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SULFATIZING ROASTING OF A COPPER SULFIDE ORE

by

Walter D. Finnegan

A Thesis

Submitted to the Department of Metallurgy
in Partial Fulfillment of the Requirements
for the Degree of Bachelor of Science in
Metallurgical Engineering

Montana School of Mines

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INTRODUCTION

NATURE OF THE INVESTIGATION:

At present copper sulfide ores are recovered by pyrometallurgical processes. While the recovery of copper from sulfide ores by hydrometallurgical means has long been considered attractive, the impurities, low recovery and mechanical difficulties have kept this process from becoming commercial. The object of such a method is to produce electrolytic copper without having to resort to expensive matte smelting and converting. The process consists of roasting a sulfide ore to form copper sulfate, leaching with dilute sulfuric acid, separation and electrolysis of the pregnant solution. In spite of the simplicity of the process it has not been developed to commercial status, and cannot, at present, compete with pyrometallurgy for the extraction of copper from sulfide ores.

The chief difficulties to be overcome before this process can compete with pyrometallurgy are:

1. Higher extraction than is now possible.
2. Reduction of the iron content in the pregnant solution.
3. Reduction of the amount of ferrites and silicates formed in the roasting operation.
4. A method to recover the gold and silver in the residue from leaching.
5. Divising new roasters to handle the material with little or no mixing effect, and still bring the gases into intimate contact with the particles.

IMPORTANCE OF THE STUDY:

This method of extracting copper from sulfide ores by leaching embraces both pyrometallurgy and hydrometallurgy, but eliminates the more expensive part of the pyrometallurgical process, namely reverbatory and convertor practice. It would also be possible to extract more than one metal from the pregnant solution, e.g. copper and zinc, and therefore, be more flexible than the present pyrometallurgical processes. It would also be possible to treat the ore directly, and since crushing the ore to about one-fourth inch would be the only step, it would eliminate the present need for grinding to minus sixty-five mesh, flotation, thickening and filtration. However, it may be necessary to concentrate by present methods a portion of the ore to enrich the sulfur content of the roaster feed.

PRESENT METHODS:

Copper is extracted from sulfide ores by pyrometallurgy. The first step is crushing and grinding to minus sixty-five mesh. Flotation is then employed to concentrate the copper and to eliminate some of the impurities of the ore. The ore is thickened and filtered to remove part of the contained water. This material is mixed with fluxes, and sent to the roasters.

The principal fluxes used are limestone and silica. Generally this material contains some gold and silver, and the barren fluxes used only when gold-silver ores are not available. While the mention of fluxes may seem irrelevant, it must be remembered that custom smelters derive part of their income from treating such ores, and any process that is to replace present smelter practice must solve not only the major problem, but also many subsidiary problems.

The problem of gold and silver recovery will be treated later, but it is well worth keeping in mind that the recovery of the contained gold and silver may represent the margin between profit and loss.

The material from the mixer is placed on the top hearth of a roaster, generally of the Wedge or Nichols Herreshoff type, and dried. The material is then passed through the roaster for partial elimination of sulfur, arsenic, antimony and bismuth. The chief problem solved by the roaster is to adjust the copper-sulfur ratio to make a suitable feed for the reverberatory furnace.

The calcine is sent to the reverberatory furnaces where the charge is melted, and the liquid metal sulfides collected. The slag is skimmed off, and the copper and iron sulfides are sent to the convertors. Here the sulfides are blown to blister copper. The blister copper is refined, cast into anodes and sent to electrolytic refining. The cathode copper is refined, melted and cast into marketable forms.

The hydrometallurgical process will not be dealt with as thoroughly as pyrometallurgy because the theory and practice will be given later in the paper as it applies to extraction of the copper from sulfide ores by hydrometallurgical means.

The process, in brief, is to bring the ore in contact with the solvent, to separate the residue from the pregnant solution, to purify the pregnant solution and to precipitate the metal. This precipitation may be accomplished by electrolysis or cementation. The advantages, cost and feasibility of these processes will be discussed later. The cathodes are fire refined and cast into marketable forms.

PREVIOUS WORK:

Considerable work has been done on this problem by Mr. E. A. Ashcroft[1] and others, but the great difficulty of mechanical application has not been solved. Briefly the process is roasting of the material in an oxidizing atmosphere to produce the sulfate directly from the sulfide, leaching with dilute sulfuric acid and depositing the copper. Mr. Ashcroft has advanced the following five rules for roasting to obtain maximum recovery:

1. Reactions in roasting proceed primarily and definitely to the formation of sulfates, not oxides, the latter, as well as the sulfur dioxide evolved, being secondary products, formed by deposition of the sulfate. Iron oxide acts as an efficient catalyst in the formation of these sulfates.

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[1] Mr. E. A. Ashcroft: Sulfate Roasting of Copper Ores and Economic Recovery of Electrolytic Copper from Chloride Solutions: <u>Electrochemical Society</u>, v. 68, pp. 23-50, 1933.

2. Iron is probably the only element, or at least the only principal element, which, by reason of the great heat of formation of the higher oxide, Fe_2O_3, is completely converted to oxide in a sufficiently oxidizing atmosphere, yielding the undecomposed acid radical to a basic material such as copper oxide or the basic constituents of the gangue.

3. As a corollary to the preceding statement, iron sulfate is not, as generally assumed, per se decomposed normally at a temperature so far below the decomposition temperature of copper sulfate that a mere roasting at a carefully regulated temperature may be employed to insure complete conversion into soluble copper and insoluble iron.

4. Formation of cupric ferrite, $CuO*Fe_2O_3$, takes place at any temperature above five-hundred and fifty degrees Centigrade when the oxides of copper and iron are brought in juxtaposition; at seven-hundred degrees such formation is prohibitively rapid.

5. The ordinary rabbled furnace is inimical to complete conversion into copper sulfate on account of the following reactions:

   $$CuSO_4 + CuS + O_2 = 2CuO + 2SO_2$$

   A similar reaction occurs under reduction conditions:

   $$CuSO_4 + CO = CuO + SO_2 + CO_2$$

While Mr. Ashcroft is not alone in this field, nearly all other investigators have based their procedures on his work, or have followed the same lines of reasoning. For this reason only Mr. Ashcroft's theory will be compared with that of the oxidization-sulfate process.

OBJECT:

The object of this paper is to prepare soluble copper from copper sulfide ore by roasting. This process differs from Mr. Ashcroft's in that the sulfides are roasted to their oxides, CuO and Fe_2O_3, and the copper converted to the sulfate by bringing a mixture of sulfur dioxide and oxygen into intimate contact with the oxide.

HISTORY:

The first use of copper by man is lost in antiquity, but Egyptian records show copper being used for many purposes as early as 1300 B.C. It is believed that gold and silver were the first metals used by man (discounting the possibility of man using the iron-nickel alloys found from meteorites), and the use of copper followed shortly thereafter. Copper was more abundant and had superior mechanical properties to either silver or gold, and therefore, was more valuable to early man. With the discovery of copper-tin alloys, progress was advanced, and man entered the Bronze Age. While copper was important to early man, with the passing of time it has grown so vital that industry, as we know it, could not exist without it. Some metals can replace copper, but because of their poorer properties, e.g. electrical conductivity, they are not as well suited to the requirement as copper.

During the Roman Era, Cyprus produced much of the world's copper, and from this came the name copper.

PROPERTIES:

Color.....Red
Specific gravity 8.91 to 8.95
Very malleable
Ductile
High tenacity (second only to iron)

Melting point 1100° C
Boiling point 2000° C
Specific heat 0.0899 at 0° C
Cofficient of linear expansion per 1° C is 0.001869
Electrical conductivity 96.4 at 13° C
Somewhat resistant to corrosion.

ECONOMICS AND STATISTICS:

During the year 1945 the production of copper in the United States of America showed a steady decline from 70,114 tons[2] in January to 58,174 short tons in December, with the total for the year being 77,894 short tons. This represented a drop of 20 percent from the 1944 total. The world production showed a decline of 15 percent below that of 1944, but the copper recovered as secondary metal showed an increase over the 1944 production. To meet the future world demand for copper, new and cheaper processes of mining and metallurgy must be evolved or the price of copper will rise so as to make its use prohibitive to industry.

