

THE DISSOLUTION OF COPPER FROM BORNITE, COVELLITE,
AND COPPER CONCENTRATES AT ELEVATED
TEMPERATURES AND PRESSURES

by

Thomas A. Moss

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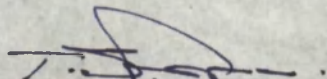
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This thesis has been approved on the date shown below:



T. G. CHAPMAN
Director of Thesis

May 16, 1958

Date

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CHAPTER I - INTRODUCTION

Leaching of Copper Ores

Treatment of oxidized copper ores by leaching increased in importance in 1915 when acid leaching first was used in large scale operations at Chuquicamata, Chile.¹ Smaller scale leaching operations that produced cement copper were used at earlier dates, but such operations were not of major importance.

Most leaching operations are carried out on oxidized or native copper minerals. For ores of these types, sulfuric acid, ammonium carbonate, or cupric-ammonium carbonate are used as the solvent depending upon the specific mineral and type of gangue in the ore. The dissolution of copper from its sulfide minerals entails the prior oxidation of the copper by air or by an oxidizing agent. In the past, at least one leaching operation treating the mineral chalcocite, cuprous sulfide, used acidified ferric sulfate which had the advantage of oxidizing and dissolving the copper with one reagent.

1. Rose, C. A., "Metallurgical Operations at the Chile Exploration Company", Engineering and Mining Journal, February 12, 1916, pp. 321-326.

When employing acid leach methods the copper is recovered from the leach liquor by means of electrolysis or by the use of metallic iron. In the electrolytic method the copper obtained is in the pure state and the equivalent acid from copper sulfate is regenerated. Copper precipitated by metallic iron is not pure and must be refined further using pyrometallurgical methods, and furthermore the equivalent acid is not regenerated.

Recovery of the copper from alkaline leach liquors entails an entirely different method of operation. The complexed copper ion in the leach solution is decomposed by boiling with steam to release ammonia and carbon dioxide and to precipitate the copper as cupric oxide. After separation of the oxide from the barren solution, the copper compound is treated by pyrometallurgical methods to recover the copper.

Commercial Leaching at Elevated Temperatures and Pressures

Leaching at elevated temperatures and pressures has been used commercially in the past for dissolving aluminum, tungsten, and other metals from ores and concentrates. J. T. Mommsen² has described the early use of autoclaves for such leaching operations.

2. Mommsen, J. T., The Dissolution of Chalcopyrite at Elevated Temperatures and Pressures, Thesis, University of Arizona, 1955, pp. 1-11.

Leaching at elevated temperatures and pressures has been applied recently to the recovery of metals from sulphide minerals. Plants which utilize this method now are operating on a commercial basis at the Sherritt-Gordon nickel property at Saskatchewan, Canada,³ and at the Calera Mining Company's cobalt-nickel-copper refinery at Garfield, Utah.⁴ The Sherritt-Gordon operation employs autoclaves for the dissolution of nickel minerals in an ammoniacal pulp followed with reduction by hydrogen of the complex nickel compound to produce metallic nickel powder.

The Garfield plant uses an oxidizing acid leach at elevated temperatures and pressures to convert cobalt and nickel sulfides into the sulfate form. The leach solution is filtered from the residue and is then neutralized using calcium and ammonium hydroxide to precipitate iron and other impurities which are separated in a second filtration step. Copper then is removed from the leach solution by cementation on metallic cobalt. The Garfield plant, originally designed to produce a metallic cobalt-nickel powder by reduction with hydrogen of the ammoniacal solution, now employs a less costly electrowinning process to recover pure cobalt.⁵

3. "Sherritt-Gordon Uses Ammonia Leach for Lyne Lake Nickel-Copper-Cobalt Sulphides", Mining Engineering, June 1953, pp. 577-581.

4. Mitchell, J. S., "Pressure Leaching and Reduction at the Garfield Refinery", Mining Engineering, November 1955, pp. 1093-1095.

5. "Continuous Recovery Cuts Cost, Boosts Yield", Chemical Week, January 11, 1958, pp. 68-69.

Experimental Work on Leaching of Copper
Minerals at Elevated Temperatures and Pressures.

In recent years considerable experimental work in the leaching of copper sulphide minerals employing elevated temperatures and pressures has been conducted at the Southwest Experiment Station of the United States Bureau of Mines. The studies were initiated in 1954 when J. T. Mommsen⁶ studied the dissolution of copper from chalcopyrite. Using a Parr rocker-type pressure reactor it was found that chalcopyrite could be oxidized at elevated temperatures and pressures and the solvent generated used to dissolve the copper content. Copper extractions of 99 per cent were obtained in one hour at 200 degrees Centigrade using an oxygen partial pressure of 300 pounds per square inch. The principal operating difficulty was corrosion of the equipment in the vicinity of valves and gaskets.

J. C. Tverberg⁷ continued the experimental work on the pressure leaching of chalcopyrite. Tverberg used an equalized pressure chamber impeller type autoclave to minimize the effects of corrosion encountered by Mommsen and to improve agitation of the pulp. Copper extraction of 97 per cent was obtained in 10 minutes at 200 degrees Centigrade using an oxygen partial pressure of 100 pounds per square inch with an impeller speed of 500 revolutions per minute which was equivalent to a peripheral speed of 261.7 feet per minute. Results of the experiment work using

6. Mommsen, op. cit., pp. 35-37.

7. Tverberg, J. C., The Dissolution of Chalcopyrite at Elevated Temperatures and Pressures, Part II, Thesis, University of Arizona, 1956, pp. 71-73.

air instead of oxygen as an oxidant at 600 pounds per square inch gauge pressure showed that a reaction period of six times as great was required as compared to when oxygen was employed.

R. S. Kirby⁸ conducted studies on chalcopyrite and chalcocite using the equalized pressure chamber impeller type autoclave and investigated the influence of such variables as pulp density, particle size, and temperature. The conclusions stated by Kirby are as follows:

Chalcopyrite

1. When using a digestion time of 30 minutes, a pulp density of 7.7 per cent of solids, a temperature of 200 degrees Centigrade, an agitation speed of 1,000 revolutions per minute, and a partial pressure of oxygen of 100 pounds per square inch; the per cent of the copper dissolved increased from 18.73 to 92.35 as the particle size was decreased from minus 35 to minus 325 mesh.
2. By extending the digestion time to 45 minutes, a comparable extraction was obtained from minus 100 plus 150 mesh chalcopyrite as was obtained from minus 325-mesh material when a digestion time of 30 minutes was used.
3. When a pulp density of 33.3 per cent of solids, consisting of a charge of 150 grams of concentrate and 300 milliliters of water was used; an extraction of 80.10 per cent of the copper was obtained using a digestion time of 90 minutes, a temperature of 200 degrees Centigrade, a partial pressure of oxygen of 100 pounds per square inch, and an impeller speed of 1,000 revolutions per minute.

8. Kirby, R. S., The Dissolution of Chalcopyrite and Chalcocite at Elevated Temperatures and Pressures, Thesis, University of Arizona, 1957, pp. 61-64.

4. A maximum of 97.31 per cent of the copper could be dissolved when using a total pressure of 600 pounds per square inch gage, a temperature of 200 degrees Centigrade, a digestion time of 60 minutes, without using a continuous flow of air through the reaction bomb. When a total pressure of 480 pounds per square inch gage was used, it was necessary to maintain a flow of air of 240 liters per hour to obtain a dissolution of 97.92 per cent of the copper. At a total pressure of 360 pounds per square inch, the maximum per cent of the copper dissolved was 11.90 when a flow of air of 240 liters per hour was used.

Chalcocite

1. Using oxygen, water, and chalcocite concentrate as the only reactants, a reaction time of one hour, a temperature of 200 degrees Centigrade, a partial pressure of oxygen of 100 pounds per square inch, an agitation speed of 1,000 revolutions per minute, and a pulp density of 4.76 per cent of solids resulted in an extraction of 35.78 per cent of the copper.
2. When sulfuric acid was added to the charge, 99.78 per cent of the copper was found to be dissolved when a reaction time of 30 minutes, a temperature of 200 degrees Centigrade, a pulp density of 4.76 per cent of solids, a partial pressure of oxygen of 100 pounds per square inch and an agitation speed of 1,000 revolutions per minute were used.
3. Consumption of the sulfuric acid which was added to the charge was found to be 0.63 pound of sulfuric acid per pound of chalcocite when an extraction of 99.16 per cent of the copper was obtained. The theoretical consumption of acid for pure chalcocite was found to be 0.62 pound of sulfuric acid per pound of chalcocite.
4. When pyrite was added in place of acid, the maximum per cent of the copper extracted was found to be 98.57 per cent when 0.67 pounds of pyrite was added per pound of chalcocite. All of the other variables were the same as when acid was used except that the pulp density was 8.3 per cent of solids.

5. When temperatures of less than 150 degrees Centigrade and a digestion time of less than 3 hours were employed using a pulp density of 4.76 per cent of solids, and an agitation speed of 1,000 revolutions per minute, the maximum per cent of the copper extracted was found to be 81.62. Using a time of 30 minutes, 97.80 per cent of the copper was extracted when using a temperature of 186 degrees Centigrade. Using a digestion time of 7 minutes and a temperature of 200 degrees Centigrade, an extraction of 98.07 per cent of the copper was obtained.
6. As the agitation speed was decreased below 650 revolutions per minute, the extraction of the copper decreased rapidly from the vicinity of 99 per cent when a time of 30 minutes, a temperature of 200 degrees Centigrade, and a pulp density of 4.76 per cent of solids were used.
7. Extractions in the neighborhood of 99 per cent may be obtained when using a pulp density of 25.9 per cent of solids, a time of 45 minutes, a temperature of 200 degrees Centigrade, an agitation speed of 1,000 revolutions per minute and a partial pressure of oxygen of 100 pounds per square inch. Solutions with a copper concentration of 20.34 per cent of copper were formed when a pulp density of 25.9 per cent of solids was used.
8. The partial pressure of oxygen, when using pure oxygen as the reacting gas, had no influence on the dissolution rate of the chalcocite when partial pressures of oxygen greater than 25 pounds per square inch were used.
9. Particle size in the range of 35 to minus 325 mesh had very little influence on the dissolution rate of the chalcocite.
10. The average oxygen consumed by the reaction was found to be 0.64 gram per gram of chalcocite. The consumption varied from 0.56 to 0.73 gram of oxygen per gram of chalcocite.
11. The time required to obtain extractions of greater than 99 per cent of the copper was found to be approximately six times as long when using air as when using oxygen with all other conditions being the same.

