A mathematical model of the chemistry of the
dump leaching of chalcopyrite

by

KNona Constance Liddell

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PhD Thesis submitted to Iowa State University

Ames Laboratory, DOE

Iowa State University

Ames, Iowa 50011

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TABLE OF CONTENTS

LIST OF SYMBOLS AND ABBREVIATIONS	iv
Abstract	v
I. INTRODUCTION	1
II. LITERATURE REVIEW	3
A. Dump Leaching Operations	3
B. Studies of Leach Dumps and Columns	7
1. Laboratory leach columns	7
2. Field studies on leach and tailings dumps	12
C. Dissolution of Chalcopyrite in Leach Dumps	14
1. Comparison of oxidation by Fe^{3+} and O_2	14
2. Reaction with Fe^{3+}	15
a. Sulfate media	16
b. Chloride media	21
c. Mixed chloride-sulfate media	23
d. Nitrate media	24
3. Reaction with O_2	24
a. Pressure leaching	24
b. Reaction at lower pressures and temperatures	27
III. DEVELOPMENT OF THE MODEL	29
A. Chemical Aspects	29
1. Irreversible heterogeneous reactions	29
2. Solution phase reactions	32
3. Hydrolysis and precipitation of Fe^{3+}	37
B. Mathematical Aspects	39
1. Derivation of equations	39
2. Method of solving the equations	53
IV. RESULTS AND DISCUSSION	57
A. Equilibrium Concentrations in Solutions of $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4 , CuSO_4 and H_2SO_4	57
B. Precipitation of Fe^{3+} as $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ and $\alpha\text{-FeOOH}$	71
C. Concentration Changes During the Dissolution Process	81

V.	CONCLUSION	110
VI.	REFERENCES	113
VII.	ACKNOWLEDGMENTS	118
VIII.	APPENDIX A	119
IX.	APPENDIX B	124

LIST OF SYMBOLS AND ABBREVIATIONS

- a_l = activity of species l
 C = analytical or initial total concentration, moles/kg solution
 gpl = g/l
 I = ionic strength
 K = equilibrium constant
 M = moles/l solution; molarity
 M_i = moles solid i /kg solution
 m = moles/kg solution; molality
 m_j = moles j /kg solution; molality
 N = equivalents/l solution
 n_j = moles j formed/mole $CuFeS_2$ reacting
 $\bar{N}_i$ = moles solid i formed/kg solution
 $\bar{n}_j$ = moles j formed/kg solution
 S_i = solid i
 s_j = dissolved species j
 γ_j = activity coefficient of j
 κ_j = charge of j
 λ_{kj} = moles moiety k contained in one mole of j
 v_l = stoichiometric coefficient of l
 ξ = fraction of solid reacted
 $()$ = moles/l solution; molarity

A mathematical model of the chemistry of the
dump leaching of chalcopyrite

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A mathematical model for the changes in solution concentrations during the dissolution of chalcopyrite in leach dumps has been developed. In a leach dump, chalcopyrite is dissolved by Fe^{3+} and by O_2 and H^+ . Comparison of the equilibrium constants of these reactions with concentration data for leach liquors indicates that neither reaction is at equilibrium under operational conditions. The solution contains Fe(III), Fe(II) and Cu(II) in an aqueous sulfate medium with a pH of about 2.

The rapid solution phase reactions can be considered to maintain their equilibria as the mineral dissolves in the much slower heterogeneous reactions. This is the physical basis of the mathematical model.

To develop and solve the model equations, the important reactions of the system must be identified and classified as irreversible or reversible. The equilibrium concentrations of all the solution species must be known when dissolution commences and kinetic data on the rates of the irreversible reactions must be available. For the chalcopyrite

system, there is one equation for each equilibrium reaction, a charge balance, material balances for Fe(III), Fe(II), Cu(II) and SO_4^{2-} and a kinetic equation. This set of equations is algebraic and linear; the unknowns are the numbers of moles of each species formed per mole of chalcopryrite reacting. A computer program was written to obtain the initial equilibrium concentrations, then solve the model equations for increments of the fraction of solid dissolved.

The equilibrium concentrations of H^+ , OH^- , SO_4^{2-} , HSO_4^- , Fe^{3+} , FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$, $\text{Fe}_2(\text{OH})_2^{4+}$, FeSO_4^+ , $\text{Fe}(\text{SO}_4)_2^-$, FeHSO_4^{2+} , Fe^{2+} , FeSO_4^0 , FeHSO_4^+ , Cu^{2+} and CuSO_4^0 were calculated for different $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4 , CuSO_4 and H_2SO_4 analytical concentrations using both ideal solution and high ionic strength apparent equilibrium constants.

Conditions under which Fe^{3+} precipitates have been investigated by including K_{Sp} values as constraints in the computer program. Jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$, precipitates except when the K^+ concentration is very small. Formation of goethite, $\alpha\text{-FeOOH}$, occurs through aging of amorphous $\text{Fe}(\text{OH})_3$; ferric hydroxide precipitation is favored by high Fe^{3+} concentrations and high pH.

With both dissolution reactions occurring, it was found that the H^+ consumed was partially restored by dissociation of HSO_4^- , FeHSO_4^{2+} and FeHSO_4^+ . With no O_2 reacting, there were only slight changes in the H^+ and HSO_4^- concentrations and FeHSO_4^+ was a product. The maximum copper concentration was obtained with high starting $\text{Fe}_2(\text{SO}_4)_3$ concentrations and little or no O_2 consumption. Too large an amount of O_2 reacting led to pH increases that caused precipitation of $\text{Fe}(\text{OH})_3$.

I. INTRODUCTION

Low-grade ore deposits are growing in importance as higher grade ore bodies are worked out. The cutoff grade for copper ores has declined from 3% to as low as 0.35% (1). At lower grades, however, the tonnages of ore do not increase greatly enough to substantially increase the total amount of recoverable metal; there appears to be a lower limit to copper ore grade beyond which recovery is geochemically impossible (20).

Leaching of waste material from open pit mines is already an important process and is becoming more so. In the United States, 450 tons of copper are recovered daily by leaching waste; the waste itself is accumulating at the rate of about 1 million tons/day (2).

Important as the leaching of waste dumps is, however, the process has been developed empirically and is poorly understood. Modeling the whole dump leaching process is an extremely complicated problem and would involve consideration of chemical kinetics and thermodynamics, mass transfer, heat generation and transfer, fluid flow patterns, particle size and methods of dump construction. Ideally, accurate predictions of leaching performance would be made for the multi-year lifespan of a dump leaching operation.

In the work presented here, the effects of various chemical factors on the dump leaching of chalcopyrite are considered. This is the most abundant copper sulfide mineral undergoing leaching (43) and is very difficult to leach.

There are two oxidants available in leach solution: ferric ion and dissolved oxygen. Laboratory studies indicate that Fe^{3+} should be the more important in dump leaching (7), but it would be desirable to confirm this. Although a number of investigators have suggested that complex ion formation has an important influence on leaching chemistry (7, 8, 10), a calculation of the distribution of species in a solution containing CuSO_4 , FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ has not been published. The effect of the high ionic strength of leach liquor has also not been thoroughly studied. Precipitation of iron from solution is a major problem in dump leaching and has often been reported in laboratory and field observations (5, 10, 11, 17, 35, 36). Conditions under which this occurs have not been elucidated, however. The particular questions this study focused on included:

- (1) How effective can Fe^{3+} and O_2 be in causing dissolution?
- (2) How do the concentrations of the soluble species change during dissolution?
- (3) How significant an effect does ionic strength have on the reactions in solution?
- (4) Under what conditions will iron compounds precipitate?

II. LITERATURE REVIEW

A. Dump Leaching Operations

Dump leaching operations have been discussed in detail in the publications by Woodcock (51) and by Sheffer and Evans (43); the following summary of information is drawn from these sources.

The copper sulfide minerals important in dump leaching are chalcopyrite, chalcocite and, to a lesser extent, covellite and bornite. At the present time, ore of higher grade than about 0.4% copper can be economically processed by other means and would not be deposited in a leach dump. The size distribution of material in a dump is very broad; run-of-mine material is dumped without size reduction.

A site suitable for dump leaching must have surfaces impermeable to leach liquor and topography that makes it convenient to collect pregnant liquor at low points. Both natural canyons and worked-out areas of open pit mines have been selected. Dump construction methods result in some sorting by size. Large boulders often roll downslope and come to rest near the bottom of a dump. Dump surfaces may be smoothed by bulldozers during construction; this tends to produce layers of fine material. A dump may consist of a series of alternating layers of coarse and fine material. Many dumps have the shape of a truncated cone.

The solution applied to a dump to effect leaching contains ferric and ferrous sulfates and has a pH between 1.5 and 3. It is

usually recycled from recovery operations. Sulfuric acid or makeup water is added to adjust the pH when necessary. The solution may be kept in large open ponds before being returned to the dump; this is intended to facilitate oxidation of Fe^{2+} by oxygen and precipitation of Fe^{3+} . The solution pH and influent and effluent Cu, Fe^{3+} and Fe^{2+} concentrations are monitored but the oxygen content typically is not.

Representative concentration data from a number of operations are given in Table 1.

Oxidizing bacteria are important in the conversion of Fe^{2+} to Fe^{3+} . The organisms that have been found to assist in the dissolution of sulfide minerals, however, require oxygen and are active over a rather narrow range of temperatures. Field studies indicate that they are not present in the interior of dumps (10, 11).

Several methods are used to introduce leach solution to a dump, including spraying solution over the dump's surface, flooding ponds or channels cut into the top and supplying solution through a system of perforated vertical pipes extending into the dump. Uniform wetting of the interior is very difficult to achieve.

At many dumps, solution is not applied continuously. Instead, application of solution is halted when the copper concentration of the pregnant liquor has become unacceptably low and the dump is rested for 6-12 months. Throughout the life of a dump, leaching and resting periods are alternated. It is believed that allowing a dump to dry out is valuable in bringing metal values from the interior to the surface of an ore particle (10).

Table 1. Concentration data for some dump leaching operations^a

Plant	Main copper mineral
Bagdad	chalcocite, chalcopyrite, oxide copper
Cananea	chalcocite
Chino	chalcocite, chalcopyrite
Copper Queen	chalcocite, chalcopyrite, bornite
Esperanza	chalcocite, chalcopyrite
Inspiration	chalcocite, chalcopyrite
Ray	chalcocite, chalcopyrite
Silver Bell	chalcocite, chalcopyrite, oxide copper
Utah	chalcopyrite, chalcocite

^aData from Woodcock (51).

Solution to dump				Solution from dump			
pH	Cu(gpl)	Fe ²⁺ (gpl)	Fe ³⁺ (gpl)	pH	Cu(gpl)	Fe ²⁺ (gpl)	Fe ³⁺ (gpl)
2.0	0.02	4.0	0.2	2.5	1.1	0.03	2.0
2.75	0.15	20.0	2.2	2.0	1.5	6.0	12.0
3.5	0.2	3.5	0.1	2.5	2.0	0.9	0.8
3.5	nil	10	nil	2.0	1.4	3.5	3.0
3.5	trace	1.3	0.1	2.6	1.1	0.01	0.1
2.65	0.24	5.0	0.5	1.9	1.9	3.3	2.7
3.4	0.08	2.4	0.06	2.4	1.0	0.7	1.3
3.3	0.01	1.7	0.04	2.4	1.1	0.01	0.6
2.4	0.1	2.5	0.02	2.5	1.2	1.0	1.0

Copper is recovered from pregnant liquor either by cementation with scrap iron or by solvent extraction and electrowinning.

Dump leaching operations have a number of interrelated problems. The most serious of these has been said to be precipitation of iron salts (43). Precipitation of iron occurs if the pH becomes too high. This reduces both the amount of oxidant available to cause leaching and the dump permeability. Reduced permeability also results from the transport of fine material by percolating solution. Decreases in permeability lead to irregularities in solution flow and localized areas where reduction reactions occur. Compaction of fine material is a frequent problem and has the same results.

B. Studies of Leach Dumps and Columns

A relatively small number of publications deals with the details of the physical and chemical processes of dump leaching. These are supplemented by reports on experiments with laboratory leach columns, which have been used to simulate dump operations on a smaller scale.

1. Laboratory leach columns

Auck and Wadsworth (4) worked with two complex ores containing chalcopyrite, digenite, chalcocite, bornite and pyrite. The ores differed in the amount of calcite they contained and hence in the extent to which their gangue minerals dissolved in acid solutions. For the high calcite ore, copper extraction was linear during an initial period when oxygen was excluded and the column was leached by sulfuric acid; the column was then drained and exposed to pure oxygen.

The copper concentration approached a maximum and was essentially unchanged after 44 days. The ferrous ion concentration increased linearly with time while the ferric ion concentration went through a maximum, disappearing from solution as the copper concentration reached its limiting value. The rate of copper dissolution was not proportional to the Fe^{3+} concentration until Fe^{3+} was nearly depleted. When copper extraction stopped, so did the dissolution of the gangue minerals and the consumption of acid. For the low calcite ore, copper release was slower and parabolic kinetics were followed. In this case, copper extraction did not level off. Both Fe^{3+} and Cu^{2+} increased slowly but linearly for the duration of the experiments. There was a rapid initial release of Mg^{2+} and Al^{3+} , followed by a slower linear release; the rate of release during the later period was directly proportional to (H^+) . For the initial leaching of copper, iron, magnesium and aluminum, the activation energy was reported to be 4.2 kcal/mol, suggesting that solution diffusion may have been rate controlling. Auck and Wadsworth believed that within the pores of an ore particle, the solution becomes basic during the leaching process, causing basic iron sulfates to precipitate. Ferric salts are more soluble at low pH and thus the mineral particle surfaces were expected to be more exposed and the channels in the ore more open under strongly acidic conditions. Such precipitation and dissolution could explain the interactions among iron concentrations, pH and oxygen uptake.

A series of column leaching experiments was performed by Brimhall and Wadsworth (13) in an attempt to elucidate the role of oxygen in dump leaching. The principal sulfide minerals in the ore used were pyrite, chalcopyrite and bornite. Before data collection began, the ore was sterilized to destroy oxidizing bacteria and leached to remove acid consuming gangue constituents. The columns were alternately filled with pure O_2 and sulfuric acid solution; this simulated the cycles commonly used in dump operations. No attempt was made to control the iron content of the solution and the action of Fe^{3+} as a leaching agent was not considered. It was believed that oxygen reacted cathodically according to

and that chalcopyrite and bornite reacted anodically as follows:

When fresh acid was added, sharp increases in copper extraction were noted. Leaching ceased when the pH had risen enough to cause basic iron sulfate precipitation, probably blocking pores in ore particles.

Averill (5) has presented results of a column leaching study on an ore containing pyrite and chalcocite with lesser amounts of covellite, chalcopyrite and bornite. Bacteria were active in the columns except when conditions were unfavorable for their growth. The

results Averill obtained with 22 kg ore samples could be scaled up to match those Madsen and Groves got with 7-9 ton lots (35, 36); the same type of ore and column design were used. With Fe^{3+} not initially present in the leach solution, the reaction rate was determined by surface reaction but after the Fe^{3+} concentration had increased sufficiently diffusion became the slow step in the reaction sequence. The reaction rate was reported to vary linearly with Fe^{3+} activity to a concentration of 5.0 gpl; the nonlinearity at this high concentration was felt to be due to the inadequacy of the extended Debye-Huckel method. When additional SO_4^{2-} (as 1 M MgSO_4) was added to the leaching solution, the dissolution rate dropped significantly. This was attributed to changes in the ferric ion activity in solution. The possibility that addition of large amounts of sulfate ions may cause large shifts in the equilibria in the leach solution was not discussed. Iron precipitated at pH 2 and 1 M added MgSO_4 but the solids formed were not reported. Iron extraction was increased by lowering the pH from 2 to 1.5. With O_2 and Fe^{3+} available, the activity of Fe^{3+} was found to be nearly the same at the inlet and outlet of the column. The reaction was slowed when air was supplied instead of pure O_2 . The ferric ion concentration was not constant when the column atmosphere consisted of N_2 ; bacterial activity and oxidation by O_2 could not occur.

A number of interesting observations on the effects of particle size distribution, oxygen availability and column permeability was made by Madsen and Groves in column leaching experiments on an ore

containing primarily pyrite, chalcocite and bornite (35, 36). Two columns were used in this work, one containing run-of-mine ore (-20 in diameter), the other containing ore from which the -1/2 inch fines had been removed. The columns were operated cyclically, being filled alternately with leach solution and air or oxygen. Fines were found to cause a large decrease in copper extraction, an effect that was attributed to decreased column permeability. When air was used during the periods of solution drainage, the oxygen content of the gas in the run-of-mine column did not increase; the O_2 content was always much lower in this column than in the other. When the column that contained fines had become nearly dormant, oxygen was injected and the rate of copper extraction increased dramatically. Madsen and Groves state that the major reason for the increase was stimulation of bacterial activity. When O_2 was added, the concentration of Fe^{3+} increased and the ferrous/ferric concentration ratio dropped; a decrease in the total soluble iron content was also noted, indicating precipitation of iron salts. Changes in ferric ion concentration could not be correlated with the rate of copper dissolution. In spite of the precipitation of iron when O_2 was injected, column permeability increased. Madsen and Groves speculated that acid producing reactions occurred in portions of the column, causing localized dissolution of the precipitated iron salts and enhancing permeability; the iron may then have reprecipitated elsewhere in the column. At the conclusion of the experiments, the leached particles were found to be coated with iron jarosite, ferric

sulfate and gypsum.

Leach columns were connected in series by Bruynesteyn et al. (18) to simulate the leaching of dumps up to 200 ft in height. The ore used was from Butte, Montana; the primary copper mineral present in this ore is chalcocite (43). With the connections between successive columns sealed, lack of oxygen reduced bacterial activity; when air was admitted to each section of column, the pH dropped and the O_2 level and copper grade increased. Even with the ends of each 20 ft section of column open, however, oxygen access was restricted by compaction of clay and fines within the columns. The copper grade decreased with time and also (when H^+ and O_2 were not limiting) with depth in the columns. A pH of 4 caused the copper grade to drop. When a stable pH had been established, the rate of extraction was nearly constant and oxygen was believed to be limiting.

2. Field studies on leach and tailings dumps

Bruynesteyn and Cooper reported on the leaching of two dumps (17). One was used as a control; the other was constructed with air pipes to increase the amount of oxygen available in its interior. Chalcocite was the major copper mineral in the ore. The copper extraction from the aerated test dump was greater than that from the unaerated control dump. In column tests, very little leaching took place inside particles of diameter 1/2 in. or greater, yet about 90% of the copper was extracted. It was concluded that the leachable minerals were situated on the exposed surfaces of the ore. Pyrite

was leached along with copper sulfides and the solution pH dropped as the experiment proceeded; this was accompanied by precipitation of $\text{HFe}_3(\text{SO}_4)_2(\text{OH})_6$. At the conclusion of the dump leaching tests, the dumps were bulldozed and a horizontal layer of clay-like material was found in each dump. While it was not certain how the layers were formed, they were 4-12 in. thick and clearly impeded the downward flow of solution. Secondary enrichment occurred within and below the layers, a sign of a reducing environment. Large quantities of precipitated CuSO_4 were also found below the obstruction.

