

# A Kinetic Study on the Pressure Leaching of Sphalerite

R. J. JAN, M. T. HEPWORTH, AND V. G. FOX

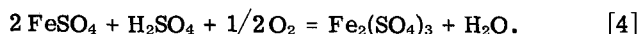
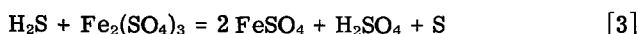
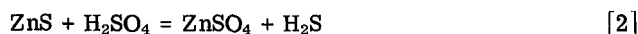
The dissolution of sphalerite (ZnS) in sulfuric acid solution under oxygen pressure was investigated. Effects of temperature, percent solids, agitation, sample size, oxygen partial pressure and foreign ions were evaluated. The effect of hydrogen pretreatment on sphalerite leaching rate was also examined. Leaching of sphalerite at 90°C and 150 psi oxygen pressure was found to occur at a constant rate. This rate was determined from the experimental data observed under the different leaching conditions mentioned above. The constant leaching rate was attributed to the chemical reaction occurring on the surface of the flat-plate type sphalerite sample. The rate-controlling step of the reaction was determined to be the oxidation of hydrogen sulfide to elemental sulfur. Oxidation of hydrogen sulfide was studied through the addition of iron and through the observation of the change in iron concentration during leaching. The oxidation was concluded to be by reaction with ferric ion rather than by direct oxygen oxidation. Leaching tests run with samples pretreated with hydrogen do not show any increase in the rate of zinc extraction.

**DIRECT** leaching of sphalerite (ZnS) at elevated temperatures and pressures has been the object of several investigations.<sup>1-8</sup> The overall reaction of the process is



It was reported as early as 1956 by Bjorling<sup>1</sup> that the reaction proceeded so slowly that it was impractical to extract zinc from zinc sulfide unless nitric acid was also present as a promoter. The nitric acid, Bjorling stated, presents obvious difficulties in the subsequent electrolysis. He concluded that because of these difficulties and the added problems of recovering sulfur from the leach residue, "acid decomposition of zincblende is unfavorable."

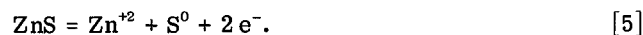
However Bjorling, Forward and Veltman<sup>2</sup> in 1959 successfully leached ZnS at 110 to 115°C, at oxygen partial pressures from 10 to 60 psi. Subsequently, research work done by Mackiw and Veltman,<sup>3</sup> and Veltman and O'Kane<sup>4</sup> enabled the great improvement of the process and the reduction of leach retention time. The reaction mechanism was proposed to be



Little explanation was made regarding the proposed mechanism and no experimental verification was reported.

The contribution from Exner, Gerlach, and Pawlek<sup>5</sup> from the Institute for Metallurgy of the Technical University, Berlin, and later published by Pawlek<sup>6</sup> proposes an entirely different mechanism for the dissolution of ZnS. Zincblende (ZnS) was chosen in their investigation of the kinetics of the reaction. An elec-

trochemical model was proposed in which leaching of zinc is analogous to the corrosion of metals. Anodic and cathodic partial reactions occur at the solid surfaces, separated locally from each other. The anodic reaction is given as:



On the other hand, the cathodic reduction of chemisorbed oxygen takes place with the uptake of the electrons produced by the anodic reaction:



For the locally separated electron exchange to take place, the solid to be dissolved must exhibit a certain conductance. The specific electrical resistance of sphalerite was found to be  $6 \times 10^9$  ohm-cm at 90°C, a value which is about ten orders of magnitude higher than that of most other metal sulfides. Also, oxygen molecules from the solution must be adsorbed before a reaction on the surface of the solid can take place. A theory of boundary chemisorption was developed to explain these events. According to the theory, the number of charge carriers in the sphalerite semiconductor can be increased by the presence of foreign atoms, by the addition of extra chemical substances to the solution to form a redox system, or by raising electrons from the valence band to the conductivity band by means of irradiation.

This semiconductor model was tested by introducing ultraviolet radiation into the system. However, the extraction could not be enhanced. Zinc sulfide was then doped with Cu and Al, and the extraction curve still lay below that of nondoped sample. However, the extraction curve of the doped zinc sulfide with UV radiation exhibited a linear rise and reached a value 3.5 times higher than the value without radiation.

The deficiency in the semiconductor model prompted the assumption of another factor hindering ZnS dissolution. This was found to be the H<sub>2</sub>S which is formed during the leaching. Experimentally, Pawlek proved that the continual removal of H<sub>2</sub>S can increase the leaching rate approximately 4-fold, while adding H<sub>2</sub>S

R. J. JAN is Process Engineer, AMAX Nickel Refining Company, Briathwaite, LA 70040. M. T. HEPWORTH, formerly with University of Denver, is now with AMAX Extractive Metallurgical Laboratories, Golden, CO 80401. V. G. FOX is with Air Products and Chemicals, Allentown, PA.

Manuscript submitted September 30, 1974.

at a pressure of 2 atm can completely suppress the reaction.

Scott and Dyson<sup>7</sup> investigated the effect of various catalysts on the pressure leaching of zinc sulfide. The presence of several metals in acid solution catalyzed the total amount of zinc leached. Increasing catalytic activity is in the order of Cu > Bi > Ru > Mo > Fe. Interestingly enough, at a leaching condition of 113°C, 250 psi oxygen partial pressure and 0.1 N H<sub>2</sub>SO<sub>4</sub>, addition of 0.6 mg Cu per gm of ZnS enabled 92 pct of the Zn to be extracted after 1 h. Addition of 14 mg Fe per gm of ZnS yielded 51 pct Zn extraction in an hour compared with 6 pct extraction when no catalyst was added. However, increasing the catalyst concentration shows little or no effect for Cu but great enhancement for the effectiveness of Fe.

A galvanic mechanism represented by Eq. [5] for the anodic and Eq. [6] for the cathodic reaction was also proposed. Therefore, the main requirements for a metal to exhibit catalytic activity appears to be:

- a) that the zinc sulfide crystal should be activated by incorporation of catalyst ions in place of zinc in the surface layers of the lattice;
- b) that the catalyst should be capable of forming a redox couple which participates in one or more of the chemical reactions between ZnS and oxygen.

