THE PRESSURE LEACHING OF COPPER SULPHIDES IN PERCHLORIC ACID SOLUTIONS

BY

FRED LOEWEN B.A.Sc., University of British Golumbia, 1964

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Department of <u>Metallurgy</u>

The University of British Columbia Vancouver 8, Canada

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ABSTRACT

The leaching of covellite (CuS), chalcocite (Cu₂S), chalcopyrite (CuFeS₂) and bornite (Cu₅FeS₄) was carried out in a shaking autoclave in perchloric acid solutions and using moderate pressures of oxygen. The temperature range of investigation was $105-140^{\circ}$ C.

It was found that covellite, chalcocite and bornite leach at approximately similar rates, with chalcopyrite being an order of magnitude slower. It was found that chalcocite leaching can be divided into two stages, first, the rapid transformation to covellite with an activation energy 1.8 Kcal/mole, followed by a slower oxidation stage identified as covellite dissolution with an activation energy of 11.4 Kcal/ mole. These two stages of leaching were also observed in bornite with chalcocite (or digenite) appearing as an intermediate step. No such transformations were observed in covellite or chalcopyrite.

Two separate reactions were recognized as occuring simultaneously for all four minerals during the oxidation process: an electrochemical reaction yielding elemental sulphur and creating pits on the mineral surface, and a chemical reaction producing sulphate. The first reaction dominates in strongly acidic conditions, being responsible for about 85% of the sulphur released from the mineral, but the sulphate to elemental sulphur ratio in solution increases with decreasing acidity. Above 120°C the general oxidation process is inhibited by molten sulphur coating the mineral particles; the sulphate producing reaction, however, is not reduced above this temperature.

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For chalcopyrite the activation energies for the sulphate producing reaction and mineral solubilized were found to be 16.0 Kcal/mole and 11.0 Kcal/mole, respectively. It is suggested that chalcopyrite may leach partially via the formation of transient covellite on the surface but since its leaching rate is faster than that for chalcopyrite, no covellite is detected after leaching.

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The Pressure Oxidation of Copper Sulphides in Perchloric Acid Solutions

INTRODUCTION

Most of the copper in the earth's crust appears as coppersulphur or copper-iron-sulphur compounds. The copper bearing sulphide ore is easily concentrated to the nearly pure mineral with little gangue material present. The classical method of the recovery of copper by pyrometallurgy produces sulphur dioxide and impure copper. One of the oldest hydrometallurgical processes for the recovery of copper, involving the leaching of roasted concentrates with sulphuric acid, also produces sulphur dioxide⁽¹⁾. More recently with the introduction of pressure oxidation leaching sulphides could be leached without roasting. Sulphur is oxidized to sulphate in ammoniacal leaching and may be recovered as ammonium sulphate^(2,3).

When sulphides are subjected to oxidation leaching in acid media elemental sulphur is frequently obtained in good yield⁽⁴⁾. For example almost 100% of the mineral sulphur is obtained in the elemental state in the oxidation of pyrrhotite⁽⁵⁾, galena^(6,7) and sphalerite⁽⁸⁾. Elemental sulphur is also obtained in acid leaching but in poor yield (less than 50%) for pyrite^(9,10). With copper sulphide minerals the production of elemental sulphur has also been reported but its yield does not appear to be reliably high.

The leaching of copper sulphides in acid solutions have been studied in various oxidizing media. For example, Jackson and Strickland⁽¹¹⁾, used chloride solutions with chlorine as an oxidant. Sullivan⁽¹²⁾

studied the chemistry and kinetics of copper sulphides leaching using acid ferric sulphate as an oxidant and found much slower rates, especially for chalcopyrite. Ferric solutions were also used as the oxidizing 'agent for the leaching of covellite by Thomas and Ingraham⁽¹³⁾. The leaching of chalcocite, chalcopyrite and covellite using oxygen as the oxidant was studied by Warren⁽¹⁴⁾ and recently by others^(15,16). From these studies the rate of leaching was found to vary with oxidizing agent according to the order $Cl_2 > Fe^{3+} > O_2$; at room temperature and atmospheric pressure, chlorine will oxidize most sulphides in a few hours, Fe³⁺ in several days, while oxygen takes years. At temperatures over 100°C oxygen will oxidize sulphides in a few hours In all of the three oxidizing media the final products of leaching are similar, i.e., sulphate and elemental sulphur. This is consistent with the proposition that the reduction of the oxidant is rate controlling, and therefore that the oxidation of the mineral proceeds along a path that is predictable from thermodynamic considerations. However, the coexistance of cupric solutions with elemental sulphur is not an equilibrium condition, in view of the fact that the equation

 $3Cu^{++} + 4H_20 + 4S^{\circ} \longrightarrow 3CuS + SO_4^{=} + 8H^{+}$ [1] is thermodynamically favourable at pH values above -4, at 25°C. The production of elemental sulphur during the dissolution of copper sulphide minerals, therefore, reflects a thermodynamically unstable condition; yet all previous investigators have observed that elemental sulphur is formed when copper is leached by acid solutions from all copper sulphide minerals. However, the conditions of Reaction [1] are sufficiently compelling to suppose that both copper recovery and elemental sulphur formation will not occur in good yield simultaneously. The deportment of sulphur to elemental sulphur and sulphate during acid leaching of copper sulphide minerals, therefore, deserves careful investigation.

Scope of this Work

In this work it is proposed to carry the study of the leaching of copper sulphides further, using perchloric acid, and oxygen as the oxidant. The four minerals, covellite, chalcocite, chalcopyrite and bornite are investigated. Answers as to the relative rates of leaching among these four minerals and the deportment of sulphur as the product will be attempted on the basis of this work and previous knowledge. Kinetic studies of these lead hopefully to the proposal of reaction steps by which the kinetic mechanism of the whole process takes place.

Identity of the acid is irrelevant if the acid anions are chemically inert in the system. Perchloric acid is known to be completely ionized, strongly resistant to reduction in dilute solutions and has the lowest tendency to form metal complexes of all known anions.

EXPERIMENTAL

Materials

Reagent grade chemicals were used exclusively. All solutions were made with distilled water. The perchloric acid used was Baker and Adamson, 60%.

The covellite, chalcocite and bornite came from Butte, Montana and were supplied by Ward's Natural Science Establishment, Inc. The chalcopyrite used in the ground form originated from Miyatamata, Japan. The solid specimen of chalcopyrite used for one run came from Rouyn, Quebec and was also supplied by Ward's.

The chalcopyrite from Japan was obtained in the ground form, coarser than 100 mesh. The other minerals were supplied in massive chunks associated with minor amounts of gangue material. The material fragments were broken off with pliers or hammer, crushed in a mortar and pestle and screened to size fractions. Enough of the mineral was ground initially for all the runs. Only -150 + 200 mesh* and -200 mesh size fractions were used.

When examining the ground material microscopically very fine particles, much smaller than the nominal particle size were seen. This

* Mesh sizes refer to Tyler standard screens.

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could be considered as dust clinging to the larger particles. When a weighed sample of -150 + 200 mesh material was washed repeatedly in water and dried, to find the percentage of such dust in the sample, a weight loss of 0.6% was obtained.

Samples of the ground minerals were analyzed for copper, iron and sulphur by Coast Eldridge Engineers and Chemists, Limited, and for copper, iron and "insolubles" by the author. The "insolubles" were the material that would not dissolve in hot, concentrated nitric acid. The result of the analyses as well as the formula compositions are presented in Table 1.

X-ray diffraction patterns* were made from -200 mesh material. The analyses show conclusive identification of covellite and chalcopyrite: every line on the pattern is matched by a prominent line on the index cards. A good identification is also obtained from the X-ray patterns of chalcocite; the only extraneous line appearing is the dominant line of bornite, as the chemical analysis would indicate. A wide range in stoichiometry is reported for chalcocite⁽¹⁸⁾ thus precluding large amounts of a second phase. The pattern for the bornite sample includes the three strongest lines of covellite; however, the weakness of these lines indicates that covellite is a minor constituent.

^{*} D-spacings with intensities from x-ray diffraction patterns together with these values obtained from the index cards are presented in the Appendix.

