

The Kinetics of Dissolution of Chalcopyrite in Ferric Ion Media

J. E. DUTRIZAC

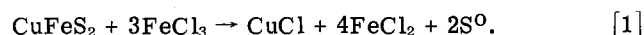
The kinetics of dissolution of chalcopyrite (CuFeS_2) in ferric chloride-hydrochloric acid and in ferric sulfate-sulfuric acid solutions have been investigated using the rotating disk technique. Over the temperature range 50 to 100°C, linear kinetics were observed in the chloride media while nonlinear kinetics were noted in the sulfate system. The apparent activation energy in the chloride system was about 11 kcal/mole. The rate increased with increasing ferric chloride concentrations but was insensitive to the concentrations of hydrochloric acid, the ferrous chloride reaction product and "inert" magnesium or lithium chlorides. Cupric chloride substantially accelerated the rate. Small amounts of sulfate in an otherwise all chloride system greatly reduce the chalcopyrite leaching rate; still larger amounts of sulfate make the system behave essentially like the slower-reacting ferric sulfate medium.

INTRODUCTION

CHALCOPYRITE (CuFeS_2) is probably the most important copper ore mineral in the world today. Traditionally, chalcopyrite concentrates have been treated using smelting technology. Both the cost-energy efficiencies and the SO_2 pollution problems associated with smelting are well known, but it should be noted that recent technological advances are tending to minimize the pollution difficulties.^{1,2} During the past few years various copper hydrometallurgical processes have been advanced, generally as a means of overcoming pollution problems involved in smelting although other potential advantages such as lower capital costs, recovery of a useful iron product, better control and automation as well as economical small scale operation have also been cited.

Chalcopyrite is quite refractory to hydrometallurgical processing and only fairly potent solutions will dissolve it. Much of the research and development activity in this area has concentrated on some form of ferric ion leaching, especially ferric chloride leaching. Ferric chloride leaching processes designed to treat chalcopyrite concentrates have been advanced from the early part of this century; the findings of these older studies have been recently discussed in a review article³ and will not be repeated at this time. It is worth noting that these earlier efforts were more or less doomed to economic failure since they simply could not compete with existing smelting processes capable of discharging unlimited amounts of SO_2 into the atmosphere and because the hydrometallurgical expertise to handle complex and corrosive chloride solutions had not been developed at that time. With the growing concern for protecting the environment, a new series of hydrometallurgical processes for treating copper concentrates was advanced and ferric ion leaching processes were prominent among these. The United States Bureau of Mines developed a ferric chloride leaching process⁴ which was able to extract over 99 pct of the copper in a chalcopyrite concentrate

during 2 h of leaching at 106°C. For the $\text{FeCl}_3/\text{CuFeS}_2$ ratios employed in that work the copper reported as cuprous chloride:



About 70 pct of the sulfur was recovered in elemental form with the remainder presumably being oxidized to sulfate. The rate was found to be strongly temperature dependent and it increased, also, as the ratio of $\text{FeCl}_3/\text{CuFeS}_2$ increased; *i.e.*, as the ferric ion concentration increased. Copper was eventually recovered by cementation on iron and the ferric chloride medium was regenerated by chlorine gas. Improvements have been effected⁵ on this process especially in the areas of elemental sulfur recovery by dissolution in ammonium polysulfide and of iron regeneration by direct air oxidation in a turboaerator. The economics of the Bureau's Process have been compared⁶ to conventional smelting with SO_2 collection by the Citrate Process, and the hydrometallurgical route was found to be competitive for both operating and capital charges. As originally conceived, the Cymet Process⁷ combined ferric chloride leaching together with anodic dissolution of chalcopyrite concentrates. Recent improvements on this process⁸ have seen the leach-anodic dissolution step replaced by a more conventional two stage leaching operation employing ferric chloride-cupric chloride. Pure cuprous chloride is crystallized from solution and copper is recovered by hydrogen reduction in a fluid bed. The FeCl_3 leaching medium is regenerated by oxidation using the HCl produced during H_2 reduction. Most of the sulfur reports in the elemental form. The Duval Corporation has developed^{9,10} a process whereby chalcopyrite concentrates are dissolved in cupric chloride-ferric chloride solution at the boiling point (107°C); silver also leaches under these conditions. The soluble cupric ions are reduced to the cuprous state in a two step process; concentrate is employed to effect the bulk of the reduction and impure copper is used to complete the reaction. Sulfur reports in the elemental form (mostly) and pyrite is only superficially attacked. An electrolytic step is used to recover copper and to oxidize some of the cuprous ion to Cu^{2+} ; a large circulating load of soluble copper is used and the process is, therefore, largely

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a cupric chloride leach. Iron is finally regenerated by air or oxygen in a suitable turboaerator. Cominco Limited¹¹ has also advanced a process based on the ferric chloride leaching of chalcopyrite concentrates. The dissolved copper is reduced to the cuprous state by addition of metallic copper and a cuprous chloride product is crystallized from solution. Copper is produced by hydrogen reduction and the HCl so produced is utilized for the oxygen regeneration of the ferric chloride lixiviant. Elkem-Spigerverket¹² has piloted a ferric chloride leaching process which is based on the dissolution of chalcopyrite in 3 M FeCl₃ at about 110°C. The dissolved copper is electrowon directly from a purified solution in a diaphragm cell. Extra iron dissolved during leaching is precipitated as an oxide product by oxy-hydrolysis at about 90°C.

Although none of the above processes is operating on a commercial scale, several are being evaluated at the pilot plant or demonstration unit level. It appears that ferric chloride leaching may soon find practical application for the treatment of chalcopyrite concentrates. The processes described above differ in their methods of handling the pregnant solutions and, especially, in their metal recovery operations, but all are based on the reaction of chalcopyrite with ferric chloride media. For such processes it is important to have a sound understanding of the mechanisms of the reactions occurring during the dissolution step. Although the dissolution of chalcopyrite in ferric chloride solutions has been looked at by several investigators, there is little agreement among the various workers concerning the form of the leaching curves, the important leaching variables or the rate controlling processes.

