as described in the following sections.
Initial Rate Analysis

Analysis of initial rate data can be accomplished by expressing the reaction rate by the simple power law model or if this fails or if better accuracy is desired, by using a Langmuir-Hinshelwood-Hougen-Watson model.

Power Law Models. The sulfidation of zinc oxide can be expressed in the form

\[-r = a S_W k C_{\text{H}_2\text{S}}^n\]  \hspace{1cm} (3)

By linearizing this expression, a plot of \(\ln(r)\) vs. \(\ln(C_{\text{H}_2\text{S}})\) gives the reaction order \(n\), as slope and \(\ln(S_W k)\) as intercept. Values of \(n\) obtained by linear regression of the data at five different temperatures revealed that although all the lines appear linear and parallel (Fig. 9), the order of reaction varied from 1.17 to 1.20. By assuming that the order was 1.0, as has been reported in the literature (Lew et al., 1992b; Westmoreland et al., 1977), the values obtained for the Arrhenius frequency factor \(k_o\) were erratic. Therefore, the values of \(n\) were averaged and using this as the reaction order, the actual values of \(S_W k\) were obtained (Fig. 10). The Arrhenius plot of \(\ln k\) vs. \(1/T\) revealed that the range of linearity was only between 541 and 697°C. This is qualitatively similar to the results obtained by Westmoreland et al. (1977) in which deviation from linearity occurred above 500°C. They had postulated that the deviation was caused by mass transfer effects which could not be eliminated at high temperature. However, in our study, we have shown that gas film diffusional effects are absent even at 750°C.

Therefore, only the linear portion was used in calculating the activation energy \(E\) (5.48 kcal/mole) and \(k_o\) (75.94 cm/min). Westmoreland et al. (1977) had observed \(E =\)
5.690 kcal/mole and \( k_0 = 0.386 \text{ cm}^2/\text{min mg-mole} \) while Lew et al. (1992b) had obtained \( E = 10.3 \text{ kcal/mole} \) and \( k_0 = 1.31 \text{ cm/s} = 78.6 \text{ cm/min} \). The values obtained for the Arrhenius factor are almost identical while those obtained for the activation energy by Lew et al. is within the same order of magnitude. It must be pointed out that Lew et al. had applied the power law model between 400 and 800°C while we found that this model does not fit the reaction above 697°C.

A plot of all the experimental initial rate data and values predicted by the power law model is seen in Fig. 11. All the points lie on the 45° diagonal and a linear fit gave an \( R^2 \) of 0.98, thus confirming the validity of this model in the temperature range 541-697°C.

As discussed in the previous section, lack of fit at high temperature of the power law model could be caused either by the reaction becoming dependent on the structural parameters of the solid sorbent at high temperature and or by the reaction rate being governed not by the concentration of reactant in the bulk but on that of adsorbed species — Langmuir-Hinshelwood-Hougen-Watson kinetics.

**Langmuir-Hinshelwood-Hougen-Watson Kinetics.** The models based on surface reaction of adsorbed species controlling (listed in Table 1) were all tested but the data did not fit any of the models. Thereby indicating that this reaction mechanism is not controlling. In order to test the adsorption and desorption controlling models some additional data are required which could not be obtained, hence the experimental data obtained could not be tested against these models. As a result the non-applicability of the LHHW models as indicated by the negative tests of the surface reaction models cannot be
extended to the adsorption/desorption models. Therefore, it is not possible at this stage to
definitely conclude that these models are not applicable and that the unexpected result
referred to earlier is due to adsorption effects. However, since practically all the gas-solid
reactions modeled so far seem to follow surface reaction models, it can be speculated that
the LHHW models fail to represent the data in the present case. This leads us to the
conclusion that the unexpected result obtained at high temperature is probably attributable
to changes in the structural parameters of the sorbent.

**Conclusions**

The kinetics of the sulfidation of zinc oxide can be successfully conducted in the
temperature range 541 to 747°C without formation of elemental sulfur (from decomposition
of H₂S).

The sulfidation reaction, when conducted without any external mass transfer
resistance, proceeds straight to zinc sulfide without the formation of any stable
intermediates.

