Silver-catalyzed bioleaching of low-grade copper ores.  
Part II: Stirred tank tests

J.A. Muñoz a, D.B. Dreisinger b,⁎, W.C. Cooper b, S.K. Young c

a Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica, Facultad de Ciencias Químicas, Universidad Complutense, 28015 Madrid, Spain
b Department of Metals and Materials Engineering, The University of British Columbia, Vancouver, Canada V6T 1Z2
c Versitech Inc., 1438 W. San Lucas Drive, Tucson, Arizona, 85704-1122 USA

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Abstract

A study of the effect of different variables (inoculation, aeration, silver complexants, [Ag], [Fe3+], temperature and chemical activation stage) on the silver-catalyzed bioleaching of two different low-grade copper ores has been carried out in stirred tanks. The catalyzed bioleaching process was greatly affected by bacterial activity. Aeration and the use of different complexing agents (thiosulfate and thiosulfate plus cupric ions) did not enhance but also did not inhibit the copper kinetics in the silver-catalyzed process. On the contrary, the presence of 5 g/L Cl− inhibited the catalytic effect of silver. The effect of silver concentration was tested on two different low-grade copper ores in the range between 10 and 500 mg Ag/kg for the lower K-ore and between 1.4 and 35.7 g Ag/kg Cu for the PVD ore, the former with a higher content of copper. Silver catalysis was effective for both ores but the PVD ore was basically unaffected by silver concentration in the range studied. Maximum copper extractions and copper dissolution rates were obtained with a very small amount of silver (3.6 g Ag/kg Cu). In all cases, the copper recovery was at least twice that in the absence of silver (∼30%). High ferric concentrations have been tested in the absence and in the presence of silver. The presence of silver was essential to improve the copper extraction from chalcopyrite in acidic ferric sulfate solutions. However, bioleaching experiments conducted with silver and 1 g/L Fe3+ produced lower copper extractions (20%) compared to experiments where ferric iron was absent (55%). The copper dissolution in the silver-catalyzed lower K-ore bioleaching is temperature dependent, with an optimum temperature around 35 °C. The activation energies of the copper dissolution process were 109.7 and 20 kJ/mol in the ranges of temperature between 15 and 28 °C and 28 and 45 °C respectively. The chemical activation stage establishes optimum conditions that promote higher copper extractions in the presence of silver.

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Keywords: Low-grade copper ores; Chalcopyrite; Silver catalysis; Stirred tanks

1. Introduction

The incomplete dissolution of chalcopyrite, typically with low copper extractions after many years of leaching, remains as one of the most striking phenomena in copper hydrometallurgy.

As it was introduced in our previous work, different metal ions have been proposed as catalysts for the dissolution of chalcopyrite in acid medium. However, none of them but silver has proven effective in the chemical and biological leaching of chalcopyrite. In addition, the amount of silver required to increase significantly the
copper yields is relatively small (McElroy and Duncan, 1974; Banerjee et al., 1990).

The mechanism of silver catalysis in chalcopyrite leaching has been profusely studied and attributed to the formation of a transient Ag$_2$S film on the chalcopyrite surface. It is believed that this film overcomes passivation through the formation of a less tenacious and more porous layer of elemental sulfur. In turn, the new film improves the electrical properties of chalcopyrite facilitating the electronic transfer to the oxidant. The mechanism proposed by Miller and Portillo (1981) establishes the following sequence of reactions:

\[
\text{CuFeS}_2 + 4\text{Ag}^+ \rightarrow \text{Cu}^{2+} + \text{Fe}^{2+} + 2\text{Ag}_2\text{S}_{\text{chalcopyrite surface}} \quad (1)
\]

\[
2\text{Ag}_2\text{S}_{\text{surface CuFeS}_2}) + 4\text{Fe}^{3+} \rightarrow 4\text{Ag}^+ + 4\text{Fe}^{2+} + \text{S}^0 \quad (2)
\]

Thus, the overall reaction, sum of both reactions, has the same stoichiometry as the uncatalyzed reaction:

\[
\text{CuFeS}_2 + 4\text{Fe}^{3+} \rightarrow \text{Cu}^{2+} + 5\text{Fe}^{2+} + 2\text{S}^0 \quad (3)
\]

Miller et al. (1981) found that, unlike copper ions, ferrous ions could passivate chalcopyrite in this process. On that basis, they concluded that the copper dissolution rate is probably controlled by reaction (2).

