

# The Dissolution of Chalcopyrite in Ferric Sulfate and Ferric Chloride Media

J. E. DUTRIZAC

The literature on the ferric ion leaching of chalcopyrite has been surveyed to identify those leaching parameters which are well established and to outline areas requiring additional study. New experimental work was undertaken to resolve points still in dispute. It seems well established that chalcopyrite dissolution in either ferric chloride or ferric sulfate media is independent of stirring speeds above those necessary to suspend the particles and of acid concentrations above those required to keep iron in solution. The rates are faster in the chloride system and the activation energy in that medium is about 42 kJ/mol; the activation energy is about 75 kJ/mol in ferric sulfate solutions. It has been confirmed that the rate is directly proportional to the surface area of the chalcopyrite in both chloride and sulfate media. Sulfate concentrations, especially  $\text{FeSO}_4$  concentrations, decrease the leaching rate substantially; furthermore,  $\text{CuSO}_4$  does not promote leaching in the sulfate system. Chloride additions to sulfate solutions accelerate slightly the dissolution rates at elevated temperatures. It has been confirmed that leaching in the ferric sulfate system is nearly independent of the concentration of  $\text{Fe}^{3+}$ ,  $k\alpha[\text{Fe}^{3+}]^{0.12}$ . In ferric chloride solutions, the ferric concentration dependence is greater and appears to be independent of temperature over the interval 45 to 100 °C.

**I**NTEREST in the hydrometallurgical processing of copper concentrates continues at a high level although it is now generally recognized that such hydrometallurgical processes will have their own special environmental problems and will likely pay an energy penalty because of the need to heat and cool large volumes of fairly dilute solutions and because copper is usually recovered from solution by electrowinning.<sup>1</sup> Among the numerous hydrometallurgical options, ferric ion leaching remains a strong contender that is enjoying some limited success at commercialization. Ferric sulfate solutions, in conjunction with bacteria, are being used to recover copper from waste rock and low grade ores by percolation leaching techniques.<sup>2</sup> Furthermore, in the United States, two pilot operations are currently determining the viability of leaching copper concentrates with  $\text{FeCl}_3\text{-CuCl}_2$  media, and, in Poland, a ferric sulfate leaching pilot operation has also been run on chalcopyrite concentrates.<sup>3</sup>

On a global scale, chalcopyrite ( $\text{CuFeS}_2$ ) is the most important copper mineral, and in many concentrates it is the sole source of copper. Because of the dual importance of chalcopyrite and ferric ion leaching, numerous investigations have been carried out to elucidate the reaction kinetics and to delineate the important leaching variables in both the ferric sulfate and ferric chloride systems. In spite of the great number of such studies and the obvious competence of most of the researchers involved, the leaching kinetics are still partly shrouded in uncertainty. There are still serious doubts about such fundamental aspects as the reaction stoichiometry or the shape of the leaching curves, and many of the more subtle, but equally important,

details have not been adequately resolved. Hence, further studies appear warranted on the leaching of chalcopyrite in ferric ion media.

In the present investigation, the recent literature has been surveyed to identify areas of consensus and to define points of controversy. Those doubtful areas were then carefully reexamined experimentally. The results of the present investigation and the discussion of the recent literature data are presented in the body of the paper below.

## EXPERIMENTAL

To avoid any possible problems associated with synthetic material, all the leaching investigations were carried out using carefully sized and cleaned natural chalcopyrite. The bulk of the work was done with chalcopyrite from Messina, Transvaal, South Africa, but confirmatory tests were also done with material from the Temagami Lake Mine, Temagami, Ontario. Selected pieces of high grade ore were dry-ground to -350 mesh and were then cyclized in 50 g lots into the following fractions: -37 + 29  $\mu\text{m}$ , -29 + 20  $\mu\text{m}$ , -20 + 14  $\mu\text{m}$  and -14 + 10  $\mu\text{m}$ . The various fractions were cleaned by repeated passage through a Franz magnetic separator sequentially set to remove impurities both more and less magnetic than  $\text{CuFeS}_2$ . The magnetically cleaned sulfides were subjected to froth flotation at both pH 6 and pH 10.5 to remove middling particles and residual gangue. The cleaned fractions were then carefully recyclosized in 15 g batches to produce the product for leaching. The sized fractions were washed thoroughly with acetone and were finally vacuum dried at room temperature.

The Transvaal chalcopyrite concentrates assayed 35.8 pct Cu, 29.0 pct Fe and 33.5 pct S; they contained over 98 pct chalcopyrite with traces of sphalerite, quartz and pyrite. The Temagami chalcopyrite con-

J. E. DUTRIZAC is Head, Metallurgical Chemistry Section, CANMET, Department of Energy, Mines and Resources, Ottawa, Canada, K1A 0G1.

Manuscript submitted August 19, 1980.

sisted of 95 pct chalcopyrite, 3 pct pyrite, 1.5 pct bornite and 0.5 pct sphalerite. Electron microprobe analysis showed both sulfides to be "chalcopyrite" of stoichiometric  $\text{CuFeS}_2$  composition. Both materials were examined using a Guinier-de Wolff precision focussing X-ray camera and it was established that both were chalcopyrite and not one of the recently discovered similar phases in the Cu-Fe-S system.<sup>4</sup>

For the leaching tests, 0.780 g of chalcopyrite was added to 2.7 l of solution in a thermostated water bath. The relative amounts of solution and chalcopyrite were such that the tests were done at approximately constant  $\text{Fe}^{3+}$  concentration, and ferric ion depletion was never a factor. The leaching solutions were automatically sampled and analyzed colorimetrically for copper with a Technicon AutoAnalyzer. The sized fractions were agitated in the leaching bath by a plastic stirrer and protective atmospheres were used to minimize air oxidation. Liquid removed from the leaching vessels, either by sampling or by evaporation, was replaced by a return feed of barren solution or water, respectively.

