Reaction Kinetics of the Ferric Chloride Leaching of Sphalerite—an Experimental Study

ZUO-MEI JIN, G. W. WARREN, and H. HENEIN

Chloride leaching processes have significant potential for treating complex sulfides. One advantage of chloride leaching is fast dissolution rates for most sulfide minerals. This experimental study is concerned with ferric chloride leaching of sphalerite, a common component of many complex concentrates. The effects of stirring, temperature, ferric ion concentration, and particle size have been examined. In addition, reaction residues at various levels of zinc extraction were examined by SEM, and the products of reaction were identified by energy dispersive X-ray analysis and X-ray diffraction. These observations indicated that the dissolution reaction is topochemical. Moreover, the leaching results fit a surface reaction control model. The activation energy was calculated to be 58.4 kJ/mole which is reasonable for a rate limiting surface reaction. The order of the reaction was 0.5 with respect to Fe^{3+} at low concentrations and zero at high concentrations. The change in reaction order occurred at similar Fe^{3+} concentrations for various particle sizes. This is believed to be indicative of an electrochemical reaction mechanism at low Fe^{3+} and an adsorption mechanism at higher Fe^{3+}. A kinetic model for the ferric chloride leaching of sphalerite was also obtained for the lower Fe^{3+} concentrations and is given by:

$$[1 - (1 - \alpha)^{1/3}] = \left\{8.86 \times 10^3[\mathrm{Fe}^{3+}]^{0.5} r_0^{-1} \exp \frac{(-5.84 \times 10^4)}{RT}\right\} t$$

This model is in excellent agreement with the experimental results for fractions of zinc extracted up to 0.95.

I. INTRODUCTION

THE kinetics of dissolution of sulfide minerals in chloride media has received considerable attention recently. There are several justifications for this interest; among them is the availability of materials of construction with improved resistance to chloride attack. More importantly, however, are the substantially faster dissolution rates exhibited by most sulfides in chloride media and the potential application of such electrolytes in the treatment of complex sulfides. To understand the fundamental behavior of a complex material and to develop a predictive strategy for process control, it is necessary to determine the oxidation behavior of the respective components. The present investigation is an experimental study of the ferric chloride leaching of ZnS (sphalerite). The results of the overall leaching reaction are consistent with the following stoichiometry:[1,2,3]

$$ZnS + 2Fe^{3+} = Zn^{2+} + 2Fe^{2+} + S^\circ \qquad [1]$$

Less than 5 pct of the sulfide is oxidized to sulfate,[3] which is consistent with the ferric leaching of other minerals such as chalcopyrite.[4,5]

Previous investigators have provided some information on the dissolution kinetics of ZnS, using both oxidative[1,3,6-9] and nonoxidative[10] conditions. Results of several of these investigations are summarized in Table I. Su[1] and Demopoulos[6] determined kinetic data with similar ranges for the variables. Both reported activation energies between 50 to 54 kJ/mole (12 to 13 kcal/mole), but the reaction was reported to be both first-order[1] and half-order[6] with respect to Fe^{3+}. A surface reaction model was also reported to fit the experimental data in the initial stages of reaction, but a mixed model including both surface reaction and diffusion was proposed for conversions larger than about 50 to 70 pct.[1,6] Venkataswamy *et al.*[7] have reported that their experimental data fit both a diffusion and a surface reaction model, but in this instance it is not clear if they used a concentrate with a sufficiently narrow size fraction or if the effect of particle diameter was incorporated into the model verification. Based upon a diffusion model, Rath *et al.*[8] have proposed that diffusion of either Fe^{3+}, Fe^{2+}, or Zn^{2+} through the product layer is the rate limiting step, but again the effect of particle diameter was not examined. In addition, it is difficult to correlate a reaction which is limited by aqueous diffusion with the reported activation energy of 90 kJ/mole (21.5 kcal/mole) and a reaction order with respect to Fe^{3+} of 1.4 as reported by Rath *et al.*[8] Such a high activation energy is more consistent with a rate limiting surface reaction while reactions limited by aqueous diffusion are first-order processes.

To date, the results of Dutrizac and MacDonald[3] seem to be the most complete. These researchers found that shrinking core, surface reaction model fit quite well, with an activation energy of 42 kJ/mole (10 kcal/mole) and a reaction order of 0.36 with respect to Fe^{3+}. Most of the experimental data was collected on rotating disc samples, but data for the leaching of particulate ZnS crystals were provided for only one size fraction. Experiments performed at various rotation speeds showed that above 100 rpm the reaction rate did not increase. Interestingly, the presence of dissolved copper significantly enhanced the rate of zinc dissolution.

Jan *et al.*[9] examined the rate of ZnS dissolution in sulfuric acid electrolytes using O_2 as an oxidant and proposed a

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Manuscript submitted July 29, 1983.

Table I. Summary of Results from Investigations Dealing with the Kinetics of ZnS Leaching. All Entries Are for $FeCl_3$ and HCl Lixiviants Except for Reference 9 Which Is Oxygen Pressure Leaching in H_2SO_4.

