HYDROMETALLURGY OF BULK CONCENTRATES OF SPANISH COMPLEX SULPHIDES: CHEMICAL AND BACTERIAL LEACHING

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Abstract—The viability of using bioleaching with a natural culture of mesophyllic organisms as a hydrometallurgical treatment of bulk concentrates of Spanish complex sulphides was studied. Bioleaching was studied as a whole treatment or as a preparatory treatment for the ore prior to chemical treatment using concentrated solutions of ammonium chloride, instead of the fine grinding step. When bioleaching was used as the sole treatment for metal extraction, recoveries of copper were in the order of 40%, while the same process only as a pre-treatment step to chemical leaching did not overcome the fine disseminations of the valuable metals through the mineral matrix. Furthermore, the rate of dissolution of sphalerite, chalcopyrite and pyrite in concentrated solutions of ammonium chloride slowed down, although less so for the first two than for the last. The advantage of using a bioleaching pretreatment lay in a higher favourable relation between the ammonia produced and the metals dissolved in the subsequent chemical leaching step, as a consequence of a greater decrease in the dissolution kinetics of the pyrite. © 1997 Canadian Institute of Mining and Metallurgy. Published by Elsevier Science Ltd

Résumé—La viabilité de l'utilisation du biolessivage avec culture naturelle d'organismes mésophylles pour le traitement hydrométallurgique de concentrés en vrac de sulfures complexes espagnols a été étudiée. Le biolessivage a été étudié comme traitement complet ou comme traitement préparatoire du minerai avant le traitement chimique utilisant des solutions concentrées de chlorure d'ammonium, au lieu de l'étape de broyage fin. Quand le biolessivage était utilisé comme seul traitement pour l'extraction du métal, la récupération du cuivre était de l'ordre de 40%, alors que le même procédé utilisé seulement comme une étape de pré-traitement du lessivage chimique n'a pas surmonté la dissemination fine des métaux valables à travers la matrice minérale. De plus, le taux de dissolution de la galène, de la chalcopyrite et de la pyrite dans les plus, le taux de dissolution de la galène, de la chalcopyrite et de la pyrite dans les solutions concentrées de chlorure d'ammonium s'est ralenti, quoique moins pour les deux premières que pour la dernière. L'avantage de l'utilisation d'un pré-traitement de biolessivage repose sur une relation nettement plus favorable entre l'ammoniaque produite et les métaux dissous à l'étape suivante de lessivage chimique, comme conséquence d'une plus grande diminution de la cinétique de dissolution de la pyrite.

INTRODUCTION

"Complex sulphides" are an extremely complicated mineralogical association basically composed of chalcopyrite, galena and sphalerite finely disseminated in a matrix of pyrite (the major component, representing more than 90% of the overall weight of the ore). The particular chemical and mineralogical characteristics of these ores means that to be beneficiated they must undergo a process of concentration by flotation. However, differential flotation does not release all the constituent phases [1] and so the differential concentrates obtained are of poor quality with a low rate of metal recovery, which seriously limits their commercial value [2].

Over the last few decades, the hydrometallurgical exploitation of bulk concentrates of Cu-Zn-Pb has been studied [3–5]. Traditionally, sulphate-based leaching solutions have been used in most cases, although recently attention has shifted to treatment in a chloride medium [6]. The principal advantages of using chloride and acid solutions as leaching agents are as follows:

- The chloride salts of most metals are more soluble than the corresponding sulphates and permit more concentrated solutions to be obtained.
- Cupric and ferric chloride solutions are aggressive oxidants of many mineral sulphides.
- The formation of chloride–metal complexes favours the dissolution of metals.
- The hydrochloric acid can be recovered from the solution, which permits the chloride ion to be regenerated and recycled during the process.

The main disadvantage of the industrial application of these hydrometallurgical processes is the high cost involved in leaching under pressure and at high temperatures. In the case of leaching in a chloride medium, these costs increase because of the need to use equipment which is resistant to the corrosive action of the chloride anion. The idea of bacterial bioleaching,
therefore, arose as an alternative to using this chemical attack in the extractive metallurgy of non-ferrous metals [7–10]. The problem, however, from an industrial viewpoint is the very slow dissolution rate in the bioleaching process.

