Influence of various factors in the bioleaching of a bulk concentrate with mesophilic microorganisms in the presence of Ag(I)

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Abstract

Various aspects concerning bioleaching of a complex sulphide in the presence of Ag⁺ cation were studied in order to improve the kinetics of sulphide leaching. The use of 9K medium, 9K medium without chlorides and Norris’ medium, together with the addition of Ag(I) in the form of Ag₂SO₄ or AgNO₃, was studied. The use of a second cation (Bi³⁺, Co²⁺ or Sn²⁺) and a two-stage bioleaching with Ag⁺ addition in the first or second stage was also evaluated.

The bioleaching medium and the form of Ag⁺ incorporated had no influence on the bulk concentrate leaching kinetics. The addition of a second cation together with the Ag⁺ cation did not improve the copper and zinc recoveries. Sn²⁺ favoured bacterial growth and, as a consequence, the dissolution rate of copper and zinc. When a two-stage bioleaching was performed with Ag⁺ addition in the first stage, copper and zinc yields were not modified and only a slight increase in copper extraction was obtained. When a two-stage bioleaching was performed with Ag⁺ addition in the second stage, both chalcopyrite and sphalerite were dissolved in the first stage and in the second stage a preferential chalcopyrite dissolution was produced. The Sn²⁺ addition helped to leach most of the sphalerite in the first stage.

1. Introduction

Nowadays, the economic potential of complex sulphide ores is becoming more interesting as a consequence of the gradual exhaustion and impoverishment of available mineral resources. It is well known that complex sulphide ores are intricate associations

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of different metallic sulphides. In the case of Spanish complex sulphide ores, they comprise chalcopyrite (CuFeS₂), sphalerite (ZnS) and galena (PbS) finely dispersed in a pyritic matrix. Because of these peculiar mineralogical characteristics it is necessary first to concentrate the ore. The development in bulk flotation technologies to obtain bulk concentrates offers new possibilities for the recovery of valuable metals contained in this type of minerals.

Pyrometallurgical processing of bulk concentrates exhibits considerable difficulties, because of their mineralogical complexity and SO₂ emissions to the atmosphere, which give rise to environmental problems. In recent years, hydrometallurgical processing [1–4] and biohydrometallurgical processing [5,6], which are less polluting, have provided alternatives to conventional pyrometallurgical processing. The bioleaching or microbial processes use the ability of certain bacteria, present in mine water, such as Thiobacillus ferrooxidans, to accelerate the oxidation of metallic sulphides. The process can be represented by:

\[
\text{MS} + 2\text{O}_2 \rightarrow \text{MSO}_4
\]

where MS is the original metallic sulphide and MSO₄ is the oxidation product. In recent decades a great deal of work has been carried out in order to reach technological applicability because of the important advantages of bioleaching, such as low reagent and energy consumption, with a subsequent decrease in overall costs. However, the main disadvantage of microbiological processes is their slow kinetics, which may hinder practical application.

In order to improve the bulk concentrate bioleaching, the addition of various ions to the leaching medium has been used [7]. These ions may modify the electrochemical dissolution mechanisms or conducting properties of metallic sulphides when they are fixed on to the different sulphide surfaces present in the concentrate. Up to now, the leaching of chalcopyrite (CuFeS₂) in the presence of Ag⁺ has been studied by several investigators [8–10], although the exaction mechanism has not been unambiguously elucidated. It has been experimentally proven that the addition of a silver salt has an accelerating effect on the chemical [11] and microbiological [12] leaching of chalcopyrite. The silver effect may be based on the transient formation of a silver sulphide on the chalcopyrite surface, which is oxidised to Ag⁺ and S⁰ by an excess of Fe³⁺, according to the following mechanism:

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

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

The generation of Ag⁺ (reaction 3) and its subsequent reaction (Eq. (2)) gives rise to a cyclic process that increases the rate of copper dissolution when silver is present.

The silver effect is amplified in the presence of iron- and sulphur-oxidising bacteria such as Thiobacillus ferrooxidans. On the one hand, they maintain a favourable ratio of Fe²⁺/Fe³⁺, contributing to the ferric-iron dependent oxidation of silver sulphide, and on the other hand, they oxidise the elemental sulphur layer produced upon Ag₂S oxidation (reaction 3).
For minerals such as bulk concentrates of Spanish complex sulphide which contain sphalerite, galena and pyrite in addition to chalcopyrite, very few studies have been made using catalytic ions and their effect on the leaching and electrochemical behaviour of different sulphides is unknown.