Throughout the paper the various leaching parameters have been discussed in terms of initial rate constants which were derived by fitting the data to a second order polynomial equation:  $\text{Cu}(\text{mg}) = a + bt + ct^2$  where  $t$  is the time in hours, and by calculating the slope at  $t = 0$ . Although this procedure is without a strong theoretical basis, it is a useful and convenient means of comparing reactions with differently shaped kinetic curves. For example, in the sulfate system the data closely obey the  $1 - 2/3\alpha - (1 - \alpha)^{2/3} = kt$  relationship which is indicative of a protective product layer. By contrast, in the chloride media the simple shrinking core model  $1 - (1 - \alpha)^{1/3} = kt$  is closely followed. In the mixed sulfate-chloride systems, neither expression is strictly obeyed, and in very concentrated solutions irregular leaching curves were sometimes produced. None of the established phenomenological models yielded straight lines under all conditions, and, hence, none gave uniquely defined constants employable for all systems. Since the objective of the present study was frequently to compare the diverse reaction rates, a universally applicable rate constant was required. Initial rate constants are easily calculated and are generally applicable. It has been found that trends identified by initial rate constants are consistent with those developed from phenomenological models although the numerical values so calculated are often slightly different as will be noted in the body of the text.

## RESULTS AND DISCUSSION

### The Effect of Surface Area

Jones and Peters<sup>5</sup> reported that the chalcopyrite leaching rate was independent of particle sizes below 100 mesh when the mineral was leached in 0.1 M ferric sulfate solution at 90 °C. In contrast, the rate in the  $\text{FeCl}_3$  system increased in direct proportion to the chalcopyrite area. The behavior in the sulfate system

was unusual and is in apparent contradiction to the widely held belief that fine grinding promotes rapid chalcopyrite reaction. This factor was also investigated by Beckstead *et al.*,<sup>6</sup> who found that the initial rate of leaching of attritor-ground chalcopyrite increased in direct proportion to the initial surface areas, as would be expected intuitively. Later, Munoz, Miller and Wadsworth<sup>7</sup> showed that the "parabolic rate constant" for the leaching of 4, 12 and 47  $\mu\text{m}$   $\text{CuFeS}_2$  particles at 90 °C in 0.25 M  $\text{Fe}_2(\text{SO}_4)_3$  also varied directly as the area of the chalcopyrite.

To clarify the above differences, a constant weight of the sized Transvaal chalcopyrite was leached at 90 °C in either 0.2 M  $\text{Fe}(\text{SO}_4)_{1.5} - 0.3$  M  $\text{H}_2\text{SO}_4$  or 0.2 M  $\text{FeCl}_3 - 0.3$  M  $\text{HCl}$  solutions. Figure 1 shows the type of leaching curves observed when the various size fractions were leached in the sulfate system. Clearly the rate increases as the mean particle size is decreased below 100 mesh. Similar behavior was observed in the chloride system, except that the rates were correspondingly more rapid. Initial rate constants were deduced from the initial slopes as determined by fitting the data to a parabolic equation:

$$y = a + bx + cx^2 \quad [1]$$

The initial rate constants so deduced were then plotted against  $1/r$ , where  $r$  is the mean particle size in micrometers. The data for both the sulfate and chloride systems are given in Fig. 2. Significantly, for both systems, there is a linear relationship between  $k_{\text{initial}}$  and  $1/r$ . If the initial leaching rate is proportional to the area, then:

$$k_{\text{initial}} (\text{mg/h}) \propto N \cdot A' \quad [2]$$

where  $N$  is the number of particles and  $A'$  is the unit particle area.

$$k_{\text{initial}} (\text{mg/h}) \propto \frac{3}{\rho} \cdot \frac{1}{r} \quad [3]$$

$$\propto 1/r \quad [4]$$

Hence, Fig. 2 clearly shows that the rates in both the sulfate and chloride media are directly proportional to the area of chalcopyrite being leached.

The present results coupled with previous findings<sup>6,7</sup> and the general observation that copper concentrate

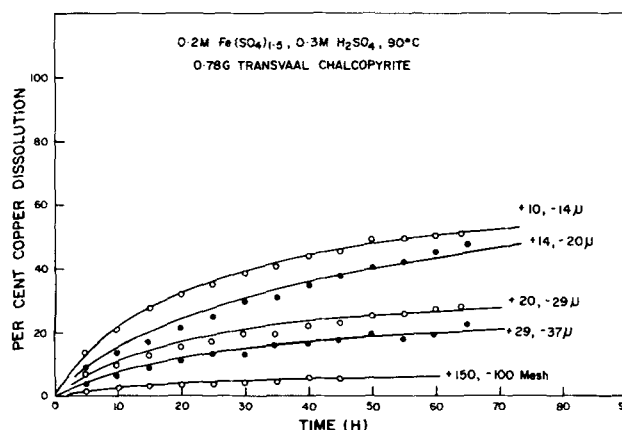


Fig. 1—Leaching curves for the dissolution of various size fractions of natural chalcopyrite in sulfate solutions.

