

# Recovery of Copper, Cobalt, Nickel, Cadmium, Zinc and Bismuth from Electrolytic Copper Solution

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An electrolytic Copper Solution (ECS) was electrolyzed using platinum electrodes. Copper was obtained in solid form. In order to precipitate Cd(II), Bi(III), As(III), Sb(III) and the rest of the Cu(II) ions, H<sub>2</sub>S gas was passed through the remaining solution. The remaining solution was evaporated to obtain metal sulphates. The sample containing metal sulphates was roasted at temperatures between 550 and 800 °C. Cobalt, nickel and zinc in the solid sample remained in the form of metal sulphates, while the iron in the sample was converted into Fe<sub>2</sub>O<sub>3</sub>. This solid sample was dissolved in water and filtered in order to crystallize the NiSO<sub>4</sub>. As a result of crystallization, a maximum yield of 86.2 % was obtained.

The solid containing metal sulphides (CuS, CdS, Bi<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>S<sub>3</sub>) was roasted at 600 °C for 3 hours. The roasted sample was dissolved in water and filtered. It was determined that the conversion of CuS into CuSO<sub>4</sub> occurred, together with the conversion of CdS and Bi<sub>2</sub>S<sub>3</sub> into CdO and Bi<sub>2</sub>O<sub>3</sub>. The samples containing CdO and Bi<sub>2</sub>O<sub>3</sub> were then leached with 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at 50 °C for one hour. The extraction yield was 97%.

## Introduction

Electrolytic copper solution contains Cu, Bi, As, Sb, Ni, Co, Zn as well as other elements. During the electrolysis of refined copper, while pure copper is collected at the cathode, some impurities, such as nickel, pass into the solution and others become anode slime. The above elements listed above pass into the solution. Acidified copper solution is used as the electrolyte during electrolysis of copper.

Methods used for the recovery of important elements in ECS can be summarized as hydrometallurgic, pyrometallurgic and extraction. In particular, most arsenic, antimony and bismuth was removed from copper solution by introducing H<sub>2</sub>S into the solution. Iron was removed with hydroxamic acid, and 45 % of arsenic and 37 % of antimony was removed with 0.5 M versetic 101 in kerosene<sup>1</sup>. Furthermore, 13 g/L arsenic was extracted into 40% TBP and 10% P<sub>2</sub>O<sub>5</sub> containing kerosene using liquid-liquid extraction<sup>2</sup>. In another study, 94.6-98.1% of arsenic was removed by roasting the solid obtained from the evaporation of ECS<sup>3</sup>. To remove bismuth from ECS, PbO was utilised and the initial concentration of bismuth was decreased to

315 ppm<sup>4</sup>. Cu(II) and Ni(II) were precipitated in the form of sulphide from ECS and separated through adjustment of the pH<sup>5</sup>. In another study, Cu, Pb, As, Sb and Bi were removed by introducing H<sub>2</sub>S into the solution so as to precipitate the metal sulfides; the remaining solution was ozonized and nickel in the solution was separated using Lwaty S 100 and Prolite C 100 cation exchangers.

The aim of this study was to develop an applicable and economically feasible method of obtaining copper, bismuth, cadmium and nickel from ECS. The basis of this study was the separation of copper by electrolysis, and the introduction of H<sub>2</sub>S into the remaining solution in order to precipitate Cu(II), As(III), Sb(III), Cd(II) and Bi(III) ions from nickel, cobalt, iron and zinc. With sulphidization, while Cu(II), As(III), Sb(III); Cd(II) and Bi(III) ions are precipitated in the form of sulphide Zn(II), Fe(II), Ni(II) and Co(II) ions remain in the solution.

## Material and Method

The electrolytic Copper Solution (ECS) used in this study was obtained by electrolyzing blister copper, supplied by the Ergani Copper Corporation. The ECS was analyzed. The results are given in Table 1.