In a previous paper, Ballester et al. [7] found that the bioleaching of Spanish complex sulphides with mesophilic cultures was catalysed by various ions, such as silver, bismuth, cobalt and tin, although only silver significantly improved the efficiency of copper recovery. As an extension of these studies, in this paper the influence of different factors in the bioleaching process catalysed by Ag\(^{+}\) has been evaluated; namely: (1) the composition of the bioleaching medium and addition of AgNO\(_3\) as catalyst; (2) the addition of two catalytic ions; and (3) the use of two-stage bioleaching in order to improve the selective bioleaching of the metals contained in the bulk concentrate and increase their further recovery. Thus, the aim of this paper is to contribute to a better understanding of the bioleaching of complex ores catalysed with Ag(I), such as bulk concentrates of complex sulphides, in order to improve and to evaluate the bioleaching process.

2. Materials and methods

2.1. Mineral

The bioleaching experiments were carried out with a bulk concentrate of a Spanish complex sulphide obtained by continuous flotation in a pilot plant. It was provided by Rio Tinto Minera, S.A. (Huelva, Spain). Its chemical and mineralogical composition is given in Table 1. The chemical analysis was carried out by atomic absorption spectrometry (AAS), except As which was determined by colorimetric methods. Analysis by X-ray diffraction showed that the most important mineral phases were sphalerite, chalcopyrite and pyrite. To determine the mineralogical composition it has been assumed that iron is stochiometrically present in chalcopyrite and pyrite and in substitutional positions in 5%.

Table 1
Chemical and mineralogical composition of the bulk concentrate

<table>
<thead>
<tr>
<th>Chemical composition (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>17.1</td>
</tr>
<tr>
<td>Pb</td>
<td>1.7</td>
</tr>
<tr>
<td>Cu</td>
<td>14.0</td>
</tr>
<tr>
<td>Fe</td>
<td>25.0</td>
</tr>
<tr>
<td>As</td>
<td>0.12</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mineral phases (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphalerite</td>
<td>27.7</td>
</tr>
<tr>
<td>Galena</td>
<td>2.0</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>40.4</td>
</tr>
<tr>
<td>Pyrite</td>
<td>24.3</td>
</tr>
</tbody>
</table>
of the zinc sites of the sphalerite lattice. The particle size of the complex sulphide concentrate was 80% less than 30 μm.

2.2. Bacteria

A mixed culture of iron- and sulphur-oxidising microorganisms, whose origin was a mine water, was used. *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans* and *Leptospirillum ferrooxidans* were identified as the main bacteria in the culture. The culture was originally enriched in shake flasks using a chalcopyrite concentrate (5% wt/vol.) as energy source. The conditions for the bacterial growth in a 9K medium modified without iron [13] were as follows: 35°C, 150 min⁻¹, pH 1.8. To obtain bacteria adapted to the different catalytic cations, successive enrichments with increasing cation concentrations were carried out. Ag₂SO₄, Bi(NO₃)₃·5H₂O, CoSO₄·7H₂O, and SnCl₂·2H₂O were used to incorporate the catalytic cation. The bacterial culture was controlled by acid production and microscopic cell counting in a Thoma’s chamber. When the bacterial solution contained around 10⁸ bacteria/ml the culture was used to inoculate a new culture or a bioleaching experiment.

2.3. Bioleaching experiments

The experiments were carried out in an orbital shaker at 150 min⁻¹, using 250 ml conical flasks, except in the two-stage experiments, where a mechanically stirred reactor with a 500 ml hemispherical flask was used [14]. Before inoculation, both catalytic cation (1 g cation/kg of concentrate) and mineral (5% pulp density) were added to the nutrient medium. All experiments were performed using 9K medium modified without iron [13]. However, to study the influence of this variable two different media were used besides the 9K medium modified without iron; namely 9K medium modified without iron and KCl and Norris’ medium [15]. The composition of the media used is given in Table 2. The pH was adjusted to 1.8 by H₂SO₄ addition.