Samples of the interstitial solution in a dump were analyzed for their Fe^{3+} , Fe^{2+} , Cu^{2+} and H^+ concentrations by Bhappu et al. (10). It was found that the Fe^{2+} in the solution applied was almost completely oxidized in the upper few feet of the dump and it was suggested that iron hydrolysis occurred primarily in this zone. Solution acidity decreased with depth. Bacterial activity was also localized at the dump's upper surface; at the surface 10^3 to 10^7 bacteria were present per gram of ore but in the dump's interior there was less than one bacterium per gram. There was a large accumulation of soluble salts in the dump, particularly close to the top.

Similar observations were made by Boorman and Watson in a study of an abandoned tailings dump (11). The 30 ft high dump had a distinct vertical zonation. The uppermost zone extended some 20 in. into the dump. Here pyrite was oxidized to ferrous then to ferric ion and chalcopyrite was leached. Oxygen was consumed and oxidizing

bacteria were active in this zone. The second zone had much lower permeability and consisted partly of precipitated iron hydroxides and oxides. In this zone almost all the dissolved iron was in the ferrous state. Below this hard pan there was a reduction zone where the tailings were unaltered and bacteria were not present.

C. Dissolution of Chalcopyrite in Leach Dumps

The dissolution of chalcopyrite under conditions relevant to dump leaching has been studied extensively but in some ways is still not well-understood. The following sections review the literature on the dissolution of chalcopyrite by Fe^{3+} and O_2 at total pressures near atmospheric and temperatures below about 100°C . In keeping with the notation most often used in these publications, Fe^{3+} is taken to indicate all solution species in which iron has an oxidation number of +3, including complex ions; (Fe^{3+}) is the total concentration of ferric species.

1. Comparison of oxidation by Fe^{3+} and O_2

The leach solution applied to a dump contains Fe^{3+} and dissolved oxygen; O_2 can also enter a dump by gas phase convection or diffusion. Until recently experimental evidence about the relative efficacy of these two oxidants has been scanty.

Yu, Hansen and Wadsworth (52) reported that under autoclave leaching conditions (160°C , 150 psia O_2 and 0.5 N H_2SO_4) addition of an unspecified amount of Fe^{3+} increased the dissolution rate of a

chalcopyrite concentrate 13%. In radiochemical experiments on the dissolution of particles of pure natural chalcopyrite at atmospheric pressure, Baur, Gibbs and Wadsworth (7) found that over a one-hour interval, $1.3 \times 10^3 \mu\text{g Cu/g CuFeS}_2$ dissolved in an O_2 -purged solution at 27°C and pH 1.25; with $\text{Fe}_2(\text{SO}_4)_3$ added to the solution, the amount of copper dissolved increased, reaching a maximum of $4.4 \times 10^3 \mu\text{g/g}$ at 0.274 M $\text{Fe}_2(\text{SO}_4)_3$.

2. Reaction with Fe^{3+}

There has been some dispute about the stoichiometry of the dissolution of CuFeS_2 by Fe^{3+} . Dutrizac, MacDonald and Ingraham (24) reported that in sulfate media the reaction is

However, Jones and Peters (29) reported that dissolution of chalcopyrite by ferric sulfate resulted in the production of both elemental sulfur and sulfate ions; in FeCl_3 solution no SO_4^{2-} was formed. More recently, Dutrizac (21) found that in chloride media a maximum of 4% of the sulfur reacting reported in solution as sulfate or other oxyanions. The present understanding, then, is that Reaction (4) is a good representation of the dissolution stoichiometry but that a small fraction of the sulfur is oxidized further and goes into solution.

FeCl_3 dissolves chalcopyrite more effectively than does $\text{Fe}_2(\text{SO}_4)_3$. In the early work of Brown and Sullivan (16), dissolution was found to be more rapid in FeCl_3 solutions. Comparing SO_4^{2-} and Cl^-

media, Jones and Peters found that in the former a higher Fe^{3+} concentration was necessary to effect the same copper dissolution (29). At all temperatures between room temperature and the solution boiling point, chloride media were more effective in dissolving chalcopyrite but the difference in reaction rate between chloride and sulfate solutions was less at lower temperatures (21).

a. Sulfate media The kinetics of the dissolution of disks of synthetic chalcopyrite by $\text{Fe}_2(\text{SO}_4)_3$ were reported to be parabolic by Dutrizac, MacDonald and Ingraham (24). An activation energy of 17 ± 3 kcal/mol was obtained from initial rate data. For the leaching of chalcopyrite concentrates by $\text{Fe}_2(\text{SO}_4)_3$, an activation energy of 20 kcal/mol has been reported (8). Later, Jones and Peters (29) reported linear kinetics when bulk samples were dissolved. For mineral particles, the dissolution curve was linear until about 40% of the copper had reacted; it then became approximately parabolic. The reaction stopped after about 70% dissolution. Dutrizac (21) repeated earlier work, again reporting parabolic kinetics for dissolution of chalcopyrite disks, but an activation energy of 8.9 kcal/mol. Recently, activation energies of 8 kcal/mol and 20 kcal/mol were reported for the phase before the sulfur layer had begun to build up and the later phase, respectively (37).

In oxygenated solutions of $\text{Fe}_2(\text{SO}_4)_3$ and H_2SO_4 , the dissolution of chalcopyrite occurred in stages, the second of which showed nonlinear kinetics at elevated temperatures; this approximately parabolic rate constant was found to be a function of the initial

total concentration of trivalent iron, leveling off at high concentrations. This behavior was said to be due to complexation of Fe^{3+} by SO_4^{2-} (7). Dissolution of chalcopyrite was rapid during the first few minutes but this was followed by a 6-10 minute period of no reaction then by an interval of somewhat slower dissolution. During the first interval, first order kinetics were observed and iron dissolved preferentially. During the second reaction period, the rate was approximately linear and copper began to dissolve faster than iron. Two possible reasons for the difference in initial dissolution rates of copper and iron were suggested: thin oxide layers may have been present on the chalcopyrite surface at first; alternatively, Fe^{3+} ions near the mineral surface may have been reduced, causing a narrow iron deficient region to form. In view of the work of Linge (32) discussed below, the first explanation seems unlikely.

Dutrizac, MacDonald and Ingraham (24) reported that the leaching rate was approximately proportional to $(\text{Fe}^{3+})^2$ below 0.01 M but unaffected by higher Fe^{3+} concentrations. However, Jones and Peters (29) found that increasing the Fe^{3+} concentration from 0.03 to 1 M had little effect on the rate of reaction in sulfate solutions. At 85°C, Baur, Gibbs and Wadsworth (7) observed that the curve of fraction dissolved vs. time reached a maximum "plateau" value which increased with Fe^{3+} concentration; they attributed this to a rapid buildup of solid products at the surface of the mineral particle. Munoz-Castillo recently reported that ferric ion has no effect on the

leaching rate (37).

The effect of adding FeSO_4 to the leach solution is also unclear. Jones and Peters (29) have reported decreased copper extraction but Baur, Gibbs and Wadsworth (7) found no change in the dissolution curves when FeSO_4 was added, as did Munoz-Castillo (37).

CuSO_4 has also been reported to have no effect (37).

Observing the leaching rate to be approximately proportional to $(\text{Fe}^{3+})^2$ below 0.01 M but unaffected by higher concentrations, Dutrizac et al. (24) believed that diffusion of Fe^{3+} inward through the sulfur product layer was rate controlling below 0.01 M and outward diffusion of Fe^{2+} was controlling above this concentration. They argued that diffusion of an aqueous species through small channels in a solid is consistent with parabolic kinetics.

This interpretation has been vigorously challenged and a number of other suggestions made. Roman and Benner (41) stated that the 17 kcal/mol activation energy reported by Dutrizac et al. implies chemical control rather than transport control; in their view, the parabolic kinetics should be attributed to second order dependence on (Fe^{3+}) . Peters (40) also pointed out that the activation energy would be expected to be lower if a mass transfer step were rate limiting. He noted that although a sulfur layer is formed on all copper sulfide minerals as they are dissolved by ferric ion, chalcopyrite is the only one with parabolic leaching kinetics. Peters remarked that unsteady state diffusion within the solid phase could account for the parabolic kinetics. Beckstead et al. (8) believed

that ferrous ion had no part in determining the overall rate and that Dutrizac et al. had been misled by not considering the formation of sulfate complexes of Fe^{3+} and Fe^{2+} . Calculating activity coefficients using the extended Debye-Huckel method, Beckstead et al. concluded that the earlier data showed a nearly linear dependence of rate on Fe^{3+} activity at low concentrations and no dependence at concentrations above 0.03 M; they reported that if corrections were made for ferric ion activity, the rate constant was independent of ferrous ion concentration. However, the solutions used by Dutrizac et al. were somewhat too concentrated for the Debye-Huckel approach to be generally applicable. Recently, Linge (32) has stated that rate control by diffusion of Fe^{3+} or Fe^{2+} cannot account for the differences in kinetics between ferric sulfate and ferric chloride solutions and argued that pore diffusion control would result in dissolution rates much higher than those observed.

It was recently stated by Munoz-Castillo that the initial rapid phase of the reaction is under surface reaction control but contributes negligibly to the overall copper extraction (37). The later phase of the dissolution was said to be controlled by the transport of electrons through the product sulfur layer from the sulfide to the solution. A shrinking core model was applied to the system.

Brown and Sullivan found that small particles of natural chalcopyrite leached faster than large ones (16). Later investigators reported that size reduction below -50 +100 mesh did not affect the leaching rate or final extraction in $\text{Fe}_2(\text{SO}_4)_3$ leaching of

chalcopyrite (29). In other work, reduction from 47 to 4 microns was found to speed the reaction (37).

Synthetic chalcopyrite dissolved much more rapidly than natural mineral samples (24). It was suggested that this could be due either to differences in surface area or to impurities in the natural samples.

Electron microscopic examinations of partly reacted chalcopyrite have indicated that there is a sharp boundary between the sulfur product and the unreacted mineral (8) and that reaction is localized, apparently at grain boundaries (29).

Ferreira and Burkin (25) studied structural changes in the solid during leaching. The reaction of synthetic α -chalcopyrite occurred without structural changes. However, three stages were observed during the leaching of synthetic β -chalcopyrite. By heating to 720°C, the nonstoichiometric β -chalcopyrite can be prepared from the stoichiometric α form; natural chalcopyrite has the α structure. By the third stage of β -chalcopyrite dissolution, the lattice spacings had become identical to those of α -chalcopyrite although the β form reacted more rapidly.

Certain impurities have been found to dramatically change the rate of chalcopyrite dissolution (23). Synthetic chalcopyrite was mixed with known amounts of impurity, pressed and sintered. Pyrite accelerated the dissolution by a factor of about three, the half-reaction taking place at the pyrite cathode and chalcopyrite anode were, respectively,

Dissolution of copper was increased only 3% when pyrite particles were added to a chalcopyrite slurry, indicating that the two minerals must be in good electrical contact for chalcopyrite leaching to be significantly affected. Ions leached from other minerals were ruled out as causes of changes in chalcopyrite leaching rates.

b. Chloride media Jones and Peters (29) reported linear kinetics for the dissolution of both bulk and particulate samples of chalcopyrite by FeCl_3 . Dutrizac (21) studied disks of chalcopyrite and also found linear kinetics. For synthetic chalcopyrite the apparent activation energy was 11.3 kcal/mol; for a natural chalcopyrite it was 9.7 kcal/mol.

Increasing the concentration of Fe^{3+} was found to increase the extraction in chloride solutions (29). In more detailed experiments, Dutrizac (21) observed that the rate constant was proportional to $(\text{Fe}^{3+})^{0.80}$ at 85°C in 0.3 M HCl. In contrast, adding up to 0.1 M FeCl_2 to a leach solution 0.1 M in FeCl_3 and 0.2 M in HCl at 90°C has been reported to have no effect (29). Later FeCl_2 was found to decrease the initial rate constant at 85°C if present in amounts greater than about 150 gpl (21). Cupric chloride enhanced the initial reaction rate for chalcopyrite dissolution (21). Mixed potentials were measured by Jones and Peters (29) in a series of experiments. Surprisingly, (Fe^{2+}) had only a negligible effect on the electrode

values although (Cu^{2+}) did affect the potential. It was concluded that the predominant cathodic reaction occurring at the mineral surface could not be the reduction of Fe^{3+} . Jones and Peters (29) proposed that in chloride solutions

is the cathodic reaction and that Fe^{3+} serves primarily to depress the concentration of Cu^+ and to raise $(\text{Cu}^{2+})/(\text{Cu}^+)$.

In one hour experiments at the boiling point of the solution, the copper extraction was essentially independent of HCl concentrations at values of 56.5 gpl or greater (26). Unfortunately, the dissolution stoichiometry at this temperature was not elucidated; substantial amounts of both Cu^{2+} and Cu^+ were formed. It was later reported that in 0.1 M FeCl_3 , the rate constant was proportional to $(\text{HCl})^{0.30}$ at 85°C but independent of the acid concentration at 45°C (21). At the lower temperature, hydrolysis was observed at about pH 1.4; at 85°C , it began at about pH 1.1. At sufficiently elevated temperatures, the leaching behavior became erratic, i.e., the curves of Cu dissolved vs. time were not smooth; this was attributed to the formation of a very thin layer of hydrolysis products.

The kinetics apparently do not depend on the chloride ion concentration. When MgCl_2 or LiCl was added, the initial leaching rate appeared to be independent of the total chloride concentration and ionic strength although the data points were somewhat scattered (21).

Use of a scanning electron microscope revealed that in chloride solutions reaction occurred over the entire chalcopyrite surface (29). The rate of copper extraction was enhanced by decreased particle size (29).

Because of the low reaction rate, relatively high activation energy and lack of dependence of the rate on the disk rotation speed, Dutrizac believed that rate control by solution phase mass transfer was not possible (21). Control by solid state diffusion was ruled out because of the linear kinetics. It was suggested instead that the rate is controlled by a chemical reaction.

c. Mixed chloride-sulfate media Dutrizac and MacDonald (22) reported that at 80°C addition of 6 gpl of NaCl to a ferric sulfate leach solution caused the kinetics to become linear and increased the extraction of copper from synthetic CuFeS_2 by a factor of 2.2 in 22 h. Leaching of natural chalcopyrite from six mines was accelerated but the dissolution of samples from two other sites was retarded. The ore responding most favorably to the NaCl addition at 80°C was then leached in columns. Below about 50°C it dissolved more slowly with the salt present.

Munoz-Ribadeneira and Gomberg (38) leached chalcopyrite concentrate with 1 N sulfuric acid to which NaCl had been added. Sealed reaction flasks were used but air was not excluded. Hence it is likely that atmospheric oxygen was a reactant. The rate was reported to be proportional to $(\text{Cl}^-)^{-1/3}$. Iron hydrolysis was observed after 12 weeks and occurred sooner in solutions with higher initial Cl^- .

concentrations.

Dutrizac (21) found that addition of MgSO_4 to a ferric chloride leaching medium caused the copper dissolution to decrease. The dissolution curve became parabolic as the MgSO_4 concentration was increased; in 2 M MgSO_4 the leaching curve was essentially the same as that of ferric sulfate.

d. Nitrate media Linge (32) dissolved a slurry of chalcopryrite in $\text{Fe}(\text{NO}_3)_3$. Early in the dissolution, about twice as much iron dissolved as did copper; this was observed even when the samples were pretreated to remove surface oxides. The subsequent phase of leaching showed parabolic kinetics and had an activation energy of 14 kcal/mol. Maintaining a constant solution potential was reported to eliminate dependence of the parabolic rate on (Fe^{3+}) and (Fe^{2+}) . A number of chalcopryrite concentrates was leached in later experiments (33) and the parabolic rate constants for copper dissolution differed over an order of magnitude; the activation energies ranged from 9 to 14 kcal/mol. Copper solubilization from pyrite-rich concentrates was about 10 times faster than from pure chalcopryrite. Solid state diffusion was suggested as the rate limiting step but the diffusing species were not identified.

3. Reaction with O_2

a. Pressure leaching Pressure leaching of chalcopryrite has received considerable attention both as a means of processing concentrates and because of its potential importance in in situ leaching.

The stoichiometry has been found to be complicated. Vizsolyi et al. (48) have reported several reactions occurring during pressure leaching of a chalcopyrite concentrate in sulfuric acid. Chalcopyrite dissolved according to

Ferrous sulfate underwent oxidation according to

Under conditions that were optimum for copper solubilization (particle size, 95 to 325 mesh; oxygen overpressure, 200 to 500 psi; and temperature, 230 to 245°F) 10-15% of the sulfide sulfur was oxidized to sulfate. As the acid was consumed iron began to hydrolyze; the main product of hydrolysis was $\text{Fe}(\text{OH})_3$ but 10-15% of the hydrolyzed iron was reportedly found as the basic ferric sulfate $\text{Fe}(\text{SO}_4)\text{OH}$. Yu, Hansen and Wadsworth (52) determined that the overall stoichiometry for pressure leaching of a concentrate was

but small quantities of Fe^{2+} and S were also formed. Experiments were performed at temperatures from 125 to 175°C, oxygen partial pressures between 75 and 400 psia and H_2SO_4 concentrations near 0.5 N.

Braithwaite and Wadsworth (12) reported that when chalcopyrite reacted with dissolved oxygen in an acidic solution, a buffer pH was eventually attained which was a function only of temperature. The ratio

of sulfate to elemental sulfur was found to depend on the initial pH, the temperature and the extent of reaction; after the buffer pH was reached, the ratio of the rates of production of sulfate and sulfur was constant.

Linear kinetics were observed during pressure leaching between 125 and 175°C (52). Below the melting point of the product sulfur layer (118°C), the apparent activation energy has been reported to be 22.2 kcal/mol (12). Other investigators reported an activation energy of 17.5 kcal/mol (31).

Fe^{2+} has been said to have no effect on the rate (52). Addition of Cu^{2+} was found in one study to increase the initial rate of copper extraction (12) and in another to cause no change (52). Addition of Fe^{3+} was reported to increase the rate of copper dissolution (52) but other investigators found that increased surface concentrations of ferric ion led to precipitation of Fe_2O_3 in the solid product layer, quickly slowing the reaction (12).

Yu et al. (52) reported that as the acid concentration was increased, the reaction rate first increased, then leveled off, then dropped; they suggested that the drop at high concentrations was due to blocking of reaction sites on the mineral surface. At 90°C and an oxygen pressure of 500 psia, the initial rate data of Braithwaite and Wadsworth (12) indicated a half order dependence on (H^+) prior to product layer formation.

As P_{O_2} was increased, Yu et al. (52) observed that the rate approached a maximum or plateau value. They believed that the following

electrochemical processes took place:

Because of the dependence of the rate on oxygen partial pressure, it was concluded that cathode reactions were rate controlling.

b. Reaction at lower pressures and temperatures Oxidation of chalcopyrite with air at 52°C and 68% relative humidity gave primarily ferric and cupric sulfates in a 4 week period; lesser amounts of ferrous and cuprous thiosulfates were also found but these were believed to be intermediate products (45). All the products were solids under these experimental conditions.