Brown and Sullivan¹³ were the first to study in any detail the ferric chloride leaching of chalcopyrite. They observed that the mineral was generally refractory to leaching (an observation which has been confirmed by all workers in the field) and that hot ferric chloride solutions were more efficacious than the corresponding sulfate media. The rate was stated to increase rapidly with increasing temperature although no activation energy was quoted. Ermilov, Tkachenko and Tseft¹⁴ investigated the kinetics of dissolution of chalcopyrite in ferric chloride solutions over the temperature interval 60 to 106°C. The rate increased moderately rapidly with increasing temperature; the apparent activation energy was about 12 kcal/mole. The rate increased directly with the ferric ion concentration for initial ferric chloride concentrations between 50 and 100 g/l. The sulfur formed during dissolution did not interfere with the dissolution kinetics. This finding is in apparent contradiction of an earlier publication of Ermilov¹⁵ where it was shown that simultaneous dissolution of the chalcopyrite and the sulfur reaction product substantially accelerated the rate of chalcopyrite attack. Presumably this indicated that the sulfur layer impeded the dissolution although it may have been that the xylene used to extract sulfur catalyzed the chalcopyrite-ferric chloride reaction in some manner.

Jones and Peters¹⁶ studied the dissolution of chalcopyrite in both ferric chloride and ferric sulfate media; ferric chloride solutions were found to be the more effective lixiviant at 90°C, and this is in agreement with the earlier study of Brown and Sullivan.¹³ For

ferric chloride solutions, linear kinetics were observed to about 90 pct dissolution and this suggests that the elemental sulfur reaction product is not impeding the reaction in the chloride system. As would be expected, the rate increased as the particle size decreased. Increasing ferric chloride concentrations (0.1 and 1.0 M) increased the leaching rate, but the presence of the FeCl₂ reaction product was found to have little effect. The influence of the leaching temperature was not given. Most recently Ammou-Chokroum, Cambazoglu and Steinmetz^{17,18} have investigated the leaching of chalcopyrite in ferric chloride solutions whose concentrations ranged from 0.01 to 0.5 M. These workers reported that the dissolution occurred in two stages; *viz*, an initially rapid part followed by a slower reaction, supposedly caused by "passivation" of the chalcopyrite. The initial rate was found to increase as the 0.3 power of the ferric ion concentration; the corresponding activation energy for this stage varied from 7 to 10 kcal/mole depending on the ferric ion concentration employed. The rate was found to be independent of the total chloride concentration (as NaCl) and of the HCl concentration over the pH range from 0 to 1.5. A complex parabolic model was advanced to explain the results which were claimed to be supported by other work^{21,24} in the ferric chloride-HCl system and in the ferric sulfate-sulfuric acid medium. For the tests in Refs. 17 and 18, unsintered disks of chalcopyrite were used, and it is the current author's opinion that the complex kinetics were caused by this experimental limitation. The unsintered disks contain both very fine and very coarse particles. The leaching of such material is characterized by a rapid initial stage where the very fine material is leached; as the fines are consumed, the reaction slows appreciably and "pseudoparabolic" or "parabolic" kinetics are apparently observed although the true kinetics are quite different. Also, the present study as well as other work^{13,16} has demonstrated substantial differences in the leaching behavior of chalcopyrite in ferric sulfate and in ferric chloride media. Hence, it appears that different mechanisms are operative for the two systems and, consequently, that data from one medium should not be used to support a mechanistic interpretation in the other.

There appears to be some consensus that the dissolution kinetics are linear; in those instances where nonlinear kinetics have been reported, changes in area that might have occurred during leaching were not taken into account. The activation energy seems to be moderately high with values between 9 to 12 kcal/mole having been noted; given the problems inherent in the deduction of the activation energy, such agreement seems very good. The rate increases with increasing ferric ion concentration, is independent of acid strength and, in general, of the presence of other chlorides. The purpose of the present study was then to try to clarify the current status of the work on the FeCl₃ leaching of chalcopyrite and to extend our knowledge of other variables operative in this commercially important leaching system. It was felt necessary to compare the reactions in the ferric chloride system with the corresponding reactions in ferric sulfate and in the mixed sulfate-chloride media which will inevitably be produced during the leaching of real concentrates on a commercial scale.

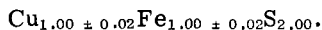
EXPERIMENTAL

For the leaching studies, both disks of synthetic chalcopyrite and carefully sized and cleaned natural chalcopyrite from the Temagami Lake Mine, Temagami, Ontario were used. The natural material was sized by wet screening and the washing was continued until all slimes and fines were removed. The screened material was then treated in an ultrasonic bath to remove the last traces of fine dust. Microscopic examination showed the sized and cleaned chalcopyrite to consist of:

- 95 pct chalcopyrite
- 3 pct pyrite
- 1.5 pct bornite
- 0.5 pct sphalerite

The synthetic CuFeS_2 was prepared from equimolar amounts of CuS and $\text{Fe}_{1.000}\text{S}$ whose synthesis procedures have been described.¹⁹ The simple sulfides were dry-ground to -150 mesh, mixed, pressed at 80,000 psi and then sinter-reacted for 2 days at 550°C to form CuFeS_2 . The initial chalcopyrite was dry-ground to -150 mesh and repressed at 80,000 psi. The disks were then sintered at 625°C for 24 h and subsequently slowly cooled. The final disks were polished through 4/0 polishing paper, ultrasonically cleaned in acetone, vacuum dried and then stored. The final disks were 25 mm in diam and were about 2 mm thick; the apparent polished surface area was 5.15 cm^2 although the true surface area presented to the leaching medium was possibly ten times greater than this.³⁰ The apparent density was 85 to 90 pct of theoretical.

