

Passivation of chalcopyrite during its chemical leaching with ferric ion at 68 °C

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ABSTRACT

The passivation of chalcopyrite in the presence of ferric sulphate solutions was investigated at 68 °C. The effect of different variables (pulp density, pH and the presence of oxygen) on both the copper dissolution rate and the formation of solid compounds was studied. The leaching tests were carried out in stirred flasks at 180 rpm with 100 mL of a $\text{Fe}^{3+}/\text{Fe}^{2+}$ sulphate solution, varying the pulp density between 0.1 and 5% and the pH between 0.5 and 2.0 and both in aerobic and anaerobic conditions. Ferric ion seems to be responsible for the oxidation of chalcopyrite but also promotes its passivation. Ferrous ion plays a key role in the process by controlling the nucleation and precipitation of jarosites, which finally cause the passivation of chalcopyrite.

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1. Introduction

The slow copper dissolution rate from chalcopyrite has been attributed to the formation of a passivating layer on the mineral surface. In this way, several theories and hypotheses have been proposed.

Burkin (1969) suggested that the leaching of chalcopyrite with Fe^{3+} favours the formation of a diffusion film over its surface made of a semiconductor bimetallic sulphide with chemical and structural properties different from chalcopyrite. Those intermediate products that proceed from solid state transformations favour the solubilization of cations from the crystal lattice at different rates. Therefore, this model assumes that the chemical reaction does not take place on the interface but across the thickness of a reaction space.

Ammou-Chokroum et al. (1977) proposed that the copper dissolution rate is controlled by the formation and evolution of a compact diffusion layer of a copper polysulphide, less reactive and with less iron content than the original chalcopyrite. The thickness of that layer would be the result of two opposite reactions: (1) the formation of a copper-rich passive layer because of the slower diffusion of copper than iron ions in solid state; this stage obeys a parabolic law; and (2) the dissolution of the passivating layer according to a linear law, in which a porous film of elemental sulphur is formed.

Muñoz et al. (1979) gave a new interpretation of the phenomenon. They considered that the limiting step of the chalcopyrite dissolution with ferric ion is the transport of electrons, needed for the

cathodic reduction reaction, through an insulating layer of elemental sulphur. Thus, in this model, the elemental sulphur formed establishes a physical barrier between the anodic and the cathodic zone, limiting the redox reaction of chalcopyrite leaching. Dutrizac (1989) and Majima et al. (1985) supported this model.

Hackl et al. (1995) proposed a mixed model of diffusion and chemical control to explain the passivation of chalcopyrite in sulphate medium. This model is complementary to the one by Ammou-Chokroum et al. (1977). Initially, iron is preferentially leached to copper and an intermediate disulphide phase is formed: $\text{Cu}_{1-x}\text{Fe}_{1-y}\text{S}_2$, where $y \gg x$ and $x + y \sim 1$. In the second stage, slower than the former one, the disulphide dissolves into a copper polysulphide, $\text{Cu}_{1-x-z}\text{S}_2$, responsible for the passivation of chalcopyrite due to its slow dissolution rate to cupric ions and elemental sulphur.

More recently, several researchers have pointed out that high redox potentials promote passivation of chalcopyrite during leaching. For instance, Hiroyoshi et al. (1997, 2000, 2001) proposed a reaction model which involves the intermediate reduction of chalcopyrite to Cu_2S and the oxidation of ferrous ion, followed by the oxidation of Cu_2S by ferric ion to cupric ions and elemental sulphur. In that model, the control step is the reduction of chalcopyrite which only takes place when the redox potential is below a critical value. In addition, Nicol and Lázaro (2003) proposed that chalcopyrite reduction can be achieved by protonic attack at potential values lower than 0.4 V, releasing Cu^{2+} , Fe^{2+} and H_2S . Then, hydrogen sulphide is oxidized by ferric ion to elemental sulphur. According to this model, the control step is the electrochemical reaction, since the oxidation rate of H_2S decreases with increasing the chalcopyrite surface potential from 0.5 to 0.7 V. Previous to these works, other authors had also found better chalcopyrite dissolution rates at relatively low potentials (Kametani and Aoki, 1985; Barr et al., 1992; Third et al., 2000, 2002; Okamoto et al., 2003).

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Recent studies (Córdoba et al., 2008) have shown that the passivation of chalcopyrite is related to high potential values (e.g. high $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio). It was concluded that the leaching solutions of ferric/ferrous sulphate reach rapidly an equilibrium at which the activities of both ions are equal. That was related with a critical potential of approximately 0.65 V vs. SHE. Thus, when the redox potential is initially very high, the tendency to that equilibrium favours the fast precipitation of ferric ion as jarosite and, then, the passivation of chalcopyrite.

The aim of the present work was to evaluate the passivation of chalcopyrite at 68 °C by studying the relationship between the redox potential and different physicochemical variables, such as: pH, pulp density and the presence or the absence of oxygen in solution.

The choice of that particular temperature, 68 °C, was based on the fact that it is the appropriate temperature for the growth of thermophilic microorganisms, which are widely used in bioleaching processes.

2. Materials and methods

2.1. Solids

The leaching tests were performed with a chalcopyrite mineral (approximately 80% of CuFeS_2) from Messina, Transvaal (South Africa), with the following chemical composition: 34.30% S, 29.65% Fe, 27.36% Cu, 0.31% Zn and 0.02% Pb. X-ray analysis of powder samples showed the presence of pyrite (FeS_2), siderite (FeCO_3) and quartz (SiO_2) as main impurities in the mineral.