Reference	Material Type	Material Sizes (μm)	Experimental Conditions $[Fe^{3+}]$	Experimental Conditions T °C	Fe^{3+} Reaction Order	E_{act} kJ/mole	Remarks
Su[1]	flotation concentrate	363 256 181 126 91	0.1 to 1.0	44 to 90	1.0	50	mixed surface and diffusion models proposed.
Dutrizac *et al.*[3]	crystals (Satander, Spain)	−212 + 150	0.001 to 1.0	25 to 100	0.36	42	sintered discs were used primarily; surface reaction model was proposed.
Demopoulos[6]	crystals (Ottawa, OK)	126 42	0.3 to 3.0	45 to 85	0.5	54	surface reaction model only fits at 3.0 M Fe^{3+}.
Venkataswamy *et al.*[7]	flotation concentrate	−212 + 150 −150 + 106 −106 + 75 −75	1.0 to 4.0	106	—	—	both surface and diffusion models are reported to fit.
Rath *et al.*[8]	synthetic	−75	0.2 to 0.8	30 to 70	1.4	90	diffusion model fits; diffusion of Fe^{3+}, Fe^{2+}, or Zn^{2+} proposed as rate-limiting.
Jan *et al.*[9]	flotation concentrate	−106 + 75	0.003 to 0.03	90 to 140	0.42	—	surface reaction model proposed; thin plate geometry.

surface model for the process. Although the emphasis of the work was somewhat different than the present study, these researchers did examine the effect of Fe^{3+} concentration over a limited range (0.003 to 0.03 M) at a constant oxygen partial pressure of 150 psi. The addition of a small amount of Fe^{3+} greatly accelerated the rate. Using the data of Jan *et al.*,[9] the reaction order was calculated to be 0.42 for Fe^{3+} as shown in Table I.

As with many minerals, zinc can be solubilized by nonoxidative dissolution in strong acids. Majima *et al.*[10] have examined the kinetics of such a reaction using HCl and NaCl electrolytes. They proposed a surface reaction model with an activation energy of 84 kJ/mole (20 kcal/mole) and a reaction order of 1.0 with respect to H^+. It is not clear from the previous work whether the reaction is limited by a surface reaction or a diffusion step. Furthermore, the reaction mechanism proposed by Majima *et al.*[10] did not conclusively show whether or not the reaction is electrochemical which often results in fractional reaction orders.[11,12]

It was the purpose of this study to investigate the reaction mechanism for the dissolution of sphalerite concentrate in ferric chloride. The effects of stirring speed, temperature, ferric ion concentration, and particle size were examined. In addition, reaction residues at various levels of zinc extraction were examined by SEM, and products of reaction were identified by energy dispersive X-ray analysis and X-ray diffraction. These data have been incorporated into a model which is consistent with a rate limiting surface reaction.

II. EXPERIMENTAL

On the basis of the chemical analysis given in Table II and X-ray diffraction, the flotation concentrate used was approximately 90 pct sphalerite with the major impurity being pyrite. No other minerals were detected by X-ray diffraction. Prior to leaching, the concentrate was washed with Na_2S solution to clean and sulfidize the surface of the mineral. The concentrate was then wet screened, to remove extremely fine particles which could bias initial leaching data, and then carefully dry screened into discrete size fractions.

Table II. Chemical Analyses of Flotation Concentrate

Element	Analyses (Pct) Size (μm) −75 +63	Analyses (Pct) Size (μm) −106 +90
Zn	61.50	60.27
Fe	3.40	3.80
Cu	0.86	0.62
Pb	0.11	0.06

For the leaching experiments, 1.0 to 1.5 g samples of a specific size fraction were placed in a 1 liter reaction vessel fitted with a thermometer, condenser, and a specially designed sampling device which permitted the withdrawal of liquid samples through a glass frit at selected intervals. The volume depletion of the liquid in the reactor was accounted for in calculating the fraction of zinc reacted for a given sample. Stirring was provided by an impeller and variable speed motor, and the temperature was controlled by immersing the reactor in a thermostatted oil bath. Leaching solutions were prepared using reagent grade $FeCl_3 \cdot 6H_2O$, HCl, and distilled, deionized water. Hydrochloric acid (10 ml) was added to the solutions to reduce the initial pH to the range 0.3 to 1.0. The standard conditions used were 0.2 M Fe^{3+}, 65 °C, −63 + 53 μm concentrate and 550 rpm stirring speed, except where each of these variables was individually examined. Zinc extraction was determined by atomic absorption and residues were washed and dried for examination by SEM, energy dispersive X-ray analysis, and X-ray diffraction.

III. RESULTS AND DISCUSSION

Stirring speeds in the reactor were varied from 250 to 900 rpm. Results from these experiments, shown in Figure 1, are expressed in terms of a, the fraction of zinc extracted. Over this range no significant effect on the reaction rate was found. Based on these data a stirring speed of 550 rpm was chosen for all subsequent experiments. The shape of the plot in Figure 1 is typical of leaching experiments and is similar to results obtained by previous investigators.

Figures 2 and 3 show the variation in extraction kinetics with temperature and particle diameter, respectively. The predicted extraction using a model to be discussed in this study is represented by the solid lines on the figures, and experimental data points are represented by symbols. The extractions reported here are higher and occurred faster than those reported elsewhere. Venkataswamy *et al.*,[7] for example, report an extraction of 53 pct in six hours for leaching conditions much more severe (1.0 M Fe^{3+}, 106 °C) than those used to obtain the data shown in Figure 1. Jan *et al.*[9] extracted 40 pct of the zinc in six hours at 90 °C, using similarly sized particles in 0.02 M Fe^{3+} and 150 psi O_2. This is still less than the roughly 55 pct extraction found in this study using 0.05 M Fe^{3+} at 65 °C. Demopoulos[6] found a maximum extraction of 44 pct in 0.3 M Fe^{3+} for −149 + 105 μm particles at 65 °C, but did not achieve this level until an elapsed time of 10 hours. This level of extraction was achieved in the present study (Figure 3) in approximately five hours. In some cases the observed difference in extraction may be due to the presence of an alternate oxidizing agent as in the case of Jan *et al.*,[9] but in other cases the reasons for the difference are not clear. As pointed out by Dutrizac,[3] some investigators may not have used material of sufficiently narrow size fractions and may not have wet screened the sample to remove fines. The extraction could also be affected significantly if the sample was not washed with Na_2S as was done in this study (Figure 4). It is believed that the Na_2S removes the flotation collector on the particle surface. This aspect is currently under investigation. Other factors such as the presence of an organic solvent or impurities could also affect the rate.