The sintered disks and the sized natural chalcopyrite were shown by X-ray diffraction analysis to consist of "chalcopyrite". The material was examined using a Guinier-de-Wolff precision focussing camera to establish that chalcopyrite, and not one of the recently found similar phases,²⁰ was being leached. Microscopic examination confirmed that the disks were essentially chalcopyrite, although small amounts of finely disseminated pyrite and bornite were also revealed. Point counting methods indicated that the impurities constituted less than 0.5 pct of the disk area. Electron microprobe analyses of a number of synthetic disks indicated the product to be:



The polished CuFeS_2 pellets were cemented to lucite stirring rods in such a manner that only the polished face was presented to the leaching medium. The disks were then leached by an established technique²¹ which consists of rotating the disk at a given speed in an acidified ferric chloride or ferric sulfate solution and periodically sampling and analyzing the dissolved copper colorimetrically with a Technicon AutoAnalyzer. Iron concentrations were obtained by standard dichromate titration of pipette samples and elemental sulfur was estimated by CS_2 extraction of air-dried pellets. The ground natural chalcopyrites were simply suspended in the leaching medium using a suitable stirrer. Protective atmospheres were used to prevent air oxidation of the sulfur or iron species. Solution removed from the leach vessel either by sampling or by evaporation was replaced by a return feed of barren solution or water, respectively.

RESULTS AND DISCUSSION

Temperature Effect in the Chloride System

Figure 1 illustrates the type of dissolution curve obtained when the disks of synthetic chalcopyrite were leached at various temperatures in 0.1 M FeCl_3 -0.3 M HCl solutions. These data are plotted on the basis of the amount of copper dissolved per unit apparent disk area and not for the true area of the sulfide that is largely unknown. The dissolution curves in these chloride solutions are essentially linear although some of them do exhibit a very slight curvature and this could be caused by slight changes in the porosity of the disks during leaching or it might indicate a very slight and limited blockage of the surface by the reaction products. Generally, though, the reaction products do not seem to be impeding the dissolution reaction in the chloride medium.

To obtain a value of the apparent activation energy for the dissolution of the synthetic chalcopyrite, initial leaching rates were evaluated by fitting the various data to an equation of the form:

$$\text{wt Cu (mg/cm}^2) = bt + ct^2 \quad [2]$$

and then calculating the slope at $t = 0$. As a check on this method, rate constants were also evaluated from the middle "linear" sections of the curves as well as from the computed slope at the end of the experiment. Figure 2 shows the Arrhenius plot realized using the initial slope calculations. An essentially identical graph with nearly the same slope was obtained when either the "linear" rates or the "terminal" rates (as defined above) were employed. The linear Arrhenius plot over the temperature range 50 to 100°C suggests that just one leaching mechanism is operative. The least squares fit to the data shown in Fig. 2 yielded the equation:

$$\log k (\text{mg Cu/cm}^2 \cdot \text{h}) = 7.425 - \frac{2469}{T} \quad [3]$$

This equation produced an apparent activation energy of 11.3 ± 0.6 (1 σ) kcal/mole, and this value did not change by more than 2 kcal/mole when the other methods were used to compute k .

To show that the synthetic chalcopyrite leached in the same manner as the natural mineral, a series of

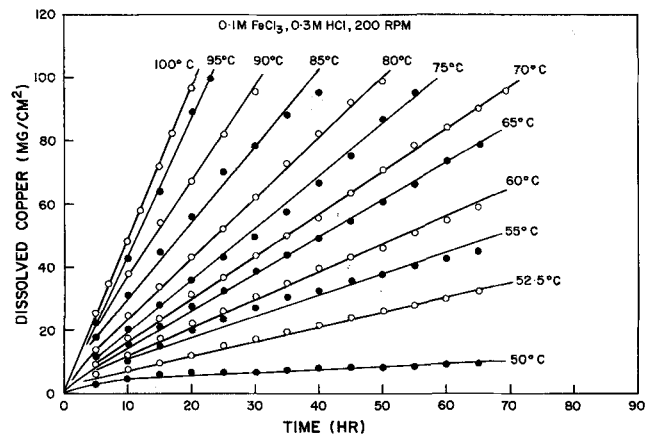


Fig. 1—The amount of copper dissolved from disks of synthetic chalcopyrite as a function of time at various temperatures in chloride solutions.

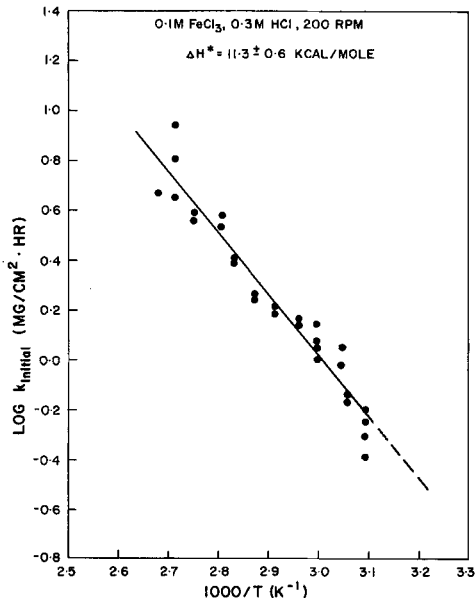


Fig. 2—Arrhenius plot for the dissolution of copper from disks of synthetic chalcopyrite between 50 and 100°C in chloride solutions.

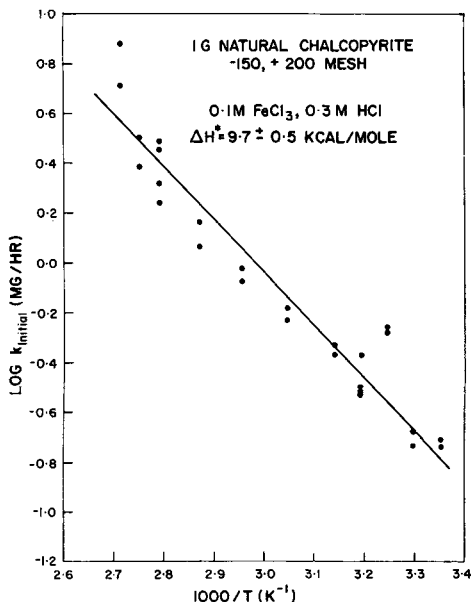


Fig. 3—Arrhenius plot for the dissolution of copper from sized and cleaned natural chalcopyrite from Temagami, Ontario.

dissolution tests at different temperatures was run. For these experiments, 1 g of -150, +200 mesh cleaned chalcopyrite from Temagami, Ontario was slurried with 2.7 l of 0.1 M FeCl_3 - 0.3 M HCl solution. Leaching curves were obtained at each temperature and initial rate constants were then deduced from these using Eq. [2]. Figure 3 shows the Arrhenius plot obtained from these data. Over the interval 25 to 100°C the data suggest a single rate controlling step, in agreement with the results on synthetic chalcopyrite. The apparent activation energy of about 10 kcal/mole found for the natural material is in fairly good agreement with the 11 kcal/mole value computed for synthetic CuFeS_2 .