If that is the case, a constant supply of oxidizing agent (Fe$^{3+}$) is required to recycle the silver ions to the process in order to maintain catalysis effective (Dutrizac, 1994). In the catalyzed chemical leaching the reoxidation of ferrous ions can be achieved by means of stronger oxidants than ferric ion. However, those chemical reagents can be expensive. The catalyzed bioleaching route avoids that cost by using a variety of microorganisms with the ability to oxidize ferrous ion at a high rate and in a natural way. Some of these microorganisms are unique in that they can also oxidize the elemental sulfur formed on the chalcopyrite surface (reaction (2)).

The enhancement in the copper extraction has been explained in terms of the galvanic theory. Initially, Ahonen and Tuovinen (1990b) postulated the formation of a CuFeS$_2$–Ag$_2$S galvanic couple with the first sulfide behaving anodically and the other cathodically. More recently, however, the opposite has been suggested (Escudero et al., 1993; Hiroyoshi et al., 2002; Hu et al., 2002) and also that the rate-controlling step during the process is the interchange reaction (1) instead of reaction (2) (Wang et al., 2004).

A new mechanism of the process proposed by Hiroyoshi et al. (2002) applies to lower potentials and involves the formation of Ag$_2$S and Cu$_2$S by the prior reduction of chalcopyrite with ferrous ion and evolution of hydrogen sulfide. In this case, the silver sulfide is not formed through reaction (1) but by the reaction of silver ions with H$_2$S. In addition, the intermediate copper sulfide leaches more easily than chalcopyrite in ferric ion. The overall reaction is given by:

\[
2\text{CuFeS}_2 + 4\text{Ag}^+ \rightarrow \text{Cu}_2\text{S} + 2\text{Fe}^{2+} + 2\text{Ag}_2\text{S} + \text{S}^0
\]

Another interesting fact is that besides silver sulfide a smaller amount of metallic silver is formed during the process (Price and Warren, 1986; Muñoz et al., 1998). The formation of metallic silver has been justified in several ways:

1) By an interchange chemical reaction similar to reaction (1) (Price and Warren, 1986):

\[
\text{CuFeS}_2 + 4\text{Ag}^+ \rightarrow \text{Cu}^{2+} + \text{Fe}^{2+} + 4\text{Ag} + 2\text{S}^0
\]

2) By an electrochemical reduction with ferrous ions (Kolodziej and Adamski, 1984):

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

3) By photochemical decomposition of AgCl (Dinardo and Dutrizac, 1985):

\[
\text{AgCl} \xrightarrow{hv} \text{Ag} + \text{Cl}^-
\]

In any case, the formation of Ag$_2$S and Ag$^0$ can be justified thermodynamically in terms of Eh-pH diagrams (Warren et al., 1984). Thus, the principal pursuit of the silver-catalyzed chalcopyrite process is to create the optimum conditions for the formation of a permanent galvanic couple between chalcopyrite and silver sulfide. In this way, the effectiveness of the catalyzed process relies on two major aspects: silver availability (applicable to both chemical and biological processes) and silver toxicity (applicable only to the biological process).

The most common reason given to interpret the low solubilization of silver in bioleaching experiments has been the deactivation of the process due to the toxicity of silver ions to microorganisms. Silver toxicity has been attributed to a competing mechanism between silver and ferrous ions for the active sites on the bacterial cell. Pooley (1982) reported the accumulation of silver sulfide on Acidithiobacillus ferrooxidans and A. thiooxidans cells.

Though there are silver-tolerant microorganisms with the ability to grow in as much as 100 ppm of Ag(I)
(Pumpel and Schinner, 1986) most bioleaching microorganisms lack that property. Norris and Kelly (1978) and Tuovinen et al. (1985) reported that the A. ferrooxidans growth was inhibited in the presence of 0.1 ppm of Ag(I). Hoffman and Hendrix (1976) and De et al. (1996) observed the inhibition of the bacterial culture at 1 ppm of Ag(I). Therefore, silver tolerance depends on the bacterial strain and also seems to be closely related to the chemical composition of the nutrient medium (Ehrlich, 1986). However, the existence of silver ions in solution during the silver-catalyzed chalcopyrite process in the absence of a complexing agent has to be very ephemeral since chemical reaction (1) is driven very fast.

On the other hand, silver availability is mainly affected by two factors: the formation of precipitates during the chemical or biological process and the mineralogical composition of the ore.

Unlike ferrous ions, ferric ions enhance the silver-catalyzed chalcopyrite process (Miller et al., 1981). But, as ferric ion in the medium builds up, the hydrolysis of ferric sulfate introduces a new limiting factor in the process: the jarosite-type precipitates formed incorporate silver as AgFe₃(SO₄)(OH)₆, with the subsequent lack of continuing catalytic effect. Ahonen and Tuovinen (1990a) estimated that about 5% of the total silver added is incorporated into jarosite-type precipitates. This effect is not observed in chloride solutions since silver is more prone to precipitate as AgCl and this compound does not react with pre-existing jarosites in sulfate solutions (Dutrizac and Lambor, 1987). On the other hand, jarosite precipitation withdraws ferric ions from the solution necessary to drive reaction (2).