The temperature was controlled and kept at 35°C. After a leaching period of 2 h, a volume of 5 ml of bacterial culture per 100 ml of solution was added to the reactor. Additionally, two control tests were performed in order to compare the effect of catalyst on the bacterial leaching: (a) a ‘reference’ test with bacteria and without catalytic ion;

<table>
<thead>
<tr>
<th>Nutrient salt</th>
<th>9K medium (g/l)</th>
<th>9K medium without chloride ions (g/l)</th>
<th>Norris’ medium (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH₄)₂SO₄</td>
<td>3.0</td>
<td>3.0</td>
<td>0.2</td>
</tr>
<tr>
<td>MgSO₄·7H₂O</td>
<td>0.5</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>K₂HPO₄</td>
<td>0.5</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>KCl</td>
<td>0.1</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ca(NO₃)₂·H₂O</td>
<td>0.01</td>
<td>0.01</td>
<td>–</td>
</tr>
</tbody>
</table>
and (b) a 'sterile' test without bacteria and with catalyst. In the latter an alcoholic solution of thymol (2wt%) was added in order to kill the microorganisms.

Periodically, when the pH was higher than 1.8, it was adjusted to this value by acid addition. However, if the pH was below 1.8, a natural evolution of this variable was allowed. The water losses by evaporation were compensated by adding distilled water. Each experiment was monitored following the copper, zinc and total iron concentrations by atomic absorption spectrophotometry (AAS). Fe$^{2+}$ was colorimetrically determined using the o-phenanthroline method [16]. Fe$^{3+}$ was calculated by difference between total iron and Fe$^{2+}$. Silver concentration was also determined by AAS.

Upon termination of the experiments, the solid residues were washed with sulphuric acid in water at pH 1.8 and examined by X-ray diffraction in order to identify the products resulting during bioleaching.

2.4. SEM studies

In order to follow the microstructural evolution of the sphalerite surface during bioleaching a series of mineral sphalerite samples were bioleached for different times in the presence and absence of Ag$^{+}$. The mineral came from Picos de Europa (Spain) and was supplied by Asturiana del Cinc, S.A. The original sphalerite samples were cut to form small pieces of about 0.8–1 cm$^2$ and included in an epoxy resin. Thereafter, they were mechanically polished with alumina and submitted to bioleaching for 3, 6, 12 and 20 days with or without Ag$^{+}$. The Ag$^{+}$ concentration was 0.05 g/l and was added to the reactor in the form of Ag$_2$SO$_4$. The experimental conditions were the same as in the bioleaching experiments of the bulk concentrate: 250 ml conical flasks at 35°C with a stirring rate of 150 min$^{-1}$ and 9K modified without iron as nutrient medium at pH 1.8. After bioleaching, samples were washed in water and dried in air. For SEM observations, samples were covered with a fine graphite thin film. A JEOL JMC-35C scanning electron microscope and EDS Kevex 7000 were used to perform the X-ray microanalyses.

3. Results and discussion

3.1. Influence of bioleaching medium composition and Ag$^{+}$ cation addition (silver nitrate)

Traditionally, the 9K nutrient medium has been most frequently used in the bioleaching experiments with *Thiobacillus ferrooxidans*, because it is very suitable for its growth and, consequently, it improves the kinetics of dissolution of the metallic sulphides. However, its high concentration of basal salts could be a drawback in the bioleaching with Ag$^{+}$ for two reasons: (1) owing to its high chloride concentration AgCl could be precipitated onto the mineral sulphides, removing Ag$^{+}$ from the solution; and (2) the high concentrations of sulphate ions could precipitate jarosites or ferric hydroxysulphates, with the composition MFe$_3$(SO$_4$)$_2$(OH)$_6$, M being H$_3$O$^+$, K$^+$, Na$^+$, NH$_4^+$ or Ag$^+$. The formation of these precipitates produces encrustations on the mineral surfaces
which retard and may even inhibit further leaching. For these reasons it is important to study the influence of bioleaching medium composition on the leaching rate of a bulk concentrate.

Three media, shown in Table 2, were used: 9K medium modified without iron, 9K medium modified without both iron and chlorides and Norris' medium. In these experiments, Ag⁺ was added to the media as Ag₂SO₄ or AgNO₃. Ag₂SO₄ is currently used to incorporate Ag⁺ to the media because the biological leaching of sulphide minerals produces sulphate as the oxidation product, or because NO₃⁻ anion has a toxic effect on the growth of *Thiobacillus ferrooxidans*. However, in this work AgNO₃ was also added in order to investigate the influence of a very low nitrate concentration.

