SEM AND AES STUDIES OF A LEAD SULPHIDE BIOLEACHING IN PRESENCE OF CATALYTIC IONS

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ABSTRACT

Scanning electron microscopy (SEM) and Auger electron spectroscopy (AES) were used to follow the surface changes occurring in galena when the bioleaching medium contained Ag(I), Hg(II) and Bi(III) ions. The results showed that the catalyst ions Ag(I), Hg(II) and Bi(III) are incorporated into the surface irrespectively of the presence of bacteria, and different reactions take place on the surface of galena depending on the cation added to the leaching medium. When the bioleaching process takes place without catalyst or with Bi(III) the galena is transformed into PbSO₄ and the growth of oxidation products is characterized by needles. Ag(I) and Hg(II) ions form a layer on the galena surface, which prevents the transformation of such surface into PbSO₄. The layer formed in this process can be like a silver sulphide and a mercury sulphide depending on the ion species. Microorganisms oxidize the surface sulphur of this layer and thus decrease the S/Ag and S/Hg ratios at the surface.

Key words
Auger Spectroscopy, PbS, bioleaching, catalytic ions

INTRODUCTION

The use of microorganisms to recover metals from low quality sulphurated ores has a promising future as an alternative to the conventional chemical extraction processes [1–3]. The two microbial species associated with the leaching process are Thiobacillus ferrooxidans and Thiobacillus thiooxidans. Both microorganisms obtain the required energy for their metabolic reactions from the oxidation of the sulphur and reduce sulphur compounds to sulphate, according to:

\[ 2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4 \]  

(1)

Thiobacillus thiooxidans oxidizes elemental sulphur more efficiently and more rapidly than Thiobacillus ferrooxidans. In addition to this, Thiobacillus ferrooxidans is able to oxidize ferrous ions, producing ferric ions and sulphuric acid, according to:

\[ 4FeS_2 + 15O_2 + 2H_2O \rightarrow 2Fe_2(SO_4)_3 + 2H_2SO_4 \]  

(2)
The literature contains a lot of information concerning the capability of *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* to oxidize copper sulphides [4] and other metallic sulphides such as NiS, CoS, HgS, ZnS, CdS, Ag₂S [5], and there have even been attempts to relate the sulphide solution rate to the solubility product of the respective sulphides [6]. However, the microbiological oxidation of PbS is not so well documented probably due to the poor solubility of the reaction products in the bacterial culture medium [7-8]. Nevertheless, it should be studied, since PbS is found in a large number of sulphurated mineral ores such as complex sulphides.

The principal inconvenience of using bioleaching processes with mineral sulphides is their slow solution kinetics, although metal extraction from these sulphides can be speeded up by adding suitable ions to the leaching solutions [9]. These ions are incorporated into the lattice of the initial sulphide through a cationic interchange reaction given by:

\[
\text{MeS} + \text{M}^{2+} \rightarrow \text{MS} + \text{Me}^{2+}
\]  

(3)

where MeS is the metal sulphide and M²⁺ the catalytic ion added to the solution.

In this study Ag(I), Hg(II) and Bi(III) were used as catalytic ions. The reason for such choice was based on the improved kinetics yields obtained in previous bioleaching experiments involving polymetallic sulphide, copper sulphide and zinc sulphide [10-13]. The principal objective was to study the changes occurring in the PbS surface when Ag(I), Hg(II) and Bi(III) ions were added to the reaction medium, in order to understand better the role of such ions in bioleaching processes of lead sulphide catalyzed by them. 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 occurring during the bioleaching attack on lead sulphide.