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Chemical Compositions of Copper-Sulphide Minerals

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Mineral	Cu	oast Fe	Eldri S	lge Sum≠	Coast. Cu	Fild. Fe	Norwalized*	Au Cu	thor Fe	Insol.	Fc Cu	rmula Fe	Comp.
Covellite (CuS)	62.8	2.49	31.7	97.0	64.7	2.6	32.7	61.9	2.84	1.67	66.4	0	33.6
Cahlcocite (Cu ₂ S)	63 . 8	5.67	25-0	-94.5	67.6	6.0	25.4	62.7	6.25	- 2.60	79.8	0	20.2
Chalcopyrite (CuFeS ₂)	33.2	30° . 4	34.6	98.2	33:8	31.0	35.2			1.90	34.5	30.5	35.0
Bornite (^{Cu} 5FeS ₄)	58 . 2	11.7	26.2	96.1		12.2	27.2	57.7	12.6.	3.15	63.3	.11.1	25.6

* Coast Eldridge assays adjusted to make Cust Fest S. = 100

Sum of Cu + Fe + S

‡

1.17

I

-- To facilitate comparison of results among the experiments approximately equal surface areas of minerals were used. Specific gravities of the mineral samples were determined and the values obtained are recorded in Table 2.

Experimental Apparatus

The reaction vessel was a shaking, titanium autoclave, manufactured by Pressure Products Industries, Inc., of 117 ml capacity and able to withstand 4500 psi working pressure. The shaking was a reciprocal motion with a stroke of 1.4 inches and 266 cycles/minute. A Flexitallic stainless steel gasket sealed the autoclave.

Heat was provided by an electrical resistance heater wound around the autoclave. The temperature was sensed by a thermistor located in a titanium well in the lid projecting to the centre of the autoclave. A Thermistemp temperature controller (Model 71, Yellow Springs Instruments Co., Inc.) in series with a voltage regulator controlled the average temperature within 1/2°C with ±1° cycles.

The total pressure in the autoclave was kept constant by a pressure regulator (0-100 psi range) which let oxygen gas from a reservoir into the autoclave as it was consumed. A transducer (Consolidated Electrodynamics Corp., Model 4-311, 0-1000 psi range) relayed a signal proportional to the pressure of oxygen in the reservoir to a Sargent strip chart recorder. Thus the rate of reaction was measured by the oxygen consumption as registered by the pressure drop in the reservoir.

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<u>Table 2</u>

Specific Gravities and Weights for Equal Areas

•

	Dana ⁽¹⁹⁾	Smith ⁽²⁰⁾	Maagurad	equal areas*
	Dana ⁽¹⁹⁾ Smith ⁽²⁰⁾ Measured and used		equal areas*	
Covellite	4.6	4.6-4.76	4.61	3.25 gm
Chalcocite	5.5-5.8	5.5-5.8	5.55	3.91
Chalcopyrite	4.1-4.3	4.1-4.3	4.26	3.00
Bornite	4.9-5.4	5.06-5.08	5.07	3.57

* Assuming cubic shape factor, Area = 475 cm^2 for -150 + 200 mesh material.

The pressure regulator was calibrated and found to read 100 when the pressure in the autoclave was 95 psig. All pressur^{es} mentioned hereafter are the corrected values.

Experimental Procedure

All runs were conducted with 70 ml of solution.

After the autoclave was sealed in preparation for a run, shaking and heating were started. When the working temperature was reached, in 10 to 15 minutes, the oxygen was let into the autoclave to initiate the run.

At the end of the run the oxygen value to the autoclave was closed, the heat was turned off, the insulating cap was removed and wet towels were wrapped around the sealing nut to promote rapid cooling. Shaking was intermittant during this time. When the temperature fell below 85°C, in 10 to 15 minutes, the autoclave was opened and the contents removed by a suction flask.

Between runs, the autoclave was washed with 50% nitric acid. A tea-spoonful of powdered silica was added if a precipitate was suspected of coating the walls of the autoclave. The autoclave was sealed and with shaking, it was allowed to reach some temperature above 70°C. The nitric acid remained in the autoclave for no less than 15 minutes.

Unless otherwise stated all experiments were carried out at 95 psi gauge pressure regardless of the temperature of the run. Therefore because of solution vapour pressure and nitrogen entrained in the autoclave at the time of closure the pressure of oxygen in the

autoclave varied with temperature as listed in Table 3.

Та	b	le	3

Temperatures and Corresponding and Oxygen Pressures Used

Temperature	Oxygen Press
105°C	77.3 psi
110	73.8
115	69.9
120	65.4
125	60.3
130	54.6
140	41.0

Unless otherwise stated, the mineral charges of all experiments were of the weights listed in Table 2 and of -150 + 200 mesh particle size.

Analytical Methods

1. The amount of sulphate in solution was estimated by the standard barium chloride precipitation and gravimetric determination $^{(21)}$. From repeated determination of the same solutions a reproducability of ±1.7% was found.

2. The concentration of copper in solution was determined by a standard electroplating procedure using platinum cathodes ⁽²¹⁾.

3. The amount of mineral leached was calculated from the weight loss of the autoclave charge corrected for elemental sulphur content. The elemental sulphur in the residue was assumed to be equal to the total sulphur in the consumed mineral minus that determined as sulphate in the solution. The residue was allowed to dry overnight in the filter paper before weighing. This estimate of the amount of mineral leached was used only for the leaching of chalcopyrite in which no composition change in the mineral occurs during leaching. Several trials in which mineral samples were shaken with pure water in the autoclave showed that the reproducability of the residue recovery method was about ±0.5%.

4. The amount of iron in the original mineral samples was estimated by the standard double precipitation and gravimetric determination $\binom{(21)}{}$.

5. The amount of oxygen consumed was estimated from the trace produced on the recorded chart. The relationship between ml of oxygen used and chart reading were established by a gas burette calibration.

6. It was originally intended to analyze for elemental sulphur by washing the dry residue in carbon disulphide to dissolve the sulphur, filtering to remove the solid residue and letting the carbon disulphide evaporate to dryness to leave behind a crust of sulphur in a preweighed beaker. The method consisted of immersing the residue for about an hour in 30 ml carbon disulphide, and then decanting it through a qualitative filter paper. The residue was again immersed and the carbon disulphide decanted. The residue was finally placed in the filter paper and washed with about 10 ml of carbon disulphide. A warmed watch-glass was

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placed over the funnel to minimize evaporation. The filtrate was allowed to evaporate overnight.

The most elemental sulphur accounted for was about 90%. The amount of oxygen consumption and the reproducability of sulphate determinations between runs indicated that the missing sulphur was not sulphate. A check with potassium permanganate indicated the absence of transient species of sulphur oxide in solution. Therefore it was thought that the above procedure was inadequate for extracting all the elemental sulphur from the residue. No results from these "analyses" are reported here.

Other investigators have encountered a similar problem (22).

RESULTS

1. Phase Changes During Leaching

Since covellite is more stable towards oxidation than other copper sulphide minerals its formation as an intermediate during oxidation of chalcopyrite, chalcocite and bornite is thermodynamically possible.

To investigate transformations of chalcocite and bornite during leaching these minerals were each leached in 1 M acid at 125°C for 30 minutes. X-ray diffraction patterns were taken of the residues after washing with carbon disulphide. Both patterns consisted of dominant lines of both chalcocite and covellite; the pattern for bornite showed no evidence of residual bornite.

To determine similar changes in chalcopyrite, 3 gm of -200 mesh material, was leached in 1 M acid at 120°C for 8 1/2 hours. The residue, after the run, was washed with carbon disulphide to remove elemental sulphur and an x-ray diffraction pattern was made of the unleached material. A similar sample of residue was sent to Coast Eldridge for chemical analysis.

The x-ray pattern revealed no evidence of covellite or chalcocite and the chemical analysis showed the residue had a composition within the accuracy range of the initial material assay. Further evidence for no mineral transformation is that the residues of all runs of chalcopyrite after being washed with carbon disulphide were identical in appearance with the initial material.

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To determine whether covellite is precipitated from a cupric solution by elemental sulphur, chalcopyrite, 1 gm of -200 mesh material, was shaken in the autoclave with 0.3 gm sulphur in 0.3 M cupric perchlorate solution at 120°C for 3 hours. Another run was performed with 3 gm of the material plus 0.3 gm sulphur in 2M cupric perchlorate—2M perchloric acid solution at 120°C for 5 hours. The chalcopyrite was added in the event that the formation of covellite should be catalyzed on the surface of the mineral, but to prevent any leaching a nitrogen atmosphere was maintained.