ORES AND METALLURGY:

The chief sulfide ores of copper are:

Chalcocite.........	Cu_2S
Covellite..........	CuS
Chalcopyrite.......	$CuFeS_2$
Bornite............	Cu_5FeS_4
Enargite...........	Cu_3AsS_4
Tetrahedrite.......	Cu_3SbS_3

The two chief means of extracting copper from its ores are:

Sulfide ores by pyrometallurgy
Oxidized ores by hydrometallurgy

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[2] *Britannica Book of the Year*, 1947.

USES:

The uses of copper are many and varied. The following table is from the *Encyclopedia Britannica* showing the estimated consumption of copper in short tons for the year 1934.

Electrical manufactures	101,000
Telephone and telegraph	18,000
Light and power lines	40,000
Wire cloth	4,600
Other rod and wire	40,000
Ammunition	12,200
Automobiles	63,300
Buildings	36,000
Castings n.c.s	36,000
Clocks and watches	1,800
Coinage	900
Copper-bearing steel	2,100
Fire-fighting apparatus	1,000
Radiators, heating	2,400
Radio receiving sets	12,600
Railway equipment	2,600
Refrigerators	16,200
Shipbuilding	3,700
Washing machines	1,900
Water heaters, household	1,500
Other uses	42,000
Manufactured for export	25,500
Total	465,000
Use in pounds per person	7.36
Shipment by refineries	**417,110**

The importance of copper to industry depends chiefly upon the following properties that copper exhibits.

1. High electrical conductivity.
2. Resistance to corrosion.
3. Thermal conductivity.
4. Forms alloys with many metals.
5. Many of these alloys show good corrosion resistance, e.g. brass.
6. Has a high scrap value.

LABORATORY APPARATUS AND PROCEDURE

APPARATUS:

The apparatus used in this investigation was as follows:

1. Electric furnace. (See Plate One)
2. Five ampere rehostat.
3. Oxygen tank.
4. Pressure reducing valve.
5. Manometer.
6. Sulfur dioxide tank.
7. Air pump.
8. Sulfur burner with glass condenser.
9. Thermocouple.
10. Various chemicals, tubing, etc.

PROCEDURE:

The sulfides were roasted in an assay furnace with a plentiful supply of air. This material was cooled and put on reserve. A test for sulfur was made on the calcine, and showed no sulfur to be present. A small portion, about five grams, was used for each of the sulfatizing roasts. The temperature, sulfur dioxide concentration and oxygen concentration were varied to determine their effect on the formation of copper sulfate.

The sulfatized material was leached for twenty-four (24) hours in a water leach or a five percent sulfuric acid leach. Fifty milliliters of water or acid were used per 0.5 grams of ore. The water soluble copper and acid soluble copper were run on each sample by the short iodide process. Iron was determined by the dichromate method, and sulfur was determined as barium sulfate. The detailed chemical procedure is given in the Appendix.

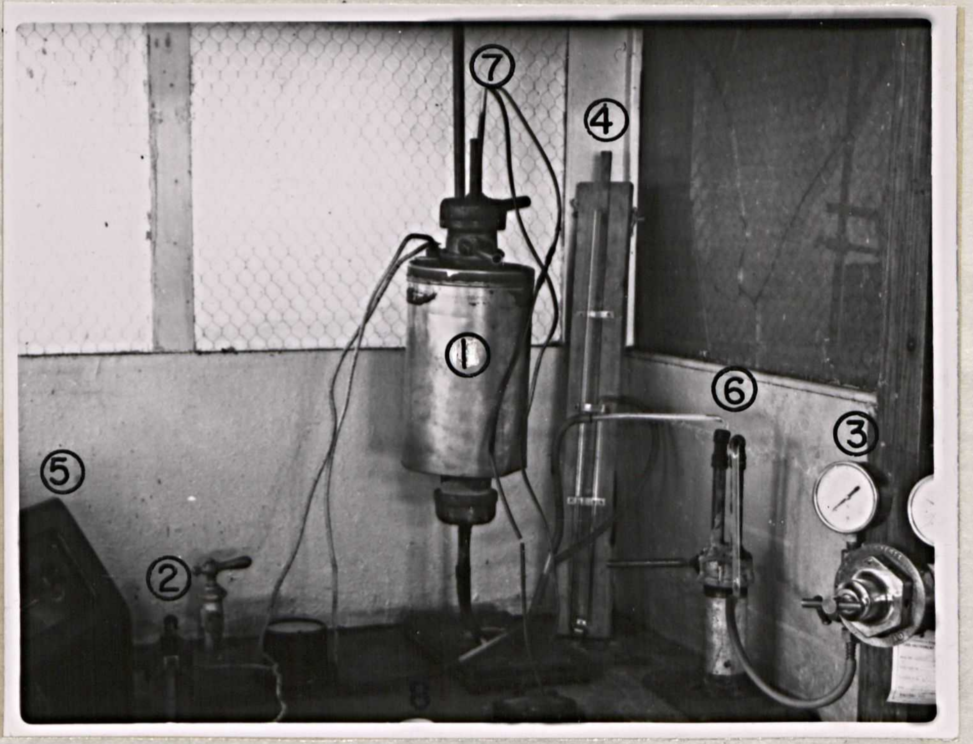


Plate I. Photograph of Labratory Equipment

1. Electric Furnace
2. Five Ampere Rehostat
3. Preassure Reducing Valve
4. Manometer
5. Air Pump
6. Sulfur Burner
7. Thermocouple
8. Crucible

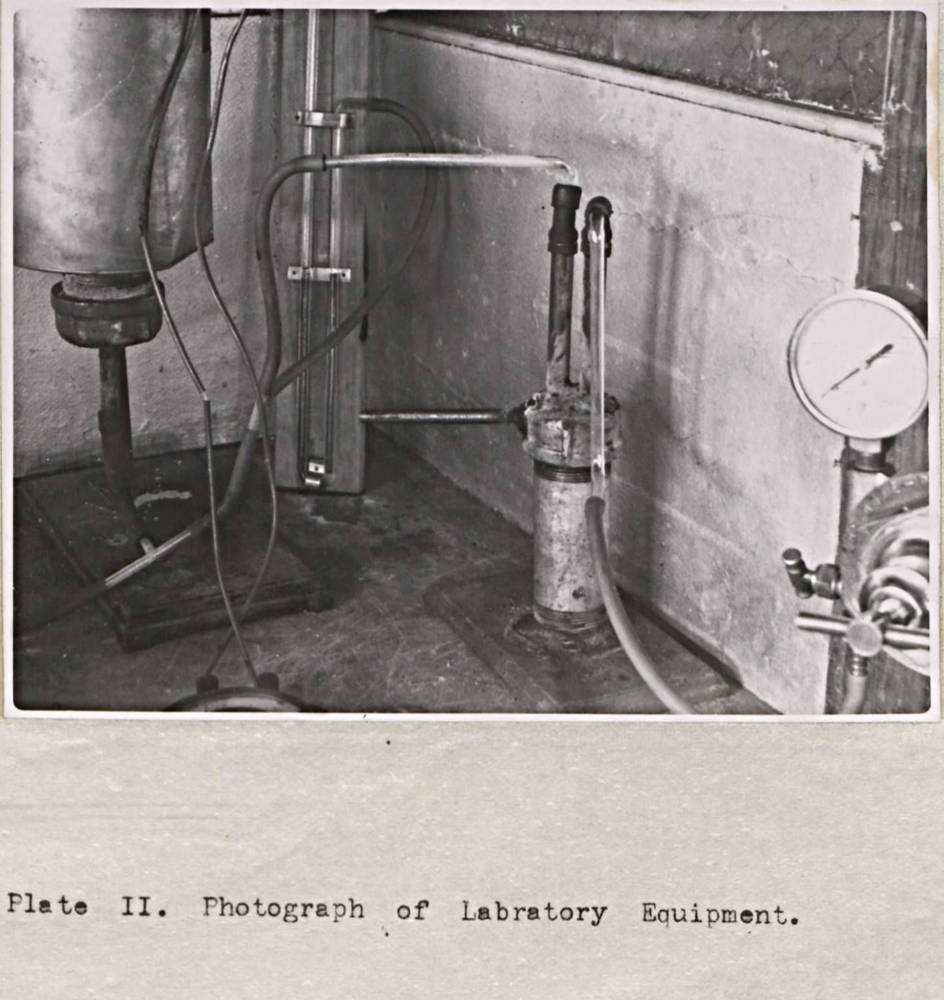


Plate II. Photograph of Labratory Equipment.

