SEM AND AES STUDIES OF CHALCOPYRITE BIOLEACHING IN THE PRESENCE OF CATALYTIC IONS

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ABSTRACT

Scanning electron microscopy (SEM) and Auger electron spectroscopy (AES) were used to study the surface changes occurring in chalcopyrite when the bioleaching medium contained Ag(I), Hg(II) and Bi(III) ions. The untreated sample revealed the presence of carbon and oxygen in addition to the chalcopyrite elements (Cu, Fe and S). AES spectra showed a sulphur enrichment on the chalcopyrite surface during bioleaching without catalytic cations. The results with catalytic cations showed that Ag(I), Hg(II) and Bi(III) are incorporated into the surface irrespective of the presence of bacteria. However, different interactions between the chalcopyrite and the cation take place, depending on the cation added to the leaching medium. Ag(I) and Hg(II) ions formed a coating of a silver sulphide and a mercury sulphide, respectively. Microorganisms oxidise the surface sulphur of this silver sulphide but not the mercury sulphide layer, so that its thickness did not increase during bioleaching. The observed changes in the shape of AES sulphur peak confirmed the formation of Ag₂S in the surface. When Bi(III) is added to the bioleaching medium an oxidised compound is formed, which suggested a different pattern of interaction with respect to Ag(I) and Hg(II). © 1997 Elsevier Science Ltd

Keywords
Sulphide ores; bioleaching; surface modification

INTRODUCTION

It is well known that certain microorganisms participate in the extraction of metals from minerals and that their role in these processes is to catalyse the dissolution reactions. The main microorganisms involved in the microbial leaching of ores are chemolithotrophic acidophilic bacteria of the genus Thiobacillus, which oxidise metallic sulphides and elemental sulphur into water-soluble sulphates [1,2]. Special importance is attached to the species Thiobacillus thiooxidans and Thiobacillus ferroxidans.

Thiobacillus thiooxidans oxidise elemental sulphur and thiosulphate to sulphate and sulphuric acid, according to:

\[ \text{S}_2\text{O}_3^{-} + 2\text{H}^+ + 2e^- \rightarrow \text{S}_2\text{O}_4^{2-} + \text{H}_2\text{O} \]

\[ \text{S}_2\text{O}_3^{-} + 2\text{H}^+ + 2e^- \rightarrow \text{S}_2\text{O}_4^{2-} + \text{H}_2\text{O} \]

\[ \text{S}_2\text{O}_3^{-} + 2\text{H}^+ + 2e^- \rightarrow \text{S}_2\text{O}_4^{2-} + \text{H}_2\text{O} \]

\[ \text{S}_2\text{O}_3^{-} + 2\text{H}^+ + 2e^- \rightarrow \text{S}_2\text{O}_4^{2-} + \text{H}_2\text{O} \]

\[ \text{S}_2\text{O}_3^{-} + 2\text{H}^+ + 2e^- \rightarrow \text{S}_2\text{O}_4^{2-} + \text{H}_2\text{O} \]
The high acid production by the bacteria lowers the pH of the leaching medium to as low as 1, and causes the dissolution of most of the metal as water-soluble sulphates. However, the more important role in the bacterial leaching processes is undoubtedly played by *Thiobacillus ferrooxidans* [1,2]. Apart from oxidising sulphur and reduced sulphur compounds to sulphates, *Thiobacillus ferrooxidans* can oxidise Fe$^{2+}$ to Fe$^{3+}$.

Chalcopyrite (CuFeS$_2$) is a mineral sulphide that can be oxidised by *Thiobacillus ferrooxidans* and related acidophilic bacteria. The overall bioleaching chalcopyrite oxidation is given by:

$$2\text{CuFeS}_2 + 8/2\text{O}_2 + \text{H}_2\text{SO}_4 \xrightarrow{\text{bacteria}} 2\text{CuSO}_4 + \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$$

However, its dissolution is inhibited as the mineral dissolves. As a consequence, in chalcopyrite bioleaching with mesophilic microorganisms, low extraction yields of copper (about 20–25%) are obtained [3]. This recalcitrance of chalcopyrite to oxidation in different leaching medium is well known [4]. It is also well known that chalcopyrite is the most resistant among the copper sulphides to hydrometallurgical processes and can be dissolved using extreme oxidant conditions only [5]. Many attempts have been made to explain the cause of this decrease in the reactivity of the mineral. In this way, Miller [6] proposed the formation of an elemental sulphur layer on the chalcopyrite surface which makes the electronic transfer difficult and hinders the dissolution reaction by establishing a diffusion barrier.

