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Electrolytic Recovery of Copper and Zinc from Brass

D. H. Swank

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ELECTROLYTIC RECOVERY OF COPPER AND ZINC FROM BRASS

BY

D. V. Swank

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 5, 1937
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INTRODUCTION

The purpose of this research was to continue the work of Thomas Barker, who worked on the recovery of copper and zinc from brass during the school year 1934-1935. Since there is such a wide variety of brasses made with usually a third alloying constituent, remelted scrap is suitable only for castings of wide tolerance in specifications. Now if the primary scrap could be electrolyzed, and pure copper and pure zinc recovered, the introduction of undesirable constituents in brass would be eliminated. Moreover, the value of the pure zinc and pure copper would be greater than that of the scrap brass.

THEORY

The anodic dissolution of an alloy is dependent on several factors. Chief among these are the miscibility of the constituents in the solid state, and the formation of compounds. If the electrode potential of a binary alloy is measured under static conditions, it is usually found to be that of the baser metal as long as two phases are present. When the two metals neither unite chemically nor dissolve one another appreciably, two phases are always present and the potential remains that of the baser metal. If a continuous series of solid solutions is formed, the potential might be expected to vary continuously with the composition. However, the nobler
phase often exerts a protective effect so that the potential is that of the nobler phase down to a certain minimum concentration of the nobler component in the alloy.

When an alloy is used as an anode in electrolysis, the least noble phase dissolves first. The potential remains constant, except for polarization, until this phase is practically gone. Then the potential of anode to electrolyte changes abruptly to a value which is dependent on the remaining phase. If a solid solution is present, both metals will dissolve simultaneously since only one phase is present.

In the commercial brasses there may be either alpha solid solution or both alpha and beta solid solutions. If beta is present it will dissolve first. However, in either case the dissolution of the anode will yield both copper and zinc ions to the solution.

The starting electrolyte used in this work was copper sulphate solution containing about 40 grams of copper and 10 cubic centimeters of concentrated $\text{H}_2\text{SO}_4$ per liter. The dissolution of the brass anode supplied copper and zinc ions to the solution. The discharge potential for the copper ion is $+0.34 + 0.285 \log C_{\text{Cu}^{++}}$ volts, and for the zinc ion it is $-0.76 + 0.285 \log C_{\text{Zn}^{++}}$ volts. Thus the copper is deposited at a smaller difference of potential than zinc. By equating the two discharge potentials Barker shows that theoretically the ratio of $\text{Zn}^{++}$ to $\text{Cu}^{++}$ must be $4 \times 10^{38}$ to 1 before
zinc will be deposited. For all practical purposes, then, a complete separation should be possible.

EXPERIMENTAL

Electrolysis was conducted in a two-liter glass cell. This was larger than should have been used for more tests could have been made if the operation had been on a smaller scale. Originally it was thought that a large cell would more closely simulate plant conditions.

In the analytical work the iodide method was used for copper, and the thiosulphate method was used for zinc.

The greatest single problem was the casting of the brass anode into a suitable shape. Cast structure was wanted since this is what would be used in plant practice. A sheet 15 centimeters by 8 centimeters by 3 millimeters was decided upon. The first attempt at casting was made in a steel mold. This mold was open at the side and was set upright for casting. A great many attempts were made to get a suitable casting, but only one usable anode was obtained. In every other case "cold shuts" ruined the casting. Even when the mold was heated in the muffle before pouring the heat flowed from the brass so quickly that it solidified before filling the mold. A mold was made from soapstone which lay horizontally during casting. Nevertheless, the brass was not fluid enough to fill the mold properly before solidifying. At the suggestion of O. J. Wick the mold was filled with oil before pouring. Of course, the oil ignited as soon
as the molten metal touched it, but this additional heat combined with the exclusion of oxygen helped. The results were not altogether satisfactory, but three more suitable anodes were obtained. In all cases the brass was made from pure copper and pure zinc with no additional constituents.