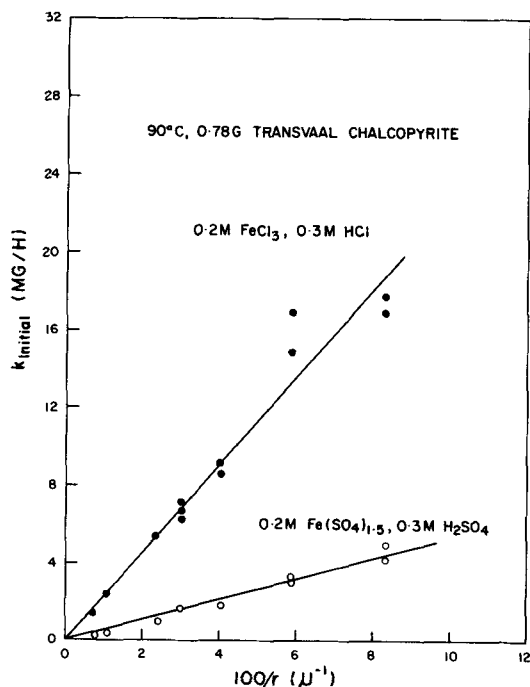


Fig. 2—Variation of the leaching rate with the chalcopyrite particle size in both sulfate and chloride media.

leaching is promoted by fine grinding all indicate a direct correlation between the rate and the surface area of the chalcopyrite. It is not known why Jones and Peters observed no area dependence for the leaching of chalcopyrite in sulfate media, but it appears that their concentrates were dry screened and this is an ineffective procedure for very fine particles.

In the ferric sulfate system, surface area and temperature are the two principal control variables, and any kinetic work must ensure an adequately characterized (or at least constant) area. Although dry screening is ineffective for separating fine particles, wet screening is acceptable if carried out thoroughly enough to wash out all fines. Of course, wet cyclosizing of small batches is an ideal method of producing a sized feed for kinetic studies. The present work has also determined that prior leaching of the chalcopyrite with cold 0.5 M H<sub>2</sub>SO<sub>4</sub> does not alter the leaching behavior of properly dried chalcopyrite samples. The mellow yellow tarnish which forms on chalcopyrite is likely a sulfide which is not readily acid soluble.

#### The Addition of FeSO<sub>4</sub>

Dutrizac *et al*<sup>8</sup> first reported the deleterious effect of the FeSO<sub>4</sub> reaction product on the leaching of synthetic chalcopyrite by 0.11 M ferric sulfate solutions at 70 °C. A later investigation<sup>9</sup> showed that the effect was confined to the sulfate medium; large concentrations of FeCl<sub>2</sub> in an FeCl<sub>3</sub> leaching solution only slightly depressed the leaching rate at 85 °C. Jones and Peters,<sup>5</sup> in comparative leaching tests, showed that the addition of 0.1 M FeSO<sub>4</sub> to a 0.1 M Fe(SO<sub>4</sub>)<sub>1.5</sub> solution caused the chalcopyrite extraction to fall from 20 pct to 4 pct under comparable conditions. In the FeCl<sub>3</sub> medium, the addition of FeCl<sub>2</sub> was

without effect. These findings are consistent with those cited above.<sup>8</sup> By contrast, Beckstead *et al*<sup>6</sup> obtained essentially identical leaching curves when either 20 or 100 g/l Fe<sup>2+</sup> as FeSO<sub>4</sub> was added to a ferric sulfate medium at 93 °C. During electrochemical (anodic) oxidation, the addition of Fe<sup>2+</sup> increases the total current,<sup>10</sup> but this is likely a result of a parallel reaction, Fe<sup>2+</sup> → Fe<sup>3+</sup>, at the anode.

Figure 3 shows the leaching curves realized in the current work when various concentrations of FeSO<sub>4</sub> were added to a 0.1 M Fe(SO<sub>4</sub>)<sub>1.5</sub> – 0.3 M H<sub>2</sub>SO<sub>4</sub> medium. The addition of even small quantities of FeSO<sub>4</sub> causes the rate to fall appreciably. For these curves, pipette samples were taken to avoid crystallization of FeSO<sub>4</sub> in the automatic sampler lines. The pipette sample was directly diluted to avoid crystallization; no salts remained in the pipette after sampling.

Initial rate constants were deduced from the initial slopes and these were plotted versus the FeSO<sub>4</sub> concentration as shown in Fig. 4. Additions of FeSO<sub>4</sub> cause the rate to drop rapidly; the presence of 0.5 M FeSO<sub>4</sub> reduces the initial dissolution rate to only 12 pct of that observed in the ferrous-free medium. Further additions of FeSO<sub>4</sub> are largely without effect. The present findings support the earlier work of Dutrizac *et al*<sup>8</sup> and Jones and Peters,<sup>5</sup> but do not

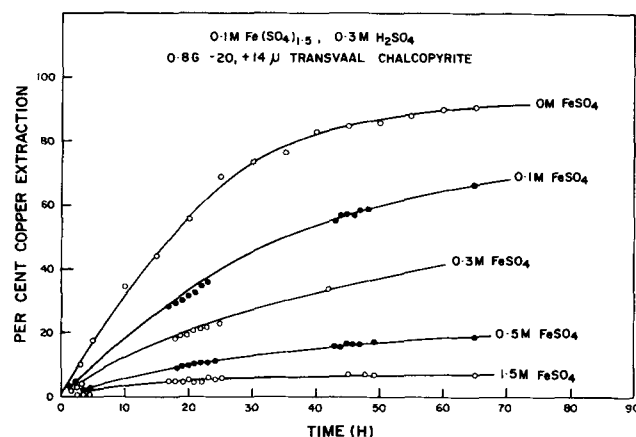


Fig. 3—Leaching curves for the dissolution of natural chalcopyrite in solutions containing various initial concentrations of FeSO<sub>4</sub>.