Temperature Effect in the Sulfate System

Figure 4 shows the type of dissolution curve realized when the disks of synthetic chalcopyrite were dissolved at various temperatures in solutions containing 0.1 M Fe^{3+} (as sulfate) and 0.3 M H_2SO_4 . Under the test conditions used, ferric sulfate solutions attack chalcopyrite more slowly than ferric chloride media; this observation is consistent with the findings of Brown and Sullivan¹³ and Jones and Peters.¹⁶ For example, in the current tests at 85°C, ferric sulfate solutions extracted about 28 mg Cu/cm^2 after 50 h of leaching while a similar chloride solution leached over 120 mg Cu/cm^2 in the same period. The dissolution curves in the sulfate system are not linear. It is the author's contention that the nonlinear kinetics observed in the sulfate system are caused by the blockage or partial blockage of the chalcopyrite surface by the elemental sulfur reaction product and/or precipitated iron compounds which can form even in fairly acidic solutions.²² The shape of the dissolution curves in sulfate media is one area of current controversy with some groups such as Beckstead *et al.*²³ and Linge²⁴ also reporting "parabolic" kinetics while other workers such as Lowe²⁵ and Jones and Peters¹⁶ observe linear reactions. Although this problem is beyond the scope of the present study, it is one area which definitely requires additional study.

In order to compare the rate data in the sulfate media with those from the chloride system, initial rate constants were deduced from the curves in Fig. 4 using Eq. [2]. These constants were then summarized on an Arrhenius plot as shown in Fig. 5. The points and the lower line correspond to the dissolution in the sulfate solutions. Although there is a fair amount of scatter, it appears that the data can be described by a single line whose equation is:

$$\log k (\text{mg Cu}/\text{cm}^2 \cdot \text{h}) = 5.261 - \frac{1937}{T} \quad [4]$$

This yields an apparent activation energy of 8.9 ± 0.7 (1 σ) kcal/mole. Because the leaching curves in the sulfate system are not linear, quite different values of ΔH^* are obtained depending on the method used to compute k (*i.e.*, linear, parabolic) and on the part of the curve used for the computations. For example, a

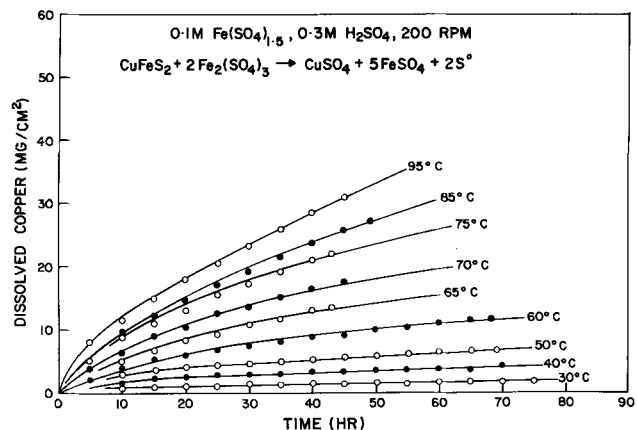


Fig. 4—The amount of copper dissolved from disks of synthetic chalcopyrite as a function of time at various temperatures in sulfate solutions.

value of 15 kcal/mole was realized when the terminal portions of the curves in Fig. 4 were used to determine k . Initial rate constants were used in this program, however, to provide a consistent basis of comparison with the chloride solutions which were of principal concern for this study. The upper line on Fig. 5 is the smoothed curve (Fig. 2) obtained for the corresponding chloride solutions. Since similar material was used for both tests and because comparable iron and acid concentrations were utilized, a direct comparison of the data seems possible. The figure shows that the chloride media are better for dissolving chalcopyrite at high temperatures ($t > 50^\circ\text{C}$), although the rate differential seems to lessen at lower temperatures.

The Dissolution Reaction

Figure 1 indicates that essentially linear kinetics are observed for the leaching of synthetic chalcopyrite in FeCl_3 - HCl solutions. To demonstrate that the natural material also dissolves according to a linear law, a test was run in which 1 g of -325, +400 mesh natural chalcopyrite from Temagami, Ontario was leached in an excess of lixiviant. The upper line and the solid points shown in Fig. 6 illustrate the kind of dissolution curve found in this system; these particular results are plotted as fraction copper dissolved (α) vs time. This particular experiment was run to about 70 pct total copper extraction. The lower line and the open points are a plot of $1 - (1 - \alpha)^{1/3}$ vs time and this relationship, of course, corrects for the shrinkage of the monosize particles during leaching. The results follow the $1 - (1 - \alpha)^{1/3}$ vs time relationship quite closely and this would seem to confirm that the rate of copper dissolution per unit area of chalcopyrite is a linear function of time in the chloride system. This finding is in agreement with the recent work of Jones and Peters¹⁶ who observed linear kinetics to about 90 pct copper dissolution when natural chalcopyrite was leached in ferric chloride solutions.