**EXPERIMENTAL**

The galena (PbS) used in this study was a high quality sulphide provided by Peñarroya-España S.A. It included only very slight traces of SiO₂. The samples used for AES were slices of about 10x8x1 mm. The samples were included in epoxy resin to perform SEM examination. All samples were mechanically polished with alumina and after that 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 9K medium consisting of 3 g/l of (NH₄)₂SO₄, 0.5 g/l of MgSO₄.7H₂O, 0.5 g/l K₃HPO₄, 0.1 g/l of KCl and 0.014 g/l of Ca(NO₃)₂, using a pyrite concentrate as growth source in order to obtain a bacterial culture with a sufficiently high concentration of microorganisms (about 10⁹ cells/ml). The main bacteria in this culture were *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans* and *Leptospirillum ferrooxidans*.

The different treatments were carried out in erlenmeyer flasks of 250 cm³ capacity containing the 9K medium. The temperature was maintained at 35°C with a stirring velocity of 150 rpm 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 were added to the reaction medium in the form of Ag₂SO₄, HgSO₄ and Bi(NO₃)₃, respectively. In the bioleaching experiments 5 ml of bacterial culture were added per 100 ml of 9K medium. Table 1 sets out the treatments of galena samples subjected to Auger spectroscopy.

In parallel experiments, a new series of galena samples were bioleached during 3, 6, 12 and 20 days with and without catalytic ions. This allows study of the microstructural evolution of PbS surface during bioleaching process.

Samples were washed in water and dried in air after every treatment. The AES characterization of the surface was carried out in a separate ultra-high vacuum system equipped with a double-pass cylindrical mirror analyzer (CMA) as described in [14]. Usual values for the CMA were 2 and 5 KeV electron energy
Lead sulphide bioleaching

and 4 and 8 eV peak to peak modulation, with an electronic current of 1mA. 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.

TABLE 1 Galena samples examined by Auger spectroscopy

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment of the galena sample</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Untreated and polished</td>
<td>—</td>
</tr>
<tr>
<td>b</td>
<td>Bioleached</td>
<td>6 days</td>
</tr>
<tr>
<td>c</td>
<td>Treated with Ag⁺, without bacteria</td>
<td>6 days</td>
</tr>
<tr>
<td>d</td>
<td>Bioleached in presence of Ag⁺</td>
<td>2 days</td>
</tr>
<tr>
<td>e</td>
<td>Bioleached in presence of Ag⁺</td>
<td>6 days</td>
</tr>
<tr>
<td>f</td>
<td>Treated with Hg²⁺, without bacteria</td>
<td>6 days</td>
</tr>
<tr>
<td>g</td>
<td>Bioleached in presence of Hg²⁺</td>
<td>6 days</td>
</tr>
<tr>
<td>h</td>
<td>Treated with Bi³⁺, without bacteria</td>
<td>6 days</td>
</tr>
<tr>
<td>i</td>
<td>Bioleached in presence of Bi³⁺</td>
<td>6 days</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Before experimental testing, a previous thermodynamic study, according to data available in the literature [15], was performed in order to determine the possible catalytic ion/galena interactions. Table 2 presents the standard Gibb’s energies (ΔG°r) for the expected reactions between PbS and Ag(I), Hg (II) and Bi(III) ions. As can be seen Ag₂S, HgS and Bi₂S₃ could be theoretically formed onto the sample surfaces.

TABLE 2 ΔG°r for cationic interchange reactions between SPb and Ag(I), Hg(II) and Bi(III) ions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔG°r (kJ)</th>
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<tbody>
<tr>
<td>PbS + 2Ag⁺ → Ag₂S + Pb²⁺</td>
<td>-120.6</td>
</tr>
<tr>
<td>PbS + Hg²⁺ → HgS + Pb²⁺</td>
<td>-140.7</td>
</tr>
<tr>
<td>3PbS + 2Bi³⁺ → Bi₂S₃ + 3Pb²⁺</td>
<td>-83.4</td>
</tr>
</tbody>
</table>

Scanning electron microscopy and X-ray analysis

Figure 1 shows a typical as-polished sample with several cracks varying in size. Galena is a fragile mineral which tends to crack easily, showing large geometric cracks as dark areas in this Figure. During mechanical polishing a large number of triangular and cubic pieces are detached. Such features can also be seen on the right hand side, on the boundaries of a crack, in Figure 1.