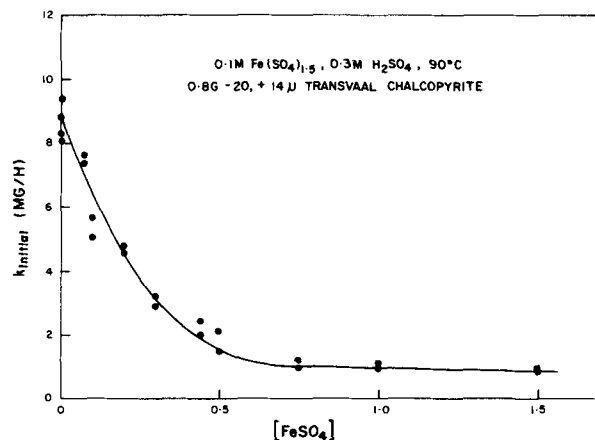


Fig. 4—Effect of the FeSO<sub>4</sub> concentration on the rate of chalcopyrite leaching.

agree with Beckstead *et al*<sup>6</sup> and there are no obvious reasons for the discrepancy.

### The Effect of Neutral Sulfates

When  $\text{FeSO}_4$  is added to a solution having a fixed  $\text{Fe}^{3+}$  concentration, three factors are involved: the oxidizing potential is reduced and the ionic strength and sulfate concentration both increase. To separate the potential effects from those caused by the increasing ionic strength and sulfate concentration, neutral sulfates were added to the ferric sulfate medium to ascertain their effect on the leaching reaction. Lithium and magnesium salts were selected since they do not form jarosite-type precipitates in ferric sulfate media.

Figure 5 shows some of the chalcopyrite leaching curves realized in the presence of lithium sulfate. The presence of  $\text{Li}_2\text{SO}_4$  causes the copper leaching rate to fall sharply but not to the extent caused by the addition of an equivalent molarity of  $\text{FeSO}_4$  (Fig. 3). The leaching curves have the same general form in the presence of  $\text{Li}_2\text{SO}_4$  or  $\text{FeSO}_4$  as in their absence. Similar tests were run with  $\text{MgSO}_4$  and similar curves were produced. Initial rate constants were computed for each leaching curve and these have been plotted vs the sulfate concentrations in Fig. 6. The presence of "inert" sulfates causes the leaching rate to decline but not to the same

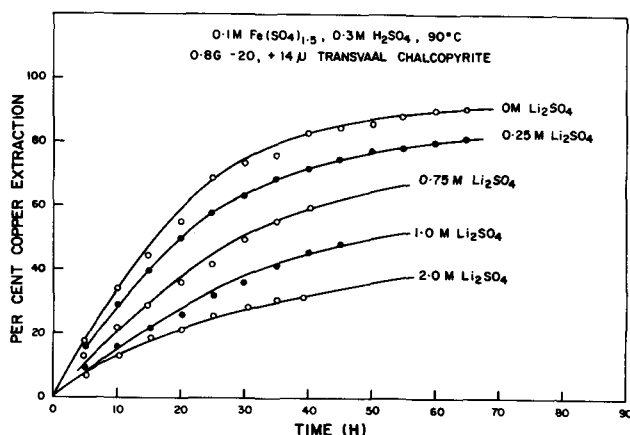


Fig. 5—Leaching curves for the dissolution of natural chalcopyrite in solutions having different  $\text{Li}_2\text{SO}_4$  concentrations.

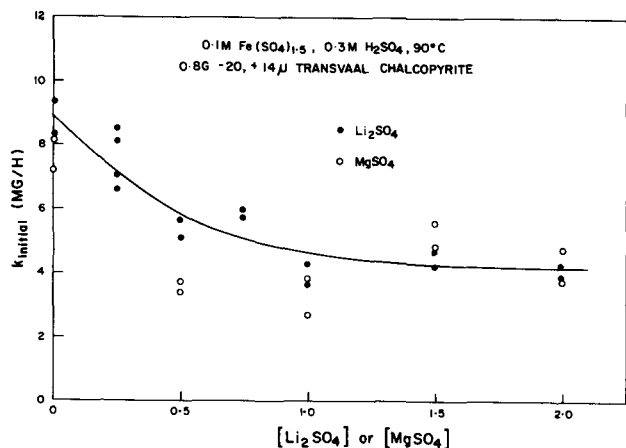


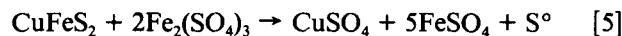
Fig. 6—Effect of  $\text{Li}_2\text{SO}_4$  or  $\text{MgSO}_4$  concentration on the rate of chalcopyrite dissolution.

dramatic extent as observed when  $\text{FeSO}_4$  was employed (Fig. 4). Both  $\text{Li}_2\text{SO}_4$  and  $\text{MgSO}_4$  depressed the reaction and the two salts behaved approximately the same. This suggests that two factors are operative; viz, one effect caused by the high sulfate ion concentration and a second factor related to the  $\text{Fe}^{2+}$  itself.

There are no other reported data on the effect of neutral sulfates on the chalcopyrite leaching rate, and this is an area which requires confirmatory studies.

### The Copper Sulfate Reaction Product

The leaching of chalcopyrite in ferric sulfate media is usually given by:<sup>6,8</sup>



where it is understood that some sulfate can be formed at the expense of elemental sulfur. It was shown above that the presence of the  $\text{FeSO}_4$  reaction product retards the reaction. It is naturally of interest to know what effect the other soluble reaction product,  $\text{CuSO}_4$ , has on the dissolution reaction. Experimentally this information is difficult to obtain directly because of the near impossibility of measuring accurately small amounts of dissolved copper against a high copper background. This problem does not exist, of course, for anodic dissolution experiments where the reaction is followed by measuring the current. Warren<sup>10</sup> observed that the presence of  $\text{CuSO}_4$  did not alter the anodic dissolution of chalcopyrite in sulfuric acid media. Since  $\text{Cu}^{2+}$  is not oxidized at the anode, this presumably shows the actual anodic reaction is independent of  $\text{CuSO}_4$ .