After the runs the chalcopyrite was removed by filtration and washed with carbon disulphide. Both the chalcopyrite and the solutions were unaltered. Barium chloride added to the solutions verified the absence of sulphate.

2. Leaching Massive Specimens

Large single specimens of covellite, chalcocite and chalcopyrite were polished smooth on one side, using for final polish 1 micron diamond paste for covellite and chalcocite and 1 micron alumina slurry on a metallurgical polishing wheel for chalcopyrite. Scratches could be observed microscopically on the polished surface. The specimens were mounted in a flat cylinder of cast sulphur reinforced with titanium wire to mount the specimens firmly during the run. The three specimens were leached at 110°C in 1M perchloric acid for 4.8, 3 and 6.5 hours respectively.

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For the covellite specimen, photomicrographs taken of the surface before and after leaching are presented in Figure 1.

The chalcocite turned from grey to black upon leaching. Microscopic examination at low magnification revealed cracks running throughout the surface of the specimen.

At low magnification the unleached surface of chalcopyrite showed inclusions of two kinds: grey, soft inclusions, probably covellite or chalcocite, and hard, yellow inclusions, probably pyrite. The hardness of the inclusions relative to the matrix is estimated by the difficulty of removing scratches from them. After leaching, the soft inclusions were completely leached out but the hard inclusions were unchanged. Photomicrographs taken at 260X magnification are presented in Figure 2. At lower magnification no change of the matrix was observed with leaching.

3. Formation of Sulphate from Elemental Sulphur.

To determine whether elemental sulphur oxidizes to sulphate under the conditions used for leaching a test was made with 0.5 gm of sulphur plus one teaspoonful of silica in 0.36M cupric perchlorate - 0.25M perchloric acid solution at 125°C.

After 2.3 hours the oxygen consumption was negligible and a barium chloride test revealed that no sulphate was present in the solution.

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Before Leaching



After Leaching

Figure 1 Surface of Massive Specimen of Covellite before and after leaching 135X



Before Leaching



After Leaching

Figure 2 Surface of Massive specimen of chalcopyrite before and after leaching 260X

4. Evolution of Hydrogen Sulphide and Sulphur Dioxide

To determine whether hydrogen sulphide or sulphur dioxide are products of the oxidation reactions chalcopyrite, 6gm of -200 mesh, was leached in 2M perchloric acid at 120°C. After 2 1/2 hours, when 0.0182 moles of oxygen had been consumed corresponding to the oxidation of about 30% of the mineral, the heat was turned off to let the autoclave cool below 100°C. With the oxygen line closed the gas in the autoclave was allowed to bubble, for about a minute each, through columns of silver nitrate, 10^{-5} M potassium permanganate and distilled water.

No precipitate was formed in the silver nitrate which indicated the absence of hydrogen sulphide. The permanganate solution retained its faint pink colour and the pH of the distilled water remained constant indicating the absence of sulphur dioxide.

5. Comparison of Leaching Rates

Covellite, chalcocite and chalcopyrite were leached in 4M perchloric acid at 110°C and 125°C and two runs were conducted with bornite in 1M acid at the same temperatures.

The oxygen consumption curves for these runs are presented in Figures 3, 4, 5 and 6. Analyses of copper and sulphate in solution after the runs are given in Table 4.

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Figure 3. Leaching covellite in 4M perchloric acid

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- 20 -





Figure 6. Leaching bornite in 1M acid

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<u>Table 4</u>

Leaching Covellite, Chalcocite and Chalcopyrite in 4M Acid and Bornite in 1M Acid for 6 Hours.

Mineral	Temp.	moles O ₂ consumed	moles [©] Cu in soln.	moles SO4 ⁼ in soln.	% S as S04 ⁼ *	% Cu in soln.
Covellite	110°C	.0079	.0111	.00145	13.0	34.7
	125	.0112	.0165	.00172	10.4	51.5
Chalcocite	110	.0170	.0261	.00206	12.0	66.5
	125	.0189	.0262	.00309	17.9	66.6
Chalcopyrite	110	.0015	.0007	N.D. ‡	N.D.	4.5
	125	.0040	.0017	N.D.	N.D.	10.8
Bornite	110	.0277	.0277	.00248	10.3	84.5
	125	.0160	.0178	.00340	24.2	54.1
			<u></u>	· · ·	. "	· · · · · · · · · · · · · · · · · · ·

- * The residues of Chalcocite and Bornite runs are assumed to be entirely transformed to Covellite.
- ‡ N.D. = not determined.

6. Variation of Acidity

A series of runs was done in which chalcocite was leached at 125°C in perchloric acid ranging in concentration from 0.1M to 4M. The lengths of these runs were 5, 6 or 9 hours. The oxygen consumption curves for these runs are given in Figure 7. The amounts of sulphate and copper in solution and the final pH values are presented in Table 5.

After the runs with 0.1M and 0.25M acid a yellow precipitate coated the inside of the autoclave and a light-brown precipitate was present with the unleached mineral. The amount of precipitate was much more extensive at the 0.1M than at the 0.25M acid run.

Chalcopyrite, 9 gm of -150 + 200 mesh, was leached at 125°C in 0.25M, 1.0M and 4M acid for 6 hours each. The oxygen consumption curves for these runs are given in Figure 8. The amount of sulphate and copper in solution and the final pH values are presented in Table 6.

7. Variation of Oxygen Pressure

Three experiments were performed using chalcocite in 1M acid at 110°C and at oxygen partial pressures in the autoclave of 25, 42 and 74 psi. The lengths of the runs were 5, 6 and 9 hours respectively.

The oxygen consumption curves for these runs are presented in Figure 9. These curves can be divided into two parts, representing an initial, rapid oxidation step followed by a period of steady, slow oxidation. The slopes of these curves are presented in Table 7 and plotted against pressure of oxygen in Figure 10.



Table 5

Leaching Chalcocite in Perchloric Acid at 125°C

	· ·	-						
Acidity	Duration of run	moles O ₂ consumed	moles Cu in soln.	moles SO4 ⁼ in soln.	% Cu in soln.	%S as SO <u>∓</u> *	final pH	precipitate
4M	6 hr. 6	.0189 .0202	.0262 .0332	.00 3 09 .00259	66.7 84.5	17.9 10.7	0 0	nil nil
2	5	.0210	.0261	.00625	66.5	36.3	0.5	nil
1	9	.0327	.0327	.0113	83.2	47.5	1.1	nil
0.5	6 5	.0356 .0363	.0280 .0284	.0137 .0140	71.2 72.3	71.7 71.8	1.0 1.35	nil nil
0.25	6	.0465	.0272	N.D.	ppt	N.D.	2.3	ppt.
0.10	6	.0228	.00715	N.D.	ppt	N.D.	3.0	ppt.

N.D. = Not determined

* Residue is assumed to be entirely transformed to covellite.



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<u>Table 6</u>

Leaching Chalcopyrite (9gm) at 125°C for 6 Hours

Acidity	Moles 02 consumed	moles Cu in soln.	moles SO ₄ in soln.	% Cu in soln.	%_S as S04	∘final… pH	precipitate
4M	.0217	.01475	.00220	31.3	7.2	0	nil
1	.0265	.0116	.00488	24.6	20.4	0.5	ppt
0.25	.0178	.00839	.00261	17.9	15.1	1.2	ppt
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<u>Table 7</u>

Chalcocite Leaching at 110°C in 1M acid at Three Oxygen Pressures

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Pressure oxygen	Initial rate	Secondary rate
25 psi	270 m10 ₂ /hr	53.8 m102/hr
42	300	57.4
74	545-830	87.5

:






8. <u>Temperature Variation</u>

Three runs were done on chalcocite in 1M perchloric acid at temperatures of 110°C, 125°C and 140°C. The lengths of these runs were 9, 9 and 3 hours respectively.

The residue from the run at 140°C was dried and washed with carbon disulphide after which 1.924 gm of it were returned to the autoclave to be leached in 1M acid at 140°C for 3 hours.

The oxygen consumption curves for these runs are given in Figure 11. The rates were measured for each of the two stages of oxidation and are presented in Table 8. The rates divided by pressure of oxygen for the two stages of leaching are shown on Arrhenius plots in Figures 12 and 13.