One possibility is to use bioleaching as a pre-treatment step prior to chemical extraction. For example, the preoxidation of certain refractory gold concentrates by biological attack results in a significant increase in the subsequent metal recovery by cyanidation [11–14]. The microorganisms break up the pyritic matrix and thus facilitate the access of the leach solutions to the valuable mineral phases. Thus, the aim of this work is to study the possibility of using bioleaching as: (a) the sole treatment of the global concentrate and (b) pre-treatment to partially release the metallic values prior to a chemical attack to extract the greatest possible percentage of these metals. For this, we studied the effect of bioleaching on two concentrates of differing composition and carried out the bioleaching experiments over different periods of time prior to submitting the residues obtained to chemical leaching with concentrated solutions of ammonium chloride using the CENIM-LNETI process [5].

**EXPERIMENTAL**

The leaching experiments (bacterial and chemical) were carried out with two bulk concentrates of different provenance: concentrate A1 was from Sotiel, Huelva (Spain) and concentrate G1 from Rio Tinto, Huelva (Spain). Their chemical compositions are shown in Table 1.

X-Ray diffraction showed FeS₂, CuFeS₂, ZnS and PbS to be the major phases in A1, while only FeS₂, CuFeS₂ and ZnS were detected in G1. Table 2 shows the approximate quantitative mineralogical composition of the concentrates, obtained according to the chemical composition and qualitative mineralogical characterization. The granulometric analysis of both concentrates was determined using a “cyclosizer” and the size distribution is shown in Fig. 1.

The microorganisms used in the bioleaching experiments came from a natural culture of minewater and were principally made up of Thiobacillus ferrooxidans, Thiobacillus thiooxidans

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**Table 1. Chemical composition of the bulk concentrates used**

<table>
<thead>
<tr>
<th>Origin</th>
<th>Concentrate</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>Fe</th>
<th>As</th>
<th>Sb</th>
<th>Ag*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sotiel</td>
<td>A1</td>
<td>2.7</td>
<td>9.2</td>
<td>32.0</td>
<td>22.0</td>
<td>0.20</td>
<td>934</td>
<td>133</td>
</tr>
<tr>
<td>Rio Tinto</td>
<td>G1</td>
<td>15.0</td>
<td>1.8</td>
<td>17.6</td>
<td>23.7</td>
<td>0.12</td>
<td>130</td>
<td>120</td>
</tr>
</tbody>
</table>

*ppm.

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**Table 2. Quantitative mineralogical composition of the bulk concentrates used**

<table>
<thead>
<tr>
<th>Origin</th>
<th>Concentrate</th>
<th>Sphalerite</th>
<th>Pyrite</th>
<th>Galena</th>
<th>Chalcopyrite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sotiel</td>
<td>A1</td>
<td>58.0</td>
<td>26.0</td>
<td>10.4</td>
<td>7.5</td>
</tr>
<tr>
<td>Rio Tinto</td>
<td>G1</td>
<td>27.7</td>
<td>24.3</td>
<td>2.0</td>
<td>40.4</td>
</tr>
</tbody>
</table>

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Fig. 1. Particle size distribution in concentrates (a) A1 and (b) G.
C. GÓMEZ et al.: HYDROMETALLURY OF BULK CONCENTRATES OF COMPLEX SULPHIDES 17

Fig. 2. Experimental apparatus used in the bioleaching experiments with mechanically stirred reactors.

and Leptospirillum ferrooxidans, grown in a nutrient medium (D2) whose composition was as follows: 0.06 g/l (NH₄)₂SO₄, 0.06 g/l MgSO₄·7H₂O, 0.02 g/l K₂HPO₄ and 0.02 g/l KCl, with a chalcopyrite concentrate as energy source.