Though many other ions, in addition to those listed catalysts, have the correct ionic radii to exchange with zinc in the ZnS lattice (*e.g.* Ag, Hg, Pb, Sn), they do not influence the kinetics of dissolution at all. Furthermore, from the half cell potentials of electrochemical reactions ( $E_h$ ), no reason can be given why some of the metals which form a redox couple with either ZnS or oxygen exhibit a catalytic effect and some do not.

The semiconductor model and the galvanic model are cited to indicate a similarity between mineral leaching and metal corrosion. Unfortunately, no correlation between theory and experimental data have yet been reached. Measurement of corrosion potential of a particle under conditions of corrosive environment and pressure is almost impossible. A leaching mechanism proposed by Veltman and O'Kane (Eqs. [2] to [4]) appears reasonable. The model they used explains the importance of H<sub>2</sub>S removal which was experimentally demonstrated by Pawlek and the catalytic effect of iron impurity. Nevertheless, the Veltman and O'Kane mechanism was proposed by looking at the zinc extraction curve at different temperatures and different oxygen partial pressure only.

It is therefore the purpose of this study to try to identify a single step which is rate-determining during sphalerite leaching. The mechanism of this rate-determining step will also be examined by the theory of leaching and verified by laboratory data.

## EXPERIMENTAL APPARATUS AND PROCEDURE

Experiments were carried out in a 1 liter titanium magnetic drive autoclave. The equipment was maintained at a constant temperature, constant oxygen partial pressure, and also permitted the withdrawal of solution sample at defined intervals.

The sample treated was a sphalerite flotation concentrate obtained through the compliments of Cominco,

Ltd., Pine Point, N.W. Territories, Canada. The concentrate is composed chiefly of sphalerite with minor amounts of pyrite, pyrrhotite, galena, and other species. A typical chemical analysis of the concentrate was obtained from three different laboratories, Cominco Ltd., Climax Molybdenum Co., Golden, Colorado and the Chemical Engineering and Metallurgy Laboratory, University of Denver. The result is shown in Table I. An average value is also shown.

Zinc composition in each size sample shows little variation and is indicated in Table II.

A -200 +325 mesh sample was used for the preliminary experiments where Zn extraction was studied as a function of temperature. Subsequently, all the experiments used -150 +200 mesh size unless the influence of sample size on Zn extraction was the objective of the specific set of tests.

A typical experiment to study the pressure leaching of sphalerite was under the conditions of 90°C, 150 psi oxygen pressure, twice the stoichiometric amount of H<sub>2</sub>SO<sub>4</sub> based on Eq. [1], 3 pct solids, 992 RPM and 6 h duration. Table III indicates the related quantities added.

A standard leach procedure was followed. The autoclave was preheated to the desired temperature. The concentrate was then pulped in a glass lining with the desired quantity of water and sulfuric acid. This glass lining was then put into the autoclave. The reaction chamber was purged three times with oxygen at a pressure of 100 psi to assure nitrogen removal. After purging, the autoclave was allowed to reach the steady state reaction temperature. Oxygen of the desired partial pressure was introduced into the chamber ac-

Table I. Chemical Analysis of Zinc Sulfide Concentrate

Constituent	Analysis, Pct			
	Cominco	Climax Molybdenum Company	Chemical Engineering Laboratory	Average
Zn	56	58.4	57.65	57.42
Pb	1.5	0.53	1.19	1.07
Fe	5	4.26	4.65	4.64
S	-	32.32	30.43	31.38
Cu	-	0.05	0.089	0.07
Ca	-	0.75	-	-

Table II. Variation of Zn Composition in Different Screen Size Sample

Size, Mesh	Zn, Pct
-50 +115	58.22
-115 +150	54.40
-150 +200	54.04
-200 +325	57.62
-325	57.80

Table III. Amount of Reagents Added

Percent Solids	ZnS	H <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> O	Total Volume
3	7.9 gm	8.7 ml	239.4 ml	250 ml
15	50.04 gm	54.9 ml	182.9 ml	250 ml

cordingly. Mixing was then started and the leaching reaction proceeded.

Periodic samples of approximately 2 ml were taken through the sampling tube. The sample was centrifuged for the solid-liquid separation. Liquid solution was drawn for pH measurement and analysis of metal ions.

Analyses for zinc, iron, copper and lead were made with a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer. The amount of elemental sulfur in the final residue was determined by distilling a definite amount of the residue solid under condition of total reflux for 24 h with an excess of  $\text{CS}_2$ . The solution was then evaporated to crystallize elemental sulfur.

### EXPERIMENTAL RESULTS AND DISCUSSION

Pressure leaching tests were performed on the sphalerite flotation concentrate by varying several common variables to determine the kinetics of its dissolution. The parameters under investigation were: 1) Temperature: from  $90^\circ\text{C}$  to  $140^\circ\text{C}$ . 2) Percent solids in the pulp solution: 3 pct and 15 pct. 3) Stirring speed: 0, 682, 992, and 1163 RPM. 4) Sample size: -50 +115 mesh, -115 +150 mesh, -150 +200 mesh, and -200 +325 mesh. 5) Oxygen partial pressure: 20, 50, 100, 150, and 200 psi. 6) Addition of Fe as  $\text{Fe}_2(\text{SO}_4)_3$ : 0, 5, 10, 20, 40 mole pct of total zinc content in the pulp solution.

The reaction temperature had a pronounced influence on the leaching of sphalerite up to  $120^\circ\text{C}$ . A rate decrease occurred at  $130^\circ\text{C}$  where the final residue appeared as several lumps instead of the powder that was obtained when the autoclave was kept below  $130^\circ\text{C}$ . This condition may be caused by the melting of elemental sulfur formed during the leaching reaction. The melting point of S and monoclinic  $\text{S}_8$  are 120 and  $119^\circ\text{C}$ , respectively. Fig. 1 shows the relationship between zinc extraction and temperature.

Since the extraction curves are straight lines, their extraction reaction exhibits zero order kinetics. The rate constants can therefore be obtained directly from the slope of the lines. A plot of the logarithm of the reaction rate vs  $1/T$  (Arrhenius plot) yields a mean value of 6.14 Kcal/g-mole (Fig. 2) for the apparent activation energy below  $120^\circ\text{C}$ . Values from the literature vary from 4.84 Kcal/g-mole<sup>10</sup> to 17.38 Kcal/g-mole.<sup>11</sup> This variation may be reasonable because sphalerite containing different impurities could cause a marked difference in leaching rate as will be explained later.