Table 8

Oxidation Rates for Leaching Chalcocite in 1M Perchloric Acid

Temperature	Pressure O ₂ psi	Primary Stage Leaching Rate	Secondary stage leaching rate
110°C	74 ·	490-540 ml0 ₂ /hr.	90 ml0 ₂ /hr.
125°C	60	425-475	140
1 40° C	41	340	150











Figure 13 Arrhenius plot for secondary stage of leaching of chalcocite in 1M acid.

Three runs were done on chalcopyrite, using 9 gm of -150 +200 mesh, in 1M acid at temperatures of 110°C, 125°C and 140°C. The lengths of these runs were 11, 6 and 3 hours respectively. The oxygen consumption curves for these runs are given in Figure 14.

9. The Catalytic Effect of Cupric Ions

In order to test for a catalytic effect of cupric ions on the leaching of copper sulphides, chalcocite was leached in 0.5M copper perchlorate - 1M perchloric acid solution at 125°C for 6 hours. Another run employed chalcopyrite, 9 gm of -150+200 mesh, in 0.5M copper perchlorate - 0.5M perchloric acid solution at the same temperature for also 6 hours. The oxygen consumption curves for these runs together with control experiments lacking initial cupric salt additions are presented in Figure 15.

10. Leaching Chalcopyrite -

A series of 2 hour runs was conducted with chalcopyrite, 3 gm of -200 mesh, in 1M acid in the temperature range of 105°C to 130°C. The solutions were analyzed for sulphate and the amount of material leached was calculated from the weight of the residue removed from the autoclave. One of the solutions (from a run at 120°C) was analyzed for ferrous content one hour after removal from the autoclave. In all runs, except one at 130°C, the oxygen consumption curves were linear, indicating constant reaction rates. The sulphate analyses at varying amounts of mineral leached are given in Table 9 and shown in Arrhenius plots in Figures 16 and 17. The ferrous titration showed that 68% of the iron present in solution was in the ferrous state.



Figure 14. Chalcopyrite leached in 1M acid at three temperatures, (9gm of mineral used).



Figure 15 The effect of Initial cupric additions on the leaching rates of Chalcocite and Chalcopyrite.

<u>Table 9</u>

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Leaching Chalcopyrite in 1M Acid for 2 Hours (3 gm of -200 mesh)

Temperature	gm Mineral leached	Moles S0 7	%. SasS0 <mark>=</mark>
•			
105°C 105	.476 .504	.000638 .000603	12.3% 11.0
110 110	.510 .545	.00078 .00111	14.0 18.7
115	.615	.00100	14.9
120 120	.750 .606	.001105 .00115	13.5 17.4
125	.648	.00143	20.2
130	.706	.001635	21.2

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Figure 16 Arrhenius plot for Chacopyrite dissolution in 1M acid

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Figure 17 Arrhenius plot for Sulphate formation from Chalcopyrite leaching in 1M acid.

DISCUSSION

1. <u>Reproducibility of Results</u>

Figure 18, showing the oxidation curves of two pairs of experiments, indicates the degree of reproduct bility that can be expected in this work. Some of the factors influencing oxygen consumption are: copper entering the solution, the formation of sulphate, transient species of sulphur oxide being formed and oxidized, ferrous ions oxidizing to ferric, and impurities in the original mineral reacting. Some of these may be influenced by minute variations in variables that may not have been controlled. Those experiments carried out above the melting point of sulphur are expected to be less reproductble than the others because of the wetting and spreading expected of the liquid sulphur and the resulting variation in area of anodic regions.

2. Phase Changes During Leaching

In the leaching of chalcocite the formation of covellite occurs rapidly according to the reaction:

$$Cu_2S + 2H^+ + \frac{10}{2}_2 \longrightarrow CuS + Cu^{++} + H_20$$
 [2]

 ΔF°_{393} - 30.37 Kcal/mole* The rapid self-diffusion of the cuprous ion in chalcocite^(23,24) is necessary for the kinetics to be as fast as observed.

* All thermodynamic data are taken from Latimer⁽²⁵⁾ with few exceptions where noted.

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From the materials analysis (Table 1) it is calculated that in the chalcocite sample used the average formal valence of copper is +1.28. For 3.91 gm of chalcocite to react to completion according to Reaction [2] 224 ml of oxygen will be consumed. Examination of the curve for the oxidation of chalcocite at 110°C in Figure 4 shows that this is near the value for the transition between the fast initial rate, identified as chalcocite-covellite transformation, and the subsequent slower oxidation rate, identified as covellite dissolution. Also, comparison of Figures 3 and 4 shows that the chalcocite curves have about the same shape as the covellite curves but are displaced upwards by about 200 ml. This indicates that the chalcocite-covellite transformation is practically completed in 30 minutes and that during this time covellite oxidation is minor. Because chalcocite is a good electrical conductor and therefore one particle can be at only one electrical potential, both covellite and elemental sulphur will not coexist on one particle of incompletely reacted chalcocite. Therefore the transformation is expected to go to completion before the next oxidation step begins. However, because all the particles of the charge will not be in electrical contact a sharp distinction between the two oxidation steps should not be expected with powdered material.

The transformation of chalcocite to covellite produces cracks in the mineral particles as a result of shrinkage in volume, since the molar volumes of chalcocite and covellite are 28.7 cc/mole and 20.7 cc/mole respectively. This would prevent the rate of transformation from decreasing due to a diffusion barrier being erected by the product forming on the particles. These cracks also increase surface area and may be responsible for the leaching rate of chalcocite at 110°C (Figure 4) being greater than the corresponding rate for covellite (Figure 3).

The appearance of both covellite and chalcocite from the leaching of bornite indicates that two transition reactions are operative, ie., $Cu_5FeS_4 + 4H^+ + 0_2 \longrightarrow 4CuS + Cu^{++} + Fe^{++} + 2H_20$ [3] $Cu_5FeS_4 + 2H^+ + \frac{10}{2}2 \longrightarrow Cu_2S + 3CuS + Fe^{++} + H_20$ [4] with ΔF°_{298} of -80.05 and -47.79 Kcal/mole respectively.*

The first reaction is the one expected from a kinetic point of view because cuprous ions in bornite are able to diffuse much faster than the ferrous ions $(^{28})$ and therefore are expected to arrive in solution at least as fast as the ferrous ions. However, thermodynamic calculations predict that iron should leach out of bornite at a lower oxidation potential than that required for copper dissolution and therefore Reaction [4] probably occurs and may even predominate. Chalcocite could be formed according to the latter reaction ohly if the reduction of oxygen is rate-determining. The presence of chalcocite in the partially leached bornite is consistent with a reversible oxidation step for the mineral $(^{27})$, and is therefore evidence for a rate-controlling step involving oxygen reduction rather than mineral oxidation. The reaction

 $Cu_5FeS_4 + 4H^+ + O_2 \longrightarrow 2Cu_2S + Cu_{}^{++} + Fe^{++} + 2S^\circ + 2H_2O$ [5] is excluded because chalcocite and elemental sulphur in intimate contact react to form covellite, the end result being equivalent to Reaction [3]. * Thermodynamic data for bornite comes form Majima and Peters⁽²⁶⁾. From previous work done with bornite it is reported that digenite is rapidly formed when bornite is heated in the temperature range of 80° to $150°C^{(28)}$. Digenite is stable above 105°C and decomposes to chalcocite and covellite below this temperature⁽²⁹⁾. This work is consistant with the results obtained here, i.e., bornite transforming to chalcocite.

The results show that chalcopyrite does not form covellite during leaching although the reaction

 $CuFeS_2 + 2H^+ + \frac{10}{2} \longrightarrow CuS + Fe^{++} + S^\circ + H_2O$ [6] has a ΔF° of -10.95 Kcal/mole at 120°C* This does not exclude the possibility that the formation of covellite may be an intermediate step in the mechanism of leaching, but because the leaching rate of covellite is faster than that of chalcopyrite (comparing Figures 3 and 5) the former would not be present in observable amounts.