The bioleaching experiments were carried out in 500 ml capacity hemispherical glass reactors stirred mechanically at 180 rpm (Fig. 2). Fifteen grams of concentrate was added to 300 ml of nutrient medium (5% pulp density) in each experiment. Before inoculation, the pH was brought to 1.8 and the system was kept at 35°C for 1 h with an air current enriched with CO₂ (1% v/v). The reactor was then inoculated with 15 ml of bacterial culture. Normal losses due to evaporation were periodically compensated by the addition of distilled water and the pH was monitored daily as a measurement of the bacterial activity. The Cu, Zn and Fe were analysed by atomic absorption spectrophotometry (AAS).

The chemical leaching experiments were carried out in a 2 l capacity titanium autoclave in oxygen at a pressure of 1.01 x 10⁵ Pa (1 atm) at 95°C and a pulp density of 24 g/l. The composition of the leaching solution was 6 molal in NH₄Cl and 0.06 molal in CuCl₂. The presence of the CuCl₂ was essential at the outset of the leaching process since the different sulphides were attacked through the copper (II) ion, the role of oxygen being to reoxidize the copper (I) ion formed [15].

Leaching time was counted from the moment the temperature of the experiment was reached. The samples of pulp were filtered and the copper, lead, zinc and silver dissolved were analysed by AAS. Similarly, the concentrations of sulphate and ammonium ions produced during leaching were determined by precipitation with BaCl₂ and by the indirect evaluation of the excess of hydrochloric acid with soda, respectively.

RESULTS AND DISCUSSION

Bioleaching as the only metal extraction step

Copper, zinc and iron are dissolved during the bioleaching of complex sulphides. Lead and silver, both generally associated in the galena, are incorporated into the residue [16] since this mineral is oxidized to PbSO₄ (anglesite), insoluble in the medium used. According to the literature [17], the kinetics of this transformation into PbSO₄ are very fast.

Figures 3–5 show the dissolution profiles of Zn, Cu and Fe for the A1 and G1 concentrates. The yield of Zn was similar for both concentrates at about 80% (Fig. 3). However, the maximum recovery of Cu obtained in A1 was double that obtained in G1 (approx. 40% compared with 18–20%) (Fig. 4). As regards the dissolution of Fe, the percentage dissolved in both concentrates showed an almost linear dependence on bioleaching time (Fig. 5), with dissolution rates similar and independent of iron content. The explanation of this behaviour of the two concentrates might be the galvanic interactions established between the constituent sulphides, in agreement with their greater or lesser degree of electrochemical activity [18]. According to the rest potentials of the sulphides, the following order can be established: pyrite > chalcopyrite > galena > sphalerite, the first being the most noble phase and the last the most active. In the results obtained here, the galvanic interactions between the different constituent sulphides are only reflected by an increase in the dissolution rate and yield of
copper from concentrate Al. This low recovery of Cu is without
doubt the principal disadvantage of using bioleaching as the
sole extraction process for these minerals.

BIOLEACHING AS A PRE-TREATMENT STEP TO
CHEMICAL LEACHING

The possibility of using a bioleaching step prior to a chemical
extraction step was studied, the idea being that the micro-
organisms might help destroy the pyrite matrix and facilitate
the access of the leaching solutions.

Bioleaching step

In order to obtain a mineral with different degrees of degra-
dation of its pyrite matrix, the Al and Gl concentrates were
submitted to bioleaching for 4, 8 and 12 days. The D2 culture
medium (with low concentration of mineral salts) was used to
decrease jarosite precipitation on the sulphide surfaces.

Table 3 shows the different percentages of metal dissolved
(zinc, copper and iron) at the different times. As can be seen,
the dissolution rates were generally low, particularly when com-
pared with the results of more prolonged exposure when bio-
leaching was considered as the only step of metal extraction.