The initial rate of reaction of H₂S with ZnO can be successfully modeled as

\[-r = 75.94 \times S_W \times \exp\left(-\frac{2.7763E3}{T}\right) C_{H_2S}^{1.18}\]

in the temperature range 541 to 697°C.

The model fails above 700°C and it is speculated that this is due to the effect of the
high temperature on the structural parameters of the sorbent.
Nomenclature

a  stochiometric coefficient, mol ZnO/mol H₂S
F  gas flow rate, cm³/min
k  reaction rate constant, cm/min
M_{ZnO}  molecular mass of ZnO, g/mol
n  reaction order
C_{H₂S}  concentration of H₂S, mol/cm³
-r  rate of reaction, mol ZnO/g ZnO min
S_w  surface area of ZnO, m²/g
W_0  initial weight of sample, mg
W_t  weight of sample at time t, mg
X  conversion at time t

References


Pineda, M; Fierro, J. L. G.; Palacios, J. M.; Cilleruelo, C.; Ibarra J. V. Kinetic Behavior and Reactivity of Zinc Ferrites for Hot Gas Desulphurization. *J. Mat. Sci.*, 1995, 30, 6171


Table 1. Detailed rate equations for the LHHW models (Sofekun and Doraiswamy, 1996)

<table>
<thead>
<tr>
<th>Model</th>
<th>Rate equation</th>
<th>Linearized form</th>
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<td>1 Single site, non-dissociative adsorption</td>
<td>[ -r = \frac{kK_A [O_2]}{1 + K_A [O_2]} ]</td>
<td>[ -\frac{1}{r} = \frac{1}{k} + \frac{1}{kK_A} \left( \frac{1}{[O_2]} \right) ]</td>
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<td>reaction ZnS + O₂*</td>
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<td>2 Single site, dissociative adsorption</td>
<td>[ -r = \frac{k(K_A [O_2])^{1/2}}{1 + (K_A [O_2])^{1/2}} ]</td>
<td>[ -\frac{1}{r} = \frac{1}{k} + \frac{1}{(kK_A)^{1/2}} \left( \frac{1}{[O_2]} \right)^{1/2} ]</td>
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<td>reaction ZnS + O*</td>
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<tr>
<td>3 Dual site, dissociative adsorption reaction</td>
<td>[ -r = \frac{k(K_A [O_2])}{(1 + (K_A [O_2])^{1/2})^2} ]</td>
<td>[ -\left( \frac{1}{r} \right)^{1/2} = \left( \frac{1}{k} \right)^{1/2} + \frac{1}{(kK_A)^{1/2}} \left( \frac{1}{[O_2]} \right)^{1/2} ]</td>
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<tr>
<td>ZnS + 2O*</td>
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Fig. 1 Elimination of External Mass Transfer
Fig. 2 XRD at Various Stages of Reaction
Fig. 3 XRD Showing Location of Sulfur Peaks
Fig. 4 Conversion - Time Plot at Different Hydrogen Sulfide Concentrations
Fig. 5 Conversion - Time Plot at Different Temperatures, $H_2S = 0.9\%$
Fig. 6 Conversion - Time Plot at Different Temperatures, H₂S = 0.7%
Fig. 7 Conversion - Time Plot at Different Temperatures, \( \text{H}_2\text{S} = 0.5\% \)
Fig. 8 Conversion - Time Plot at Different Temperatures, \( \text{H}_2\text{S} = 0.3\% \)
Fig. 9 Linearized Rate Equation at Different Temperatures
Fig. 10 Arrhenius Plot of Reaction Rate Constant
Fig. 11 Comparison of Model and Experimental Data
CHAPTER 6. CONCLUSIONS AND RECOMMENDATIONS

General Conclusions

Zinc oxide appears to be a good desulfurization candidate. Regeneration of the oxide by oxidation of the sulfide, which had been reported to be problematic, was found to be fast and complete when conducted under conditions in which external mass transfer resistance was negligible. In the presence of external mass transfer resistance, an oxysulfate intermediate is formed but this decomposes when the reaction is extended to completion. The formation of zinc sulfate was not observed at any point in our studies.