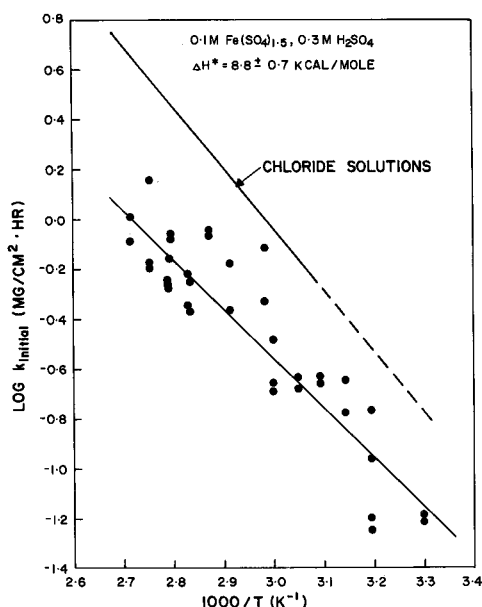


Fig. 5—Arrhenius plot for the dissolution of copper from disks of synthetic chalcopyrite in sulfate media.

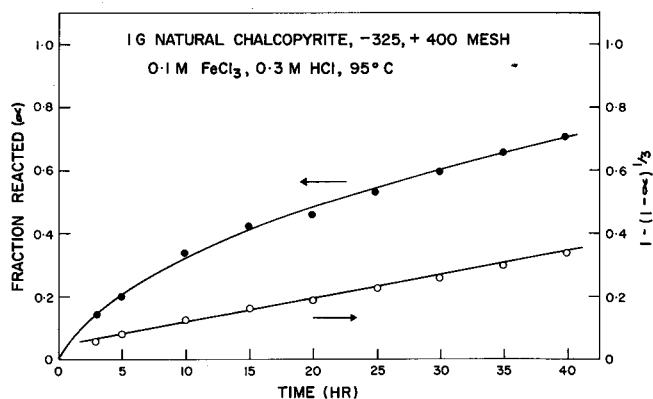
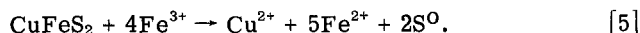


Fig. 6—Dissolution-time curve for the leaching of sized and cleaned natural chalcopyrite from Temagami, Ontario.

Table I. Analytical Data Obtained for Sulfur Species Produced During Leaching

Temperature, °C	Leaching Time, h	S^0 , mg	SO_4 , mg	$\text{S}^0/\text{Cu}^{2+}$
50	72	35	<2	1.98
80	17	218	n.d.	1.88
80	24	387	<2	1.91
80	48	444	<2	1.94
80	72	343	<2	1.93

During the current tests in chloride media, the chalcopyrite was found to react essentially according to the reaction:



Direct determination of dissolved sulfate indicated that less than 1 pct of the oxidized sulfide ion reported in that form. Equation [5] predicts a $\text{S}^0/\text{Cu}^{2+}$ molar ratio of 2. Table I which presents the results of 5 independent leaching tests indicates this ratio to be in the range of 1.88 to 1.98, with an "average" value of about 1.93. This indicates about 96 pct of the oxidized sulfide reports as S^0 . The difference between the 96 pct S^0 production obtained by direct sulfur determination and the 99 pct S^0 generation deduced from SO_4 determinations could be due to one or more of the following:

- 1) Physical loss of suspended S^0 during analysis,
- 2) Failure of all S^0 to dissolve in CS_2 ,
- 3) Precipitation of basic iron sulfates,
- 4) Production of thiosalts rather than SO_4 .

Equation [5] also predicts a $\text{Fe}^{2+}/\text{Cu}^{2+}$ molar ratio of 5, and values slightly above this were commonly obtained during the test program. Thus, it appears that Eq. [5] fairly accurately predicts the leaching behavior in chloride media; a more precise determination of the products and their relative amounts would necessitate a separate study directed towards this problem.

Effect of Ferric Ion Concentration

Figure 7 shows some of the leaching curves obtained when the disks of synthetic chalcopyrite were leached at 85°C in solutions containing various initial concentrations of FeCl_3 and a constant background acid

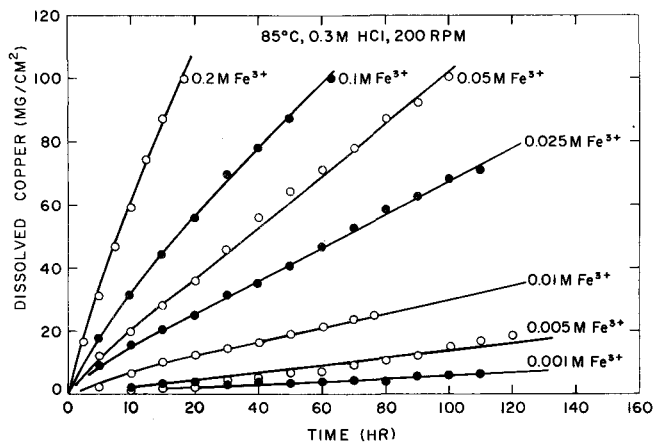


Fig. 7—The dissolution of disks of synthetic chalcopyrite in solutions containing various initial concentrations of FeCl_3 .

concentration of 0.3 M HCl. The reaction curves at all ferric ion concentrations are essentially linear although some of them do exhibit a slight curvature. The rate appears to accelerate steadily from 0.001 M Fe^{3+} to the highest value studied. Incidentally, the experiments at the lower ferric ion concentrations were done using large volumes (16 l) of solution so that ferric ion depletion was not a problem during any of the tests; *i.e.*, the experiments were done at essentially constant FeCl_3 concentration. The response of chalcopyrite to increasing ferric ion concentrations in the chloride system differs considerably from that in sulfate media where the rate is essentially independent of concentrations greater than about 0.01 M $\text{Fe}(\text{SO}_4)_{1.5}$ (Refs. 21, 24). From a practical point of view this difference is significant because it permits the rate of a chloride based leaching process to be increased simply by increasing the FeCl_3 concentration. In the sulfate system this cannot be done to any significant degree and the leaching proceeds at the “maximum” rate possible which is substantially lower than the corresponding rate in the chloride medium.