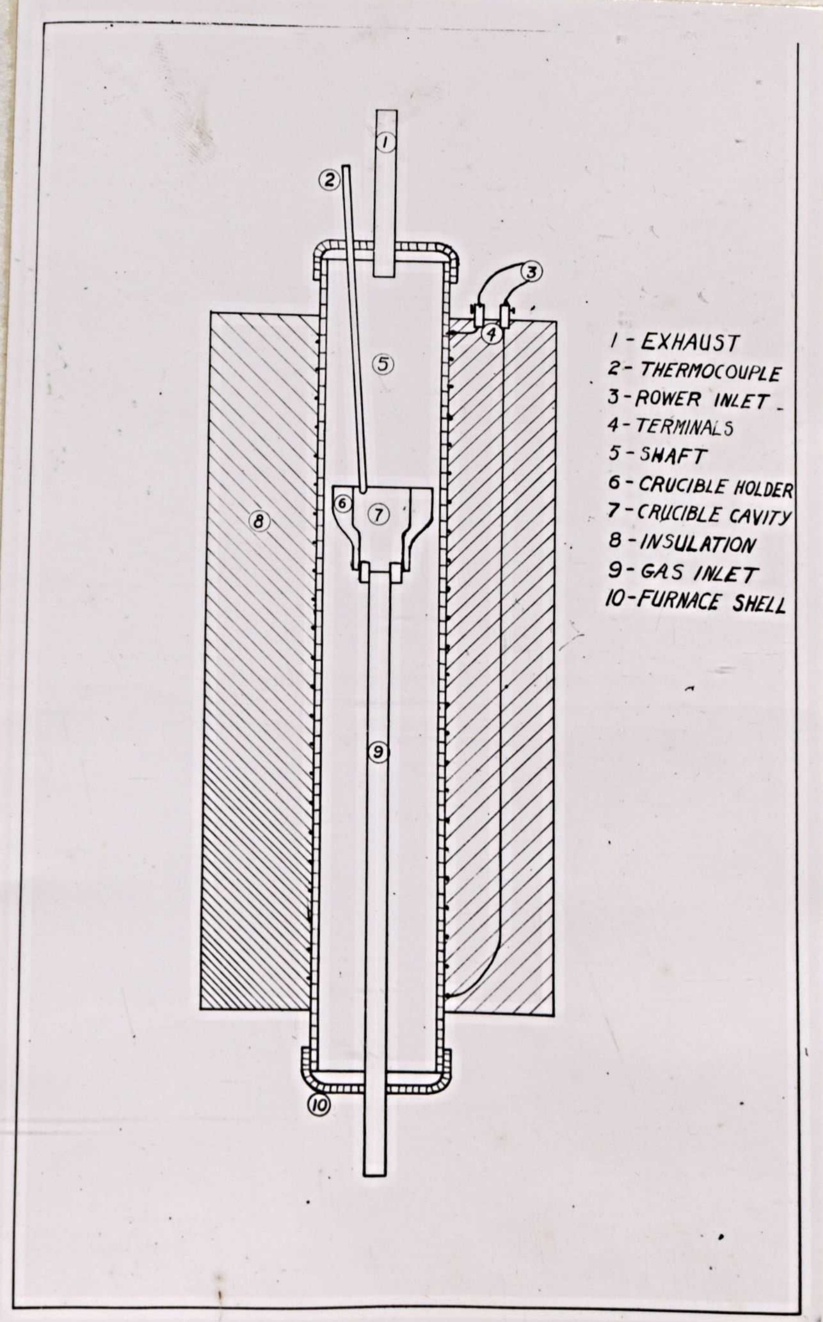


Plate III. Sectional View of Furnace

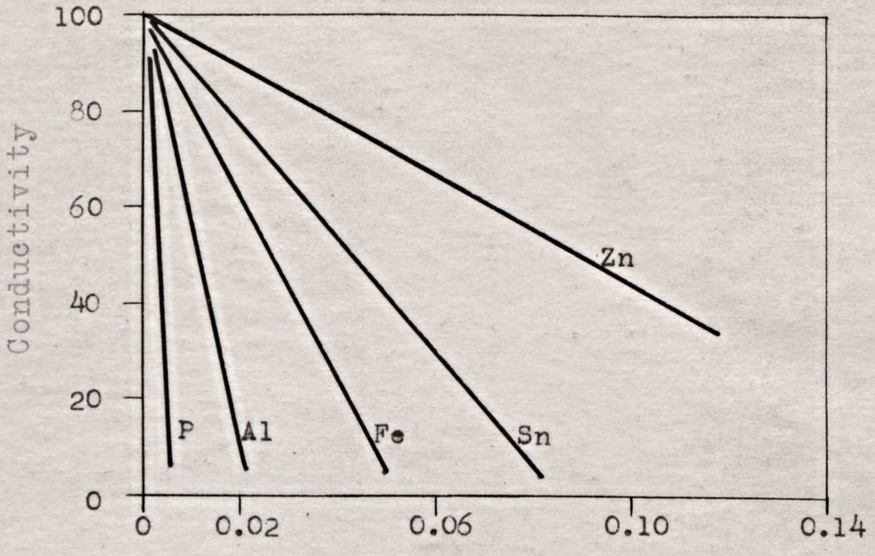
THEORETICAL CONSIDERATIONS

THEORY:

Copper sulfide ores are insoluble in dilute sulfuric acid, but cupric oxide and copper sulfate are readily soluble in a dilute sulfuric acid solution. Therefore, it is necessary to have the copper present as cupric oxide or copper sulfate to obtain a high extraction of copper. It is also important to have the solution as free as possible of impurities. These impurities may be divided into two groups; those that will deposit with the copper, and those that will attack the deposited copper. The first group is characterized by arsenic, and less than one percent of this impurity will greatly reduce the conductivity of the copper (Plate 2). The second group is characterized by iron. A small amount of iron present in the ferric state will reduce the current efficiency (Plate 3). For these reasons we must strive to keep the solution as free from impurities as possible.

ROASTING:

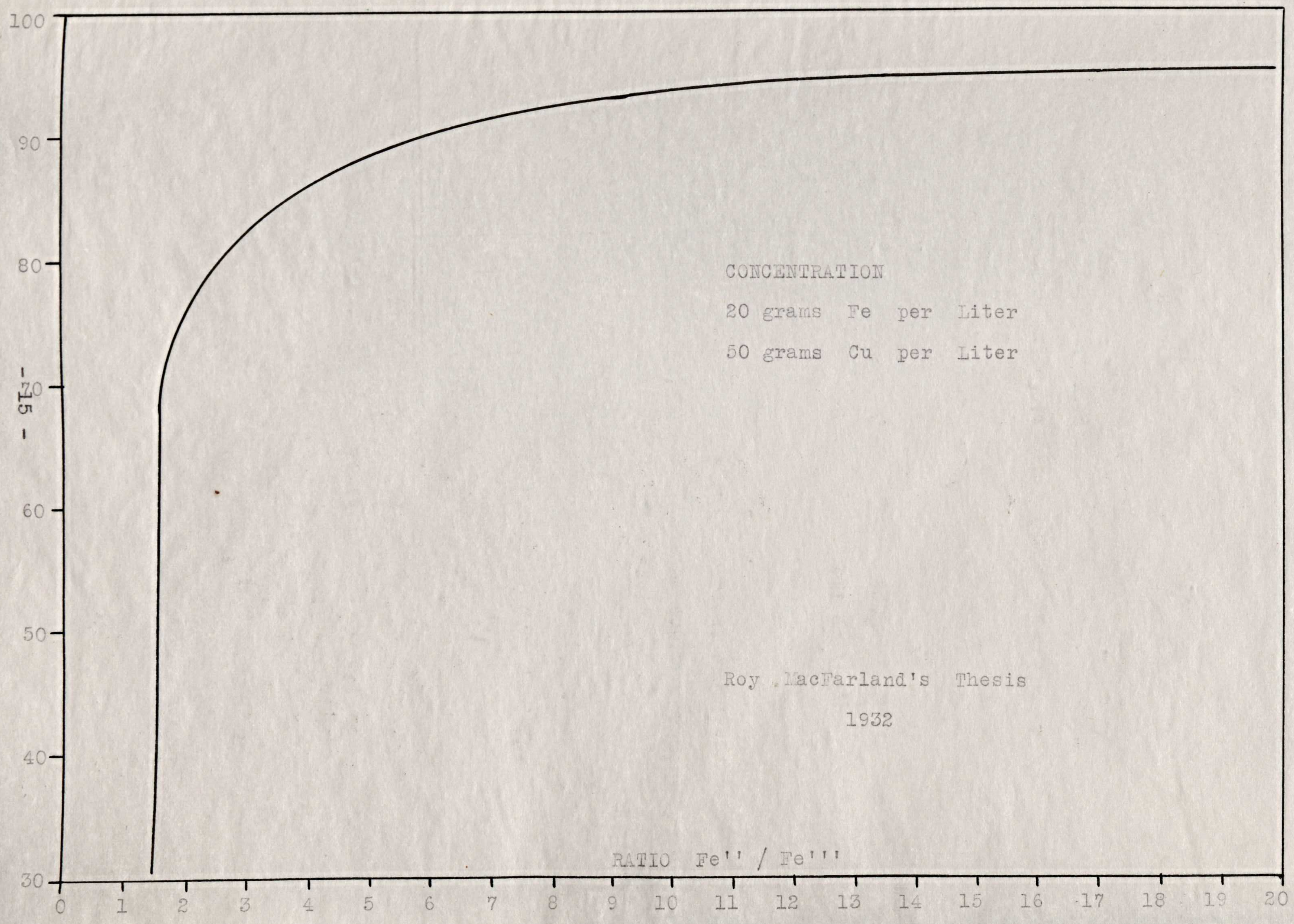
The aim of roasting is to make all of the copper soluble, and to make all of the iron insoluble. Since the most soluble form of copper is cupric oxide or copper sulfate, and the most insoluble form of iron is ferric oxide, a strong oxidizing roast is essential. Therefore, the first step is an oxidizing roast to convert all of the copper and iron to their higher valent oxides. This oxidization takes place in two stages.



Percent of impurity

Figure 1. Effect of Impurities on the Conductivity of Copper

For other impurities see Metallurgy of Copper, Hofman and Hayward, McGraw- Hill Book Company, New York, New York (1924).



CONCENTRATION

20 grams Fe per Liter

50 grams Cu per Liter

Roy MacFarland's Thesis

1932

In the first stage the copper sulfide is oxidized to cuprous oxide, and the iron sulfide to ferrous oxide. A small amount of ferrous and cupric sulfate may also form as well as a magnetic iron oxide, probably $FeO*Fe_2O_3$. The reactions for this phase are:

$$FeS_2 + 2\tfrac{1}{2}O_2 = FeO + 2SO_2$$

$$2CuS + 2\tfrac{1}{2}O_2 = Cu_2O + 2SO_2$$

$$2FeCuS_2 + 5\tfrac{1}{2}O_2 = 2FeO + Cu_2O + 4SO_2$$

Part of the arsenic and antimony are driven off as their oxides during this and the second stage of roasting.

$$2AsS + 3\tfrac{1}{2}O_2 = As_2O_3 + 2SO_2$$

The second stage is a demagnetizing period, and its purpose is to convert the ferrous iron and the cuprous oxide to their higher valent states. From the reaction

$$2CuO + SO_2 = Cu_2O + SO_3$$

it is evident that all sulfides, the source of the sulfur dioxide, must be absent before the oxidization of this stage is completely underway. The temperature of this portion of the roast is carried out at nine-hundred and eighty degrees Fahrenheit, which is not critical but which should be approximated. If the temperature is allowed to rise much higher than this (980°F.), copper silicates will form, and these are insoluble in dilute sulfuric acid. As the calcine progresses through this stage, the magnetic properties disappear, and the material becomes a brick red when cooled. The reactions of this stage are:

$$2FeO + 1\frac{1}{2}O_2 = Fe_2O_3$$

$$Cu_2O + \frac{1}{2}O_2 = 2CuO$$

The third phase of the roast is to convert part of the charge to a sulfate. Since the reactions possible are

$CuO + SO_2 + \frac{1}{2}O_2 = CuSO_4$ Delta H = -68.5 Kcal.

$Fe_2O_3 + 3SO_2 + 1\frac{1}{2}O_2 = Fe_2(SO_4)_3$ Delta H = -225.2 Kcal.

it seems reasonable to assume that both the iron and copper will form sulfates. Since the iron would be soluble if left as a sulfate, it must be decomposed. Since the sulfate of iron cannot exist above four-hundred and eighty (480) degrees Centigrade, and copper sulfate does not begin to decompose until the temperature exceeds six-hundred and seventy (670) degress Centigrade, it appears that the iron could be decomposed to its oxide by a simple control of temperature . This would leave the copper as the desired sulfate, and the iron as the desired oxide. However, the decomposition product of ferric sulfate is not ferric oxide, but is a form of basic ferric sulfate ($Fe_2O_3*2SO_3$) which will not decompose into ferric oxide below a temperature of one-thousand and forty (1040) degrees Fahrenheit. Within this temperature range, 1040-1238, the iron will decompose to its ferric oxide, and the copper will remain as, and even form, the desired copper sulfate. Therefore, the iron acts as a semi-catalytic agent. The reaction may be represented by the equation:

$$Fe_2(SO_4)_3 + 3CuO = Fe_2O_3 + 3CuSO_4$$

MISCELLANEOUS

GOLD AND SILVER:

Gold and silver may be recovered by the cyanide process, and, according to Mr. Ashcroft, the residual copper is not a cyanacide.

ELECTROLYTIC DEPOSITION VS. CEMENTATION:

Assuming a 90 percent anode efficiency there is regenerated 1.5 tons of sulfuric acid per ton of copper deposited at the cathode. If iron is used to deposit the copper, all of this acid is lost. It also takes about two and one-half pounds of iron to deposit one pound of copper, and the relative cost of cementation is nearly four times that of the electrolytic deposition.

EXPERIMENTAL WORK AND DISCUSSION

FURNACE PROCEDURE:

A small crucible (commonly called a Gooch crucible) was filled with a five-gram charge, placed in the furnace and heated for ten minutes to bring it up to furnace temperature. When the charge reached the proper temperature, the mixture of gases, sulfur dioxide plus air or oxygen, was forced through the charge. After the gases had passed through the charge for the specified time, they were turned off, and the crucible extracted from the furnace. The material was weighed, leached and the desired constituents determined.

To determine the effect of temperature, concentration of sulfur dioxide and time, each was varied, and the others held constant. The effect that each gave will be discussed later.

EFFECT OF IMPURITIES:

Iron gave little trouble in furnace runs, and the percent present in the leach solution was negligible. Iron acts as an efficient catalytic agent in producing sulfur trioxide, and the amount present as a ferrite was nearly nil.

Silica gave considerable trouble in the recovery of copper by tying up the copper as a silicate, and this silicate was insoluble in a dilute sulfuric acid leach.

Aluminum formed a soluble compound, and was present in the leach solution. Other elements gave no ill effects, or their effect was not noticed.

FURNACE RUNS AND LEACHES:

A furnace run was made to determine the effect of the decomposing roast on the water soluble copper (Fig. 3). The exact effect of this roast was not realized, but some sulfate decomposed to yield copper sulfate. Since the amount of soluble iron was only a trace, and the amount of soluble aluminum decreased as the roast continued, I believe it was the decomposition of the aluminum sulfate, or some sulfate of aluminum, that furnished the sulfur trioxide. The iron did not form a sulfate, therefore, the iron could not supply the sulfur trioxide. Aluminum sulfate decomposes at 1418°F., and this roast was carried on at 1060°F. Subsequent investigation is necessary to determine the source of the sulfur phase that is converted to copper sulfate.