From the available data shown in Fig. 2, it is not conclusive whether the line above  $120^\circ\text{C}$  should be drawn by connecting 120 and  $140^\circ\text{C}$  points or by connecting 130 and  $140^\circ\text{C}$  points. But the apparent discontinuity between 120 and  $130^\circ\text{C}$  is reasonable because during the tests run above the melting point of sulfur, the molten sulfur formed globules which wetted and occluded the unoxidized sulfide. This sulfur formation may cause the diffusion of reactants or products in or out of the sulfide surface to become so low that a low activation energy resulted. Below the melting point of sulfur, the elemental sulfur formed was finely divided and had much less effect on the diffusion of reactants and products.

In order to describe mineral leaching process, the

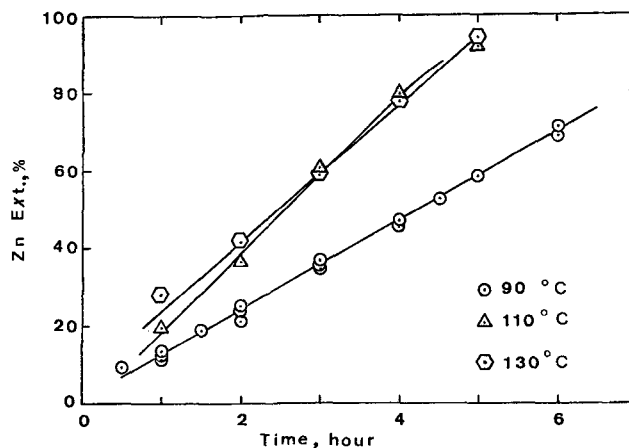


Fig. 1—Influence of temperature on the Zn extraction at twice stoichiometric  $\text{H}_2\text{SO}_4$  and 150 psi oxygen partial pressure. Sample size -200 +325 mesh.

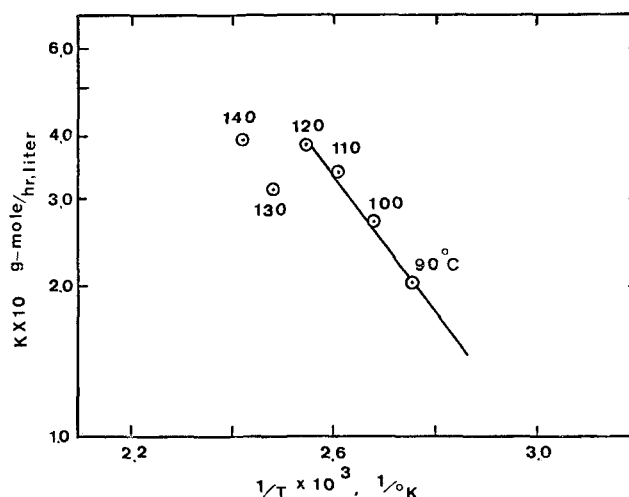


Fig. 2—Arrhenius Plot showing the effect of temperature on the rate of dissolution of sphalerite at twice stoichiometric  $\text{H}_2\text{SO}_4$  and 150 psi oxygen partial pressure.

rate-determining step of the reaction can first be classified as one or a combination of the following: a) Diffusion of a reactant  $R$  from the bulk of the solution through a liquid film to the mineral surface. b) Reaction of the reactants at the mineral surface to form a soluble product or products. c) Diffusion of one of the products,  $P$ , away from the surface.

When a porous solid product is forming during leaching, two additional possibilities are: d) Diffusion of the reactant  $R$  in through the porous product layer. e) Diffusion of product  $P$  out through the porous product layer.

For a leaching reaction, dispersion of gas is always an important factor. Therefore another possibility which might determine the sphalerite leaching rate is: f) Oxygen dispersion from gas to liquid phase.

The value of activation energy can in most cases enable one to distinguish between liquid diffusion (steps a), c), d), and e)) and reaction controlled phenomena (step b)). The value of 6.14 Kcal/g-mole observed in sphalerite leaching is higher than most diffusion controlled processes. This value is considerably lower than for a reaction controlled process. Therefore no definite conclusion can be made regarding the

rate-determining step, whether it be diffusion or reaction control. Tests were run with 3 pct solids and 15 pct solids. No significant difference in the percentage zinc extraction was revealed. This strongly indicated that the concentration of products (or intermediate products) in the lixiviant had little effect on the zinc dissolution rate.

In addition, the linearity of the rate curves shown in Fig. 1 suggests that the concentration of sphalerite surface sites which contribute to the reaction remains constant during leaching. Also, the mineral surface is not obstructed by products of the reaction. An analysis of the data based upon an approach suggested by Wadsworth<sup>13</sup> indicates that for a reaction model which assumes that the reaction surface moves inward to the center of the particle at a constant velocity, the percent extracted *vs* time curve will result in a straight line only when the mineral particles being leached are in a disk or a flat-plate shape.

The rate-determining step of the sphalerite leaching under present conditions therefore could be: 1) diffusion of reactants through a liquid film to the sphalerite surface if the sphalerite particle is in disk or flat-plate shape, or 2) surface reaction if the sphalerite particle is a disk or flat-plate shape, or 3) dispersion of oxygen from gas to liquid phase.

Each step will be checked experimentally and explained in the following discussions.

The rate of dispersion of oxygen from the gas to the liquid phase is constant for a given mixing system at a given temperature. This could be the rate-determining step when the surface reaction involving dissolved oxygen is extremely fast.<sup>12</sup> If this is the case, a plot of percent extraction *vs* time will be a straight line. The slope of the line is dependent upon oxygen dispersion rate.

The dissolved oxygen content measured during the sphalerite leaching registered a concentration of at least 8 ppm, indicating sufficient oxygen is in the dissolved state. Dispersion of oxygen is concluded not to be a controlling factor in the sphalerite reaction, not at least under the conditions studied.

#### Influence of Sample Size

The exclusion of an oxygen-dispersion rate-determining step can further be established by examining the influence of sample size on zinc extraction. The total surface area will greatly affect the reaction rate when diffusion to the solid surface or reaction on the solid surface is rate-determining; however, the leaching rate will not be affected by the surface area of the mineral particles if oxygen dispersion is rate-determining. Surface area effects shown in Fig. 3 confirm this conclusion.

With the exclusion of oxygen dispersion as a possible rate-determining step, the other two possibilities may exist only when the sphalerite particle has a disk or flat-plate type shape.

To explore this further, scanning electron micrographs of the sample, before and after leach, were taken. Typical micrographs are shown in Figs. 4 and 5. The micrograph indicates that the sphalerite does appear in a flat-type shape. The change of the mineral surface area is therefore minimal during leaching.