In order to catalyse the chemical and biological kinetics of dissolution of chalcopyrite, small quantities of Ag$^+$ ions have been used by researchers [7, 8]. This ion enhances copper leaching rates and extractions. This positive effect of Ag$^+$ on the reactivity of chalcopyrite was explained by the formation of an intermediate Ag$_2$S film, which prevents the formation of the protective and non-porous sulphur formed in the absence of Ag$^+$. Following this hypothesis, the effect of other cations on the biological leaching of several Spanish concentrates of complex sulphides have been studied in earlier works [3, 9]. The main conclusion was that Hg(II) and Bi(III) ions also increase the bioleaching rate of the chalcopyrite contained in such concentrates, but to a lesser extent than in the case of Ag$^+$, and these cations have not influenced the recovery yields. Thus, the main objective of the present work has been to study changes occurring in the CuFeS$_2$ surface when Ag(I), Hg(II) and Bi(III) were added to the reaction medium, in order to understand the role of such ions in the bioleaching processes of CuFeS$_2$. With this aim, Scanning Electron Microscopy (SEM), Energy Dispersion Spectroscopy (EDS) and Auger Electron Spectroscopy (AES) were used to follow topographic and chemical surface changes taking place during the bioleaching reaction on CuFeS$_2$–

### EXPERIMENTAL

All studies were carried out on massive samples of chalcopyrite from the Transvaal (South Africa). The chemical composition was Cu=35%, Fe=30.1% and S=34.7%. The metallographic examination revealed a very pure chalcopyrite, including occasionally very slight traces of ZnS and FeS$_2$. The samples used for AES were slices of about 10x8x1 mm. The samples were mounted in epoxy resin to perform SEM examination. All samples were mechanically polished with alumina, then submitted to different chemical leaching (solution with or without added ions) and bioleaching processes (solution using a bacterial medium with or without added ions).

The bacteria, obtained from a mine water, were grown in a modified 9K medium without Fe$^{2+}$, consisting of 3 g/l of (NH$_4$)$_2$SO$_4$, 0.5 g/l of MgSO$_4$. 7H$_2$O, 0.5 g/l K$_2$HPO$_4$, 0.1 g/l of KCl and 0.014 g/l of Ca(NO$_3$)$_2$, using a copper concentrate as growth source, in order to obtain a bacterial culture with a sufficiently high concentration of microorganisms (about 10$^9$ cells/ml). Microbiological studies showed the presence of different bacteria, mainly *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans* and *Leptospirillum ferrooxidans*.

Bioleaching and leaching experiments were performed in erlenmeyer flasks of 250 cm$^3$ capacity containing the modified 9K medium. The temperature was maintained at 35$^\circ$ C with a stirring velocity of 150 min$^{-1}$
and a pH of 2.0. The concentration of the catalytic ions (Ag(I), Hg(II) and Bi(III)) was in every case 0.1 g/l and these ions were added to the reaction medium in the form of Ag$_2$SO$_4$, HgSO$_4$ and Bi(NO$_3$)$_3$, respectively. In the bioleaching experiments 5 ml of bacterial culture were added per 100 ml of 9K medium. Table 1 lists out the treatments of chalcopyrite samples subjected to Auger spectroscopy. The experiments were carried out for 10 days.

**TABLE 1** Chalcopyrite samples examined by Auger spectroscopy.

*Time of treatment was 10 days.*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment of the chalcopyrite sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Untreated and polished</td>
</tr>
<tr>
<td>b</td>
<td>Bioleached</td>
</tr>
<tr>
<td>c</td>
<td>Treated with Ag$^+$, without bacteria</td>
</tr>
<tr>
<td>d</td>
<td>Bioleached in presence of Ag$^+$</td>
</tr>
<tr>
<td>e</td>
<td>Treated with Hg$^{2+}$, without bacteria</td>
</tr>
<tr>
<td>f</td>
<td>Bioleached in presence of Hg$^{2+}$</td>
</tr>
<tr>
<td>g</td>
<td>Treated with Bi$^{3+}$, without bacteria</td>
</tr>
<tr>
<td>h</td>
<td>Bioleached in presence of Bi$^{3+}$</td>
</tr>
</tbody>
</table>

In parallel experiments, a new series of chalcopyrite samples for SEM examination were bioleached for 3, 6, 12 and 20 days with and without catalytic ions. This allows the microstructural evolution of the chalcopyrite surfaces to be observed during the bioleaching process.