In the present study, the effect of copper sulfate on the leaching rate was followed by measuring both the ferrous ion and elemental sulfur reaction products generated by Equation 10 and assuming the relative amounts were independent of the copper sulfate concentration. Individual leaching-time curves were produced for the amount of  $\text{Fe}^{2+}$ , but only the final (48 h) amount of elemental sulfur was measured. Figure 7 shows the influence of  $\text{CuSO}_4$  on the initial rate constant for  $\text{Fe}^{2+}$  production. An approximately similar curve was found for the amount of elemental sulfur except that the scatter was slightly greater. The data

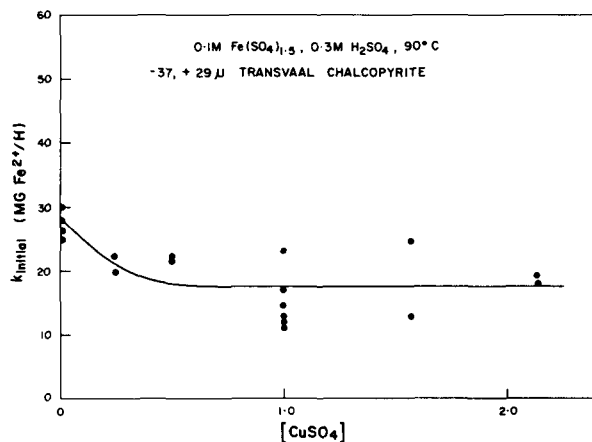


Fig. 7—Effect of  $\text{CuSO}_4$  concentration on the chalcopyrite leaching rate.

of Fig. 7 indicate that the  $\text{CuSO}_4$  reaction product slightly depresses the leaching rate, but that the effect is less than for an equivalent concentration of  $\text{Li}_2\text{SO}_4$ . Unlike the chloride system<sup>9</sup> where the cupric chloride reaction product accelerates the reaction sharply, the cupric sulfate reaction product in the ferric sulfate medium will likely retard the dissolution slightly. The effect seems closely related to the high sulfate concentration and not to the actual presence of  $\text{Cu}^{2+}$ .

#### Effect of Neutral Chlorides

At temperatures above  $50^\circ\text{C}$  and for  $\text{Fe}^{3+}$  concentrations  $>0.01\text{ M}$ , it is fairly well established that the ferric chloride system is a more effective lixiviant for chalcopyrite than the ferric sulfate system. Several years ago, Dutrizac and MacDonald<sup>11</sup> showed that minor  $\text{NaCl}$  additions to a ferric sulfate solution promoted the chalcopyrite leaching reaction above  $50^\circ\text{C}$ , but were apparently without effect at lower temperatures where, admittedly, meaningful rates are difficult to determine. Ammou-Chokroum, Steinmetz and Malve<sup>12</sup> found that the anodic dissolution of chalcopyrite in  $\text{HCl}$  media was independent of the total chloride concentration, and this finding is in essential agreement with the leaching data in  $\text{FeCl}_3$ - $\text{HCl}$  media.<sup>9</sup>

In the current study, the leaching behavior of chalcopyrite in ferric sulfate solutions was studied in the presence of various concentrations of  $\text{LiCl}$ . Lithium chloride was selected to avoid any possible precipitation of alkali jarosites.<sup>13</sup> Individual leaching curves were measured and initial slopes were deduced for each curve; the resulting data are displayed in Fig. 8. The addition of chloride ion causes a gradual increase in the leaching rate; the presence of  $4\text{ M Cl}^-$  increases the rate by about 2.6 times. Higher concentrations of  $\text{LiCl}$  caused  $\text{Li}_2\text{SO}_4$  to precipitate because of the common ion effect. Figure 2 shows that, for the chosen conditions, the ferric chloride system is about three times more aggressive towards chalcopyrite than the ferric sulfate system. Hence substantial neutral chloride additions, as in Fig. 8, can transform the sulfate system to a pseudo-chloride medium at least for the

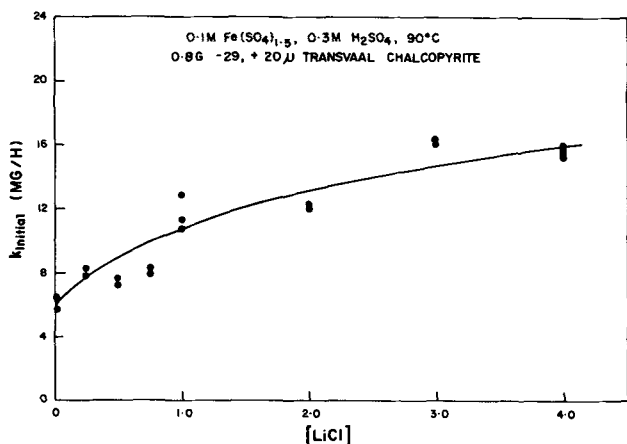


Fig. 8—The variation of the chalcopyrite leaching rate with increasing  $\text{LiCl}$  concentrations in an otherwise all sulfate medium.

relatively dilute  $\text{Fe}_2(\text{SO}_4)_3 - \text{H}_2\text{SO}_4$  media employed in these investigations.