3. Leaching Massive Specimens

Examination of the photomicrographs of Figure 1 for the leaching of covellite reveals that before leaching the covellite contained veins of light grey material, probably chalcocite or bornite; the chemical analysis suggests the presence of bornite. After leaching the presence of pits and channels indicate non-uniform attack on the surface of the covellite. The scratch marks still visible show that little uniform attack

* Thermodynamic data for chalcopyrite is taken from Golomzik⁽³⁰⁾.

has occurred. The photographs show that the pits were initiated at locations of the original light grey phase. If this phase is chalcocite or bornite, this is consistent with the findings discussed in the above section that if in electrical contact then covellite should not leach until chalcocite and bornite have transformed completely to covellite. In the transformation process the grey phase will open up cracks in the mineral. The pits and channels extend over a larger area than the original light grey phase and this indicates that the region adjacent to this phase becomes anodic.

Nonuniform attack on electrical conductors is indicative of the occurrence of electrochemical processes (17). In the leaching of covellite with acid and oxygen the anodic and cathodic reactions may be written as follows:

CuS
$$\longrightarrow$$
 Cu⁺⁺ + S° + 2e [7]
2H⁺ + $\frac{10}{2}$ + 2e \longrightarrow H₂O [8]

On some corroding materials the anodic and cathodic areas may migrate, giving the appearance of general corrosion. However the photographs show the areas were reasonably fixed during the length of this run, with Reaction [7] initiating and propagating pits, and Reaction [8] occuring on the virtually unattacked surface. An explanation for this is that in pits the concentration of oxygen is expected to be less than on the flat surface. Therefore Reaction [7] would continue and propagate the pits, whereas Reaction [8] is unlikely in pits since it involves the diffusion of oxygen and protons to the surface of the mineral. Since chalcocite and bornite transform to covellite during the initial step of leaching, the dissolution characteristics of covellite discussed here should also apply to the final leaching of chalcocite and bornite.

During leaching the solid specimen of chalcocite it became black and developed cracks on the surface showing its transformation to covellite and a simultaneous shrinkage in volume.

The photomicrographs from leaching the specimen of chalcopyrite, Figure 2, show traces of local attack at 260X magnification, however, considering the slowness of the leaching of chalcopyrite the available evidence is insufficient to exclude the possibility of general attack.

4. Formation of Sulphate from Elemental Sulphur

The results indicate that with oxygen and in 0.25M perchloric acid sulphur does not oxidize to sulphate although the reaction $S^{\circ} + \frac{30}{2} + H_2^{\circ} \longrightarrow S_4^{\circ} + 2H^{+}$ [9] has a $\checkmark F^{\circ}$ of -119.39 Kcal/mole at 125°C.

Sulphur that oxidizes to sulphate through cataysis by the surface of the mineral would not be distinguishable from sulphate formation with sulphur originating from the mineral itself. 5. The Evolution of Hydrogen Sulphide and Sulphur Dioxide

Hydrogen sulphide is not a product of the leaching reaction even in solutions of 2M acid as predicted by thermodynamic calculations, since the reaction

 $H_2S + Cu^{++} \longrightarrow CuS + 2H^+$ [10] has a ΔF°_{298} of -19.34 Kcal/mole and is rapid in the direction as written.

Sulphur dioxide also cannot be expected in these solutions because its oxidation by oxygen is rapid, although the reaction

$$CuS + \frac{30}{2} + 2H^{+} \longrightarrow Cu_{4}^{++} + H_{2}SO_{3}$$
 [11]

has a ΔF°_{298} of -101.36 Kcal/mole. Sulphate formation through SO₂ or H₂SO₃ as an intermediate cannot be excluded.

6. Comparison of Leaching Rates

From the oxidation curves of covellite, chalcocite and bornite of Figures 3, 4, and 6, it can be seen that the curves for leaching at 125°C have a higher initial slope than the 110°C curves, as expected, but have continuously decreasing slopes over their range, whereas, the 110°C curves, after an initial steep section, assume constant slopes. The decrease in the reaction rates at 125°C can be attributed to liquid sulphur covering the mineral and thereby stifling the reaction, since the melting point of sulfur is 119°C. This conclusion was also reached by many previous investigators ^(14,15,16). If the anodic reaction occurs in pits on the mineral, stifling of the reaction is especially likely. In the leaching of covellite, Figure 3, it would be expected for the steady rate section of the 110°C oxidation curve to pass through the origin, but bornite and/or chalcocite impurities in the covellite react rapidly at first and a linear rate is reached when only covellite remains.

The chalcocite curves are the same shape as the covellite curves but displaced upwards by an amount necessary to produce the chalcocite-covellite transformation, as discussed earlier. The fact that the 110°C steady leaching rate for chalcocite is steeper than for covellite, even though both can be considered to be the leaching of covellite, may be explained by the increase in surface area of chalcocite by the cracks formed during the chalcocite-covellite transformation.

It is incorrect to compare the bornite oxidation curves rigorously with the others since the acidities are different. It is noticed from Figure 7 that there is a significant difference between leaching chalcocite in 1M and 4M acid. The fact that a varying amount of sulfate is produced, and that the iron from bornite oxidizes almost completely to ferric tend to make the oxygen consumption curves less meaningful. These factors permit only qualitative interpretations of the curves.

The 110°C oxidation curve is steeper for bornite than for chalcocite and covellite probably because the greater volume change during transformation amplifies the cracks and probably because the transformation of chalcocite (or digenite) to covellite, since it is a secondary reaction, would be spread over a longer time period than the equivalent transformation

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in original chalcocite. Thus the final steady rate for 110°C leaching of bornite is probably not only the leaching of covellite but a simultaneous transformation to some extent. The fact that the 125°C curve after 1 hour is steeper than the chalcocite curve can be explained in the same way. That it is less subject to stifling by molten sulfur may again be evidence that the transformation is spread out over a longer period.

The leaching of chalcopyrite (Figure 5) is an order of magnitude slower than that of other copper minerals. After six hours the oxygen consumption was still too small to detect stifling by elemental sulphur at 125°C. Apparently fast initial rates may be due to dust or traces of other minerals and are therefore not necessarily characteristic of chalcopyrite.

7. Variation of Acidity

An examination of the oxidation curves for leaching chakocite in perchloric acid of varying strengths (Figure 7) shows that the total oxygen consumption increases from the 4M run to a maximum at the 0.25M run. The sharp decrease in reaction rate after about one hour for the 4M and 2M cases may be attributed to liquid sulphur coating the mineral and inhibiting further leaching. This phenomenon would normally be expected to be operative in all runs in this series.

From Table 5 it is seen that the decrease of acidity from 4M to 0.5M is accompanied by an increase in the yield of sulphate. This is not surprising considering that sulphur is never produced when sulphides are leached in basic solutions^(2,31), and that with increasing pH values elemental sulphur becomes less stable. The observation that the oxidation rate during the latter half of each run increases with decreasing acidity leads to the possibility that either the stifling of the reaction has been eliminated, e.g., sulphur is being removed, or other reactions that consume oxygen become increasingly dominant.

It has already been shown that sulphur is not removed by oxidation to sulphate in an acid, cupric solution. This experiment, was conducted in 0.25M acid and is not more favourable at higher acidities. An alternative is for the reaction producing sulphate directly to become dominant, and/or is not subject to liquid sulphur stifling. Assuming chalcocite is completely converted to covellite, the sulphate producing reaction is

$$\operatorname{CuS} + 20_2 \longrightarrow \operatorname{Cu}^{++} + \operatorname{SO}_4^{=}$$
 [12]

a reaction which not only consumes four times as much oxygen as that yielding elemental sulphur, but also does not consume acid.

The suggestion that Reaction [12] may be occurring at locations other than the anodic sites arises from the probability that it is not subject to sulphur stifling. If this is the case the sulphating reaction may be chemical in nature and occur somewhat uniformly on the surface of the mineral. It is not likely for sulphate to be formed as the counterpart of the cathodic Reaction [8], ie, to proceed $CuS + 4H_20 \longrightarrow Cu^{++} + S0_4^{=} + 8H^{+} + 8e^{-}$ [13] $\Delta F_{298} = -76.65Kcal/mole$ because of the unfavourable entropy changes involved when this many water molecules are taken up to yield a single sulphate ion.

It is not necessary for a heterogeneous chemical reaction to exhibit uniform attack on the surface of a particle since preferrential adsorption and selective activities, and hence varying reaction rates among crystal lattice planes of different orientation have been observed in some systems (38). However the attack is expected to vary no more than the orientation of the exposed faces and therefore pronounced preferrential attack leading to the creation of pits is not expected for chemical processes.