**Table 1.** Analysis of Electrolytic Copper Solution

| Ions    | Amount (g/mL) |
|---------|---------------|
| Cu(II)  | 7.85          |
| Ni(II)  | 3.97          |
| Fe(III) | 1.89          |
| Zn(II)  | 0.74          |
| Co(II)  | 0.0517        |
| Bi(III) | 0.0048        |
| Cd(II)  | 0.00066       |

## Apparatus Used

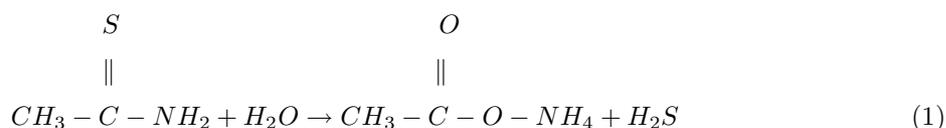
Analyses were carried out with a Varian Techtron 1200 Model Atomic Absorption Spectrometer (AAS). The samples were roasted in a Heraus Hanau Model furnace. The pH the measurements were carried out with a NEL 890 pH meter. The extraction experiments were carried out with a NUVE ST 400 constant-temperature bath. The electrolysis experiments were carried out in a vessel made by hand and an EDA-marked power supply of (0-30 V, 0-600 A) was used.

## Experimental

### Removal of Copper

The electrolytic copper solution was electrolyzed to separate the copper from other ions using platinum electrodes. Electrolyzation was carried out with a constant potential of 2.95 V and a current of approximately 0.4 A for 24 hours. It was determined that 99.3 % of the Cu(II) ions in the solution collected at the cathode.

Thioacetamide was added to the remaining solution in order to precipitate Bi(III), Cd(II), As(III), Sb(III) and the remaining Cu(II) ions in the form of metal sulfide according to the following reactions;



where  $M^{2+}$  is Cu(II) and Cd(II),  $M^{3+}$  is B(III), Sb(III) and As(III) ions. The precipitate was then filtered.

## Roasting of Metal Sulphate

The remaining solution was evaporated to obtain solid metal sulphate. This solid sample was dried at 110 °C and analyzed (8.5 % Ni, 2.1 % Fe, 1.15 % Zn and 0.0087 % Co).

About 1 g of the samples was taken and roasted at 600 °C, 650 °C, 700 °C, 750 °C and 800 °C for 2.0, 2.5, 3.0 and 4.0 hours, respectively. After roasting, the samples were dissolved in water and analyzed. These results are given in Table 2.

**Table 2.** Roasting of Solid Sample Containing Metal Sulphate

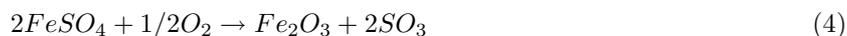
| Roasting Time (Hours) | Amount of Fe, Ni, Co and Zn passed into solution (%) |     |     |     |     |                |     |     |     |     |                |     |     |     |     |                |     |     |     |     |
|-----------------------|--|-----|-----|-----|-----|----------------|-----|-----|-----|-----|----------------|-----|-----|-----|-----|----------------|-----|-----|-----|-----|
|                       | Fe   |     |     |     |     | Ni             |     |     |     |     | Co             |     |     |     |     | Zn             |     |     |     |     |
|                       | Temperature °C                                       |     |     |     |     | Temperature °C |     |     |     |     | Temperature °C |     |     |     |     | Temperature °C |     |     |     |     |
|                       | 600  | 650 | 700 | 750 | 800 | 600            | 650 | 700 | 750 | 800 | 600            | 650 | 700 | 750 | 800 | 600            | 650 | 700 | 750 | 800 |
| 20                    | 7  | -   | -   | -   | -   | 72             | 66  | 47  | -   | -   | 87             | 85  | 52  | -   | -   | 64             | 88  | 57  | 44  | 33  |
| 25                    | 6  | -   | -   | -   | -   | 65             | 54  | 37  | -   | -   | 62             | 74  | 41  | -   | -   | 51             | 76  | 42  | 41  | 32  |
| 30                    | 5  | -   | -   | -   | -   | 52             | 47  | 29  | -   | -   | 55             | 56  | 37  | -   | -   | 47             | 62  | 39  | 37  | 30  |
| 35                    | 1  | -   | -   | -   | -   | 47             | 42  | 1   | -   | -   | 42             | 45  | 32  | -   | -   | 40             | 58  | 30  | 30  | 22  |
| 40                    | -  | -   | -   | -   | -   | 33             | 34  | 06  | -   | -   | 37             | 40  | 29  | -   | -   | 37             | 44  | 20  | 20  | 16  |