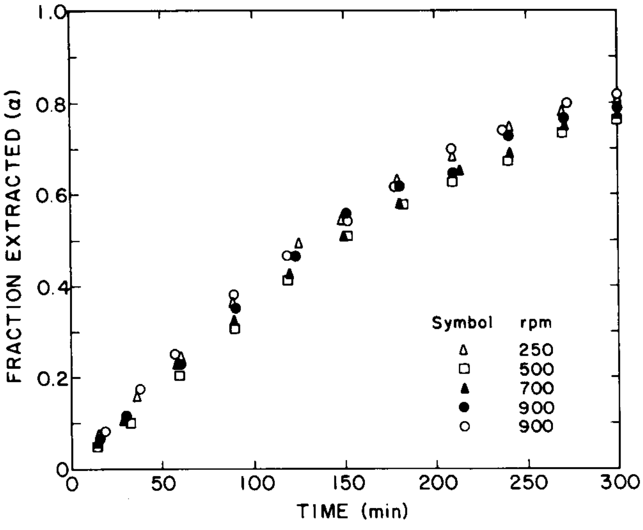


Fig. 1—Leaching results for various stirring speeds, 0.2 M Fe^{3+}, −63 + 53 μm size, 65 °C, and 0.1 M HCl.

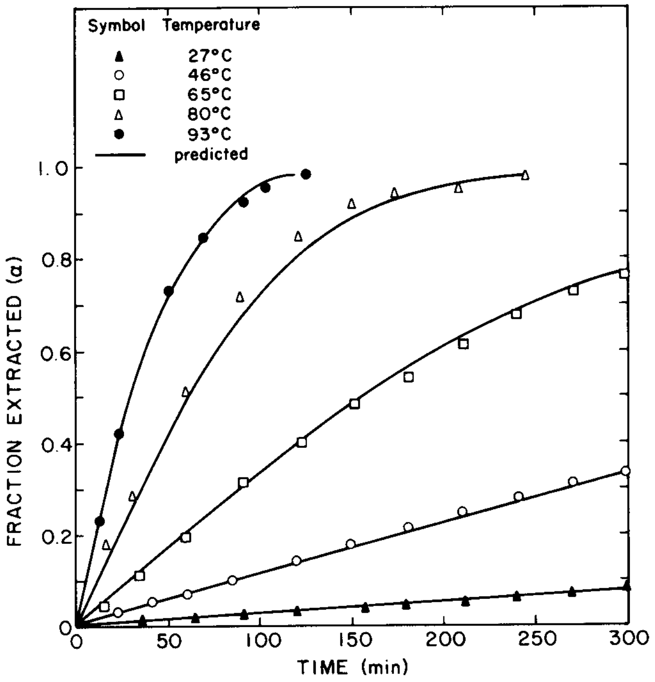


Fig. 2—Leaching results for 0.2 M Fe^{3+}, −63 + 53 μm size and 0.1 M HCl showing the effect of temperature.

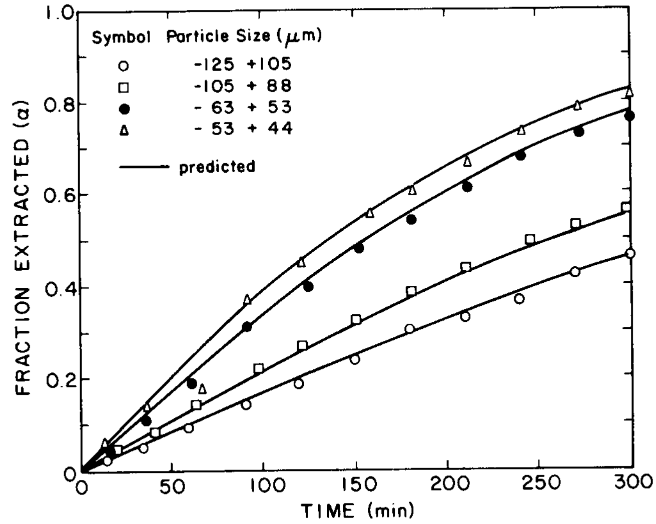


Fig. 3—Leaching results for 0.2 M Fe^{3+}, 65 °C, and 0.1 M HCl showing the effect of particle size.

A. *Characterization of Reaction Products*

Several investigators have utilized kinetic models which are based on a reaction which is topochemical in nature. Careful examination and identification of the solid reaction products are important segments of the study of any heterogeneous reaction. Residues from several leaching experiments at various temperatures and levels of extraction were examined using a scanning electron microscope and X-ray diffraction. A visual examination of the cross-section of partially reacted particles can be especially helpful in determining whether the reaction is topochemical.