In oxidizing sulfuric acid media, radiochemical techniques were used by Baur, Gibbs and Wadsworth to study the initial stages of dissolution of small particles of pure natural chalcopyrite (7). Synthetic samples reacted faster than natural ones. Reaction with O_2 was slower than reaction with $\text{Cr}_2\text{O}_7^{2-}$, H_2O_2 or Fe^{3+} . However, the oxygen dissolution process was more complicated than the others. Over the range 0 atm (N_2 purge) to 0.84 atm, oxygen partial pressure did not affect the amount of copper dissolved at ambient temperature. The reaction process had three distinct phases: an initial period of rapid

reaction, an intermediate stage when there was no dissolution and a second, somewhat slower, period of reaction that lasted for the duration of the experiment. For the second reaction phase, the stoichiometry is given by

The initial stage of the reaction had an activation energy of about 4.8 kcal/mol; solution diffusion may be rate controlling. The kinetics were linear at room temperature and the rate was independent of P_{O_2} . The kinetics of the second reaction interval were approximately linear near ambient temperature. In both cases the rate constants were approximately independent of pH over the interval between 1 and 2.5. The second stage of reaction became nonlinear at higher temperatures. This was interpreted as indicating that during this stage the overall rate was under the control of both a surface reaction with linear kinetics and a transport process with parabolic kinetics. The linear rate constant was independent of potential, indicating that the hypothesized rate controlling surface reaction could not involve charge transfer. For the linear and parabolic processes activation energies of 12.5 and 10.2 kcal/mol, respectively, were reported. At 85°C, the rate constants of both processes were found to increase O_2 partial pressure, leveling off above about 0.3 atm. The fractional extraction at which the hiatus in reaction occurred was nearly independent of P_{O_2} . It was reported that basic ferric sulfates were deposited in the product sulfur layer.

III. DEVELOPMENT OF THE MODEL

A. Chemical Aspects

As the literature surveyed above indicates, two desiderata in dump leaching are maximizing the dissolution of copper bearing minerals and preventing precipitation of iron. The model has been developed with the aim of understanding how the concentrations of the various species in leaching solution can be manipulated to accomplish these objectives.

1. Irreversible heterogeneous reactions

The dissolution reactions considered are given in Table 2. Free energy of formation data tabulated by Barner and Scheuerman (6) have been used to calculate equilibrium constants for these reactions. The values given in Table 2 apply at 298 K. If typical values for dump effluent concentrations (see Table 1) are substituted into the mass action expressions for the dissolution reactions, the resulting numbers are many orders of magnitude smaller than the K values. The dissolution of chalcopyrite in a leach dump is not an equilibrium process.

There appears to be no data available about the rate at which O_2 enters a dump and is absorbed by leach solution. It is likely that this rate is highly variable and depends on such factors as permeability, particle size distribution and the spatial heterogeneity of the size distribution. It has been assumed that oxygen is replenished as quickly as it reacts, i.e., that it is not a limiting reagent and

Table 2. Reactions for dissolution of chalcopyrite in leach dumps

	K_{298}
$\text{CuFeS}_2 + 4\text{Fe}^{3+} \rightarrow \text{Cu}^{2+} + 5\text{Fe}^{2+} + 2\text{S}^0$	6.76×10^{20}
$\text{CuFeS}_2 + \text{O}_2 + 4\text{H}^+ \rightarrow \text{Cu}^{2+} + \text{Fe}^{2+} + 2\text{S}^0 + 2\text{H}_2\text{O}$	8.62×10^{54}

that the dissolved oxygen concentration is maintained at steady state.

It should be noted that elemental sulfur, the predominant sulfur containing reaction product in low temperature kinetic studies, is not thermodynamically stable relative to the -2 and +6 oxidation states.

For computational purposes, however, it has been assumed that S^0 (s) is formed quantitatively.

The reaction

could also be considered; ferrous ion is always present in liquor returned to a dump from a precipitation plant and is also produced by oxidation of iron containing sulfide minerals. However, Equation (16) is not independent of the dissolution reactions of Table 2; subtracting the latter two gives Equation (16).

In developing the model, it is necessary to have kinetic information on the dissolution reactions in order to obtain a complete set of equations. The only ambient temperature data available that permits comparison of the rates of these two reactions are those of Baur, Gibbs and Wadsworth (7); Figure 1 is taken from their report. These data have been replotted in Figure 2 with the variables transformed to match those of the model equations (see below); ξ is the fraction of chalcopyrite dissolved averaged over each 10 minute interval and $\bar{n}_{O_2}$ and $\bar{N}_{CuFeS_2}$ are the number of moles of O_2 and $CuFeS_2$ reacting per kg of solution over a 10 minute interval. The reaction time in these experiments was one hour so the data must be extrapolated. The

parabolic curves for reaction with both Fe^{3+} and O_2 level off so quickly that they effectively become linear within one hour; both reaction processes may be taken to follow linear kinetics beyond this. Because the solutions were purged with O_2 , the ratio of total moles CuFeS_2 reacting to moles O_2 reacting may be taken to be a lower limit that applies to solutions saturated with oxygen and containing moderate concentrations of $\text{Fe}_2(\text{SO}_4)_3$.

2. Solution phase reactions

There is a large number of solution phase reactions occurring as leach liquor percolates through a dump. These include complexation reactions involving sulfate and bisulfate ions, acid-base reactions and olation reactions; they may be considered to be rapid reactions which remain at equilibrium as the solid chalcopyrite slowly goes into solution.

Dilemmas of two kinds must be faced in dealing with the solution chemistry of transition metal sulfates: for some frequently studied systems the formation or stability constants reported differ greatly even when the measurements were made by the same technique under closely similar conditions; for other systems the values of the equilibrium constants have been investigated only rarely and reports of the existence of certain complex ions are of dubious veracity.

The published values of stability constants for FeSO_4^0 , CuSO_4^0 , FeSO_4^+ and $\text{Fe}(\text{SO}_4)_2^-$ have been evaluated and recommended values given by Smith and Martell (44). Several complex ions involving HSO_4^- ligands

and iron ions have also been reported. In cases where there is more than one published value for an equilibrium constant for a bisulfate complex, the recommended values of Smith and Martell were used to help decide which value was more reasonable; in most papers, formation or stability constants for several complexes are given and the values for the sulfate complexes can be compared with those in Smith and Martell to detect systematic errors.

A value for the equilibrium constant for formation of FeSO_4^0 at high ionic strength has been given by Wells and Salam (50) but may not be reliable because the value of the formation constant of FeSO_4^0 at $I = 0$ given by these workers is smaller by a factor of 10 than the value of Smith and Martell (44). There appears to be no other published work giving this constant at 25°C and a high ionic strength. Hence it is necessary to estimate a value. Smith and Martell (44) give the formation constants of CuSO_4^0 and FeSO_4^+ for 3 and 4 values of I , respectively. Plots of $\log K$ vs. I show that K decreases sharply between $I = 0$ and 1 and levels off at larger I values. The value of K for FeSO_4^0 at $I = 3$ can be estimated by subtracting the average of the decreases between $I = 0$ and 3 for the other two complexes from the FeSO_4^0 formation constant in ideal solution; the result is 2.06.

The equilibrium constant for FeHSO_4^+ was first given by Beukenkamp and Herrington (9) but apparently neither the H_2SO_4 concentration nor the temperature was kept constant during the experiments so the value of 0.61 for the formation constant is clearly

unreliable. Beckstead et al. (8) reported that the dissociation constant is 0.263; the temperature and ionic strength were not specified but examination of other constants in the same tabulation suggests that they were 25°C and $I = 0$. This value is the best one to use in an ideal solution. Wells and Salam (50) reported a formation constant of 1.94 for this constant at 25°C and an ionic strength of 4.0. This value was used in the calculations because it follows the general trend of decreased formation constant with increased ionic strength.

Work on FeHSO_4^{2+} has been reported by Sykes (46), Lister and Rivington (34) and Sapieszko et al. (42). Sykes gave a value of 60 for the formation constant at 19°C and an ionic strength of 0.15. This value was selected for use under ideal solution conditions. Lister and Rivington gave a formation constant of 6 at an ionic strength of 1.2. They also reported the existence of $\text{FeSO}_4\text{HSO}_4$, a complex not reported by other investigators. Sapieszko et al. gave 4 as the value of the formation constant of FeHSO_4^{2+} in 2.67 M NaClO_4 at 25°C.

A large number of olation reactions is known but most of them are unimportant under the acidic conditions of interest. At a pH of 2, only those shown in Table 3 have a concentration ratio of complex to free metal ion greater than 10^{-6} . Hydroxo complexes of Cu(II) and Fe(II) are not significant near this pH.

K values for the olation reactions and the bisulfate-sulfate reaction and water dissociation are available in Smith and Martell (44).

The values of all the complexation, olation and acid-base constants used in the computations are summarized in Table 3.

Table 3. Equilibrium constants for reactions in solution

Reaction	K_{298}	Conditions	Source
$H^+ + OH^- \rightleftharpoons H_2O$	9.93×10^{13}	25°C I = 0	Smith & Martell (44)
	1.51×10^{14}	25°C I = 3	Smith & Martell (44)
$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$	9.77×10^1	25°C I = 0	Smith & Martell (44)
	8.13×10^0	25°C I = 3	Smith & Martell (44)
$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+$	6.50×10^{-3}	25°C I = 0	Smith & Martell (44)
	1.07×10^{-3}	25°C I = 3	Smith & Martell (44)
$FeOH^{2+} + H_2O \rightleftharpoons Fe(OH)_2^+ + H^+$	3.11×10^{-4}	25°C I = 0	Smith & Martell (44)
	5.13×10^{-4}	25°C I = 3	Smith & Martell (44)
$2FeOH^{2+} \rightleftharpoons Fe_2(OH)_2^{4+}$	3.02×10^1	25°C I = 0	Smith & Martell (44)
	1.51×10^3	25°C I = 3	Smith & Martell (44)
$Fe^{3+} + SO_4^{2-} \rightleftharpoons FeSO_4^+$	1.10×10^4	25°C I = 0	Smith & Martell (44)
	8.51×10^1	25°C I = 3	Smith & Martell (44)
$FeSO_4^+ + SO_4^{2-} \rightleftharpoons Fe(SO_4)_2^-$	2.19×10^1	25°C I = 0	Smith & Martell (44)
	1.51×10^0	25°C I = 3	Smith & Martell (44)
$Fe^{3+} + HSO_4^- \rightleftharpoons FeHSO_4^{2+}$	6.00×10^1	19°C I = 0.15	Sykes (46)
	4.00×10^0	25°C I = 2.67	Sapieszko <u>et al.</u> (42)
$Fe^{2+} + SO_4^{2-} \rightleftharpoons FeSO_4^0$	1.58×10^2	25°C I = 0	Smith & Martell (44)
	2.06×10^0	25°C I = 3	estimated from data in Smith & Martell (44)

Table 3. (continued)

Reaction	K_{298}	Conditions	Source
$\text{Fe}^{2+} + \text{HSO}_4^- \rightleftharpoons \text{FeHSO}_4^+$	3.81×10^0	25°C I = 0	Beckstead <u>et al.</u> (8)
	1.94×10^0	25°C I = 4	Wells & Salam (50)
$\text{Cu}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{CuSO}_4^0$	2.29×10^2	25°C I = 0	Smith & Martell (44)
	5.01×10^0	25°C I = 3	Smith & Martell (44)

3. Hydrolysis and precipitation of Fe^{3+}

The hydrolysis and precipitation of Fe^{3+} is extremely complicated and has been extensively studied. The mechanism of the precipitation is not understood (51). It is known that the solution pH, total ferric ion concentration, anions present and temperature all affect the precipitation process.

In acidic sulfate solutions at room temperature, one of the final solid products is goethite, $\alpha\text{-FeOOH}$ (3, 30). The initial product is amorphous $\text{Fe}(\text{OH})_3$, which crystallizes into goethite upon aging; the results of Hsu (28) suggest that the initial supersaturation of the solution with respect to amorphous $\text{Fe}(\text{OH})_3$ determines the size distribution of the precipitating particles, their stability and crystallinity. If other anions are present, other crystalline forms of FeOOH are produced.

Smith and Martell (44) have given solubility products for amorphous $\text{Fe}(\text{OH})_3$ and $\alpha\text{-FeOOH}$ at ionic strengths of 0 and 3.

Arden (3) also reported finding $(\text{Fe}_2(\text{OH})_5)_2\text{SO}_4$ but this compound has not been reported in other studies and is not considered further.

The jarosites are a series of related compounds of the general formula $\text{XFe}_3(\text{SO}_4)_2(\text{OH})_6$ where $\text{X} = \text{H}_3\text{O}^+$, Na^+ , K^+ , NH_4^+ , or Ag^+ ; the compound $\text{PbFe}_6(\text{SO}_4)_4(\text{OH})_{12}$ is also known. The best known is jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$. All of the jarosites are very insoluble (39). Jarosites form simultaneously with hydrolysis in ferric sulfate solution if Na^+ , K^+ or NH_4^+ ions are also present (30). There is extensive $\text{K}^+\text{-Na}^+\text{-H}_3\text{O}^+$ substitution in both natural and synthetic

minerals (14); higher temperatures during synthesis lead to more substitution of H_3O^+ for K^+ . In synthetic work at 25°C , Brown (15) found that pure hydronium jarosite formed only if alkali metal ions were absent.

Thermodynamic data have been reported for only one of this family of compounds, pure (or very nearly so) jarosite. For the dissolution reaction

at 25°C and an ionic strength of 1, Brown (15) gave an equilibrium constant of 3.205×10^{-8} . Vlek et al. (49) reported a pK value of 98.56 for the reaction

The ΔG_f^0 value for jarosite given by these workers has been used together with data from Barner and Scheuerman (6) to calculate a K value of 1.47×10^{-2} for

Vlek et al. reported that amorphous $\text{Fe}(\text{OH})_3$ precipitated simultaneously with the jarosite; Na^+ was present in some of their experiments as well. The values of Brown have been used because they may be more

accurate and in any event will give a more conservative estimate of the concentrations at which Fe precipitation may be expected.

The equilibrium constants used for these reactions are given in Table 4.

B. Mathematical Aspects

1. Derivation of equations

In an aqueous solution of $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4 and CuSO_4 , such as leach liquor not in contact with soluble solids, the reactions listed in Table 3 are important. There are 16 dissolved species involved in these reactions, not counting H_2O . These 16 species satisfy 11 mass action expressions, a charge balance and mass balances for the sulfate moiety, Fe(III), Fe(II) and Cu(II). Simultaneous solution of these nonlinear algebraic equations gives the concentration of each species. The mass action equations for this system are given in Table 4, the material and charge balances in Table 5. Water molecules are ordinarily considered to be present in constant amounts in aqueous solutions since, as the solvent, water has a much higher concentration than any of the solutes. If it were desired to take the concentration of H_2O into account, the mass action expressions would need to be written. The most convenient way to do this would be to write an equation expressing the conservation of the number of H atoms.

When the solution enters a leach dump, the situation becomes somewhat more complicated. As suggested above, the reactions taking

Table 4. Equilibrium constants for precipitation of Fe^{3+} in sulfate media

Reaction	K_{298}	Conditions	Source
$\text{Fe}(\text{OH})_3(\text{s}) \rightleftharpoons \text{Fe}^{3+} + 3\text{OH}^-$	1.58×10^{-39}	25°C I = 0	Smith & Martell (44)
	2.51×10^{-39}	25°C I = 3	Smith & Martell (44)
$\alpha\text{-FeOOH}(\text{s}) \rightleftharpoons \text{Fe}^{3+} + 3\text{OH}^-$	3.16×10^{-42}	25°C I = 0	Smith & Martell (44)
	7.94×10^{-42}	25°C I = 3	Smith & Martell (44)
$K_{0.98}(\text{H}_3\text{O})_{0.02} \text{Fe}_3(\text{SO}_4)_2(\text{OH})_6 + 6.98 \text{H}_3\text{O}^+$ $\rightleftharpoons 0.98 \text{K}^+ + 3\text{Fe}^{3+} + \text{HSO}_4^- + \text{SO}_4^{2-} + 13\text{H}_2\text{O}$	3.20×10^{-8}	25°C I = 1	Brown (15)

Table 5. Material and charge balances for a solution of $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4 , H_2SO_4 and CuSO_4 at equilibrium^a

$$C_{\text{SO}_4} = m_{\text{SO}_4^{2-}} + m_{\text{HSO}_4^-} + m_{\text{FeSO}_4^+} + 2m_{\text{Fe}(\text{SO}_4)_2^-} + m_{\text{FeHSO}_4^{2+}} + m_{\text{FeSO}_4^0} \\ + m_{\text{FeHSO}_4^+} + m_{\text{CuSO}_4^0}$$

$$2C_{\text{Fe}_2(\text{SO}_4)_3} = m_{\text{Fe}^{3+}} + m_{\text{FeOH}^{2+}} + m_{\text{Fe}(\text{OH})_2^+} + 2m_{\text{Fe}_2(\text{OH})_2^{4+}} + m_{\text{FeSO}_4^+} \\ + m_{\text{Fe}(\text{SO}_4)_2^-} + m_{\text{FeHSO}_4^{2+}}$$

$$C_{\text{FeSO}_4} = m_{\text{Fe}^{2+}} + m_{\text{FeSO}_4^0} + m_{\text{FeHSO}_4^+}$$

$$C_{\text{CuSO}_4} = m_{\text{Cu}^{2+}} + m_{\text{CuSO}_4^0}$$

$$0 = m_{\text{H}^+} - m_{\text{OH}^-} - 2m_{\text{SO}_4^{2-}} - m_{\text{HSO}_4^-} + 3m_{\text{Fe}^{3+}} + 2m_{\text{FeOH}^{2+}} + m_{\text{Fe}(\text{OH})_2^+} \\ + 4m_{\text{Fe}_2(\text{OH})_2^{4+}} + m_{\text{FeSO}_4^+} - m_{\text{Fe}(\text{SO}_4)_2^-} + 2m_{\text{FeHSO}_4^{2+}} \\ + 2m_{\text{Fe}^{2+}} + m_{\text{FeHSO}_4^+} + 2m_{\text{Cu}^{2+}}$$

^a C_i = analytical concentration of i, moles/kg solution; m_i = equilibrium concentration of i, moles/kg solution.

place in a leach dump may be divided into two classes: (i) the dissolution reactions, which do not reach equilibrium and (ii) rapid reactions involving only dissolved species that maintain their equilibria as the irreversible reactions proceed.

This type of situation has been treated in the geochemical literature (27) and termed "partial equilibrium". In the case of sulfide mineral leaching, as in many others, the partial equilibrium concept can be used to derive equations linking the concentrations of the soluble species to the progress of the reactions involving solids.

Taking a basis of 1 kg of solution, the chemical equation for the overall irreversible dissolution of a solid can be written

$$\sum_i \bar{N}_i S_i + \sum_j \bar{n}_j s_j = 0 . \quad (\text{Eq. 20})$$

Here $\bar{N}_i$ is the number of moles of solid S_i formed and $\bar{n}_j$ is the number of moles of the j th dissolved species s_j formed. $\bar{N}_i$ and $\bar{n}_j$ are negative for reactants and positive for products. If several independent dissolution reactions occur simultaneously, Equation 20 is the sum of these; i.e., it gives the net stoichiometry observed. In this case, the ratios $\bar{N}_i : \bar{n}_j$ would change with time if the independent reactions followed different kinetics. If there is only a single dissolution reaction, $\bar{N}_i$ and $\bar{n}_j$ are conventional stoichiometric coefficients. The extent of dissolution is given by ξ , a progress variable for the fraction of solid reacted; $0 \leq \xi \leq 1$.