After every treatment, samples were washed in water and dried in air. Surface analysis was performed by Auger Electron Spectroscopy (AES). The Auger spectrometer was a cylindrical type incorporated to an electron gun operating at 3kV with a voltage modulation of 3V peak to peak. The intensity of the electron beam measured on the sample was 30 nA and the spot diameter was 30 μm. In order to check homogeneity of surface composition, AES spectra were recorded on different points of the surface sample, by moving the sample with respect to the electron beam. For SEM examination, the samples were covered with a fine graphite thin film. A JEOL JSM-35C scanning electron microscope and a EDS Kevex 7000, to perform the X-ray microanalysis, were used.

**RESULTS AND DISCUSSION**

**Scanning electron microscopy and X-ray analysis**

The as-polished chalcopyrite samples showed a surface with a few defects, some isolated cracks and pores varying in size. These defects were interpreted as mineral genetic defects. An as-polished chalcopyrite surface including some of these pores can be seen in Figure 1.
A SEM observation of the bioleached samples without catalytic ions (Figure 2) showed no important changes when compared to as-polished samples. However, it seems that the edges of typical as-polished mineral defects had been rounded and smoothed. Moreover, on the surface some precipitates introduced with the inoculum (a) and some microorganisms (b) can be seen.

![Fig.1 Typical as-polished chalcopyrite surface (grey background) with some pores (dark zones).](image)

![Fig.2 Detail at high magnification of one pore after bioleaching for 6 days, showing some precipitates (a) and microorganisms (b).](image)

The chalcopyrite samples bioleached with Ag(I) differed from the bioleached samples without catalytic cations. At first sight, the greyish colour of the as-polished surface turns blueish, although the shine remains. A SEM examination of the bioleached chalcopyrite with Ag(I) showed a rougher surface, which was interpreted as a coating. In Figure 3 this coating can be observed in a zone close to a crack. EDS microanalysis showed the presence of silver on all samples bioleached for different times and there was already a noticeable quantity of silver after 3 days of bioleaching (Figure 4) although the quantity of silver increased with the bioleaching time.

![Fig.3 Detail of a zone close to a crack showing the silver coating.](image)

The chalcopyrite surface bioleached with Hg(II) had a similar appearance to the bioleached chalcopyrite without catalytic ions, with a slightly darker colour and a less metallic shine. SEM examination showed a very smooth surface, not etched and with HgCl₂ precipitates on it, as a consequence of the reactivity of Cl⁻ ions present in the 9K medium and the added Hg (II) cations. No mercury was detected by EDS microanalysis, even after long periods of time.

A peculiar behaviour was observed in samples containing pyrite impurity zones after bioleaching in the
presence of Hg(II). Figure 5 shows two phases: pyrite (py), darker phase in the centre of the micrograph, and a matrix of chalcopyrite (cha), grey phase. As can be seen, the pyrite has plenty of cracks, produced as a consequence of bacterial leaching. The chalcopyrite however, has a very smooth surface, not etched. EDS microanalysis did not detect Hg after bioleaching in the pyrite zones. It is well known that in the absence of catalytic cations in galvanic chalcopyrite-pyrite couples, chalcopyrite is firstly bioleached and then the pyrite [10]. However, as observed in Figure 5, the addition of Hg (II) changes the dissolution order between both sulphides. This fact could be explained by a Hg (II)/chalcopyrite interaction. In the bioleaching with Hg, this cation could be incorporated on the chalcopyrite surface to inhibit its dissolution. However, because Hg was not detected on the chalcopyrite surface by EDS microanalysis, this hypothesis should be checked using other superficial analysis techniques, such as Auger Spectroscopy.

Fig.3 Chalcopyrite bioleached with Ag(II) for 12 days. The surface has been covered by a silver coating.

Fig.4 X-ray microanalysis of chalcopyrite bioleached with Ag(I) for 3, 6 and 12 days.
A SEM examination of the chalcopyrite bioleached with Bi(III) showed no important changes in comparison to the chalcopyrite bioleached in the absence of catalytic cation (Figure 6) and no bismuth was detected by microanalysis.