For comparison, Figure 5 depicts typical unreacted particles. Figure 6 shows a particle which has been partly reacted at 65 °C, and Figure 7 shows one which has been

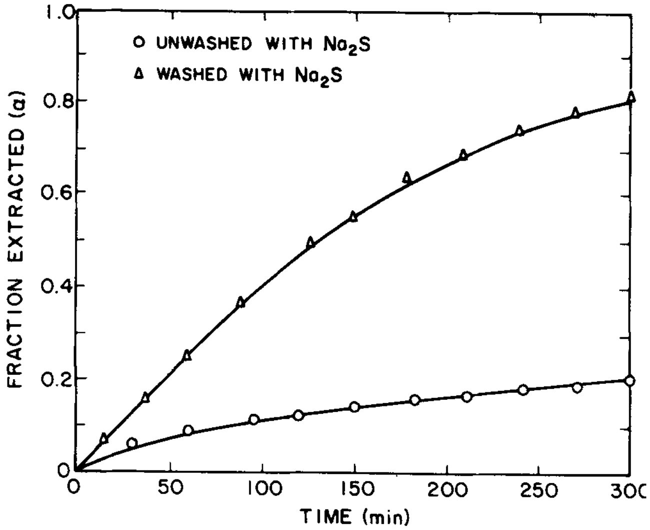


Fig. 4—Leaching results for 0.2 M Fe^{3+}, 65 °C, 0.1 M HCl and −63 + 53 μm size showing the effect of washing the concentrate with Na_2S solution.

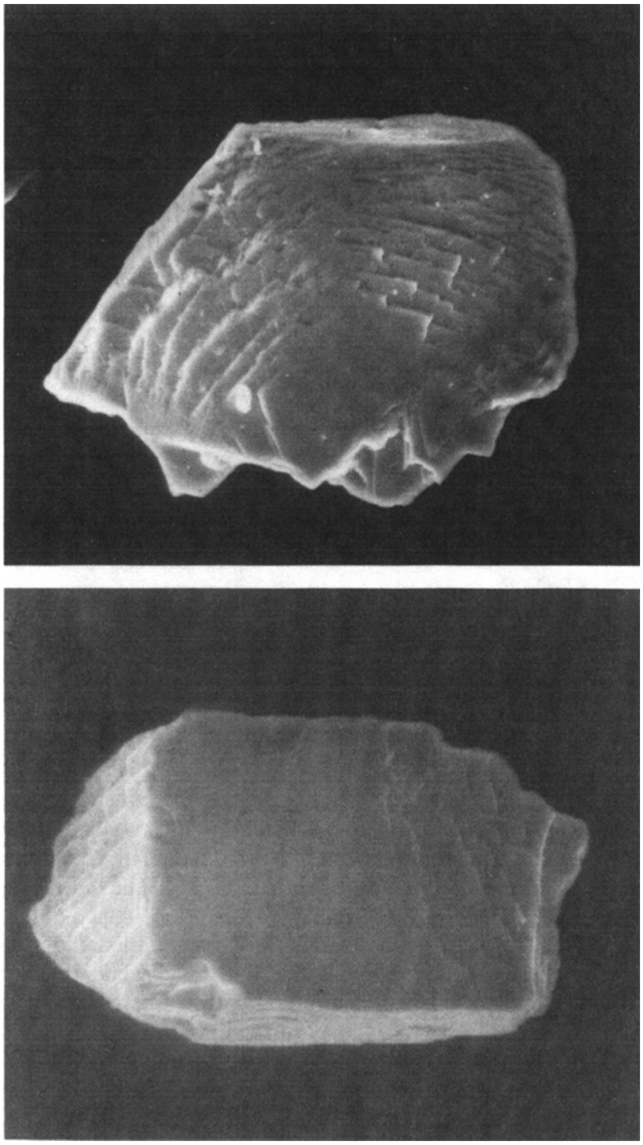


Fig. 5—Photographs of typical unrelated particles, −63 + 53 μm. Magnification 523 times.

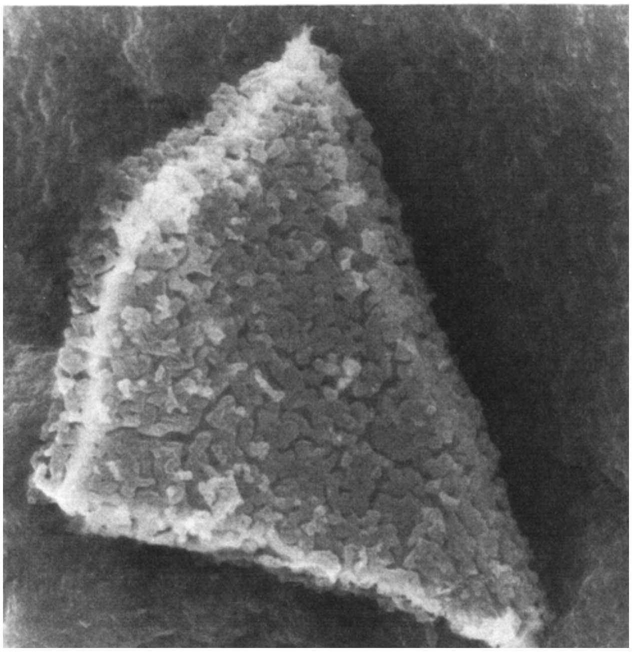


Fig. 6—Porous surface of a particle, −63 + 53 μm, at α = 0.5 which has been reacted at 65 °C and 0.2 M Fe^{3+}. Magnification 741 times.

