COPPER RECOVERY BY ELECTROLEACHING OF CHALCOPYRITE

Vânia Mori (PQ)\textsuperscript{1}, Marco A. S. Aguiar (PQ)\textsuperscript{2}, Paulo A. Medeiros da Silva\textsuperscript{3} e
Luis G. S. Sobral (PQ)\textsuperscript{4}
2. Instituto Nacional de Propriedade Industrial - INPI, DIQUIM II,Rua. Mauá, 7- Centro- RJ
3. Mineração Caraíba S/A, Fazenda Caraíba, s/n, Jaguariaí/BA.
vamori@cetem.gov.br

ABSTRACT

Copper occurs in the crust of the earth, predominantly, as sulphides. Among the copper sulphide minerals, the chalcopyrite is the most abundant and the most refractory to the conventional oxidative processes. This work aims at developing an electrolytic process for treating a copper sulphides flotation concentrate, more precisely chalcopyrite (CuFeS\textsubscript{2}) and bornite (Cu\textsubscript{5}Fe\textsubscript{4}S\textsubscript{9}) in the percentages of 70 and 30\%, respectively.

The electroleaching tests of the flotation concentrate were accomplished in a suitable reaction system, had been carried through in reactor Pyrex a glass of 1L with cover leaked for rank of the electrodes (cathode/anode), where the sulphides particles were suspended by magnetic stirring and the current supplied by a power Source MCE 8257 0-18 V / 0-20 A. The pH of the reaction system was monitored every 30 minutes and controlled by adding concentrate hydrochloric acid, and so was the redox potential.

The success of the electroleaching of sulphide concentrates depends, to some extent, on the effective generation of hypochlorite ions and hypo-chlorous acid, due to the electrochemical chloride evolution and hydroxyl ions in the surface of the polarized electrodes. The first tests were carried out using NaCl 2.0 mol.dm\textsuperscript{-3}, for 25 hours, at a pH approximately 1.5 and anodic current density of 1.2 A.dm\textsuperscript{-3}.

Through the electroleaching tests nearly the total dissolution of sulphides could be observed and the recovery of copper was approximately 70\%. Those tests make clear that the electroleaching process makes possible the production of chloride ions that dissolve the aforementioned sulphides, with formation of copper soluble species that are simultaneously reduced in the cathode surface.

KEY-WORDS: Copper, electroleaching and chalcopyrite.
1. INTRODUCTION

Copper occurs in the crust of the earth, predominantly, as sulphides. Among the copper sulphide minerals, the chalcopyrite is the most abundant and the most refractory to the conventional oxidative processes. Solutions of ferric chloride are used in the hydrometallurgy of sulphides copper ores as source of ferric ions ($Fe^{3+}$), a strong oxidant agent. The oxidation of chalcopyrite through ferric ions is stoichiometrically represented by the following global reaction, in accordance with Gupta & Mukherjee (1990):

$$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2e^- \quad (1)$$

However, during the leaching of chalcopyrite, the mineral surface passivation, phenomenon that reduces the reaction rate, and, consequently, making the metal ions of interest available in solution. The chalcopyrite passivation takes place due to the formation of a film of sulphur that hinders the pursuit of the dissolution reaction, this was shown in the works of Warren et al., (1982); Mateos et al. (1987); Hadd et al. (1995) and Elsherief (2002). The chalcopyrite passivation has been researched, nowadays, a great deal due to their practical implications. Lu et al. (2000) studied the effect of chloride ions in the dissolution of that mineral in oxygenated acid solutions and they concluded that the presence of sodium chloride (NaCl), in the leaching solution, promoted the diffusion of the leaching reagents through that film (product of the reaction) and the reaction continuation in the surface of the mineral. The addition of NaCl in the copper sulphides leaching solution was studied also by Winand (1991) that attributed to the formation of copper chloride complex ions as being a decisive factor for increasing the leaching rate, for increasing the copper solubility in the system Cu/Cu(II) and/or Cu(I), suggesting that NaCl acts on the elemental sulphur layer and also on the solubility of copper complexes in the reaction system.

The electro-oxidation technique has been applied, mainly, in the digestion of mercury species, such as elemental mercury and mercury sulphide (HgS), on the surface of activated carbon, previously impregnated with sulphur, from the natural gas cleaning process, from gold mining residues (residues from the gravity concentrate gold amalgamation process), from residues of the chlor-alkali industry and, still, from exhausted fluorescent lamps. That process is characterized by the action of strong oxidizing agents, generated in a suitable reaction system, during the electrolytic oxidation of chloride ions present in that system (the cell electrolyte). In that process, differently of the aforementioned pre-oxidative processes, the copper and the precious metals, contained in the copper sulphides flotation concentrate, can be recovered along the electro-oxidation process through the deposition of those metals in the cathode surface under suitable cathode potential.