For the j th dissolved species, changes in the activity a_j and molality m_j are related by

$$da_j = d(\gamma_j m_j) \quad . \quad (\text{Eq. 21})$$

The activity coefficient is denoted γ_j .

As the solid S_i dissolves, the concentration m_j of the j th soluble species changes. The change in concentration can be related to the dissolution progress variable by

$$\bar{n}_j d\xi = dm_j \quad (\text{Eq. 22})$$

or

$$\frac{da_j - m_j d\gamma_j}{\gamma_j} = dm_j$$

$$\frac{1}{\gamma_j} da_j - m_j d\ln\gamma_j = dm_j \quad . \quad (\text{Eq. 23})$$

For the solid

$$\bar{N}_i d\xi = dM_i \quad (\text{Eq. 24})$$

where dM_i is the differential change in the number of moles of solid i present per liter of solution.

Each solution reaction has an associated mass action expression

$$K = \prod_{\ell} a_{\ell}^{\nu_{\ell}} \quad (\text{Eq. 25})$$

where K is the equilibrium constant and the ν_{ℓ} are the stoichiometric coefficients. The equilibria shift as the solid dissolves so the a_{ℓ} are functions of ξ . Taking logarithms and differentiating,

$$0 = \frac{d \ln K}{d \xi} = \sum_{\ell} \nu_{\ell} \frac{d \ln a_{\ell}}{d \xi} .$$

Assuming that only the activities of the solute species s_j vary appreciably during dissolution, this can also be written

$$0 = \frac{d \ln K}{d \xi} = \sum_j \nu_j \frac{d \ln a_j}{d \xi} . \quad (\text{Eq. 26})$$

Substituting from Equations 21 and 22, this becomes

$$\begin{aligned} 0 &= \sum_j \frac{\nu_j \bar{n}_j}{\gamma_j m_j} \frac{d(\gamma_j m_j)}{d m_j} \\ &= \sum_j \nu_j \bar{n}_j \left[\frac{1}{m_j} + \frac{d \ln \gamma_j}{d m_j} \right] . \end{aligned} \quad (\text{Eq. 27})$$

In a multicomponent electrolyte solution, the concentration of a single species will not have much influence on the ionic strength I and hence

$$\frac{d \gamma_j}{d m_j} = \frac{d \gamma_j}{d I} \frac{d I}{d m_j} \approx 0 . \quad (\text{Eq. 28})$$

Thus

$$0 = \sum_j \frac{\nu_j \bar{n}_j}{m_j} . \quad (\text{Eq. 29})$$

In addition, a mass balance equation can be written for each species which is conserved or which undergoes a concentration change determined by the stoichiometry of the irreversible reactions. This is

$$0 = \sum_k (\lambda_{kj} \bar{n}_j + \lambda_{ki} \bar{N}_i) \quad (\text{Eq. 30})$$

where λ_{kj} is the number of k moieties in species s_j . A charge balance

$$0 = \sum_j \kappa_j \bar{n}_j \quad (\text{Eq. 31})$$

can also be written for the solution phase. Here κ_j is the charge on s_j .

Such a set of equations is not complete and additional information must be supplied. Kinetic information on the irreversible reactions may be available to add to the set of equations. There is no particular advantage in using rate data directly because mineral dissolution rates are highly dependent on the source and methods of preparing the sample. It is convenient to use fractional dissolution, ξ , as the independent variable rather than time and, for the unknowns that participate only in irreversible reactions, to introduce $\bar{n}_j$ or $\bar{N}_i$ as the dependent variable. In general, each $\bar{n}_j$ and $\bar{N}_i$ will be a function of ξ . The equations to be added to the set will be algebraic rather than differential equations. In certain cases the explicit dependence on ξ can be removed, as for example if for the species not at equilibrium the unknowns are linearly related.

If the irreversible reactions of Table 2 are added to those of Table 3, the number of unknowns increases and the system of equations must be modified. For the equilibria, there are 11 equations of the form of Equation 29. The charge and concentration of sulfate moieties are conserved, giving 2 balance equations. The total Fe(III) concentration decreases and the Fe(II) and Cu(II) concentrations increase with dissolution. For Fe(III),

$$\bar{N}_{\text{CuFeS}_2} = \frac{1}{4} \bar{n}_{\text{Fe(III)}} + \bar{n}_{\text{O}_2}$$

or

$$4(\bar{N}_{\text{CuFeS}_2} - \bar{n}_{\text{O}_2}) = \bar{n}_{\text{Fe}^{3+}} + \bar{n}_{\text{FeOH}^{2+}} + \bar{n}_{\text{Fe(OH)}_2^+} \quad (\text{Eq. 32})$$

$$+ 2 \bar{n}_{\text{Fe}_2(\text{OH})_2^{4+}} + \bar{n}_{\text{FeSO}_4^+} + \bar{n}_{\text{Fe(SO}_4)_2^-} + \bar{n}_{\text{FeHSO}_4^{2+}} .$$

For Fe(II) and Cu(II),

$$-\frac{5}{4} \bar{n}_{\text{Fe(III)}} - \bar{n}_{\text{O}_2} = \bar{n}_{\text{Fe(II)}}$$

$$-5 \bar{N}_{\text{CuFeS}_2} + 4 \bar{n}_{\text{O}_2} = \bar{n}_{\text{Fe}^{2+}} + \bar{n}_{\text{FeSO}_4^0} + \bar{n}_{\text{FeHSO}_4^+} \quad (\text{Eq. 33})$$

and

$$\begin{aligned} -\bar{N}_{\text{CuFeS}_2} &= \bar{n}_{\text{Cu(II)}} \\ &= \bar{n}_{\text{Cu}^{2+}} + \bar{n}_{\text{CuSO}_4^0} . \end{aligned} \quad (\text{Eq. 34})$$

A mass balance for total H atoms cannot be written without introducing H₂O as a variable. It is not convenient to consider H₂O and S because the concentration of the former is effectively constant while the latter does not react further; neither, therefore, affects the solution concentrations.

Figure 1 presents kinetic data from Baur, Gibbs and Wadsworth (7) that can be used to add another equation to the set. Extrapolation

Figure 1. Dissolution of chalcopyrite by $Fe_2(SO_4)_3$ and O_2 . Solutions purged by O_2 . Data from Baur *et al.* (7).

of the curves in Figure 2 indicates that

$$\frac{\bar{N}_{\text{CuFeS}_2}}{\bar{n}_{\text{O}_2}} = R \quad (\text{Eq. 35})$$

where R is a constant that has a lower limit of 2 in solutions saturated with O_2 and containing moderate concentrations of $\text{Fe}_2(\text{SO}_4)_3$. Fortuitously, this additional equation is linear.

There is a total of 17 unknowns here but only 16 equations. It is convenient to divide by $-\bar{N}_{\text{CuFeS}_2}$ and define new variables, e.g.,

$$n_{\text{H}^+} = \frac{\bar{n}_{\text{H}^+}}{-\bar{N}_{\text{CuFeS}_2}} = \frac{\text{moles H}^+ \text{ formed}}{\text{moles CuFeS}_2 \text{ reacting}} \quad (\text{Eq. 36})$$

Inclusion of the minus sign preserves the sign convention introduced earlier. With this modification, the set of equations given in Table 6 is obtained.

For Equation 29 to be solvable, the concentration m_j must be specified. It is necessary to obtain the concentrations of the species in solution before the solid begins to dissolve; this can be done by solving the set of nonlinear algebraic equations given in Tables 3 and 5. It is necessary that the solution initially contain at least a small amount of copper. This assumption is physically reasonable because leach liquor is recycled and contains traces of Cu(II) at all times.

Figure 2. Copper dissolved as a function of the fraction of chalcopyrite reacted.

Table 6. Scaled partial equilibrium equations for chalcopryrite dissolution^a

$$0 = \frac{n}{m} \frac{H^+}{H^+} + \frac{n}{m} \frac{OH^-}{OH^-}$$

$$0 = \frac{n}{m} \frac{H^+}{H^+} + \frac{n}{m} \frac{SO_4^{2-}}{SO_4^{2-}} - \frac{n}{m} \frac{HSO_4^-}{HSO_4^-}$$

$$0 = \frac{n}{m} \frac{Fe^{3+}}{Fe^{3+}} - \frac{n}{m} \frac{H^+}{H^+} - \frac{n}{m} \frac{FeOH^{2+}}{FeOH^{2+}}$$

$$0 = \frac{n}{m} \frac{FeOH^{2+}}{FeOH^{2+}} - \frac{n}{m} \frac{H^+}{H^+} - \frac{n}{m} \frac{Fe(OH)_2^+}{Fe(OH)_2^+}$$

$$0 = \frac{2n}{m} \frac{FeOH^{2+}}{FeOH^{2+}} - \frac{n}{m} \frac{Fe_2(OH)_2^{4+}}{Fe_2(OH)_2^{4+}}$$

$$0 = \frac{n}{m} \frac{SO_4^{2-}}{SO_4^{2-}} + \frac{n}{m} \frac{Fe^{3+}}{Fe^{3+}} - \frac{n}{m} \frac{FeSO_4^+}{FeSO_4^+}$$

$$0 = \frac{n}{m} \frac{SO_4^{2-}}{SO_4^{2-}} + \frac{n}{m} \frac{FeSO_4^+}{FeSO_4^+} - \frac{n}{m} \frac{Fe(SO_4)_2^-}{Fe(SO_4)_2^-}$$

^a n_i = moles i formed/mole $CuFeS_2$ reacting; m_j = moles j /kg solution.

Table 6. (continued)

$$0 = \frac{n}{m} \frac{\text{HSO}_4^-}{\text{HSO}_4^-} + \frac{n}{m} \frac{\text{Fe}^{3+}}{\text{Fe}^{3+}} - \frac{n}{m} \frac{\text{FeHSO}_4^{2+}}{\text{FeHSO}_4^{2+}}$$

$$0 = \frac{n}{m} \frac{\text{SO}_4^{2-}}{\text{SO}_4^{2-}} + \frac{n}{m} \frac{\text{Fe}^{2+}}{\text{Fe}^{2+}} - \frac{n}{m} \frac{\text{FeSO}_4^0}{\text{FeSO}_4^0}$$

$$0 = \frac{n}{m} \frac{\text{HSO}_4^-}{\text{HSO}_4^-} + \frac{n}{m} \frac{\text{Fe}^{2+}}{\text{Fe}^{2+}} - \frac{n}{m} \frac{\text{FeHSO}_4^+}{\text{FeHSO}_4^+}$$

$$0 = \frac{n}{m} \frac{\text{SO}_4^{2-}}{\text{SO}_4^{2-}} + \frac{n}{m} \frac{\text{Cu}^{2+}}{\text{Cu}^{2+}} - \frac{n}{m} \frac{\text{CuSO}_4^0}{\text{CuSO}_4^0}$$

$$0 = n_{\text{H}^+} - n_{\text{OH}^-} - 2n_{\text{SO}_4^{2-}} - n_{\text{HSO}_4^-} + 3n_{\text{Fe}^{3+}} + 2n_{\text{FeOH}^{2+}} + n_{\text{Fe(OH)}_2^+}$$

$$+ 4n_{\text{Fe}_2(\text{OH})_2^{4+}} + n_{\text{FeSO}_4^+} - n_{\text{Fe}(\text{SO}_4)_2^-} + 2n_{\text{FeHSO}_4^{2+}} + 2n_{\text{Fe}^{2+}} + n_{\text{FeHSO}_4^+}$$

$$+ 2n_{\text{Cu}^{2+}}$$

Table 6. (continued)

$$0 = n_{\text{SO}_4^{2-}} + n_{\text{HSO}_4^-} + n_{\text{FeSO}_4^+} + 2n_{\text{Fe}(\text{SO}_4)_2^-} + n_{\text{FeHSO}_4^{2+}} + n_{\text{FeSO}_4^0}$$

$$+ n_{\text{FeHSO}_4^+} + n_{\text{CuSO}_4^0}$$

$$-4 - 4n_{\text{O}_2} = n_{\text{Fe}^{3+}} + n_{\text{FeOH}^{2+}} + n_{\text{Fe}(\text{OH})_2^+} + 2n_{\text{Fe}_2(\text{OH})_2^{4+}} + n_{\text{FeSO}_4^+}$$

$$+ n_{\text{Fe}(\text{SO}_4)_2^-} + n_{\text{FeHSO}_4^{2+}}$$

$$5 + 4n_{\text{O}_2} = n_{\text{Fe}^{2+}} + n_{\text{FeSO}_4^0} + n_{\text{FeHSO}_4^+}$$

$$1 = n_{\text{Cu}^{2+}} + n_{\text{CuSO}_4^0}$$

$$\frac{1}{R} - n_{\text{O}_2} = 0$$

Solutions of the partial equilibrium equations are subject to the physical constraint that the amount of each solution phase reactant consumed in an increment of dissolution cannot exceed the amount present at the start of that increment.

2. Method of solving the equations

The computational procedure may be outlined as follows:

(1) Obtain the initial equilibrium concentrations by solving the nonlinear equations simultaneously. Use the solubility products of Table 4 to check for precipitation. Stop if it occurs.

(2) Choose values of n_{O_2} , $\bar{N}_{CuFeS_2}$ and $\Delta\xi$.

(3) Solve the equations of Table 6 for the n_j .

(4) Calculate concentration changes using

$$\Delta m_j \approx \bar{n}_j \Delta\xi = n_j (-\bar{N}_{CuFeS_2}) \Delta\xi \quad . \quad (\text{Eq. 37})$$

(5) Calculate new concentrations.

(6) Check to see whether any of the new concentrations are negative. If so, reduce the increment size and repeat steps (5) and (6).

(7) Check the solubility products again. Stop if precipitation occurs.

(8) Check whether Fe(III) is depleted. Stop if this happens.

(9) Repeat beginning with step (3).

Flowcharts of the main program and subroutines are given in Appendix A.

In general, species present in very low concentrations were determined less accurately than those with higher concentrations. The hydroxide ion concentration is of the same order of magnitude as the

precision with which the linear equations of Table 6 can be solved; changes in this concentration therefore were calculated indirectly from the equilibrium constant for the dissociation of H_2O . Precision of the other calculated reactant concentrations began to deteriorate around 10^{-6} m.

The mathematical problem is first the solution of a system of nonlinear equations, then the solution of a system of linear equations.

Although for favorable cases a set of simultaneous nonlinear algebraic equations can readily be combined to yield a single equation containing a single unknown, large sets of equations are usually not reduced in this way but are solved by an iteration process involving all the unknowns.

The well-known Newton-Raphson method has been chosen for this study. Using the Newton-Raphson technique has the advantage that the Gauss-Jordan elimination used as part of the multidimensional Newton-Raphson method can also be used in solving the linear system of equations given in Table 6.

In solving a single nonlinear equation, the value of the unknown $x_{(N+1)}$ obtained from the (N+1)st iteration is given by

$$x_{(N+1)} = x_{(N)} - \frac{f(x_{(N)})}{f'(x_{(N)})} \quad (\text{Eq. 38})$$

To use the Newton-Raphson method, one supplies an initial guess $x_{(0)}$ and evaluates the function and its derivative at each stage in the iteration.

This technique can be generalized to solve a system of n equations $\{f_i\}$ in n unknowns $\{x_j\}$. Matrix techniques must then be introduced. Equation 39 is analogous to Equation 38 but is written in matrix notation.

$$\underline{x}_{(N+1)} = \underline{x}_{(N)} - [\underline{f}'(\underline{x}_{(N)})]^{-1} \underline{f}(\underline{x}_{(N)}) \quad (\text{Eq. 39})$$

or

$$\underline{x}_{(N+1)} = \underline{x}_{(N)} + \underline{\delta}_{(N)} \quad (\text{Eq. 40})$$

where $\underline{\delta}_{(N)}$ is the solution to the linear system

$$\underline{f}'(\underline{x}_{(N)}) \underline{\delta}_{(N)} = -\underline{f}(\underline{x}_{(N)}) \quad (\text{Eq. 41})$$

Here $\underline{f}'$ is the Jacobian matrix whose elements are

$$f'_{ij} = \frac{\partial f_i}{\partial x_j} \quad (\text{Eq. 42})$$

In effect, a nonlinear problem has been made linear. From this point on, the same matrix manipulations are performed in obtaining the initial concentrations and in determining the subsequent changes in number of moles of each species.

An exact solution of a set of nonhomogeneous linear equations can be obtained by Gauss-Jordan elimination if the coefficient matrix is nonsingular (19). Considering the general nonhomogeneous linear system

$$\underline{B} \underline{x} = \underline{C} \quad (\text{Eq. 43})$$

an augmented matrix $\underline{A}$ with the form

$$\underline{A}_{\text{initial}} = [\underline{B} : \underline{C} : \underline{I}] \quad (\text{Eq. 44})$$

is first constructed. The first n columns on the lefthand side of $\underline{A}$ are the coefficient matrix $\underline{B}$, the middle column is the column matrix of constants, $\underline{C}$, and on the right is an $n \times n$ identity matrix $\underline{I}$.

For a system of n equations, the augmented matrix has dimensionality $n \times (2n + 1)$ or $n \times m$. Working down row by row, the augmented matrix is normalized so that each element a_{kk} of $\underline{A}$ is unity; each element a_{kj} is replaced by a_{kj}/a_{kk} ($j = n+m, n+m-1, \dots, k$). Then all elements to the left of a_{kk} and in the k th row or a lower row are reduced to zero as a_{ij} is replaced by $a_{ij} - a_{ik}a_{kj}$ ($j = n+m, n+m-1, \dots, k; i = 1, 2, \dots, n$ but $i \neq k$). After the Gauss-Jordan elimination, Equation 44 has the form

$$\underline{A}_{\text{final}} = [\underline{I} : \underline{x} : \underline{B}^{-1}] . \quad (\text{Eq. 45})$$

There is an identity matrix on the left and the inverse of matrix $\underline{B}$ appears on the right. In the central column are the solutions to Equation 43.

IV. RESULTS AND DISCUSSION

The major results of this work include (i) calculation of the equilibrium distribution of species in solutions of $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4 , CuSO_4 and H_2SO_4 at high and low ionic strength, (ii) elucidation of the conditions under which trivalent iron precipitates from such solutions and (iii) calculation of the changes in solution concentrations during dissolution of chalcopyrite under dump leaching conditions, with particular emphasis on the relative effectiveness of Fe(III) and O_2 lixiviants and the prevention of precipitation. Implications for the operation of leach dumps are discussed at the same time.

A. Equilibrium Concentrations in Solutions of
 $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4 , CuSO_4 and H_2SO_4

Using the thermodynamic equilibrium constants, the concentrations of the species present in 0.1 m FeSO_4 , 0.001 m CuSO_4 , 0.01 m H_2SO_4 and 0.050, 0.025, 0.010 and 0.005 m $\text{Fe}_2(\text{SO}_4)_3$ were calculated. These data are given in Table 7 and the distributions of the Fe(III) species are shown as a function of the analytical concentration of $\text{Fe}_2(\text{SO}_4)_3$ in Figures 3 and 4.

The H^+ concentration declines as $C_{\text{Fe}_2(\text{SO}_4)_3}$ is increased. The SO_4^{2-} concentration increased 28% as $C_{\text{Fe}_2(\text{SO}_4)_3}$ increased from 0.005 to 0.05 m. The bisulfate ion concentration also increased but only 9%.