<table>
<thead>
<tr>
<th>Concentrate</th>
<th>Duration of bioleaching step (days)</th>
<th>% Zn dissolved</th>
<th>% Cu dissolved</th>
<th>% Fe dissolved</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>4</td>
<td>16.0</td>
<td>1.2</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>20.0</td>
<td>5.0</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>24.0</td>
<td>4.0</td>
<td>10.5</td>
</tr>
<tr>
<td>Gl</td>
<td>4</td>
<td>3.7</td>
<td>0.1</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>20.3</td>
<td>8.9</td>
<td>9.8</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>38.5</td>
<td>19.3</td>
<td>12.0</td>
</tr>
</tbody>
</table>

Tables 4 and 5 shows the results of the chemical analysis of
the residues obtained at the different leaching times. In Table 4
(A1) there is a slight decrease in the percentage of zinc and the
level of copper remains constant as bioleaching progresses.
These results are partly due to the fact that the dissolution of
copper and zinc which occurs during bioleaching leads to a loss
of weight on the residue and partly to the fact that the lead from
the galena remains totally in the residue as PbSO₄, resulting in
a slight increase in weight, which is not sufficient to compensate
for the previously mentioned loss. The net result, therefore, is
an increase in the concentrations of lead and silver in the resi-
due. To ascertain the quantity of PbS transformed into PbSO₄
(angleite), the concentration of SO₄²⁻ and the [SO₄²⁻]/[Pb] ratio
in the A1 concentrate and in each of residues was determined.

The sulphate content of the residues was caused by the trans-
formation of PbS into PbSO₄ during bioleaching. Since the
leached lead is around 97% (3% Pb is inaccessible, for example
inside the particles) this transformation can be considered total
in the samples taken at 8 and 12 days.

An analysis of the results of Table 5 leads to similar
conclusions, although the concentration of galena was very low
in the residues of the Gl bulk concentrate and there was no
great increase in weight. The copper hardly dissolved at all.

As can be seen, in Table 5 the [SO₄²⁻]/[Pb] molar ratio in the
Gl bulk concentrate and in the residues was close to unity or
higher. This suggests that all the lead existed as PbSO₄ and
some additional sulphates from the original Gl concentrate
could be present. In order to determine these last sulphates two
chemical tests on the Gl concentrate (without treatment)
were performed: (a) with distilled water to determine the cupric,
ferrous or ferric and zinc sulphates; and (b) with a 5 M NaCl
solution to determine additionally PbSO₄ which is soluble in
this medium. The results confirmed that in the Gl concentrate
there was a surface oxidation of the sulphides, so that, initially,
all the lead existed as PbSO₄, 0.05% of the copper as CuSO₄,
0.45% of the zinc as ZnSO₄, and 0.13% of the iron as ferrous
sulphate or acid ferrous sulphate.

Observations of the bioleaching residues of the A1 bulk con-
centrate by SEM showed they had undergone no important
changes compared with the biologically untreated concentrate
(Fig. 6). The angular forms of the particles submitted to bio-
leaching had, generally speaking, been rounded and smoothed
and their surface was covered by an incipient precipitate. In no
case was there evidence of a localized attack, cracks or any
other strong surface damage.

Chemical leaching step

The chemical leaching method chosen was the most impor-
tant part of the CENIM-LNETI process recently developed for
the hydrometallurgical treatment of complex sulphides [19].
This consists of leaching with oxygen in concentrated solutions
of ammonium chloride at neutral pH, in which ammonia is
generated to facilitate the dissolution of copper and zinc
through the formation of complex metal ammines. This form
of attack achieves the joint and practically total dissolution of
the metallic values of interest (Cu, Zn, Pb and Ag), while the
pyrite is comparatively lightly attacked.

According to Limpo et al. [20], the overall reactions produced
during the oxygen attack, in the presence of copper, for each of
the metallic sulphides of the bulk concentrate are as follows:
Table 4. Chemical analysis of the Al bulk concentrate from Sotiel and of the residues obtained by bacterial leaching for different times