The concentration of sulfur dioxide was varied, and the conclusion was reached that a high sulfur dioxide concentration will produce more water soluble copper than a low concentration. A concentration of 50 percent sulfur dioxide will give at least ten percent more copper soluble than a 33 1/3 percent concentration (Fig. 2)

The time factor has an interesting and eccentric behavior (Fig. 3-4). As the time is increased, the copper first forms the desired sulfate at a rapid rate, but drops off after a short period and decreases. It then begins to increase at a slow and fairly steady rate.

TABLE I

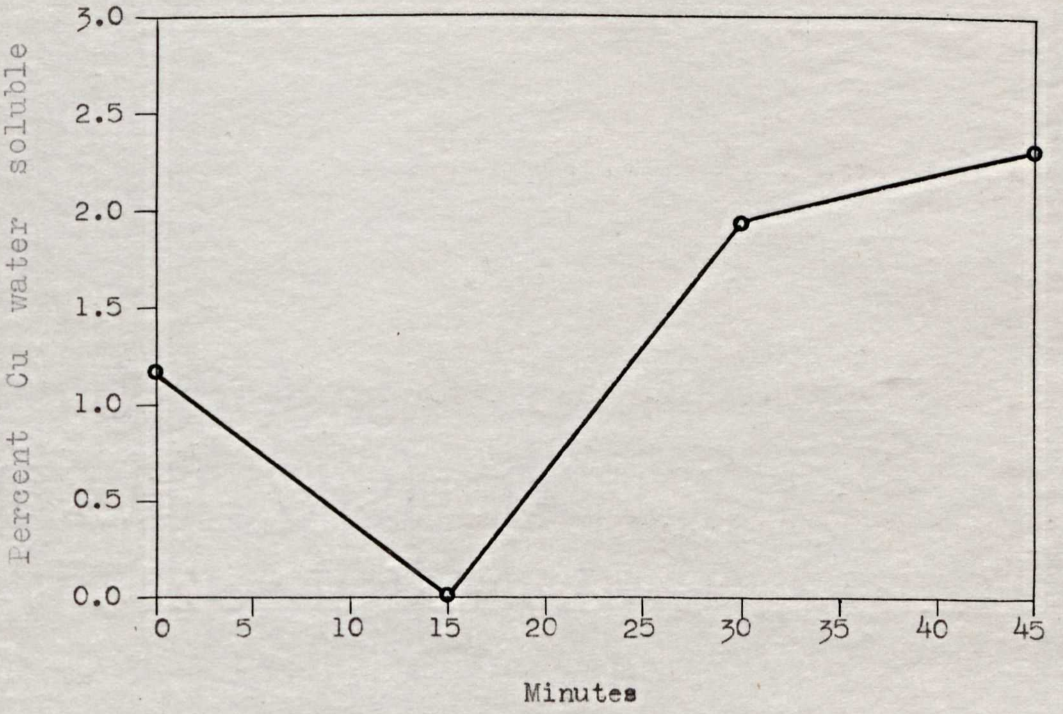
Test No.	Cu Sol. H_2O	Cu Acid Sol.	Cu Insoluble		SO_2:O_2	Temp. °F	Time Min.	$BaSO_4$
			H_2O	H_2SO_4				
1	53.7	92.1	46.3	7.9	1:1	1060	8	
						1300	60	
2	32.2	86.0	67.8	14.0	1:1	670	60	
						1650	60	
3	48.8	87.4	51.2	12.6	1:1	800	15	
						1060	60	
4	9.64	52.2	90.36	47.8	NO SO_2	1060	15	
5	1.18		98.82		1:1	800	60	.0288
	0.00		100.00			1060	15	.0107
	1.95		98.05			1060	30	.0627
	2.32		97.68			1060	45	.0563
6	25.0	75.4	75.0	24.6	Air:SO_2 1:1	800	60	
						1060	60	
7	1.41	56.5	98.59	43.5	Air:SO_2 2:1	800	15	.0250
	4.25	46.4	95.75	53.6		800	40	.0358
	2.83	52.5	97.17	47.6		800	60	.0759
	0.00	40.6	100.00	59.4		1060	30	.0623
	10.9	46.7	89.10	53.3		1060	60	.0885
	6.36	50.8	93.64	49.2		1060	90	.0786
8	11.3		88.7			800	15	
	11.3		88.7			930	15	
	15.5		84.5			1200	15	
	32.8		67.2			1330	15	
9	15.5	58.6	84.5	38.0	1:1	1330	1	.0550
	17.3	61.2	82.7	33.0		1330	2	.1137
	7.4	60.0	92.57	37.4		1330	3	.1040
	5.0	56.6	95.05	40.2		1330	4	.0687
	2.1	52.3	97.88	43.5		1330	6	.0387

TABLE I (Cont.)

Test No.	Cu Sol. H_2O	Cu Acid Sol.	Cu Insoluble H_2O	Cu Insoluble H_2SO_4	$SO_2:O_2$	Temp.	Time Min.	$BaSO_4$
10		60.4			1:1	800	3	
						800	12 Hours	
11		62.5			1:1	800	2	
		62.9				800	7	
		60.8				800	30	
		70.0				800	60	
12		83.5			1:1	900	0	
	25.8	78.6				730	5	
	36.4	80.2				730	10	
	36.4	51.3				730	15	
	26.5	77.0				730	20	

Test No.	Cu Sol. H_2O	Cu Acid Sol.	Percent H_2SO_4	$SO_2:O_2$	Temp.	Time Min.
13	36.4	80.2	5	1:1	750°F	10
		85.4	10			
		93.9	15			
		98.5	20			
		89.4	25			

Test No.	Fe Sol. H_2O	Fe Acid Sol.	Precent H_2SO_4	$SO_2:O_2$	Temp.	Time Min.
13B	0.00	Trace	5	1:1	750°F	10
		3.01	10			
		3.14	15			
		3.28	20			
		3.12	25			



Decomposition 1060°F.

Figure 3. Effect of Decomposing Time on Extraction.