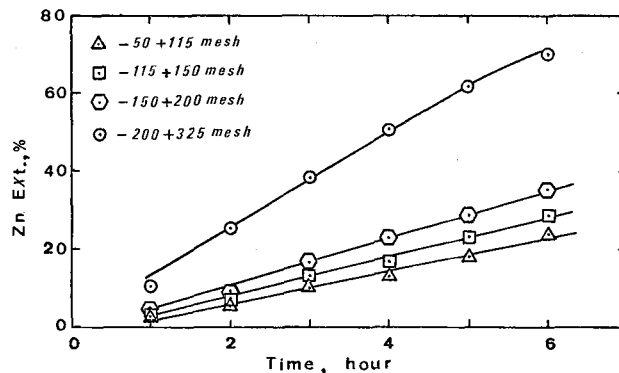


Fig. 3—Influence of sample size on Zn extraction at 90°C, twice stoichiometric H<sub>2</sub>SO<sub>4</sub> and 150 psi oxygen partial pressure.

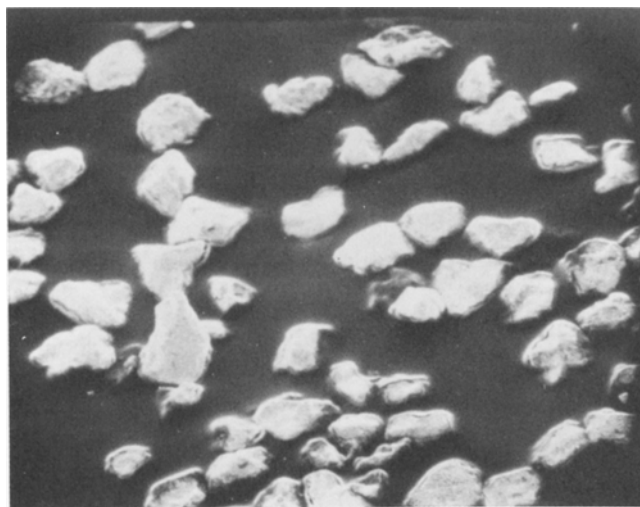


Fig. 4—Scanning electron micrograph of the sphalerite sample taken at 45 deg angle (angle between sample and microscope). Sample size -150 +200 mesh.

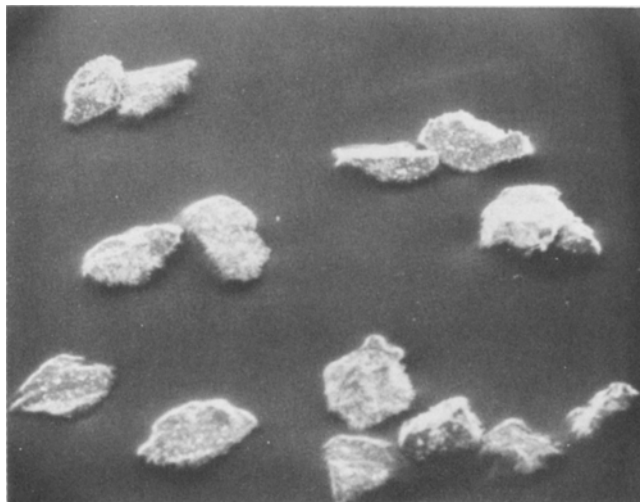


Fig. 5—Scanning electron micrograph of sphalerite leach residue. Sample initial size -150 +200 mesh. Leach conditions 90°C, twice stoichiometric H<sub>2</sub>SO<sub>4</sub>, 100 psi O<sub>2</sub> and 6 h.

## Influence of Agitation

Agitation is often important in liquid-solid reaction. If  $\delta$  represents the thickness of the liquid layer surrounding the solid particle, as agitation is increased  $\delta$  approaches  $\delta_m$ , where  $\delta_m$  is the thickness of a limiting boundary layer of stagnant solution adjacent to the solid surface. Diffusion across this film no longer is influenced by agitation. It should be emphasized that diffusion through this liquid film may still be rate controlling. Zinc extraction was studied as a function of stirring rate as shown in Fig. 6. The results indicate that agitation of 992 RPM in this study had reduced the boundary layer of stagnant solution adjacent to the solid particles to a minimum and constant thickness. Under this condition, reaction rate should be directly proportional to the concentration of the diffusion species. If, however, the concentration of the diffusion species remains constant throughout the leaching reaction, the leaching rate should remain constant. This conclusion can be derived from Fick's first law of diffusion written in overall reaction rate form

$$R = DA \frac{(C)_b - (C)_i}{\delta}$$

Here  $R$  is the overall reaction rate,  $D$  is the diffusivity of the diffusion species and  $A$  is the total surface area of the mineral particles. For a reaction proceeding at constant rate,  $(C)_i$ , which is the concentration of the diffusing species at the solid-liquid interface, can be considered as constant. When the thickness of the diffusion layer  $\delta$  approaches  $\delta_m$ , the reaction rate is proportional to the concentration of the diffusing species at the bulk liquid phase  $(C)_b$ .

The possible reactants which could be the diffusing species are, from Eq. [1], dissolved oxygen, sulfuric acid, and ferric ion. As will be seen from the following discussion of the experimental data observed on the "influence of oxygen partial pressure" and "influence of addition of Fe," none of the above diffusing species could be considered as rate-determining.

### Influence of Oxygen Partial Pressure

Fig. 7 shows the influence of oxygen partial pressure on zinc extraction. The slope of the curves is plotted for several oxygen partial pressure and is shown in Fig. 8. These tests reveal that the rate of dissolution of zinc sulfide increases linearly with increasing oxygen partial pressure. The rate increase levels off and becomes essentially unaffected when the oxygen partial pressure in the autoclave reaches 150 psig. The leveling off is not in agreement with that predicted by Fick's law of diffusion if dissolved oxygen diffusion is the slowest step in leaching.

The amount of sulfuric acid used throughout the study is twice the stoichiometric amount of total zinc content. The reaction rate difference exhibited by different oxygen partial pressure not only indicates the influence of dissolved oxygen, but also excludes the diffusion of sulfuric acid as a rate-determining mechanism. This conclusion can be explained by further examination of Fig. 7. Should the rate-determining step be the diffusion of sulfuric acid to the mineral particles, the diffusivity of sulfuric acid at 100 psi

oxygen pressure (about 20 pct Zn extraction) will then be about two times higher than the diffusivity at 50 psi (about 10 pct Zn extraction) and five times higher than that of 20 psi value (4 pct Zn extraction). This drastic change of diffusivity is inconceivable and therefore suggests that sulfuric acid diffusion is not rate-determining step.