<table>
<thead>
<tr>
<th>Leaching time</th>
<th>% Cu</th>
<th>% Zn</th>
<th>% Pb</th>
<th>% Fe</th>
<th>% Ag</th>
<th>% SO_4^-</th>
<th>SO_4^-/Pb Molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 days</td>
<td>2.70</td>
<td>32.0</td>
<td>9.2</td>
<td>22.0</td>
<td>0.0133</td>
<td>0.39</td>
<td>0.091</td>
</tr>
<tr>
<td>4 days</td>
<td>2.70</td>
<td>30.8</td>
<td>9.2</td>
<td>21.6</td>
<td>0.0135</td>
<td>0.38</td>
<td>0.097</td>
</tr>
<tr>
<td>8 days</td>
<td>2.70</td>
<td>28.0</td>
<td>10.1</td>
<td>22.6</td>
<td>0.0150</td>
<td>4.46</td>
<td>0.952</td>
</tr>
<tr>
<td>12 days</td>
<td>2.70</td>
<td>24.4</td>
<td>11.4</td>
<td>24.0</td>
<td>0.0165</td>
<td>5.04</td>
<td>0.955</td>
</tr>
</tbody>
</table>

Table 5. Chemical analysis of the Gl bulk concentrate from Rio Tinto and of the residues obtained by bacterial leaching for different times

<table>
<thead>
<tr>
<th>Leaching time</th>
<th>% Cu</th>
<th>% Zn</th>
<th>% Pb</th>
<th>% Fe</th>
<th>% Ag</th>
<th>% SO_4^-</th>
<th>SO_4^-/Pb Molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 days</td>
<td>15.00</td>
<td>17.63</td>
<td>1.76</td>
<td>23.73</td>
<td>0.0120</td>
<td>1.84</td>
<td>2.25</td>
</tr>
<tr>
<td>4 days</td>
<td>14.25</td>
<td>16.13</td>
<td>1.91</td>
<td>24.00</td>
<td>0.0125</td>
<td>1.14</td>
<td>1.30</td>
</tr>
<tr>
<td>8 days</td>
<td>15.13</td>
<td>15.25</td>
<td>1.90</td>
<td>22.75</td>
<td>0.0132</td>
<td>0.93</td>
<td>1.05</td>
</tr>
<tr>
<td>12 days</td>
<td>15.50</td>
<td>14.38</td>
<td>1.89</td>
<td>22.88</td>
<td>0.0132</td>
<td>0.87</td>
<td>1.00</td>
</tr>
</tbody>
</table>

\[
4\text{PbS} + \frac{7}{2}\text{O}_2 + 6\text{NH}_4^+ \rightarrow \text{SO}_4^{2-} + 3\text{S} + 4\text{Pb}^{2+} + 3\text{H}_2\text{O} + 6\text{NH}_3
\] (1)

\[
4\text{Zn}_{(1-x)}\text{Fe}_x\text{S} + \frac{7 + 2x}{2}\text{O}_2 + (6 - 8x)\text{NH}_4^+ \rightarrow \text{SO}_4^{2-} + 3\text{S} + 4(1 - x)\text{Zn}^{2+} + 2x\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O} + (3 - 6x)\text{H}_2\text{O} + (6 - 8x)\text{NH}_3
\] (2)

\[
2\text{FeCuS}_2 + 4\text{O}_2 + 2\text{NH}_4^+ \rightarrow \text{SO}_4^{2-} + 3\text{S} + 2\text{Cu}^{2+} + \frac{15}{4}\text{Fe}_2\text{O}_3 \cdot \frac{5}{2}\text{H}_2\text{O} + 2\text{NH}_3
\] (3)

\[
\text{FeS}_2 + \frac{15}{4}\text{O}_2 + \frac{5}{2}\text{H}_2\text{O} \rightarrow 2\text{SO}_4^{2-} + 4\text{H}^+ + \frac{1}{2}\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}
\] (4)

Although the optimal operational conditions for Spanish sulphides are: 105°C, a partial oxygen pressure of 1.5 x 10^5 Pa (1.5 atm) and neutral pH, the chemical leaching of the bioleaching residues was carried out at 95°C in order to decrease the velocity of the attack and thus be able to detect any kinetic differences between the bioleached samples and those which had not undergone any previous treatment.

In this experiment the behaviour of the different partially bioleached concentrates was compared with that of the untreated concentrate. The use of leaching with oxygen in concentrated ammonium chloride solutions made it possible to evaluate the individual attacks on the different mineral phases of the sphalerite, chalcopyrite, galena, pyrite) since each phase has a particular stoichiometry [20].