In addition, this precipitate was ground through -90 mesh and roasted at 550 °C, 600 °C, 650 °C and 700 °C. The amounts of iron, cobalt, nickel and zinc which passed into the solution are given in Table 3.

**Table 3.** The amounts of Fe, Co, Ni and Zn Passing into the solution after roasting -90 mesh of sample containing metal sulphates.

| Element | Temperature (°C) | Roasting Time (Hours) |      |      |      |      |      |      |
|---------|------------------|-----------------------|------|------|------|------|------|------|
|         |                  | 1.0                   | 1.5  | 2.0  | 2.5  | 3.0  | 3.5  | 4.0  |
| Fe      | 550              |                       |      | 27.0 | 18.9 | 16.8 | 12.8 | 12.5 |
|         | 600              | -                     | -    | -    | -    | -    | -    | -    |
|         | 650              | -                     | -    | -    | -    | -    | -    | -    |
|         | 700              | -                     | -    | -    | -    | -    | -    | -    |
|         | 750              | -                     | -    | -    | -    | -    | -    | -    |
| Ni      | 550              |                       |      | 61.2 | 55.0 | 38.8 | 35.9 | 24.3 |
|         | 600              | 98.8                  | 91.2 | 84.3 | 79.3 | 69.4 | 53.4 | 49.7 |
|         | 650              |                       |      | 25.0 | 22.9 | 18.5 | 13.5 | 10.4 |
|         | 700              | 11.2                  | 6.3  | 4.2  | 2.7  | -    | -    | -    |
|         | 750              |                       |      |      |      |      |      |      |
| Co      | 550              |                       |      | 92.4 | 88.5 | 76.2 | 60.0 | 56.0 |
|         | 600              | 100                   | 97.5 | 95.8 | 92.3 | 88.0 | 76.0 | 72.4 |
|         | 650              |                       |      | 87.6 | 79.6 | 62.4 | 52.6 | 44.0 |
|         | 700              | 96.2                  | 94.0 | 89.7 | 84.0 | 70.9 | 65.3 | 71.2 |
|         | 750              |                       |      |      |      |      |      |      |
| Zn      | 550              |                       |      | 99.8 | 97.6 | 96.0 | 95.4 | 92.0 |
|         | 600              | 99.9                  | 99.2 | 98.9 | 98.8 | 96.6 | 92.4 | 87.6 |
|         | 650              |                       |      | 97.2 | 89.0 | 85.2 | 79.3 | 71.2 |
|         | 700              | 84.6                  | 75.7 | 72.0 | 68.7 | 65.0 | 59.0 | 52.5 |
|         | 750              |                       |      |      |      |      |      |      |

As can be seen in Tables 2 and 3, while temperature and time increased, the ratio of the iron passing into the solution decreased. For this reason, iron and nickel salts decomposed into their oxides.



where, Me is Co, Ni and Zn. As can be seen in Table 3, while iron in the sample underwent total conversion into  $Fe_2O_3$  when roasted at  $600^\circ C$  for one hour the amounts of nickel, cobalt and zinc passing into the solution were 98.8 %, 99.9 % and 99.9 %, respectively.

