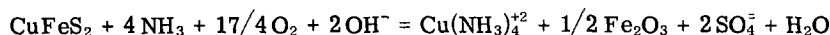# Ammonia, Oxidation Leaching of Chalcopyrite —Surface Deposit Effects

L. W. BECKSTEAD AND J. D. MILLER

The reaction for the ammonia, oxidation leaching of chalcopyrite,

$$CuFeS_2 + 4NH_3 + 17/4\,O_2 + 2OH^- = Cu(NH_3)_4^{+2} + 1/2\,Fe_2O_3 + 2SO_4^= + H_2O$$

was studied using monosize particles in an intensely stirred reactor at moderate oxygen pressures. For dilute solids concentration, the rate is controlled by an electrochemical surface reaction. Under conditions of low stirring speeds and low oxygen pressure, the hematite reaction product passivates the surface and the reaction virtually stops. Even though stirring speed influences the rate of the electrochemical reaction, this effect is due to changes in the morphology of the hematite deposit which alters the surface reaction kinetics, rather than being indicative of mass transfer limitations.

CONCERN about the impact of technological development on the environment has been responsible, to a certain extent, for a continued interest in copper hydrometallurgy. This interest is also a result of the prospect that hydrometallurgy can compete directly with smelting for recovery of metals from sulfide ores and minerals. Leaching of copper sulfide minerals has demanded considerable attention as a result of proven recovery from waste dumps and because the development of a hydrometallurgical nonsmelting process may provide the necessary technology to meet recently imposed clean air standards.

Many oxidants such as peroxides, persulfates, bromates, chlorates, *etc*, can be used in ammoniacal solution to leach copper sulfides, but the most available, low cost oxidant is oxygen. The chemistry of the oxidation is complex and is influenced by temperature, oxidant concentration, ammonia concentration, ammonium salts and metal ammines. For example, the reaction of covellite with oxygen can be represented as:

$$CuS + 4NH_3 + 2O_2 = Cu(NH_3)_4^{+2} + SO_4^=. \qquad [1]$$
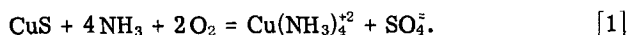
Leaching is possible due to the stabilization of cupric in the alkaline solution as the tetraamine complex. The reaction is complicated by the fact that the sulfide is not directly oxidized to sulfate, but goes through intermediates such as thiosulfate, $S_2O_3^=$, thionate, $S_3O_6^=$, polythionate, $S_4O_6^=$, and sulphamate, $NH_2SO_3^-$, all of which may be present in varying amounts. For copper sulfides containing iron, the reaction is further complicated by the fact that the iron is oxidized to ferric and precipitated as hematite, Fe_2O_3, which under certain circumstances alters the kinetics of the reaction.

Nucleation and growth of the hematite phase on the surface of copper-iron sulfides, particularly chalcopyrite, appears to account for a significant reduction in the rate of reaction and in many instances seems to passivate the surface. Stanczyk and Rampacek[1] showed that chalcocite, Cu_2S, covellite, CuS, and

bornite, Cu_5FeS_4, were more readily leached at lower temperatures, and oxygen pressures than chalcopyrite, $CuFeS_2$, under similar conditions. The reduced extent of reaction in the case of chalcopyrite was attributed to the formation of the hematite reaction product. The low iron content of bornite apparently is insufficient to significantly affect the reaction kinetics. Evans, *et al*[2] found similar results in their studies, in that chalcocite and covellite were much more readily dissolved due to the absence of a ferric oxide reaction product layer. The initial rates of reaction for the copper-iron sulfides were rapid. However, as the reaction proceeded, the rate decreased dramatically and the authors suggested that the reaction rate became controlled by diffusion through the hematite, reaction product layer.

The formation of the hematite phase was found to be important in the studies on ammonia leaching of copper sulfides as practiced by Sherritt-Gordon.[3] They found that agitation above a certain stirring speed was detrimental from the standpoint that the hematite was abraded as a colloidal dispersion, allegedly causing problems in subsequent thickening and filtering operations. On the other hand, the Arbiter process[4] makes use of intense mixing to achieve satisfactory leaching rates thus eliminating the need for high pressure autoclaves. It is reported that the intense mixing provides for good oxygen transport rates and also abrades the hematite phase from the copper-iron sulfide surface thus exposing fresh surface for reaction.

In another publication,[5] it was established that the reaction kinetics for ammonia, oxidation leaching of chalcopyrite

$$CuFeS_2 + 4NH_3 + 17/4\,O_2 + 2OH^-$$
$$= Cu(NH_3)_4^{+2} + 1/2\,Fe_2O_3 + 2SO_4^= + H_2O \qquad [2]$$
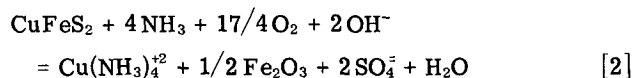
at dilute solid phase concentration, could be described accurately by an electrochemical reaction mechanism. Important kinetic parameters such as reaction order, temperature and particle size were discussed. The subject of this paper is the passivation phenomenon observed during the ammonia, oxidation leaching of chalcopyrite, the conditions under which passivation occurs and techniques which might be used to prevent passivation.