Furthermore, Banerjee et al. (1990) pointed out that the mineralogical composition of the ore is one of the most important factors in the silver-catalyzed chalcopyrite process. Similarly to chalcopyrite, other mineral sulfides can retain in their crystal lattice traces of the silver added. Price and Warren (1986) found that ZnS and PbS entrapped silver on its surface in the form of elemental silver.

It has also been reported that the silver salt used could have an important role in the catalyzed chalcopyrite dissolution process. Besides silver sulfate, the most common source of silver used, other different silver salts have been tested. Ahonen and Tuovinen (1990a) used nitrate salt and Sato et al. (2000) reported that the copper dissolution rate from chalcopyrite was higher with silver chloride than with silver sulfate. It has also been suggested the use of silver-bearing ores, cheaper than silver chemical compounds, as an effective catalyst for chalcopyrite dissolution (Hu et al., 2002).

Different authors have considered the addition of silver to enhance the rate and extent of copper dissolution from chalcopyrite ores using acidic ferric sulfate solutions under both chemical (Miller and Portillo, 1981; Price and Warren, 1986; Hiroyoshi et al., 2002) and biological conditions. Moreover, in the latter case, different types of microorganisms have been used: mesophiles (Lawrence et al., 1985; Bruynesteyn et al., 1986; Ahonen and Tuovinen, 1990a; Banerjee et al., 1990; Sukla et al., 1990; Coto et al., 1993; Gómez et al., 1997), moderate thermophiles (Gómez et al., 1999; Cancho et al., 2005) and extreme thermophiles (Muñoz et al., 1998; Blázquez et al., 1999).

Researchers of the University of Seville in Spain have developed two different sulfate hydrometallurgical processes to treat metal sulfide concentrates with the participation of silver ions: the IBES (Indirect Bioleaching with Effect Separation) and BRISA process (Fast Indirect Bioleaching with Actions Separation) (Carranza et al., 1997; Romero et al., 1998; Palencia et al., 2002). Identically, in both processes silver is used as catalyst of chalcopyrite in ferric sulfate medium and is later recovered from the residue by acidic brine leaching. Both processes share the same flow sheet concept by separating the chemical from the biological (reoxidation of ferrous iron by mesophilic bacteria) stage. Pooley et al. (1987) had already applied the separate generator concept to bioleaching processes in order to perform both operations (chemical and bacterial) under optimum conditions. Carranza et al. (1997) have taken advantage of this concept by: a) performing the chemical leaching at high temperature and b) avoiding the inhibitory effect of silver to bacteria and the harmful abrasive effect on bacteria of high pulp densities during leaching.

The transient catalytic effect of silver has led to the consideration of the addition of complexing agents to improve the process. Lawrence et al. (1985) and Bruynesteyn et al. (1986) developed the B.C. Research process described as a silver-catalyzed biological process in stirred tanks for the electrochemical dissolution of chalcopyrite by means of the Cu⁺/Cu²⁺ couple. The B.C. Research Process employs copper sulfate (20 g/L Cu²⁺) and thiosulfate (15.5 g Na₂S₂O₃·5 H₂O/g Ag⁺) as activating reagents in the Ag-catalyzed biological leaching of chalcopyrite using a pulp density of 22%. Those additives control the redox potential below 680 mV rendering elemental sulfur instead of sulfate in the process. The reaction mechanism is presumed to involve the formation of cuprous-thiosulfate complexes through cupric reduction and later decomposition into cuprous sulfide, a more easily oxidizable compound than chalcopyrite.
In the present work, silver-catalyzed chalcopyrite bioleaching has been investigated with two different low-grade copper ores in stirred tanks. The aim of this study was to establish the optimum leaching conditions regarding different variables: [Ag], [Fe^{3+}], aeration, temperature, etc.

2. Materials and methods

2.1. Low-grade ores

Two different low-grade copper ores supplied by Magma Copper Company were used: the lower Kalamaezoo ore, named lower K-ore, already tested in shake flasks and the Pinto Valley Dump ore, named PVD ore. The copper was concentrated almost entirely into the sulfide fraction as chalcopyrite mineral.

The chemical analysis of the as-received ores is given in Table 1. For both ores, X-ray diffraction analysis showed the presence of quartz and silicates as the main components and chalcopyrite, pyrite and galena as minor phases.