The main advantage of that kind of electrolysis is that the material to be treated can be used in its original form, i.e. as particulate material. Another important characteristic of the electro-oxidation process is that some steps of high costs are eliminated, when compared to other processes with similar objectives, as the dissolved metals (copper, gold etc.) are deposited in the cathode simultaneously to the sulphides digestion process.

2. EXPERIMENTAL

2.1. Chemical and Instrumental Analyses of the Flotation Concentrate

At first, the sample was homogenized and a representative fraction separated for chemical analyses of elements of interest. The chemical and instrumental characterizations were accomplished by using scanning electronic microscopy (SEM), using the LEO S440 equipment, X-ray diffraction (XRD), using a Siemens/Brocker - AXS D5005, equipped with Goebel mirror for X-rays parallel beam, graphite monochromator, whenever necessary, and NaI detector of solid state. A semi-quantitative chemical analysis was accomplished by X-ray fluorescence, in order to verify the metal components of the concentrate under study.

The copper content in the sample was quantified by atomic absorption spectrometry (AAS). The used equipment was a VARIAN spectrometer model AA.
2.2. Electroleaching Tests

The electroleaching tests of the flotation concentrate, containing essentially chalcopyrite and bornite, were accomplished in a 1 liter Pyrex glass reactor with hole-containing lid for attaching the electrodes (cathode and anode), being the particulate material suspended by magnetic stirring. The current and potential control were accomplished using a power supplier MCE 8257 0-18 V / 0-20 A. The electrolyte pH and cell voltage were monitored every 25 minutes. The Figure 1 shows the outline of the reaction system used in the electroleaching process.

![Diagram of reaction system](image)

*Figure 1: Reaction system used in the electroleaching tests.*

The leaching of sodium chloride was prepared and transferred for the cylindrical glass reactor. The pH of the leaching solution was, then, adjusted by adding concentrated HCl. The electroleaching tests were accomplished in five steps of 5 hours each, maintaining the relationship solid/liquid ratio of 1:10 (0.1). After each step, the leached material was analysed to verify the copper content. Samples of the leaching liquor were analysed aiming at quantifying the copper concentration, through Atomic Absorption spectrometry (AAS).

3. RESULTS AND DISCUSSION

3.1. Chemical and Instrumental Analysis of The Flotation Concentrate

According to Atomic Absorption analysis, the initial copper content in the flotation concentrate was of 37.3%.

The semi-quantitative analyses of the mineralogical species present in the flotation concentrate under study showed that the mineralogical constituents were the chalcopyrite, major constituent (CuFeS2), sulphides very refractory to the oxidative processes.

The results of the semi-quantitative analyses (X-ray diffraction and fluorescence) of the flotation concentrate mineralogical species, show that the concentrate under study contains high copper content, element of interest in this study, which is confirmed by the high sulphur and iron contents, elements associated to the copper sulphides (chalcopyrite and bornite).
3.2. Electroleaching Tests

The success of the sulphides electroleaching process depends, largely, on the effective reaction of hypochlorite ions and hypochlorous acid, due to the electrochemical generation of chlorine and hydroxyl ions on the surface of the polarized electrodes, anode and cathode, respectively.

The electroleaching process begins, once supplied the current, with the oxidation of chloride ions to chlorine gas, according to reaction (2).

\[ 2Cl^- \leftrightarrow Cl_2 + 2e^- \]  \hspace{1cm} (2)

On the other hand, in the cathode surface the water is, initially, reduced producing hydrogen gas and hydroxyl ions, according to reaction (3).

\[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \]  \hspace{1cm} (3)

Simultaneously, hypochlorous acid is generated in the bulk solution through the chemical reaction of chlorine, generated in the anode, with the aqueous phase:

\[ Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \]  \hspace{1cm} (4)

That acid is dissociated to form hypochlorite and hydrogen ions, reaction depending directly on the pH of the aqueous phase.

\[ HClO \leftrightarrow ClO^- + H^+ \]  \hspace{1cm} (5)

Those hydrogen ions react with the hydroxyl ions, product of the cathode reaction, to form water, according to the following reaction.