A preliminary test was made with the anode cast in the steel mold. This brass was 62.0 percent copper and 38 percent zinc. The electrolyte contained 64.6 grams of copper and 10 cubic centimeters of concentrated \( \text{H}_2\text{SO}_4 \) per liter. A sheet copper cathode placed 6 centimeters from the anode was used. The current density was 15 amperes per square foot. During the test 33.213 grams of copper were deposited. The bath contained 62.2 grams of copper per liter at the end of the test. This showed the tendency for the copper to deposit faster than it was dissolved from the anode.

A test was made with a rolled sheet of commercial brass. The analysis given for this was:

\[
\begin{align*}
\text{Cu} &= 70.38 \text{ percent} \\
\text{Zn} &= 28.38 \text{ "} \\
\text{Sn} &= 1.17 \text{ "} \\
\text{Pb} &= 0.05 \text{ "} \\
\text{Fe} &= 0.02 \text{ "}
\end{align*}
\]

This is an example of a brass to which a third constituent, tin, has been added purposely. The lead and iron are accidental. The bath contained 41.2 grams of copper and 10 cubic centimeters of concentrated \( \text{H}_2\text{SO}_4 \) per liter before electrolysis. The current density was 14 amperes per square foot. The results are tabulated below.
Time| Amperes| Volts
---|---|---
3:30 PM| 2| 2.05
3:45| 2| 2.05
4:00| 2| 2.00

Electrolysis stopped. Restarted next morning at 11:00.
11:00 AM| 2| 1.85
1:30 PM| 2| 1.80
3:30| 2| 1.55

Electrolysis stopped. Restarted next morning at 11:00.
11:00 AM| 2| 1.00
1:00 PM| 2| 0.10

Electrolysis stopped. Electrolyte filtered and anode cleaned. 10cc. H₂SO₄ added. Restarted at 2:00 PM.
2:00 PM| 1| 0.90
3:00| 1| 0.70
4:00| 1| 0.60

Electrolysis run all night.
9:30 AM| 1| 0.40

Electrolysis stopped.

The anode corroded entirely from the back. The side facing the cathode became coated with a black film shortly after electrolysis was begun. Obviously this was Pb₃O₄ and it made the brass act as an insoluble anode on one side. Note that the voltage dropped to 0.1 volts after eight hours. When the film was cleaned from the anode, the voltage rose. The current density was also cut in half. Nevertheless, the voltage again dropped gradually. At the beginning of the test the bath contained 41.2 grams of copper per liter. After the total of 27.5 hours of electrolysis, the copper content was down to 12.8 grams per liter.

The next test was made with an anode which had been cast under oil in the soapstone mold. It contained 83 percent copper and 17 percent zinc. The original plan was to take single potential readings of the brass
anode against a normal calomel half-cell during electrolysis. However, the current density caused so great a polarization that its measurement was abandoned. The current density used in this test was 7 amps per square foot.

<table>
<thead>
<tr>
<th>Time</th>
<th>Amperes</th>
<th>Volts</th>
<th>Cu gms/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:00 PM</td>
<td>1</td>
<td>1.64</td>
<td>41.2</td>
</tr>
<tr>
<td>4:00</td>
<td>1</td>
<td>1.40</td>
<td></td>
</tr>
<tr>
<td>5:15</td>
<td>1</td>
<td>1.55</td>
<td></td>
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</tbody>
</table>

Electrolysis stopped. Restarted next afternoon at 2:00.

<table>
<thead>
<tr>
<th>Time</th>
<th>Amperes</th>
<th>Volts</th>
<th>Cu gms/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:00 PM</td>
<td>1</td>
<td>1.60</td>
<td></td>
</tr>
<tr>
<td>4:00</td>
<td>1</td>
<td>1.40</td>
<td></td>
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</tbody>
</table>

Electrolysis stopped. Restarted next afternoon at 2:40.