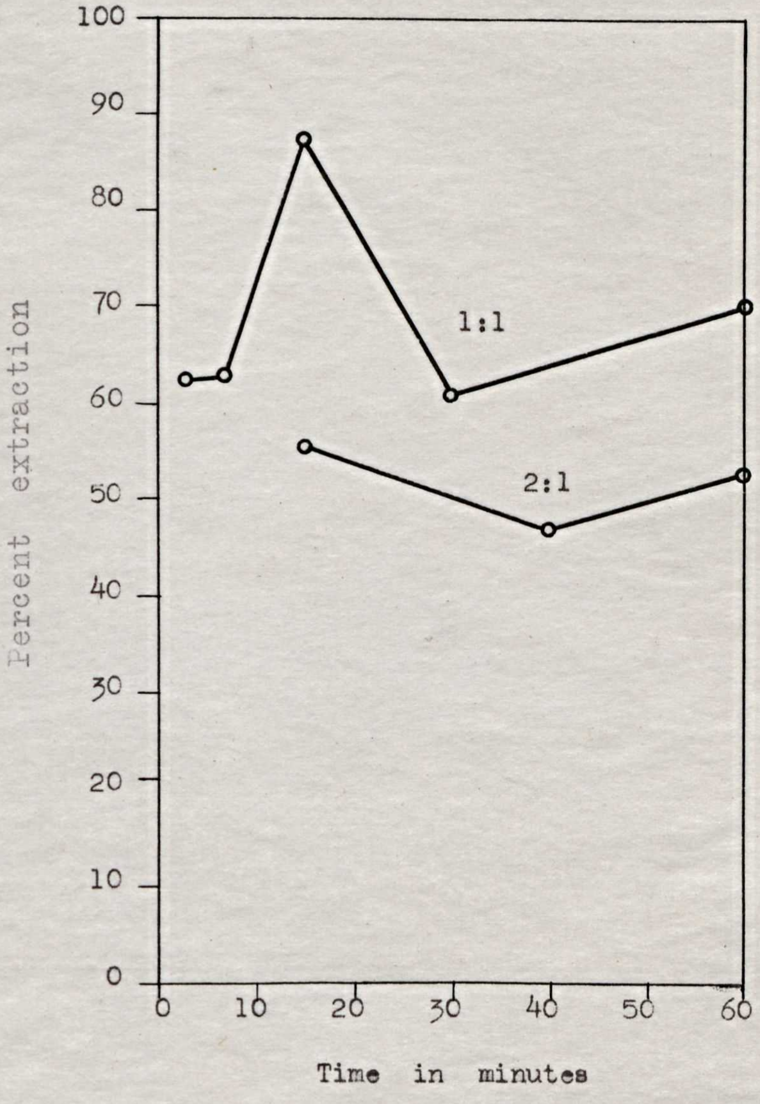
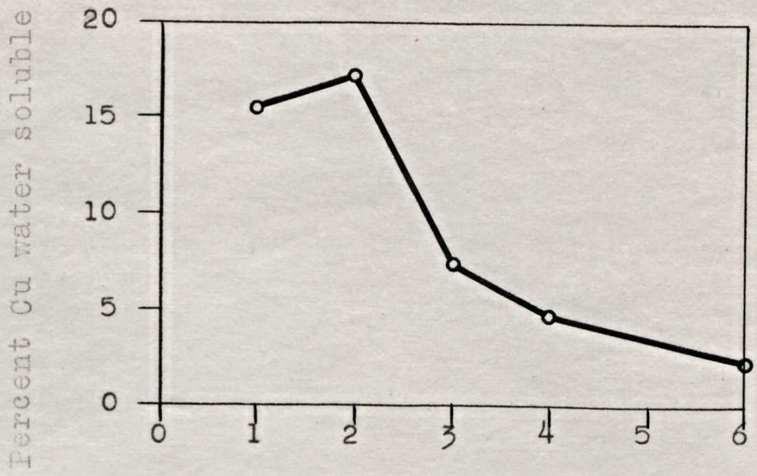
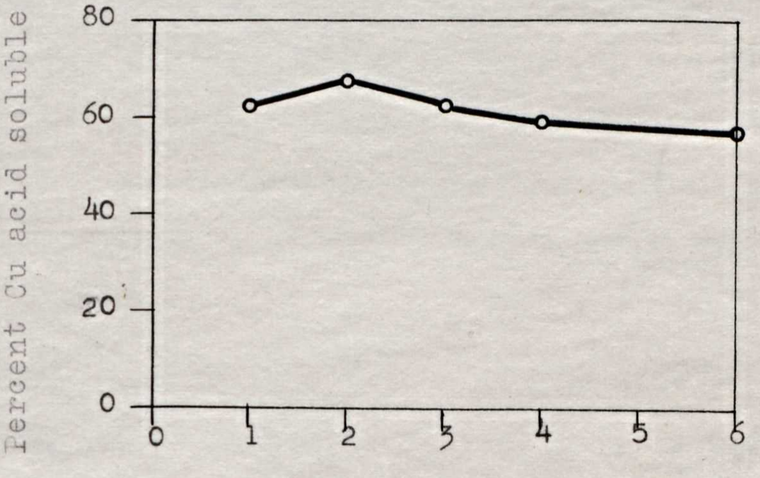


Figure 4. Effect of Concentration of SO_2 on Extraction.



Copper water soluble at 1330°F.

Figure 5. Effect of Sulfatizing Time on Water Soluble Copper



Copper acid soluble at 1330°F.

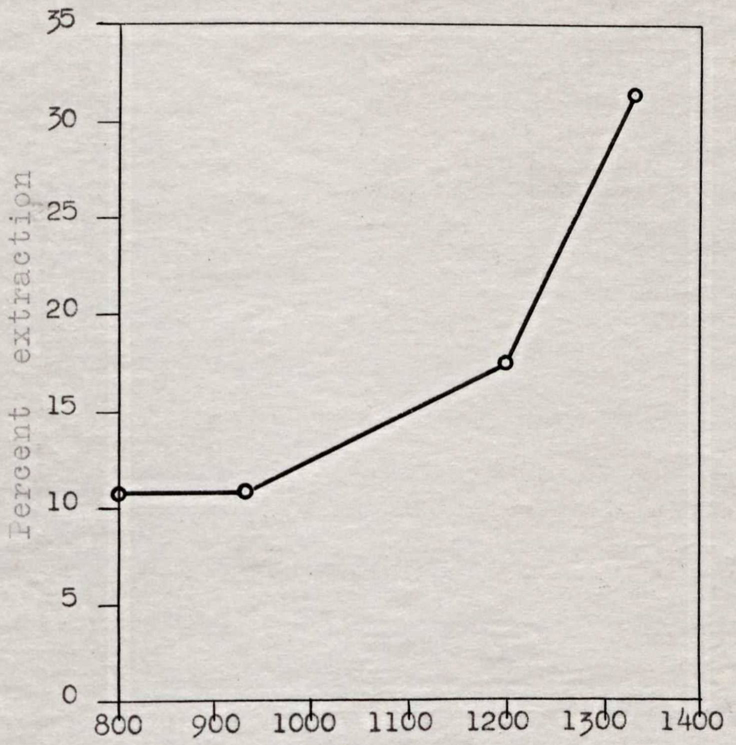
Figure 6. Effect of Sulfatizing Time on Acid Soluble Copper

Figure 7 indicates that the formation of acid soluble copper is constant between 800°F and 930°F. Actually the extraction drops off, see time factor Figure 3, and then increases to the same value as the 800° roast. This figure shows that a compound decomposes to yield copper in its soluble form after thirty minutes. Since Figure 3 also shows this condition, it is inferred that the time and not the temperature is the controlling factor. As expected, Figure 3 shows that as the temperature increases, the rate of decomposition also increases.

Figures 8, 9 and 10 show the relation of soluble copper to the presence of the sulfate radical. It will be noted that an increase of the sulfate radical increases the extraction, but that an increase in extraction can also take place with a decrease in the sulfate radical.

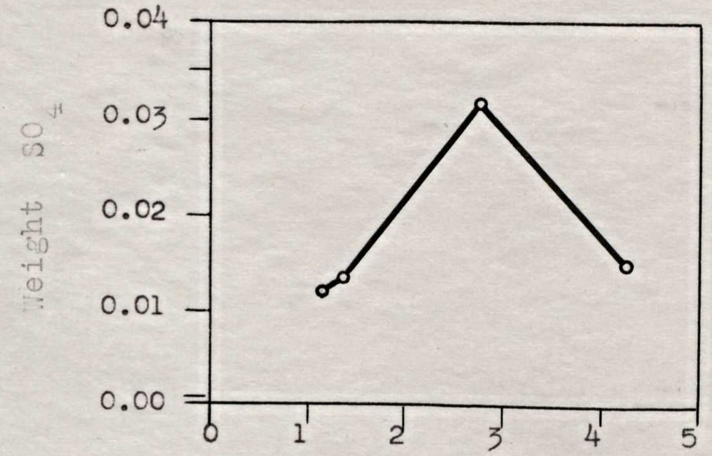
Figures 11 and 12 show the relation of the sulfate radical to the percent extraction of copper. It is seen that the extraction of copper in a water leach is dependent upon the amount of SO_3^{--} present, but in an acid leach the extraction is not dependent upon the amount of SO_3^{--} present. The decomposition product from copper sulfate is copper oxide, and this is soluble in dilute sulfuric acid.

A low temperature oxidizing roast, maximum temperature 900°F., was made to determine if the extraction could be improved. Figure 11 shows that extraction was greatly improved by this low temperature roast. It is believed that silicates form at temperatures much in excess of 900°F.,



All samples treated for 15 minutes at the indicated temperature plus the treatement given at lower temperature e.g. the sample at 1200 received 15 minutes at 800, 15 minutes at 930 and 15 minutes at 1200°F.

Figure 7. Effect of Temperature on Extraction.

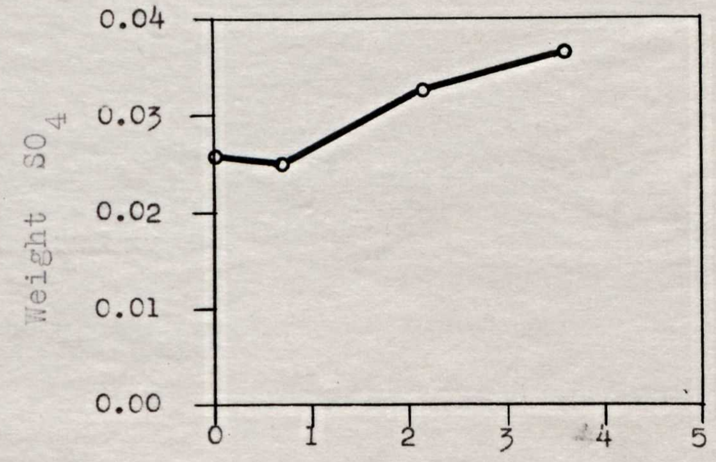


Percent water soluble copper

at 800°F.