EXPERIMENTAL

The equipment used to conduct the majority of the leaching experiments was a Model 1-E-150-DFKU reactor, manufactured by Bench Scale Equipment Co., as described previously.[5] The reactor was fully baffled to insure good mixing conditions and hydraulically driven such that stirring speeds of 6,000 rpm could be achieved.

Several experiments were conducted in a 1 liter glass reactor assembly in which oxygen was allowed to bubble through the system at atmospheric pressure. The equipment consisted of a 1 liter, baffled, cylindrical glass reactor with a clamp held lid containing four fitted openings. A thermometer, solution sampler, condenser, and stirrer were placed into the reactor through these openings. The reactor was submerged in a circulating oil bath which maintained the temperature to $\pm 0.5°C$. In one set of experiments, the size distributed Pima flotation concentrate[5] was wet ground for 3 h in an attrition mill.[6] The ground product was characterized with respect to surface area and particle size and the leaching reaction kinetics determined.

The oxygen, compressed air, and chemicals used in this study have been described elsewhere.[5] The same Pima flotation concentrate was used and the monosize particles were prepared in the manner reported previously.[5] The rate of reaction was determined by copper analysis of the leach solution at selected time intervals with an atomic absorption spectrophotometer. This technique proved to be both convenient and reproducible. One of the more important aspects of this study was the characterization of reaction products. Solid leach residues were carefully observed both with an optical microscope and a scanning electron microscope in order to describe the nucleation and growth of the hematite phase on the chalcopyrite surface as a function of the reaction variables. X-ray diffraction was used to identify the hematite phase and no other solid reaction products were identified.

EXPERIMENTAL RESULTS

Again, as in the previous publication[5] "standard experimental conditions" of 1 pct solids, 90°C, 3,200 rpm, 1.8 M ($NH_3 + NH_4^+$), 2.18 atm oxygen pressure and 200 × 250 mesh particles will represent a point of reference. Variations in any of these conditions will be specifically noted.

Reaction Initiation

The importance of the hematite phase and how it can alter the leaching rate was demonstrated very early during the course of this investigation. Fig. 1 shows kinetic data collected for two different experimental procedures at different oxygen pressures. The top two curves represent results obtained using the standard procedure in which the reaction was initiated by breaking a glass vial containing the chalcopyrite into the solution at the specified temperature and pressure.[5] The lower two curves represent results obtained when the chalcopyrite was allowed to heat to the desired temperature in the leach
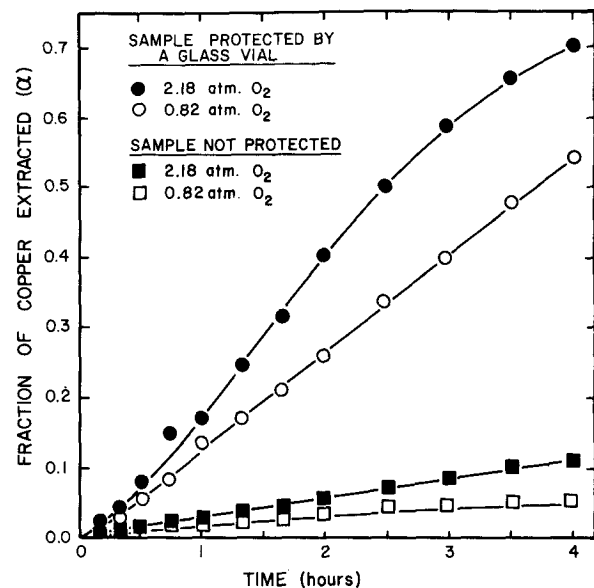

Fig. 1—Fraction extracted vs time plots at 90°C, 1 pct solids, 1.8 M [$NH_4^+ + NH_3$] pH 10.20, 200 × 250 mesh particles, 2,000 rpm at different oxygen pressure and for different methods of sample introduction.

solution—*not* protected by a glass vial. The reaction in this latter case was initiated by turning on the stirrer and introducing oxygen into the system. During the period in which the stagnant suspension was heating, less than 0.5 pct of the material reacted prior to initiation of the experiment. However, it appears that even for this extent of reaction, the hematite reaction product passivates the chalcopyrite surface. Under these circumstances, the rate may become controlled by diffusion of reactants through a protective product layer. This type of phenomenon would be similar to that which is observed in acid ferric sulfate leaching of chalcopyrite in which a protective sulfur layer forms.[6] Alternately, the passivation may be more of an electrochemical effect rather than a physical effect which inhibits mass transfer.