A particle size of <0.6 mm for the lower K-ore and <3.56 mm for the PVD ore was used. For that, the as-received ore was initially screened through −0.6 and −3.56 mm respectively and the remaining coarse fraction crushed. The particle size distribution of both ores is shown in Fig. 1.

2.2. Bacterial cultures

All bioleaching tests were inoculated with active maintenance cultures of thiobacilli and leptospirilli constantly renewed. Bacterial cultures were maintained routinely in an orbital shaker at 35 °C and grown in 75 mL of the Fe-free 9 K, named 0 K, nutrient medium (3.0 g (NH₄)₂SO₄, 0.5 g KH₂PO₄, 0.5 g MgSO₄·7H₂O, 0.1 g KCl and 0.01 g Ca(NO₃)₂·4H₂O) with the pH adjusted to 2.0, 4 g of lower K or PVD ore as the solely source of energy and 5 mL aliquots of exponential-phase bacterial culture.

Two different mesophilic cultures were subcultivated: in the absence and in the presence of silver as Ag₂SO₄. Silver resistance was enhanced by subsequent adaptation of the bacterial culture to different silver concentrations. Periodically, pH, Eh and bacterial population of the cell suspensions were measured and bacteria transferred to a new fresh nutrient medium after reaching the exponential growth phase.

For the sake of reproducibility of data, the same bacterial culture was used as inoculum in the study of each variable.

2.3. Bioleaching tests

Bioleaching experiments were performed in stirred tank reactors at 800 rpm and 35 °C, unless otherwise stated, using 2 L cylindrical covered reactors with four baffles and a gas inlet pipe into the bottom of the reactor to improve hydrodynamics of the system. Each stirred
tank contained 1.875 L of 1/10th strength 0 K medium at pH 2.0 (except in tests where this variable was studied), 200 g of low-grade copper ore (10% pulp density), with or without additions of silver (as Ag₂SO₄) and 125 mL of inoculum grown in the absence or presence of silver. Unless otherwise stated, a gas mixture of air and 1% CO₂ was supplied to each tank at a flowrate of 250 mL/min.

After 1 day of chemical conditioning, the pH of the leach suspensions was adjusted to 2.0 and 125 mL of an active microbial culture, previously adapted to the ore used, was added. In the control experiments (abiotic tests), 125 mL of 2 g/L thymol in methanol was added instead of the inoculum.

The redox potential was measured using a Pt combination redox electrode with a Ag/AgCl reference electrode. pH was monitored using a gel-filled combination pH probe with a Ag/AgCl reference electrode. Evaporation water losses were compensated by adding deionized water. Periodically, pH was readjusted to 2.0 with 6 M H₂SO₄, the redox potential measured and 0.5 mL of sample removed from the leach solutions and analyzed for copper, iron and silver by atomic absorption spectrophotometry. The sample removed was replaced with 1/10 0 K nutrient medium. Bacterial population was determined weekly using a counting chamber and an optical microscope.

At the end of the experiments, the solids were filtered and the chemical analysis of the residues was used to complete the mass balance for the calculation of final copper and iron extractions.

3. Results and discussion

Previous shake flask experiments had confirmed that the copper dissolution mechanism from the low-grade ore is related to the oxidizing conditions in the medium and indirectly to the bacterial activity. Those experiments also showed that silver remains primarily in the residue but, during the early stages of bioleaching, silver in solution could have a harmful effect on bacterial growth.

3.1. Influence of inoculation

Different studies in the absence and in the presence of silver have demonstrated the beneficial effect of a previous inoculation on copper dissolution.

Similar tests to those carried out in shake flask experiments were performed in stirred tanks but considering only the addition of silver (14.3 g Ag/kg Cu). At this time, the sterilized experiment with thymol was replaced by heating the solid sample at 110 °C 1 h/day for 5 consecutive days in a convection oven.

The differences in copper dissolution observed in shake flasks experiments are less noticeable in these experiments (Fig. 2a). This seems to be related to the improvement of hydrodynamics for bacterial growth and the difficulty of getting sterile conditions for longer periods of time in stirred tank reactors. The onset on the copper extraction in the uninoculated experiments would be due to the presence of active bacteria associated to the ore which were able to grow after 4 days and after 7 days in the uninoculated and in the sterilized experiments respectively.

Similar to the shake flasks tests, the redox potential curve of the inoculated experiment was characterized by an initial drop followed by a rise up to 850 mV (Fig. 2b). In the non-inoculated experiments the onset of oxidizing...
conditions showed up at longer times once bacterial activity started. This contamination of the non-inoculated experiments was confirmed by the material balance of the residues (Table 2).

