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The Electrowinning of Copper from Roasted Sulphides

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THE ELECTROWINNING OF COPPER
FROM ROASTED SULPHIDES

by

Thomas B. Linn

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
Butte, Montana
May 6, 1937
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ELECTROWINNING OF COPPER FROM ROASTED SULPHIDES

INTRODUCTION

A hydrometallurgical process for the recovery of copper from flotation concentrates has long been considered an attractive possibility. The object of such a method is to produce electrolytic copper without resorting to expensive matte smelting and converting. The treatment would be similar to that used in the hydrometallurgical production of zinc. It would consist of roasting, leaching with dilute sulphuric acid, and separation and electrolysis of the resulting solution. In spite of the great simplicity of this treatment as compared to the pyrometallurgical methods now in use for sulphide ores, it has not yet been developed to the stage where it can successfully compete with the pyrometallurgical method.

The chief difficulties to be solved before the method can become a serious competitor are: 1. The extraction of copper in the leaching process is too low. This is believed to be due to the formation of insoluble copper ferrites and copper ferrates in roasting. 2. The leach solutions contain ferric iron, which seriously interferes in the electrolysis by dissolving copper from the cathode. 3. The gold and silver, which are a substantial item in the value of many ores, are not readily recoverable.

1.
The object of this paper is to describe some experiments which were made with a copper concentrate from the Anaconda Reduction Works. This concentrate contained 24.4 per cent copper and 35.5 per cent sulphur.

**ROASTING**

Copper occurs in the concentrate chiefly as chalcocite (Cu$_2$S), bornite (Cu$_5$FeS$_4$), and enargite (Cu$_3$AsS$_4$). Covellite (CuS), tetrahedrite (Cu$_5$SbS$_3$), and chalcopyrite (CuFeS$_2$) are present in lesser amounts. The object of the roasting is to convert the copper to oxides and sulphates which will be soluble in dilute sulphuric acid. Tests were made to determine the optimum temperature for roasting.

The roasting was done in a gas-fired assay muffle. In each case 20 grams of dry concentrate on a large scorifying dish were placed in the muffle when it had been brought to the desired temperature. One-half hour roasts were made at 500 deg. C., 550 deg. C., 600 deg. C., 650 deg. C., and 700 deg. C. Temperatures were measured with a Hoskins base-metal thermocouple placed across the edge of the scorifying dish, just above the charge. The door of the muffle was left partially open to admit a plentiful supply of air, and each charge was thoroughly stirred after fifteen minutes of roasting. The resulting calcines were
analyzed for water-soluble iron, water-soluble copper, acid-soluble iron, and acid-soluble copper.

Water-soluble iron was determined by boiling 2 grams of calcine with 100 cc. of water for 10 minutes. The resulting solution was acidified with 10 cc. of sulphuric acid. Zinc was added to reduce the iron and precipitate the copper. The solution was then filtered, cooled, and titrated with standard potassium permanganate solution.

Water-soluble copper was determined by boiling 1 gram of calcine with 50 cc. of water for ten minutes. The solution was filtered and made ammoniacal. Standard potassium cyanide solution was added until the blue color was faint. Then the hydroxides were filtered off, and the titration with potassium cyanide continued to a very faint color.

Determinations of acid-soluble iron and acid-soluble copper were made as above except that the calcine was boiled with dilute hydrochloric acid (one part of hydrochloric acid to seven parts of water) instead of water in the first step.

The analyses of the calcines are given in Table I. The figures given are percentages of the total weight of the calcine.
<table>
<thead>
<tr>
<th>Temp. (deg. C)</th>
<th>Water-soluble iron</th>
<th>Acid-soluble iron</th>
<th>Water-soluble copper</th>
<th>Acid-soluble copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0.35</td>
<td>9.15</td>
<td>14.2</td>
<td>24.8</td>
</tr>
<tr>
<td>550</td>
<td>0.10</td>
<td>14.2</td>
<td>10.2</td>
<td>28.7</td>
</tr>
<tr>
<td>600</td>
<td>0.15</td>
<td>10.55</td>
<td>5.3</td>
<td>28.1</td>
</tr>
<tr>
<td>650</td>
<td>0.30</td>
<td>19.25</td>
<td>0.9</td>
<td>31.4</td>
</tr>
<tr>
<td>700</td>
<td>0.05</td>
<td>19.5</td>
<td>0.0</td>
<td>31.7</td>
</tr>
</tbody>
</table>

Analysis of Calcines
The water-soluble copper represents copper as copper sulphate. The effect of temperature on the formation of copper sulphate is shown in Fig. 1.

