Characterization of the Products and By-products Obtained in the Electrolytic Refining of Copper Using Scraps

MIHAI BUZATU¹, PETRU MOLDOVAN², DIONEZIE BOJIN², MIHAI BUDU³, IÖZSEF JUHASZ², ELENA POP²

¹University Politehnica of Bucharest, Faculty of Materials Science and Engineering, Splaiul Independenței 313, 060042, Bucharest, Romania
²North University of Baia Mare, Mineral Resources and Environment Faculty, Dr.Victor Babeș 62A, 430083, Maramures, Romania

Experimental data from electrolytic refining of copper anodes obtained from scraps are presented in this paper. Alloying elements behaviour from the secondary copper was studied by SEM microscopy, EDAX chemical characterization, and atomic emission spectroscopy.

Keywords: electrolytic refining, secondary copper, scraps, remnant anodes

Known and used as industrial process for more than a century, the electrolytic refining of copper remains the main production method to meet the standards for most consumers in electrotechnique, energetic, electronic, microelectronic and communication industries.

Some improvements have been made to increase the technical and economical outputs, especially the quality of the electrolytic copper. Cathode copper quality is usually regarded as purity being the main parameter in the electrolyse process.

Cathode deposit quality depends on many technological factors, like: anode nature and electrolyte chemical composition, anodic current density, electrolyte temperature, electrolyte flow rate, active materials added, etc.; most of these factors can be controlled and maintained within some strict limits [1-4].

There is a tendency for impurities as Sb, As, Bi, Ni, Co to increase their concentration in the electrolyte beyond the critical concentration. It is why an efficient system to recycle and purify the electrolyte must be installed, to reduce and restrain sludge by few impurities as possible in the electrolyte. This is done mostly by filtering of the electrolyte and replacing of 0.1-0.5 m³ cathode electrolyte in the electrolyte. This is done mostly by filtering of the electrolyte and replacing of 0.1-0.5 m³ cathode electrolyte with a fresh pure one [5, 6].

As a result of exponentially grows of copper demand, alongside with the decrease of useful mineral in ores and respecting the world environmental policies, the electrolytic copper obtained from secondary materials gains more importance. This work presents experimental results obtained from electrolytic refining of secondary copper anodes.

State of the art in copper electrolytic refining technologies

The refined copper production from primary and secondary sources has highly increased in the last years as a result of developments in copper production technologies.

The operating parameters for conventional copper refining are: 35-45g Cu²⁺/L, 150-200g H₂SO₄/L, 55-65°C electrolytic temperature, 160-400 A/m² current density, 15-20 L/min circulation rate, walls of electrolytic cell covered with PVC or pure lead [1, 5].

ISA has remained the main process, and a marker for industrial performance evaluation, after more than 20 years. The process allowed great improvement regarding productivity grows, decreasing operating costs and most important production of high quality cathode copper. Updates refer to the followings:

- removing the start-up sheets and introducing reusable steel cathode sheets;
- automated copper deposits stripping from the brut stainless steel;
- mechanization for anode removal and spacing;
- cell voltage computer monitoring.

Electrolyte composition may suffer big fluctuations because of increasing level of impurities in the raw materials and therefore for the anodes, especially for secondary metallurgy.

Impurities as Sb, As, Bi, Ni, Co and others have the tendency to increase their concentration in the electrolyte up to the critical values where they can reduce on cathode (Ni, Co) or make floating sludges (As, Sb, Bi).

During the obtaining electrolytic copper from scraps, one of the secondary copper electrolysis characteristics, compared to other refining processes, is the high presence of impurities in electrolyte. Thus, by dissolution of the raw materials many impurities such as Fe²⁺, Mn²⁺, Al³⁺, Ca²⁺, Ni²⁺, Co²⁺ enter the electrolyte. Their effects on copper electrolysis were studied regarding the influence on the process main parameters (current efficiency, deposit morphology etc.) [7, 8].

It has been observed that Zn²⁺ ionic impurities have some effect on deposit morphology, although looking at their positions in the electrode potential series they should not deposit in the same time at cathode.

In order to select the most rational way to regenerate and use barren solutions from copper refining, both the usual CuSO₄ and H₂SO₄ solutions, and the waste electrolyte from copper refining in processing technology have been studied on a national and international level.

All improvements and updates for electrolytic copper refining, on a global scale can be put across the following main technical and economical characteristics:
- current efficiency 90-95%;
- electrical energy consumption 250-300 KW/h/t CuE;
- electrolytic copper with a high quality, less 200 ppm impurities (Cu 99.97%);
- superior quality for copper and useful metals in used electrolyte, as CuE, CuSO₄·5H₂O, NiSO₄ and/or Sb and As salts.