It was the object of the experimental work described in this paper to complete the study on the leaching at elevated temperatures and pressures of copper sulfide minerals by experimental work with bornite and covellite.

It was also the objective of this paper to undertake experimental work on the leaching of cement copper and commercial copper concentrates.

CHAPTER II
MATERIALS, EQUIPMENT, AND EXPERIMENTAL PROCEDURES

Bornite Concentrates

The bornite used in the tests was hand picked from specimen grade material obtained from the Magma Copper Company, Superior, Arizona. The material used for most of the tests was dry crushed, wet ground, and the bornite separated by flotation from an alkaline pulp using ethyl xanthate collector and methylisobutylcarbinol frother. A partial chemical analysis of the concentrate follows:

<u>Constituent</u>	<u>Per Cent</u>
Copper	64.73
Iron	9.3
Sulfur	24.1
Zinc	0.7
Insoluble	0.2
	<u>99.03</u>

A sizing analysis of the product is given below:

<u>Size, Mesh</u>	<u>Weight, Per Cent</u>
Minus 100 plus 150	3.0
" 150 " 200	7.3
" 200 " 270	9.2
" 270 " 325	7.3
" 325 " 20 *	61.2
" 20 *	12.0

* Microns

Another concentrate of the mineral also was prepared by wet grinding the dry crushed bornite to minus 35-mesh and floating by the procedure outlined above.

This concentrate was screened to produce different sized fractions between 35 and 270 mesh for tests to determine the influence of particle size on the dissolution rate of bornite. Assays of the various sized products are given below:

Size, Mesh	Assays, Per Cent				
	Copper	Iron	Sulfur	Zinc	Insoluble
Minus 35 plus 65	64.05	9.26	21.9	0.2	0.5
" 65 " 100	63.27	9.30	24.3	0.15	1.0
" 100 " 200	63.68	9.13	24.1	0.2	1.0
" 200 " 270	63.67	9.18	23.6	0.3	1.1

Covellite Concentrate

A small specimen of relatively pure covellite, obtained from the Geology Department of the University of Arizona, was used for the tests involving covellite. The specimen was dry crushed and dry ground in a porcelain mortar. The ground material was sized and the individual sizes were concentrated with a Frantz Isodynamic Magnetic Separator which yielded bornite, pyrite, and covellite as separate products. The individual minerals were separated by making use of characteristic magnetic susceptibilities. The bornite exhibited the highest susceptibility or paramagnetism and pyrite the least. The sample of covellite thus obtained assayed as follows:

<u>Constituent</u>	<u>Per Cent</u>
Copper	66.32
Iron	0.7
Sulfur	30.0
Insoluble	0.5
	<u>97.52</u>

A sizing analysis of the covellite is given below:

<u>Size, Mesh</u>	<u>Weight, Per Cent</u>
Minus 65 plus 100	1.5
" 100 " 200	59.3
" 200 " 325	39.2

Commercial Copper Concentrates

Typical copper flotation concentrates of Arizona were obtained from the Magma Copper Company, Superior; the Old Dick Concentrator of the Cyprus Mines, Incorporated, Bagdad; the Bagdad Copper Corporation, Bagdad; and the Lavender Pit Concentrator of the Phelps Dodge Corporation, Bisbee. A partial chemical analysis of each concentrate was as follows:

	Per Cent					Ounces Per Ton	
	Copper	Iron	Zinc	Sulfur	Insoluble	Gold	Silver
Magma	24.72	24.85	0.2	31.1	8.6	0.11	4.5
Cyprus	26.68	24.96	10.0	32.6	0.9	0.01	3.05
Bagdad	33.63	19.19	0.3	27.5	15.1	-	-
Phelps Dodge	16.09	32.59	-	41.76	6.2	-	-

A screen analysis of each concentrate gave the following results:

Size, Mesh	Weight, Per Cent			
	Magma	Cyprus	Bagdad	Phelps Dodge
Plus 65	0.6	-	6.2	0.4
Minus 65 " 100	3.0	0.4	13.6	2.4
" 100 " 150	4.9	0.4	17.8	7.4
" 150 " 200	7.2	1.4	14.0	10.2
" 200 " 270	7.6	3.0	8.6	9.6
" 270 " 325	7.2	17.8	7.4	13.0
" 325 " 20 *	59.7	67.4	24.6	50.2
" 20 * " "	10.0	9.6	7.8	6.8

* Microns

The mineral analysis of the different concentrates was made by microscopic examination of polished briquette surfaces of the concentrates with a reflecting microscope.

The principal copper mineral of the Magma concentrate was chalcopyrite which was associated with minor amounts of pyrite, quartz, bornite, siderite, specularite, sphalerite, and sporadic grains of chalcocite and covellite. The gangue particles of quartz and siderite contained numerous inclusions of chalcopyrite and pyrite which were approximately 1 to 5 microns in diameter.

The Cyprus concentrate was composed predominantly of chalcopyrite with minor amounts of sphalerite, chalcocite, bornite, covellite, pyrite, quartz, and galena. The larger portion of the minerals were free, but there was some interlocking between the chalcopyrite and sphalerite in the coarser grains.

The Bagdad concentrate was composed of about equal amounts of chalcopyrite and chalcocite-covellite intergrowth with lesser amounts of pyrite, quartz, and sporadic grains of feldspars, calcite, and muscovite. Most of the chalcopyrite grains were partly altered to chalcocite along the cleavage and fracture planes.

Examination of the Bisbee concentrate showed that it was composed principally of pyrite with some chalcocite, covellite, bornite, chalcopyrite, sphalerite, quartz, and altered feldspars. Some of the pyrite particles were partly rimmed with thin coatings of chalcocite and covellite.

Cement Copper

A sample of Lavender Pit cement copper precipitate was obtained from the Phelps Dodge Corporation, Bisbee, Arizona. A partial chemical analysis of the precipitate follows:

<u>Constituent</u>	<u>Per Cent</u>
Copper	80.02
Iron	5.16
Sulfur	0.58
Lead	0.55
Zinc	0.20
Tin	0.46
Nickel	0.03
Insoluble	1.40

A sizing analysis of the precipitate is given below:

<u>Size, Mesh</u>	<u>Weight, Per Cent</u>
Plus 65	22.4
Minus 65 " 100	7.2
" 100 " 150	0.6
" 150 " 200	13.0
" 200 " 270	6.0
" 270 " 325	4.4
" 325 " 400	4.0
" 400 " 20 *	17.8
" 20 *	22.6

* Microns

Pyrite Concentrate

A flotation concentrate of pyrite was prepared from a mineral sample obtained from G. H. Roseveare of the Arizona Bureau of Mines. The specimen was dry crushed, wet ground, and the pyrite was separated by flotation from a slightly alkaline pulp using ethyl xanthate collector and methylisobutylcarbinol frother.

A chemical analysis of the minus 325 plus 20 micron fraction of the product is given below:

<u>Constituent</u>	<u>Per Cent</u>
Copper	0.05
Iron	46.4
Sulfur	52.3
Zinc	1.1
Insoluble	0.1
	<u>99.95</u>

Autoclave

The experimental work was performed in the autoclave designed by Tverberg⁹ which is shown in Figure 1. The autoclave was a two-chamber type which equalized the pressure of the impeller shaft packing gland and therefore minimized leakage through the packing. The packing consisted of a graphite and oil impregnated asbestos material wound around the impeller shaft and pressed between two cones of the packing gland. All components which were subjected to corrosion were constructed of type 316 stainless steel. The volume of the reaction chamber was 2.1 liters and the pulp was agitated by a 2-inch diameter downward pitch impeller driven by a 1/12 horsepower, variable speed, electric motor. An electric generator-tachometer was connected to the motor to indicate the speed of the impeller. Both pressure chambers were fitted with valves for the introduction of compressed gases and the bleeding of

9. Tverberg, op. cit., pp. 6-40.

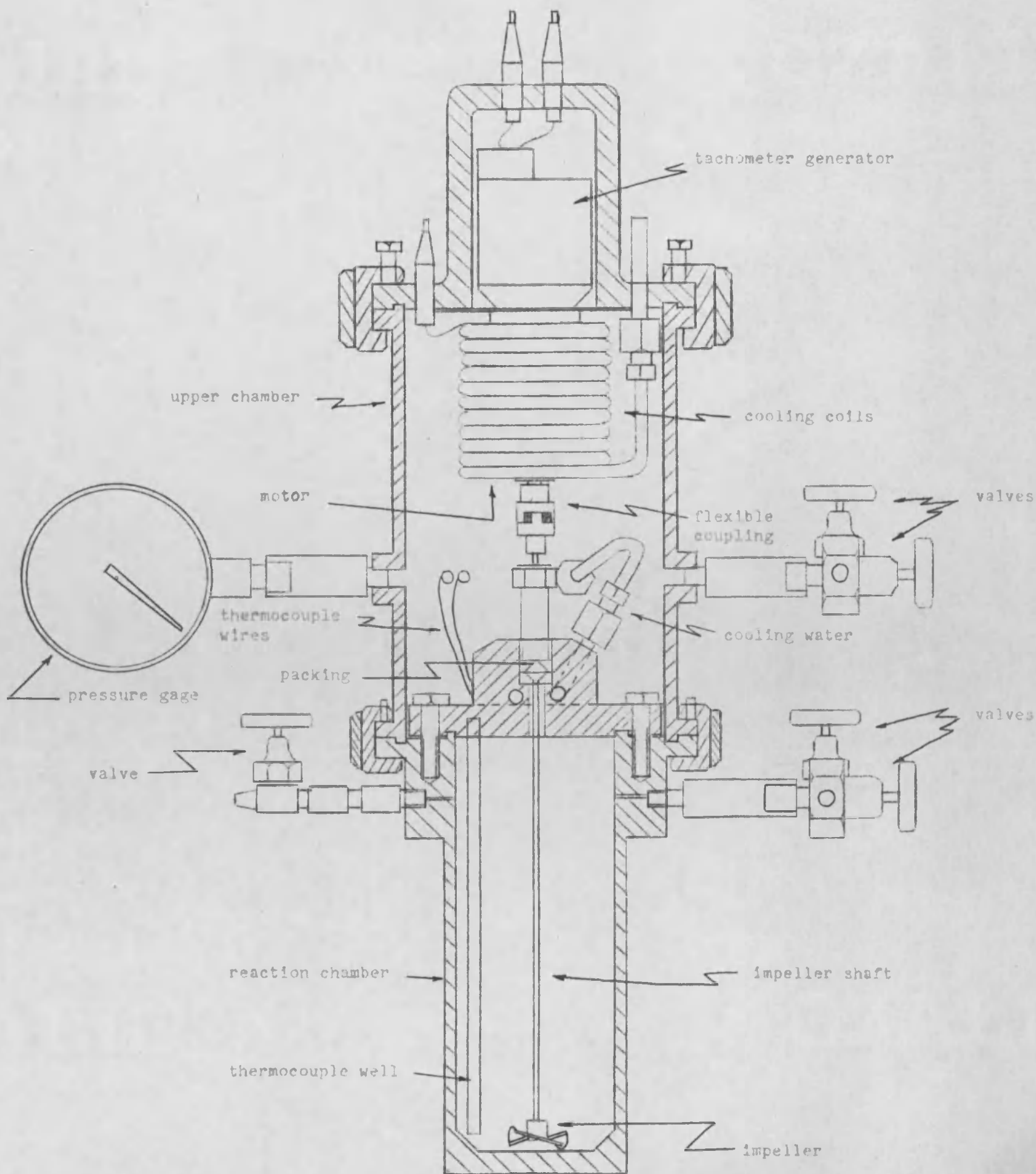


Figure 1. Assembled Autoclave (scale 1:3)