### Crystallization of $NiSO_4$

The sample containing solid  $FeSO_4$ ,  $NiSO_4$ ,  $CoSO_4$  and  $ZnSO_4$  was roasted at  $600^\circ C$  for one hour so that  $FeSO_4$  was converted into  $Fe_2O_3$  and the roasted sample was dissolved in water and filtered to remove  $Fe_2O_3$ . The solution containing Ni(II), Co(II) and Zn(II) was evaporated in order to obtain a solid sample, which was dried at  $100^\circ C$ . 20 g of this sample was dissolved in 20 mL of water, heated, filtered and then washed with 10 mL of water. 30 mL of this solution was evaporated until 15 mL remained and then it was cooled slowly. The precipitated  $NiSO_4$  crystals were filtered, washed with 5 mL of water and analyzed. It was determined that 70.2 % of  $NiSO_4$  was crystallized, and that cobalt and zinc were not converted into crystals. The solution was evaporated to a volume of 10 mL washed with 5 mL of water and analyzed. It was determined that 16% of  $NiSO_4$  was precipitated in the second crystallization, and that cobalt and zinc did not crystallize. Of the remaining 15 mL, 7.5 mL was evaporated, filtered, washed with 2.5 mL water and analyzed. It was determined that cobalt and zinc precipitated together with the nickel. As a result, the crystallization was considered finished. A total of 86.2 % of the  $NiSO_4$  was crystallized.

### Separation of Bismuth and Cadmium from Antimony

Thioacetamide was added to the solution remaining after electrolysis of the ESC in order to precipitate Cu(II), Bi(III), As(III) and Sb(III) ions in the form of metal sulfide. The precipitate was filtered, dried and analyzed (0.7 % Cu, 7.8 % Bi, 0.4 % Cd and 4.0 % Sb).

To separate Sb and As in this sample,  $Na_2S$  extraction was performed 0.2 g of the samples were leached successively with 0.02 0.04, 0.06, 0.08, 0.1, 0.5, 1.0 and 1.5 M  $Na_2S$  solution at  $50^\circ C$ . The results are given in Table 4.

**Table 4.** Leaching of sample containing Cu, Bi, Cd and Sb.

| Concentration of $Na_2S$ Solution (M) | Extracted Metals (%) |      |      |      |
|---------------------------------------|----------------------|------|------|------|
|                                       | Bi                   | Cd   | Cu   | Sb   |
| 0.02                                  | 0.01                 | 0.02 | 0.05 | 0.6  |
| 0.04                                  | 0.70                 | 0.08 | 0.20 | 13.2 |
| 0.06                                  | 0.75                 | 0.20 | 0.37 | 19.8 |
| 0.08                                  | 1.32                 | 0.90 | 1.10 | 31.3 |
| 0.10                                  | 1.30                 | 0.80 | 0.90 | 34.4 |
| 0.50                                  | 0.36                 | 0.70 | 0.02 | 89.6 |
| 1.00                                  | 0.31                 | 0.05 | 0.02 | 99.2 |
| 1.50                                  | 0.31                 | 0.04 | 0.02 | 99.2 |
| 2.00                                  | 0.33                 | 0.02 | 0.01 | 99.2 |

## Separation of Sulfide Compounds by Roasting

5g samples containing CuS, CdS, Bi<sub>2</sub>S<sub>3</sub>, As<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>S<sub>3</sub> were roasted at 600°C for 3 hours. The reactions which occurred are as follows;



The sample formed was dissolved in 100 mL water, filtered and analyzed. It was determined that copper in the sample passed completely into the solution. The precipitate was dissolved in HNO<sub>3</sub> and analyzed. The amounts of Bi and Cd in the precipitate were determined to be 7.8% and 0.42%, respectively. Of this precipitate 0.1 g was leached with 0.2, 0.3, 0.5 and 1.0 M H<sub>2</sub>SO<sub>4</sub> solution at 50°C for 1 hour. The experimental results are given in Table 5.