<table>
<thead>
<tr>
<th>Test</th>
<th>Non-inoculated sterilized (Ag)</th>
<th>Non-inoculated (Ag)</th>
<th>Inoculated (Ag)</th>
</tr>
</thead>
<tbody>
<tr>
<td>%Cu</td>
<td>63.6</td>
<td>78.6</td>
<td>93.6</td>
</tr>
<tr>
<td>%Fe</td>
<td>21.0</td>
<td>28.2</td>
<td>31.0</td>
</tr>
<tr>
<td>Fe/Cu</td>
<td>1.9</td>
<td>2.0</td>
<td>1.9</td>
</tr>
<tr>
<td>S(H₂SO₄)/Cu</td>
<td>4.5</td>
<td>4.6</td>
<td>2.8</td>
</tr>
</tbody>
</table>

![Fig. 3. Effect of aeration on the silver-catalyzed bioleaching of the lower K-ore: a) copper extracted and b) evolution of redox potential after 14 days.](image)

3.2. Influence of aeration

Aeration of the solution can be important in bacterial oxidation processes as a source of both oxygen and carbon dioxide. These experiments were carried out in the presence of silver (14.3 g Ag/kg Cu) with or without an air/1%CO₂ supply at a flow rate of 0.25 L/min.

This variable had a slight effect on the parameters controlled during the process. The major difference observed was related to a higher acid consumption in the experiment without aeration. Copper extraction was unaffected by aeration (Fig. 3a) whereas iron dissolution decreased with aeration (results not shown). A similar evolution of the redox potential was obtained for both tests (Fig. 3b).
Although oxygen and carbon dioxide transfer from the gaseous phase is not a concern in agitated reactor systems, it may restrict the rate of bacterial oxidation reactions in static processes such as those in column leaching reactors that will be discussed in the next work.

3.3. Influence of the presence of chloride in the nutrient medium

The presence of small amounts of chloride ion in the nutrient medium could have an effect on the silver-catalyzed copper dissolution. Visual proof of precipitation of AgCl at the starting of the experiments was observed when silver was added as a liquid to the nutrient medium (1/10 0 K or 0 K).

These experiments were performed with 14.3 g Ag/kg Cu and 1/10 0 K nutrient medium with and without chloride.

The presence of chloride in the nutrient medium improved the copper extraction very slightly (Fig. 4a). The evolution of the redox potential was practically the same for both conditions tested (Fig. 4b).

![Graphs](a) Copper extraction, (b) Iron extraction, (c) Eh, (d) Metal extraction.

Table 3
Final metal extractions and molar ratios based on material balances with and without the presence of chloride ion - after 14 days of bioleaching

<table>
<thead>
<tr>
<th>Test</th>
<th>1/10 0 K</th>
<th>Cl-free 1/10 0 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>%Cu</td>
<td>93.6</td>
<td>91.4</td>
</tr>
<tr>
<td>%Fe</td>
<td>31.0</td>
<td>31.6</td>
</tr>
<tr>
<td>Fe/Cu</td>
<td>1.9</td>
<td>2.0</td>
</tr>
<tr>
<td>S(H₂SO₄)₃/Cu</td>
<td>2.8</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Fig. 5. Effect of complexing agents on the silver-catalyzed bioleaching of the lower K-ore: copper (a) and iron extractions (b) and redox potential (c) versus time; and final Cu and Fe extractions after 14 days.
Material balances of the residues confirmed that the variable under study practically does not affect the chemistry of the silver-catalyzed bioleaching process of the lower K-ore (Table 3).

### 3.4. Influence of different complexing agents

Three different complexing agents were tested for the copper dissolution from the lower K-ore using 14.3 mg Ag/kg Cu: thiosulfate (15.5 g Na₂S₂O₃·5H₂O/g Ag); thiosulfate plus cupric ions (15.5 g Na₂S₂O₃·5H₂O/g Ag⁺ 2 g/L Cu²⁺ as CuSO₄·5H₂O) and chloride (5 g/L Cl⁻ as NaCl).

Copper extractions were not enhanced by the presence of any of the complexing agents tested (Fig. 5a). Although in both thiosulfate tests the copper kinetics were basically similar to the experiment without complexant, the iron dissolution rate was accelerated in these systems (Fig. 5b). This agrees with a better bacterial growth observed in the presence of thiosulfate (results not shown), probably due to the ability of bacteria to use it as an energy source. Conversely, 5 g/L of Cl⁻ had an adverse effect on copper dissolution in agreement with the evolution of the redox potential (Fig. 5c).

The effect of different complexing agents on the final metal extractions is shown in Fig. 5d. Table 4 shows similar values of final metal extractions and molar ratios except for the system with 5 g/L of Cl⁻. Therefore, the silver-catalyzed bioleaching of the low-grade copper ore can reach maximum copper extractions without the addition of complexing agents.