Fig. 2 presents a sequence of scanning electron photomicrographs of reacted chalcopyrite surfaces which correspond to the rate data presented in Fig. 1. The unleached mineral is relatively clean and smooth as shown by photograph (a) of Fig. 2. When the sample was not protected prior to initiating the reaction, a dense film of hematite was found to cover the mineral surface and inhibit the reaction as shown in photograph (b) of Fig. 2. This phenomenon was observed for reaction initiation at both 0.82 and 2.18 atm oxygen pressure. Analysis of the mineral surface by EDAX confirmed that the chalcopyrite particle was covered with the hematite reaction product. Photograph (c) of the same figure shows the surface of the reacted chalcopyrite particle (not protected by the glass vial) at 2.18 atm oxygen pressure magnified to 20,000 times to show the dense nodular growth of the hematite phase. The average size of the nodules in the photograph can be estimated to be between 0.2 and 0.5 μ. This estimate of the average nodule size compares well with independent size distribution measurements. For example, the size distribution

presented in Fig. 3 corresponds to the dispersed hematite phase found at the end of the experiment represented by the closed circle data in Fig. 1. The size analysis was made with a Micromeritics Sedi-Graph and shows that the hematite has an average particle size of 0.37 μ, similar to the surface hematite nodule size estimated from the SEM photomicrographs.

When the chalcopyrite particles are protected from the solution by a glass vial prior to leaching, the reacted particles have a distinctly different surface morphology as shown by photograph (d) in Fig. 2. Under these conditions, the hematite forms in patches and extensive passivation of the reaction is not observed. Since the reaction has been shown to be controlled by an electrochemical surface reaction,[5] both the cathodic and anodic areas are important parameters which determine the reaction rate and

may be modulated by the growth and character of the hematite phase.

Stirring Speed

Experiments were conducted to investigate the effect of stirring speed on the rate of reaction. Stirring speed has been shown to be a very important variable in ammonia leaching of copper sulfides.[4] Fig. 4 shows fraction extracted vs time plots for which the stirring speed was varied. This figure shows an effect similar to that observed in Fig. 1, in that at low stirring speeds the rate and extent of reaction are significantly reduced. Fig. 5 shows the initial rate of reaction plotted as a function of rpm. The type of curve obtained is very similar to what might be expected for systems in which the reaction rate is limited by mass transfer. However, a one-half order depend-
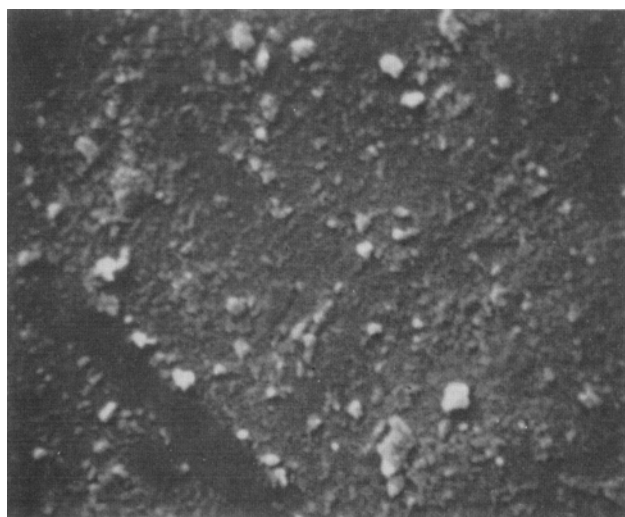
(a)
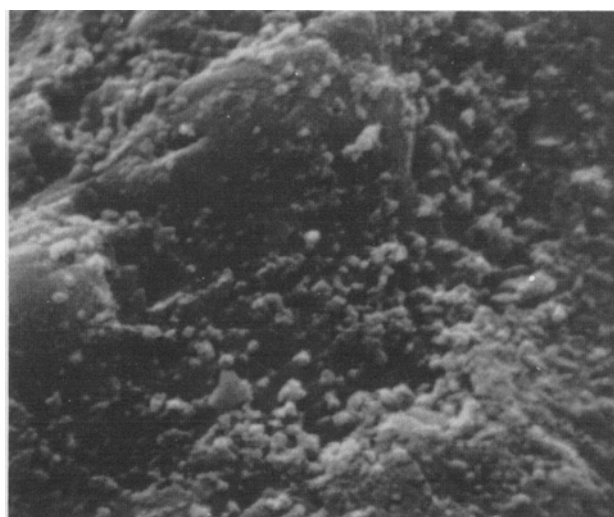
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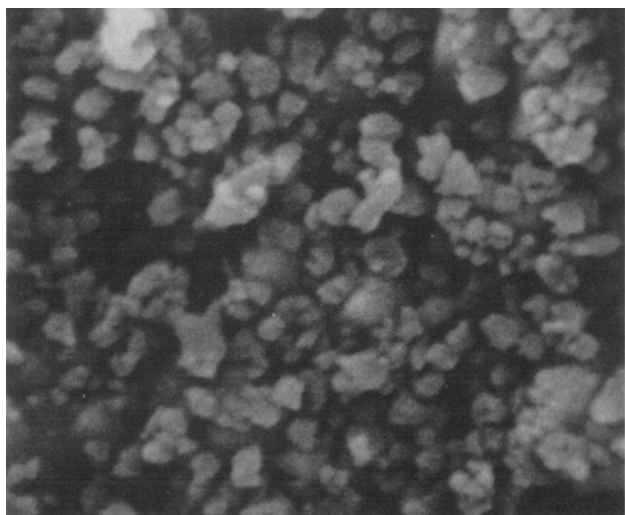
(c)

(d)