#### Temperature Dependence in Sulfate and in Chloride Media

Although the leaching temperature is one of the most important control parameters in the hydrometallurgical processing of copper concentrates, it has proved difficult to determine this effect really accurately for chalcopyrite in ferric ion media. Part of the difficulty has been associated with obtaining an adequately pure chalcopyrite sample for leaching. The presence of secondary copper mineralization, even in minor quantities, can seriously affect the leaching, especially at low temperatures where the total dissolution is small. It is known that other noncopper minerals can also alter the leaching rates<sup>14</sup> but there is no evidence available concerning the effect of such minerals on the activation energy for chalcopyrite dissolution. An additional complicating factor is that the activation energy depends somewhat on the method employed for calculating the rates. If the leaching curves are not strictly linear, then different activation energies will be produced depending on whether linear fits, initial slopes or terminal slopes are utilized to define the rate. The fits are also somewhat dependent on the number of points and the total reaction time employed; these factors are usually not constant even within a given test program. Given the above experimental difficulties, close agreement ( $\pm 5\text{ kJ/mol}$ ) in reported activation energies should not be expected. Table I shows the activation energies reported for the dissolution of reasonably pure chalcopyrite by various authors; these data are taken from the works of Dutrizac and MacDonald<sup>15</sup> and Munoz, Miller and Wadsworth,<sup>7</sup> but have been updated where necessary.

Given the general problems associated with the determination of activation energies, the agreement among the various works is acceptable. In the ferric chloride system, the activation energy is in the range of 38 to 63  $\text{kJ/mol}$ , with the most probable value being 42 to 46  $\text{kJ/mol}$ . The 63  $\text{kJ/mol}$  value reported for "Present Study" was obtained on natural chalcopyrite containing  $\sim 2\%$  pct bornite impurity and was chosen to show the influence of such impurities. The value is higher than the 46  $\text{kJ/mol}$  activation energy found for bornite-free material. The activation energy in the ferric sulfate system seems to be higher than in the chloride system, but the value is strongly dependent on the method employed for calculating the individual leaching rate constants.<sup>9</sup> An average activation energy in the ferric sulfate system would be about 75  $\text{kJ/mol}$ . The activation energy in the nitrate system appears to be intermediate, but, independent confirmatory work would be required to establish this point conclusively. The activation energy reported for the anodic dissolution of chalcopyrite in chloride media is similar to that found in  $\text{FeCl}_3$  leaching. In the chloride system, the electrochemical activation energy is substantially lower than in  $\text{Fe}_2(\text{SO}_4)_3$  leaching. This may indicate electrochemical control in

**Table I. Reported Activation Energies for the Leaching of Chalcopyrite in Ferric Chloride and in Ferric Sulfate Media**

Material	Leaching Medium	Activation Energy, kJ/mol	Reference
Natural chalcopyrite	Ferric chloride 60 to 106 °C	50	Ermilov <i>et al</i> (1969) Ref. 21
Synthetic chalcopyrite	Ferric chloride 25 to 75 °C anodic dissolution	38 ± 4 (anodic reaction only)	Ammou-Chokroum <i>et al</i> (1977) Ref. 16
Synthetic chalcopyrite	Ferric chloride 50 to 100 °C	46 ± 4	Dutrillac (1978) Ref. 9
Natural chalcopyrite	Ferric Chloride 30 to 100 °C	42 ± 4	Dutrillac (1978) Ref. 9
Natural chalcopyrite	Ferric chloride 40 to 100 °C	63 ± 8	Present Study (1980)
Synthetic chalcopyrite	Ferric sulfate 50 to 94 °C	71 ± 13	Dutrillac <i>et al</i> (1969) Ref. 8
Natural chalcopyrite	Ferric sulfate 32 to 50 °C	75	Lowe (1970) Ref. 17
Natural chalcopyrite	Ferric sulfate 27 to 92 °C	84	Baur <i>et al</i> (1974) Ref. 18
Natural chalcopyrite	Ferric sulfate 60 to 90 °C	84	Munoz <i>et al</i> (1979) Ref. 7
Natural chalcopyrite	H <sub>2</sub> SO <sub>4</sub> 25 to 90 °C Anodic Dissolution	54	Warren (1978) Ref. 10
Synthetic chalcopyrite	Ferric sulfate 30 to 95 °C	38 - 63	Dutrillac (1978) Ref. 9
Natural chalcopyrite	Ferric nitrate 25 to 40 °C	95	Linge (1976) Ref. 19

chloride media and nonelectrochemical (*e.g.*, mass transfer) control in sulfate systems.

#### Agitation and Acid Effects

There is general agreement<sup>15</sup> that agitation does not promote the leaching of chalcopyrite; *i.e.*, the rate is not controlled by mass transfer across the liquid boundary layer. Sufficient agitation must be provided to suspend the particles (to prevent their caking) and to eliminate gross solution inhomogeneities, but further agitation seems to be without effect in the chloride, nitrate or sulphate systems.<sup>6,18,19</sup>

Acid concentration is without effect in any ferric ion leach system at least for acid concentrations less than 1 M.<sup>15,9,6,12</sup> It is important that sufficient acid be present to prevent ion precipitation and hydrolysis (>0.1 M), but greater concentrations are without significant effect.

#### Effect of Ferric Ion Concentration

Early work<sup>20</sup> on the leaching of chalcopyrite concentrates in ferric sulfate solutions indicated that the leaching rate was independent of the concentration of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in the range of 0.25 to 5 pct. Subsequent investigations on fairly pure chalcopyrite<sup>8,17,18</sup> confirmed that the rate was nearly independent of the Fe<sup>3+</sup> concentration above about 0.01 M, but was sharply ferric concentration dependent at lower levels. More recently, Munoz *et al*<sup>7</sup> showed that 0.06 and 0.5 M Fe(SO<sub>4</sub>)<sub>1.5</sub> solutions attacked chalcopyrite at essentially identical rates; Beckstead *et al*<sup>6</sup> observed similar leaching rates at 0.5, 1.0 and 2.0 M Fe(SO<sub>4</sub>)<sub>1.5</sub> concen-

trations. Jones and Peters<sup>5</sup> investigated this effect at three Fe<sup>3+</sup> concentrations, but their results were inconclusive. Increasing the concentration from 0.03 to 0.1 M Fe(SO<sub>4</sub>)<sub>1.5</sub> increased the leaching rate slightly, but a further increase to 1.0 M Fe(SO<sub>4</sub>)<sub>1.5</sub> concentration yielded a leaching rate slower than that found for the 0.03 M Fe(SO<sub>4</sub>)<sub>1.5</sub> solution.