The low copper extraction obtained in the presence of 5 g/L Cl⁻ could be due to the formation of a silver complex during the chemical stage unable to react with the mineral surfaces in a subsequent stage. In order to check the extent of the chloride effect a new experiment was carried out with 5 g/L Cl⁻ in the absence of silver. The results indicate that copper and iron extractions were slightly enhanced by the addition of silver to a system with 5 g/L Cl⁻ (Fig. 6a). Nevertheless, the copper extraction values only approached 10% after 15 days of leaching. Minor variations in the evolution of the redox potential were observed between both tests (Fig. 6b).

### 3.5. Influence of silver concentration

The effect of silver concentration was studied in the range between 0.7 and 71.4 g Ag/kg ore for the lower K-ore (Fig. 7) and between 1.4 and 35.7 g Ag/kg Cu for the PVD ore (Fig. 8).

For both ores, copper dissolution was dramatically affected in the presence of small amounts of silver (Figs. 7a and 8a). For instance, the addition of silver at any concentration was able to double at least the copper extraction with respect to the experiment without silver. But even more important, the copper kinetics sped up. The copper dissolution during the chemical stage was

### Table 4

<table>
<thead>
<tr>
<th>Test</th>
<th>Without complexant</th>
<th>Thiosulfate</th>
<th>Thiosulfate + Cu²⁺</th>
<th>Chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>%Cu</td>
<td>93.6</td>
<td>91.4</td>
<td>90.7</td>
<td>18.6</td>
</tr>
<tr>
<td>%Fe</td>
<td>31.0</td>
<td>29.6</td>
<td>31.0</td>
<td>15.2</td>
</tr>
<tr>
<td>Fe/Cu</td>
<td>1.9</td>
<td>1.8</td>
<td>1.9</td>
<td>4.6</td>
</tr>
<tr>
<td>S(H₂SO₄)/Cu</td>
<td>2.8</td>
<td>2.8</td>
<td>3.2</td>
<td>8.1</td>
</tr>
</tbody>
</table>

![Fig. 6. Effect of chloride ions (5 g/L) on the silver-catalyzed bioleaching of the lower K-ore: a) copper extracted and b) evolution of redox potential after 14 days.](image-url)
higher for the PVD ore (∼10%) than for the lower K-ore (∼5%) in accordance with a higher amount of acid soluble copper in the former ore. At the same time, copper dissolution kinetics was initially faster for the PVD ore than for the lower K-ore and less amount of silver was required to catalyze the copper extraction from the PVD than for the lower K-ore. Nevertheless, the optimum copper extraction for the lower K-ore was achieved with small amounts of silver (ranging between 15 and 25 mg Ag/kg ore). The effect of silver concentration in the range tested was less marked in the case of the PVD. Conversely, high amounts of silver can be harmful on the copper dissolution process of the lower K-ore.

Iron extractions display linear kinetics with recoveries slightly higher for the experiments with silver (Figs. 7b and 8b). Once again, an increase of the silver concentration led to a higher release of iron from the ore. Silver in solution was not detected during these experiments except for a minimum amount of silver at the end of the experiments (results not shown).

From the Eh curves it is clear that the oxidizing conditions are reached in stirred tanks in a shorter time than in shake flasks experiments, indicating that hydrodynamics and gas-liquid mass transfer play an important role in the catalytic process (Figs. 7c and 8c).

X-ray diffraction analyses performed on the residues of the lower K-ore without silver and with 14.3 g Ag/kg ore did not show appreciable differences in chemical composition, all peaks corresponding to the unleached material (mainly silicoaluminates and quartz).

The effect of silver concentration on the final metal extractions is shown in Figs. 7d and 8d for the lower K-ore and for the PVD ore respectively. Material balances confirmed that when silver catalysis is effective, less iron
is leached and less acid is consumed per mol of copper extracted (Table 5a and b).

Based on the Fe/Cu molar ratios of material balances, the degree of copper selectivity was more favorable for the K-ore than for the PVD and for the same ore when silver was added. However, variations in [Ag] had a minor effect. For both ores, the addition of silver diminished the consumption of acid during the process. The PVD ore is a higher acid consumer than the lower K-ore. This is due to a different level of gangue acid consumption.

3.6. Influence of $[Fe^{3+}]$

3.6.1. Abiotic experiments

Our previous shake flasks experiments demonstrated that high ferric iron concentrations speed up the copper extraction from the lower K-ore tested. Four short-term experiments (11 h) in the absence of bacteria with or without silver (14.3 g Ag/kg Cu) and high $[Fe^{3+}]$ (>3 g/L) were performed at 35 °C and in 1/10 0 K medium at pH 2.0. These ferric ion concentrations were chosen to establish initially high oxidizing conditions in the chemical process.