\[ H^+ + OH^- \rightarrow H_2O \]  \hspace{1cm} (6)

During the electrolytic process, after a while, the production of hypochlorite ions (ClO-) does not increases any more as expected, which is attributed to the chemical generation of chlorate ions (ClO3-), through the following reaction:

\[ 2HClO + ClO^- \rightarrow ClO_3^- + 2H^+ + 2Cl^- \]  \hspace{1cm} (7)

or electrochemically:

\[ 6ClO^- + 3H_2O \leftrightarrow 2ClO_3^- + 6H^+ + 4Cl^- + 3/2O_2 + 6e \]  \hspace{1cm} (8)

Once produced the HClO (hypochlorous acid) species and/or ClO3- (hypochlorite ion) the sulphides oxidation begins, just as the pyrite, expressed, according to the reactions (9) and (10).

\[ 2FeS_2 + 15ClO^- + H_2O + 2H^+ \leftrightarrow 2Fe^{3+} + 4HSO_4^- + 15Cl^- \]  \hspace{1cm} (9)
2FeS₂ + 15ClO⁻ + H₂O ⇄ 2Fe³⁺ + 4HSO₄⁻ + 13Cl⁻  

The electrolytic leaching of chalcopyrite goes by the oxidation of sulphide to elemental sulphur, sulphate and other oxidants. The global electrochemical reactions that take place during the oxidative leaching of chalcopyrite can be represented by the following semi-reactions:

CuFeS₂ ⇄ Cu²⁺ + Fe³⁺ + 2S + 5e⁻  

SH⁻ + 5/2O₂ + 5e⁻ ⇄ 5/2H₂O  

In sufficiently oxidant solutions and in pH below 3, the Fe³⁺ ions are, soon afterwards, oxidised to ferric ions (Fe⁵⁺), as in the following reaction:

Fe²⁺ ⇄ Fe³⁺ + e⁻  

The Fe⁵⁺ ions are, by itself, oxidant agents and can participate of the oxidation reaction of the refractory mineralogical species. However, the pyrite is considered inert, in particular, to the action of ferric ions, but its performance as oxidant agent is catalysed in the presence of other several species, such as cupric ions (Cu²⁺) and activated carbon.

The electrochemical techniques have been used for obtaining detailed information on the electroleaching process. Those studies have been showing that the kinetics of low favoured leaching is the result of the anodic passivation by the generation of elemental sulphur layer on the chalcopyrite surface.

During the electrolysis, the generation of the hypochlorous acid (HClO) and hypochlorite ions (ClO⁻) depends on the pH of the bulk solution and the oxidation power increases as the pH decreases, as the generation of hypochlorous acid is favoured. The pH control was necessary, so as to avoid the formation of elemental sulphur during the oxidation process of sulphide ions into sulphate.

The tests accomplished with 100g of flotation concentrate sample in one litter of a 2.0 mol.L⁻¹ NaCl solution, during 25 hours, being the pH of the suspension controlled in 1.5 by adding concentrated HCl. The applied potential was of 3.0 V and the current density was of 1.2 A.dm⁻².

The Table 1 shows the copper concentrations in each one of the samples in the final residue (obtained after the electroleaching experiments) and in the filtrate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction Time (h)</th>
<th>Residual Copper Mass (g)</th>
<th>Extraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>63.40</td>
<td>2.3</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>45.85</td>
<td>29.4</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>28.06</td>
<td>56.8</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>19.44</td>
<td>70.0</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>18.70</td>
<td>71.2</td>
</tr>
</tbody>
</table>

The influence of the digesting time of the sample is represented in the graph the figure 2.
Through the results of the graph 2, it is observed that the copper extraction through the electroleaching process, after 25 hours of experiment, is of approximately 71.2% at room temperature.

4. CONCLUSIONS

Through the electroleaching process, nearly the total dissolution of the sulphides could be observed.

Those tests evidenced that the electroleaching process makes possible the production of chloride ions that dissolve the copper sulphides releasing copper ions to solution, which are simultaneously reduced in the cathode surface. In addition, in such process, bearing in mind other similar copper concentrate leaching techniques for recovering that metal, some steps of high cost are eliminated.

The elemental sulphur formation on the surface of the sulphide particles, as a result of the electrolyte saturation with sulphate ions, encapsulates those particles leading to an interruption of the sulphides digestion process.

Through the electroleaching process a reversible iron redox reaction takes place ($\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+} + e^-$), which consumes part of the applied current to the reaction system.

5. REFERENCES