gases from the pressure chambers. Each chamber was equipped with a pressure gauge and a safety valve for protection against excessive pressures. A detailed description of the autoclave was given by Tverberg.

Accessory equipment to the autoclave included a 1,000-watt electrical heating unit, separate rheostats for controlling the heating unit and the impeller motor. The temperature of the reaction chamber was measured with an alumel v.s. chromel thermocouple connected to a Wheelco Model 330 potentiometer. The thermocouple extended inside the reaction chamber and into the reacting solution. A gas metering cylinder was used to determine the amount of gas introduced into the reaction chamber. The cylinder was fitted with a pressure gauge, inlet and outlet valves, and a thermometer. Gas, bled from the reacting chamber, was measured by a "Precision" Wet Test Meter manufactured by the Precision Scientific Company.

Analytical Procedures

Standard analytical procedures were used for determining copper, iron, sulfur, nickel, chromium, zinc, gold, silver, lead, and molybdenum, contents of the solutions and residues.¹⁰

10. Scott, W. W., Standard Methods of Chemical Analysis, Volume I, ed. by N. H. Furman, D. Van Nostrand Company, Inc., 1939, pp. 370, 473, 908, 619, 291, 1060, 835, 512, 589.

A modified method of Keyes¹¹ was used to determine the sulfuric acid content of the leach solutions. The method was as follows: potassium iodide was added to the sample until the solution turned a clear dark brown color and sodium thiosulfate then was added dropwise until the solution turned colorless. Several drops of bromophenol blue indicator were added and the solution was titrated with a standard solution of sodium hydroxide until the first permanent blue color appeared.

The waste gases were analyzed for oxygen by means of an Orsat apparatus and the pH of the leach solutions were measured by an electric Beckman pH meter.

Standard Test Procedure

A 20-gram charge of concentrate was placed into the reaction chamber of the autoclave with 400 milliliters of distilled water to form a slurry which had a pulp density of 4.76 per cent of solids. After the autoclave was assembled oxygen was introduced at a partial pressure of 50 pounds per square inch gauge and then discharged to the atmosphere. This purging procedure was repeated three times to assure a substantially pure oxygen atmosphere in the reaction chamber.

With all valves closed the autoclave then was heated to a temperature of about 185 degrees Centigrade with intermittent agitation to prevent sintering of the concentrate. At this temperature oxygen at a partial pressure of 100 pounds per square inch was charged into the reaction chamber and continuous agitation was

11. Keyes, N. A., Innovations in Copper Leaching Employing Ferric Sulfate-Sulfuric Acid, U. S. Bureau of Mines Bulletin 321, 1930, p. 64.

initiated at 1,000 revolutions per minute or a peripheral speed of 523.6 feet per minute. Immediately after oxidation of the concentrate began, the exothermic nature of the reaction caused the temperature to rise to the desired temperature of 200 degrees Centigrade in a period of about 2 minutes. The reaction was allowed to continue for a period of one hour with the temperature being maintained as nearly as possible at 200 degrees Centigrade and the partial pressure of oxygen at 100 pounds per square inch. After one hour the agitation was stopped and the test considered completed.

The autoclave unit was removed from the heater and was cooled by quenching in water. The waste gases then were bled from the reaction chamber through a precision wet test meter and into a collecting bottle. Analysis of the gases was made by means of an Orsat gas analyser. The consumption of oxygen was calculated by subtracting the weight of oxygen in the waste gases from the weight of oxygen introduced into the reaction chamber. The weight of the oxygen introduced into the reaction chamber was found by the equation $W = 90.89 \cdot Q(P_1 - P_2)/T$ where W was the weight of oxygen in grams; P_1 and P_2 , the initial and final pressures of the gas in the metering cylinder; T , the absolute temperature; Q , the per cent of oxygen in the gas entering the reaction chamber; and 90.89, a constant which was determined by considering the universal gas constant, the volume of the metering cylinder, and necessary conversion factors. The weight of oxygen in the waste gases was determined by the equation $W = 0.513 \cdot PVQ/T$ where W , Q , and T were the same as

described above; P was the barometric pressure in millimeters of mercury; V_r the volume of waste gases; 0.513, a constant arrived at by considering the universal gas constant and the necessary conversion factors.

After the removal of the waste gases the autoclave was disassembled and its contents removed. The leach liquor and leach residue were separated by filtration. The volume of the leach liquor was measured, the pH determined, and a sample taken for analysis. The residue was washed with distilled water until the addition of ammonia to the filtrate failed to indicate the presence of copper. The volume of the wash solution was then measured and a sample taken for assay. The resulting residue was dried in an oven at 100 degrees Centigrade, weighed, sampled, and then assayed.

The extractions given in the tables which follow have been calculated from the assays of the heads and residues. A comparison of the extractions based on the assays of the residues and the extractions based on the assays of the liquors has shown agreement within one per cent of each other.

In the tests which follow any deviation from the standard procedure as described is noted.

CHAPTER III

EXPERIMENTAL WORK ON BORNITE AND COVELLITE

In the experimental work involving the dissolution of copper from bornite, eleven series of tests were made to study the affects of time, additions of acid or pyrite, temperature, degree of agitation, partial pressure of oxygen, particle size, the substitution of air for oxygen, and pulp density. Due to the difficulty of obtaining sufficient covellite only one test was made.

Series I - Influence of Time on the Dissolution of Copper from Bornite Under Oxidizing Conditions.

This series of tests was conducted to determine the effect of time on the dissolution of copper from a slurry of bornite and water using oxygen as the oxidant. The sulfuric acid produced from the oxidation of the bornite supplies the sulfate ion required for dissolution of the copper. The test procedure employed was the same as the standard test procedure previously described. The reaction period was varied from 15 to 120 minutes. The results of the tests are given in Table 1, analysis of the residues and leach solutions are shown in Table 2.

Table 1. - Influence of Time on the Dissolution of Copper from Bornite under Oxidizing Conditions.

Dissolution time, minutes	Copper dissolved, per cent	Free acid, lb. sulfuric acid per lb. bornite	pH of leach solutions
15	28.39	0.0	3.3
30	56.05	0.0	3.5
60	58.83	0.0	3.4
90	59.79	0.0	3.1
120	60.52	0.0	3.3

Table 2. - Assays of Residues and Leach Solutions.

Dissolution time, minutes	Assays of leach liquor grams per liter			Residue assay, per cent		
	Copper	Iron, Fe ^{II}	Iron, Fe ^{III}	Copper	Iron	Sulfur
15	9.30	0.31	0.02	52.22	9.5	16.8
30	17.28	0.03	0.04	41.53	12.7	9.6
60	17.41	0.03	0.02	41.64	13.3	8.0
90	23.89	0.04	0.03	41.64	13.2	7.2
120	19.76	0.29*	0.00	41.22	13.9	7.2

* Cannot be explained by author.

Interpretation of Results:

As was expected, the sulfur content of the bornite was inadequate to supply all of the sulfate ion needed for complete dissolution of the copper. Dissolution of 56.05 per cent of the copper was obtained in 30 minutes and by extending the time to 120 minutes the dissolution was increased to only 60.52 per cent. The consumption of oxygen amounted to 1.70 pounds per pound of copper dissolved and, as noted, in Table 2, free acid was not found in the leach liquors. The maximum amount of iron

found in solution was 2.65 per cent of the total iron of the bornite. The larger portion of the iron formed a hydrated iron oxide which gave the residue a reddish brown color.

Series II - Effect of the Addition of Sulfuric Acid on the Dissolution of Copper from Bornite.

The use of sulfuric acid for supplying sulfate ion, in addition to that formed by the oxidation of sulfur in the charge, was investigated to ascertain if complete dissolution of the copper could be obtained. The standard procedure was followed except that various amounts of acid were added to the charge. The results of these tests are summarized in Tables 3 and 4.

Table 3. - Effect of the Addition of Sulfuric Acid on the Dissolution of Copper from Bornite for a Reaction Period of One Hour.

Sulfuric acid		Copper dissolved, per cent	Free acid, lb. sulfuric acid per lb. bornite	pH of leach liquor	Oxygen consumption lb. per lb. of copper dissolved
lb. per lb. of bornite	per cent of solution				
0.00	0.0	58.85	0.00	3.4	1.70
0.25	1.2	90.43	0.00	2.9	1.51
0.50	2.4	98.96	0.13	1.4	0.92
0.75	3.6	99.35	0.26	1.0	-
1.00	4.8	99.59	0.47	0.7	0.83
1.25	5.9	99.75	0.58	0.6	0.82

Table 4. - Assays of Residues and Leach Liquors.