The results show that copper extraction was largely improved by the addition of silver independently of $[Fe^{3+}]_{\text{initial}}$ (Fig. 9a). Initial iron precipitation took place but, after that, the iron in solution remained constant for the rest of the experiments (Fig. 9b). For the same $[Fe^{3+}]$, Eh was lower in the presence than in the absence of silver (Fig. 9c) and this was a good indicator of the extent of reaction between the ore and the leaching medium.

3.6.2. Biotic experiments

Two different biotic experiments were carried out with 0.7 g Ag/kg Cu with and without the addition of
Table 5
Final metal extractions and molar ratios based on material balances of lower K and PVD ores

<table>
<thead>
<tr>
<th>Substances</th>
<th>Lower K-ore bioleaching</th>
<th>PVD ore bioleaching</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ag] (g/kg Cu)</td>
<td>0</td>
<td>1.4</td>
</tr>
<tr>
<td>%Cu</td>
<td>82.7</td>
<td>84.8</td>
</tr>
<tr>
<td>%Fe</td>
<td>37.1</td>
<td>32.1</td>
</tr>
<tr>
<td>Fe/Cu</td>
<td>1.4</td>
<td>3.2</td>
</tr>
<tr>
<td>S(H₂SO₄)/Cu</td>
<td>5.3</td>
<td>7.1</td>
</tr>
</tbody>
</table>

b) For the PVD ore after 14 days of bioleaching

<table>
<thead>
<tr>
<th>Substances</th>
<th>PVD ore bioleaching</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ag] (g/kg Cu)</td>
<td>0.7</td>
</tr>
<tr>
<td>%Cu</td>
<td>84.8</td>
</tr>
<tr>
<td>%Fe</td>
<td>3.7</td>
</tr>
<tr>
<td>Fe/Cu</td>
<td>3.2</td>
</tr>
<tr>
<td>S(H₂SO₄)/Cu</td>
<td>1.0</td>
</tr>
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</table>

1 g/L of Fe³⁺ as Fe₂(SO₄)₃. This ferric ion concentration was chosen on the basis of the [Fe]final found in bioleaching tests (~1 g/L). Both tests were compared with the previous abiotic test performed with 3 g/L of Fe³⁺.

Copper dissolution shows parabolic and linear kinetics in the absence and in the presence of Fe³⁺ respectively (Fig. 9d). However, the final copper extractions were much higher in the absence of ferric ions. The similar response of the inoculated and non-inoculated experiments with ferric ions suggests that Fe³⁺ suppressed bacterial action in favour of a chemical mechanism.

For these experiments, pH and acid consumption decreased with increasing ferric concentration as a result of iron precipitation as jarosite (Fig. 9e). Although this could have affected copper dissolution rates through the formation of a protective layer of jarosite on the chalcopyrite surface, this does not seem the case after the copper linear kinetics observed in these experiments.

The redox potential values were mainly controlled by bacterial activity in the bioleaching experiments and by chemical reactions in the non-inoculated tests (Fig. 9f). However, the potential curves indicate that the oxidizing conditions in the presence of 1 g/L Fe³⁺ were reached at a slower step than in its absence. Probably, bacteria were able to tolerate this concentration but its presence in the bulk affects ferrous biooxidation adversely.

3.7. Influence of temperature

The optimum temperature at which the sulfide mineral oxidizes faster may not coincide with the optimum value for the growth of the bacterial culture. Each bacterial culture has a preferred growth temperature, which will depend on the environmental conditions (nutrients, toxic substances, pH, Eh, ore, etc.).

The effect of temperature was studied in the range between 15 and 45 °C. All experiments were carried out under the same experimental conditions using 14.3 mg Ag/kg Cu.

Copper and iron extractions (Fig. 10a and b) showed a marked dependency on temperature, the effect being more pronounced in the case of copper. Bacteria grown at temperatures lower than 20 °C showed a mild oxidizing activity giving as a result lower copper recoveries (<15%). High temperatures can, however, have not only a chemical influence on the process but also on microbial metabolism which can affect negatively the growth of the bacterial culture. From these results it is clear that thermal activation plays an important role in this process.

The onset of oxidizing conditions depended on temperature with an anomalous behaviour at 45 °C that could be related to a modification of the nature of the culture due to the presence of moderately thermophilic bacteria (Fig. 10c). However, the experiments at temperature <20 °C were unable to create oxidizing conditions.