At 0.005 m $\text{Fe}_2(\text{SO}_4)_3$, 17% of the total sulfate concentration is present as SO_4^{2-} , 10% as HSO_4^- and 61% as FeSO_4^0 ; at 0.05 m, these figures are 11, 5 and 31%, respectively.

Table 7. Equilibrium concentrations in solutions of 0.1 m FeSO_4 , 0.001 m CuSO_4 , 0.01 m H_2SO_4 and $\text{Fe}_2(\text{SO}_4)_3$ at $I = 0^a$

	0.005 m $\text{Fe}_2(\text{SO}_4)_3$	0.01 m $\text{Fe}_2(\text{SO}_4)_3$	0.025 m $\text{Fe}_2(\text{SO}_4)_3$	0.05 m $\text{Fe}_2(\text{SO}_4)_3$
H^+	6.0829×10^{-3}	5.9326×10^{-3}	5.5734×10^{-3}	5.1720×10^{-3}
OH^-	1.6555×10^{-12}	1.6974×10^{-12}	1.8068×10^{-12}	1.9470×10^{-12}
SO_4^{2-}	2.1585×10^{-2}	2.2442×10^{-2}	2.4695×10^{-2}	2.7630×10^{-2}
HSO_4^-	1.2835×10^{-2}	1.3014×10^{-2}	1.3454×10^{-2}	1.3969×10^{-2}
Fe^{3+}	2.8462×10^{-5}	5.4080×10^{-5}	1.1902×10^{-4}	2.0438×10^{-4}
FeOH^{2+}	3.0423×10^{-5}	5.9270×10^{-5}	1.3885×10^{-4}	2.5694×10^{-4}
$\text{Fe}(\text{OH})_2^+$	1.5561×10^{-6}	3.1084×10^{-6}	7.7513×10^{-6}	1.5457×10^{-5}
$\text{Fe}_2(\text{OH})_2^{4+}$	2.7954×10^{-8}	1.0610×10^{-7}	5.8225×10^{-7}	1.9939×10^{-6}
FeSO_4^+	6.7365×10^{-3}	1.3308×10^{-2}	3.2227×10^{-2}	6.1920×10^{-2}
$\text{Fe}(\text{SO}_4)_2^-$	3.1811×10^{-3}	6.5335×10^{-3}	1.7410×10^{-2}	3.7428×10^{-2}
FeHSO_4^{2+}	2.1914×10^{-5}	4.2221×10^{-5}	9.6055×10^{-5}	1.7127×10^{-4}
Fe^{2+}	2.2373×10^{-2}	2.1710×10^{-2}	2.0142×10^{-2}	1.8410×10^{-2}
FeSO_4^0	7.6533×10^{-2}	7.7213×10^{-2}	7.8826×10^{-2}	8.0611×10^{-2}

^a m_i = moles l/kg solution.

Table 7. (continued)

	0.005 m $\text{Fe}_2(\text{SO}_4)_3$	0.01 m $\text{Fe}_2(\text{SO}_4)_3$	0.025 m $\text{Fe}_2(\text{SO}_4)_3$	0.05 m $\text{Fe}_2(\text{SO}_4)_3$
FeHSO_4^+	1.0939×10^{-3}	1.0764×10^{-3}	1.0323×10^{-3}	9.7966×10^{-4}
Cu^{2+}	1.6821×10^{-4}	1.6283×10^{-4}	1.5021×10^{-4}	1.3643×10^{-4}
CuSO_4^0	8.3179×10^{-4}	8.3717×10^{-4}	8.4979×10^{-4}	8.6357×10^{-4}

Figure 3. Equilibrium concentrations of Fe^{3+} , FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}_2(\text{OH})_2^{4+}$ using ideal solution equilibrium constants.

Figure 4. Equilibrium concentrations of Fe^{3+} , FeSO_4^+ , $\text{Fe}(\text{SO}_4)_2^-$ and FeHSO_4^{2+} using ideal solution equilibrium constants.

Concentrations of the Fe(II) species shift with increasing $\text{Fe}_2(\text{SO}_4)_3$ concentration so that the amount of FeSO_4^0 increases while the amounts of Fe^{2+} and FeHSO_4^+ drop; the order of these concentrations, $\text{FeSO}_4^0 > \text{Fe}^{2+} > \text{FeHSO}_4^+$, is maintained.

CuSO_4^0 is the more important Cu(II) species; its concentration increased as $C_{\text{Fe}_2(\text{SO}_4)_3}$ rose while that of Cu^{2+} declined.

The dominant Fe(III) species are FeSO_4^+ and $\text{Fe}(\text{SO}_4)_2^-$. At 0.005 m $\text{Fe}_2(\text{SO}_4)_3$, 67% of the total Fe(III) concentration is present as FeSO_4^+ and 32% as $\text{Fe}(\text{SO}_4)_2^-$; at 0.05 m $\text{Fe}_2(\text{SO}_4)_3$, these fractions are 62 and 37%, respectively. The order of the Fe(III) concentrations remains $\text{FeSO}_4^+ > \text{Fe}(\text{SO}_4)_2^- > \text{FeOH}^{2+} > \text{Fe}^{3+} > \text{FeHSO}_4^{2+} > \text{Fe}(\text{OH})_2^+ > \text{Fe}_2(\text{OH})_2^{4+}$.

The situation in high ionic strength solutions differs significantly and has been studied in more detail because high ionic strength is more characteristic of the liquors used in metallurgical processes. Equilibrium concentrations calculated using apparent equilibrium constants at $I = 3$ are given in Tables 8-10. Figures 5 and 6 show the distribution of Fe(III) species.

In 0.1 m FeSO_4 , 0.001 m CuSO_4 and 0.01 m H_2SO_4 , increasing the $\text{Fe}_2(\text{SO}_4)_3$ concentration from 0.005 to 0.05 m resulted in a slightly decreased H^+ concentration. The sulfate ion concentration increased 36% and the bisulfate ion concentration increased 30%. These increases, especially the second, are more dramatic than when the $I = 0$ constants are used.

Table 8. Equilibrium concentrations in solutions of 0.01 m $\text{Fe}_2(\text{SO}_4)_3$, 0.001 m CuSO_4 , 0.01 m H_2SO_4 and FeSO_4 at $I = 3^a$

	0.1 m FeSO_4	0.2 m FeSO_4
H^+	1.0686×10^{-2}	7.6262×10^{-3}
OH^-	6.1966×10^{-13}	8.6832×10^{-13}
SO_4^{2-}	9.4966×10^{-2}	1.5747×10^{-1}
HSO_4^-	8.2508×10^{-3}	9.7633×10^{-3}
Fe^{3+}	1.9162×10^{-3}	1.1208×10^{-3}
FeOH^{2+}	1.9186×10^{-4}	1.5726×10^{-4}
$\text{Fe}(\text{OH})_2^+$	9.2117×10^{-6}	1.0580×10^{-5}
$\text{Fe}_2(\text{OH})_2^{4+}$	5.5588×10^{-5}	3.7344×10^{-5}
FeSO_4^+	1.5487×10^{-2}	1.5021×10^{-2}
$\text{Fe}(\text{SO}_4)_2^-$	2.2210×10^{-3}	3.5719×10^{-3}
FeHSO_4^{2+}	6.3241×10^{-5}	4.3772×10^{-5}
Fe^{2+}	8.2532×10^{-2}	1.4888×10^{-1}
FeSO_4^0	1.6147×10^{-2}	4.8299×10^{-2}
FeHSO_4^+	1.3210×10^{-3}	2.8198×10^{-3}
Cu^{2+}	6.7761×10^{-4}	5.5900×10^{-4}
CuSO_4^0	3.2239×10^{-4}	4.4100×10^{-4}

a_{m_i} = moles i/kg solution.

Table 9. Equilibrium concentrations in solutions at 0.005 m $\text{Fe}_2(\text{SO}_4)_3$, 0.001 m CuSO_4 , FeSO_4 and H_2SO_4 at $I = 3^a$

	0.01 m H_2SO_4 0.1 m FeSO_4	0.01 m H_2SO_4 0.2 m FeSO_4	0.005 m H_2SO_4 0.1 m FeSO_4
H^+	1.0820×10^{-2}	7.6667×10^{-3}	5.5601×10^{-3}
OH^-	6.1201×10^{-13}	8.6374×10^{-13}	1.1910×10^{-12}
SO_4^{2-}	9.0902×10^{-2}	1.5446×10^{-1}	9.0572×10^{-2}
HSO_4^-	7.9965×10^{-3}	9.6274×10^{-3}	4.0942×10^{-3}
Fe^{3+}	1.0037×10^{-3}	5.7364×10^{-4}	9.9011×10^{-4}
FeOH^{2+}	9.9249×10^{-5}	8.0058×10^{-5}	1.9054×10^{-4}
$\text{Fe}(\text{OH})_2^+$	4.7064×10^{-6}	5.3578×10^{-6}	1.7583×10^{-5}
$\text{Fe}_2(\text{OH})_2^{4+}$	1.4875×10^{-5}	9.6788×10^{-6}	5.4824×10^{-5}
FeSO_4^+	7.7647×10^{-3}	7.5406×10^{-3}	7.6320×10^{-3}
$\text{Fe}(\text{SO}_4)_2^-$	1.0659×10^{-3}	1.7589×10^{-3}	1.0439×10^{-3}
FeHSO_4^{2+}	3.2103×10^{-5}	2.2091×10^{-5}	1.6215×10^{-5}
Fe^{2+}	8.3140×10^{-2}	1.4960×10^{-1}	8.3715×10^{-2}
FeSO_4^0	1.5570×10^{-2}	4.7604×10^{-2}	1.5621×10^{-2}
FeHSO_4^+	1.2897×10^{-3}	2.7939×10^{-3}	6.6488×10^{-4}
Cu^{2+}	6.8709×10^{-4}	5.6395×10^{-4}	6.8787×10^{-4}
CuSO_4^0	3.1291×10^{-4}	4.3625×10^{-4}	3.1213×10^{-4}

^a m_i = moles i/kg solution.

Table 10. Equilibrium concentrations in solutions of 0.001 m CuSO_4 , 0.01 m H_2SO_4 , $\text{Fe}_2(\text{SO}_4)_3$ and FeSO_4 at $I = 3^a$

	0.025 m $\text{Fe}_2(\text{SO}_4)_3$ 0.1 m FeSO_4	0.05 m $\text{Fe}_2(\text{SO}_4)_3$ 0.1 m FeSO_4	0.025 m $\text{Fe}_2(\text{SO}_4)_3$ 0.2 m FeSO_4
H^+	1.0436×10^{-2}	1.0274×10^{-2}	7.5753×10^{-3}
OH^-	6.3451×10^{-13}	6.4455×10^{-13}	8.7416×10^{-13}
SO_4^{2-}	1.0653×10^{-1}	1.2408×10^{-1}	1.6623×10^{-1}
HSO_4^-	9.0394×10^{-3}	1.0364×10^{-2}	1.0238×10^{-2}
Fe^{3+}	4.2360×10^{-3}	7.1812×10^{-3}	2.6249×10^{-3}
FeOH^{2+}	4.3428×10^{-4}	7.4789×10^{-4}	3.7075×10^{-4}
$\text{Fe}(\text{OH})_2^+$	2.1350×10^{-5}	3.7350×10^{-5}	2.5111×10^{-5}
$\text{Fe}_2(\text{OH})_2^{4+}$	2.8481×10^{-4}	8.4468×10^{-4}	2.0758×10^{-4}
FeSO_4^+	3.8407×10^{-2}	7.5836×10^{-2}	3.7135×10^{-2}
$\text{Fe}(\text{SO}_4)_2^-$	6.1789×10^{-3}	1.4210×10^{-2}	9.3218×10^{-3}
FeHSO_4^{2+}	1.5316×10^{-4}	2.9772×10^{-4}	1.0749×10^{-4}
Fe^{2+}	8.0840×10^{-2}	7.8386×10^{-2}	1.4681×10^{-1}
FeSO_4^0	1.7743×10^{-2}	2.0038×10^{-2}	5.0276×10^{-2}
FeHSO_4^+	1.4175×10^{-3}	1.5760×10^{-3}	2.9156×10^{-3}
Cu^{2+}	6.5200×10^{-4}	6.1665×10^{-4}	5.4561×10^{-4}
CuSO_4^0	3.4800×10^{-4}	3.8335×10^{-4}	4.5439×10^{-4}

^a m_i = moles i/kg solution.

Figure 5. Equilibrium concentrations of Fe^{3+} , FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}_2(\text{OH})_2^{4+}$ using apparent equilibrium constants at high ionic strength $C_{\text{FeSO}_4} = 0.1$ m.

Figure 6. Equilibrium concentrations of Fe^{3+} , FeSO_4^+ , $\text{Fe}(\text{SO}_4)_2^-$ and FeHSO_4^{2+} using apparent equilibrium constants at high ionic strength $C_{\text{FeSO}_4} = 0.1$ m.

The Fe(II) concentrations decrease in the order $\text{Fe}^{2+} > \text{FeSO}_4^0 > \text{FeHSO}_4^+$. The complex ions become more important at higher values of $C_{\text{Fe}_2(\text{SO}_4)_3}$. Also in contrast to the situation at low ionic strength, Cu^{2+} is the dominant Cu(II) species at $I = 3$. It becomes slightly less important as the $\text{Fe}_2(\text{SO}_4)_3$ concentration increases.

As indicated in Figures 5 and 6, at 0.05 m $\text{Fe}_2(\text{SO}_4)_3$ the Fe(III) concentrations decrease in the order $\text{FeSO}_4^+ > \text{Fe}(\text{SO}_4)_2^- > \text{Fe}^{3+} > \text{Fe}_2(\text{OH})_2^{4+} > \text{FeOH}^{2+} > \text{FeHSO}_4^{2+} > \text{Fe}(\text{OH})_2^+$ while at 0.005 m the order changes to $\text{FeSO}_4^+ > \text{Fe}(\text{SO}_4)_2^- > \text{Fe}^{3+} > \text{FeOH}^{2+} > \text{FeHSO}_4^{2+} > \text{Fe}_2(\text{OH})_2^{4+} > \text{Fe}(\text{OH})_2^+$. In the former case, 76% of the Fe(III) is present as FeSO_4^+ , 14% as $\text{Fe}(\text{SO}_4)_2^-$ and 7% as Fe^{3+} ; in the latter, 77% is FeSO_4^+ , 11% $\text{Fe}(\text{SO}_4)_2^-$ and 10% Fe^{3+} .

The dominant sulfate-containing species at 0.005 m $\text{Fe}_2(\text{SO}_4)_3$ are SO_4^{2-} (14% of the total sulfate concentration) and FeSO_4^0 (12%). At 0.05 m $\text{Fe}_2(\text{SO}_4)_3$, 48% is in the form of SO_4^{2-} , 29% FeSO_4^+ and 8% FeSO_4^0 .

Increasing the FeSO_4 concentration to 0.2 m causes striking effects.

At 0.05 m $\text{Fe}_2(\text{SO}_4)_3$, 0.2 m FeSO_4 , 0.001 m CuSO_4 and 0.01 m H_2SO_4 , the solubility product of amorphous $\text{Fe}(\text{OH})_3$ is exceeded and precipitation occurs. This is discussed further below.

At 0.025 m $\text{Fe}_2(\text{SO}_4)_3$, the H^+ concentration drops 27% when C_{FeSO_4} increases from 0.1 to 0.2 m. At the same time, the SO_4^{2-} concentration increases 56% and the HSO_4^- concentration increases 13%.

Concentrations of all the Fe(II) species increase; Fe^{2+} by 81%, FeSO_4^0 by 183% and FeHSO_4^+ by 106%. The concentration of CuSO_4^0 increases

to take up some of the additional sulfate and the concentration of Cu^{2+} drops.

Of the Fe(III) species, Fe^{3+} , FeOH^{2+} , $\text{Fe}_2(\text{OH})_2^{4+}$, FeSO_4^+ and FeHSO_4^{2+} show decreased concentrations. The concentrations of $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}(\text{SO}_4)_2^-$ rise.

The same trends are observed at 0.01 and 0.005 m $\text{Fe}_2(\text{SO}_4)_3$.

The concentration distributions of the trivalent iron species at analytical concentrations of 0.01 m H_2SO_4 , 0.2 m FeSO_4 and 0.001 m CuSO_4 are shown in Figures 7 and 8. Excepting the different horizontal scales, these curves look very similar to those of Figures 5 and 6. The only difference is that at 0.2 m FeSO_4 , the curve for FeSO_4^+ apparently does not cross that for Fe^{3+} at low ferric sulfate concentrations.

Precipitation of amorphous $\text{Fe}(\text{OH})_3$ occurs when the analytical concentration of sulfuric acid is dropped to 0.005 m unless the concentration of $\text{Fe}_2(\text{SO}_4)_3$ is also very low.

In 0.005 m $\text{Fe}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 and 0.001 m CuSO_4 , decreasing the H_2SO_4 concentration from 0.01 to 0.005 m results in a 49% drop in the H^+ concentration. The SO_4^{2-} concentration remains almost the same, decreasing only 0.4% while HSO_4^- is down 49%.

The concentrations of Fe^{2+} and FeSO_4 increase slightly while that of FeHSO_4^+ drops 48%. Cu^{2+} and CuSO_4 show virtually no change.

Among the Fe(III) species, Fe^{3+} , FeSO_4^+ , $\text{Fe}(\text{SO}_4)_2^-$ and FeHSO_4^{2+} decline 1, 2, 2 and 49% while FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}_2(\text{OH})_2^{4+}$ rise 91, 274 and 269%. These concentrations decrease in the order $\text{FeSO}_4^+ > \text{Fe}(\text{SO}_4)_2^- > \text{Fe}^{3+} > \text{FeOH}^{2+} > \text{FeHSO}_4^{2+} > \text{Fe}_2(\text{OH})_2^{4+} > \text{Fe}(\text{OH})_2^+$ at

Figure 7. Equilibrium concentrations of Fe^{3+} , FeSO_4^+ , $\text{Fe}(\text{SO}_4)_2^-$ and FeHSO_4^{2+} using apparent equilibrium constants at high ionic strength $C_{\text{FeSO}_4} = 0.2$ m.

Figure 8. Equilibrium concentrations of Fe³⁺, FeSO₄⁺, Fe(SO₄)₂⁻ and FeHSO₄²⁺ using apparent equilibrium constants at high ionic strength $C_{\text{FeSO}_4} = 0.2$ m.

0.01 m H_2SO_4 while at 0.005 m H_2SO_4 the end of the sequence is $\text{Fe}_2(\text{OH})_2^{4+} > \text{Fe}(\text{OH})_2^+ > \text{FeHSO}_4^{2+}$.

It is evident that at high ionic strength a lower fraction of each of the metallic species (Fe(III) , Fe(II) and Cu(II)) is present in the form of complexes. The effect is particularly notable for Fe(II) and Cu(II) but is also important for Fe(III) .

This suggests that reduction of the trivalent iron might well be faster at high ionic strength. With Fe^{3+} a greater fraction of the total Fe(III) concentration, the reaction rate could be enhanced because Fe^{3+} could react without the steric hindrance of an attached ligand and there would be no ligand to be simultaneously or subsequently stripped off.