For those tests shown in Fig. 7, sulfuric acid had an initial concentration of 64 gpl (grams per liter). The concentration dropped to 54 gpl for the tests with oxygen partial pressure of 150 and 200 psi and to about 58 gpl, 60 gpl, 62.5 gpl accordingly for the tests with 100 psi, 50 psi and 20 psi oxygen. The change in sulfuric acid concentration did not appear to be significant.

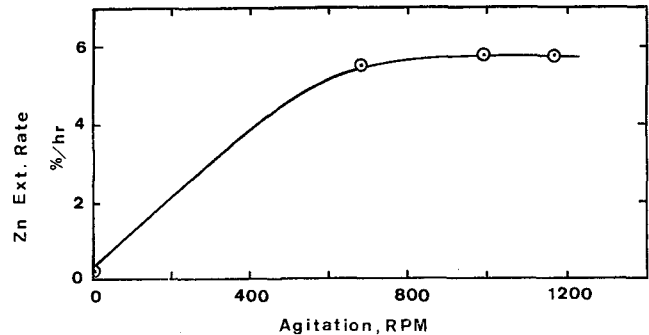


Fig. 6—Influence of agitation on Zn extraction rate at 90°C, twice stoichiometric  $H_2SO_4$  and 150 psi oxygen partial pressure.

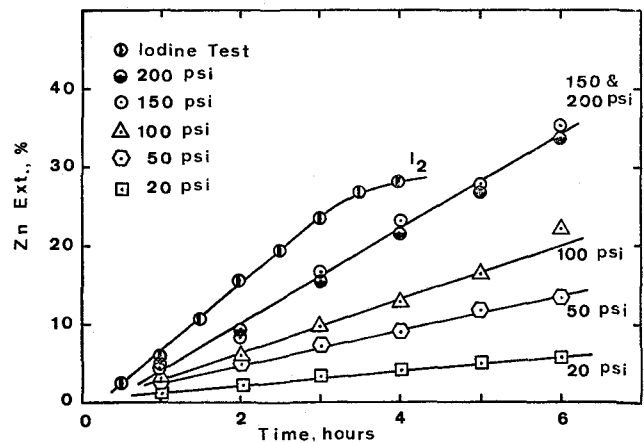


Fig. 7—Influence of oxygen partial pressure on Zn extraction at 90°C and twice stoichiometric  $H_2SO_4$ .

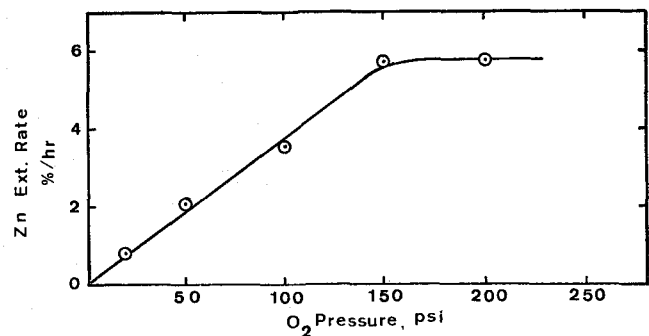


Fig. 8—Influence of oxygen partial pressure on Zn extraction rate at 90°C and twice stoichiometric  $H_2SO_4$ .

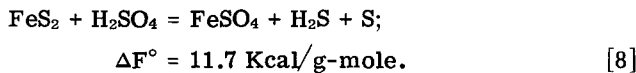
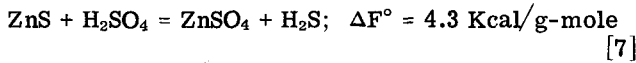
### Influence of Fe Addition

Amounts of ferric ion added in mole percent of total zinc presented in pulp solution and its influence on the zinc extraction are shown in Fig. 9. A plot on a reaction rate basis (Fig. 10) indicates that the dissolution rate is not linearly increased with respect to the addition of ferric ion. Similar data were reported by Pawlek. Although no satisfactory explanation can be given why the slope of the curve in Fig. 10 increases to a maximum when approaching 20 mole pct Fe addition and then levels off, the nonlinear rate increase behavior does indicate that ferric ion diffusion is not likely to be a rate-determining step in the sphalerite leaching.

The rate-determining step for the sphalerite pressure leaching is therefore concluded to be the "reaction occurring on the mineral surface."

### Chemical Reactions

All the important chemical reactions involved in the leaching of sphalerite exhibit a strong spontaneous reaction characteristic except the following two:



The equilibrium constant of Eq. [7] calculated from its free energy change of 4.3 Kcal/g-mole at 25°C is  $3.7 \times 10^{-4}$ , or

$$K_{\text{eq}} = \frac{a_{\text{ZnSO}_4} \cdot a_{\text{H}_2\text{S}}}{a_{\text{H}_2\text{SO}_4} \cdot a_{\text{ZnS}}} = 3.7 \times 10^{-4} \text{ at } 25^\circ\text{C} \quad [9]$$

where  $a$  is chemical activity based upon infinite dilution as the reference state.

From the mean activity coefficient values given by Maron and Prutton<sup>14</sup> at 25°C, the mean activity of  $\text{H}_2\text{SO}_4$  under leaching conditions is calculated to be 0.095 mole/liter. At the same time, when 50 pct Zn extraction is reached, the mean activity of  $\text{ZnSO}_4$  in the solution is 0.018. Assuming solid  $\text{ZnS}$  has unit activity, then the mean activity of  $\text{H}_2\text{S}$  at which Eq. [7] reaches equilibrium is

$$a_{\text{H}_2\text{S}} = 7 \times 10^{-5} \text{ mole/liter.}$$

In other words, when the activity of  $\text{H}_2\text{S}$  in solution reaches this value, Eq. [7] reaches equilibrium. Beyond this point no more  $\text{ZnS}$  dissolution could occur. The standard free energy change of reaction [7] decreases from 4.3 Kcal/g-mole at 25°C to approximately 3.3 Kcal/g-mole at 150°C. Equilibrium value of  $a_{\text{H}_2\text{S}}$  at 150°C is not available due to insufficient activity data related to  $\text{ZnSO}_4$  and  $\text{H}_2\text{SO}_4$  solution at high temperature.