A chemical reaction such as Equation [12] involves molecular oxygen rather than water molecules and is completely chemical, i.e., it is not associated with separate anodic or cathodic processes. However, it may, in fact, take place in several steps on the mineral surface, i.e.

$$CuS + 0_2 - Cu^{++} + SO_2^{-}$$
 (ads) [14]

$$SO_2^{-} (ads) + O_2^{-} SO_4^{-}$$
 [15]

The amount of copper in solution for the runs in which no precipitate was formed remained approximately constant as seen in Table 5. This indicates that as Reaction [12] increases Reaction [7] must decrease correspondingly. It is also seen that with decreasing acidity the slopes of the initial sections of the oxidation curves are lowered (Figure 7). Thus it seems that both the chalcocite-covellite transformation and the subsequent covellite leaching without sulphate formation (reactions that consume acid) diminish in rate with decreasing acidity. The slopes of the curves for leaching at 0.25M and 0.1M acid indicate that sulphate formation

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becomes important after some time has elapsed, perhaps when the sulphur producing reaction is nearly stopped because of rising pH or liquid sulphur stifling.

The oxygen consumption curves for 6 hours of leaching chalcopyrite in 4M, 1M and 0.25M acid (Figure 8) are comparable to the curves of Figure 7 for the first 2 1/2 hours of leaching chalcocite.

The 4M curve shows the lowest final oxidation rate indicating the highest degree of stifling by sulfur. The curve for leaching in 1M acid has the greatest final slope probably because it has the highest sulphate formation (Table 3). It may be that as a result of the slow leaching rate of chalcopyrite the curve at 0.25M acid may be the lowest of the three curves and show a moderate amount of sulphate in solution after six hours but a longer leaching time would lead to more rapid oxygen consumption and a much higher percentage production of sulphate. See, for example, the chalcocite curve (Figure 7) for the same acidity.

8. Oxygen Pressure Variation

From the oxygen consumption curves of Figure 12 and the oxidation rates plotted against oxygen pressure on Figure 13, it is suggested that the rate of both the chalcocite-covellite transformation and the covellite leaching reaction are dependent on the pressures of oxygen in the reaction vessel. The experiments are inadaquate for any relationship between oxygen pressure and reaction rate to be postulated; however, if a Langmuir adsorption isotherm applies, it seems that at below the pressure of 80 psi the adsorption of oxygen on the mineral is incomplete and that the reaction rates would be of first order in oxygen pressure. The dependence of leaching rates on the pressure of oxygen as found here justifies the plotting of log (rate/press 0_2) versus 1/T for Arrhenius plots.

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9. Temperature Variation

The activation energy obtained by plotting log (Rate/PO₂) versus 1/T is approximately 1.8 Kcal/mole for the primary stage of leaching chalcocite (Figure 12). This low activation energy indicates that the reaction rate is probably controlled by diffusion, either as part of the cathodic reaction, ie., diffusion of oxygen or protons through a liquid boundary layer, or the diffusion of cuprous ions through the chalcocite lattice. Jost reports an activation energy for the diffusion of cuprous ions in chalcocite as approximately 1 Kcal/mole⁽³²⁾; another source assigns a value of about 5 Kcal/mole to this⁽²⁴⁾.

The cathodic reaction is similar for both stages of chalcocite leaching but may exhibit an entirely different rate for each stage. It is reasonable to expect that the cathodic reaction rate is proportional to and greatly enhanced by the arrival of cuprous ions at the surface of the mineral since the cuprous ions in solution oxidize rapidly to cupric and will reduce adsorbed oxygen in doing so. There is evidence for the occurance of this for the leaching of chalcocite in ferric solutions⁽¹²⁾. When the chalcocite-covellite transformation is complete the cathodic reaction must take place on the covellite surface without the aid of cuprous ions and may occur at a rate slow enough to control the rate of the whole process. If the chalcocite-covellite transformation is rate controlled by diffusion through a liquid boundary layer, the transformation rate should increase with agitation.

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The activation energy of 11.4 Kcal/mole for the secondary stage of leaching (Figure 13) can be considered to be that for the dissolution of covellite. This value is comparable with that of 11.7 Kcal/mole reported elsewhere for the activation energy for the leaching of covellite ⁽¹⁴⁾. These values are greater than can be expected for a liquid phase diffusion controlled process. When consideration of the dependence of rate on oxygen pressure is taken into account, this suggests that the rates of dissolution of transformed covellite are controlled by heterogeneous processes at the surface of the mineral. Such a process could be a part of the cathodic reaction; for example, the adsorption of oxygen on the surface of the mineral, the transfer of electrons to the oxygen, the combination with protons or the desorption of reaction products. A rate controlling step at the surface would infer that the rate of mineral dissociation would be proportional to the initial surface area of the mineral, a conclusion reached by other investigations⁽¹⁷⁾.

It could be that both stages of the leaching of chalcocite are rate controlled by the cathodic Reaction [8] although the apparent activation energies found are widely different. In the initial stage it may be that the chalcocite-covellite transformation is rapid enough to induce the cathodic reaction to speed up to the point were this reaction could be controlled by diffusion, (Both reactions must occur to the same degree). but the subsequent covellite dissolution may be slow enough for diffusion to keep up, making a chemical step the slowest in the whole process.

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When part of the residue of the run at 140°C was washed in carbon disulphide and returned to the autoclave for further leaching, its initial oxidation rate was greater than the final rate of the run from which it came. This is further evidence that molten sulphur coating the mineral surface is responsible for inhibiting leaching at temperatures above the melting point of sulphur.

Figure 14 shows no evidence for more than one step in the oxidation of chalcopyrite. The runs at 125°C and 140°C show stifling of the reaction after a time of leaching.

10. The Catalytic Effect of Cupric Ions

Figure 15 shows that there is probably no catalytic effect on the leaching rate of chalcocite by the addition of cupric ions, but a large increase in the oxidation rate of chalcopyrite especially in the intermediate time period of leaching is observed. The increased oxygen consumption rate of chalcopyrite due to the initial addition of cupric salts, exceeds the amount required for complete oxidation of iron in solution to ferric—an oxidation catalyzed by cupric ions^(9,33,34).

It is tempting to relate the catalytic effect of cupric ions on chalcopyrite oxidation to the well established ferrous-ferric oxidation in solution. However it is difficult to associate the depletion of ferrous ions from solution with increased mineral oxidation, and the ferric content of the solution is kept constant by hydrolysis, thus preventing it also from affecting the leaching rate. A better explanation is probably surface substitution of iron by copper in the mineral lattice,

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with or without superficial transformation to covellite, and the mineral surface may then develop enhanced leaching rates more comparable to covellite. Substitution of iron by copper on iron sulphide minerals is well known in flotation practice^(35,36).

The difference in leaching rates is expected to decrease after some period of leaching because copper from the mineral is available for catalysis as leaching progresses.

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11. Leaching Chalcopyrite

The activation energies for chalcopyrite consumed and sulphate produced are 11.0 Kcal/mole and 16.0 Kcal/mole respectively as found from the Arrhenius plots of Figures 16 and 17. The points on the graph for chalcopyrite leached at 120°C, 125°C and 130°C are ignored because these are believed to be too low as a result of liquid sulphur stifling.

Evidence for the supposition that the rate controlling mechanism is the same for the leaching of chalcocite and chalcopyrite may be construed from the similarity of their activation energies (11.4 and 11.0 Kcal/mole). Their vastly different leaching rates in this case indicate different cathodic area fractions for these two minerals, and therefore, the suggestion that they possess like rate controlling steps leads to the proposition that their cathodic reactions are similar and the slowest step in the process. It was pointed out before that it is thermodynamically favourable for chalcopyrite to convert of covellite during leaching, according to the reaction

$$CuFeS_2 \longrightarrow CuS + Fe^{++} + S^\circ + 2e.$$
[16]

but because of the faster leaching rate of covellite it does not appear in observable amounts. However microareas of covellite may be formed temporarily and cover a certain fraction of the mineral surface in dynamic equilibrium. This covellite may not be massive enough to form a separate phase. Three reactions may occur on the covellite, ie.,

$$CuS + 20_2 \longrightarrow Cu^{++} + S0_4^{-}$$
 [12]

$$CuS \longrightarrow Cu^{++} S^{\circ} + 2e$$
[7]

$$4H^{+} + O_2 + 4e \longrightarrow 2H_2O$$
 [8]

The chemical Reaction [12] and the electrochemical Reaction [7] destroy covellite, whereas, Reaction [8] is the cathodic complement to Reactions [16] and [7] as well as to the reaction

 $CuFeS_2$ $Cu^{++} + Fe^{++} + 2S^\circ + 4e$ [17] which breaks chalcopyrite into its elements.