In order to prevent precipitation and supply H^+ for the dissolution of CuFeS_2 , a low pH should be maintained. With corresponding analytical concentrations, the H^+ concentration is approximately twice as high at $I = 3$ as at $I = 0$. At $I = 3$, it is about 30% higher at 0.1 than at 0.2 m FeSO_4 but decreases only slightly with a tenfold increase in $C_{\text{Fe}_2(\text{EO}_4)_3}$ from 0.005 to 0.05 m.

B. Precipitation of Fe^{3+} as $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ and $\alpha\text{-FeOOH}$

In studying the conditions under which Fe^{3+} precipitates from leach liquor, all the solution chemistry must be considered. There is no single concentration that, by itself, indicates whether precipitation will occur.

For amorphous $\text{Fe}(\text{OH})_3$, the concentrations of Fe^{3+} and OH^- determine whether the solid forms. For jarosite, the situation is more complex; the potassium concentration must be known but is essentially independent of the other concentrations in leach solution since potassium ion is neither a reactant nor a product in copper dissolution and does not form strong complexes. In the computations reported here, it has been treated as a separate parameter.

At an ionic strength of 0.0 m, the minimum potassium ion concentration that causes jarosite to precipitate increases from 2.4×10^{-10} m at 0.05 m $\text{Fe}_2(\text{SO}_4)_3$ to 1.5×10^{-6} m at 0.005 m $\text{Fe}_2(\text{SO}_4)_3$. This is shown in Figure 9 and Table 11. Changing the equilibrium constants in the calculation to those prevailing at $I = 3$ leads to a considerable drop in the K concentration needed for jarosite precipitation, as can be seen in Table 11. The minimum m_{K^+} values needed for jarosite formation at high ionic strength range from 8.1×10^{-13} at 0.05 m $\text{Fe}_2(\text{SO}_4)_3$ to 7.6×10^{-10} at 0.005 m $\text{Fe}_2(\text{SO}_4)_3$. All these computations were performed with H_2SO_4 , FeSO_4 and CuSO_4 concentrations of 0.01, 0.1 and 0.001 m, respectively.

At the higher ionic strength, increasing the analytical concentration of FeSO_4 from 0.1 to 0.2 m causes the K^+ concentration necessary for $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ formation to decline by a factor of about 4, as may be seen in Figure 10. Examination of data in Table 11 indicates that decreasing the H_2SO_4 concentration from 0.01 to 0.005 m leads this concentration to drop more sharply, by a factor of 50.

Figure 9. Minimum potassium ion concentration necessary to precipitate jarosite. Ideal solution equilibrium constants used.

Table 11. Minimum K^+ concentration to precipitate $KFe_3(SO_4)_2(OH)_6$ ^a

I = 0:

$C_{H_2SO_4}, m$	C_{FeSO_4}, m	C_{CuSO_4}, m	$C_{Fe_2(SO_4)_2}, m$	C_{K^+}, m
0.01	0.1	0.001	0.050	9.6286×10^{-10}
0.01	0.1	0.001	0.025	9.5582×10^{-9}
0.01	0.1	0.001	0.010	1.7945×10^{-7}
0.01	0.1	0.001	0.005	1.5461×10^{-6}

I = 3:

$C_{H_2SO_4}, m$	C_{FeSO_4}, m	C_{CuSO_4}, m	$C_{Fe_2(SO_4)_3}, m$	C_{K^+}, m
0.01	0.1	0.001	0.050	8.1303×10^{-13}
0.01	0.1	0.001	0.025	5.9049×10^{-12}
0.01	0.1	0.001	0.010	9.2526×10^{-11}
0.01	0.1	0.001	0.005	7.5721×10^{-10}
0.01	0.2	0.001	0.050	2.2071×10^{-13}
0.01	0.2	0.001	0.025	1.4907×10^{-12}
0.01	0.2	0.001	0.010	2.2212×10^{-11}
0.01	0.2	0.001	0.005	1.7776×10^{-10}
0.009	0.1	0.001	0.005	1.4627×10^{-11}

^a C_i = analytical concentration of i, moles i/kg solution.

Figure 10. Minimum potassium ion concentration necessary to precipitate jarosite, showing effect of $FeSO_4$ concentration. High ionic strength apparent equilibrium constants used.

Under all the conditions investigated, the equilibrium constant for α -FeOOH is exceeded. As discussed earlier, however, this substance does not form directly by precipitation from solution but instead is produced by aging of amorphous $\text{Fe}(\text{OH})_3$. The parent material has a solubility product constant several orders of magnitude larger than the constant for goethite. Solutions in which $m_{\text{Fe}^{3+}} m_{\text{OH}^-}^3$ lies between the two constants are solutions in which goethite formation is favored thermodynamically but does not occur because of the lack of a suitable kinetic pathway.

Values of the product $m_{\text{Fe}^{3+}} m_{\text{OH}^-}^3$ are given in Table 12 for a variety of initial analytical concentrations and for ionic strengths of 0 and 3 m.

Figure 11 shows $m_{\text{Fe}^{3+}} m_{\text{OH}^-}^3$ as a function of $C_{\text{Fe}_2(\text{SO}_4)_3}$ for the same FeSO_4 , CuSO_4 and H_2SO_4 concentrations when both the $I = 0$ and $I = 3$ equilibrium constants are used. The curves are quite close together but at $I = 3$ m the K_{Sp} of amorphous $\text{Fe}(\text{OH})_3$ is almost twice as high. Precipitation therefore occurs more readily at low ionic strength.

At the higher ionic strength, the value of the product $m_{\text{Fe}^{3+}} m_{\text{OH}^-}^3$ was determined for a variety of analytical concentrations. The data are plotted in Figure 12. Increasing the FeSO_4 concentration from 0.1 to 0.2 m increases the product somewhat but decreasing the amount of sulfuric acid from 0.01 to 0.005 m has a more striking effect. In a solution that is 0.005 m in H_2SO_4 , 0.1 m in FeSO_4 and 0.001 m in

Table 12. Value of $m_{\text{Fe}^{3+}} m_{\text{OH}^-}^3$ ^a

I = 0:

$C_{\text{H}_2\text{SO}_4}, m$	C_{FeSO_4}, m	C_{CuSO_4}, m	$C_{\text{Fe}_2(\text{SO}_4)_3}, m$	$m_{\text{Fe}^{3+}} m_{\text{OH}^-}^3$
0.01	0.1	0.001	0.050	1.5085×10^{-39}
0.01	0.1	0.001	0.025	7.0201×10^{-40}
0.01	0.1	0.001	0.010	2.6448×10^{-40}
0.01	0.1	0.001	0.005	1.2913×10^{-40}

I = 3:

$C_{\text{H}_2\text{SO}_4}, m$	C_{FeSO_4}, m	C_{CuSO_4}, m	$C_{\text{Fe}_2(\text{SO}_4)_3}, m$	$m_{\text{Fe}^{3+}} m_{\text{OH}^-}^3$
0.01	0.1	0.001	0.050	1.9229×10^{-39}
0.01	0.1	0.001	0.025	1.0821×10^{-39}
0.01	0.1	0.001	0.010	4.5594×10^{-40}
0.01	0.1	0.001	0.005	2.3007×10^{-40}
0.01	0.2	0.001	0.050	3.1217×10^{-39}
0.01	0.2	0.001	0.025	1.7534×10^{-39}
0.01	0.2	0.001	0.010	7.3380×10^{-40}
0.01	0.2	0.001	0.005	3.6965×10^{-40}
0.005	0.1	0.001	0.050	6.4984×10^{-39}
0.005	0.1	0.001	0.025	5.1788×10^{-39}
0.005	0.1	0.001	0.010	2.9773×10^{-39}
0.005	0.1	0.001	0.005	1.6727×10^{-39}

^a C_1 = analytical concentration of i, moles i/kg solution.

Figure 11. Value of $m_{\text{Fe}^{3+}} m_{\text{OH}^-}^3$ using both ideal and apparent equilibrium constants.

Figure 12. Value of $m_{Fe^{3+}} m_{OH^-}^3$ showing effect of FeSO₄ and H₂SO₄ concentrations. High ionic strength apparent equilibrium constants used.

CuSO_4 , ferric hydroxide forms when there is only 0.008 m $\text{Fe}_2(\text{SO}_4)_3$ present. With 0.01 m H_2SO_4 , 0.2 m FeSO_4 and 0.001 m CuSO_4 , precipitation occurs at 0.037 m $\text{Fe}_2(\text{SO}_4)_3$; changing the FeSO_4 concentration to 0.1 m causes the $\text{Fe}_2(\text{SO}_4)_3$ concentration needed for precipitation to rise to about 0.061 m.

The potassium concentrations that will lead to precipitation of jarosite from leach liquor are clearly very small and might well be exceeded under conditions of dump operation. This problem can be minimized by maintaining the solution's ionic strength at a low rather than a high value and using low concentrations of ferric sulfate. To a lesser extent, it is also helpful to maintain low ferrous sulfate concentrations and high sulfuric acid concentrations.

To prevent formation of $\text{Fe}(\text{OH})_3$ and $\alpha\text{-FeOOH}$, it is desirable to maintain a high ionic strength, use high sulfuric acid concentrations, low FeSO_4 concentrations and low $\text{Fe}_2(\text{SO}_4)_3$ concentrations.

The recommended choice of ionic strength to prevent precipitation is in conflict for jarosite and $\text{Fe}(\text{OH})_3$. Knowledge of the concentration of K^+ or other univalent cations in leach liquor would make it possible to assess the likelihood of jarosite precipitation and make the best choice between these two alternatives. No operational data are available, however.

C. Concentration Changes During the Dissolution Process

The computations discussed in this section were performed at intervals in n_{O_2} of 0.1. This corresponds physically to 10% intervals in the fraction of copper dissolved by reaction with O_2 and protons; n_{O_2} has been defined as a negative number because O_2 is a reactant. The K^+ concentration was taken to be sufficiently low that $KFe_3(SO_4)_2(OH)_6$ would not precipitate at any time during the dissolution. Data from the computer runs are given in Appendix B.

Availability of O_2 was assumed to be unrestricted, i.e., a finite steady state dissolved oxygen concentration was assumed.

With these assumptions, the dissolution process can be halted in two ways: $Fe(OH)_3$ may eventually precipitate as the concentrations change or Fe(III) may be depleted. In this computation, Fe(III) was taken to be depleted when the total concentration of trivalent iron dropped to 10^{-4} m. The choice of this value is somewhat arbitrary but it should be set well above the point at which the concentrations of the dominant Fe(III) species begin to be unreliable.

The final concentration of Cu(II) achieved in a closed system containing chalcopyrite and leach liquor is governed by the solution phase reactants Fe(III), H^+ and O_2 .

Figure 13 shows the effect of the initial analytical ferric sulfate concentration and the fraction of the copper dissolution due to O_2 on the final total copper extraction. As would be expected Cu recovery at first increases with increased $|n_{O_2}|$ at initial $Fe_2(SO_4)_3$ concentrations of 0.025, 0.010 and 0.005 m but the gradual increase

Figure 13. Final Cu(II) concentration as a function of n_{O_2} for various initial $Fe_2(SO_4)_3$ concentrations. $C_{FeSO_4} = 0.1$ m.

is abruptly terminated by a sharp dropoff. This is due to precipitation of amorphous $\text{Fe}(\text{OH})_3$. With increased $|n_{\text{O}_2}|$, more acid is consumed, the OH^- concentration rises and ferric hydroxide precipitates. If the fraction of copper dissolved by O_2 is too large, precipitation is essentially immediate. This happens at high ferric sulfate concentrations and high pH values although the exact conditions for precipitation depend on all the initial analytical concentrations. With 0.05 m $\text{Fe}_2(\text{SO}_4)_3$, precipitation already occurs at an n_{O_2} value of -0.1. Additional oxygen can increase copper leaching only to a limited extent. At 0.025 m $\text{Fe}_2(\text{SO}_4)_3$, the maximum in the curve is 0.003 m above the value at $n_{\text{O}_2} = -0.0$; at 0.005 m $\text{Fe}_2(\text{SO}_4)_3$, this distance is 0.00375 m. The difference is insignificant compared to the effect of initial $\text{Fe}(\text{III})$ level on the final copper concentration, yet at the higher ferric sulfate concentration, $|n_{\text{O}_2}|$ has to be much lower to avoid precipitation. To dissolve the greatest amount of copper, therefore, it is best to use a high $\text{Fe}_2(\text{SO}_4)_3$ concentration and a very low level of oxygen. With a high ferric sulfate concentration, moreover, the amount of oxygen reacting must be controlled within narrow limits or precipitation will take place before the maximum possible copper recovery is approached.

Changes in pH during dissolution are of interest because pH is monitored and adjusted during dump leaching processes and, other concentrations being equal, precipitation of both ferric hydroxide and jarosite occurs as the solution pH rises. In Figures 14-16 are plotted the pH at $\text{Fe}(\text{III})$ depletion vs. the fraction of copper

Figure 14. pH at depletion of Fe(III) when $C_{\text{FeSO}_4} = 0.1 \text{ m}$.

Figure 15. pH at depletion of Fe(III) when $C_{FeSO_4} = 0.2$ m.

Figure 16. pH at depletion of Fe(III). Shows effect of initial H_2SO_4 concentration.

dissolved by the acid consuming reaction with oxygen. Trivalent iron was taken to be depleted when its concentration had fallen to 10^{-4} m. These graphs give some indication of how sharply the pH changes as a function of the initial concentrations and n_{O_2} . Were the curves to be extended to the right by 0.1 unit, precipitation would take place immediately.

Figure 14 shows the dependence of the final pH on $|n_{O_2}|$ at analytical concentrations of 0.01 m for H_2SO_4 , 0.1 m for $FeSO_4$, 0.001 m for $CuSO_4$ and three different $Fe_2(SO_4)_3$ concentrations. Without any H^+ consumed in dissolving chalcopyrite ($n_{O_2} = -0.0$), the terminal pH values are close together. At higher $|n_{O_2}|$ values, the curves begin to spread apart, rising most steeply for the highest value of $C_{Fe_2(SO_4)_3}$ shown, 0.025 m. The highest final pH value is attained for the lowest initial ferric sulfate concentration, 0.005 m.

Figure 15 shows the effect of changing the ferrous sulfate concentration to 0.2 m. At high values of C_{FeSO_4} , the range of n_{O_2} values that can be used without $Fe(OH)$ precipitation is reduced and this effect is more pronounced at high ferric sulfate concentrations.

Figure 16 shows that reducing the H_2SO_4 concentration has the same type of effect that increasing the $FeSO_4$ concentration had in Figure 15. At the lower $C_{H_2SO_4}$ value, 0.005 m, the curve is higher and terminates at $|n_{O_2}| = 0.3$ rather than 0.6 as when $C_{H_2SO_4}$ is 0.01 m. Lowering the initial acid concentration therefore decreases the range

over which $C_{\text{Fe}_2(\text{SO}_4)_3}$ and n_{O_2} may be varied without having $\text{Fe}(\text{OH})_3$ precipitate.

The effect of initial H_2SO_4 concentration on copper recovery at 0.005 m initial ferric sulfate is shown in Figure 17. Doubling the initial H_2SO_4 concentration from 0.005 to 0.010 m results in almost a 60% increase in the maximum final copper concentration. The two curves are almost the same but that for the low starting acid concentration drops off between $n_{\text{O}_2} = -0.3$ and -0.4 while the other continues to rise through $n_{\text{O}_2} = -0.6$. A high initial level of acid plays a dual role: it provides a high reactant concentration for the oxygen-acid dissolution reaction and it forestalls precipitation.

Figure 18 is the same type of curve as the one preceding it but is for an initial ferrous sulfate concentration of 0.2 m. An initial $\text{Fe}_2(\text{SO}_4)_3$ concentration of 0.05 m leads to immediate precipitation and at lower ferric sulfate levels the maximum copper concentration is lower than in the corresponding cases shown in Figure 13. A high ferrous sulfate concentration therefore affects the complexation equilibria in such a way that precipitation occurs sooner in the leaching process than it otherwise would.

Figures 19-23 illustrate how the concentrations of the $\text{Fe}(\text{III})$ species change during chalcopyrite dissolution. Figures 19 and 20 show the effect of an increase in the fraction of copper dissolution due to the oxygen-acid reaction. With iron the only oxidant reacting (Figure 15), all the $\text{Fe}(\text{III})$ concentrations decline smoothly and the curves retain their relative spacing. When, as in Figure 20, 20% of

Figure 17. Final $Cu(II)$ concentration. Shows effect of initial H_2SO_4 concentration.

Figure 18. Final $Cu(II)$ concentration, $C_{FeSO_4} = 0.2$ m.

Figure 19. Concentration changes for Fe(III) species during CuFeS_2 leaching. $n_{\text{O}_2} = -0.0$. Initial $\text{Fe}_2(\text{SO}_4)_3$ concentration 0.025 m.

Figure 20. Concentration changes for Fe(III) species during CuFeS_2 leaching. $n_{\text{O}_2} = -0.2$. Initial $\text{Fe}_2(\text{SO}_4)_3$ concentration 0.025 m.

Figure 21. Concentration changes for Fe(III) species during CuFeS_2 leaching. $n_{\text{O}_2} = -0.0$. Initial $\text{Fe}_2(\text{SO}_4)_3$ concentration 0.01 m.

Figure 22. Concentration changes for Fe(III) species during CuFeS_2 leaching. $n_{\text{O}_2} = -0.2$. Initial $\text{Fe}_2(\text{SO}_4)_3$ concentration 0.01 m.

Figure 23. Concentration changes for Fe(III) species during CuFeS_2 leaching. $n_{\text{O}_2} = -0.4$. Initial $\text{Fe}_2(\text{SO}_4)_3$ concentration 0.01 m.

the copper is dissolved by oxygen and acid, the curves for Fe^{3+} , FeSO_4^+ and $\text{Fe}(\text{SO}_4)_2^-$ could essentially be superimposed on the corresponding curves in Figure 19. However, the curve for FeOH^{2+} does not decline as sharply in Figure 20 and the $\text{Fe}(\text{OH})_2^+$ concentration actually rises slightly before dropping. Two competing effects are at work here; with both irreversible chalcopyrite dissolution reactions underway, both $\text{Fe}(\text{III})$ and H^+ are consumed. The equilibria for the ololation reactions shift to maintain equilibrium among Fe^{3+} , FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$ and H^+ . The concentrations of Fe^{3+} and H^+ cannot both be raised (or both lowered) by a change in the amount of FeOH^{2+} , however, because they are on opposite sides of the chemical equation. An analogous statement may be made about FeOH^{2+} , H^+ and $\text{Fe}(\text{OH})_2^+$. The FeHSO_4^{2+} curve drops much more sharply in Figure 20 than in Figure 19. When H^+ is consumed in copper leaching, it is partially replenished by dissociation of HSO_4^- . This further reaction forces the FeHSO_4^{2+} dissociation to shift further in the direction of Fe^{3+} and HSO_4^- than it otherwise would, causing the steep drop in Figure 20. Figures 21, 22 and 23 show similar curves for an initial analytical ferric sulfate concentration of 0.010 m. With no O_2 reacting, the curves in Figure 21 almost match those of Figure 19 but they have been shifted down somewhat. Figure 23 is similar to Figure 20 and Figure 21 is intermediate between Figures 21 and 23. Qualitatively, the changes in the relative concentrations of the $\text{Fe}(\text{III})$ species are the same at different concentrations. The shifts in the distribution of species occur over a smaller range of n_{O_2} values at higher concentrations.