The difference between acid-soluble copper and water-soluble copper is the copper as oxide. The effect of temperature of roasting on the formation of copper oxide is shown in Fig. 2.

Fig. 1 shows that the amount of copper sulphate present in the calcine decreases as the temperature of roasting is raised until 700 deg. C. is reached, at which temperature all the copper sulphate is decomposed in half an hour.

Fig. 3 shows that the amount of oxide copper in the roast increases as the temperature is raised to 700 deg. C., at which temperature all the soluble copper is present as oxide.

A roast at 600 deg. C. appears to be the most advantageous. At that temperature the amounts of sulphate copper and acid-soluble iron are low.
Fig 1
Effect of Temperature of Roasting on the Formation of Copper Sulphate.

![Graph showing the effect of temperature on the formation of copper sulphate.](image-url)
Fig. 2
Effect of Temperature of Roasting on the Formation of Copper Oxide
Fig. 3
Effect of Temperature of Roasting on the Formation of Acid-Soluble Iron
LEACHING

The material used in the leaching tests was prepared by roasting 2 kilograms of concentrate in a laboratory Herrinsoffing unit. This roaster has a mechanical rabbling arm and is fired with natural gas. The roasting was continued for four hours at a moderate roasting temperature, but no effort was made to control the temperature accurately.

Leaching tests were made to determine what strength of dilute sulphuric acid solution yielded the greatest extraction of copper. In each case 10 grams of roasted ore were leached in small bottles with twice the amount of acid theoretically required to dissolve all the copper. The acid strengths used were 5%, 10%, 15%, and 20%. The leaching was continued for one hour with intermittent agitation. The solutions were filtered and 25 cc. of each taken for analysis. The recoveries are given in Table II.

Table II

<table>
<thead>
<tr>
<th>Acid strength % H₂SO₄</th>
<th>Extraction of Cu % of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>57.5</td>
</tr>
<tr>
<td>10</td>
<td>59.5</td>
</tr>
<tr>
<td>15</td>
<td>60.3</td>
</tr>
<tr>
<td>20</td>
<td>61.9</td>
</tr>
</tbody>
</table>

Effect of Acid Strength on Extraction of Copper
A second series of leaching tests was made to determine what amount of acid yielded the best results. The acid used was 20% sulphuric acid. The amounts used were: 1. The theoretical amount required to dissolve all the copper, 2. One and one-half the theoretical amount, 3. Twice the theoretical amount. The leaching was done as in the preceding tests, and extractions were calculated from analysis of the solutions. The results are given in Table III.

Table III

<table>
<thead>
<tr>
<th>Amount of acid</th>
<th>Excess acid</th>
<th>Extraction of Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% H$_2$SO$_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Theo. amount</td>
<td>0</td>
<td>46.0</td>
</tr>
<tr>
<td>1½x Theo. amt.</td>
<td>50</td>
<td>54.8</td>
</tr>
<tr>
<td>3x Theo. amt.</td>
<td>100</td>
<td>54.3</td>
</tr>
</tbody>
</table>

Effect of Excess Acid on the Extraction of Copper

The leaching tests show that the strength of acid affects the extraction of copper only moderately. 50% excess acid improves the extraction markedly, but the extraction is slightly lower when 100% excess is used.

The most significant fact brought out by the leaching tests is the very low extractions of copper obtained when the temperature of roasting is not carefully controlled. This is due to the formation of insoluble
compounds of copper and iron oxides. In this connection Floe\textsuperscript{1) \textsuperscript{1}} states: "From 97 to 98 per cent extraction of copper from roasted concentrates can be obtained by baking with $\text{H}_2\text{SO}_4$ solution followed by water leaching. This is accomplished by first baking the acid-calcine mixture at temperatures below 300 deg. C., followed by heating at about 600 deg. C. The latter treatment sulphates the ferrite copper, so that a better extraction is obtained than with ordinary sulphuric acid leaching."