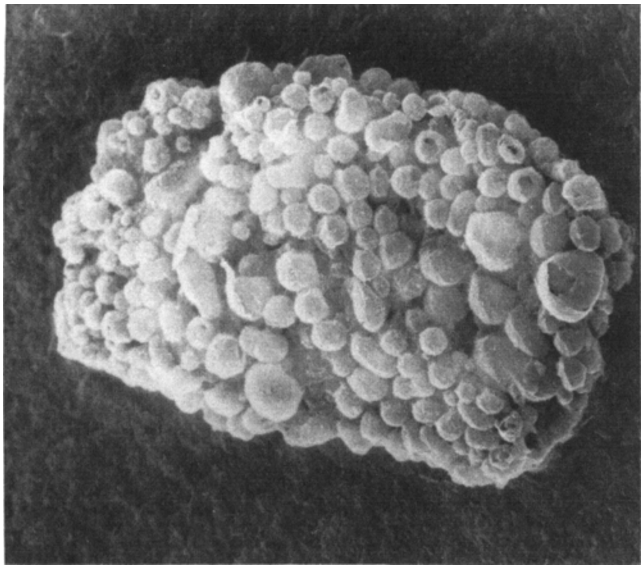
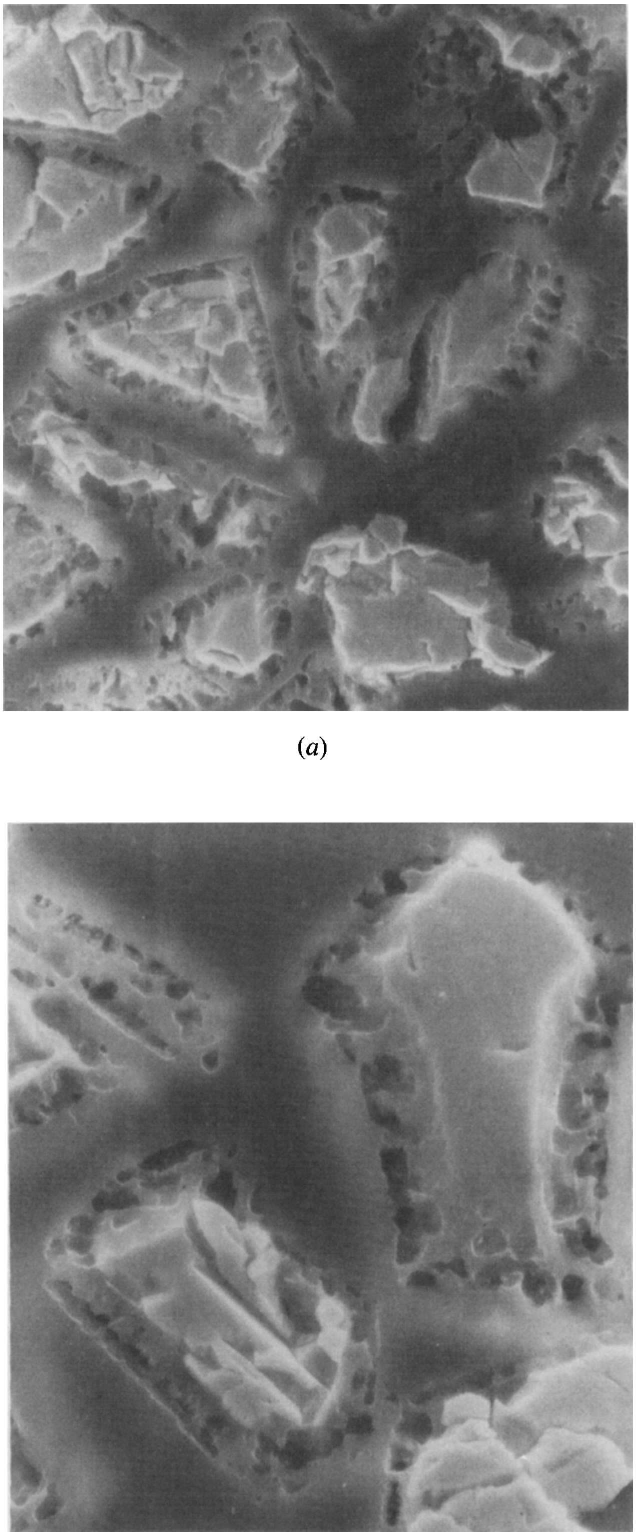


Fig. 7—Porous surface of a particle, −63 + 53 μm, at α = 1.0 which has been reacted at 80 °C and 0.2 M Fe^{3+}. Magnification 741 times.

nearly fully reacted at 80 °C. After reaction the surface is very rough and appears to be quite porous. Energy dispersive X-ray analysis of the surface of such particles showed greatly increased levels of sulfur, and the presence of elemental sulfur was confirmed by X-ray diffraction. No evidence of zinc chloride as a reaction product could be found by X-ray diffraction. The most interesting microscopic evidence found in this study is provided in the cross-sections shown in Figures 8(a) and 8(b). Reacted particles (α = 0.75) were mounted in a low viscosity embedding media and then polished to reveal the product layer which rims the unreacted core of each particle. Energy dispersive X-ray analysis showed greatly increased levels of sulfur and



(a)

(b)

Fig. 8—Cross-section of porous particles, $-63 + 53$ μm at $\alpha = 0.75$, reacted at 65 °C, and 0.2 M Fe^{3+}. Magnification of (a) 371 times and of (b) 760 times.

diminished zinc levels in the outer layer. These photographs strongly indicate that the reaction is indeed topochemical in nature and that the sulfur product layer which forms is extremely porous. It is possible that some of the sulfur product may have been plucked out during polishing. This loss of sulfur would probably be more severe for a highly porous product layer (Figures 6, 7) as opposed to a dense, impervious layer. These results are in agreement with the observations made by Dutrizac and MacDonald[3] on sphalerite cubes and sintered disks.