Changes in Fe^{2+} , FeSO_4^0 and FeHSO_4^+ concentrations during dissolution are shown in Figures 21-24. The initial conditions for Figures 24 and 25 are 0.025 m $\text{Fe}_2(\text{SO}_4)_3$, 0.001 m CuSO_4 , 0.01 m H_2SO_4 and 0.1 m FeSO_4 . They are the same for Figures 26 and 27 except that the FeSO_4 concentration increases to 0.2 m. Without any copper dissolution due to oxygen and acid (Figures 24 and 26), the concentrations of all three Fe(II) species increase continuously until the trivalent iron is exhausted. When a fraction of the copper leaching occurs by the $\text{O}_2\text{-H}^+$ reaction, however, FeHSO_4^+ becomes a reactant rather than a product. The need to supply HSO_4^- to maintain the $\text{H}^+ \text{-HSO}_4^-$ equilibrium overcomes the need to form complexes to take up the Fe(II) produced by both of the dissolution reactions. The same changes in the distribution of Fe(II) species in the solution are seen regardless of the initial concentration of FeSO_4 .

As the results above suggest, the $\text{H}^+ \text{-HSO}_4^-$ - bisulfate complex concentration distributions show strong dependencies on initial concentrations and on the fraction of dissolution by O_2 and H^+ .

Starting with 0.025 m $\text{Fe}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 , 0.001 m CuSO_4 and 0.01 m H_2SO_4 , the SO_4^{2-} concentration rises as chalcopyrite dissolves (Figures 28 and 29). Nearly the same final concentration of free sulfate ions is reached regardless of the value of n_{O_2} . If the reaction with Fe(III) is the only dissolution reaction taking place, the H^+ concentration declines slightly and the HSO_4^- concentration rises slightly. These changes are all due to the irreversible consumption of Fe(III) and production of Fe(II) and Cu(II) and the resulting

Figure 24. Concentration changes for Fe(II) species during CuFeS_2 leaching. $n_{\text{O}_2} = -0.0$. Initial $\text{Fe}_2(\text{SO}_4)_3$ concentration 0.025 m; initial FeSO_4 concentration 0.1 m.

Figure 25. Concentration changes for Fe(II) species during CuFeS_2 leaching. $n_{\text{O}_2} = -0.2$. Initial $\text{Fe}_2(\text{SO}_4)_3$ concentration 0.025 m; initial FeSO_4 concentration 0.1 m.

Figure 26. Concentration changes for Fe(II) species during CuFeS_2 leaching. $n_{\text{O}_2} = -0.0$. Initial $\text{Fe}_2(\text{SO}_4)_3$ concentration 0.025 m; initial FeSO_4 concentration 0.1 m.

Figure 27. Concentration changes for Fe(II) species during CuFeS_2 leaching. $n_{\text{O}_2} = -0.1$. Initial $\text{Fe}_2(\text{SO}_4)_3$ concentration 0.025 m; initial FeSO_4 concentration 0.1 m.

Figure 28. Concentration changes for H^+ , SO_4^{2-} and HSO_4^- during CuFeS_2 leaching. $n_{\text{O}_2} = -0.0$.

Figure 29. Concentration changes for H^+ , SO_4^{2-} and HSO_4^- during $CuFeS_2$ leaching. $n_{O_2} = -0.2$.

changes in the amount of sulfate and bisulfate ions complexed by the transition metals. If, as in Figure 29, $|n_{O_2}|$ is 0.2, the SO_4^{2-} concentration increases to almost the same value as in Figure 28 but both the H^+ and HSO_4^- concentrations decline sharply. Initially the H^+ concentration is higher but its decline is steeper and the two curves cross. Bisulfate ion is the major source of protons to replace those consumed in the irreversible dissolution reaction because the dissociation constant for H_2O is so small compared to the other solution phase equilibrium constants and the concentrations of the $Fe^{3+}-OH^-$ complexes are small to begin with. Only a fraction of the H^+ used up in dissolving $CuFeS_2$ is replenished by the HSO_4^- , however. Concentration distributions for H^+ , HSO_4^- , $FeHSO_4^{2+}$ and $FeHSO_4^+$ at an initial $Fe_2(SO_4)_3$ concentration of 0.005 m are shown in Figures 30-33. Figures 30 and 31 have a $C_{H_2SO_4}$ value of 0.01 m while Figures 32 and 33 are for an initial sulfuric acid concentration of 0.005 m. The only major difference between the two pairs of graphs is in the order of the concentrations: $H^+ > HSO_4^- > FeHSO_4^+ > FeHSO_4^{2+}$ at $C_{H_2SO_4} = 0.01$ m, but $FeHSO_4^+ > H^+ > HSO_4^- > FeHSO_4^{2+}$ at $C_{H_2SO_4} = 0.005$ m. With the O_2-H^+ reaction not contributing to chalcopyrite leaching (Figures 30 and 32), the H^+ concentration decreases very slightly, the HSO_4^- level remains effectively unchanged and the $FeHSO_4^+$ concentration rises a little. $FeHSO_4^{2+}$ drops off steeply. This drop is somewhat more abrupt at the lower sulfuric acid concentration. When the fraction of copper

Figure 30. Concentration changes for H^+ , HSO_4^- , FeHSO_4^{2+} and FeHSO_4^+ during CuFeS_2 leaching. $n_{\text{O}_2} = -0.0$. Initial H_2SO_4 concentration 0.01 m.

Figure 31. Concentration changes for H^+ , HSO_4^- , FeHSO_4^{2+} and FeHSO_4^+ during CuFeS_2 leaching. $n_{\text{O}_2} = -0.3$. Initial H_2SO_4 concentration 0.01 m.

Figure 32. Concentration changes for H^+ , HSO_4^- , FeHSO_4^{2+} and FeHSO_4^+ during CuFeS_2 leaching. $n_{\text{O}_2} = -0.0$. Initial H_2SO_4 concentration 0.005 m.

Figure 33. Concentration changes for H^+ , HSO_4^- , FeHSO_4^{2+} and FeHSO_4^+ during CuFeS_2 leaching. $n_{\text{O}_2} = -0.3$. Initial H_2SO_4 concentration 0.005 m.

dissolved by oxygen and acid increases to 30%, concentrations of all four species decline as the copper concentration increases. For H^+ , HSO_4^- and FeHSO_4^+ , the decrease is steeper at the lower initial H_2SO_4 concentration although the final Cu(II) level is the same. The decline in the FeHSO_4^{2+} concentration is also more abrupt at the lower value of $C_{\text{H}_2\text{SO}_4}$ but it is steep in both cases.

V. CONCLUSION

The chemical species that are important in a solution of $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4 , CuSO_4 and H_2SO_4 , such as those used in dump leaching processes, have been identified through a survey of the literature. They include H^+ , SO_4^{2-} , HSO_4^- , Fe^{3+} , FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$, $\text{Fe}_2(\text{OH})_2^{4+}$, FeSO_4^+ , $\text{Fe}(\text{SO}_4)_2^-$, FeHSO_4^{2+} , Fe^{2+} , FeSO_4^0 , FeHSO_4^+ , Cu^{2+} and CuSO_4^0 . The reactions by which CuFeS_2 is dissolved in leach dumps were shown to be not at equilibrium.

A mathematical model was developed to treat systems, such as this one, in which there are irreversible heterogeneous reactions and simultaneous fluid phase reactions always at equilibrium. Applied to chalcopyrite leaching, the model equations include one linear equation for each of the reversible reactions, mass balances for $\text{Fe}(\text{III})$, $\text{Fe}(\text{II})$, $\text{Cu}(\text{II})$ and SO_4^{2-} , a charge balance and a kinetic equation drawn from the experimental data of Baur *et al.* (7). These data indicate that, after a brief interval of surface reaction, the ratio of the amounts of copper leached by O_2 and H^+ and by ferric ion is a constant. Because of the constancy of this ratio, the kinetic equation, like the other model equations, is linear. The set of equations has been solved by Gauss-Jordan elimination.

The initial equilibrium concentrations in the leach liquor were obtained by Newton-Raphson iteration from a nonlinear set of equations consisting of mass action expressions and material and charge balances. Equilibrium constants applicable at both low and high ionic strength

were used. The latter case is more typical of dump leaching. With the same analytical concentrations of $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4 , CuSO_4 and H_2SO_4 , use of high ionic strength apparent equilibrium constants gave greater fractions of the total Fe(III), Fe(II) and Cu(II) concentrations present as free Fe^{3+} , Fe^{2+} and Cu^{2+} . The relative importance of the various species was also altered by changing the equilibrium constants. The equilibrium concentrations of H^+ , SO_4^{2-} , Fe^{3+} , FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$, $\text{Fe}_2(\text{OH})_2^{4+}$, FeSO_4^+ , FeHSO_4^{2+} , Fe^{2+} , FeHSO_4^+ and Cu^{2+} increased when the constants were changed from ideal solution to apparent high ionic strength values. By far the sharpest increase was for $\text{Fe}_2(\text{OH})_2^{4+}$, whose concentration increased by about three orders of magnitude. Concentrations for the other species dropped. The effects of changing the analytical concentrations of $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4 and H_2SO_4 were also investigated.

Precipitation of ferric ion is a major problem in leaching operations and the conditions under which this occurs were investigated. High ionic strength, high FeSO_4 concentration, high $\text{Fe}_2(\text{SO}_4)_3$ concentration and low H_2SO_4 concentration are all factors that tend to lead to precipitation, although the system is a complex one and no single factor can be singled out as an indicator of whether precipitation will occur. Formation of goethite is thermodynamically favored throughout the concentration regime studied, from 0.005 to 0.05 m $\text{Fe}_2(\text{SO}_4)_3$, 0.1 to 0.2 m FeSO_4 , 0.005 to 0.01 m H_2SO_4 and 0.001 m CuSO_4 . Precipitation of amorphous $\text{Fe}(\text{OH})_3$, from which goethite forms by an aging process, is favored by high Fe^{3+}

concentrations and low H^+ concentrations. The mineral jarosite, $KFe_3(SO_4)_2(OH)_6$, forms except when the potassium ion concentration is extremely small.

Several striking effects manifest themselves in the data obtained from solving the model equations for successive dissolution increments. For each set of initial analytical concentrations, runs were made for various values of n_{O_2} , the fraction of copper dissolved by reaction with O_2 and acid. As this fraction was increased, the final Cu(II) recovery gradually rose until precipitation of $Fe(OH)_3$ occurred rather than depletion of Fe(III). For the highest copper recovery, the ferric ion concentration should be high and the dissolved oxygen level low. With both dissolution reactions going on, $FeHSO_4^+$, an Fe(II) species, is consumed. Concentrations of HSO_4^- , $FeHSO_4^{2+}$ and $FeHSO_4^+$ all decline as protons are used up during dissolution; the supply of H^+ is partly, but not completely, made up by shifts in the solution equilibria. This emphasizes that the dissolution reactions and solution chemistry should not be considered apart from one another for they interact in subtle ways.

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VIII. APPENDIX A

Figure A1. Flowchart of the main program in the partial equilibrium calculation.

Figure A2. Flowchart of the subroutine that calculates the initial concentrations.

Figure A3. Flowchart of the subroutine for back-substitution in the Gauss-Jordan elimination.

Figure A4. Flowchart of the subroutine for Gaussian elimination.

IX. APPENDIX B

Table B1. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.05 m $\text{F}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.0

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
10274	124080	10364	78386	20038	1576	617	383
9794	129240	10311	87537	23211	1752	2148	1352
9347	134460	10257	96542	26535	1923	3650	2350
8932	139720	10203	105400	30009	2089	5114	3386
8548	145030	10152	114120	33630	2252	6541	4459
8193	150370	10104	122690	37397	2410	7930	5570
7867	155760	10063	131130	41306	2566	9281	6719
7568	161180	10031	139420	45356	2720	10596	7904
7294	166630	10008	147580	49546	2873	11875	9125
7170	169390	10003	151590	51710	2950	12496	9754
7050	172150	10000	155560	53909	3026	13109	10391
6936	174920	9998	159500	56151	3102	13711	11039
6828	177650	9996	163330	58396	3176	14293	11687

Fe^{3+} m x 10 ⁶	FeOH^{2+} m x 10 ⁶	$\text{Fe}(\text{OH})_2^+$ m x 10 ⁶	$\text{Fe}_2(\text{OH})_2^{4+}$ m x 10 ⁶	FeSO_4^+ m x 10 ⁶	$\text{Fe}(\text{SO}_4)_2^-$ m x 10 ⁶	FeHSO_4^{2+} m x 10 ⁶
7181	748	37	845	75836	14210	298
6155	676	36	682	68154	13362	254
5213	603	33	536	60471	12395	213
4347	530	31	405	52798	11307	177
3552	456	28	292	45141	10097	144
2820	381	24	196	37508	8762	113
2148	305	20	118	29905	7299	86
1530	229	16	59	22340	5707	61
963	152	11	20	14818	3978	38
704	114	9	10	11084	3042	28
457	76	6	3	7366	2071	18
222	38	3	1	3671	1056	9
3	1	0	0	57	17	0

Table B2. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.05 m $\text{Fe}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.1^a

H^+ m x 10 ⁶	SO_4^{2-} m x 10 ⁶	HSO_4^- m x 10 ⁶	Fe^{2+} m x 10 ⁶	FeSO_4^0 m x 10 ⁶	FeHSO_4^+ m x 10 ⁶	Cu^{2+} m x 10 ⁶	CuSO_4^0 m x 10 ⁶
10274	124080	10364	78386	20038	1576	617	383
9438	129060	9937	86821	22998	1681	2149	1351
8641	134090	9486	95137	26097	1765	3651	2349

^a $\text{Fe}(\text{OH})_3$ precipitates.

Table B3. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.025 m $\text{Fe}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.0

H^+ m x 10 ⁶	SO_4^{2-} m x 10 ⁶	HSO_4^- m x 10 ⁶	Fe^{2+} m x 10 ⁶	FeSO_4^0 m x 10 ⁶	FeHSO_4^+ m x 10 ⁶	Cu^{2+} m x 10 ⁶	CuSO_4^0 m x 10 ⁶
10436	106530	9039	80840	17743	1418	652	348
9942	112010	9075	90203	20709	1587	2270	1230
9495	117580	9119	99394	23849	1757	3852	2148
9094	123230	9172	108410	27160	1926	5391	3109
8743	128990	9238	117220	30685	2097	6873	4127
8427	134770	9307	125760	34378	2266	8288	5192

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	$\text{Fe}(\text{OH})_2^+$ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe}(\text{SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
7181	748	37	845	75836	14210	298
6227	709	38	758	68802	13462	246
5349	669	40	672	61784	12614	200

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	$\text{Fe}(\text{OH})_2^+$ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe}(\text{SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
4236	434	21	285	38407	6179	153
3173	346	18	169	30746	5264	115
2221	258	14	83	23052	4208	81
1372	170	10	26	15342	3003	51
639	84	5	4	7644	1596	24
5	1	0	0	59	13	0

Table B4. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.025 m $\text{Fe}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.1

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
10436	106530	9039	80840	17743	1418	652	348
9513	111760	8683	89478	20509	1513	2271	1229
8641	117070	8300	97978	23432	1590	3855	2145
7820	122460	7892	106340	26510	1648	5398	3102
7048	127910	7466	114570	29742	1686	6898	4102
6341	133470	7024	122630	33170	1702	8343	5157
5977	136550	6777	126960	35127	1700	9109	5758

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	$\text{Fe}(\text{OH})_2^+$ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe}(\text{SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
4236	434	21	285	38407	6179	153
3262	373	20	204	31460	5365	112
2386	307	18	132	24512	4435	77
1601	235	16	70	17575	3384	48
900	155	12	23	10660	2203	24
297	61	6	1	3787	840	7
4	1	0	0	59	14	0

Table B5. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.025 m $\text{Fe}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.2

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
10436	106530	9039	80840	17743	1418	652	248
9085	111520	8291	88752	20309	1439	2271	1229
7799	116580	7495	96556	23017	1427	3858	2142
6577	121720	6651	104250	25866	1380	5404	3096
5415	126910	5760	111850	28854	1296	6910	4090
4308	132160	4821	119350	31983	1172	8374	5126
3265	137510	3817	126710	35298	990	9783	6217
3018	138810	3563	128480	36128	937	10116	6489

Table B6. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.025 m $\text{Fe}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.3^a

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
10436	106530	9039	80840	17743	1418	652	348
8656	111270	7900	88026	20109	1365	2272	1228
6970	116100	6704	95128	22604	1268	3860	2140

^a $\text{Fe}(\text{OH})_3$ precipitates.

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	$\text{Fe}(\text{OH})_2^+$ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe}(\text{SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
4236	434	21	285	38407	6179	153
3350	400	22	240	32175	5465	108
2550	361	23	194	25951	4656	72
1829	315	24	144	19751	3749	44
1180	259	24	93	13589	2739	22
601	185	22	40	7483	1622	8
111	53	9	1	1481	343	1
3	2	0	0	46	11	0

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	$\text{Fe}(\text{OH})_2^+$ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe}(\text{SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
4236	434	21	285	38407	6179	153
3439	427	25	275	32889	5566	105
2712	420	29	266	27367	4873	67

Table B7. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.01 m $\text{Fe}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.0

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
10686	94966	8251	82532	16147	1321	678	322
10445	97834	8313	87280	17563	1407	1518	732
10218	100730	8379	91977	19029	1494	2347	1153
10009	103670	8449	96612	20556	1582	3159	1591
9814	106580	8518	101120	22114	1669	3941	2039

Table B8. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.01 m $\text{Fe}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.1

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
10686	94966	8251	82532	16147	1321	678	322
9720	100410	7977	91296	18787	1417	2359	1141
8845	106060	7681	99841	21665	1494	3984	2016
8662	107310	7612	101680	22324	1508	4330	2217

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	$\text{Fe}(\text{OH})_2^+$ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe}(\text{SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
1916	192	9	56	15487	2221	63
1382	143	7	27	11633	1735	46
881	94	5	9	7764	1210	30
423	46	2	1	3882	630	14
6	1	0	0	61	10	0

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	$\text{Fe}(\text{OH})_2^+$ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe}(\text{SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
1916	192	9	56	15487	2221	63
946	112	6	9	8536	1352	29
157	22	1	0	1548	267	5
2	0	0	0	24	4	0

Table B9. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.01 m $\text{Fe}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.2

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
10686	94966	8251	82532	16147	1321	678	322
9236	100120	7579	90564	18594	1342	2360	1140
8552	102760	7217	94517	19897	1336	3182	1568
7887	105430	6844	98438	21239	1323	3992	2008
7257	108100	6461	102260	22615	1298	4773	2457

Table B10. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.01 m $\text{Fe}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.3

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
10686	94966	8251	82532	16147	1321	678	322
8753	99824	7180	89832	18401	1266	2360	1140
6917	104810	6032	97039	20796	1166	4008	1992
5463	109160	4982	103020	22973	1026	5352	2758

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	Fe(OH)_2^+ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe(SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
1916	192	9	56	15487	2221	63
1046	131	8	20	9293	1453	29
669	93	6	9	6191	1006	17
317	51	4	1	3090	529	7
5	1	0	0	48	9	0

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	Fe(OH)_2^+ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe(SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
1916	192	9	56	15487	2221	63
1145	149	9	31	10050	1555	30
469	93	7	7	4617	792	7
7	2	0	0	71	13	0

Table B11. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.01 m $\text{Fe}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.4

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
10686	94966	8251	82532	16147	1321	678	322
8270	99531	6782	89101	18208	1191	2361	1139
5975	104220	5219	95602	20395	1003	4011	1989
3819	109050	3530	102020	22741	734	5610	2890
3145	110620	2951	104070	23529	627	6109	3191

Table B12. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.01 m $\text{Fe}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.5^a

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
10686	94966	8251	82532	16147	1321	678	322
7786	99238	6383	88369	18015	1115	2362	1138
5040	103640	4415	94160	19996	845	4015	1985

^a $\text{Fe}(\text{OH})_3$ precipitates.