**Table 5.** Effect of H<sub>2</sub>SO<sub>4</sub> concentration on the leaching of Bi and Cd.

| Concentration of H <sub>2</sub> SO <sub>4</sub><br>(M) | Extracted Metal (%) |      |
|--|---------------------|------|
|  | Bi                  | Cd   |
| 0.2  | 3.1                 | 87.8 |
| 0.3  | 3.8                 | 95.3 |
| 0.4  | 5.0                 | 95.3 |
| 0.5  | 5.2                 | 96.2 |
| 0.7  | 8.1                 | 96.8 |
| 0.9  | 9.8                 | 96.8 |
| 1.0  | 9.6                 | 96.5 |
| 1.2  | 15.8                | 97.1 |
| 1.5  | 16.0                | 97.2 |

Different amounts of the sample containing CdO and Bi<sub>2</sub>O<sub>3</sub> were extracted with H<sub>2</sub>SO<sub>4</sub>. The experimental results are given in Table 6.

**Table 6.** The effect of the amount of sample on the leaching of Bi and Cd.

| Amount of Sample (g) | Extracted Metal (%) |      |
|----------------------|---------------------|------|
|                      | Bi                  | Cd   |
| 0.2259               | 9.1                 | 77.1 |
| 0.4301               | 6.5                 | 66.1 |
| 0.6324               | 3.8                 | 52.5 |
| 0.8907               | 3.7                 | 50.1 |
| 0.9489               | 3.1                 | 49.5 |
| 1.9779               | 0.6                 | 47.7 |

In order to decrease the solubility of the bismuth, H<sub>2</sub>O<sub>2</sub> was added to the medium. The experimental results are given in Table 7.

**Table 7.** The effect of H<sub>2</sub>O<sub>2</sub> on the leaching of Bi and Cd.

| Number of drop added<br>H <sub>2</sub> O <sub>2</sub> (30%) | Extracted Metal (%) |      |
|---|---------------------|------|
|   | Bi                  | Cd   |
| 1   | 0.7                 | 96.9 |
| 5   | 0.5                 | 96.9 |
| 9   | 0.4                 | 96.9 |
| 11  | 0.4                 | 96.8 |

## Results and Discussions

In industry, during electrolytic purification of blister copper, some impurities from the copper used in the anode pass into the solution. In the insoluble-anode process, copper in the solution is electrolysed so that it is separated from Co(II), Ni(II), Zn(II), Fe(II), Bi(III), Sb(III) and As(III). The determination of other ions is carried out using different methods.

In this study, our purpose was to precipitate Cu(II), Bi(III), Sb(III) and As(III) in the form of metal sulphide and to convert Co(II), Ni(II), Zn(II), Fe(II) ions into sulphates in the remaining solution after electrolytic separation of the copper, and then to investigate whether the sulphides could be separated from each other and whether the sulphates could be separated by roasting at different temperatures for different periods of time.

Mixtures of metal sulphides were roasted at 600°C. The conversions of CuS into CuSO<sub>4</sub>, CdS and Bi<sub>2</sub>S<sub>3</sub> to CdO and Bi<sub>2</sub>O<sub>3</sub> were observed. CuSO<sub>4</sub> was dissolved in water and the residue containing CdO and Bi<sub>2</sub>O<sub>3</sub> was leached with 0.5 M H<sub>2</sub>SO<sub>4</sub>. The extraction yield was 96.3% and 99.6% of the Bi<sub>2</sub>O<sub>3</sub> remained in the solid.

The solution containing Zn(II), Fe(II), Ni(II) and Co(II) ions were evaporated in order to obtain solid metal sulphates. The solid samples were roasted between 500 and 800°C. While iron was converted into Fe<sub>2</sub>O<sub>3</sub>, nickel, zinc and cobalt remained in sulphate form. This sample was dissolved in water and filtered so that it crystallized. Nickel was separated from cobalt, iron and zinc as NiSO<sub>4</sub> by fractional crystallization. The yield was 86.2%.

In this process, 99.3% Cu and 96.3% Cd leached, 86.2% nickel was crystallized and 99.6% of the bismuth remained in the solid.

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