To compare directly the leaching rates in Fig. 7, the individual leaching data were fitted by Eq. [2] and initial rate constants were deduced for each test. These data have been summarized on the $\log k$ vs $\log \text{Fe}^{3+}$ plot shown in Fig. 8. The curve is linear over the concentration range from 0.001 to 0.3 M and this suggests that the same mechanism operates at all iron concentrations. The equation of the presented line is:

$$\log k \text{ (mg Cu/cm}^2 \cdot \text{h)} = 1.241 + 0.796 \log [\text{Fe}^{3+}] \quad [6]$$

which yields

$$k \propto [\text{Fe}^{3+}]^{0.80} \quad [7]$$

The 0.80 power dependence is somewhat lower than the 1.0 dependence reported by Ermilov¹⁴ but is considerably higher than the 0.3 power dependence noted by Ammou-Chokroum^{17,18} or the very slight effect reported by Jones and Peters¹⁶ for just two iron concentrations.

Effect of Acid Concentration

To investigate the effect of acid concentration on the rate of chalcopyrite dissolution, leaching tests were carried out at both 45 and 85°C. Individual leaching

curves were obtained and initial rate constants were deduced from each curve; these rate data are shown in Fig. 9. At 85°C, the rate increases very slightly as the acid concentration increases:

$$k \propto [\text{HCl}]^{0.30} \quad [8]$$

At 45°C, the rate is virtually independent of the HCl concentration. Although the rates are only slightly affected by the solution pH, acid plays an important role in preventing iron hydrolysis and precipitation. The acid concentration at which “visible” extensive hydrolysis occurred is marked on the figure for each temperature. As a generalization, lower acid concentrations could be tolerated at lower temperatures; at 85°C, 0.1 M HCl prevented visible iron hydrolysis but lower acid levels resulted in extensive hydrolysis within a few hours.

Although visible iron hydrolysis may not occur, there is some evidence that “invisible” iron precipitation is occurring on the sulfide surface and that this is interfering with the leaching process. Figure 10 shows some dissolution curves obtained at various temperatures in the presence of 0.1 M HCl. At 50°C the leaching curve is “normal” (Fig. 1) but as the temperature is varied, the leaching behavior becomes more irregular. At 85°C the curve is almost parabolic in form; at 90°C the initial part is linear but the rate stops fairly abruptly. At 95°C the dissolution behavior

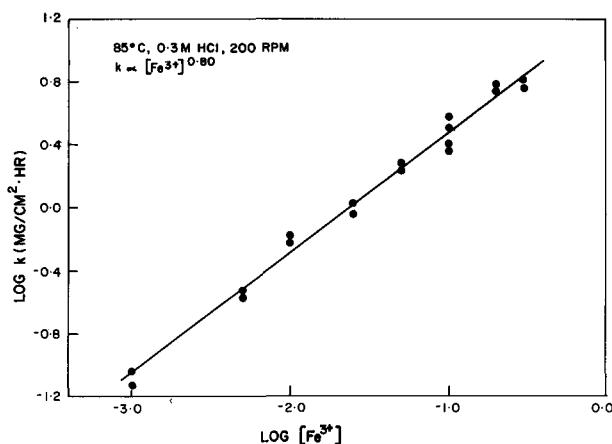


Fig. 8—The effect of ferric ion concentration on the rate of dissolution of synthetic chalcopyrite.

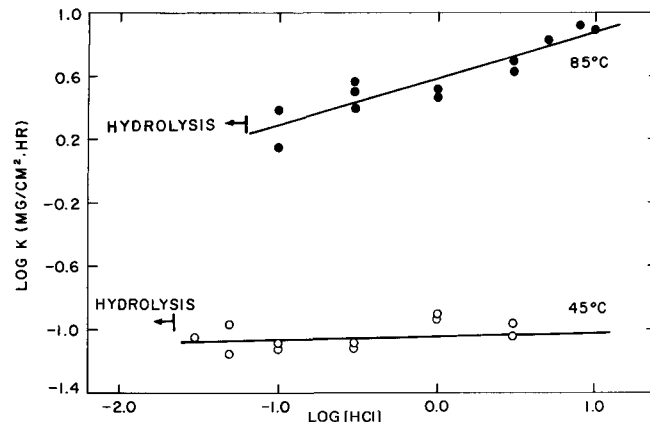


Fig. 9—The effect of HCl concentration on the rate of dissolution of synthetic chalcopyrite in 0.1 M FeCl_3 and at 200 rpm disk rotation speed.

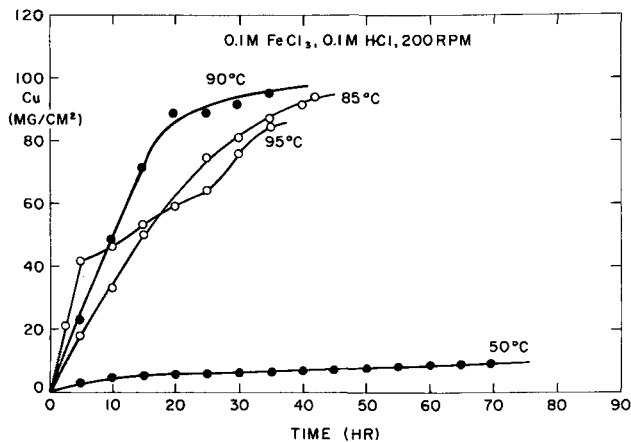


Fig. 10—Dissolution-time curves realized for synthetic chalcopyrite leached at a "low" acid concentration.

is simply erratic. It is important to note that visible hydrolysis products were never observed in any of these experiments. Presumably a thin layer of some iron compound is forming on the surface and is gradually inhibiting the reaction. This figure points out fairly dramatically the need for a fairly acidic medium to keep iron in solution even though the acid does not play a major role in the actual leaching reaction.

Possibility of Mass Transport Control

Mass transport control as a rate limiting step can be discounted for the following three reasons. Firstly, as illustrated in Table II, the measured rates are much slower than those required for liquid diffusion control. Secondly, the measured activation energy of 11 kcal/mole is too high for liquid diffusional control; thirdly, the leaching rate is virtually independent of the rotation speed (Fig. 11). These three factors would seem to confirm that the leaching rate is controlled by a chemical reaction.