Nevertheless, removal of  $\text{H}_2\text{S}$  is clearly essential for the continual dissolution of  $\text{ZnS}$ . This fact was also demonstrated experimentally by Pawlek.<sup>5</sup> A 2 atmospheric partial pressure of  $\text{H}_2\text{S}$  in 10 atm autoclave total pressure proved more than enough to stop the  $\text{ZnS}$  leaching completely.

In spite of the low equilibrium constant indicated by Eq. [9], the reaction rate according to Eq. [7] proceeds rather fast. This is shown by the result of iodine test

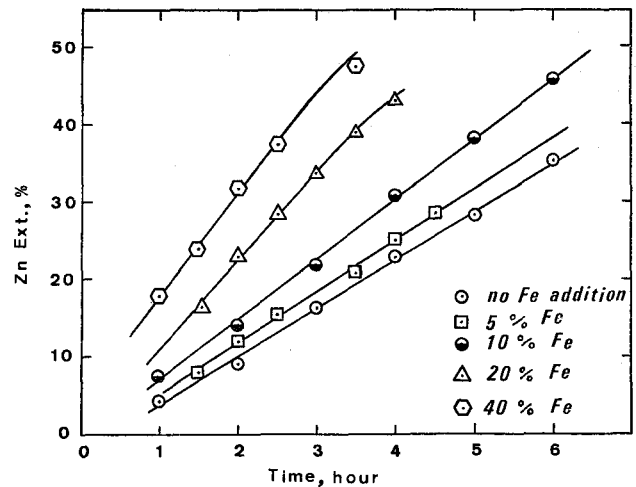


Fig. 9—Influence of iron addition on Zn extraction at 90°C, twice stoichiometric  $\text{H}_2\text{SO}_4$  and 150 psi oxygen partial pressure. (Iron addition in unit of mole percent of total zinc).

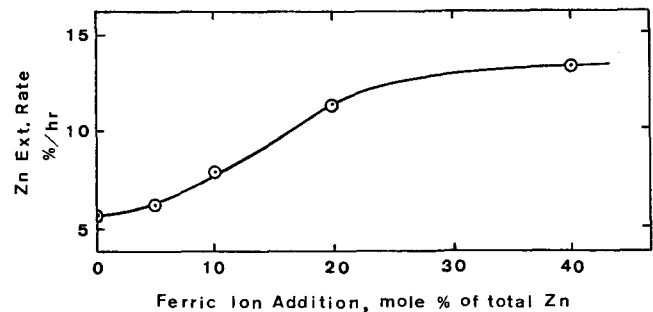
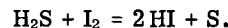
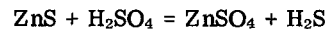


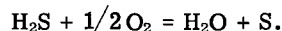
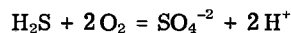
Fig. 10—Influence of iron addition on Zn extraction rate at 90°C, twice stoichiometric  $\text{H}_2\text{SO}_4$  and 150 psi oxygen partial pressure.

in Fig. 7. The iodine test was performed in a controlled at 90°C plastic vessel where  $\text{ZnS}$ , acid and one stoichiometric amount of zinc of iodine dissolved in KI solution were mixed by a magnetic stirrer. No oxygen or air was introduced during the test. The test involves the following two-step reaction:



The reaction of  $\text{I}_2$  with  $\text{H}_2\text{S}$  is essentially instantaneous. The relatively high reaction rate (higher than oxygen at 150 psi in substitution for  $\text{I}_2$  test) indicates that the formation of  $\text{H}_2\text{S}$  (Eq. [7]) proceeds relatively fast. It is the oxidation of  $\text{H}_2\text{S}$  that is slow and rate-determining.

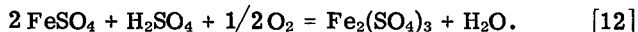
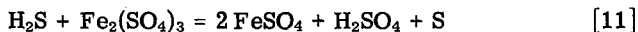
Direct oxidation of  $\text{H}_2\text{S}$  is according to the following equations:



Walas<sup>15</sup> reported that direct oxidation without catalyst required a temperature as high as 750°F. The leaching rate of pure  $\text{ZnS}$  at high  $\text{O}_2$  pressure had been reported by Bjorling<sup>1</sup> as negligible. Veltman *et al.*<sup>2-4</sup> concluded that the impurities in the sphalerite helped its leaching. All of these plus the catalytic effect reported by Scott and Dyson<sup>7</sup> on the leaching of pure  $\text{ZnS}$  lead to the conclusion that oxidation of  $\text{H}_2\text{S}$  is not

directly by oxygen but rather through the help of a catalyst.

Since the amount of ferric ion presented in the leach solution had a great effect on the rate of leaching as indicated by Figs. 9, 10 and 11, it is logical to assume Eqs. [10] to [12] as a mechanism for sphalerite leaching and Eq. [11] as the rate-controlling reaction.



The assumption is in good agreement with the following observations:

1) A higher leaching rate was observed when iodine was used in place of oxygen (Fig. 7). The higher reaction rate is attributed to the consequence of instantaneous reaction between hydrogen sulfide and iodine.

2) A close examination of Fig. 11 reveals the consistent relationship between iron and zinc concentration. The higher the iron content in the leach solution, the higher the sphalerite extraction rate. This is also in accord with reaction described by Eq. [11]. The higher the ferric ion concentration in the solution, the lower the equilibrium  $\text{H}_2\text{S}$  remained free in the solution and therefore the higher Zn dissolution rate predicted by Eq. [10]. The constant values of iron concentration in the solution after the first two hours of leaching also resulted in the constant zinc extraction rate.

3) Experimental data (Fig. 12) indicated that at low sulfuric acid concentration, zinc extraction rate decreased greatly possibly due to the shift of the rate-controlling step to Eq. [10]. Supplying more than twice the stoichiometric amount of  $\text{H}_2\text{SO}_4$  did not increase the dissolution rate. The effect of increased  $\text{H}_2\text{S}$  partial pressure generated by higher  $\text{H}_2\text{SO}_4$  concentration was balanced since  $\text{H}_2\text{SO}_4$  itself is involved in the product side of Eq. [11].

4) Solution pH value was dropping from an initial 1.7 to 1.4 in the tests where  $\text{Fe}_2(\text{SO}_4)_3$  addition was exercised indicating the production of  $\text{H}_2\text{SO}_4$ . When no  $\text{Fe}_2(\text{SO}_4)_3$  was added, solution pH value remained relatively constant at 1.7.