Fig. 5 Chalcopyrite bioleached with Hg(II) for 12 days. Detail of the galvanic couple chalcopyrite-pyrite with a preferent dissolution of pyrite.

Fig. 6 Chalcopyrite bioleached with Bi\(^{3+}\) for 20 days.

Auger Spectroscopy

Figure 7 shows the AES spectra for the chalcopyrite samples after the indicated biological and chemical treatments with Ag(I), Hg(II) and Bi(III). The untreated chalcopyrite (a) is also presented for comparison purpose. Peaks corresponding to S(150 eV), C(270 eV), O(512 eV), Cu(920 eV) and Fe(712 eV) were observed in all the spectra. In the case of samples treated with metallic ions the attenuation of Fe and Cu signals is within the noise level of the instrument scale (curves c to h). The C and O signals may be due partly to the presence of bacteria and/or atmospheric contamination since, as is known by surface spectroscopists, carbon and oxygen are seen on any surface exposed to the atmosphere [11]. The AES peaks corresponding to Ag(357 eV), Hg(76 eV) and Bi(96 eV) are always observed when chalcopyrite is treated with the corresponding catalytic ion, irrespective of the presence of bacteria. Furthermore, Cl (182 eV) and Ca (291 eV) are observed in samples treated with Ag (I) and Hg (II) cations. The presence of Cl and Ca is due to the fact that these elements are present in the 9K medium and they became included into the
surface, depending on their capability to form compounds with the catalytic ion.

Table 2 summarises relative concentrations of the elements in the samples whose treatment is outlined in Table 1, calculated according to the standard method and corrected by sensitivity factors [12]. These results correspond to the mean values of five different AES measurements. The most significant difference between untreated (a) and bioleached samples without catalytic cations (b) is the increase in sulphur concentration. This means that the S concentration increases in the presence of bacteria. Such behaviour agrees reasonably well with models already accepted, in which the bioleaching does not progress, as a consequence of sulphur surface enrichment either by the formation of a layer of metal-deficient polysulphide and porous sulphur [5] or by the formation of elemental sulphur [6]. However, due to the insensitivity of the AES technique to distinguish the chemical state of sulphur, our results are unable to confirm any of the above-mentioned models.

As mentioned above, in samples treated with Ag(I) the presence of this element was detected irrespective of the presence of bacteria. Ag could also be observed with X-ray microanalysis, where Ag was already found after 3 days of bioleaching (Figure 4). Cu and Fe concentrations drastically fall, reaching zero. Cu and Fe signals are due to the chalcopyrite composition, and this decrease could be explained by the formation of a layer, which does not contain these elements. This layer was also observed by SEM. The S signal remains practically constant and the relative concentration of O decreases in comparison to the untreated chalcopyrite, ruling out the presence of an oxidised compound or silver sulphate. All this indicates

![AES spectrum of chalcopyrite samples after a bioleaching treatment in presence of (a) Ag(I), (b) Hg(II) and (c) Bi (III).](image)
that the layer formed would be similar to silver sulphide. These results agree with the mechanism already
proposed by Miller [6], in which the catalytic effect of the Ag(I) is due to the precipitation of Ag₂S on the
surface, according to the reaction:

\[ \text{CuFeS}_2 + 4\text{Ag}^+ \rightarrow 2\text{Ag}_2\text{S} + \text{Cu}^{2+} + \text{Fe}^{2+} \quad (3) \]

This reaction occurs in both cases, e.g. with or without the presence of bacteria. However, bacteria catalyse
the \( \text{Fe}^{2+} \) oxidation to \( \text{Fe}^{3+} \) [1]. This step is summarised by the reaction:

\[ \text{Fe}^{2+} \xrightarrow{\text{bacteria}} \text{Fe}^{3+} + \text{e}^- \quad (4) \]

The \( \text{Ag}_2\text{S} \) formed on the chalcopyrite surface then reacts with the \( \text{Fe}^{3+} \) according to the reaction:

\[ \text{Fe}^{3+} + \text{Ag}_2\text{S} \rightarrow 2\text{Ag}^+ + \text{S}^0 + \text{Fe}^{2+} \quad (5) \]

These \( \text{Ag}^+ \) ions generated via reaction (5) again precipitate on the chalcopyrite surface and, in turn, more
\( \text{Cu}^{2+} \) and \( \text{Fe}^{2+} \) ions will be liberated according to reaction (3). This establishes a cyclic process in the
presence of ferrooxidising bacteria, which yields a progressive dissolution of the massive chalcopyrite. Thus,
this mechanism reaction process explains the higher silver concentrations in biotreated samples (see Table 2). On the other hand, the \( \text{S}^0 \) formed in reaction (5) is oxidised by microorganisms to sulphate, by
microorganisms which is soluble in the reaction medium [1,2] and, as a consequence, the amount of
elemental sulphur decreases. This model is in agreement with our data (Table 2) where the S and Ag
concentrations decrease and increase, respectively, in bioleached samples.