In Fig. 1 the influence of both bioleaching medium and Ag⁺ addition, as AgNO₃ or Ag₂SO₄, on the leaching of copper (Fig. 1a), zinc (Fig. 1b) and iron (Fig. 1c) is shown. For comparison purposes a bioleaching experiment without Ag⁺, denoted as reference, is also represented. In all experiments involving Ag⁺ the copper and zinc leaching profiles were similar irrespective of the medium composition and the salt form of Ag⁺ cation added to the medium. The toxic effect on the *Thiobacillus ferrooxidans* expected by the addition of AgNO₃ does not take place, presumably due to the low nitrate concentration of 0.5 mM. This concentration is very low in comparison with that referred to by Imai et al. [17] as inhibitory to bacterial growth.

Fig. 1. Microbiological leaching catalysed by Ag⁺. The influence of nutrient medium on the dissolutions of: (a) copper; (b) zinc; and (c) iron.
The curves concerning copper dissolution (Fig. 1a) show that silver has an important catalytic effect on the chalcopyrite bioleaching. This cation increased the leaching rate and the copper extraction from about 20% (reference) to nearly 60%. However, the Ag⁺ addition had an opposite effect on zinc extraction (Fig. 1b). This value was about 20% lower than the corresponding value in the experiments with no silver addition.

In the experiments with Ag⁺ three regions can be observed in the evolution of the iron concentration (Fig. 1c), which could be related to the evolution of bacterial growth. The first region shows a long lag period (approximately 8 days) in which no dissolution occurred. Thereafter, bacterial growth takes place and, as a consequence, the amount of dissolved iron increases. In the last bioleaching stage a decrease in the iron concentration is observed. In the case of 9K medium and Ag₂SO₄ as catalyst this stage began after 12 days, 6 days earlier than the other media. This decrease could be due to the precipitation of iron compounds (jarosites), which were detected by X-ray diffraction in all bioleaching residues. Note that, as in the case of zinc, in the reference experiment the amount of dissolved iron was higher than in the experiments catalysed by Ag⁺.

The evolution of the silver concentration for every nutrient medium is shown in Table 3. During the first 8 days a decrease in the amount of dissolved silver was observed, which was in coincidence with the lag phase (Fig. 1c). This decrease was due to the precipitation of Ag⁺ cation onto the concentrate sulphides [11,18,19]. In the case of chalcopyrite, a cationic exchange reaction took place [1] and Ag₂S was produced. A value of −175 kJ for ΔG°₂₉₈, calculated from the data available in the literature [20], indicated that this reaction is thermodynamically possible. When the microorganisms began to grow (between 8 and 14 days), the iron (Fig. 1c) and silver concentration tended to increase, as a consequence of the reaction [2]. However, as can be seen in Table 3, the silver concentration depended on the different media. At the final stage of leaching, starting from 19 days, a new decrease in the silver concentration was produced which coincided with the decrease in the iron concentration (Fig. 1c). Both phenomena could be explained by the formation of argentojarosite. However, X-ray diffraction of the bioleaching residues was not possible to identify this product, because its diffraction peaks were very close to those of potassium and ammonium jarosites and the amount of

### Table 3
Silver concentration (mg/l) in the leaching solutions

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>9K medium without KCl (Ag₂SO₄)</th>
<th>9K medium (Ag₂SO₄)</th>
<th>Norris' medium (Ag₂SO₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>150</td>
<td>170</td>
<td>140</td>
</tr>
<tr>
<td>1/2</td>
<td>1.6</td>
<td>1.1</td>
<td>0.7</td>
</tr>
<tr>
<td>3</td>
<td>0.9</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>8</td>
<td>0.6</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td>11</td>
<td>4.8</td>
<td>2.6</td>
<td>0.2</td>
</tr>
<tr>
<td>12</td>
<td>4.4</td>
<td>2.6</td>
<td>0.6</td>
</tr>
<tr>
<td>14</td>
<td>0.8</td>
<td>5.2</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>19</td>
<td>0.2</td>
<td>2.2</td>
<td>0.4</td>
</tr>
<tr>
<td>24</td>
<td>0.4</td>
<td>2.4</td>
<td>0.2</td>
</tr>
</tbody>
</table>

- Ag⁺ addition had an opposite effect on zinc extraction.
- Silver has a catalytic effect on copper dissolution.
- Iron concentration decreases in the last stage.
- Silver concentration decreases due to precipitation in the lag phase.
- Silver concentration depends on the medium type.
silver added to the medium was very low. At the end of the bioleaching the decrease in the silver concentration could be due to its incorporation in the bioleaching residues [9,10,12] or could be accumulated inside *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* as Ag₂S, as affirmed by Pooley [21].