The activation energy of the silver-catalyzed lower K-ore bioleaching in the range of temperature studied was calculated from the kinetic constants and the semi-logarithmic plot of the Arrhenius equation. The parabolic rate constants, k, were derived from all the leaching curves obtained in the range of temperature between 15 and 45 °C.

In the case of copper, a consistent set of data was obtained with a single rate-controlling process operative over the 15–28 °C temperature range, different from that over the 28–45 °C range. The apparent activation energy calculated from the Arrhenius plot was 109.7 kJ/mol between 15 and 28 °C and 20 kJ/mol between 28 and 45 °C. For iron, a value of 38.1 kJ/mol was obtained in the range between 15 and 40 °C. In this sense, chemical rate-control usually has a large temperature dependence compared to mass-transfer rate control.

The effect of temperature on the final metal extractions is shown in Fig. 10d. Material balances confirmed that the silver-catalyzed lower K-ore bioleaching has an optimum temperature around 35–40 °C (Table 6).

3.8. Influence of the chemical stage

The chemical stage in this study refers to a step for the chemical activation of chalcopyrite by addition of silver. In this way, the chemical stage was part of the experimental procedure followed in the bioleaching tests. It consisted of 3 days of contact between the ore and the leaching medium during which chemical reactions took place and prepared the mineral surfaces for the bioleaching process.
Fig. 9. Effect of ferric ion on the silver-catalyzed chemical and bacterial leaching of the lower K-ore after 14 days: copper (a) and iron extractions (b) and redox potential (c) versus time.
Two experiments were carried out under similar experimental conditions with 14.3 g Ag/kg Cu, added before or after the chemical stage, prior to the bioleaching process.

Copper extractions only showed differences during the first days (Fig. 11a). On day 4, the copper extraction was ∼15% higher with the ore treated with silver before the chemical stage started. After 7 days, coinciding with the rise of Eh, the test with silver added after the chemical stage was able to reach a similar copper extraction right to the end of the experiments.

The onset of oxidizing conditions was clearly affected by this variable and accounted for the differences observed during the copper dissolution: with the increase of the redox potential in a shorter time for the experiment where silver was added before the chemical leaching stage (Fig. 11b). Table 7 confirms the small effect of this variable.

Nevertheless, short-term experiments demonstrated that during the initial stages of the chemical leaching stage, a pronounced drop of Eh of the solution occurs in a

![Figure 10](image)

**Table 6**

<table>
<thead>
<tr>
<th>Test</th>
<th>15 °C</th>
<th>20 °C</th>
<th>25 °C</th>
<th>28 °C</th>
<th>35 °C</th>
<th>40 °C</th>
<th>45 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>%Cu</td>
<td>24.3</td>
<td>29.3</td>
<td>83.6</td>
<td>83.6</td>
<td>91.4</td>
<td>96.4</td>
<td>97.1</td>
</tr>
<tr>
<td>%Fe</td>
<td>6.9</td>
<td>6.9</td>
<td>28.6</td>
<td>31.5</td>
<td>28.6</td>
<td>31.2</td>
<td>14.2</td>
</tr>
<tr>
<td>Fe/Cu</td>
<td>1.6</td>
<td>1.3</td>
<td>1.9</td>
<td>1.9</td>
<td>1.4</td>
<td>1.8</td>
<td>0.8</td>
</tr>
<tr>
<td>S(H₂SO₄)/Cu</td>
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<td>8.3</td>
<td>2.5</td>
<td>2.2</td>
<td>1.6</td>
<td>1.7</td>
<td>2.2</td>
</tr>
</tbody>
</table>
very short time when the leaching solution, silver and ore are brought into contact (Fig. 11c and d). The analysis of the solution after the chemical stage demonstrated that copper and iron were extracted in similar proportions (3.3% Cu and 3.9% Fe) whereas silver remained mainly precipitated (0.02 ppm Ag in solution which correspond to <0.1%). These results point out the importance of the chemical stage in the deposition of silver on chalcopyrite surfaces.

4. Conclusions

The optimum conditions for the bioleaching of the lower K-ore in stirred tank were as follows: 1/10 0 K nutrient medium, ∼35 °C, pH ∼2.0, no supply of air/1% CO₂ is required and [Ag] ∼3.5–14.3 mg Ag/kg ore. In addition, the PVD ore, with a coarser particle size (<3.56 mm), can be treated with good copper recoveries.

The use of complexing agents (thiosulfate or thiosulfate plus cupric ions) did not affect the yields of copper and iron extraction. But high chloride concentrations (5 g/L) suppressed the silver catalytic effect.
The effect of temperature on the copper extraction has a marked effect above 25 °C, with an optimum temperature about 35–40 °C.

References