Figure 8. Effect of the Sulfate Radical Present on

Water Soluble Copper 800°F.



Percent water soluble copper

at 1060°F.

Figure 9. Effect of the Sulfate Radical Present on

Water Soluble Copper 1060°F.

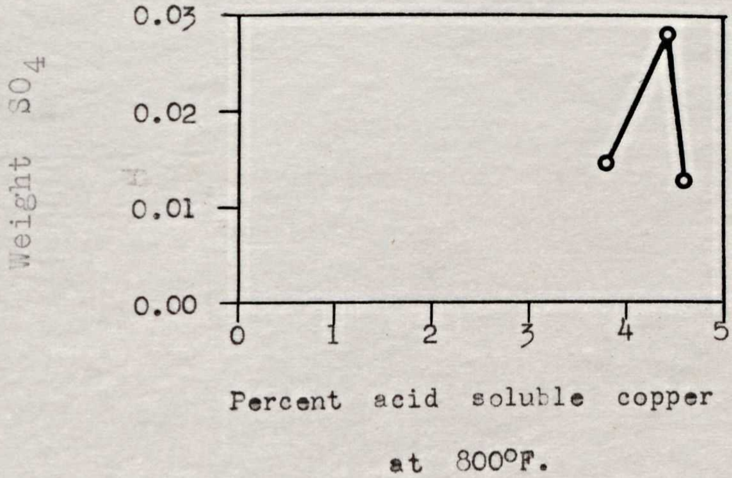
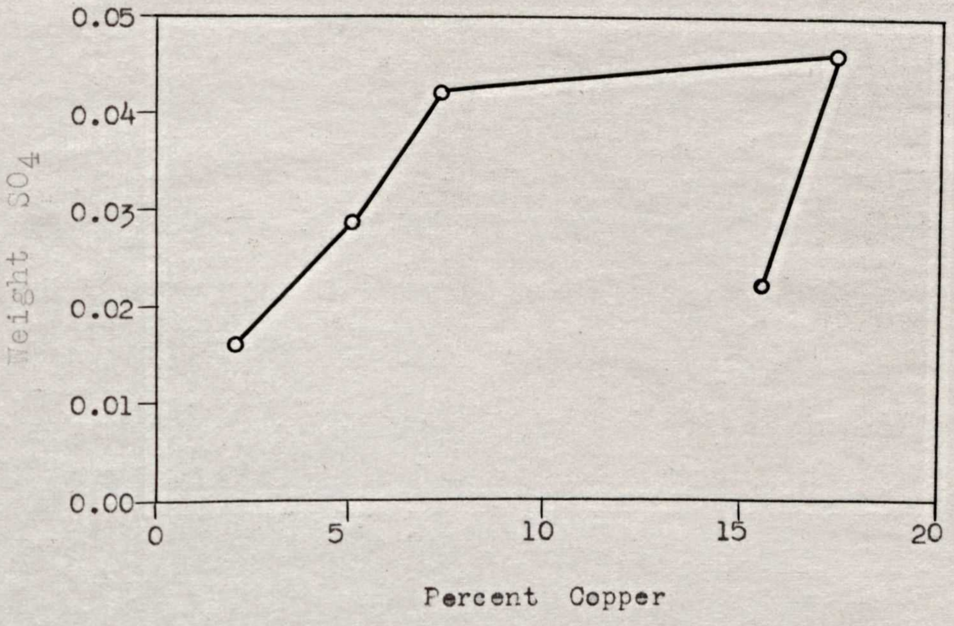


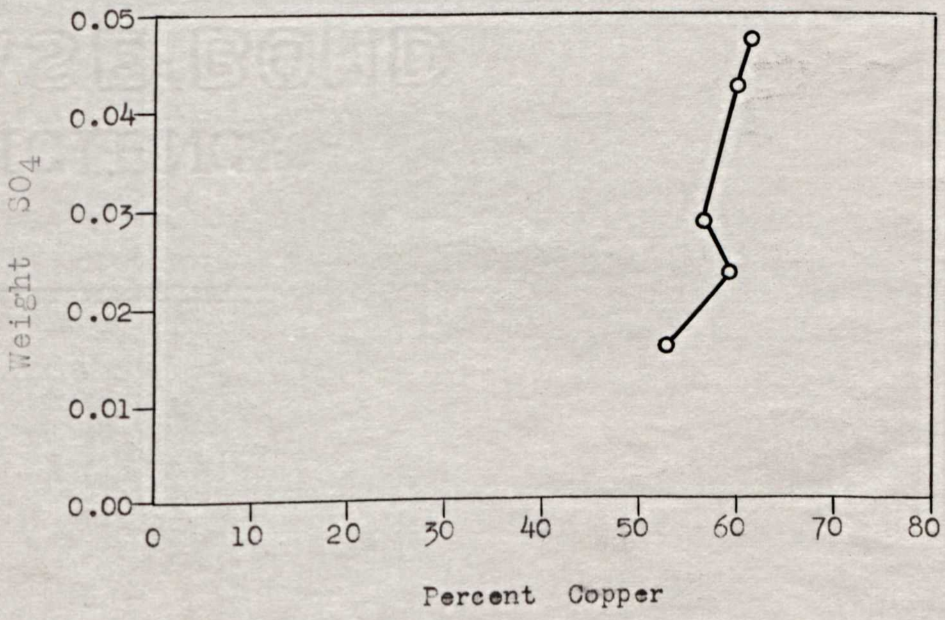
Figure 10. Effect of the Sulfate Radical Present on Acid Soluble Copper 800°F.



Water soluble at 1330°F.

Figure 11. Effect of the Sulfate Radical Present on

Water Soluble Copper 1330°F.



Acid soluble copper at 1330°F.

Figure 11. Effect of the Sulfate Radical Present on

Acid Soluble Copper 1330°F.

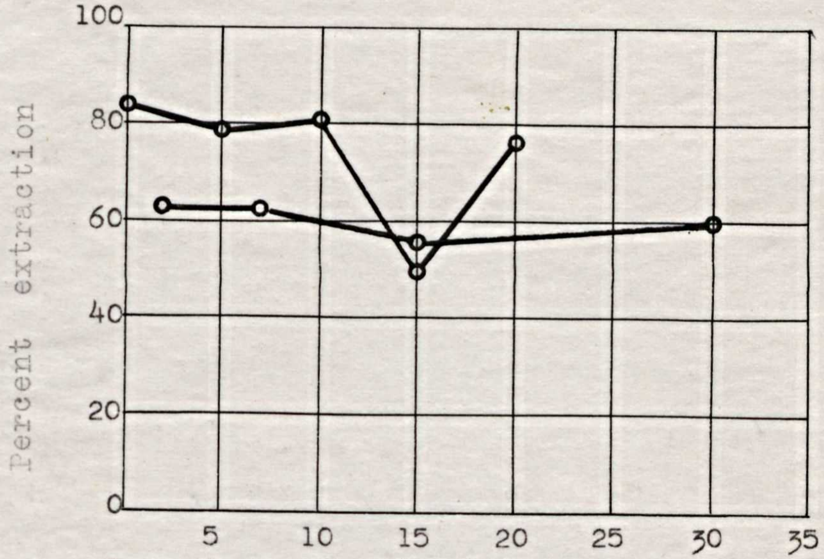
and these are insoluble in dilute sulfuric acid. Figure 13 shows the effect of a low temperature roast on the formation of water soluble copper.

Figures 15 and 16 show the effect of acid concentration on the extraction of copper and the percent of soluble iron in the leaching solution. It will be noted that as the concentration of acid increases, the extraction and the soluble iron content also increase.