* email: mihai_batu@webmail.pub.ro; Tel.: 0747033884

REV. CHIM. (București) ♦ 59 ♦ Nr. 6 ♦ 2008
Electrolytic refining using copper scraps

Importance of such a process depends mostly on the concentration of sulphuric acid in solution, as well as on the high purity of electrolyte, obtained especially by electrochemical methods. If usual anodes, made from copper scraps, are used there will be large amounts of impurity elements in anodes, leading to changes of thermodynamic and kinetic conditions.

An example of a technological operation diagram to purify and reuse the depleted electrolyte is presented in figure 1 [5].

\[
\text{Copper Electrefining} \xrightarrow{\text{used electrolyte}} \text{purifying} \xrightarrow{\text{filtration}} \text{Residue} \xrightarrow{\text{electrolytic copper extraction}} \text{H}_2\text{SO}_4 \text{residual solution} \xrightarrow{\text{regeneration}} \text{regenerated solution H}_2\text{SO}_4
\]

**Fig. 1. Technological operation diagram of purifying and reusing the depleted electrolyte in cooper electrorefining**

The distribution of main impurities between anodic slimes and electrolyte for copper electrorefining is presented in table 1 [1-3].

From the shown data it can be observed that the biggest tendencies to pass into electrolyte are for Co, As, Sb, Ni and Fe. Among other impurities lead precipitates almost entirely as sulphate. Bi passes into electrolyte as much as As and Sb. Iron is eliminated mostly by thermorefining, thus it doesn't raise any specific problems for electrolyse.

**Table 1**

<table>
<thead>
<tr>
<th>Impurity</th>
<th>% in anodic slime</th>
<th>% in electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>&gt; 99</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Ag</td>
<td>98</td>
<td>2</td>
</tr>
<tr>
<td>Se and Te</td>
<td>98</td>
<td>2</td>
</tr>
<tr>
<td>Pd and Sn</td>
<td>98</td>
<td>2</td>
</tr>
<tr>
<td>Sb</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>As</td>
<td>25</td>
<td>75</td>
</tr>
<tr>
<td>Ni and Co</td>
<td>5</td>
<td>95</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt; 1</td>
<td>&gt; 99</td>
</tr>
</tbody>
</table>

Between the elements with the most significant importance for electrolysis, As, Sb and Bi stand out, especially because they couldn't be advanced eliminated in the first stage by thermorefining.

The depleted electrolyte contains less than 0.5 g/L Cu and has Ni and possibly Fe as the most important impurities. Evaporating and then crystallizing will remove the Ni and Fe as sulphates, the obtained solution being highly acid and suitable to be used to prepare the fresh electrolyte.

In the first steps of the refining, when copper ion concentration is over 10 g/L, the main electrochemical reactions are:

- At cathode: \[
\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}^0 \quad \text{(1)}
\]
  \[
\varepsilon = 0.337 + 0.0295 \log(\text{Cu}^{2+}), \text{V}
\]

- At anode: \[
2\text{OH}^- - 2e^- \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \uparrow \quad \text{(2)}
\]

So, with decreasing of copper concentration sulphuric acid becomes more concentrated in the electrolyte, its concentration raises 1.54 times the concentration of copper ion drops.

In the acid electrolyte solution As species can be either as As\(^{5+}\), in H\(_3\)AsO\(_4\), or as As\(^{3+}\) in HAsO\(_2\) and AsO\(^-\).

As\(^{5+}\) has a great influence over Sb\(^{3+}\) and Bi\(^{3+}\) ions as it forms antimony arsenate (SbOHAsO\(_4\) or SbAsO\(_4\)) and bismuth arsenate (BiAsO\(_3\)), which can't be dissolved by electrolyte. Thus As\(^{5+}\) plays a significant role in partial elimination of Sb and Bi in the anode slime.

Antimony, like arsenic, can be present in acid solutions as Sb\(^{3+}\) or Sb\(^{5+}\). Most of Sb\(^{5+}\) hydrolyzes in SbO\(_2\)·nH\(_2\)O, this being the main cause for the floating slags that could lead to cathode impurification.

As\(^{3+}\), Sb\(^{3+}\) and Bi\(^{3+}\) ions have better stability in electrolyte, and if copper ions are in little concentration (less than 10 g/L) can participate in some cathode reactions, leading to their elimination from the electrolyte.