Sulfuric acid added, lb. per lb. of bornite	Assays of leach liquors, grams per liter			Assays of residues, per cent			
	Copper	Iron, Fe ^{II}	Iron, Fe ^{III}	Copper	Iron	Sulfur as sulfide	Sulfate ion
0.00	17.41	0.03	0.02	41.64	13.3	5.91	7.02
0.25	28.67	0.07	1.60*	19.06	36.5	2.97	4.18
0.50	31.64	0.08	0.09	1.60	47.4	1.77	2.30
0.75	35.13	0.02	0.13	0.87	48.0	1.79	2.56
1.00	31.90	0.02	0.59	0.60	48.9	2.33	3.23
1.25	32.09	0.05	0.60	1.18	27.2*	3.19	3.11

* Cannot be explained by the author.

Interpretation of Results:

The addition of sulfuric acid in the amount of 0.50 pound per pound of bornite was sufficient to give a copper extraction of 98.96 per cent. This is above the 0.20 pound of sulfuric acid per pound of bornite which is theoretically needed and the difference was attributed to an excess of acid needed for equilibrium and to the unavailable sulfate ion which was absorbed by the residue.

Severe corrosion of the 316-Stainless Steel and the odor of hydrogen sulfide were encountered in the tests with acid additions of 1.00 and 1.25 pounds per pound of bornite. Free sulfur was found in the reaction chamber from the latter test.

Series III - Effect of Substitution of Pyrite for Sulfuric Acid on the Dissolution of Copper from Bornite.

The purpose of this series was to determine if the sulfur in pyrite could be converted to the sulfate ion and utilized in the dissolution of the copper.

The standard procedure was used except that various amounts of pyrite were added to the charge. Tables 5 and 6 give the results of this series.

Table 5. - Effect of the Addition of Pyrite on the Dissolution of Copper from Bornite for a Reaction Period of One Hour.

Pyrite added,		Copper dissolved, per cent	Free acid, lb. per lb. of bornite	pH of leach liquors
lb. per lb. of bornite	equivalent acid per lb. of bornite			
0.00	0.00	58.83	0.00	3.4
0.25	0.41	98.33	0.13	1.4
0.50	0.82	97.81 *	0.51	0.8
1.00	1.64	99.00	1.13	0.4
1.25	2.05	99.00	1.23	0.2

* Cannot be explained by author.

Table 6. - Assays of Leach Liquors and Residues.

Pyrite added, lb. per lb. bornite	Assays of leach liquors grams per liter			Assays of residues, per cent		
	Copper	Iron, Fe ^{II}	Iron, Fe ^{III}	Copper	Iron	Sulfur
0.00	17.4	0.03	0.02	41.64	13.3	8.0
0.25	32.4	0.03	0.32	3.26	60.3	2.6
0.50	30.1	0.03	0.27	2.83	60.5	2.4
1.00	31.2	0.13	2.73	0.80	61.3	2.3
1.25	30.7	0.20	6.37	0.46	46.9	10.7

Interpretation of Results:

The acid produced by the oxidation of the pyrite was utilized in the dissolution of the copper from the bornite. The addition of 0.25 pound of pyrite per pound of bornite, which was equivalent to 0.41 pound of sulfuric acid, permitted a copper dissolution comparable to the 0.50 pound sulfuric acid per pound of bornite tested in Series II. The failure to obtain copper extractions greater than 99 per cent was attributed to soluble copper being absorbed by the residue.

When pyrite was added in excess of that necessary to provide the acid to dissolve the copper the ferric ion increased in the leach liquors.

Series IV - Effect of Time on the Dissolution of Copper from Bornite with the Addition of 0.50 pound of Sulfuric Acid per Pound of Bornite.

The purpose of this series was to determine the effect of time on the dissolution of the copper when sulfuric acid was added to supply the deficiency of sulfate ion. Since the addition of 0.50 pound of sulfuric acid per pound of bornite was found to be sufficient to give 98.96 per cent dissolution of the copper in Series II, the same amount was chosen for this series. The standard procedure was followed except that

acid was added to the charge and the reaction time was varied from 7 to 60 minutes.

The results of this series are listed in Table 7.

Table 7. - Effect of Time on Dissolution of Copper with the Addition of 0.50 Pound of Sulfuric Acid per Pound of Bornite.

Dissolution time, minutes	Copper dissolved, per cent	Free acid in leach solution, lb. per lb. of bornite	Added acid consumption, lb. per lb. of bornite	Iron in leach liquors grams per liter	
				Iron, Fe ^{II}	Iron, Fe ^{III}
7	91.80	0.16	0.34	0.25	0.12
15	97.66	0.15	0.35	0.05	0.01
60	98.96	0.13	0.37	0.08	0.09

Interpretation of Results:

Dissolution of the copper from the bornite was rapid in the presence of excess acid and 91.80 per cent of the dissolution of the copper was obtained in 7 minutes. The latter increase in dissolution of copper was probably due to the small percentage of larger sized particles of bornite in the charge. Since the major portion of the reaction must take place at the surface of the particles the larger particles, having a smaller area unit volume than the smaller sized particles, required a longer reaction time.

The larger amount of iron reported in solution during the 7-minute test was believed to be due to the iron sulfide of the bornite reacting with the free sulfuric acid which was present at the beginning of the test. Upon completion of all the tests most of the iron was found in the residue as hydrated iron oxide.

Series V - Effect of Time on the Dissolution of Copper from Bornite with the Addition of 0.25 Pound of Pyrite per Pound of Bornite.

It was the purpose of this series to investigate the rate at which sulfate ion, obtained from the oxidation of pyrite, could be utilized in the dissolution of the copper. The procedure used was the same as the standard procedure except that pyrite was added to the charge and the reaction period was varied between 30 and 120 minutes. The addition of 0.25 pound of pyrite per pound of bornite was shown to be sufficient to give 98.33 per cent dissolution of the copper in Series III and therefore the same amount was employed in this series. This amount of pyrite is equivalent to 0.41 pound of sulfuric acid. Table 8 gives the results of the series.

Table 8. - Effect of Time on Dissolution of Copper with the Addition of 0.25 Pound of Pyrite per Pound of Bornite.

Dissolution time, minute	Copper dissolved, per cent	Free sulfuric acid, lb. per lb. of bornite	pH of leach liquors	Iron in leach liquors	
				Fe ^{II}	Fe ^{III}
30	95.16	0.06	1.8	0.05	0.30
60	98.33	0.13	0.8	0.03	0.27
120	98.32	0.12	0.7	0.03	0.12

Interpretation of Results:

Dissolution of 98.33 per cent of the copper was obtained in a period of 60 minutes. A longer period failed to increase copper extraction or to increase the free sulfuric acid content in the leach liquor.

An increased reaction period lowered the amount of ferric iron in solution from 0.30 gram per liter in 30 minutes to 0.12 gram per liter in 120 minutes. A value of 0.03 gram of ferrous iron per liter in solution appears to be the equilibrium amount under the conditions encountered in the reaction chamber.

Series VI - Effect of Temperature on the Dissolution of Copper with 0.50 Pound of Sulfuric Acid Added per Pound of Bornite.

The purpose of this series was to determine the effect of temperature on the dissolution of the copper from bornite. The standard procedure was followed except that the temperature was varied from 100 to 200 degrees Centigrade and 0.50 pound of sulfuric acid was added per pound of bornite. The results are shown in Table 9.

Table 9. - Effect of Temperature on Dissolution of Copper for a Reaction Period of One Hour.

Temperature, degree Centigrade	Copper dissolved, per cent	Assays of leach solutions, grams per liter		
		Copper	Iron, Fe ^{II}	Iron, Fe ^{III}
100	34.30	10.52	0.01	0.03
150	90.37	29.43	0.06	0.00
200	98.96	31.64	0.08	0.09

Interpretation of Results:

The results indicated that the rate of dissolution of the copper increased with an increase in the temperature. Tests were not made to determine the possibility of increasing the dissolution by employing an extended reaction time at 150 degrees Centigrade.

Series VII - Effect of the Degree of Agitation of the Pulp with 0.50 Pound of Sulfuric Acid Added per Pound of Bornite.

The tests of this series were made to determine the influence of the speed of agitation on the dissolution of copper from bornite for a reaction period of 60 minutes when 0.50 pound of sulfuric acid per pound of bornite was added. The procedure used was the same as the standard procedure except that acid was added to the charge and the speed of agitation was varied from 250 to 1,000 revolutions per minute. The results are shown in Table 10.

Table 10. - Effect of the Degree of Agitation of the Pulp on Dissolution of Copper.

Speed of Agitation		Copper dissolved, per cent	Assay of leach liquors, grams per liter		
Revolutions per minute	Peripheral speed, feet per minute		Copper	Iron, Fe ^{II}	Iron, Fe ^{III}
250	130.9	99.46	29.49	0.07	0.00
500	261.8	98.65	30.34	0.04	0.05
1000	523.6	98.96	31.64	0.08	0.09

Interpretation of Results:

The results indicated that the speed of agitation did not affect the dissolution of copper when acid was added to the charge and a reaction period of 60 minutes was used. The environment in the pulp became more oxidizing with increased agitation as shown by the amount of ferric ion in solution.

Although the results did not indicate an appreciable difference in the dissolution of the copper for different degrees of agitation for a period of 60 minutes, it cannot be assumed that a difference would not appear in a period of 30 minutes.

Series VIII - The Effect of the Partial Pressure of Oxygen on the Dissolution of the Copper with 0.25 Pound of Pyrite Added per Pound of Bornite.

This series had two objectives; the first was to determine the effect of various partial pressures on the rate of dissolution of copper and the second was to determine if higher dissolution of copper could be obtained at relatively low oxygen partial pressures if extended reaction periods were employed. The standard procedure was followed for both objectives except that in the first the oxygen partial pressure was varied using a reaction period of 30 minutes, and in the second the time was varied and the partial pressure of oxygen was held at 25 pounds per square inch gage. An addition of 0.25 pound of pyrite per pound of bornite was made to furnish needed sulfate ion. The results are given in Tables 11 and 12.

Table 11. - Effect of the Partial Pressure of Oxygen on the Rate of Dissolution of Copper.

Partial pressure of oxygen, pounds per square inch gage	Copper dissolved, per cent	Assays of leach liquors, grams per liter		
		Copper	Iron, Fe ^{II}	Iron, Fe ^{III}
25	33.52	11.11	0.36	0.21
100	95.16	29.90	0.05	0.30
200	98.96	32.09	0.05	0.03

Table 12. - Effect of Longer Reaction Periods at an Oxygen Partial Pressure of 25 Pounds per Square Inch Gauge on the Dissolution of Copper.