Figure 7 shows the percentage of copper, zinc, silver and lead dissolved from the Al concentrate. The results reveal that there was hardly any difference between the attacks on the different bioleaching residues nor between these and the previously untreated sample.

As regards the attack on the sphalerite [Fig. 7(a)], the dissolution rates in the bioleached samples were slightly lower than those in the previously untreated samples. Furthermore the dissolution rate decreased as the bioleaching time increased in the partially bioleached concentrates.

The chemical attack on the chalcopyrite was similar to that on the sphalerite [Fig. 7(b)]. The leaching rate was lower in the previously bioleached samples and fell as the bioleaching time increased. In this case, however, the determination of the attack rate on the chalcopyrite was less precise, since a certain concentration of copper was initially necessary in the leaching solution (0.8 g Cu²⁺/l). This copper, once leached, had to be determined by difference between the copper in dissolution and the initial copper and, although the quantities involved were small, the results must have contained higher relative errors.

As we have already seen, galena was the first sulphide to be oxidized in the prior bioleaching, so that oxidation was com-
Fig. 7. Chemical leaching of concentrate A1 after different periods of bioleaching. Evolution of the percentage of dissolved (a) Zn, (b) Cu, (c) Pb and (d) Ag.

Since iron was insoluble in the leaching medium, being precipitated as hydrated ferric oxide, the degree of pyrite degradation was calculated indirectly from the balance of sulphates in solution.

The chemical attack on the pyrite of the A1 concentrate (Fig. 8) showed the same tendency as the sphalerite and chalcopyrite, with a smaller percentage being attacked in the previously bioleached samples. However, in the case of the pyrite, the decrease was more pronounced as previous treatment times increased. Thus in the residues obtained after 12 days of bioleaching the rate of attack fell to half that of the untreated sample.

The decrease in the attack on the pyrite was also revealed by the following:
- According to the reactions (1), (2) and (3), each mineral sulphide produces a specific amount of ammonia, which, in the aqueous solution is distributed in the form of different ionic species: binary ammonia metal complexes $\text{Me(NH}_3)_2^+$, ternary ammonia chloride metal complexes
MeCl\(_n\)(NH\(_3\))\(_{2-n}^+\) and ammonia free (Me = Cu or Zn and from \(n=1\text{--}4\)) \([21\text{--}23]\). The total concentration of ammonia is equal to the sum of the concentrations of all these ionic species and is determined by back titration, adding an excess of standardized NaOH using dimethyl yellow as an indicator \([23]\). The total ammonia produced in the case of the galena, is 1.5 mol per mole of lead dissolved. For the sphalerite Fe\(_{0.5}\)Zn\(_{0.5}\)S (\(x=0.05\) for the Gl concentrate and 0.08 for the Al) this amount is, respectively, 1.47 and 1.45 mol of NH\(_3\) per mole of zinc dissolved and for the chalcopyrite 1.0 mol NH\(_3\) per mole of copper dissolved. If we say \(R=NH_3/\Sigma Me\), where \(NH_3\) and \(Me\) are the moles of \(NH_3\) formed and metals dissolved, there is a different value for \(R\) for each concentrate, depending on the mineralogical composition and increasing with increased contents of chalcopyrite. This value for \(R\) corresponds to the maximum limit value reached in the presence of pyrite.

According to eqn (4), if the concentrate contains pyrite then the maximum limit \(R\) cannot be attained since, due to the pyrite being attacked, an acid is formed which neutralizes the ammonia formed.

If the values of the molar ratio \(R\) are represented as a function of the attack time and the moles of metal dissolved, \(t/\Sigma Me\), a straight line is obtained for the equation:

\[
\frac{NH_3}{\Sigma Me} = R - k \frac{t}{\Sigma Me}
\]

The ordinate on the origin is the maximum limit, \(R\), of the bulk concentrate and the slope of the line, \(k\), is the kinetic constant for the attack on the pyrite. To obtain eqn (5), it must be hypothesized that the quantity of pyrite attacked depends linearly on time, which holds true only if a small percentage of pyrite is attacked, as occurs in this process.