\textsuperscript{1)} Carl Frederick Floe: "Extraction of Copper from Roasted Concentrates by Sulphuric Acid Baking", A.I.M.E. Tech. Pub. No. 768 (1937).
ELECTROLYSIS

300 grams of the roast made in the leaching experiments were leached for 3 hours with 1100 cc. of 20% sulphuric acid solution. The material was then filtered and electrolyzed in a liter beaker with a sheet lead anode and a copper cathode. The electrical connections are shown in Fig. 4.

Fig. 4. Arrangement of Cell
The conditions of the electrolysis were as follows:

Initial copper content of the electrolyte...33 g.m./l.
Width of electrodes.......................2-13/16 in.
Depth of immersion of electrodes........3 in.
Current........................................1 amp.
Current density.........................17 amps/sq.ft.
Distance between electrodes.................1/4 in.
E.M.F..........................2.2 volts

The cathode was weighed, and the solution was electrolyzed continuously for 21 hours and 20 minutes. Then the electrolysis was stopped and the cathode weighed. The average current efficiency over this period was found to be 74.6%. The electrolysis was then resumed. For the next 3 hour 52 minute period, the current efficiency was found to be 17.6%. At the end of these two runs, 19.7 grams of copper, or 51.9% of the initial content, had been deposited from solution.

In order to obtain more definite information regarding the effect of time on electrolysis on current efficiency, a second leach was made as before. The solution was electrolyzed under the conditions enumerated above. The current efficiency was determined after each hour of electrolysis by weighing the cathode. The current was kept constant by adjusting the slide-wire resistance. Current measurements were made with an ammeter which was calibrated against a copper coulometer.
The results of these current efficiency determinations are given in Table IV.

Table IV

<table>
<thead>
<tr>
<th>Hour of electrolysis</th>
<th>Current efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>95.8%</td>
</tr>
<tr>
<td>3</td>
<td>97.8%</td>
</tr>
<tr>
<td>4</td>
<td>97.5%</td>
</tr>
<tr>
<td>5</td>
<td>94.6%</td>
</tr>
<tr>
<td>6</td>
<td>95.8%</td>
</tr>
<tr>
<td>7</td>
<td>94.5%</td>
</tr>
<tr>
<td>8</td>
<td>94.0%</td>
</tr>
<tr>
<td>9</td>
<td>92.6%</td>
</tr>
<tr>
<td>10</td>
<td>88.3%</td>
</tr>
<tr>
<td>11</td>
<td>89.6%</td>
</tr>
<tr>
<td>12</td>
<td>90.1%</td>
</tr>
</tbody>
</table>

Variation of Current Efficiency with Time

The erratic variations in some of the figures are due to temperature changes. The first five determinations were made on different days at the temperature of the laboratory, which varied. Tests 6 to 10 inclusive were made in one day and at constant temperature (31 deg.C.).

The decrease in current efficiency as the electrolysis proceeds is shown in Fig. 5. The current efficiency for the second hour was not obtained.
Fig 5
Variation in Current Efficiency with Time

Current Efficiency %

Hour of Electrolysis
SUMMARY

1. Low temperature roasts produce too much copper sulphate to be suitable for sulphuric acid leaching and electrolysis where any effort is made to regenerate the solvent. High temperature roasts produce excessive amounts of acid-soluble iron. Roasting at an intermediate temperature (600 deg. C.) gives the best results with the concentrates tested.

2. Roasting without careful temperature control yields calcines from which only about 60% of the copper can be extracted with cold, dilute sulphuric acid.

3. 20% sulphuric acid solution gives better extractions than weaker solutions. 50% excess acid improves the extraction, but 100% excess acid yields no better results than 50% excess.

4. The current efficiency of copper deposition falls off to less than 18% after 25 hours of electrolysis, due to the reaction,

$$2\text{Fe}^{++} + \text{Cu}^+ = 2\text{Fe}^{+} + \text{Cu}^{2+}$$

taking place at the cathode.
ACKNOWLEDGEMENT

I wish to express my appreciation of the assistance given me by the following members of the faculty of Montana School of Mines: Curtis L. Wilson, Ettore A. Perretti, and Alfred E. Koenig, all of the Department of Metallurgy, and to Miss Margery Bedinger, Librarian.