If the cathodic Reaction [8] is greatly enhanced on the covellite surface, the covellite may constitute a small fraction of the total mineral surface but be responsible for the bulk of the oxygen reduction. When this reaction is rate determining, this theory, therefore, leads to equal activation energies for chalcopyrite and the other three minerals, since the reaction occurs mainly on a covellite surface in all cases. The temporary covellite areas may be cathodic during their life, and when they have disappeared the chalcopyrite surface may again be anodic.

The difference in activation energies for the leaching of chalcopyrite between 11.0 Kcal/mole found here and 23 Kcal/mole found by Warren⁽¹⁴⁾ may partially be due to the following factors: A different temperature range was employed for the two studies--Warren's work being done in a generally higher temperature range. Also, the copper in solution was measured as the rate of reaction by Warren; in this work the weight loss of the mineral was used.

The difference in activation energies may be explained by the chalcopyrite-covellite proposition by reasoning that if the cathodic reaction has an activation energy of 23 Kcal/mole on chalcopyrite and 11 on covellite, and if the net area of covellite on the chalcopyrite shrinks or disappears with increasing temperature, then a rise in temperature would force the main fraction of the cathodic reaction onto the chalcopyrite and an activation energy of 23 Kcal/mole would then be observed at higher temperatures.

At 120°C the wide separation between the two points of chalcopyrite leached (Figure 16) may indicate that stifling by sulphur may or may not occur at this temperature. This is reasonable because the melting point of sulphur is 119°C and the temperature controller caused temperature cycles of ±1°C during its operation.

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Because the activation energy for sulphate production is somewhat larger than that for chalcopyrite leaching an increase in the percentage of sulphate formed would be expected and approximate correlation with this can be seen from Table 9.

That the production of sulphate is not inhibited above the melting point of sulphur may be deduced from the fact that the points above that temperature do not fall below the line on the Arrhenius plot (Figure 17) and also that the scatter for these points is less than that for chalcopyrite leached. Thus the percentages of sulphate produced for temperatures above 120°C increases because the reaction producing sulphate goes on uninhibited whereas the overall reaction producing sulphur is hindered. This is evidence for the occurrence of the two reactions at different surface regions for chalcopyrite leaching, as was also stated for chalcocite leaching.

If the reaction yielding sulphate is chemical in nature it is then expected to occur more or less uniformly on the surface of the mineral. Such a reaction may be the one already described, ie.,

$$CuS + 20_2$$
 $Cu^{++} + S0_4^{=}$ [12]
which would lead to the same sulphate producing reaction for all four
minerals. A chemical reaction for sulphate formation directly on

chalcopyrite is the following:

$$CuFeS_2 + 40_2 \longrightarrow Cu^{++} + Fe^{++} + 2S0_4^{=}$$
 [18]

Alternatively a chemical reaction may occur which produces both sulphur and sulphate, ie.,

$$CuFeS_2 + 5/2 O_2 + 2H^+ - Cu^{++} Fe^{++} + SO_4 + S^\circ + H_2O$$
 [19]

Because the rate of sulphur production is reasonably fast, the reaction may be partly chemical and partly electrochemical. This would require less stringent atomic configurations during the formation of the sulphate radical since all steps of the reaction mechanism need not occur at one location.

If sulphate is formed by an electrochemical process, the total reaction may be split into its cathodic and anodic parts, ie.,

 $8H_2^0 + CuFeS_2 \longrightarrow Cu^{++} + Fe^{++} + 2SO_4^- + 16H^+ + 16e^-$ [20]

In this process the sulphur is required to break up the water molecules in oxidizing to sulphate. Because of the stability of the water molecule and the high configurational entropy required for reaction with water, it is more likely for the sulphur to oxidize with the oxygen dissolved in the solution. This makes the chemical Reactions [12] or [18] more likely.

From the vastly different leaching rates observed for bornite and chalcopyrite it is suggested that the role of iron in these two minerals is not merely chemical but involves the structure of the mineral so as to produce two widely different leaching characteristics. In this respect the part played by iron in this case is parallel to that in pyrite and pyrrhotite ⁽³⁷⁾ - minerals which display two different characteristics in/spite of being composed of the same elements.

CONCLUSIONS

1. The order of leaching rates for copper minerals from the slowest to the fastest was found to be in the order, chalcopyrite, covellite, chalcocite, and bornite.

2. The leaching of chalcocite and bornite can be divided into two steps: first, the transformation to covellite, and second, the dissolution as covellite. No transformations occur in the leaching of covellite or chalcopyrite.

3. The major portion of the leaching of covellite is by non-uniform attack on its surface resulting in the creation of pits.

4. The production of sulphate and elemental sulphur as products of leaching occur by two distinct reactions. Evidence indicates that the reaction yielding elemental sulphur is electrochemical in nature occuring at localized areas on the mineral and that the reaction yielding sulphate is chemical in nature and therefore may occur uniformly on the surface of the mineral.

5. The activation energy for the first stage of the leaching of chalcocite was found to be 1.8 Kcal/mole; the rate was believed to be the diffusion controlled, either in the liquid phase, or by cuprous diffusion in the mineral. The second stage of chalcocite leaching was thought to be controlled by a step in the cathodic reaction mechanism, with an activation energy of 11.4 Kcal/mole. For the leaching of chalcopyrite and the accompanying production of sulphate the activation energies were found to be 11.0 and 16 Kcal/mole.

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6. For the leaching of chalcocite, the percentage of sulphur appearing as sulphate increased with decreasing acidity, being about 14% in 4M and 71% in 0.5M acid. A similar effect is expected for the other three minerals.

7. The presence of cupric ions in solution catalyzes the leaching of chalcopyrite but their effect is not detected in chalcocite.

8. The reaction seems to be about first order in oxygen pressure at lower pressures, although an adsorption isotherm form of dependence is not excluded.

Suggestions for Future Work

This study has uncovered several areas of work which may be usefully followed.

1. It should be determined whether sulphate is formed by an electrochemical or a chemical process. This could be done by using oxygen-18 as the reactant gas. For example for covellite the chemical reaction

 $CuS + 20_2 \longrightarrow SO_4^{=} + Cu^{++}$

would include only oxygen-18 in the sulphate, whereas, the electrochemical reactions

 $8H^{+} + 2O_{2} + 8e^{-} + 4H_{2}O$ CuS + $4H_{2}O - Cu^{++} + SO_{4}^{-} + 8H^{+} + 8e^{-}$

would produce sulphate containing little oxygen-18.

2. To determine whether sulphate is formed from elemental sulphur or from sulphur originating from the mineral radioactive sulphur-35 could be added initially with the mineral and the extent of its oxidation to sulphate during the run may be noted.

3. Tests can be carried out in which an electrical potential is imposed on polished, massive specimens of the mineral during leaching. The effect of this on the leaching rate may elucidate the reaction mechanism.

4. Experiments should be carried out in which the effect of a rising pH value is determined. The experiments done with low acidity and extensive leaching underwent a pH change of several units during the length of the run. The sulphuric acid-sulphate salt system can be used to buffer the solution at low pH values.

5. Any effect of sulphate in the solution on the leaching rate of minerals or on the resulting deportment of sulphur could be checked by experiments in which sulphate is added to the solution initially or removed from solution as it forms by an initial barium chloride addition.

6. The suggestion that chalcopyrite forms covellite during leaching and the effect of this on the sulphate and cathodic reactions merits investigation. It may be possible to detect such covellite on chalcopyrite by low energy electron diffraction. By knowing the rate equations for covellite formation on chalcopyrite and for its dissolution, a mathematical expression for the fraction of surface covered by covellite could be calculated.