After mechanical polishing the galena has a brilliant metallic shine. The samples of bioleached galena without catalyzing ions completely lose the shine of recently polished galena and turn black as a consequence of this process. This transformation does not occur in those samples submitted to the chemical action of the 9K medium.

Figures 2a to 2c show the surface morphologic changes after 3 and 20 days of bioleaching. As can be seen in Figure 2a, the transformation has already taken place after three days. Two different contrasts can be observed according to the transformation grade; a clear grey colour, corresponding to a little etched zone, and a darker grey to a more etched zone. A magnification (×10) of the latter one shows that this
transformation does not occur homogeneously over the whole surface (Figure 2b). Some kind of needles can be seen in pits produced during the process. As the bioleaching time increases the transformation is more pronounced and goes deeper into the surface, so that the surface of the galena sample is thoroughly transformed after 20 days (Figure 2c).

Fig.1 Detail of a typical crack in polished galena.

Fig.2a Surface of galena bioleached for 3 days.

Fig.2b Detail of galena bioleached for 3 days.
The galena samples bioleached with Ag(I) show a different pattern of transformation to those bioleached without catalytic ions. At first sight, the greyish colour of the as-polished surface turns blueish, although the shine remains. An SEM photograph of bioleached galena with Ag(I) is shown in Figure 3. As can be observed, after 20 days of treatment the surface became smoother than bioleached samples without catalytic ions (Figure 2c). EDS microanalysis showed the presence of silver in all samples and there was already a substantial quantity of this element after 3 days of treatment (Figure 4). The quantity of silver increased up to 6 days, after which time the already substantial levels did not show any increase. X-ray map of samples treated at different times showed in all cases a homogenous distribution of silver.

The surface of the galena samples bioleached with Hg(II) was only slightly etched and still showed the same metallic shine and colour as the original polished surface, even after 20 days of bioleaching treatment. SEM examination of samples bioleached with Hg (II) after 20 days of treatment showed a very smooth surface not transformed (Figure 5). No mercury was detected by microanalysis.

The appearance of the galena surface bioleached with Bi(III) was similar to that of galena bioleached without catalyst and different to that observed in the presence of Ag(I) and Hg(II). A comparison of bioleached galena (Figure 2c) and that of the bioleached samples in the presence of Bi(III) (Figure 6) showed the formation of needles in both cases, whose number increased with bioleaching time. This transformation suggests a similar kind of etching during the bioleaching treatment. No bismuth was detected by microanalysis.
Fig. 4 X-ray microanalysis of galena bioleached with Ag(I) for 3 days.

Fig. 5 Galena bioleached with Hg for 6 days.

Fig. 6 Galena bioleached with Bi for 20 days. There is a substantial solution of PbS in some areas with formation of large needles.
Auger Spectroscopy

Figure 7 shows the AES spectra for the galena samples bioleached with Ag(I), Hg(II) and Bi(III). Peaks corresponding to S(150 eV), C(270 eV), O(512 eV) and Pb(91 eV) were observed in all the spectra, together with Ag(355 eV), Hg(75 eV) and Bi(101 eV) according to the catalytic ions used. In addition Cl(182 eV) and N(385 eV) were detected in the samples treated with Ag(I) and Hg(II), and P(120 eV) in the samples treated with Bi(III). The presence of Cl, N, and P is due to the fact that these elements are found in the 9K medium and they are fixed to a greater or lesser extent on the surface, depending on their capability to form compounds with the catalytic ion. Thus Ag(I) and Hg(II) form chlorides while P reacts with Bi(III). The C and O might 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. As mentioned above, AES spectra revealed the presence of three catalytic ions, Hg, Bi, and Ag, although Ag was the only one detected by X-ray microanalysis. This suggests a layer modification onto the surface and this layer was below the detection limits for EDS in mercury and bismuth in our experimental conditions.