Fig. 2—Scanning electron photomicrographs of the reacted chalcopyrite surface at various oxygen pressures and different methods of sample introduction. Leaching conditions were 90°C, 1 pct solids, 1.8 M [NH_4^+ + NH_3], pH 10.20 and 2,000 rpm. (The hematite phase is the light area of clustered nodules). (a) Unleached chalcopyrite, magnification 10,000 times; (b) O_2 pressure—0.82 atm, conversion—5 pct, leach time—4 h; sample not protected; magnification 10,000 times; (c) O_2 pressure—2.18 atm, conversion—12 pct, leach time—4 h; sample not protected; magnification 20,000 times; (d) O_2 pressure—0.82 atm, conversion—54 pct, leach time—4 h; sample protected by glass vials; magnification 10,000 times.

ence on oxygen pressure at 2,000 rpm and an activation energy of approximately 10 kcal/mole at the same speed do not support mass transfer as the rate limiting process.[5]

To evaluate the significance of mass transfer resistance at the solid/liquid interface, the reaction rate constant can be calculated assuming rate control by oxygen transfer. Under these circumstances, the rate of reaction for spherical monosize particles of initial diameter, d_0, can be written in terms of the fraction reacted, α, as follows:

$$\frac{d\alpha}{dt} = \frac{6(b/a)M_B\, k(O_2)}{\rho_B\, d_0}(1 - \alpha)^{2/3} \qquad [3]$$

where

α = fraction chalcopyrite reacted at time, t,
k = reaction rate constant,
(b/a) = stoichiometry factor, moles of chalcopyrite per mole of oxygen,
ρ_B = density of chalcopyrite,
d_0 = initial particle diameter,
(O_2) = bulk concentration of oxygen, and
M_B = molecular weight of chalcopyrite.

For the initial kinetic response, Eq. [3] becomes

$$\left(\frac{d\alpha}{dt}\right)_{t \to 0} = \frac{6(b/a)M_B\, k(O_2)}{\rho_B\, d_0} = K_i \qquad [4]$$

where K_i is the initial rate of reaction, expressed in units of time^{-1}, from which the reaction rate constant can be determined. At 90°C, 0.82 atm oxygen pressure, 200 × 250 mesh particles, 1.8 M [NH$_4^+$ + NH$_3$], pH 10.20 and 2,000 rpm, the initial rate was determined to be 1.55×10^{-3} min^{-1}. From Eq. [4] the reaction rate constant, k, can be calculated from

$$k = \frac{K_i d_0 \rho_B}{6(b/a)M_B\, P_{O_2} K_h} \qquad [5]$$
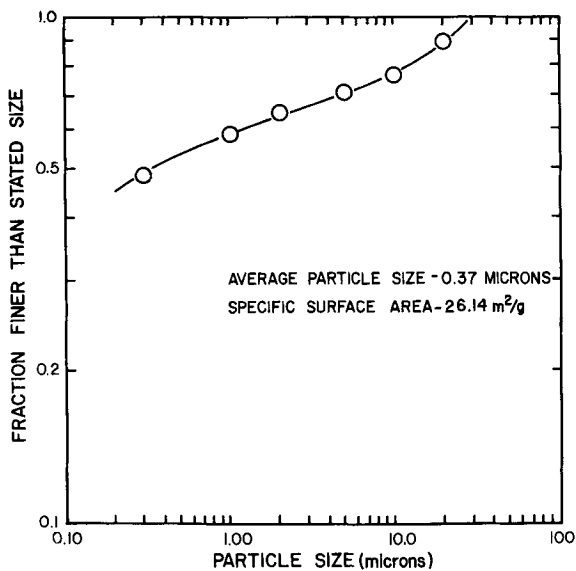
using the following data:

ρ_B = 4.1 g cm^3,
d_0 = 70 × 10^{-4} cm,
(b/a) = mole ratio chalcopyrite to oxygen, 4/17,
P_{O_2} = oxygen pressure, atmospheres, 0.82 atm,
K_h = Henry constant, mole cm^{-3} atm^{-1}, and
M_B = 183.5 g per mole.

At 90°C, the value of the Henry constant for oxygen in water is 7.507×10^{-7} moles cm^{-3} atm^{-1} (Ref. 7). From these data, the rate constant calculated from Eq. [5] is found to be 4.6×10^{-3} cm/s. This is assuming that the chalcopyrite particles are spherical and have a shape factor, f, of one. The shape factor would be inversely related to the rate constant as
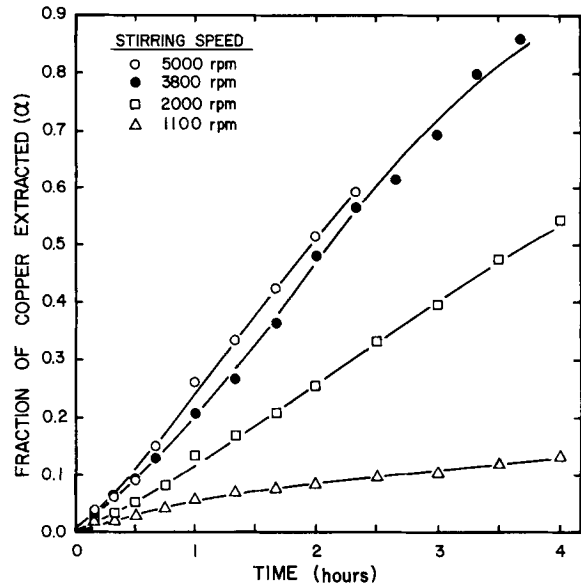

Fig. 4—Fraction extracted vs time plots for different stirring speeds at 90°C, 1 pct solids, 1.8 M [NH$_4^+$ + NH$_3$], pH 10.20, 200 × 250 mesh particles and 0.82 atm oxygen pressure. The data at 2,000 rpm are both for oxygen as needed by the reaction (standard procedure) and for oxygen flow through at 500 ml/min.