In order to explain the decrease in the zinc dissolution kinetics in the bioleaching in the presence of Ag⁺ (Fig. 1b) the superficial evolution of mineral sphalerite samples after microbiological leaching in the presence and absence of Ag⁺ was followed. Scanning electron microscopy (SEM) and X-ray microanalysis were used to observe the morphologic and composition changes on the mineral surface. Sphalerite is a very brittle and soft mineral (its hardness value is 3.5 according to Mohs' scale). Due to these characteristics when the mineral is polished it tends to crack at the grain boundaries, as can be observed in Fig. 2, which shows an as-polished surface. A lot of cracks and defects of different sizes can be seen. Between the cracks there was a zone nearly free of
defects with some characteristic genetic pores. In bioleached sphalerite samples without Ag+ an increase in the number and size of superficial defects (cracks, peaks, etc.) with the bioleaching time was produced and some small cracks appeared between the native cracks (Fig. 3). This appearance is the result of the chemical attack of the ferric sulphate produced by *Thiobacillus ferrooxidans* and *Leptospirilum ferrooxidans* according to the reaction:

$$
\text{ZnS} + 2\text{Fe}^{3+} + \text{S}^2- + \text{Zn}^{2+} + 2\text{Fe}^{2+}
$$

(4)

and already referenced in the literature [22].

However, in the sphalerite samples with Ag+ bioleached for 3 days, a silver coating was detected but no increase in the number and size of cracks was observed. A magnification of the sphalerite surface bioleached with Ag+ for 12 days (Fig. 4) also showed the presence of this silver coating. EDS microanalysis showed the presence of silver homogeneously distributed in all samples even after 3 days of treatment (Fig. 5). Thus, the decrease in yield and zinc bioleaching rate in the presence of the Ag+ cation could therefore be attributed to the formation of a silver compound on the sphalerite surface, which hinders further leaching.

3.2. Using two catalytic ions in a single-stage bioleaching

As can be seen above, Ag+ cation strongly enhanced both the rate and the leaching yield of chalcopyrite. However, this cation had a noxious effect on the sphalerite bioleaching, decreasing the zinc yield strongly. On the other hand, as reported in previous papers [7,14], the addition of Sn2+, Bi3+ and Co2+ increased the rate of sphalerite leaching and the rate of chalcopyrite leaching slightly.

From the above considerations, and in order to optimise the copper and zinc dissolutions, the addition of two catalytic ions was tried. Ag+ was fixed as one of these ions and the other ones were Co2+, Bi3+ and Sn2+. The concentrations of every cation...
were 1 g/kg of bulk concentrate. In order to minimise the metal toxicity on *Thiobacillus ferrooxidans*, the bacteria used to inoculate these experiments were adapted to these cation concentrations.

Fig. 6 shows the influence of Ag\(^{+}\)-Sn\(^{2+}\), Ag\(^{+}\)-Bi\(^{3+}\) and Ag\(^{+}\)-Co\(^{2+}\) addition on the chalcopyrite and sphalerite microbiological leaching and the evolution of ferric ion concentration. In order to compare the effect of the added ions, the results of three additional experiments are also represented: bioleaching with Ag\(^{+}\), bioleaching without catalyst addition (reference) and chemical leaching with Ag\(^{+}\) addition (sterile). As can be observed, incorporating Ag\(^{+}\)-Bi\(^{3+}\) and Ag\(^{+}\)-Co\(^{2+}\) did not change the copper (Fig. 6a) and zinc (Fig. 6b) bioleaching kinetics as compared with exclusively Ag\(^{+}\) addition. However, when Sn\(^{2+}\) is used together with Ag\(^{+}\), an increase in both leaching rates and recoveries of copper and zinc were obtained. Note that, in the above results, in all processes catalysed by Ag\(^{+}\) the chalcopyrite leaching rate was much higher than in those experiments without Ag\(^{+}\). This fact confirms again the catalytic effect of Ag\(^{+}\) on the microbiological leaching of chalcopyrite.