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	Fe(OH)_2^+ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe(SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
1916	192	9	56	15487	2221	63
1245	168	10	42	10807	1657	30
648	134	11	25	6131	1018	9
144	62	9	3	1506	274	1
5	3	1	0	58	11	0

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	Fe(OH)_2^+ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe(SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
1916	192	9	56	15487	2221	63
1345	187	11	53	11564	1758	30
828	181	51	49	7631	1238	9

Table B13. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.005 m $\text{Fe}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.0

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
10820	90902	7996	83140	15570	1290	687	313
10701	92363	8037	85525	16267	1333	1113	512
10587	93831	8079	87897	16976	1377	1536	714
10477	95309	8122	90251	17702	1421	1954	922
10373	96747	8163	92518	18419	1464	2354	1127

Table B14. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.005 m $\text{Fe}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.1

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
10820	90902	7996	83140	15570	1290	687	313
10332	93669	7879	87543	16868	1339	1539	711
9869	96489	7756	91887	18229	1384	2375	1125
9777	97066	7730	92763	18513	1392	2543	1211

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	Fe(OH)_2^+ $\text{mm} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe(SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
1004	99	5	15	7765	1066	32
737	74	4	7	5829	817	24
480	49	2	2	3890	558	16
235	24	1	0	1946	286	8
8	1	0	0	61	9	0

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	Fe(OH)_2^+ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe(SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
1004	99	5	15	7765	1066	32
522	56	3	2	4279	620	16
91	11	1	0	778	118	3
8	1	0	0	67	10	0

Table B15. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.005 m $\text{Fe}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.2

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
10820	90902	7996	83140	15570	1290	687	313
10081	93514	7680	87176	16773	1301	1540	710
9369	96170	7348	91168	18028	1303	2378	1122
9034	97471	7182	93087	18655	1301	2778	1327

Table B16. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.005 m $\text{Fe}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.3

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
10820	90902	7996	83140	15570	1290	687	313
9829	93359	7480	86809	16678	1263	1540	710
8865	95849	6946	90452	17822	1226	2383	1117
8086	97971	6479	93467	18821	1182	3074	1471

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	Fe(OH)_2^+ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe(SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
1004	99	5	15	7765	1066	32
574	64	3	4	4663	671	17
182	23	1	0	1554	235	5
6	1	0	0	49	8	0

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	Fe(OH)_2^+ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe(SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
1004	99	5	15	7765	1066	32
625	71	4	6	5048	722	18
272	38	2	0	2328	352	7
6	1	0	0	57	9	0

Table B17. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.005 m $\text{Fe}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.4

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
10820	90902	7996	83140	15570	1290	687	313
8337	95507	6566	89743	17595	1161	2394	1106
6803	98669	5544	94013	19036	1029	3483	1658

Table B18. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.005 m $\text{Fe}_2(\text{SO}_4)_3$, 0.01 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.5

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
10820	90902	7996	83140	15570	1290	687	313
7834	95198	6168	89009	17405	1086	2395	1105
5075	99620	4210	94724	19364	795	4029	1932

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	$\text{Fe}(\text{OH})_2^+$ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe}(\text{SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
1004	99	5	15	7765	1066	32
350	57	4	2	3100	479	5
5	1	0	0	48	8	0

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	$\text{Fe}(\text{OH})_2^+$ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe}(\text{SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
1004	99	5	15	7765	1066	32
453	72	5	7	3868	581	7
6	2	0	0	59	10	0

Table B19. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.005 m $\text{Fe}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.6

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
10820	90902	7996	83140	15570	1290	687	313
7332	94888	5769	88275	17214	1010	2395	1105
4058	99056	3382	93376	18986	637	4063	1937
2525	101120	2156	95841	19889	419	4853	2358

Table B20. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.005 m $\text{Fe}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.7^a

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
10820	90902	7996	83140	15570	1290	687	313
6830	94579	5371	87542	17024	935	2396	1104

^a $\text{Fe}(\text{OH})_3$ precipitates.

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	Fe(OH)_2^+ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe(SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
1004	99	2	15	7765	1066	32
555	87	6	11	4638	683	9
168	57	6	4	1518	241	1
5	4	1	0	46	8	0

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	Fe(OH)_2^+ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe(SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
1004	99	5	15	7765	1066	32
658	102	7	16	5406	785	11

Table B21. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.025 m $\text{Fe}_2(\text{SO}_4)_3$, 0.2 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.0

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
7575	166230	10238	146810	50276	2916	546	454
7287	171430	10169	154840	54601	3056	1902	1598
7023	176670	10111	162750	59058	3194	3234	2766
6782	181950	10066	170520	63643	3332	4537	3963
6568	187270	10037	178140	68388	3472	5801	5199
6373	192580	10018	185550	73239	3609	7018	6462

Table B22. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.025 m $\text{Fe}_2(\text{SO}_4)_3$, 0.2 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.1

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
7575	166230	10238	146810	50276	2916	546	454
6962	171250	9718	154240	54341	2915	1902	1598
6376	176300	9187	161580	58526	2895	3235	2765
5819	181370	8648	168810	62831	2854	4540	3960
5288	186470	8103	175950	67254	2795	5816	5184
4793	191620	7559	182960	71825	2714	7055	6445
4535	194450	7258	186740	74388	2661	7716	7151

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	$\text{Fe}(\text{OH})_2^+$ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe}(\text{SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
2625	371	25	208	37135	9322	107
2011	298	21	126	29611	7725	82
1441	224	17	64	22124	6008	58
913	150	12	21	14680	4166	37
436	75	6	4	7301	2158	17
3	1	0	0	57	17	0

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	$\text{Fe}(\text{OH})_2^+$ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe}(\text{SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
2625	371	25	208	37135	9322	107
2064	322	24	152	30316	7892	79
1542	267	22	101	23549	6363	55
1058	207	19	55	16838	4733	34
610	138	14	19	10186	2996	18
207	55	7	1	3612	1112	5
3	1	0	0	56	18	0

Table B23. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.025 m $\text{Fe}_2(\text{SO}_4)_3$, 0.2 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.2^a

H^+ m x 10 ⁶	SO_4^{2-} m x 10 ⁶	HSO_4^- m x 10 ⁶	Fe^{2+} m x 10 ⁶	FeSO_4^0 m x 10 ⁶	FeHSO_4^+ m x 10 ⁶	Cu^{2+} m x 10 ⁶	CuSO_4^0 m x 10 ⁶
7575	166230	10238	146810	50276	2916	546	454
6637	171070	9267	153640	54080	2775	1902	1598

^a $\text{Fe}(\text{OH})_3$ precipitates.

Table B24. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.01 m $\text{Fe}_2(\text{SO}_4)_3$, 0.2 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.0

H^+ m x 10 ⁶	SO_4^{2-} m x 10 ⁶	HSO_4^- m x 10 ⁶	Fe^{2+} m x 10 ⁶	FeSO_4^0 m x 10 ⁶	FeHSO_4^+ m x 10 ⁶	Cu^{2+} m x 10 ⁶	CuSO_4^0 m x 10 ⁶
7626	157470	9763	148880	48299	2820	559	441
7490	160170	9756	152920	50436	2894	1254	996
7360	162870	9752	156920	52609	2969	1940	1560
7239	165590	9753	160880	54825	3044	2617	2133
7126	168280	9757	164740	57047	3118	3272	2709

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	Fe(OH)_2^+ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe(SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
2625	371	25	208	37135	9322	107
2116	345	26	179	31020	8058	76

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	Fe(OH)_2^+ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe(SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
1121	157	11	37	15021	3572	44
820	118	8	19	11249	2736	32
532	78	6	6	7484	1867	21
259	39	3	1	3734	953	10
4	1	0	0	58	15	0

Table B25. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.01 m $\text{Fe}_2(\text{SO}_4)_3$, 0.2 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.1

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
7626	157470	9763	148880	48299	2820	559	441
6999	162650	9281	156360	52315	2822	1948	1552
6419	167920	8797	163690	56510	2803	3301	2699
6297	169070	8689	165270	57450	2795	3591	2956

Table B26. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.01 m $\text{Fe}_2(\text{SO}_4)_3$, 0.2 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.2

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
7626	157470	9763	148880	48299	2820	559	441
6644	162440	8814	155770	52057	2676	1949	1551
5719	167470	7840	162540	55968	2490	3306	2694
5281	169970	7352	165840	57949	2383	3959	3272

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	Fe(OH)_2^+ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe(SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
1121	157	11	37	15021	3572	44
576	94	7	7	8217	2071	20
99	18	2	0	1484	394	3
2	0	0	0	23	6	0

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	Fe(OH)_2^+ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe(SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
1121	157	11	37	15021	3572	44
633	109	9	14	8947	2243	20
198	44	4	1	2964	783	5
3	1	0	0	46	13	0

Table B27. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.01 m $\text{Fe}_2(\text{SO}_4)_3$, 0.2 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.3

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
7626	157470	9763	148880	48299	2820	559	441
6290	162230	8348	155170	51799	2530	1949	1551
5011	167030	6898	161400	55411	2192	3316	2684
3985	171150	5633	166580	58584	1852	4438	3672

Table B28. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.01 m $\text{Fe}_2(\text{SO}_4)_3$, 0.2 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.4

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
7626	157470	9763	148880	48299	2820	559	441
5936	162010	7881	154580	51540	2384	1949	1551
4320	166610	5959	160220	54886	1890	3317	2683
2785	171260	3976	165820	58362	1315	4650	3850
2300	172760	3314	167610	59504	1108	5069	4232

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	Fe(OH)_2^+ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe(SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
1121	157	11	37	15021	3572	44
690	124	10	22	9698	2414	21
295	78	9	6	4428	1174	5
4	2	0	0	68	19	0

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	Fe(OH)_2^+ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe(SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
1121	157	11	37	15021	3572	44
747	140	12	29	10438	2585	21
401	113	13	18	5898	1534	6
92	53	10	2	1443	397	0
4	3	1	0	56	16	0

Table B29. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.01 m $\text{Fe}_2(\text{SO}_4)_3$, 0.2 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.5^a

H^+ m x 10 ⁶	SO_4^{2-} m x 10 ⁶	HSO_4^- m x 10 ⁶	Fe^{2+} m x 10 ⁶	FeSO_4^- m x 10 ⁶	FeHSO_4^+ m x 10 ⁶	Cu^{2+} m x 10 ⁶	CuSO_4^0 m x 10 ⁶
7626	157470	9763	148880	48299	2820	559	441
5581	161800	7414	153980	51282	2238	1950	1550

^a $\text{Fe}(\text{OH})_3$ precipitates.

Table B30. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.005 m $\text{Fe}_2(\text{SO}_4)_3$, 0.2 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.0

H^+ m x 10 ⁶	SO_4^{2-} m x 10 ⁶	HSO_4^- m x 10 ⁶	Fe^{2+} m x 10 ⁶	FeSO_4^- m x 10 ⁶	FeHSO_4^+ m x 10 ⁶	Cu^{2+} m x 10 ⁶	CuSO_4^0 m x 10 ⁶
7667	154460	9627	149600	47604	2794	564	436
7600	155820	9629	151620	48669	2832	914	711
7536	157190	9632	153640	49742	2871	1262	988
7473	158560	9636	155640	50827	2909	1607	1268
7414	159900	9640	157570	51888	2946	1938	1542

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	$\text{Fe}(\text{OH})_2^+$ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe}(\text{SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
1121	157	11	37	15021	3572	44
803	155	13	36	11179	2757	21

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	$\text{Fe}(\text{OH})_2^+$ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe}(\text{SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
574	80	5	10	7541	1759	22
425	60	4	5	5651	1334	16
279	40	3	2	3764	900	11
138	20	1	0	1880	455	5
4	1	0	0	59	14	0

Table B31. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.005 m $\text{Fe}_2(\text{SO}_4)_3$, 0.2 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.1

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
7667	154460	9627	149600	47604	2794	564	436
7352	157080	9396	153350	49605	2797	1264	986
7050	159720	9164	157050	51651	2794	1954	1546
6990	160260	9116	157800	52072	2793	2093	1661

Table B32. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.005 m $\text{Fe}_2(\text{SO}_4)_3$, 0.2 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.2

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
7667	154460	9627	149600	47604	2794	564	436
7170	156970	9160	153050	49476	2723	1264	986
6689	159500	8688	156470	51387	2642	1956	1544
6460	160730	8457	158120	52327	2599	2287	1819

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	$\text{Fe}(\text{OH})_2^+$ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe}(\text{SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^+ $\text{m} \times 10^6$
574	80	5	10	7541	1759	22
305	46	3	1	4137	995	11
54	9	1	0	750	185	19
5	1	0	0	64	16	0

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	$\text{Fe}(\text{OH})_2^+$ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe}(\text{SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^+ $\text{m} \times 10^6$
574	80	5	10	7541	1759	22
334	52	4	3	4512	1081	12
108	19	2	0	1499	369	3
3	1	0	0	47	12	0

Table B33. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.005 m $\text{Fe}_2(\text{SO}_4)_3$, 0.02 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.3

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
7667	154460	9627	149600	47604	2794	564	436
6988	156860	8925	152750	49347	2649	1265	985
6325	159270	8215	155890	51119	2493	1959	1541
5786	161310	7613	158490	52633	2349	2530	2015

Table B34. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.005 m $\text{Fe}_2(\text{SO}_4)_3$, 0.2 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.4

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
7667	154460	9627	149600	47604	2794	564	436
5946	159040	7753	155310	50833	2356	1966	1534
4874	162110	6483	159010	53044	2020	2865	2275

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	Fe(OH)_2^+ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe(SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
574	80	5	10	7541	1759	22
363	58	4	4	4887	1167	12
161	31	3	0	2246	554	5
4	1	0	0	55	14	0

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	Fe(OH)_2^+ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe(SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
574	80	5	10	7541	1759	22
210	47	4	2	2983	748	4
3	1	0	0	46	12	0

Table B35. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.005 m $\text{Fe}_2(\text{SO}_4)_3$, 0.2 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.5

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
7667	154460	9627	149600	47604	2794	564	436
5583	158820	7282	154720	50576	2209	1966	1534
3640	163200	4899	159710	53631	1541	3316	2646

Table B36. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.005 m $\text{Fe}_2(\text{SO}_4)_3$, 0.2 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.6

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
7667	154460	9627	149600	47604	2794	564	436
5219	158600	6812	154120	50319	2061	1966	1534
2905	162820	3928	158620	53146	1234	3341	2659
1814	164880	2489	160800	54554	795	3995	3216

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	$\text{Fe}(\text{OH})_2^+$ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe}(\text{SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
574	80	5	10	7541	1759	22
268	59	5	5	3733	920	5
4	2	0	0	57	15	0

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	$\text{Fe}(\text{OH})_2^+$ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe}(\text{SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
574	80	5	10	7541	1759	22
326	71	6	7	4483	1093	6
101	47	7	3	1464	374	1
3	3	1	0	44	12	0

Table B37. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.005 m $\text{Fe}_2(\text{SO}_4)_3$, 0.2 m FeSO_4 , 0.01 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.7^a

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
7667	154460	9627	149600	47604	2794	564	436

^a $\text{Fe}(\text{OH})_3$ precipitates.

Table B38. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.005 m $\text{Fe}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 , 0.005 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.0

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
5560	90572	4094	83715	15621	665	688	312
5344	93514	4068	88525	17026	699	1541	709
5188	96501	4076	93178	18488	737	2361	1119

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	$\text{Fe}(\text{OH})_2^+$ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe}(\text{SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
574	80	5	10	7541	1759	22

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	$\text{Fe}(\text{OH})_2^+$ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe}(\text{SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
990	191	18	55	7632	1044	16
468	97	10	1	3854	561	8
7	2	0	0	60	9	0

Table B39. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.005 m $\text{Fe}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 , 0.005 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.1

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
5560	90572	4094	83715	15621	665	688	312
5104	93367	3884	88153	16931	666	1541	709
4686	96228	3679	92530	18307	663	2378	1122
4603	96814	3636	93413	18594	661	2545	1209

Table B40. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.005 m $\text{Fe}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 , 0.005 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.2

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
5560	90572	4094	83715	15621	665	688	312
4863	93220	3701	87781	16836	633	1541	709
4190	95910	3288	91805	18105	590	2380	1120
3872	97229	3081	93740	18738	565	2781	1325

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	$\text{Fe}(\text{OH})_2^+$ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe}(\text{SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
990	191	18	55	7632	1044	16
517	115	12	11	4217	609	8
90	23	3	0	767	116	1
8	2	0	0	66	10	0

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	$\text{Fe}(\text{OH})_2^+$ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe}(\text{SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
990	191	18	55	7632	1044	16
565	133	14	22	4580	657	8
179	54	7	1	1526	230	2
5	2	0	0	47	7	0

Table B41. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.005 m $\text{Fe}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 , 0.005 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.3

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
5560	90572	4094	83715	15621	665	688	312
4622	93073	3517	87408	16741	600	1542	708
3702	95600	2912	91079	17899	522	2385	1115
2940	97743	2370	94124	18906	441	3077	1468

Table B42. Concentration changes during CuFeS_2 dissolution; initial concentrations: 0.005 $\text{Fe}_2(\text{SO}_4)_3$, 0.1 m FeSO_4 , 0.005 m H_2SO_4 , 0.001 m CuSO_4 ; fraction dissolved by O_2 0.4^a

H^+ m x 10^6	SO_4^{2-} m x 10^6	HSO_4^- m x 10^6	Fe^{2+} m x 10^6	FeSO_4^0 m x 10^6	FeHSO_4^+ m x 10^6	Cu^{2+} m x 10^6	CuSO_4^0 m x 10^6
5560	90572	4094	83715	15621	665	688	312
4382	92926	3333	87036	16646	568	1542	708

^a $\text{Fe}(\text{OH})_3$ precipitates.

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	Fe(OH)_2^+ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe(SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
990	191	18	55	7632	1044	16
614	150	17	32	4943	705	8
265	95	14	8	2266	342	2
6	3	1	0	55	9	0

Fe^{3+} $\text{m} \times 10^6$	FeOH^{2+} $\text{m} \times 10^6$	Fe(OH)_2^+ $\text{m} \times 10^6$	$\text{Fe}_2(\text{OH})_2^{4+}$ $\text{m} \times 10^6$	FeSO_4^+ $\text{m} \times 10^6$	$\text{Fe(SO}_4)_2^-$ $\text{m} \times 10^6$	FeHSO_4^{2+} $\text{m} \times 10^6$
990	191	18	55	7632	1044	16
663	168	19	42	5306	753	8