**TABLE 2 Relative concentrations of main elements for different samples.**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Cu</th>
<th>Fe</th>
<th>S</th>
<th>C</th>
<th>Cl</th>
<th>Ca</th>
<th>N</th>
<th>O</th>
<th>Ag</th>
<th>Hg</th>
<th>Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Untreated</td>
<td>6</td>
<td>7</td>
<td>46</td>
<td>29</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(b) Bioleaching</td>
<td>4</td>
<td>5</td>
<td>63</td>
<td>19</td>
<td>-</td>
<td>-</td>
<td>9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(c) Leaching Ag⁺</td>
<td>-</td>
<td>-</td>
<td>45</td>
<td>20</td>
<td>2</td>
<td>-</td>
<td>6</td>
<td>25</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(d) Bioleaching Ag⁺</td>
<td>-</td>
<td>-</td>
<td>36</td>
<td>18</td>
<td>7</td>
<td>4</td>
<td>2</td>
<td>33</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(e) Leaching Hg⁺</td>
<td>-</td>
<td>-</td>
<td>40</td>
<td>27</td>
<td>10</td>
<td>-</td>
<td>10</td>
<td>-</td>
<td>13</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(f) Bioleaching Hg⁺</td>
<td>-</td>
<td>-</td>
<td>43</td>
<td>23</td>
<td>11</td>
<td>-</td>
<td>2</td>
<td>7</td>
<td>-</td>
<td>16</td>
<td>-</td>
</tr>
<tr>
<td>(g) Leaching Bi⁺</td>
<td>-</td>
<td>-</td>
<td>41</td>
<td>38</td>
<td>1</td>
<td>1</td>
<td>16</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>(h) Bioleaching Bi⁺</td>
<td>-</td>
<td>-</td>
<td>26</td>
<td>26</td>
<td>-</td>
<td>6</td>
<td>35</td>
<td>-</td>
<td>-</td>
<td>7</td>
<td>-</td>
</tr>
</tbody>
</table>

Similar behaviour is observed in the samples treated with Hg(II). As can be seen in Table 2, Cu and Fe
signals decrease, becoming zero and there is no increase in the O signal in comparison to the untreated
sample. However, the S signal remains constant and similar to the untreated sample, irrespective of the
presence of microorganisms. As with the samples treated with Ag(I), a coating of a mercury sulphide is
formed on the chalcopyrite surface. However, in this case, Hg is not detected by EDS due to the mercury
sulphide layer being thinner. On the other hand, the similarity of the relative concentration of the main
elements in the leached and bioleached samples (experiments e and f respectively) shows that the presence
of bacteria slightly influences the mercury sulphide layer, because it provides an unsuitable substrate for
the microorganisms [13] and it is leached with ferric sulphate and other oxidising solutions with great
difficulty [14]. All this would explain why after bioleaching with Hg(II) in coupled chalcopyrite/pyrite
systems, chalcopyrite is passivated (Figure 5). Mercury sulphide formed on the chalcopyrite would hinder its dissolution, accelerating the pyrite bioleaching.

In samples treated with Bi (III) an opposite behaviour to Ag(I) and Hg (II) is observed. Table 2 shows the lowest values in the catalytic cation concentrations in the case of Bi (III). Moreover, Bi (III) leads to relatively higher O concentration and no increase in S concentration in the bioleached sample. All this suggests the formation of an oxidised compound of bismuth. According to the literature [15] and a previous AES work on galena [16], this compound may be a bismuth salt and not a bismuth sulphide.