Therefore, it can be inferred that the influence of a second cation (Co\(^{2+}\), Bi\(^{3+}\) or Sn\(^{2+}\)) on the chalcopyrite and sphalerite bioleaching was not very important. However, when Sn\(^{2+}\) was added a notable decrease in the time needed to achieve the copper and zinc maximum recoveries was observed. A explanation of the behaviour of Sn\(^{2+}\) in this bulk concentrate bioleaching has been already described in [7]. This cation produces a quick bacterial growth at the beginning of the experiment and, as a consequence, an increase in the Fe\(^{3+}\) concentration occurred (Fig. 6c) and no initial lag period was observed. However, with Ag\(^{+}\)-Co\(^{2+}\) or Ag\(^{+}\)-Bi\(^{3+}\) a longer lag period was observed and bacterial growth started after 10 days. From this time on there was an increase in the amount of iron, copper and zinc leached (Fig. 6).
3.3. Two-stage bioleaching

3.3.1. Influence of silver sulphate concentration in the first stage
An improvement in the copper and zinc recoveries of a bulk concentrate could be obtained in a two-stage bioleaching. This idea has been previously developed by Snell [23] in a ferric sulphate oxidative leaching with Ag⁺. A two-stage leaching increased copper extraction up to 99%, which made the process technically viable.

In order to study the influence of silver cation concentration, 1 and 0.2 g of Ag⁺ per kg concentrate were tested. Ag⁺ was added at the first stage, which finished when the microbial growth began the stationary phase; that is, at the end of the exponential phase. The leach liquor was removed and the same volume of nutrient medium was added to the reactor. The change of stage was carried out at that time for two main reasons: (1) the leach liquor contained a high concentration of copper, zinc and ferric ions, which could be toxic for microorganisms, decreasing their activity and, as a consequence, the sulphide leaching; and (2) the microbial growth just started to decline. This point marks the transition to the stationary phase, where the net growth rate becomes zero. Replacing the medium with another fresh one would increase the bacterial activity, so that bacteria could keep on leaching the mineral. Moreover, it is not necessary to have inoculation in the second stage because, according to Carranza [24], only 3.4% of the Thiobacilli present are in the solution; the rest remain stuck to the mineral substrate.
As can be seen in Fig. 7, by introducing a second stage in the bioleaching the copper yields (Fig. 7a) increased only 8% with a concentration of 1 g Ag+/kg concentrate. No improvement could be observed in the case of the lower concentration, 0.2 g Ag+/kg concentrate. On the other hand, the catalytic concentration noticeably influenced both the leaching rate and the copper yield in the first stage. Both parameters were duplicated in the experiment with the higher Ag+ concentration.

The curves related to zinc leaching (Fig. 7b) show that the inclusion of a second stage did not increase the zinc recovery. Note that the effect of zinc dissolution is the same in all the experiments described in this work; that is, in the experiments involving Ag+ the percentage of zinc leached was slightly lower than in the experiment without Ag+ (reference). However, the zinc leaching rate for 1 g Ag+/kg concentrate was similar to the experiment without Ag+ (reference), but it was higher than in the experiments with the lowest Ag+ concentration. This behaviour can be explained by inspection of Fig. 7c, which shows the evolution of Fe3+ concentration. It confirms that in the experiment with the highest Ag+ concentration the bacterial activity was more important. The same figure also shows that the change of stage took place at the end of the exponential bacterial growth phase, which corresponds to a rapid oxidation of ferrous iron and an increase in the total iron concentration.

On the other hand, in the second stage the ferrous cation concentration was nearly zero, but an increase of ferric cation total could be observed (Fig. 7c), which indicated
that minerals continued to be leached. In this stage, the amount of dissolved iron came from the chalcopyrite and pyrite dissolution, although mainly the latter mineral was dissolved.

Summing up, the experimental results showed that the introduction of a second stage in the bioleaching with Ag$^+$ did not remarkably improve the leaching of non-ferrous sulphides (chalcopyrite and sphalerite) of the bulk concentrate. In the second stage the pyrite was the mineral phase mainly dissolved, the improvement in the copper extraction was small (8–10%) and zinc recovery did not increase.