Time, minutes	Copper dissolved, per cent	Assays of leach liquors, grams per liter		
		Copper	Iron, Fe ^{II}	Iron, Fe ^{III}
30	33.52	11.11	0.36	0.21
60	98.17	31.86	0.10	0.03
120	98.25	31.96	0.03	0.10

Interpretation of Results:

From the results shown in Table 11 it was determined that an increase in partial pressure of oxygen increased the rate of dissolution of the copper. The author offers three possible explanations for this effect on the dissolution. First, an increase in the partial pressure would increase the amount of oxygen dissolved in the pulp making its environment more oxidizing. Second, since the reactions proceeded with a decrease in volume of gases, increased pressure favored the formation of the products due to an application of the LeChatelier-Braun principle of mobile equilibrium. Third, if during the oxidation of the particles of bornite the unreacted sulfides became enclosed in an iron oxide envelope through which the oxygen diffused inward to react with the sulfides, then an increase in the oxygen partial pressure would aid the diffusion process. It seems reasonable to assume that all the factors would apply, each to a varying degree.

The results shown in Table 12 demonstrated that 98.25 per cent of the copper could be dissolved using an oxygen partial pressure of only 25 pounds per square inch gauge and an extended reaction period of 120 minutes.

Series IX - Effect of Particle Size on the Dissolution of Copper with 0.50 Pound of Sulfuric Acid added per Pound of Bornite.

This series of tests was run to investigate the influence of particle size on the rate of dissolution of copper from bornite. The standard procedure was followed except sized bornite was used and 0.50 pound of sulfuric acid was added per pound of bornite. The results of this series are given in Table 13.

Table 13. - Effect of Particle Size on Dissolution of Copper.

Particle size, mesh	Copper dissolved, per cent	Assays of leach liquor, grams per liter		
		Copper	Iron, Fe ^{II}	Iron, Fe ^{III}
Minus 35 plus 65	95.81	30.09	0.08	0.18
" 65 " 100	98.04	31.34	0.01	0.10
" 100 " 200	99.19	31.84	0.03	0.06
" 200 " 270	99.14	31.46	0.04	0.03

Interpretation of Results:

An increase in particle size caused a decrease in the dissolution of the copper. Particles finer than minus 100-mesh showed only a slight change in the dissolution rate of the copper with a reaction period of 60 minutes.

Series X - The Effect of the Rate of Flow of Air on the Dissolution of Copper from Bornite with 0.25 Pound of Pyrite Added per Pound of Bornite.

The purpose of this series was to determine the effect of the rate of flow of air on the dissolution of copper when the oxygen present in air was used as the oxidant. The standard procedure was followed except that a continuous flow of air at a total pressure of 340 pounds per square inch gage was used in the reaction chamber and 0.25 pound of pyrite per pound of bornite was added to the charge. The results of this series is given in the following table for a one-hour digestion period.

Table 14. - Effect of Rate of Flow of Air on the Dissolution of Copper.

Air Flow, liters per hour	Copper dissolved per cent	Assays of leach liquors grams per liter			Free Acid, lb. per lb. of bornite	pH of leach solutions
		Copper	Iron, Fe ^{II}	Iron, Fe ^{III}		
160	95.81	61.42	0.18	0.10	0.12	1.1
320	97.30	73.43	0.20	0.41	0.11	1.1

Interpretation of Results:

A dissolution of 97.30 per cent of the contained copper was obtained in 60 minutes with an air flow of 320 liters per hour. This compares with 98.33 per cent dissolution of copper obtained in Series V where an identical reaction time and amount of pyrite were used with an oxygen atmosphere. The 95.81 per cent dissolution obtained during the test using 160 liters of air per hour compares favorably to the 30-minute test of Series V where 95.16 per cent dissolution of the copper occurred.

The continuous flow of air through the reaction chamber maintained the oxygen concentration at a level which permitted oxidation of the bornite and pyrite to proceed. Additional heat was required during this series since the air introduced into the reaction chamber was at room temperature and there was evaporation of the water into the unsaturated atmosphere of flowing air.

Series XI - Effect of the Pulp Density on the Dissolution of Copper with Additional Sulfur Supplied.

The purpose of this series was to determine if complete dissolution of the copper could be obtained at higher pulp densities thus allowing better utilization of machine capacity and recovery of copper sulfate crystals from saturated solutions. The tests were carried out using the standard procedure except that the pulp density was varied, the necessary additional sulfate ion was furnished, and the filtering operation was modified. Upon quenching of the autoclave, copper sulfate crystallized out of solution and was contaminated with ferric hydroxide which made the separation of the ferric hydroxide by filtration impossible. This obstacle could have been overcome by either reheating the solution or by diluting it. A combination of the two was

finally used. In the tests of this series, the quenched pulp was diluted with 200 to 800 milliliters of boiling water just prior to filtering which proved to be successful in allowing the separation of the ferric hydroxide. Crystals of copper sulfate were recovered from the diluted filtrate upon cooling. The results of this series are given in Table 15 and the solubilities of copper sulfate in water at temperatures up to 130 degrees Centigrade are given in Table 16.

Table 15. - Effect of Pulp Density on the Dissolution of Copper.

Pulp density, per cent solids	Copper dissolved, per cent	Addition of sulfate ion			Assays of leach liquors,* grams per liter		
		Method	Time	Amount, lb. per lb. of bornite	Copper	Iron, Fe ^{II}	Iron, Fe ^{III}
4.8	98.96	acid	start	0.50	31.6	0.1	0.1
10.0	99.63	acid	start	0.50	75.1	0.0	0.4
25.0	96.63	acid	start	0.50	312.7	3.0	29.4
35.0	99.36	acid	start	0.50	476.4	13.9	27.0
35.0	99.16	acid	stage	0.50	475.4	16.2	29.0
35.0**	97.20	pyrite	start	0.25	271.2	4.6	3.5

* Based on original volume of leach liquors.

** Solids included bornite and pyrite.

Table 16. - Solubility of Copper Sulfate in Water.*¹²

Temperature, degrees Centigrade	Copper sulfate, grams per liter	Copper, grams per liter
20	208	83
25	224	89
30	244	97
40	287	114
50	334	133
56	365	146
60	390	155
70	456	182
80	542	216
90	672	268
100	752	300
101	765	305
110	788	311
120	797	317
130	810	323

* Based on calculations from data in International Critical Tables.

Interpretation of Results:

Pulp density failed to produce a pronounced effect on the dissolution of copper for reaction periods of one hour if the deficiency of sulfate ion was furnished by acid.

Analysis of the crystals separated from the saturated solutions showed a pure copper sulfate content of 99.52 per cent for the intermittent acid leach and 99.77

12. Bronsted, J. N., "Solubility of Salts and of Strong Acids and Bases in Water", International Critical Tables, Vol. IV, ed. by E. Washburn, McGraw-Hill Book Company, Inc., New York, 1928, p. 222.

per cent for the pyrite substitution. To avoid dilution of the leach liquors it was suggested that a heated pressure filter chamber be used for the separation of the ferric hydroxide from the pregnant liquor. If this equipment were used up to 72 per cent of the copper theoretically could be recovered as the sulfate when the filtrate was cooled to 50 degrees Centigrade as indicated quantitatively in Table 15.

As the pulp density was increased the high initial acid concentration caused severe corrosion whereas the intermittent addition of the acid reduced the corrosion and the substitution of pyrite for acid remedied it completely.

When the deficiency of the sulfate ion was furnished by the oxidation of pyrite the indicated dissolution of the copper was 1.96 per cent lower than when sulfuric acid was used at the same pulp density. The author believes that the lower extraction when the pyrite was used was partially due to the time lag in the formation of acid from pyrite and partially due to the absorption of soluble copper sulfate by the comparatively large amount of ferric hydroxide formed from the pyrite.

The high increase of iron in solution might be explained by the action of the strong initial sulfuric acid upon the mineral to form sulfates and hydrogen sulfide before oxidation started.

Series XII - Effect of Elevated Temperatures and Pressures of the Dissolution of Copper from Covellite.

Although a series of tests was planned for the experimental work on covellite sufficient pure covellite could not be obtained for more than one test. The test was made with the addition of 0.25 pound of sulfuric acid per pound of covellite to insure an excess of sulfate ion in solution. The standard procedure was followed except that

the weight of the covellite was of necessity limited to 9 grams and the reaction period was 120 minutes. The results of the test are given in Table 17.

Table 17. - Effect of Elevated Temperatures and Pressures on the Dissolution of Copper.

Dissolution time, minutes	Copper dissolved, per cent	Assay of leach liquors, grams per liter		
		Copper	Iron, Fe ^{II}	Iron, Fe ^{III}
120	96.03	12.16	0.04	0.04

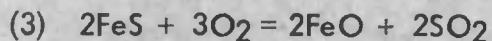
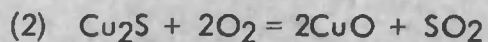
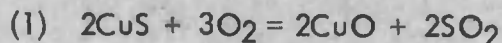
Interpretation of Results:

Dissolution of 96.03 per cent of the copper was obtained in 120 minutes thus showing that covellite was susceptible to leaching at elevated temperatures and pressures. This dissolution was achieved in the absence of an appreciable amount of ferric sulfate. It is the author's belief that the failure to produce higher dissolution of copper was due to mechanical losses inherent to a batch operation. It is quite possible that the reaction time of this test was excessive and the same dissolution might have been obtained in a shorter time.

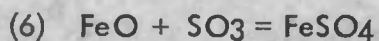
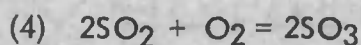
Chemistry of Leaching Bornite at Elevated Temperatures and Pressures

Based on the evidence obtained from the experimental work, the author concluded that the following principal chemical reactions occurred during the dissolution period:

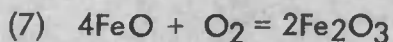
Primary oxidation converted the copper, sulfur, and possibly the iron present in the bornite to the oxides by the reactions described in equations 1, 2 and 3. The bornite, Cu_5FeS_4 , was considered as being a mixture of CuS , $2\text{Cu}_2\text{S}$, and FeS for simplicity in writing the chemical equations.



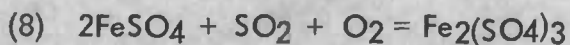
Assuming the presence of a catalytic agent the sulfur dioxide was oxidized to sulfur trioxide and reacted with either the cupric oxide or ferrous oxide to form cupric or ferrous sulfate



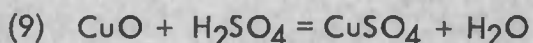
If a deficiency of sulfur trioxide existed in the vicinity of the ferrous oxide, it is possible that the iron would be oxidized to the ferric state and thus account for the presence of ferric oxide in the residue.