<table>
<thead>
<tr>
<th>Time</th>
<th>Amperes</th>
<th>Volts</th>
<th>Cu gms/L</th>
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<tbody>
<tr>
<td>2:40 PM</td>
<td>1</td>
<td>1.65</td>
<td>38.2</td>
</tr>
<tr>
<td>4:00</td>
<td>1</td>
<td>1.65</td>
<td>36.2</td>
</tr>
<tr>
<td>5:00</td>
<td>1</td>
<td>1.45</td>
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</table>

Electrolysis run all night.

<table>
<thead>
<tr>
<th>Time</th>
<th>Amperes</th>
<th>Volts</th>
<th>Cu gms/L</th>
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<tbody>
<tr>
<td>1:30 PM</td>
<td>1</td>
<td>1.40</td>
<td>34.2</td>
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<tr>
<td>4:00</td>
<td>1</td>
<td>1.35</td>
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Electrolysis run all night.

<table>
<thead>
<tr>
<th>Time</th>
<th>Amperes</th>
<th>Volts</th>
<th>Cu gms/L</th>
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<tbody>
<tr>
<td>10:15 AM</td>
<td>1</td>
<td>1.35</td>
<td>28.6</td>
</tr>
<tr>
<td>4:00 PM</td>
<td>1</td>
<td>1.35</td>
<td>27.0</td>
</tr>
</tbody>
</table>

Electrolysis run all night, next day (Sunday), and that night.

<table>
<thead>
<tr>
<th>Time</th>
<th>Amperes</th>
<th>Volts</th>
<th>Cu gms/L</th>
</tr>
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<tbody>
<tr>
<td>9:00 AM</td>
<td>1</td>
<td>1.55</td>
<td>25.1</td>
</tr>
<tr>
<td>4:00 PM</td>
<td>1</td>
<td>1.45</td>
<td>23.0</td>
</tr>
</tbody>
</table>

Electrolysis stopped at 5:00 PM. The anode was practically gone. The total time of the test was 102.5 hours. The remaining copper could have been precipitated by addition of zinc dust. Instead it was stripped by using a lead anode. The results are tabulated below.
Time | Amperes | Volts | Cu gms/L.
--- | --- | --- | ---
10:30 AM | 1 | 3.5 | 23.0
12:30 PM | 1 | 3.4 | 21.4

Stripping stopped at 5:30. Restarted next morning at 2:55.

8:55 AM | 1 | 3.0 | 17.7
4:00 PM | 1 | 3.0 | 13.1

Electrolysis run all night.

1:15 PM | 1 | 2.0 | 0.0

The remaining solution was electrolyzed with a lead anode and an aluminum cathode to recover the zinc.

Barker suggested the following flow sheet for a commercial plant.

Copper
Brass
Roadter
Electrolysis
Electrolyte Slime Cathode copper
Zinc dust addition
Copper ppt. Solution
Purification
Zinc electrolysis
Spent electrolyte Cathode zinc

The possibility of making copper sulphate by roasting the copper precipitate and anode slime with $\text{H}_2\text{SO}_4$ was investigated. The resulting calcine was almost completely soluble in dilute $\text{H}_2\text{SO}_4$ and the solution was very satisfactory for a starting bath.

CONCLUSION

The electrolysis of brass containing only copper and zinc would certainly be possible, especially those brasses high in copper. Yet the one test with the
commercial sheet of brass shows that actually the recovery of copper and zinc from commercial brass could not be put into practice, when al little as 0.05 percent of lead stops the process. Scrap brass obtained from all sources and cast into anodes would certainly contain more than 0.05 percent lead.
Bibliography

Glasstone - "Electrochemistry of Solutions
Barker - Senior Thesis 1935, Montana School of Mines
Sawyer - Senior Thesis 1934, Montana School of Mines
Acknowledgement

I wish to acknowledge the assistance of Doctors Wilson, Koenig, and Peretti during the past year.