Figure 9 shows the experimental values obtained for \(NH_3/\Sigma Me\) in relation to \(t/\Sigma Me\) in the Al concentrate. The data can be fitted to a series of straight lines whose maximum value for \(NH_3/\Sigma Me\) of 1.45 practically coincides with the 1.40 obtained theoretically from eqns (1)-(3). The slope of these straight lines, however, differs according to the treatment. The maximum value for the kinetic constant of the pyrite, \(k\), corresponded to the sample which had not been treated previously and this decreased with the bioleaching time, i.e. the dissolution rate of the pyrite was less in samples which had been bioleached for longer periods of time.

The behaviour of concentrate G1 was similar to that of Al. Figure 10 shows the percentage of zinc, copper, lead and silver dissolved at various chemical leaching times in samples of G1 both partially bioleached and with no previous treatment. The dissolution curves corresponding to the residue after 4 days bioleaching are not represented since they are similar to those obtained at 8 days. The results show that the dissolution rates for sphalerite, chalcopyrite and galena in the bioleached samples were slightly less than those obtained in the original untreated concentrate. However, no significant differences arose between the different bioleaching times since the chemical compositions of the residues obtained were very similar (Table 5).

Figure 11 shows the percentage of pyrite attacked chemically in the untreated G1 concentrate and the residues obtained after bioleaching. The leaching rate was lower in the bioleached samples, although the decrease was less pronounced than in the Al concentrate, basically because the degree of pyrite degradation was similar in the different bioleached samples of G1.

In conclusion, the leaching rates of the different mineral species were lower in samples previously exposed to a bioleaching process than in untreated concentrates. This was probably due to either a decrease in particle surface area or a coating produced in the pre-treatment step which was deposited on the surface. As mentioned above, in Fig. 6 an incipient precipitate formed on the surfaces of the sulphides particles. This could be PbSO\(_4\) (Tables 4 and 5) which was formed in the pre-treatment or jarosites, ferric hydroxy sulphate of composition \(MFe_2(SO_4)\_3(OH)\_6\) where \(M\) is one of several cations, including H\(_2\)O\(^+\), K\(^+\), Na\(^+\) and NH\(_4\)^+. PbSO\(_4\) is, however, soluble in concentrated chloride solutions and its formations would not justify the decrease in the observed leaching rates. Besides, no Pb
was detected by X-ray microanalysis on the mineral surfaces. However, there is strong evidence in the literature \cite{24-26} that jarosite precipitation occurs in different bioleaching media in the presence of microorganisms, especially in nutrient media with relatively high concentrations of NH$_4^+$ and K$^+$, such as 9K medium \cite{27}. On the other hand, previous studies on the same Al and G1 bulk concentrates showed that massive jarosites precipitations was detected by X-ray diffraction in the residues after a bioleaching process performed in similar experimental conditions \cite{28}. All this suggested that the jarosites would be the solid product that limited the oxidation reactions during the chemical leaching.

**CONCLUSIONS**

The possibility of applying a bioleaching treatment to bulk concentrates of Spanish complex sulphide concentrates was studied. The main drawback of bioleaching as sole treatment was the low rate of copper dissolution (40\% maximum). During this treatment about 80\% of the zinc and substantial quantities of iron (12-22\%) were dissolved.

Bioleaching as a pre-treatment step to chemical leaching with concentrated solutions of ammonium chloride did not destroy the pyrite matrix. The attack tended to smooth the irregular forms rather than to destroy the structure. As a result, bioleaching as a pre-treatment step in a hydrometallurgical process cannot be considered as an alternative to grinding and as a way of overcoming the fine dissemination of metallic values in a pyrite ore.

In addition, bioleaching pre-treatment of bulk concentrates did not improve the sphalerite, chalcopryite or pyrite leaching rates. In fact, there was a reduction, which, although small in the case of sphalerite and chalcopryite, was greater in that of pyrite. These lesser leaching rates were attributed to the solid products, jarosites that passivate the sulphide surfaces. As a
render the subsequent treatment of resulting fertile solutions more effective.

the metals dissolved during chemical leaching, which would there was a higher ratio between the ammonia produced and concentrates.

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