3.4. Silver sulphate addition in the second stage

The above results showed that Ag$^+$ addition at the first stage decreases the zinc yield. In order to improve the zinc recovery a two-stage bioleaching with Ag$^+$ addition in the second stage was tested. In this way the sphalerite dissolution would be favoured in the first stage and the chalcopyrite dissolution in the second one. Likewise, the change of stage took place when bacterial growth began, at the stationary phase. Then, the culture medium was substituted by fresh medium and 1 g Ag$^+$/kg of bulk concentrate was added to the reactor.

Fig. 8 shows the copper (Fig. 8a), zinc (Fig. 8b) and iron (Fig. 8c) bioleaching profiles obtained in shake flasks. In the first stage, the recoveries of these metals was
similar to the first stage reference. As can be seen, the addition of Ag+ in the second stage increased the copper recovery approximately 25%, although to a lower amount if the catalyst was added in the first stage. The percentage of dissolved iron stayed constant (around 15%), although an increase due to the chalcopyrite dissolution was to be expected. This fact can be explained by the precipitation of iron compounds (jarosites) which were detected by X-ray diffraction in the bioleaching residue.

### 3.5. Sn^{2+} and Bi^{3+} addition in the first stage and Ag^{+} in the second one

In order to improve the bioleaching kinetics of the bulk concentrate a series of experiments were carried out in mechanically stirred reactors. The influence of Bi^{3+} and Sn^{2+} in the first bioleaching stage was also studied. These cations improve the sphalerite dissolution in single-stage bioleaching [7].

In the first stage the copper dissolution (Fig. 9a) showed a different behaviour depending on the added cation. Sn^{2+} addition provided the highest copper yield, whereas with Bi^{3+} addition the recovery was even lower than in the reference experiment. The addition of Ag^{+} in the second phase increased the copper dissolution in all cases (25–30%).

In Fig. 9b it can be observed that the addition of Ag^{+} in the second stage did not modify the zinc recovery. However, at the end of the first stage the zinc recovery was about 75–80% in the presence of Sn^{2+} and Bi^{3+}; that is, 20% more than in the reference experiment. These differences are in agreement with previous results reported in the literature about the role of Sn^{2+} and Bi^{3+} in a bulk concentrate bioleaching [7]. A measurement of bacterial growth showed that, in experiments with Bi^{3+} and Sn^{2+}, it was faster than in the reference, indicating that the effect of these ions was to improve bacterial activity (Fig. 10).
In summary, the best results in a two-stage bioleaching were obtained when \( \text{Sn}^{2+} \) was incorporated in the first stage and \( \text{Ag}^+ \) in the second one. In this case, in the first stage a preferential zinc dissolution (about 80%) together with a 40% copper dissolution were obtained. In the second stage, copper (about 40%) was selectively leached.

4. Conclusions

The experimental results explained above confirmed that chalcopyrite was catalysed by the presence of silver. However, this cation has a noxious effect on the bioleaching kinetics for other sulphides of the bulk concentrate, such as sphalerite. \( \text{Ag}^+ \) formed a silver compound on the sphalerite surface, which hinders its further bioleaching. The composition of the bioleaching medium and the form of \( \text{Ag}^+ \) addition have no effect on the dissolution rate of the bulk concentrate. The use of a second ion (\( \text{Co}^{2+}, \text{Bi}^{3+} \) or \( \text{Sn}^{2+} \)) together with \( \text{Ag}^+ \) did not improve the copper and zinc recoveries in a single-stage bioleaching in comparison with the exclusive use of \( \text{Ag}^+ \). However, the role of \( \text{Sn}^{2+} \) is to accelerate the bacterial growth with a significant reduction of the total time of bioleaching.

On the other hand, a two-stage bioleaching with \( \text{Ag}^+ \) addition in the first stage did not improve the valuable non-ferrous recoveries. The most interesting results were obtained in a two-stage bioleaching with \( \text{Ag}^+ \) addition in the second stage. \( \text{ZnS} \) was preferentially dissolved in the first stage and \( \text{CuFeS}_2 \) dissolution was favoured in the second one. Additionally, if, in a two stage bioleaching, the first stage is catalysed by \( \text{Sn}^{2+} \) or \( \text{Bi}^{3+} \), zinc recovery was 30% higher than when \( \text{Ag}^+ \) was incorporated in the first stage. Moreover, when \( \text{Ag}^+ \) was added in the second stage, the amount of leached
copper was higher by 20–25% compared with the amount dissolved in the first stage (20–30%). However, the total copper recovery was slightly lower that the one obtained by addition of Ag⁺ in the first stage (around 65%).

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