B. *Kinetic Models*

Since the rate of a heterogeneous reaction is directly proportional to the surface area of the reacting solid, kinetic models for such reactions must account for the diminishing surface area of the solid. The general expression* for the overall reaction rate has been given by Wadsworth[13] as

$$\frac{dn}{dt} = k_0' A \prod_i C_i^{\nu_i} \qquad [2]$$

Thus, the rate depends directly upon the area, A, and initial shape of the particles. Particles which are small in one dimension such as thin plates or discs will have a minimum variation in area. For such a case the rate will not appear to change as the reaction progresses. Such a model has been proposed by Jan *et al.*[9] for oxgyen pressure leaching of ZnS. Based on the observed reaction kinetics and SEM examination of the concentrate and reaction residues these investigators assumed that the particles can be approximated by thin plate geometry. Using Eq. [2] and expressing the reaction rate in terms of the fraction reacted, α, yields:

$$\frac{d\alpha}{dt} = \frac{2k_0' VC}{l_0} \qquad [3]$$

Integrating Eq. [3] yields a linear relationship with time (*i.e.*, linear kinetics):

$$\alpha = \frac{2k_0' VC}{l_0} t \qquad [4]$$

This behavior was found experimentally by Jan *et al.* and could also apply in the present case for those experiments in which the extent of reaction is low, for example the curves for 25 °C and 45 °C in Figure 2. In general, however, for a larger extent of reaction there is significant deviation from Eq. [4] which arises due to a significant change in the particle surface area as the reaction proceeds. This could well be the case if the initial geometry of the particles was closer to a sphere than to a thin disc.

In this case beginning with Eq. [2] and assuming spherical geometry for the particles results in the relationship:[13]

$$1 - (1 - \alpha)^{1/3} = k_s t \qquad [5]$$

A similar relationship is obtained even if the particles are assumed to be cubes or other such isometric shapes. This model assumes that a surface reaction is the rate limiting step and that the product layer, elemental sulfur in this case, is sufficiently porous that it provides no diffusion barrier. Hence, in such a case the rate of diffusion of dissolved reactants and products is much faster than the surface reaction rate. The details of the development of Eq. [5] are available elsewhere,[13] but it would be useful to examine more closely those terms which make up the rate

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*Symbols are described in the nomenclature section.

constant, k_s:

$$k_s = \frac{Vk_0'C}{r_0} \qquad [6]$$

The surface concentration, C, is usually not known but is characteristic of the material, the bulk concentration of reactant, and is assumed to be constant. Therefore, for any particular set of experimental conditions, the rate constant k_s is inversely proportional to the initial particle radius, with all other variables being constant.

If the limiting step in the reaction mechanism is the diffusion through a product layer of aqueous reactants or products to or from the reaction interface, then appropriate models can be derived from Fick's Law,[13] which are again dependent on the geometry of the particles. For thin plate geometry the rate equation takes the familiar parabolic form:

$$\alpha^2 = k_p t \qquad [7]$$

For spherical geometry the rate equation becomes somewhat more complex since the changing area must be accounted for:

$$1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3} = k_d t \qquad [8]$$

Based on a comparison of the models represented by Eqs. [4], [5], [7], and [8] with the data in Figures 2 and 3, a topochemical surface reaction may be proposed as the limiting step in the mechanism. For values of fraction reacted less than approximately 40 pct, the change in area is negligible and Eq. [4] fits the data quite well. Furthermore, the topochemical nature of the reaction is supported by the SEM photographs. For those experiments in which the fraction reacted is substantially larger, the diminishing surface area of ZnS must be accounted for. A plot of the data in Figure 2 according to Eq. [5] is shown in Figure 9, which indicates that the surface reaction is indeed the rate limiting step in the extraction process. The model fits exceptionally well up to about 0.95 fraction reacted. In order to substantiate further this mechanism, additional work was performed to elucidate the effects of particle diameter, temperature, and Fe^{3+} concentration.

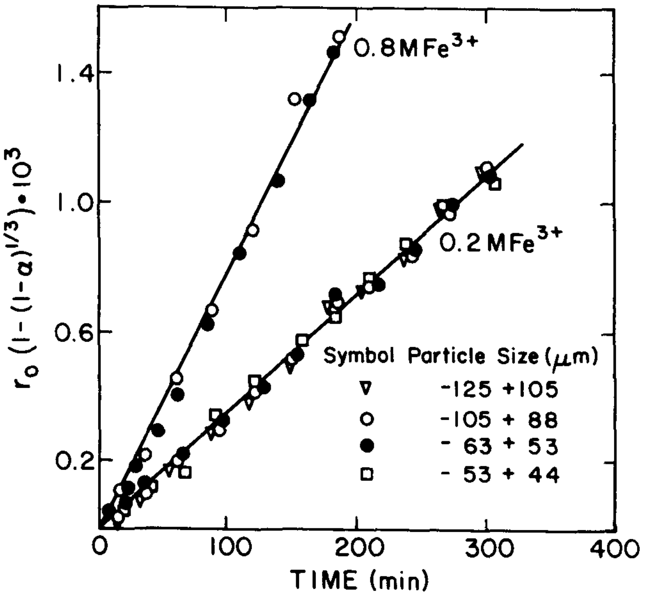

Fig. 9—Surface reaction model for the leaching data presented in Fig. 3.

C. *Particle Size Effect*

The effect of particle diameter on the rate of zinc extraction was examined by measuring the kinetics of reaction for four size fractions (Figure 3). As expected, a smaller particle size results in a faster rate of dissolution, and the data when plotted according to Eq. [5] are linear as shown in Figure 9. The slopes of each of the lines in Figure 9 are the apparent rate constants, k_s, given by Eq. [6]. It should also be noted that the intercepts pass through the origin. Particle sizes and rate constants from Figure 9 were used to produce Figure 10 which yields the linear relationship predicted by Eq. [6].