Influence of Ferrous Chloride and Cupric Chloride

When chalcopyrite is leached in ferric chloride-hydrochloric acid solutions, both ferrous chloride and cupric chloride are produced as reaction products. It is important to know the effect of these products on the chalcopyrite leaching rate since both will be present in substantial amounts in any real leaching process. Initial rate constants were deduced from a series of tests done in the presence of various FeCl_2 concentrations and these are plotted vs the FeCl_2 concentration in Fig. 12. The addition of ferrous chloride in amounts to 100 g/l had little effect on either the form of the leaching curve or the rate of reaction. Much higher FeCl_2 concentrations slightly retard the dissolution process and, also, seem to make the leaching curves somewhat erratic, although this latter problem could be associated with analytical difficulties involved in determining copper in high chloride media. It would appear that the ferrous chloride concentrations encountered in actual leaching practice, likely 100 to 150 g/l FeCl_2 , would have a negligible effect on the leaching kinetics. This behavior is in sharp contrast to that noted in the corresponding ferric sulfate system where the accumulation of the FeSO_4 reaction product sharply reduces the

leaching rate.^{21,24} The relative insensitivity of the ferric chloride leaching reaction to FeCl_2 was noted by Jones and Peters.¹⁶

The effect of cupric chloride on the leaching rate of CuFeS_2 was evaluated in a manner similar to that used to ascertain the influence of FeCl_2 . A series of experiments was run with different initial concentrations of cupric chloride, and the course of the reaction was monitored as a function of time. Because it is very difficult to measure small changes in copper concentration against a high copper background, these particular tests were followed by determining the ferrous chloride reaction product and assuming Eq. [5] to apply. Figure 13 shows the influence of dissolved cupric chloride on the initial rate constant as defined by the amount of ferrous ion generated. The addition of cupric ion to the solution greatly promotes the dissolution of chalcopyrite for all copper concentrations likely to be encountered in practice; this finding is consistent with the reported reactivity of CuCl_2 towards CuFeS_2 .²⁹ The positive influence of CuCl_2 on the leaching rate together with the nearly neutral influence of FeCl_2 suggests that the accumulation of the reaction products during leaching will not adversely

Table II. Comparison of the Measured Rate Constants to those Calculated From the Levich Equation^{26,28}

Temperature, °C	k Calculated	k Measured
25	7 mg Cu/cm ² ·h	0.1 mg Cu/cm ² ·h
85	24 mg Cu/cm ² ·h	3.5 mg Cu/cm ² ·h

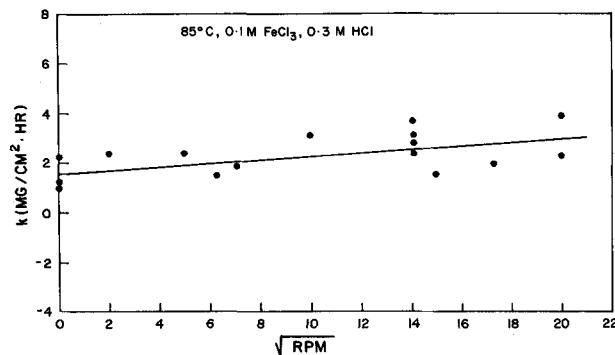


Fig. 11—Effect of the disk rotation speed on the rate of leaching of synthetic chalcopyrite.

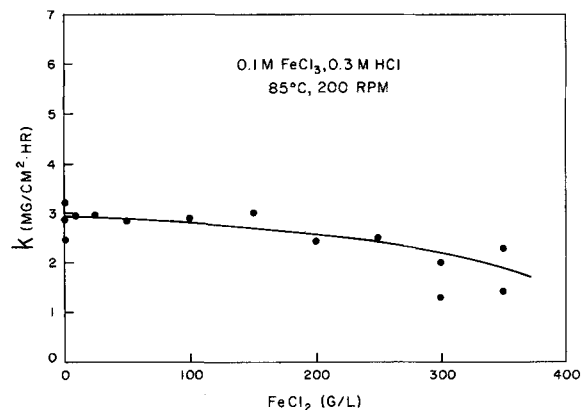


Fig. 12—Effect of ferrous chloride concentration on the rate of dissolution of synthetic chalcopyrite.

affect the rate. In fact, a slight net beneficial influence would be expected.

For the data shown in Figs. 12 and 13 the total chloride concentration varied as the amount of ferrous chloride or cupric chloride increased. Previous

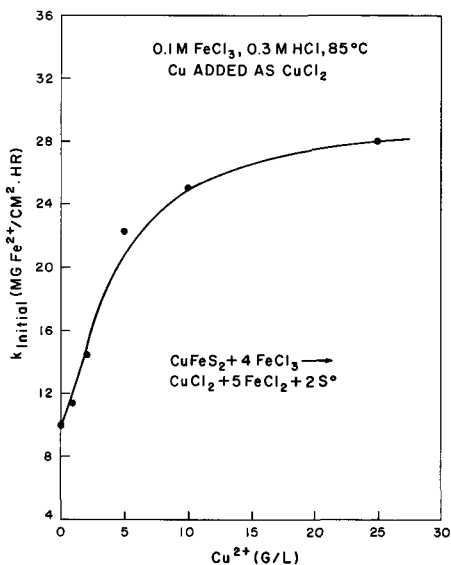


Fig. 13—The effect of CuCl_2 on the rate of leaching of synthetic chalcopyrite.

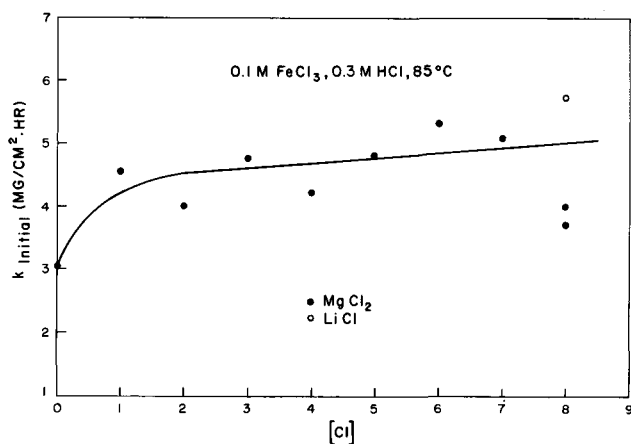


Fig. 14—Effect of total chloride concentration on the rate of dissolution of synthetic chalcopyrite.