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REFERENCES

1.	Liddell D.M., "Handbook of Nonferrous Metallurgy - Recovery of the Metals" McGraw-Hill (1945).
2.	Forward F.A., Trans. Can. Inst. Min. Met. <u>56</u> , 363 (1953).
3.	Vizsolyi A., Veltman H., and Forward F.A., Met. Soc. Conf. <u>24</u> , 326 (1963).
4.	Turchaninov V.V., and Sinakevich A.S., Nauchn. Tr., Irkutsku Gos. Nauchn. – Issled. Inst. Redkikh Metal. <u>11</u> , 301 (1963).
5.	Downes K.W., and Bruce R.W., Trans. Can. Inst. Min. Met. <u>58</u> , 77 (1955).
6.	Vizsolyi A., Veltman H., and Forward F.A., Trans. AIME 227, 215 (1963).
7.	Sherman M.I., and Strickland J.D.H., J. Metals <u>9</u> , 795 (1957).
8.	Forward F.A., and Veltman H., J. Metals <u>11</u> , 836 (1959).
9.	McKay D.R., and Halpern J., Trans. AIME 212, 301 (1958).
10.	Warren I.H., Aust. J. of Appl. Sci. <u>7</u> , 346 (1956).
11.	Jackson K.J., and Strickland J.D.H., Trans. AIME 212, 373 (1958).
12.	Sullivan J.D., Trans. AIME <u>106</u> , 515 (1933).
13.	Thomas G., and Ingraham T.R. (1967) unpublished.
14.	Warren I.H., Aust. J. Appl. Sci. <u>9</u> , 36 (1958).
15.	Veltman H., Pellegrini S., and Mackiw V.N., "Direct Acid Pressure Leaching of Chalcocite Concentrates", paper presented at 95th Annual Meeting of AIME, 1966.
16.	Vizsolyi A., Veltman H., Warren I.H., and Mackiw V.N., "Copper and Elemental Sulphur from Chalcopyrite by Pressure Leaching", paper presented at 96th Annual Meeting of AIME, 1967.
17.	Woodcock J.T., review article, Aust. Inst. Min. Met. Proc. No. 198, 47 (1961).
18.	Gaudin A.M., and Dicke G., Econ. Geol. <u>34</u> , 49 (1939).
19.	Dana E.S., "A Textbook of Minerology", 4th Ed., J. Wiley.

20. Smith O.C., "Identification and Qualitative Chemical Analysis of Minerals", 2nd Ed., D. Van Nostrand Co.

- 21. Vogel I., "A Textbook of Quantitative Inorganic Analysis Theory and Practice", 2nd Ed., Longmans, Green and Co., pp. 401, 407, 518.
- 22. Ingraham T.R., private communications
- 23. Wagner J.B., and Wagner C., J. Chem. Phys. 26, 1602 (1957).
- 24. Pavlyuchenko M.M., Pokrovskii I.I., and Tikhonov A.S., Dokl. Akad. Nauk. Belorussk. SSR <u>9</u> (4) 235 (1965).
- 25. Latimer W.M., "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions", 2nd Ed., Prentice-Hall, Inc. (1952).
- 26. Majima H., and Peters E., private communication.
- 27. Garrels R.M., and Christ C.L., "Solutions, Minerals and Equilibrium", Harper and Row (1965).
- Takeuchi T., and Nambu M., Ganseki-kobutsu-koisho Gakkai-shi <u>36</u>, 33 (1952).
- 29. Edwards A.B., "Textures of the Ore Minerals", 1st Ed., Aust. Inst. Min. Met.: Melbourne (1947).
- Golomzik A.I., Izv. Vysshikh Uchebn Zavedenii Tsvetn. Met. 7 (2) 47 (1964).
- 31. Majima H., and Peters E., "Oxidation Rates of Sulfide Minerals by Aqueous Oxidation at Elevated Temperatures", paper presented at 95th Annual Meeting of AIME, 1966.
- 32. Jost W., "Diffusion", p. 168, Academic Press: New York (1952).
- 33. Huffman R.E., Davidson N., J. Amer. Chem. Soc. 78, 4836 (1956).
- 34. George P., J. Chem. Soc. (London) 280, 4349 (1954).
- Bushell C.H.G., Krauss C.J., and Brown G., Trans. Can. Inst. Min. Met. <u>65</u>, 185 (1962).
- 36. Bushell C.H.G., Krauss C.J., and Brown G., Trans. Can. Inst. Min. Met. <u>64</u>, 177 (1961).
- 37. Hähne H., Doctoral Dissertation, Technishen Universität Berlin (1964).
- 38. Laidler K.J., "Chemical Kinetics", 2nd Ed., p. 304, McGraw Hill (1965).

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APPENDIX

Butte Covellite			CuS Index			
d A°	I/ _{Im}		d	I/ _{Im}		
3.21	30	3	3.220	28		
3.05	70	3	3.048	67		
2.80	90 [.]	2	2.813	100		
2.72	100	2	2.724	56		
2.32	20	2	2.317	10		
2.04	20	2	2.043	7		
1.96	10	1	L.902	25		
1.90	70	1	L.896	75		
1.73	50	1	L.735	34		
1.55	40	1	L.556	37		

X-Ray Diffraction Patterns

Chalcopyrite, Japan		CuFeS2 Index			
	d	I/ _{Im}	đ	I/I _m	
-	3.02	100	3.03	100	
	2.63	5	2.63	5	
	1.87	20	1.865	40	
	1.86	40	1.854	80	
	1.59	20	1.591	60	

Butte Born	ite	Cu ₅ FeS ₄ I	ndex	CuS In	dex
đ	I/ _{Im}	d	I/ _{Im}	d	I/ _{Im}
 3.30	30	3.32	30		
3.16	50	3.16	30		
3.02	10			3.048	67
2.94	20				
2.81	20			2.813	100
2.74	50	2.75	30	2.724	56
2.51	30	2.52	30		
1.94	100	1.94	100		
1.65	5	1.65	10		

Butte Chalcocite		lcocite	Cu ₂ S Index				
	d	I/ _{Im}	d	I/ _{Im}			
	3.40	10	3.412	25			
	3.335	40	3.330	50			
	3.16	10	3.181	75			
	3.07	10	3.051	75			
	2.95	100	2.950	75			
	2.85	10	2.864	50			
	2.65	10	2.665	75			
	2.55	10	2.560	50			
	2.51	10	2.528	75			
	2.39	50	2.401 2.398	100 100			
	2.32	10	2.328	50			
	2.02	10	2.206	50			
	1.96	60	1.972	100			
	1.94	30	1.94	100			
	1.87	70	1.879	100			
	1.80	30	1.795	50			

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	Bornite leached 30 minutes		Cu ₂ S I	Cu ₂ S Index		- lex
	d .	I/ _{Im}	d	I/ _{Im}	đ	I/ _{Im}
<u></u>		40	<i>4</i> 97 .	50		
	4.25	40	4.27	50		
	3.32	10	3.33	50	2	
	3.20	20	2.181	/5	3.220	28
	3.08	20				
	3.04	100			3.048	67
	2.93	50	2.930	75		
	2.80	50			2.813	100
	2.72	40	2.724	75	2.724	56
	1.89 -1.85	100	1.879 1.875	100 50	1.896	75
	1.79	40	1.795	50		
	Bornite leached 6 hours		CuS Index		Cu ₂ S Index	
	d	I/ _{Im}	d	I/ _{Im}	đ	I/ _{Im}
<u> </u>	/. DE	10				
	4.25	10			4.27	50
	3.32	80			3.330	75
	3.21	20	3.220	28	3.181	75
	3.04	100	3.048	67		
	2.93	60	2.930	75		
	2.81	30	2.813	100		
	2.72	30	2,724	56		
	1.90	30	2.724	75	1.908	7.5
	1.07	80	~ • <i>1 ~</i> ~ 7	, ,	1 070	100
	1.01	00			1.012	100
					1.875	50

Chalcocite leached 30 minutes		Cu ₂ S 1	Cu ₂ S Index CuS Inde		ndex	×	
d	I/ _{Im}	d	I/ _{Im}	đ	I/ _{Im}		
3.33	10	3.330	50				
3.20	10	3.181	75	3.220	28		
3.04	50	3.051	75	3.048	67		
2.93	100	2.930	75				
2.80	60.	2.822	50	2.813	100		
2.73	40	2.731	75	2.734	56		
2.42	10	2.401	100				
1.89	60	1.895	50	1.896	75		
1.86	10	1.879 1.862	100 25				
1.80	40	1.795	50				
1.74	20			1.735	34		
1.57	10			1.572	15		
1.55	10			1.556	37		
1.53	20						

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