The corresponding reactions are:

- AsO\(^+\) + 2H\(^+\) + 3e\(^-\) \rightarrow As (on cathode) + H\(_2\)O
  \[
  \varepsilon = 0.254 - 0.0394 \text{pH} + 0.0197 \log(\text{AsO}^+), \text{V}
  \]

- HAsO\(_2\) + 3H\(^+\) + 3e\(^-\) \rightarrow As (on cathode) + 2H\(_2\)O
  \[
  \varepsilon = 0.248 - 0.0591 \text{pH} + 0.0197 \log(\text{HAsO}_2), \text{V}
  \]

- As (on cathode) + 3H\(^+\) + 3e\(^-\) \rightarrow H\(_3\)As
  \[
  \varepsilon = -0.608 - 0.0591 \text{pH} - 0.0197 \log(\text{H}_3\text{As}), \text{V}
  \]

- SbO\(^+\) + 2H\(^+\) + 3e\(^-\) \rightarrow Sb (on cathode) + H\(_2\)O
  \[
  \varepsilon = 0.212 - 0.0394 \text{pH} + 0.0197 \log(\text{H}_3\text{Sb}), \text{V}
  \]

- Bi\(^{3+}\) + 3e\(^-\) \rightarrow Bi (on cathode)
  \[
  \varepsilon = 0.215 + 0.0197 \log(\text{Bi}^{3+}), \text{V}
  \]

- Bi (on cathode) + 3H\(^+\) + 3e\(^-\) \rightarrow H\(_3\)Bi
  \[
  \varepsilon = -0.8 - 0.0591 \text{pH} - 0.0197 \log(\text{H}_3\text{Bi}), \text{V}
  \]

where: logarithm arguments are the ion concentrations for indicated compounds, in ions g/L or thermodynamic activities of chemical compounds;

\(\varepsilon^\circ\) - standard electrode potential for the corresponding electrochemical couples.

The chemical reactions presented before indicate some very toxic hydrides, which impose taking special measures to catch and neutralize them.
Experimental part

The operating parameters for experiments were:
- current density: 200 A/m²;
- circulation rate: 15-20 L/min;
- electrolyte temperature: 45°C;
- cell voltage: 2-2.5 V.

Microstructure of cathodic copper and residues were analysed using SEM, chemical analysis EDAX and optic emission spectrometry. An electronic microscope XL-30-ESEM TMP was the main equipment.

Results and discussion

In this work we present experimental data from electrorefining of secondary copper anodes. Copper extraction from solution and alloying elements were both observed, because if some elements reach a certain concentration will greatly alter electrolytic copper properties.

Depending on observed parameters the initial and final concentration of copper in electrolyte has widely fluctuated. Also the current efficiency will vary within a wide range.

After electrorefining of secondary copper anodes it has been obtained metallic copper and a residue (fig. 2).

Chemical analysis for electrolytic residue is shown in table 2. The powder was dried, pressed (15 tf) and metallographic processed for performing this analysis.

Electron microscopy - composition SEM with EDAX analysis - made on sample B on different points, has revealed chemical composition in mass percents for selected areas.

Thus, in figures 3-5 there are different coloured areas representing partial oxidized metallic copper, partial oxidized metallic lead as well as areas richer in metallic oxides, specifically lead and copper based oxides.

Copper cathode resulted after electrolysis has been analysed to determine chemical composition, and to determine standard class to be classified by. Table 3 shows results from optical spectrometry.

According to STAS 170/1-88 regarding the copper cathodes, maximum impurities allowed in Romania for electrolytic copper are presented in table 3. It can be easily observed that none of the discussed impurities meets the standard.
Fig. 3. SEM composition microstructure, and EDAX analysis (compact grey particle, composed of 97.99% Cu and 2.01% O).
EDAX diagrams have coordinates: counts [a.u. - arbitrary units] on the ordinate, and energy [keV] abscissa.

Fig. 4. SEM composition microstructure, and EDAX analysis (compact dark grey particle, composed of 57.24% Si, 42.76% O - up) (dark grey porous area, composed of 82.50% Cu, 0.65% Ca, 4.84% S, 12.0% O - left). EDAX diagrams have coordinates: counts [a.u. - arbitrary units] on the ordinate, and energy [keV] abscissa.

Fig. 5. SEM composition microstructure, and EDAX analysis (white area, composed of 91.98% Pb, 8.02% O - up) (compact light grey particle, composed of 3.12% Cu, 82.61% Pb, 14.27% O - left). EDAX diagrams have coordinates: counts [a.u. - arbitrary units] on the ordinate, and energy [keV] abscissa.
Electrolytic copper obtained from copper and copper alloys scraps ought to be situated in a standardization class with less demand regarding impurity levels. In our experiments, the initial anode composition is much richer in contaminants and the products must undertake a new stage of refining (a supplementary refining process using anodes made from the electrolytic copper obtained before).

Anode residues from secondary copper anodes electrorefining show a chemical composition that impose their introducing in the liqation phase of the primary copper technological flow, followed by next operations. Because of the high concentration of alloy elements, lead precipitates as an oxide not as a sulphate.

As a final conclusion, the electrolytic copper obtained from scrap based anodes, may only be used to produce lead bronze, and only after silicon is reduced below the standard level.

References
1. CONSTANTIN, I., Copper Metallurgy, I, Polytechnic Institute of Bucharest, 1989
4. FREE, M.L., JOM, 59, nr. 5, 2007, p. 28

Manuscript received: 6.03.2008