In the present study, the effect of the ferric sulfate concentration on the leaching of the Transvaal chalcopyrite was re-determined in the concentration range 0.01 to 2.0 M Fe<sup>3+</sup>; the results are given in Fig. 9 in terms of initial rate constant versus ferric ion concentration. Clearly, the leaching rate in the sulfate system is only marginally dependent on the concentration of ferric sulfate. The current results suggest the rate varies

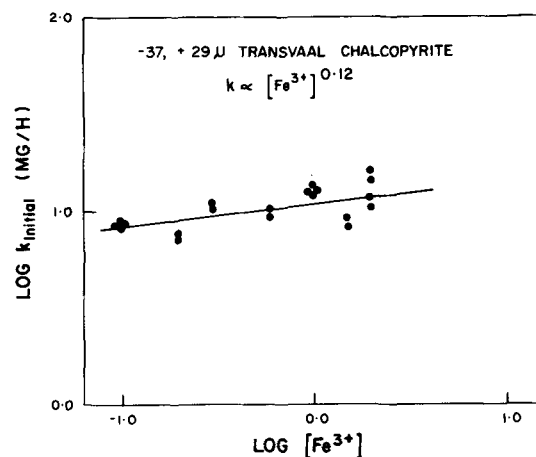


Fig. 9—Variation of the chalcopyrite leaching rate with increasing concentration of Fe<sup>3+</sup>, as Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.

as the 0.12 power of the  $\text{Fe}^{3+}$  concentration, a finding which is in essential agreement with the previous studies.

The ferric ion dependence in the chloride system is less well defined. Ermilov *et al*<sup>21</sup> reported a first power dependence on the concentration of  $\text{FeCl}_3$ , but later workers have consistently found the reaction to be less sensitive to  $\text{FeCl}_3$ . Ammou-Chokroum *et al*<sup>16</sup> observed a 0.3 power dependence for  $\text{FeCl}_3$ , and Jones and Peters<sup>5</sup> observed that increasing the  $\text{FeCl}_3$  concentration from 0.1 to 1 M approximately doubled the rate, also suggesting a 0.3 power dependence. Later, Dutrizac<sup>9</sup> studied the effect of the  $\text{FeCl}_3$  concentration on the rate of leaching of disks of synthetic chalcopyrite and reported a 0.8 power dependence.

In the current work, the effect of the  $\text{FeCl}_3$  concentration on the dissolution of -20, +14  $\mu\text{m}$  Transvaal chalcopyrite was studied at 95, 65 and 45 °C. Individual leaching curves were produced and initial rate constants were deduced for each run. Meaningful dissolutions were noted in all experiments at 95 and 65 °C, but the tests using dilute solutions at 45 °C gave dissolved copper values which were only marginally significant. The results of the experiments are presented graphically in Fig. 10. At all temperatures the rate increases fairly sharply with increasing ferric chloride concentration. At both 95 and 65 °C, the rate increases approximately as the 0.3 power of the  $\text{FeCl}_3$  concentration in agreement with previous work<sup>5,16</sup> also done with natural chalcopyrite, but not in good agreement with the 0.8 power dependence observed for synthetic chalcopyrite.<sup>9</sup> At 45 °C, there is some indication of a higher power dependence but the accuracy of the low-temperature data is insufficient to permit any definitive statement. It should be noted, however, that similar results were obtained using the natural chalcopyrite from Temagami, Ontario.

#### Areas Requiring Additional Study

As can be seen from the above discussion, many aspects of the reaction between chalcopyrite and ferric ion are fairly well resolved, or require only moderate clarification. There are still, however, some important topics where agreement is far from evident. Until all the important parameters are firmly established, there is little point in evolving complex mechanisms to explain the dissolution although such endeavours might be useful for guiding experimentation. The following areas would appear to require additional investigation.

1) Although linear kinetics are usually reported for the leaching of chalcopyrite in  $\text{FeCl}_3$ -HCl media, there is no consensus concerning the form of the curve produced in ferric sulfate solutions. In particular, it should be ascertained why independent studies report linear, parabolic or complex kinetics.

2) Given the importance of ferric concentration in any commercial leaching process, there is probably a need for an independent re-determination of this parameter.

3) In the ferric sulfate system there is little agree-

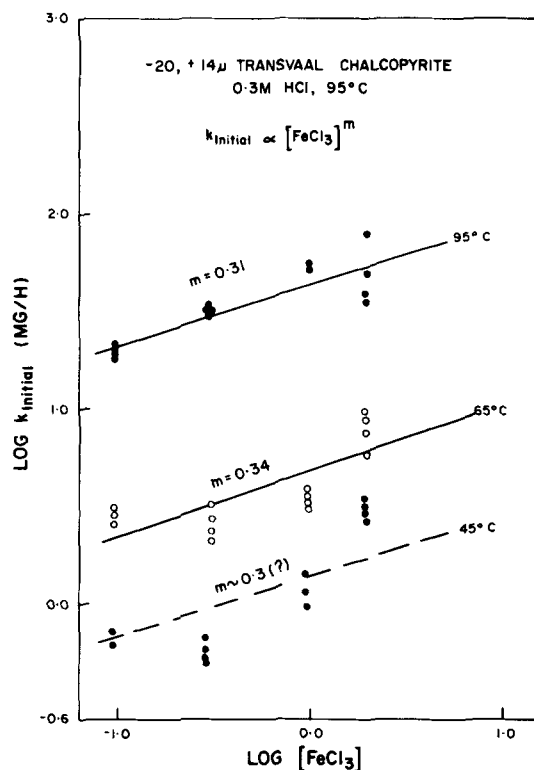


Fig. 10—The effect of ferric chloride concentration on the rate of chalcopyrite leaching at 45, 65 and 95 °C.