![AES spectrum of galena samples after a bioleaching treatment in presence of (a) Ag(I), (b) Hg(II) and (c) Bi (III).](image)

Table 3 shows the relative concentrations of the elements calculated according to the standard method and corrected by sensitivity factors [18] in the samples whose treatment is outlined in Table 1. These results correspond to the medium values of five different AES measurements. In Table 3 the coefficient of variation (\(v=\sigma/x\)) for the most significant elements C, Pb, S and O is also shown. It has been determined from the standard deviation (\(\sigma\)) and the mean (\(x\)) expressed as percentage. The coefficient of variation of C is less than the remaining elements, indicating that the C concentration does not depend on the treatment of the samples and suggesting that C is basically present as a result of atmospheric contamination. The untreated galena (a) is also presented for comparison purposes, in order to show the effect of the atmosphere on the galena surface. It has a relatively high concentration of C(75%), accompanied by O(7%), S(8%) and Pb(10%).
TABLE 3  A Relative concentrations of main elements for different samples.
Variation coefficient (%) = σ/x.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Pb</th>
<th>S</th>
<th>C</th>
<th>Cl</th>
<th>P</th>
<th>N</th>
<th>O</th>
<th>Ag</th>
<th>Hg</th>
<th>Bi</th>
<th>S/cat</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Untreated</td>
<td>10</td>
<td>8</td>
<td>75</td>
<td>—</td>
<td>—</td>
<td>7</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(b) Bioleaching 6 days</td>
<td>9</td>
<td>4</td>
<td>67</td>
<td>1</td>
<td>—</td>
<td>19</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(c) Leaching Ag(^+) 6 days</td>
<td>5</td>
<td>12</td>
<td>63</td>
<td>3</td>
<td>—</td>
<td>12</td>
<td>5</td>
<td>—</td>
<td>—</td>
<td>1.0</td>
<td>—</td>
</tr>
<tr>
<td>(d) Bioleaching Ag(^+) 2 days</td>
<td>—</td>
<td>8</td>
<td>75</td>
<td>3</td>
<td>—</td>
<td>10</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(e) Bioleaching Ag(^+) 6 days</td>
<td>1</td>
<td>12</td>
<td>59</td>
<td>4</td>
<td>—</td>
<td>2</td>
<td>6</td>
<td>16</td>
<td>—</td>
<td>—</td>
<td>0.7</td>
</tr>
<tr>
<td>(f) Leaching Hg(^{2+}) 6 days</td>
<td>3</td>
<td>16</td>
<td>54</td>
<td>8</td>
<td>—</td>
<td>8</td>
<td>11</td>
<td>—</td>
<td>—</td>
<td>1.5</td>
<td>—</td>
</tr>
<tr>
<td>(g) Bioleaching Hg(^{2+}) 6 days</td>
<td>—</td>
<td>23</td>
<td>43</td>
<td>8</td>
<td>—</td>
<td>5</td>
<td>3</td>
<td>18</td>
<td>—</td>
<td>1.3</td>
<td>—</td>
</tr>
<tr>
<td>(h) Leaching Bi(^{3+}) 6 days</td>
<td>3</td>
<td>8</td>
<td>80</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>6</td>
<td>—</td>
<td>—</td>
<td>3</td>
<td>2.7</td>
</tr>
<tr>
<td>(i) Bioleaching Bi(^{3+}) 6 days</td>
<td>5</td>
<td>6</td>
<td>58</td>
<td>1</td>
<td>6</td>
<td>16</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>8</td>
<td>0.7</td>
</tr>
<tr>
<td>Variation coefficient (%)</td>
<td>86</td>
<td>51</td>
<td>17</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>63</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