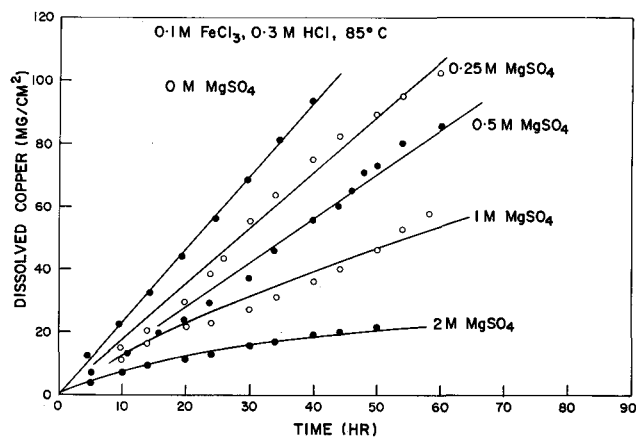


Fig. 15—Leaching curves obtained when synthetic chalcopyrite was leached in chloride solutions containing various amounts of sulfate.

work had shown that the rate was independent of the total chloride concentration^{17,18} and it was considered important to confirm this dependence. To this end, a series of experiments was run at 85°C using solutions containing 0.1 M FeCl_3 -0.3 M HCl but various concentrations of the "inert" chlorides MgCl_2 or LiCl . Initial rates were deduced for each leaching curve and these have been summarized in Fig. 14. Increasing the total chloride concentration seems to cause a slight initial rate acceleration but, thereafter, the rate is fairly insensitive to total chloride concentration. These data suggest that the changes observed when FeCl_2 or CuCl_2 are added to the solution are due to the metal ions and not just to the associated change in the ionic strength of the medium. Also, it would appear that the chief reason for adding inert chlorides to a leaching solution³⁰ is to elevate the solution boiling point and to increase the solubility of lead and silver; chloride levels have a rather minimal effect on the actual leaching rates.

Mixed Chloride-Sulfate Systems

The dissolution of chalcopyrite in ferric chloride solutions yields elemental sulfur as the principal sulfidic species. Although less than 1 pct of the oxidized sulfide reports as sulfate in the chloride system, even this small amount will lead to an eventual sulfate buildup during the recycling of commercial leach solutions. The oxidation of other sulfide minerals present in copper concentrates could also contribute to an eventual sulfate buildup. To investigate the effect of sulfate ion in an otherwise all chloride system, a series of experiments was run in which various concentrations of MgSO_4 were added to the 0.1 M FeCl_3 -0.3 M HCl leaching medium. Figure 14 suggests that the magnesium ion itself does not affect the leaching rate. Figure 15 shows the kind of leaching curve produced when sulfate ion was added. The addition of SO_4 causes the dissolution rate to fall quite rapidly and, furthermore, seems to influence the shape of the leaching curve. Small amounts of sulfate make the leaching curves erratic while larger amounts (>1 M) tend to produce "parabolic" kinetics. The leaching curve obtained in the presence of 2 M MgSO_4 is essentially that noted in the corresponding ferric sulfate-sulfuric acid system.

Figure 16 is a plot of the initial rate constant for copper dissolution *vs* the amount of sulfate added. The presence of SO_4 causes the rate to fall sharply and then level off. Sulfate concentrations as low as 10 g/l are sufficient to reduce the leaching rate, and higher SO_4 contents make the system behave essentially like a ferric sulfate-sulfuric acid medium. In a commercial chloride-based leaching process some care would have to be exercised to prevent the accumulation of large amounts of sulfate in solution. Sulfate control could probably be maintained during the iron precipitation stages or by the addition of calcium ion.

SUMMARY

The kinetics of dissolution of both natural and synthetic chalcopyrite have been studied in the FeCl_3 - HCl system and, to a lesser degree, in the $\text{Fe}(\text{SO}_4)_{1.5}$ - H_2SO_4 and mixed sulfate-chloride media. In the chloride solutions, linear kinetics with an associated activa-

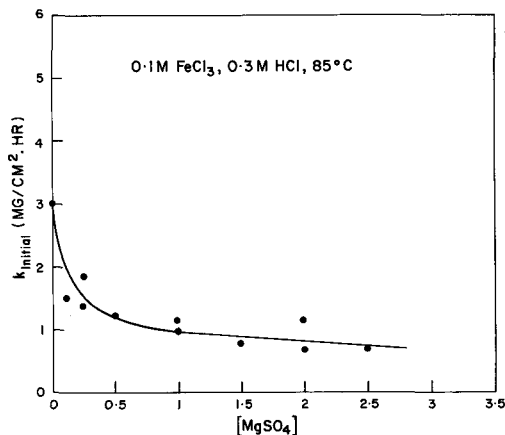


Fig. 16—Effect of sulfate concentration on the rate of dissolution of synthetic chalcopyrite in an otherwise all chloride system.

tion energy of 10 to 11 kcal/mole were noted; non-linear reaction curves were observed in the sulfate media. Chloride solutions were many times more potent than the simple sulfate solutions. Addition of sulfate ion to an otherwise all chloride solution caused the rate to decline and the kinetics to become non-linear. In the chloride solutions, the rate increased as the 0.80 power of the ferric chloride concentration but was insensitive to the concentrations of hydrochloric acid, the ferrous chloride reaction product and inert magnesium or lithium chlorides. Cupric chloride greatly accelerated the reaction.

In the chloride system, rate control by mass transport limitations in the liquid phase was ruled out on the basis of the high activation energy, of rates slower than those predicted by the Levich Equation and of the insensitivity of the reaction to the disk rotation speed. The linear kinetics preclude solid state diffusional control. Hence, the rate must be chemically controlled although insufficient confirmed data exist at this time to permit a more precise characterization of the rate controlling step. Additional research is required both to confirm the influence of the leaching variables and to identify the rate controlling steps before the kinetics of this commercially important system will be fully understood.

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