D. *Effect of Temperature*

The rate of zinc extraction was studied over the temperature range 27° to 93 °C; results are given in Figures 2 and 11. As expected, increasing temperature greatly accelerates the reaction rate. The apparent rate constants, k_s, obtained from the slopes of the lines in Figure 11 were used to determine an activation energy of 58.4 kJ/mole (14 kcal/mole) as shown in Figure 12. This value falls in the range expected

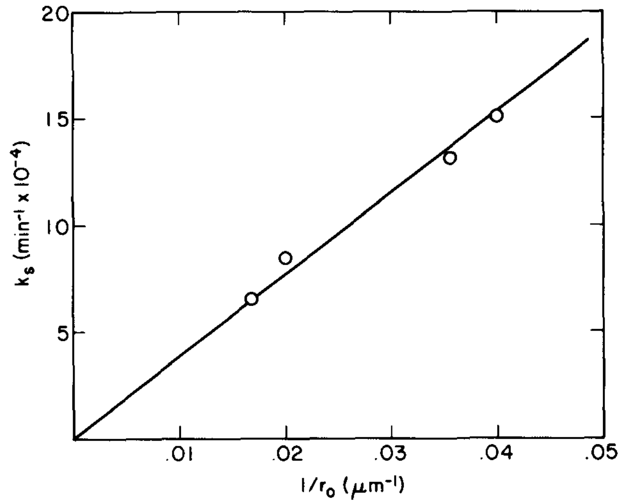

Fig. 10—The effect of particle size shown here in a plot of the apparent reaction rate constant, k_s, as a function of $1/r_0$, according to Eq. [6].

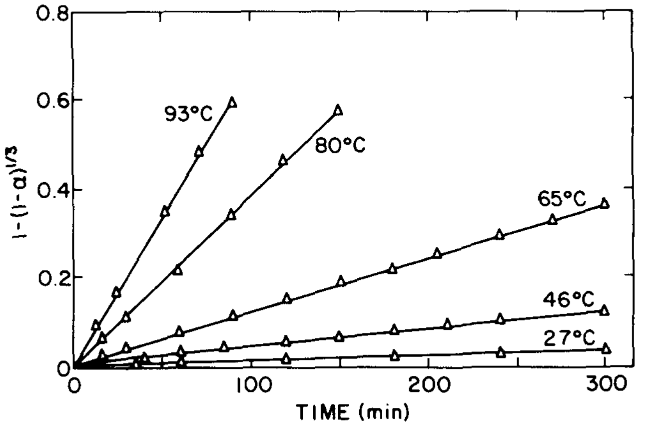

Fig. 11—A plot of the data presented in Fig. 2 according to Eq. [5].

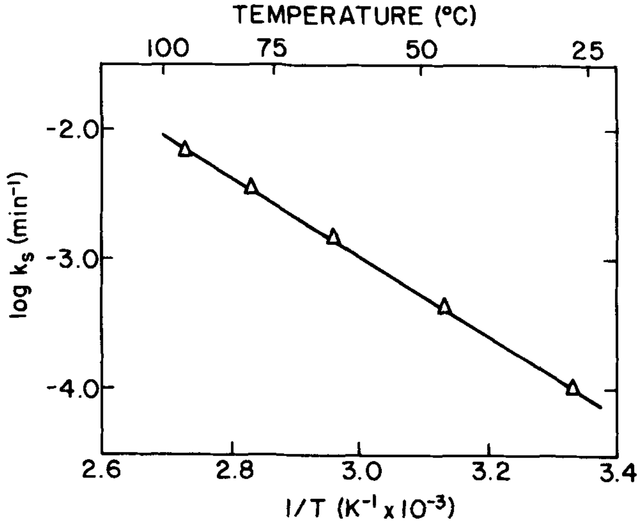

Fig. 12—The activation energy, determined using the surface reaction kinetic model for an isometric particle, is 58.4 kJ/mole.

for a rate limiting surface reaction and is consistent with that found by previous investigators.[1,3,6,8]

E. *Effect of Ferric Ion Concentration*

The effect of ferric ion concentration, as given by the total amount of ferric ion added as $FeCl_3$, on the rate of zinc extraction has been examined for two size fractions of ZnS concentrate. From the results shown in Figure 13 for the $-63 + 53$ μm size fraction, it can be seen that increasing [Fe^{3+}] increased the rate of reaction up to a concentration of 0.8 M above which no further increase could be detected. Similar results (Figure 14) were obtained for the larger size fraction, $-125 + 105$ μm, except that the rate increased up to 0.6 M [Fe^{3+}] and did not increase for the higher concentrations. All of the data shown in Figures 13 and 14 were found to fit Eq. [5] for the surface reaction model. From these data the experimental rate constants, k_s, were obtained and plots of log k_s *vs* log [Fe^{3+}] were made as shown in Figure 15 for both particle sizes. The slopes of the resulting plot indicate that the reaction is one half order with respect to ferric ion for lower concentrations. This result agrees well with previous researchers[6,9] but is somewhat higher than that observed by Dutrizac and MacDonald.[3] The insensitivity of the reaction to higher concentrations of [Fe^{3+}] may be the result of an adsorption phenomenon involving ferric ion or ferric-chloro complexes. Additional work is necessary to test this hypothesis.

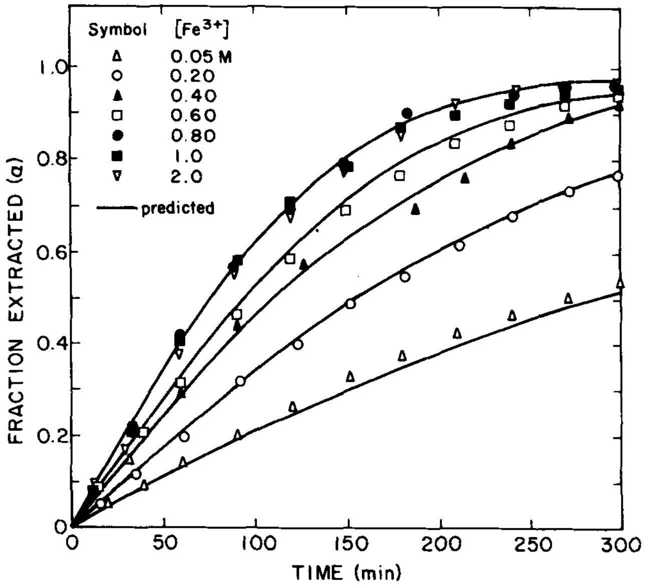

Fig. 13—The effect of Fe^{3+} concentration for $-63 + 53$ μm particles leached at 65 °C and 0.1 M HCl.