A comparison of the sample bioleached without catalyst (b) and the untreated samples (a) shows a decrease of relative concentration of S and a substantial increase in O. These changes could indicate a galena (PbS) oxidation to anglesite (PbSO\(_4\)), but no chemical identification of oxidation products has been done with AES. However, the analysis by X-ray diffraction showed lead sulphate (PbSO\(_4\)) as oxidation product, which is insoluble in the bioleaching medium. On the other hand, the literature reports that bacteria catalyze the oxidation of galena (PbS) to anglesite (PbSO\(_4\)) [15–17] according to the reaction:

\[
PbS + H_2SO_4 + 1/2O_2 \rightarrow PbSO_4 + H_2O + S_0
\] (4)

This would indicate that the product formed during the bioleaching treatment is PbSO\(_4\), so that we can conclude that the unevenness observed in Figures 2a to 2c correspond to PbSO\(_4\), which was formed in the galena oxidation.

The data in Table 3 show that the Pb signal drastically falls down in samples treated with Ag (I), becoming zero in bioleached samples. Pb signal is due to the galena composition, and this decrease could be explained by the formation of a layer on the galena surface, which does not contain this element. On the other hand, the oxygen concentration is similar to the untreated sample (a), indicating that the oxygen on the surface is only due to atmospheric contamination and not due to the presence of PbSO\(_4\). However, the S signal increases and Ag is detected in all samples. All this would indicate that the layer formed would be a sulphur/silver compound, like a silver sulphide, even though by AES it is not possible to identify the stoichiometry of the coating.

Comparing the relative concentrations of the samples leached and bioleached with Ag\(^+\) for 2 and 6 days (c, d and e), it can be seen that the presence of microorganisms influences the S/Ag ratio. The value of such ratio without bacteria is 1, whereas it decreases with bioleaching to 0.8 and 0.7 after 2 and 6 days respectively. Furthermore, the presence of microorganisms results in an increased concentration of Ag on the galena surface (c and e) suggesting that the bacteria oxidize mainly the sulphur of this layer, according to the bioleaching processes outlined in equation (1). These results are in perfect agreement with the observations, where an homogeneous silver coating, which prevents the oxidation of galena, was noticed (Figure 3 and 4).

A similar behaviour pattern is observed in the samples treated with Hg(II). As can be seen in Table 3, the Pb signal decreases becoming nearly zero in bioleached samples and there is no increase in the O signal in comparison with the untreated sample (a). On the other hand the S signal increases and Hg is detected on the surface. As with the treatment with Ag(I) a coating of a mercury sulphide is formed on the galena
surface. Comparing leached and bioleached samples in the presence of Hg(II) (f and g) the ratio S/Hg decreases from 1.5 to 1.3, respectively. Bacteria then play the same role as when Ag(I) is used, namely they oxidize the sulphur of the layer.

In the case of Bi (III) we can observe that the use of this ion leads to a relatively high concentration of O in the bioleached sample (i), in which P is also detected, suggesting the formation of an oxidized compound of both elements, presumably bismuth phosphate according to the literature [19]. This compound would form an inhomogeneous layer, since Pb was detected in both bioleached and leached samples. SEM observation revealed a strong surface attack (Figure 6), similar to that occurring in the bioleached sample (Figures 2a to 2c), suggesting the same type of transformation in both cases, namely the oxidation to anglesite without forming a coating of bismuth sulphide.

CONCLUSIONS

Bioleached samples with or without Bi(III) studied by SEM showed a needle growth and high surface roughness, whereas in Ag(I) and Hg(II) cases the surface is smoother. AES showed the presence of catalytic ions onto the surface, that is not related to the presence of bacteria. Ag(I) and Hg(II) form a layer of silver and mercury sulphides which prevent the oxidation of galena to PbSO₄. The presence of bacteria decreases the ratios S/Ag and S/Hg ratios of this layer, which suggest that bacteria oxidize the sulphur of this layer. Higher concentrations of oxygen were observed in the case of bioleached samples with or without Bi (III), which is an indication of oxidation to a lead sulphate-like compound.

REFERENCES