If sufficient sulfur trioxide was present, the ferrous sulfate formed was oxidized to ferric sulfate by the following equation:



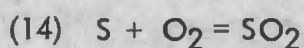
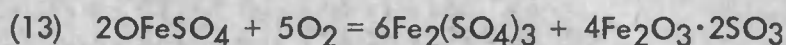
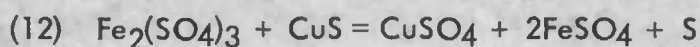
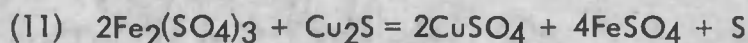
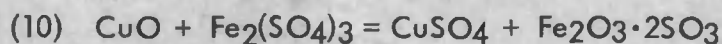
The sulfuric acid added also reacted with the cupric oxide to form cupric sulfate.



The only explanation for the formation of the oxide from ferric or ferrous sulfate is either by decomposition or hydrolysis. A search of the literature failed to reveal any evidence the decomposition proceeded at the temperature of the autoclave or that hydrolysis occurred at the pH of the leach liquors. Furthermore,

information pertaining to the influence of pressure on the formation of ferric oxide was not available.

The presence of ferric sulfate probably aids in the dissolution process by the mechanisms shown in the following equations:



The Alteration of Bornite During Leaching

Microscopic examination under reflected light of embedded polished surfaces of the residues showed that the particles of bornite, Cu_5FeS_4 , upon being subjected to the environment of the autoclave altered to chalcopyrite, CuFeS_2 , and covellite, CuS . This method allowed cross sections of the particles to be observed and it could be seen that the covellite had formed around the periphery of the particle leaving the center composed of bornite with chalcopyrite between the covellite and bornite. At a magnification of 400 diameters the field that appeared to be pure chalcopyrite at lower magnification was resolved to show a Widmanstätten structure where the chalcopyrite had formed along certain preferred crystallographic planes of the bornite, as shown in Figures 2, 3, and 4.

There could be two possible explanations for this structure. First, that interstitial leaching had taken place altering the bornite to chalcopyrite and covellite. Interstitial leaching, however, would have involved the acid solvents

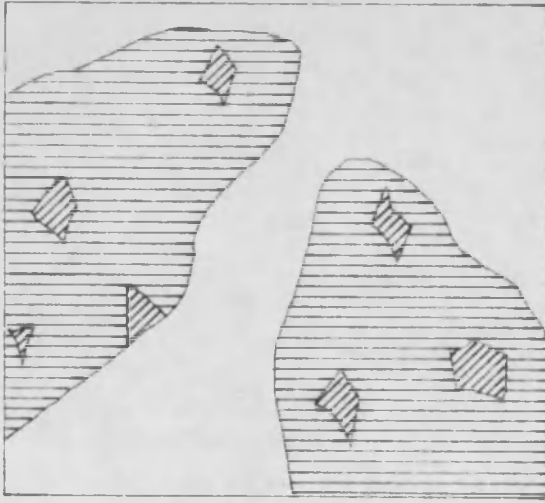


Figure 2 - Original polished surfaces of particles magnified to 400X showing inclusions of chalcocite.



Figure 3 - Polished surfaces of residue particles leached for 30 minutes with acid and oxygen magnified at 100X.

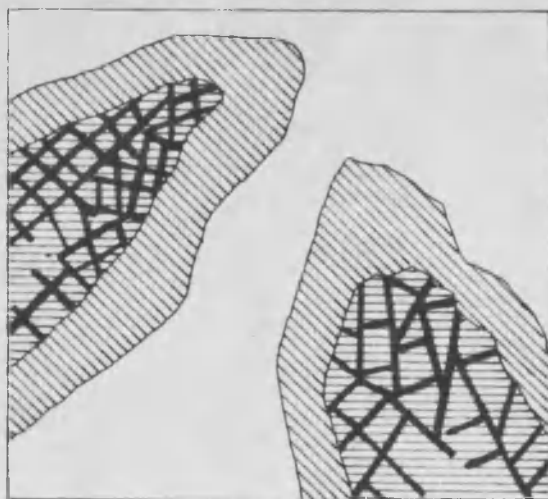


Figure 4 - The same polished surfaces as of Figure 3 magnified to 400X showing the Widmanstätten structure of the chalcopyrite.

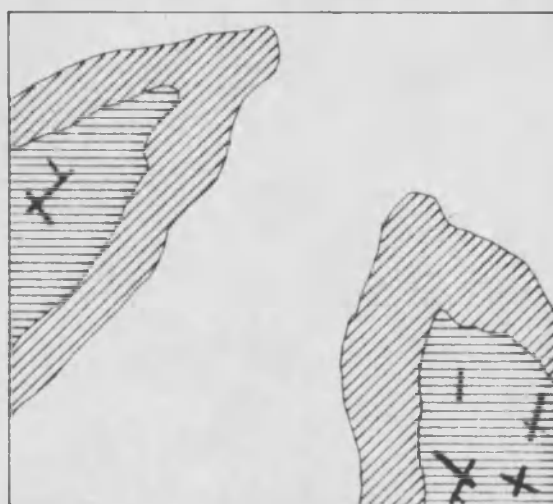


Figure 5 - Polished surfaces of residue particles after being submitted to 200 degrees Centigrade for 120 minutes in a nitrogen atmosphere without the addition of acid solvents.

penetrating into the interstitial spaces of the particles, leaching preferentially, and the migration of the soluble salts to the periphery of the particles by capillarity and diffusion. Since the minerals before and after leaching appeared equally dense this theory was abandoned.

The second explanation involves the diffusion of atoms to form the new minerals. The evidence revealed by the microscope indicated that copper and sulfur atoms migrated from the interior of the particles to the periphery while iron atoms migrated in the opposite direction. In order to determine the effect of temperature, pressure, oxidation, and leaching upon diffusion of the atoms as described a test was conducted using distilled water and sized bornite for the pulp and nitrogen as the atmosphere in the autoclave. A temperature of 200 degrees Centigrade and a nitrogen over pressure of 100 pounds per square inch gauge were employed and the original bornite was minus 35 plus 65 mesh. After a reaction period of two hours the charge was filtered and no evidence of oxidation or leaching was found, although the particles showed signs of abrasion and slight discoloration. The addition of ammonia to the colorless filtrate failed to disclose the presence of copper in solution.

A microscopic examination of particles from the above residue revealed a structure similar to that found in the leached particles. The periphery of the particles was composed of chalcocite, Cu_2S , and the center was predominately bornite with a few lines of chalcopyrite where the Widmanstätten structure had begun to form as shown in Figure 5. The alteration of the bornite to chalcopyrite

and chalcocite was not due to leaching, but a consequence of the temperatures and pressures generated in the autoclave. The diffusion of atoms had taken place.

The presence of an oxidizing and leaching environment appeared to increase the rate of diffusion and to alter the chalcocite to covellite.

Corrosion of Equipment

The environment inside the reaction chamber was inherently corrosive since at elevated temperatures and pressures, the presence of free acid, and in some instances hydrogen sulfide impaired overall corrosion resistance. It was apparent that there were two types of corrosion present during the reaction period; each attacking the stainless steel of the autoclave by its own method. One type was relatively slow and was noticeable only as pits in the stainless steel. The other type progressed rapidly and was visually noticeable after certain tests as a uniform surface corrosion.

Uhlig¹³ stated that for stainless steels corrosion pits begin by a breakdown of passivity at favored nuclei on the metal surface followed by the formation of an electrolytic cell, the anode which is a minute area of active metal and the cathode which is a large area of passive metal. The potential difference characteristics of this cell accounts for a considerable flow of current with the attendant rapid corrosion at the small anode. Increases in temperature, acidity, or oxygen dissolved in the solutions accelerates the rate of pitting. However, Uhlig also stated that the presence of copper sulfate and ferric sulfate, both of which are found in the leach

13. Uhlig, H. H., "Pitting in Stainless Steels and Other Passive Metals", Corrosion Handbook, ed. by H. Uhlig, John Wiley and Sons, Inc., New York, 1948, pp. 165-173.

solutions of this investigation, retarded the pitting of stainless steels.

The afore paragraph probably explained the pits in the 316 stainless steel which were found below the solution line of the reaction chamber. The author also concluded from Uhlig's discussion that the pitting rate was reduced in the latter stages of a test since the amount of copper and ferric sulfate in solution increased as the tests progressed.

The severe corrosion encountered in tests which used a high initial concentration of acid was attributed to hydrogen sulfide. The action of the stronger concentrations of sulfuric acid upon sulfide minerals prior to the beginning of oxidation was to produce hydrogen sulfide gas and soluble sulfates. Binder¹⁴ stated that moist hydrogen sulfide gas will attack stainless steel and that the rate of corrosion is increased when the temperature is raised. In one test which he cited the stainless steel sample was totally converted to sulfide. This corrosion by hydrogen sulfide first became noticeable in the experimental work described in this paper at an acid concentration of 3.6 per cent; therefore the optimum acid concentration, to safely avoid production of hydrogen sulfide, appeared to be between 2.5 and 3.0.

14. Binder, W. O., "Chromium-Iron, Austenitic Chromium-Nickel-Iron, and Related Heat-Resistant Alloys", Corrosion Handbook, ed. by H. Uhlig, John Wiley and Sons, Inc., New York, 1948, pp. 651-652.

CHAPTER IV

DISSOLUTION OF COPPER FROM COMMERCIAL CONCENTRATES AND CEMENT COPPER AT ELEVATED TEMPERATURES AND PRESSURES

Since the experimental work on the dissolution of copper at elevated temperatures and pressures was started at the Southwest Experiment Station of the United States Bureau of Mines in 1954, all work has been performed on relatively pure copper sulfide minerals. This chapter deals with the application of the past three years experience to the dissolution of copper from commercial copper concentrates and cement copper.

Samples of copper concentrates, which are described in Chapter II, were obtained from the Magma Copper Company at Superior, Arizona, the Old Dick Concentrator of the Cyprus Copper Corporation at Bagdad, Arizona, the Bagdad Copper Corporation at Bagdad, Arizona, and the Bisbee, Arizona, Branch of the Phelps Dodge Corporation.