Fig. 3—A typical size distribution plot for the hematite reaction product formed at 90°C, 1 pct solids, 1.8 M [NH$_4^+$ + NH$_3$], pH 10.20, 200 × 250 mesh particles, 2,000 rpm and 2.18 atm, oxygen pressure.
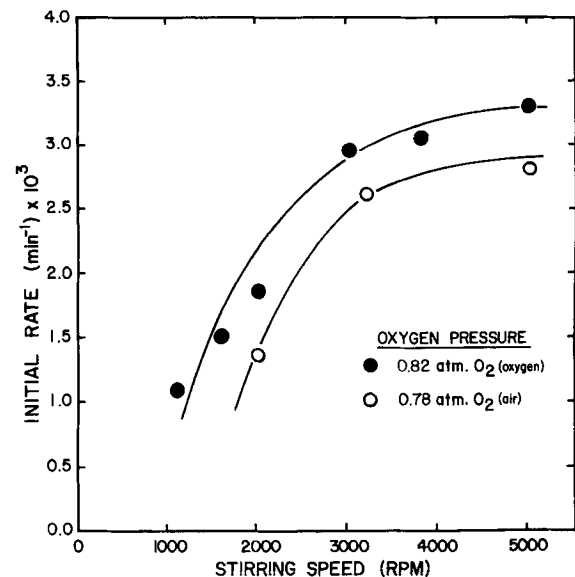

Fig. 5—Initial rate of reaction vs stirring speed at two different oxygen pressures.

$$k = \frac{4.6 \times 10^{-3} \text{ cm/s}}{f}. \qquad [6]$$

A realistic value of f might be 4 (Ref. 8), in which case k is equal to 1.16×10^{-3} cm/s. Harriot[9] has investigated methods by which the physical mixing conditions in a system can be coupled with the Sherwood correlation to predict the value of the mass transfer coefficient at the solid/liquid interface for suspended particles in stirred reactors. Using Sherwood Number correlation mass transfer coefficient can be estimated to be on the order of 10^{-1} cm/s (Ref. 10). The experimental value for the rate constant, (4.6×10^{-3} cm/s to 1.16×10^{-3} cm/s) is two orders of magnitude smaller than what would be expected if mass transfer at the solid/liquid interface were rate limiting. Thus, it would appear that resistance due to mass transfer at the solid/liquid interface is not important in this system, even at lower stirring speeds.

With regard to possible rate control by oxygen mass transfer at the gas/liquid interface, the data presented in Fig. 4, for a stirring speed of 2,000 rpm suggest that this resistance is not significant. The data shown in Fig. 4 are for standard conditions in which oxygen was allowed to enter the system as needed by the reaction. However, a similar experiment was made at 2,000 rpm in which oxygen was dispersed and allowed to flow through the solution at 500 ml per min. The data for this experiment were identical to the data in which oxygen was not bubbled through the system. It would appear that the diffusion of oxygen at the gas/liquid interface is not rate controlling for this system at dilute solids concentration.