Elimination of internal (ash layer) diffusional resistance proved to be unattainable even though very small particles (<200 mesh) were reacted.

The initial rate data for the oxidation of zinc sulfide were found to fit the LHHW surface reaction model with no dissociation of oxygen rather than the simple power law model. The kinetic parameters of this model were statistically determined.

Data obtained on changes in the sorbent structure revealed that the oxidation of zinc sulfide leads to an increase in surface area and pore volume in the absence of sintering. However, when reaction occurs in the presence of sintering, a maximum was noticed in the surface area-conversion plot. At all temperatures, this maximum was attained at ca 75% conversion. In general, reaction at high temperatures caused lower sorbent surface areas and pore volume.
It was also observed that samples with the same surface areas tended to have very different pore size distributions which could significantly affect their reaction capabilities.

The sulfidation kinetics of zinc oxide was found to be adequately represented by the power law model with $n = 1.18$ and not $n = 1.0$ as reported in the literature. This relationship is only valid between 541 and 697°C. Above 700°C, changes in sorbent structural parameters caused a lack of fit of the power law model.

**Recommendations for Future Work**

A fundamental understanding of the kinetics of the reaction of hydrogen sulfide and zinc oxide is required in order to develop a zinc oxide based sorbent. The results in this study have shown that zinc oxide has most of the characteristics desired in a high temperature sorbent but there are still some aspects that require investigating. Therefore the following experiments are recommended to serve as a starting point for future studies:

1. The evolution of structural changes in the sulfidation of zinc oxide should be investigated. This would serve to confirm or refute the speculations made in Chapter 4 of this thesis.

2. The multicycle performance of zinc oxide should be re-examined without addition of any reducing gases to the reactant gas. This would provide unadulterated information on the capabilities of zinc oxide.

3. Both the sulfidation and regeneration reactions should be conducted using pellets. This would provide data that can be used in the development of a predictive model for the cyclic process.
4. The breakthrough levels of $\text{H}_2\text{S}$ and the levels of $\text{SO}_2$ in the effluent should be monitored.
Table 1. Initial rate data (dX/dt) for oxidation of zinc sulfide

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<th>Temperature (°C)</th>
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Table 2. Initial rate data (dX/dt) for oxidation of zinc sulfide

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\[-\tau = \left( \frac{1}{M_{\text{ZnO}}} \right) \frac{dX}{dt} .\]
Table 3. Surface area and pore volume variation during oxidation of ZnS at 640°C

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<tr>
<th>Oxygen %</th>
<th>Time (min.)</th>
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<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
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Table 4. Surface area and pore volume variation during oxidation of ZnS at 575°C

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<th>Oxygen %</th>
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<th>Conversion</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
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APPENDIX 2. CORRECTION APPLIED TO SURFACE AREA AND PORE VOLUME MEASUREMENTS

The surface area of a sample consisting of $\approx 10$ m$^2$ of ZnS (unreacted, room temperature) was determined by N$_2$ adsorption to be 8.267 m$^2$/g. Krypton gas was then used to determine the surface area of 14 mg of the same sample. By adjusting the cross sectional area $A_m$ of Kr, the value obtained by Kr was adjusted till it matched that obtained by N$_2$. The value of $A_m$ was determined to be 0.24 nm$^2$.

The reliability of gas adsorption in determining pores with diameter greater than 60 nm is questionable. Although the ASAP 2010 carried 300 nm as default, the range was narrowed by adjusting sum area to match the N$_2$ BET surface area. It is generally accepted that if the prevailing assumptions used in calculating the pore volume and cumulative pore surface area are valid, the cumulative pore area should be within 5% of the N$_2$ BET surface area. In order to assure this, the upper limit was reduced to 120 nm for all data in this study.
REFERENCES


Focht, G. D; Sa, L. N.; Ranade, P. V.; Harrison, D. P.; Structural Property Changes in Metal Oxides Hot Coal Gas Desulfurization Sorbents. DOE/MC/21166-2163 (DOE86016041), Louisiana State University, Baton Rouge, LA, 1986.


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Finally and most importantly, I give thanks to the Almighty God, for through HIM everything is possible.