Series XIII - Dissolution of Copper from the Magma Concentrate.

This series of tests was run to determine if the Magma concentrate contained sufficient sulfur for a satisfactory dissolution of the copper and, if so, to determine the per cent dissolutions of the copper for 30 and 60 minute periods of agitation. Since dissolution of gold and silver contained in copper concentrates had not been studied

in previous experimental work it was also an objective of this series to determine the dissolution of gold and silver from the Magma concentrate. The standard procedure was used except that the time was varied. The results of this series are shown in Table 18.

Table 18. - Dissolution of Copper from the Magma Copper Concentrate.

Time, minutes	Copper dissolved, per cent	Assays of leach liquors, grams per liter			Assays of residues, per cent		Free acid lb. per lb. of conc.
		Copper	Iron, Fe ^{II}	Iron, Fe ^{III}	Copper	Iron	
30	99.14	12.18	0.08	0.40	0.43	44.43	0.47
60	99.07	12.32	0.05	0.70	0.44	45.11	0.45

Interpretation of Results:

The Magma copper concentrate contained sufficient sulfur for 99.14 per cent dissolution of the copper during a reaction period of 30 minutes and extending the time to 60 minutes did not improve the per cent of dissolution.

Analysis of a composite sample of residues from five tests of one hour duration disclosed the dissolutions of 4.6 per cent of the gold and 11.1 per cent of the silver present in the concentrate. Considerably more work should be done on the dissolution of gold and silver to verify these figures.

Series XIV - Dissolution of Copper from the Old Dick Concentrate.

The object of this series was to determine the behavior of the Old Dick concentrate when subjected to leaching at elevated temperatures and pressures. The standard procedure was followed except that the time interval was varied and in the latter two tests an addition of 0.25 pound of sulfuric acid per pound of concentrate was made.

Table 19 shows the results of this series.

Table 19. - Dissolution of Copper from the Old Dick Concentrate.

Time, minutes	Copper dissolved, per cent	Acid added, lb. per lb. of conc.	Assays of leach liquors, grams per liter			Free acid, lb. per lb. of conc.
			Copper	Iron, Fe ^{II}	Iron, Fe ^{III}	
15	58.99	0.00	9.71	0.18	0.05	0.02
30	84.58	0.00	14.00	0.08	0.02	0.09
60	94.01	0.00	15.32	0.05	0.08	0.17
120	97.71	0.00	15.52	0.03	0.07	0.24
15	83.30	0.25	10.17	0.18	0.12	0.43
60	99.17	0.25	16.37	0.08	0.37	0.59

Interpretation of Results:

Extended reaction periods without the addition of sulfuric acid from 15 to 120 minutes increased the dissolution of the copper from 58.99 to 97.71 per cent. The longer dissolution period required for this concentrate was explained by the relatively coarse size of the concentrate as shown in Chapter II.

In order to increase the dissolution above 97.71 per cent it was necessary to increase the free acid concentration which was accomplished with the addition of sulfuric acid. The addition of 0.25 pound of acid per pound of concentrate increased the dissolution to 99.17 per cent in a 60 minute period.

Series XV - Dissolution of Copper from the Bagdad Concentrate.

The object of this series was to determine the time required for a satisfactory dissolution of the copper from the Bagdad concentrate. The standard procedure was followed except that the time interval was varied. The results of this series are given in Table 20.

Table 20. - Dissolution of Copper from the Bagdad Concentrate.

Time, minutes	Copper dissolved, per cent	Assays of leach liquors, grams per liter			Assays of residues, per cent		Free acid, lb. per lb. of conc.
		Copper	Iron, Fe ^{II}	Iron, Fe ^{III}	Copper	Iron	
15	99.0	12.95	0.08	0.17	0.62	55.51	0.34
30	98.9	12.59	0.03	0.17	0.71	55.28	0.36
60	98.9	12.57	0.03	0.12	0.71	56.16	0.36

Interpretation of Results:

Referring to Table 20, the rate of formation of the sulfate ion was sufficiently rapid due to the relatively fine material to allow a dissolution of 99.0 per cent of the copper in a 15 minute period. Extending the time to 60 minutes did not improve the per cent of dissolution.

Series XVI - Dissolution of Copper from the Phelps Dodge Concentrate.

The purpose of this series was to determine if the Phelps Dodge concentrate was susceptible to leaching at elevated temperatures and pressures. The standard procedure was followed except that the reaction time was varied. The results of these tests are shown in Table 21.

Table 21. - Dissolution of Copper from the Phelps Dodge Concentrate.

Time, minutes	Copper dissolved per cent	Assays of leach liquors, grams per liter			Assays of residues, per cent		Free acid lb. per lb. of conc.
		Copper	Iron, Fe ^{II}	Iron, Fe ^{III}	Copper	Iron	
7	82.38	6.86	0.40	0.25	3.94	42.74	0.24
15	98.32	7.88	0.64	3.68	0.59	49.27	0.59
60	98.69	7.76	0.72	1.71	0.42	52.28	0.71

Interpretation of Results:

Referring to Table 21, the results showed a dissolution of 82.38 per cent of the copper in 7 minutes. The rapid rate of dissolution for this concentrate was believed to be due to the relative fine material and the presence of considerable pyrite. Extending the time to 15 minutes improved the dissolution of 98.32 per cent and a further increase in time did not materially increase the dissolution.

Series XVII - Dissolution of Copper from Various Concentrates Employing Pulp Densities of 35 Per Cent of Solids.

It was the object of this series to determine the affect of high pulp density upon the dissolution of copper from various copper concentrates. The standard procedure was followed except that a pulp density of 35 per cent of solids was employed. Due to high concentrations of copper in the pregnant solution at this high pulp density the pulp was diluted with boiling water prior to filtering to avoid crystallization of copper sulfate. A reaction time equal to that which allowed high dissolution of copper from the particular concentrate at 4.76 per cent solids was used in this series. Table 22 contains the results of this series.

Table 22. - Dissolution of Copper from Various Copper Concentrates Employing Pulp Densities of 35 Per Cent Solids.

Concentrate	Time, minutes	Copper dissolved, per cent	Assays of leach liquors, *		
			Copper	Iron, Fe ^{II}	Iron, Fe ^{III}
Magma	30	93.91	172	1.5	31.4
Old Dick	30	33.41	83	3.7	22.5
Bagdad	30	94.69	187	4.6	1.5
Phelps Dodge	15	59.82	71	48.2	0.6

* Based on volume of original leach liquor.

Interpretation of Results:

Referring to the results of Table 22, the per cent dissolutions of copper were less by 5 to 40 per cent as compared with equal times of agitation for pulps of 4.76 per cent of solids and also the amount of iron contained in the solutions was considerably higher.

It is probable that due to the higher concentration of copper in the leach solutions at the higher pulp densities the speed of the reaction was reduced. It is also probable that with the amount of oxygen constant and a larger amount of material to be oxidized that the time necessary to obtain the higher dissolutions was increased.

The results also indicated that the concentrates with the finer sizes of grains yielded higher extractions but these higher extractions were not comparable to those obtained at 4.76 per cent solids.

In planning this series of tests consideration was given to maintaining the amount of solid material constant as compared to that used for 4.76 per cent solids. Such charges, however, could not be agitated satisfactorily.

This series was run during the last stages of the experimental work and time was not available for additional tests of longer time periods. It appears reasonable however to expect that satisfactory results could be obtained if longer periods were employed.

Series XVIII - Dissolution of Copper from Various Concentrates Employing a Continuous Flow of Air as the Atmosphere.

The object of this series was to determine if a continuous flow of air could be substituted for commercial oxygen as the oxidizing atmosphere in the autoclave. The standard procedure was followed except that an air flow of 500 liters per hour

at a pressure of 340 pounds per square inch gauge used. The results of this series are given in Table 23.

Table 23 - Dissolution of Copper from Various Concentrates Using an Air Flow of 500 Liters per Hour.

Concentrate	Copper dissolved, per cent	Assays of leach liquors, grams per liter		
		Copper	Iron, Fe ^{II}	Iron, Fe ^{III}
Magma	98.76	37.69	0.38	2.96
Old Dick	84.45	12.94	0.23	0.07
Bagdad	99.00	12.81	0.38	0.57
Phelps Dodge	97.73	18.98	1.55	0.07

Interpretation of Results:

The dissolution of 99.00 and 97.73 per cent of the copper from the Bagdad and Phelps Dodge concentrates respectively were obtained in 60 minutes using an air flow of 500 liters per hour whereas similar dissolutions were previously obtained in one - fourth this time employing oxygen.

The 98.76 and 84.45 per cent dissolutions yielded from the Magma and Old Dick concentrates when air was used were similar to results obtained with oxygen in an agitation period one - half as long.

Series XIX - Dissolution of Copper from Cement Copper.

It was the purpose of this series to determine if copper present in cement copper could be dissolved at a rapid rate when using elevated temperatures and pressures. Also the behavior of the lead, zinc, tin, and nickel from the solder used in the manufacture of the cans upon which the copper was precipitated was to be studied. The standard procedure was followed except that the reaction time was varied and the theoretical

amounts of sulfate ion were provided by the addition of sulfuric acid or pyrite. The results are shown in Tables 24 and 25.

Table 24. - Dissolution of Copper from Cement Copper when Sulphate Ion Was Provided with Pyrite and Sulfuric Acid Addition.

Time, minutes	Copper dissolved, per cent	Reagent added		Assays of leach liquors, grams per liter		
		Kind	Amount lb. per lb. cement copper	Copper	Iron, Fe ^{II}	Iron, Fe ^{III}
7	88.85	Acid	1.23	33.13	0.07	0.08
15	1.27	Pyrite	0.75	0.13	trace	trace
60	65.90	Pyrite	0.75	25.83	0.12	0.03

Table 25. - Assays of Leach Liquor and Residue from the 7 Minute Test Using 1.23 Pounds of Sulfuric Acid per Pound of Cement Copper.

Assays of leach liquor, grams per liter				Assays of Residues, per cent			
Lead	Zinc	Tin	Nickel	Lead	Zinc	Tin	Nickel
Trace	0.05	0.02	0.03	1.73	0.16	0.46	0.01

Interpretation of Results:

The relatively low dissolution of 88.85 per cent of the copper when sulfuric acid was added might have been due to the speed of oxidation of the copper or a deficiency in sulfate ion.