5) Table IV indicates the formation of elemental sulfur from ZnS occurs nearly quantitatively.

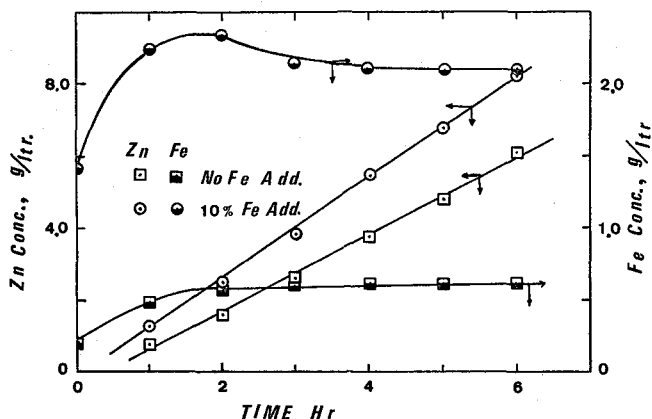
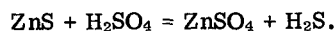
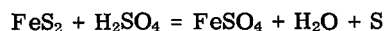
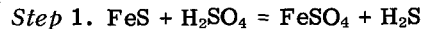


Fig. 11—Relationship between solution Zn and Fe concentration during leaching (90°C, twice stoichiometric  $\text{H}_2\text{SO}_4$ ).

## Reaction Mechanism

Examination of all the experimental data permits the conclusion that the reaction mechanism is:



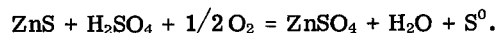
Dissolution of pyrrhotite and pyrite occurs very rapidly. Reaction of sphalerite with sulfuric acid is also fast when the solution has a low initial  $\text{H}_2\text{S}$  concentration.

Step 2.  $2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + 1/2\text{O}_2 = \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$ . Ferrous sulfate produced from Step 1 is oxidized to ferric sulfate. The reaction rate and conversion yield increase proportionally with oxygen pressure.

Step 3.  $\text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{S} = 2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{S}^0$ . Oxidation of  $\text{H}_2\text{S}$  is by ferric sulfate. The reaction produces sulfuric acid, elemental sulfur, and ferrous sulfate. Ferrous sulfate thus formed is oxidized again by Step 2.

Step 4. Steps 1, 2, and 3 reach a steady-state rapidly. Subsequently, the iron concentration remains constant while the dissolution of Zn proceeds at constant rate. No satisfactory reason can be found to explain why the iron concentration shown in Fig. 11 remains relatively constant throughout the leaching.

Overall Reaction:



## Effect of Hydrogen Pretreatment on the Sphalerite Leaching

Romankiw and de Bruyn<sup>16</sup> studied the dissolution of crystalline zinc sulfide in concentrated sulfuric acid solution in the absence of oxidizing conditions. They suggest that the dissolution process must be preceded by the rupture of the zinc sulfide bonds which are predominantly covalent in character and subsequent electron transfer to yield  $\text{Zn}^{+2}$  and  $\text{S}^{-2}$  ions. A rough calculation of the ionic nature of the Zn-S bond, based upon Pauling's<sup>17</sup> data, indicates that it is approximately

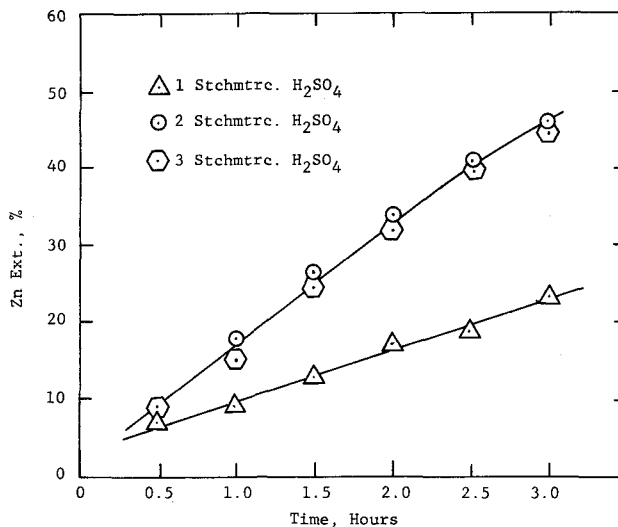


Fig. 12—Influence of sulfuric acid concentration on zinc extraction at 90°C and 150 psi oxygen partial pressure. (Sample size -200 +325 mesh).

Table IV. Formation of Elemental Sulfur in the Pressure Leaching of Sphalerite at 90°C, Twice Stoichiometric H<sub>2</sub>SO<sub>4</sub> and 150 psi Oxygen Partial Pressure

Test Conditions	S <sup>-2</sup> Oxidized from ZnS	S <sup>0</sup> Formed in Residue	Pct S <sup>-2</sup> Converted to S <sup>0</sup>
-115 +150 mesh, 6 h	0.59 gm	0.58 gm	98
-150 +200 mesh, 6 h	0.72 gm	0.70 gm	97
-150 +200 mesh, 6 h, 10 pct Fe addition	0.96 gm	0.90 gm	94
-150 +200 mesh, 4 h, 20 pct Fe addition	0.90 gm	0.81 gm	90

20 pct ionic in character. The more ionic in nature the bond is made to become, the more soluble it should be. They also observed an increasing rate of dissolution as iron or manganese content of the Zn-S lattice was increased, and attributed the behavior to the greater ionic character of the lattice as a result of the "doping" with iron or manganese.

Dutrizac, MacDonald and Ingraham<sup>18</sup> compared the kinetics of the dissolution of natural and synthetic chalcopyrite in sulfuric acid and oxygen under pressure. They observed that the parabolic rate constant of synthetic chalcopyrite is 50 times that of the rate constant for the natural mineral! No satisfactory explanation was made concerning this difference in rate. In a conversation between Profs. E. Peters, M. T. Hepworth and V. G. Fox,<sup>19</sup> the surprising difference in rates measured by Ingraham *et al* is explained as follows: natural chalcopyrite is formed slowly and allowed to anneal for geologic times; whereas, the synthetic mineral was metathesized and annealed for a relatively short time, *i.e.*, three days at 550°C. It is speculated therefore that the synthetic mineral would have a greater number of lattice defects and consequently be more susceptible to attack.