It is most probable that the dependence of the reaction rate on stirring speed is, in fact, related to the growth and nucleation of the hematite reaction product on the chalcopyrite surface. For example, it has been shown in electrolysis that the form of the electrode deposit is quite sensitive to the hydrodynamics of the system.[11] Fig. 6 shows scanning electron photomicrographs of the leached chalcopyrite surface
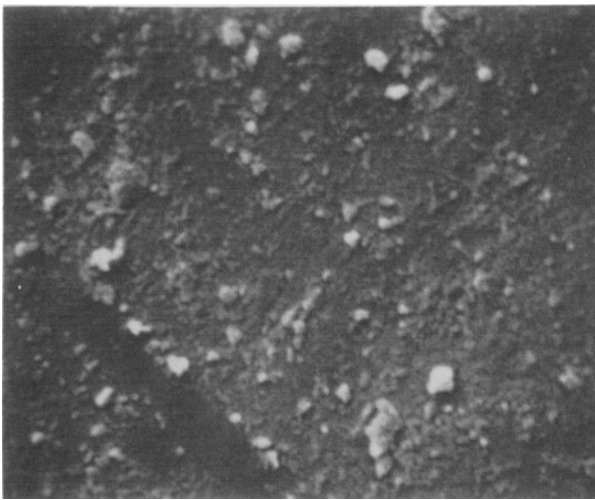
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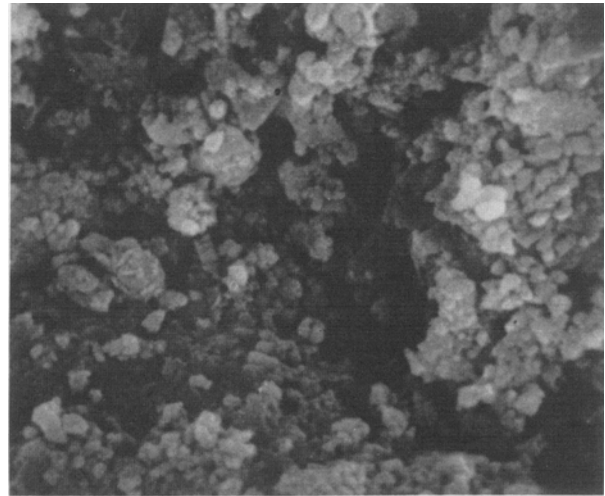
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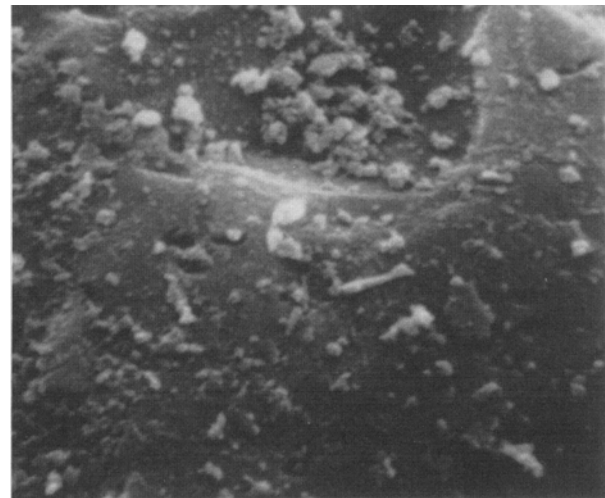
(d)

Fig. 6—Scanning electron photomicrographs (magnification 10,000 times) of the reacted chalcopyrite surface at various stirring speeds. Leaching conditions were 90°C, 1 pct solids, 1.8 M [$NH_4^+ + NH_3$], pH 10.20 and 0.82 atm, oxygen pressures. (a) Unreacted chalcopyrite; (b) stirring speed–1,100 rpm, conversion–11 pct, leach time–4 h; (c) stirring speed–2,000 rpm, conversion–54 pct, leach time–4 h; (d) stirring speed–3,200 rpm, conversion–82 pct, leach time–4 h.

at different stirring speeds; otherwise the conditions of the experiments were identical. As can be seen, the chalcopyrite surface develops a dense layer of hematite at 1,100 rpm and the reaction is passivated, similar to the results observed when the particles were not protected prior to reaction initiation as was shown in Fig. 2, photograph (b). At higher stirring speeds the surface is much cleaner and relatively free of the hematite product. As the rate of stirring is increased, the turbulence of the system abrades the mineral surface thus exposing fresh surface sites for reaction. Furthermore, the nature of the deposit itself may change with stirring speed as was observed in the electrodeposition study.[11] Above approximately 3,000 rpm it appears that the surface is maintained fairly free of hematite, a constant surface morphology is reached and increased stirring does not affect the rate appreciably. At low stirring speeds, the amount of hematite on the mineral surface may be greater than at high stirring speeds. In addition, the nature of the hematite deposit may be altered causing the hematite reaction product to spread over the particle surface and as a consequence offer significant resistance to the rate of reaction. If the reaction kinetics are controlled by the electrochemical reaction mechanism previously proposed,[5] even a small amount of a tight coherent hematite deposit could result in a very large interfacial ohmic potential drop resulting in electrochemical passivation.

Particle Size

In relation to particle size effects, the leaching response of attritor ground Pima concentrate was examined. The attritor ground chalcopyrite (3 h grind time) has an average particle size of 0.45 μ, and a specific surface area (BET) of 12 m^2/g. Fig. 7 shows fraction reacted vs time plots for the attritor
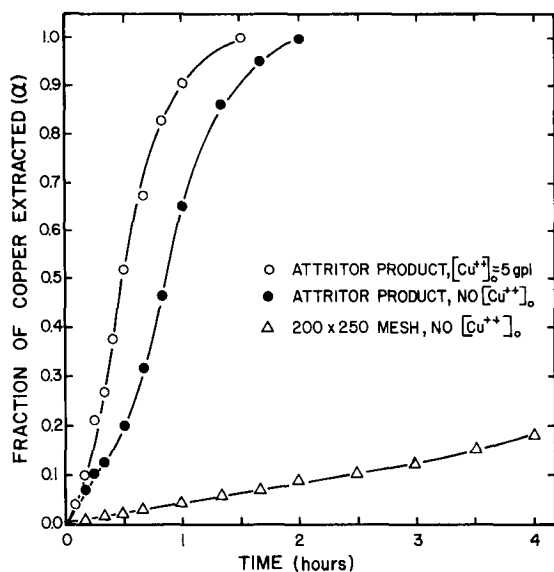

Fig. 7—Fraction extracted vs time plots for monosize chalcopyrite particles and 3 h attritor ground concentrate. A glass reactor was used and experimental conditions were 90°C, 1 pct solids, 1.8 M [NH_4^+ + NH_3], 2,000 rpm with flow through oxygen at 1 atm pressure.

ground Pima concentrate when leached in a glass reactor by bubbling oxygen through the system at atmospheric pressure, 90°C, 1 pct solids, 1.8 M [NH_3 + NH_4^+], and pH 10.20. Also shown by way of comparison is the leaching response of 200 × 250 mesh particles under the same leaching conditions. For the attritor ground chalcopyrite, 100 pct extraction is easily obtained in 2 h. The 200 × 250 mesh particles leach much slower in comparison. The sigmoidal curve in the case of the attritor ground material arises due to cupric catalysis.[5] An initial addition of cupric smooths the curve and increases the rate of reaction indicating that an electrochemical surface reaction continues to control the kinetic response.