A thermodynamic study, according to data available in the literature [17], has been performed in order to determine the catalytic ion/chalcopyrite interactions. Table 3 presents the standard Gibb’s energies ($\Delta G^0_r$) for the expected reactions between chalcopyrite and Ag(I), Hg (II) and Bi(III) ions. As can be seen, $\text{Ag}_2\text{S}$ and $\text{HgS}$ could be theoretically formed onto the chalcopyrite, but not $\text{Bi}_2\text{S}_3$. This theoretical study on the bulk of the mineral is in agreement with the AES studies above explained.

**TABLE 3** $\Delta G^0_r$ for cationic interchange reactions between $\text{CuFeS}_2$ and Ag(I), Hg(II) and Bi(III) ions. For every cation the value of $\Delta G^0$ for the unionised state has been considered.

<table>
<thead>
<tr>
<th>REACTION</th>
<th>$\Delta G^0_r$ (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CuFeS}_2 + 4\text{Ag}^+ \rightarrow 2\text{Ag}_2\text{S} + \text{Cu}^{2+} + \text{Fe}^{2+}$</td>
<td>-173.4</td>
</tr>
<tr>
<td>$\text{CuFeS}_2 + 2\text{Hg}^{2+} \rightarrow 2\text{HgS} + \text{Cu}^{2+} + \text{Fe}^{2+}$</td>
<td>-216.1</td>
</tr>
<tr>
<td>$\text{CuFeS}_2 + 4\text{Bi}^{3+} \rightarrow 2\text{Bi}_2\text{S}_3 + 3\text{Cu}^{2+} + 3\text{Fe}^{2+}$</td>
<td>+29.57</td>
</tr>
</tbody>
</table>

It is well known that, in the case of S, in addition to elemental analysis, information related to the chemical state can also be obtained from AES spectra [18]. Thus, an attempt has been made to record the sulphur Auger peak with 1 eV peak to peak modulation to ensure that line shape distortion would not be introduced by overmodulation. Figure 8 shows the S Auger peak for both leached and bioleached chalcopyrite with Ag$^+$ (experiments d and e, respectively). Because $\text{Ag}_2\text{S}$ and $\text{Ag}_2\text{SO}_4$ are the most probable layers formed on the chalcopyrite surface, the S Auger peak in both $\text{Ag}_2\text{SO}_4$ (experiment a) and

![Fig.8 Sulphur Auger peak of: a) $\text{Ag}_2\text{SO}_4$, b) $\text{Ag}_2\text{S}$, c) untreated chalcopyrite, d) leached chalcopyrite with Ag (I) and e) bioleached chalcopyrite with Ag(I).](image)
Ag₂S (experiment b) are also shown together with the untreated chalcopyrite (experiment c) for comparison purposes. As can be seen, Ag₂SO₄ presents two peaks centred at 146 eV and 130 eV. In the case of Ag₂S a main peak at 150 eV together with a small one at 135 eV appears in the spectrum. At first sight, it can be noticed that none of the chalcopyrite samples treated with Ag⁺ show a peak at 130 eV, indicating that the S is not present as sulphate. On the other hand, the AES spectra for both leached and bioleached with Ag (I) show a similar shape to Ag₂S, with main peaks at 150 eV and small ones at 135 eV. This would indicate the formation of Ag₂S on their surfaces as a consequence of the treatment with Ag (I). In chalcopyrite treated with Hg(II) and Bi(III) ions no chemical changes of S Auger peak are observed, due to the thickness of the mercury and bismuth layers.

CONCLUSIONS

The changes on chalcopyrite surfaces by the addition of Ag(I), Hg(II) and Bi (III) cations in bioleaching have been studied by AES and SEM. AES spectra showed the presence of these cations on the surface and their fixation is irrespective of the presence of bacteria. In the bioleached chalcopyrite without catalytic cations a sulphur enrichment is observed. The concentration of catalytic ion on the surface depended on the cation added; following the order: Ag(I) > Hg(II) > Bi (III), being much higher in the case of Ag (I) than in the other cases. Ag (I) and Hg (II) form a layer of a silver and mercury sulphide, respectively. However, mercury sulphide is not readily oxidised by the ferric sulphate produced by microorganisms, and its thickness did not increase. Changes in the AES peak shape of sulphur confirmed that Ag + is incorporated as Ag₂S. Microorganisms oxidise the sulphur of this layer, so that the surface sulphur concentration decreased during bioleaching. A different interaction of Bi (III)/chalcopyrite than in the case of Ag(I) and Hg (II) occurred and an oxidised bismuth product was formed and not bismuth sulphide.

REFERENCES

Chalcopyrite bioleaching