On the basis of these observations, it seems conceivable that an *altered sphalerite*, which would be produced by increasing the deviation from stoichiometry by partial reduction with hydrogen to produce a more highly metal excess semiconducting mineral, would have a higher zinc extraction than those of *natural sphalerite* under the same leaching conditions.

A fluidized bed was then set up to treat the natural sphalerite in the temperature range of 220°C to 600°C. A hydrogen-nitrogen gas mixture of 15 pct hydrogen was used as a reducing gas. The reduction of sphalerite was determined by chemically analyzing the amount of hydrogen sulfide in the exit gas. The hydrogen pretreated sample was then leached at 90°C, twice stoichiometric amount of H<sub>2</sub>SO<sub>4</sub> and 150 psi oxygen pressure. The overall zinc and iron extraction after 6 h leaching were plotted on Fig. 13. The ordinate axis on the left hand side of this figure gives the Zn extraction at the percentage of sulfur removal of that test. The ordinate axis on the right gives the Fe extraction corresponding to the sulfur removal of the test. The zero percent sulfur removal reading shown on the figure indicates the Zn and Fe extraction of natural sphalerite. The Zn or Fe extraction of each point on the figure are calculated from the volume the Zn or Fe content in the final leach solution.

Although the Zn and Fe extraction show a relative increase with increasing sulfur removal, all the hy-

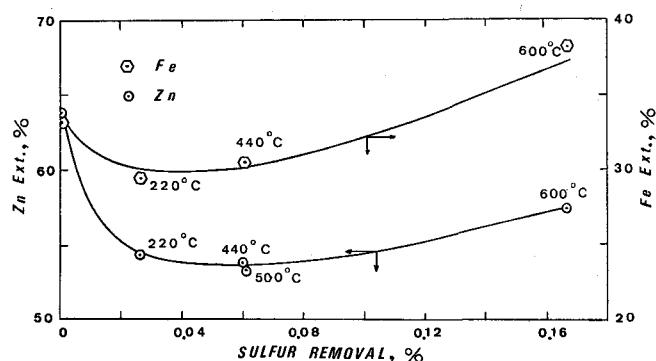


Fig. 13—Zn and Fe extraction from 20 min hydrogen pretreated sphalerite. (Pretreatment temperatures are shown on the graph). Leaching conditions: 90°C, twice stoichiometric H<sub>2</sub>SO<sub>4</sub>, 150 psi oxygen, and 6 h. Sample size -200 +325 mesh.

drogen pretreated sphalerite show less zinc extraction than that without pretreatment. The sphalerite has a resistance of  $6 \times 10^9$  ohm-cm at 90°C, but no measurement on the change of its resistance after pretreatment was made. However it is possible that sphalerite is so poor a conductor (resistance is about ten times higher than that of most other sulfides), that this small percentage sulfur removal does not change its covalent bond characteristic at all. On the contrary, other unknown factors cause the pretreatment to be unfavorable. Pretreatment of longer periods of time to remove much more sulfur may be necessary in order to produce an enhancement on the leaching result. However, this longer time will be economically unfeasible. The higher Zn extraction rate observed in Fig. 13 at higher sulfur removal percentage may be the result of higher Fe extraction instead of higher sphalerite conductivity.

## CONCLUSIONS

The kinetic results permit the following summary of the conclusions to be drawn regarding the mechanism of the reactions and the nature of the slow or rate-controlling stage.

- 1) The sphalerite is a flat-plate type particle resulting in the constant Zn extraction rate.
- 2) The rate-controlling step of leaching reaction is a heterogeneous process occurring on the sphalerite surface and not a homogeneous reaction in the solution. This is indicated by the rate dependence on the sphalerite surface area.
- 3) The rate-determining step during leach appears to be the oxidation of H<sub>2</sub>S occurring on the sphalerite surface, *i.e.* Eq. [11].
- 4) Oxidation of H<sub>2</sub>S is by ferric ion. Its reaction rate increases with increasing amounts of ferric ion. Addition of iron in the lixivium did increase the zinc extraction rate. The oxidation reagent, ferric sulfate, is then reduced to ferrous sulfate.
- 5) Reproduction of ferric sulfate is by oxygen conversion of ferrous sulfate. This reaction rate and conversion yield is low at room temperature. Reaction rate and conversion yield increases with increasing oxygen partial pressure.
- 6) Presence of ferrous sulfate is through the dissolution of pyrite and pyrrhotite. This dissolution occurs quickly at the initial moment of leaching and



reaches an equilibrium value. Thus throughout the leaching the amount of iron in the solution remains constant. If all other leaching conditions remain the same, the continual increase in the iron concentration will also increase the zinc extraction rate, and a linear Zn extraction rate could then not be observed.

7) Zinc extraction rate is first order with respect to oxygen partial pressure below 150 psi, although it is half order predicted by stoichiometry. This is conceivable since some side reactions consume oxygen too. In addition, it is the dissolved oxygen that affects the reaction rate but not the oxygen partial pressure. Also, oxygen dissociates into atoms and reacts (results in a first order reaction) is unlikely under this condition.

8) Oxygen consumption curve for leaching of sphalerite reported by Majima and Peters<sup>20</sup> showed an initial low rate with substantial increase and reached a constant value after 1 h. This is consistent with most of the experimental data seen in the study except that initial low rate appears in shorter periods of time. Probably the iron concentration has not reached a steady-state value causing this initial low rate. After this short period of time, iron concentration reached a steady state value and therefore Zn extraction proceeded at constant rate.

9) Pretreatment of sphalerite samples by hydrogen does not show any favorable extraction results.

10) Further study on the details of how the dissolution of pyrite and pyrrhotite proceeds during sphalerite leaching is important and may shed more light on the kinetics of pressure leaching of sphalerite.

#### ACKNOWLEDGMENTS

The authors wish to express their appreciation for the financial support of the Department of Chemical Engineering and Metallurgy, College of Engineering, University of Denver. Thanks especially to Professor L. W. Ross for his enthusiasm and helpful discussions.

Thanks are extended to Climax Molybdenum Com-

pany, Golden, Colorado, especially to Dr. R. S. Rickard, for their help in analyzing the sphalerite concentrate and in the use of their titanium autoclave. Also the generosity of Cominco Ltd., Canada, in supplying the sphalerite concentrate is acknowledged.

Special thanks to Professor M. E. Wadsworth of the University of Utah for his helpful and valuable suggestions.

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