DISCUSSION

It has been shown that, in the absence of passivation effects, the rate of reaction is limited by an electrochemical reaction at the chalcopyrite surface.[5] From consideration of half cell reactions and the respective Butler-Volmer equations for the partial currents, which involve the mixed potential (E_m), the following expression was derived and found to describe the reaction kinetics:

$$\frac{d\alpha}{dt} = \frac{127 f \, (OH^-)^{1/2}}{d_0} \left(\frac{K_1 P_{O_2}}{1 + K_2 P_{O_2}} \right)^{1/2}$$
$$\times \, [k_1 + k_2(Cu^{+2})_0 + k_2' \alpha]^{1/2}(1 - \alpha)^{2/3}. \qquad [7]$$

This equation accurately accounted for experimental kinetic data in the absence of passivation and excellent agreement regarding reaction orders as well as geometric factors was obtained. The above equation can be simplified to,

$$\frac{d\alpha}{dt} = K_0[k_1 + k_2(Cu^{+2})_0 + k_2' \alpha]^{1/2}(1 - \alpha)^{2/3} \qquad [8]$$

where

$$K_0 = \frac{127 f}{d_0} (OH^-)^{1/2} \left(\frac{K_1 P_{O_2}}{1 + K_2 P_{O_2}} \right)^{1/2}.$$

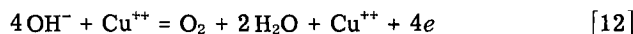The equation then can be rearranged and integrated from $t = 0$, $\alpha = 0$ to $t = t$ and $\alpha(t)$ to obtain

$$\int_0^{\alpha(t)} \frac{d\alpha}{(1 - \alpha)^{2/3}[k_1 + k_2(Cu^{+2})_0 + k_2' \alpha]^{1/2}} = K_0 t. \qquad [9]$$

The integral in Eq. [9] can be evaluated numerically for a given set of data and the resulting values when plotted as a function of time are found to be linear in the absence of passivation.

Eq. [9] was derived by considering the reaction to be controlled by an electrochemical, charge transfer surface reaction, shown schematically in Fig. 8. Any electrochemical reaction requires the presence of two distinct areas for discharge of the respective half cells. The anodic reaction,

$$CuFeS_2 + 19 \, OH^- = Cu^{++} + 1/2 \, Fe_2O_3 + 2 \, SO_4^=$$
$$+ \, 19/2 \, H_2O + 17e \qquad [10]$$
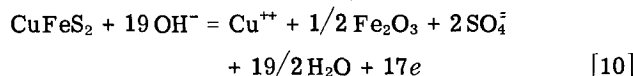
takes place at anodic sites, A_a, on the surface, while the cathodic reactions,

$$4 \, OH^- = O_2 + 2 \, H_2O + 4e \qquad [11]$$
$$4 \, OH^- + Cu^{++} = O_2 + 2 \, H_2O + Cu^{++} + 4e \qquad [12]$$

Cathodic Reactions

$$O_2 + 2H_2O + 4e \longrightarrow 4OH^-$$

$$O_2 + 2H_2O + Cu^{++} + 4e \longrightarrow Cu^{++} \quad 4OH^-$$

REDUCTION IN EFFECTIVE ANODIC AREA BY THE HEMATITE REACTION PRODUCT LEADING TO PASSIVATION

Anodic Reaction

$$CuFeS_2 + 19OH^- \longrightarrow Cu^{++} + \tfrac{1}{2}Fe_2O_3 + 2SO_4^= + \tfrac{19}{2}H_2O + 17e$$
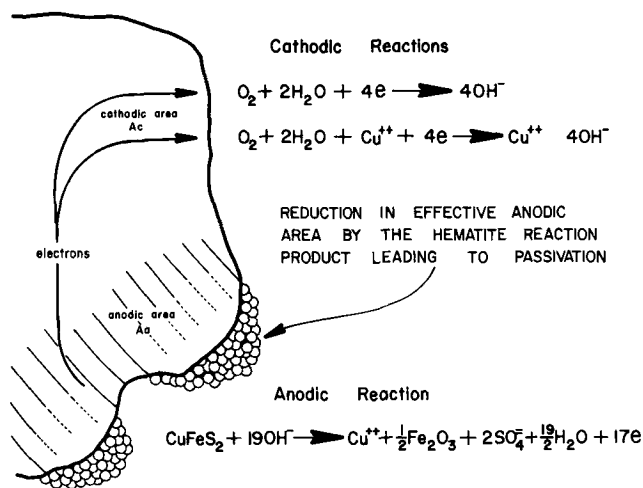
Fig. 8—Schematic representation of the electrochemical reaction and the reduction of the anodic area by the hematite reaction product.

take place at cathodic sites, A_c, on the surface. The sum of both areas is the total area, A, at which the reaction occurs. Due to the fact that the ammonia, oxidation leaching of chalcopyrite is limited by an electrochemical surface reaction, both area terms are important, and changes in either one will affect the rate of reaction.