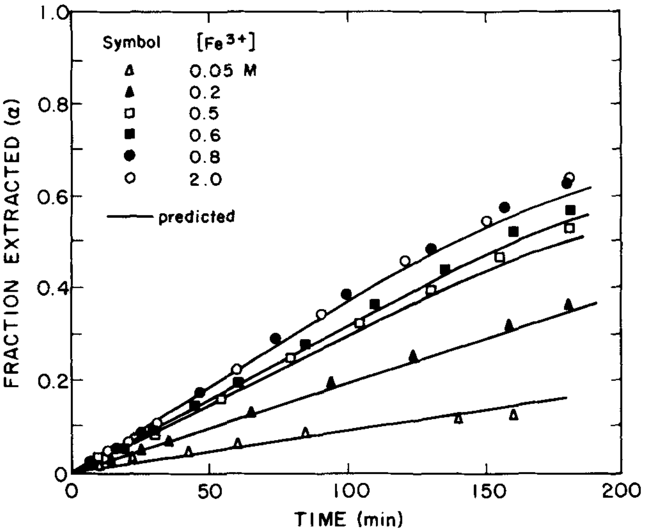

Fig. 14—The effect of Fe^{3+} concentration for $-125 + 105$ μm particles leached at 65 °C and 0.1 M HCl.

IV. SUMMARY

For all experiments, a generalized rate equation was determined based on the surface limiting reaction where the

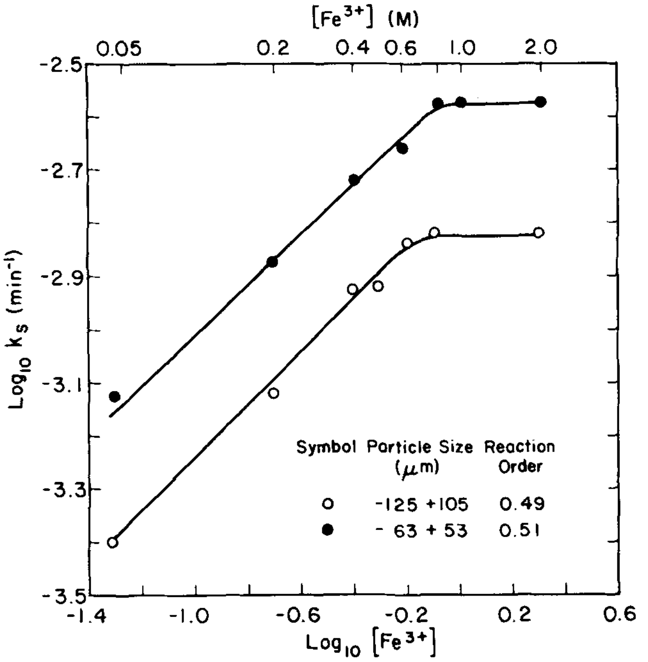

Fig. 15—The order of reaction with respect to Fe^{3+} determined for the data shown in Figs. 13 and 14.

order with respect to $[\mathrm{Fe}^{3+}]$ was one-half:

$$1 - (1 - \alpha)^{1/3} = \left\{(8.86 \times 10^{3})[\mathrm{Fe}^{3+}]^{0.5} r_0^{-1} \exp\left[\frac{-5.84 \times 10^{4}}{\mathrm{R}T}\right]\right\} t \qquad [9]$$

The average value of the surface reaction rate constant had a standard deviation of

$$950 \frac{l^{1/2}\ \mathrm{cm}}{\mathrm{gmole}^{1/2}\mathrm{min}} \qquad [10]$$

for all experiments. This model was used to draw the curves presented in this paper in Figures 2, 3, 13, and 14. Very good agreement is obtained between the model and the experimental results over nearly the complete duration of the reaction. The significance of the rate constant, reaction order, and activation energy with respect to a proposed reaction mechanism is the subject of an ongoing investigation.

NOMENCLATURE

A	Particle surface area
C	Surface concentration of ZnS capable of reaction
$[\mathrm{Fe}^{3+}]$	Molar concentration of ferric ion
R	Universal gas constant
T	Temperature
V	Molar volume of ZnS
k_0'	Specific reaction rate constant (including shape factor)
k_d	Apparent reaction rate constant for diffusion in an isometric particle
k_p	Apparent reaction rate constant for diffusion in a thin plate
k_s	Apparent reaction rate constant for surface reaction for an isometric particle
l_0	Initial plate thickness
r_0	Initial particle radius
t	Elapsed time
α	Fraction of ZnS reacted
n	Number of moles of reactant remaining at time t
ν_i	Order of reaction with respect to species i

ACKNOWLEDGMENTS

The authors are grateful to Mr. Steve Balsone for his help in the early stages of this experimental work. Appreciation is also expressed to Mr. Steve James and Mr. David Esterl of St. Joe Minerals Corporation for providing the concentrate and for financial support provided by St. Joe Minerals Corporation and The Pennsylvania Science and Engineering Foundation (Contract Nos. 81-44, 82-40).

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