ment concerning the quantitative distribution of reaction products. In particular, what is the ratio of  $\text{Fe}^{2+}/\text{Cu}^{2+}$  and does this really change with time? What effect does the short-time initial reaction observed in electrochemical tests have on the chemical leaching? How much sulfate is produced and how do the experimental conditions affect the  $\text{S}^0/\text{SO}_4$  ratio?<sup>22</sup>

4) Lastly, there is the lingering problem of whether chalcopyrites from different sources leach substantially differently. This is of paramount importance to commercial practice and to our understanding of the dissolution mechanism.

#### CONCLUSIONS

The recent literature on the ferric ion leaching of chalcopyrite has been surveyed, and new experimental studies were carried out to elucidate points still in dispute. The leaching rates are more rapid in chloride media than in ferric sulfate solutions; the activation energy in chloride solutions is about 42 kJ/mol and in sulfate solutions the corresponding value is about 75 kJ/mol. In both systems the rate is essentially independent of acid concentration and degree of agitation. It was confirmed that the rate is directly proportional to the surface area of the chalcopyrite in both sulfate and chloride media. The presence of  $\text{FeSO}_4$ ,  $\text{Li}_2\text{SO}_4$  or  $\text{MgSO}_4$  substantially decreased the leaching rate; furthermore,  $\text{CuSO}_4$  also slightly suppressed the reaction. The addition of chloride ion to a sulfate system progressively accelerated the leaching of the chalcopyrite. In ferric sulfate solutions the rate increased as the 0.12 power of the ferric ion concentration, but in ferric chloride media the ferric ion con-

centration dependence is greater and seems to be independent of temperature from 45 to 100 °C.

#### ACKNOWLEDGMENT

The assistance of D. J. Hardy, technologist, CANMET, with the experimental work is recognized.

#### REFERENCES

1. L. A. Haas and J. L. Shafer: *J. Metals*, 1979, vol. 31, no. 7, pp. 40-47.
2. H. W. Sheffer and L. G. Evans: USBM I.C.-8341, 1968.
3. F. Letowski, B. Kolodziej, M. Czernecki, A. Jedrczak and Z. Adamski: *Hydromet.*, 1979, vol. 4, pp. 169-184.
4. L. J. Cabri: *Econ. Geol.*, 1973, vol. 68, no. 4, pp. 443-54.
5. D. L. Jones and E. Peters: *Extractive Metallurgy of Copper*, J. C. Yannopoulos and J. C. Agarwal, eds., vol. 2, pp. 633-53, AIME, N.Y., 1976.
6. L. W. Beckstead, P. B. Munoz, J. L. Sepulveda, J. A. Herbst, J. D. Miller, F. A. Olson and M. E. Wadsworth: *Extractive Metallurgy of Copper*, vol. 2, J. C. Yannopoulos and J. C. Agarwal, eds., 1976 AIME, N.Y. pp. 611-32.
7. P. B. Munoz, J. D. Miller and M. E. Wadsworth: *Metall. Trans. B*, 1979, vol. 10B, pp. 149-58.
8. J. E. Dutrizac, R. J. C. MacDonald and T. R. Ingraham: *Trans TMS-AIME*, 1969, vol. 245, pp. 955-59.
9. J. E. Dutrizac: *Metall. Trans. B*, 1978, vol. 9B, pp. 431-39.
10. G. W. Warren: Ph.D. Thesis, University of Utah, 1978.
11. J. E. Dutrizac and R. J. C. MacDonald: *Metall. Trans. B*, 1971, vol. 2B, pp. 2310-12.
12. M. Ammou-Chokroum, D. Steinmetz, and A. Malve: *Bull. Mineral (Fr.)*, 1978, vol. 101, pp. 26-43.
13. J. E. Dutrizac and S. Kaiman: *Can. Mineral.*, 1976, vol. 14, pp. 151-58.
14. J. E. Dutrizac and R. J. C. MacDonald: *Can. Metal. Quart.*, 1973, vol. 12(4), pp. 409-20.
15. J. E. Dutrizac and R. J. C. MacDonald: *Minerals Sci. Eng.*, 1974, vol. 6(2), pp. 3-100.
16. M. Ammou-Chokroum, M. Cambozoglou and D. Steinmetz: *Bull. Soc. Mineral. Cristallogr.*, 1977, vol. 100, pp. 149-61.
17. D. F. Lowe: Ph.D. Thesis, University of Arizona, 1970.
18. J. P. Baur, H. L. Gibbs and M. E. Wadsworth: USBM RI-7823, 1974.
19. H. G. Linge: *Hydrometallurgy*, 1976, vol. 2, pp. 51-64.
20. J. D. Sullivan: *Trans. AIME*, 1933, vol. 106, pp. 515-546.
21. V. V. Ermilov, O. B. Tkachenko and A. L. Tseft: *Tr. Inst. Met., Obogashch, Alma Ata*, 1979, vol. 30, pp. 3-14.
22. B. L. Tiwari, J. Koibe and H. W. Hayden: *Metall. Trans. B*, 1980, vol. 11B, pp. 89-93.