The reaction rate constants, k_1, k_2, and k_2' of Eq. [9] are complex and consist of the product of several terms:

$$k_1 = \overleftarrow{k}_{c1}\overrightarrow{k}_a K_b^2 \qquad [13]$$

$$k_2 = \overleftarrow{k}_{c2}\overrightarrow{k}_a K_b^2 \qquad [14]$$

and

$$k_2' = k_2\left(\frac{0.33\,W_0}{V M_c}\right) \qquad [15]$$

where $\overrightarrow{k}_a$, $\overleftarrow{k}_{c1}$, $\overleftarrow{k}_{c2}$, are the respective half cell rate constants for the anodic (Eq. [10]) and cathodic (Eqs. [11] and [12]) reactions, W_0 is the initial weight of chalcopyrite, 0.33 is the fraction of copper in the chalcopyrite, V is the volume of the aqueous phase and M_c is the atomic weight of copper. The constant K_b has been defined as,

$$K_b = \left(\frac{b}{b+1}\right)\left(\frac{1}{b}\right)^{1/2} \qquad [16]$$

where b is the ratio of cathodic to anodic area, A_c/A_a (see Fig. 8).

In the derivation of Eq. [9] it was assumed that the ratio of the cathodic area, A_c, to the anodic area, A_a, is constant for a given set of conditions. It is quite possible that the ratio of the cathodic area to the anodic area will vary with a number of system parameters, such as stirring speed, electrolyte composition, particle size, temperature, etc. This is especially true in the case of stirring speed in that it has been clearly demonstrated in an electrodeposition study[11] that the surface morphology is determined, in part, by the hydrodynamics of the system. Surface deposit effects have been observed to

influence the interpretation of heterogeneous reaction kinetics and have been discussed extensively in the case of cementation reactions.[12] In the ammonia oxidation leaching of chalcopyrite at low stirring speeds it has been shown (see Fig. 6) that the hematite on the surface of the chalcopyrite has a different morphology than at higher stirring speeds possibly reducing the anodic area, A_a. A decrease in the anodic area, A_a, increases the value of the parameter b, (A_c/A_a). The term, K_b, decreases resulting in a decrease in the rate of reaction.

At higher stirring speeds, it appears from the photomicrographs that the growth of the hematite phase is diminished. Since this nucleation and growth originates at anodic sites it seems this could represent an increase in the anodic area. A smaller value of b increases the value of the parameter, K_b, and the rate of reaction should and does increase (see Fig. 4). If this analysis is correct, it follows that at stirring speeds greater than 3,000 rpm, b is no longer a function of stirring speed (see Fig. 5) and a constant surface deposit morphology is reached above 3,000 rpm such that b (the ratio A_c/A_a) remains constant.

From calculations made, it appears that mass transfer at the solid/liquid interface is not an important consideration under the experimental conditions of this study. Even when the interfacial area was increased by more than an order of magnitude (the 3 h attritor ground chalcopyrite), the kinetic response still reflected control by an electrochemical surface reaction. Further, recall that the attritor ground chalcopyrite can be reacted to completion at moderate conditions (2,000 rpm 90°C, and oxygen at atmospheric pressure) under which the unground concentrate normally passivates. These results suggest that particle size and/or the rate of reaction may influence the morphology and growth of the hematite reaction product. The fact that the stirring speed dependence is revealed in the initial kinetic response seems to indicate that, the surface deposit effect becomes a critical issue almost instantaneously. Even for very short reaction times, the environment (hydrodynamics and reactants' concentrations) determines the extent of activation of electrochemical sites and whether or not the system passivates.

CONCLUSIONS

The following conclusions were made regarding passivation effects in the ammonia, oxidation leaching of chalcopyrite. SEM photomicrographs of reacted particles were invaluable in characterizing surface morphology and in reaching these conclusions.

1) Early experiments proved that when chalcopyrite is not protected from the leach solution prior to the initiation of an experiment, the formation of a hematite reaction product at the chalcopyrite surface severely inhibits the rate and extent of reaction.

2) The stirring speed significantly influenced the rate of reaction below 3,000 rpm. Above 3,000 rpm, the rate of reaction became insensitive to stirring speed. The reaction rate dependence on stirring speed is the result of surface deposit effects and/or electrochemical site activation—not a result of mass transfer control in the system.

3) The fact that the attritor ground concentrate did not passivate and was shown to leach rapidly in comparison to unground concentrate particles under moderate leaching conditions, suggests that there may be an interaction between particle size and surface deposit morphology. Furthermore even with the high interfacial area, the electrochemical reaction controls the rate as evidenced by cupric catalysis.

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