ORE:

The ore used for this investigation was from the Washoe Smelter, Anaconda, Montana, and analyzed as follows:

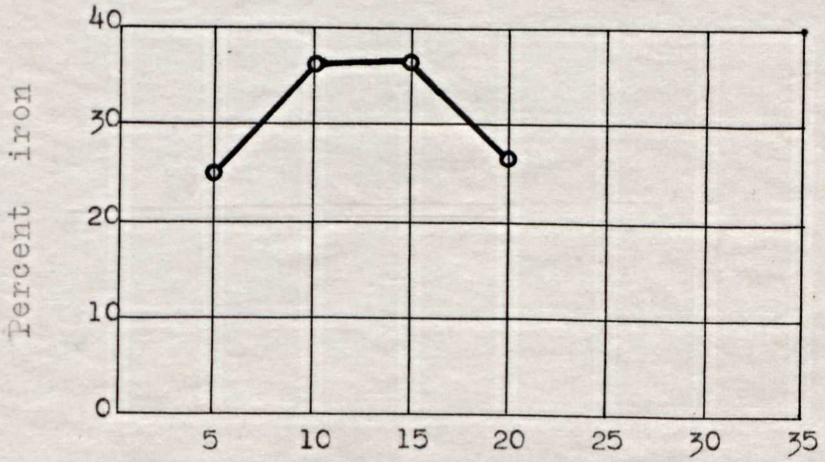
Cu	16.91%
Fe	19.30%
S	27.39%
Insol	14.00%



Comparison of extraction in percent of previous curve and curve from Roast 13

800°F.

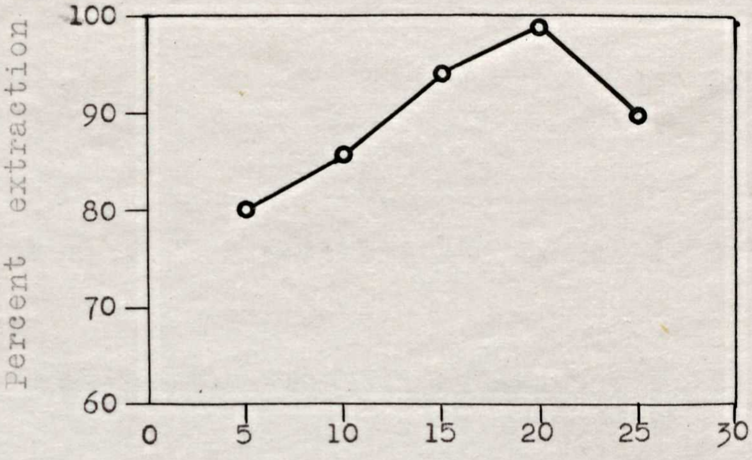
Figure 13. Extraction of Copper with Sulfatizing Time.



Water soluble copper from Roast No. 13

800°F.

Figure 14. Water Soluble Copper with Sulfatizing Time.



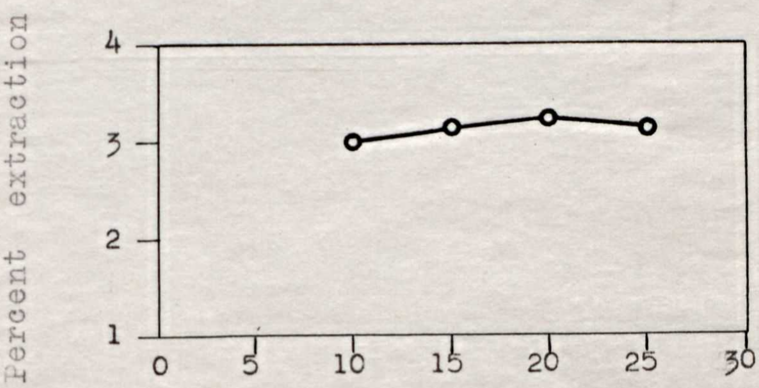
Strength of acid in percent

Figure 15. Extraction with Strength of Acid.

Temperature held below 900°F.

in oxidizing roast, and at

750°F. in sulfatizing roast.



Strength of acid in percent

Figure 16. Soluble Iron with Strength of Acid.

CONCLUSIONS:

1. The leaching solution that gave the highest extraction contained 20 percent sulfuric acid. This solution gave a copper extraction of 98.5 percent, and a soluble iron content of 3.28 percent.

2. As the acid concentration is increased, the extraction and soluble iron content are also increased.

3. The percent of the copper that is water soluble depends upon the amount of sulfate formed, but the amount of sulfate radical present is no indication of the water soluble copper.

4. At elevated temperatures a compound forms that decreases the extraction. This compound is believed to be a silicate of copper.

5. The higher the sulfur dioxide concentration, the faster and more complete the formation of water soluble copper.

6. At low temperatures aluminum forms a soluble compound that is believed to decompose at elevated temperatures with the formation of copper sulfate.

7. Good extraction can be obtained with a short roast, and with an extension of time. The extraction first decreases and then begins to increase at a slow but fairly constant rate. At 800°F., with a concentration of 50 percent sulfur dioxide, the same extraction is obtained with roasts of 10 and 60 minutes duration.

8. Best extraction was obtained by using the following conditions:

Oxidizing roast
- 1. Temperature not to exceed 900°F.

Sulfatizing roast
- 1. Temperature 750°F.
- 2. 50 percent concentration of SO_2
- 3. Time 10 minutes.

Leaching
- 1. 20 percent sulfuric acid

The results obtained from this run were:

Copper
- 1. Water soluble...36.4 percent
- 2. Acid soluble
    - a. 5% solution...80.2%
    - b. 10% solution...85.4%
    - c. 15% solution...93.9%
    - d. 20% solution...98.5%
    - e. 25% solution...89.4%

Iron
- 1. Water soluble...trace
- 2. Acid soluble
    - a. 5% solution...trace
    - b. 10% solution...3.01%
    - c. 15% solution...3.14%
    - d. 20% solution...3.28%
    - e. 25% solution...3.12%

While the results of this investigation point to success, the data is far from complete, and many points must be cleared-up before commercial application is possible.

RECOMMENDATIONS:

1. Determination of the optimum temperature for the decomposing roast; probably around 1060°F.

2. Determination of the optimum concentration of sulfur dioxide and oxygen.

3. Determination of the compounds formed that reduce the extraction of copper. I believe these compounds are copper silicates. My determinations were made by assuming that the insoluble copper was present as ferrites, sulfides or silicates. The amounts of ferrites and sulfides were negligible, and it was assumed that the major portion of the copper was present as silicates. Microscopic examination helped to confirm this conclusion.

4. Determination of the optimum time for sulfatizing. This time will probably be under 15 minutes.

5. Determination of the optimum size for sulfatizing.

6. Determination of the soluble impurities in the leach solution that may effect the physical properties of copper, e.g. arsenic, and designing methods to reduce or eliminate these impurities.

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APPENDIX

CHEMICAL PROCEDURES

COPPER:

Weigh out 0.5 grams of sample and dissolve in 10 ml. of HNO_3 + about 2 grams of $KClO_3$. When fuming is over, add 5 ml. of HCl. Boil until no brown fumes are evolved. (For oxidized material weigh out 0.5 grams of calcine and dissolve in 10 ml. of HCl) Cool and add NH_4OH until a slight permanent precipitate forms. Avoid an excess. Add 5 ml. of acetic acid and dilute to 75 ml. Add about 2 grams of NaF (solution is now a light blue), 10 ml. of 30% KI and titrate with standard thiosulfate.

SULFATE:

Dissolve in 10 ml. HNO_3 + 2 grams $KClO_3$. Fume, add 5 ml. of HCl, bring to dryness, add 5 ml. HCl and again bring to dryness. Take up with 5 ml. HCl and dilute to 100 ml. Add 10-15 ml. of 10% $BaCl_2$. Digest for one hour, filter, wash, dry, burn and weigh as $BaSO_4$.

IRON:

Weigh out 0.5 grams of ore (sulfide ore is given a previous fusion with sodium carbonate) and bring into solution with 30 ml. of 1:1 HCl. Heat until solution is affected, and then add $SnCl_2$ until white or clear. Cool and add 10 ml. of mercuric chloride solution, dilute to 150 ml., add 20 ml. 1:4 H_2SO_4 and 10 ml. of H_3PO_4, and titrate with standard potassium dichromate using 8 drops of diphenylamine as an inside indicator. The end point is blue.

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