> Referring to the tests in which pyrite additions were made, the very low dissolution of 1.27 per cent in 15 minutes and 65.90 per cent in 60 minutes were probably due to insufficient time for the oxidation of the pyrite and copper to occur and a deficiency of sulfate ion.

It is likely that additional sulfate ion and increased time of agitation would produce satisfactory dissolutions.

Calculations based on the results of Table 25 indicated that 25 per cent of the lead, 80 per cent of the zinc, 75 per cent of the tin, and 75 per cent of the nickel present in the cement copper were dissolved during the reaction period.

Series XX - Dissolution of Copper from a Mixture of Phelps Dodge Concentrate and Cement Copper.

The purpose of this series was to determine if a concentrate which contained excess pyrite could be used in conjunction with cement copper to allow a satisfactory dissolution of the copper in both the concentrate and the cement copper. The mixture contained 10 per cent of cement copper by weight. The tests were carried out using the standard procedure except the reaction time was varied. The results of these tests are shown in Table 26.

Table 26. - Dissolution of Copper from a Synthetic Concentrate Composed of a Mixture of the Phelps Dodge Concentrate and Cement Copper.

Time, minutes	Copper dissolved, per cent	Assays of leach liquors, grams per liter		
		Copper	Iron, Fe ^{II}	Iron, Fe ^{III}
15	94.33	10.47	0.27	0.21
30	97.89	11.48	0.27	0.93

Interpretation of Results:

A dissolution of 94.33 per cent of the copper was obtained in 15 minutes and by increasing the time to 30 minutes a dissolution of 97.89 per cent was obtained.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

The important results of the experimental work which have been described herein have been summarized as follows:

Bornite.

1. Without the addition of acid as a solvent and employing a temperature of 200 degrees Centigrade, a pulp density of 4.76 per cent of solids, an impeller peripheral speed of 524 feet per minute, and a partial pressure of oxygen of 100 pounds per square inch gauge; the dissolution of the copper increased from 28.39 to 60.52 per cent as the period of agitation was increased from 15 to 120 minutes.
2. With the addition of sulfuric acid as the solvent and varying the amounts of sulfuric acid added to the charge up to a maximum of 1.25 pounds of sulfuric acid per pound of bornite the percentage dissolution of the copper increased from 58.85 to 99.75 when an agitation period of one hour, a pulp density of 4.76 per cent of solids, a temperature of 200 degrees Centigrade, a partial pressure of oxygen of 100 pounds per square inch gauge, and an impeller speed of 524 feet per minute were employed.
3. By substituting pyrite for acid in amounts varying up to a maximum of 1.25 pounds per pound of bornite and keeping the other conditions constant the dissolution of copper increased from 58.83 to 99.00 per cent.
4. By varying the reaction time from 7 to 60 minutes and employing the addition of 0.50 pound of sulfuric acid per pound of bornite while maintaining the other conditions constant, the per cent of dissolution of the copper increased from 91.80 to 98.96.

5. Employing 0.25 pound of pyrite per pound of bornite and maintaining the other variables constant, the percentage of dissolution of copper ranged from 95.16 to 98.32 as the reaction time was varied from 30 to 120 minutes.
6. Maintaining a pulp density of 4.76 per cent of solids, an oxygen partial pressure of 100 pounds per square inch gauge, an impeller speed of 524 feet per minute, a reaction period of 60 minutes, and the addition of 0.50 pound of sulfuric acid; the dissolution of the copper increased from 34.30 to 98.96 per cent when the temperature was raised from 100 to 200 Centigrade.
7. Within the range of impeller speeds from 131 to 524 feet per minute the degree of agitation did not appear to affect the percentage of dissolution of the copper when using 0.50 pound of sulfuric acid per pound of bornite, a temperature of 200 degrees Centigrade, and maintaining the other conditions constant.
8. The dissolution of the copper increased from 33.52 to 98.96 per cent as the partial pressure of oxygen was raised from 25 to 200 pounds per square inch gauge when using 0.25 pound of pyrite per pound of bornite and maintaining the other conditions constant. A dissolution of 98.25 per cent of the copper was obtained by increasing the time to 120 minutes and using an oxygen partial pressure of only 25 pounds per square inch gauge.
9. Particles coarser than 100-mesh size decreased the rate of dissolution when using 0.50 pound of sulfuric acid per pound of bornite, a partial pressure of oxygen of 100 pounds per square inch gauge, a temperature of 200 degrees Centigrade, an impeller speed of 524 feet per minute, and a reaction period of 60 minutes.
10. When air additions of 160 and 320 liters per hour at a total pressure of 340

pounds per square inch gauge were substituted for oxygen during tests employing 0.25 pound of pyrite per pound of bornite and the other conditions held constant; dissolutions of 95.81 and 97.30 per cent of the copper were obtained respectively. Similar extractions were obtained with oxygen in 30 minutes.

11. Increases of pulp density up to 35 per cent of solids failed to produce a pronounced affect on the dissolution of the copper for reaction periods of one hour if the deficiency of sulfate ion was furnished by 0.50 pound of sulfuric acid per pound of bornite and the other conditions were held constant.

Covellite.

12. A copper dissolution amounting to 96.03 per cent was obtained in 120 minutes when employing a pulp density of 2.2 per cent of solids, a temperature of 200 degrees Centigrade, a partial pressure of oxygen of 100 pounds per square inch gauge, an impeller speed of 524 feet per minute, and the addition of 0.25 pound of sulfuric acid per pound of covellite. As previously mentioned, the difficulty of obtaining more covellite did not permit additional tests.

Commercial Concentrates.

13. A dissolution of 99.14 per cent of the copper contained in the Magma concentrate was obtained in 30 minutes when using a temperature of 200 degrees Centigrade, a pulp density of 4.76 per cent of solids, an impeller speed of 524 feet per minute, and a partial pressure of oxygen of 100 pounds per square inch gauge.

14. When the time was increased from 15 to 120 minutes, the dissolution of copper from the Old Dick concentrate increased from 58.99 to 97.71 per cent when the other variables were held constant. Using a 60-minute period and the addition of 0.25 pound

of sulfuric acid per pound of concentrate the dissolution increased to 99.17 per cent. This concentrate was more refractory than the others tested due to the coarseness of the material.

15. The Bagdad concentrate yielded a dissolution of copper of 99.0 per cent in 15 minutes without the addition of acid and with other conditions maintained constant.

16. During a reaction period of 15 minutes the Phelps Dodge concentrate allowed the dissolution of 98.32 per cent of the copper with other conditions constant.

17. At a pulp density of 35 per cent of solids, a reaction period of 30 minutes, and the other conditions constant the Magma, Old Dick, and Bagdad concentrates yielded per cent dissolutions of 93.91, 33.41, and 94.69, respectively. The Phelps Dodge concentrate gave a dissolution of 59.82 per cent in 15 minutes. It is quite probable that these dissolutions could be increased by changing variables, especially time.

18. When a flow of air of 500 liters per hour at a total pressure of 340 pounds per square inch was substituted for oxygen the Bagdad and Phelps Dodge concentrates required a time period four fold as long to achieve dissolutions comparable to those employing oxygen. The Magma and Old Dick required only twice as long a period.

Cement Copper

19. Employing the addition of 1.23 pounds of sulfuric acid per pound of cement copper, a temperature of 200 degrees Centigrade, a speed of agitation of 524 feet per minute, a pulp density of 4.76 per cent of solids, and a partial pressure of oxygen of 100 pounds; 88.85 per cent of the copper in the cement copper was dissolved in 7 minutes. When 0.75 pound of pyrite per pound of cement copper was used, 65.90

per cent of the copper dissolved.

20. A mixture of 80 per cent of Phelps Dodge concentrate and 20 per cent of cement copper yielded copper dissolutions of 94.33 and 97.89 per cent in periods of 15 and 30 minutes, respectively, when the other conditions were held constant.

The author believes that the following recommendations will be helpful if further experimental work on copper sulfide minerals is planned.

1. Since the development and use of the new packing gland composed of graphite and oil impregnated asbestos material which was sold under the trade name, GARLOCK number 117, proved to be successful, consideration should be given to the elimination of the upper chamber of the autoclave for ease of operation. The Parr modified autoclave, which did not have the equalized pressure chamber, operated satisfactorily with this packing at pressures of 1,000 pounds per square inch gauge.

2. For the filtering of high copper content pregnant solutions consideration should be given to the design and construction of an accessory pressure filter chamber to permit filtration before crystallization of copper sulfate takes place.

BIBLIOGRAPHY

1. Binder, W. O., "Chromium - Iron, Austenitic Chromium - Nickel - Iron, and Related Heat Resistant Alloys", Corrosion Handbook, ed. by H. Uhlig, John Wiley and Sons, Inc., New York, 1948.
2. Bronsted, J. N., "Solubility of Salts and of Strong Acid and Bases in Water", International Critical Tables, Vol. IV, ed. by E. Washburn, Mc Graw - Hill Book Company, Inc., New York, 1928.
3. Editors, "Continuous Recovery Cuts Cost, Boasts Yield", Chemical Week, January 11, 1957.
4. Editors, "Sherritt - Gordon Uses Ammonia Leach for Lyné Lake Nickel - Copper - Cobalt Sulfides", Mining Engineering, June 1953.
5. Keyes, N. A., Innovation in Copper Leaching Employing Ferric Sulfate - Sulfuric Acid, U. S. Bureau of Mines Bulletin 321, 1930.
6. Kirby, R. S., The Dissolution of Chalcopyrite and Chalcocite at Elevated Temperatures and Pressures, Thesis, University of Arizona, 1957.
7. Mitchell, J. S., "Pressure Leaching and Reduction at the Garfield Refinery", Mining Engineering, November 1955.
8. Mommsen, J. T., The Dissolution of Chalcopyrite at Elevated Temperatures and Pressures, Part I, Thesis, University of Arizona, 1955.
9. Rose, C. A., "Metallurgical Operations at the Chile Exploration Company", Engineering and Mining Journal, February 12, 1916.
10. Scott, W. W., Standard Methods of Chemical Analysis, Volume I, ed. by N. H. Furman, D. Van Nostrand Company, Inc., 1939.
11. Tverberg, J. C., The Dissolution of Chalcopyrite at Elevated Temperatures and Pressures, Part II, Thesis, University of Arizona, 1956.
12. Uhlig, H. H., "Pitting in Stainless Steels and Other Passive Metals", Corrosion Handbook, ed. by H. Uhlig, John Wiley and Sons, Inc., New York, 1948.