The mineral was dry ground using a ball mill. The particle size distribution was determined by laser pulse, with an average particle size around 70 μm . In addition, a BET surface area of 0.07 m^2/g was determined.

2.2. Leaching solutions

Three solutions with different redox potentials were used: 400, 600 and 667 mV vs. Ag/AgCl. They were obtained mixing ferric and

ferrous sulphates of analytical grade in deionized water, keeping constant a total iron concentration of 5 g/L at pH 1.8 (except for tests on the influence of that variable, in which pH ranged between 0.5 and 2.0). The stock solutions of ferric and ferrous sulphate were prepared with Norris nutrient medium (0.4 g/L $(\text{NH}_4)_2\text{SO}_4$; 0.5 g/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.2 g/L K_2HPO_4 , Norris and Barr, 1985), normally used in bioleaching with thermophilic microorganisms.

2.3. Leaching tests

All leaching tests were performed in an orbital shaker at 180 rpm and 68 °C. Aerobic tests were carried out in 250 mL Erlenmeyers covered with hydrophobic cotton that allowed the access of oxygen but reduced water loss through evaporation. 100 mL flasks hermetically closed were used in anaerobic tests. A low pulp density of 0.5% (100 mL of leaching solution and 0.5 g of mineral), except for tests on the influence of that variable, was chosen to avoid sharp changes of the redox potential of the liquid medium during the first moments of leaching.

Periodically, water evaporation was restored, pH adjusted when above the initial value, redox potential recorded and 1 mL samples removed from the liquid to obtain kinetic information on metal dissolution by atomic absorption spectrophotometry (Cu and Fe_{Total}) and by photocolourimetry (Fe^{2+}). Finally, solid residues were characterized by XRD (X-ray Diffraction) and SEM-EDS (scanning electron microscopy–energy dispersive spectroscopy).

3. Results and discussion

3.1. Influence of pH

In previous studies (Córdoba et al., 2008), the authors collected evidences on the passivation of chalcopyrite during its chemical leaching with ferric sulphate at 68 °C. That leaching process seems to be greatly affected by the formation of a layer of jarosite on the chalcopyrite surface. Thus, the copper dissolution rate could be indirectly affected by pH because of iron hydrolysis. In this study,

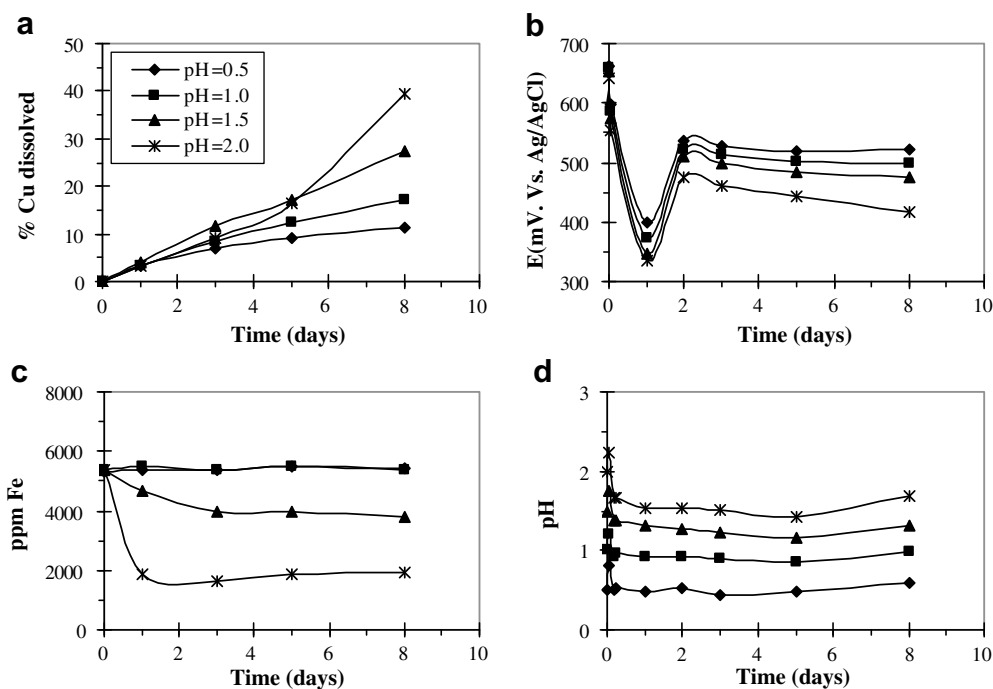


Fig. 1. Influence of pH on the chalcopyrite leaching at 68 °C.

a ferric sulphate solution of 5 g/L Fe (667 mV vs. Ag/AgCl) was used.

pH was carefully controlled with diluted H_2SO_4 during the first 5 h of leaching in order to stabilize the value slightly below the initial value (0.5, 1.0, 1.5 and 2.0). Alkaline reagents, such as NaOH or NH_3 , were not added to avoid iron hydrolysis.

Unexpectedly, higher copper extractions were obtained at higher pH, 1.5 and 2.0 (Fig. 1a). Paradoxically, however, iron hydrolysis took place preferentially in tests at the higher pH values as shown in Fig. 1c.

The sharp drop of the redox potential during the first day of leaching seems to be associated to an increase of ferrous concentration, initially absent in solution, as a reaction product of the chalcopirite dissolution (Fig. 1b).

The SEM study of the leaching residue at low pH (0.5) showed attacked chalcopirite particles with a porous reaction product (Fig. 2a), identified as S° , and pyrite particles with a strong pitting

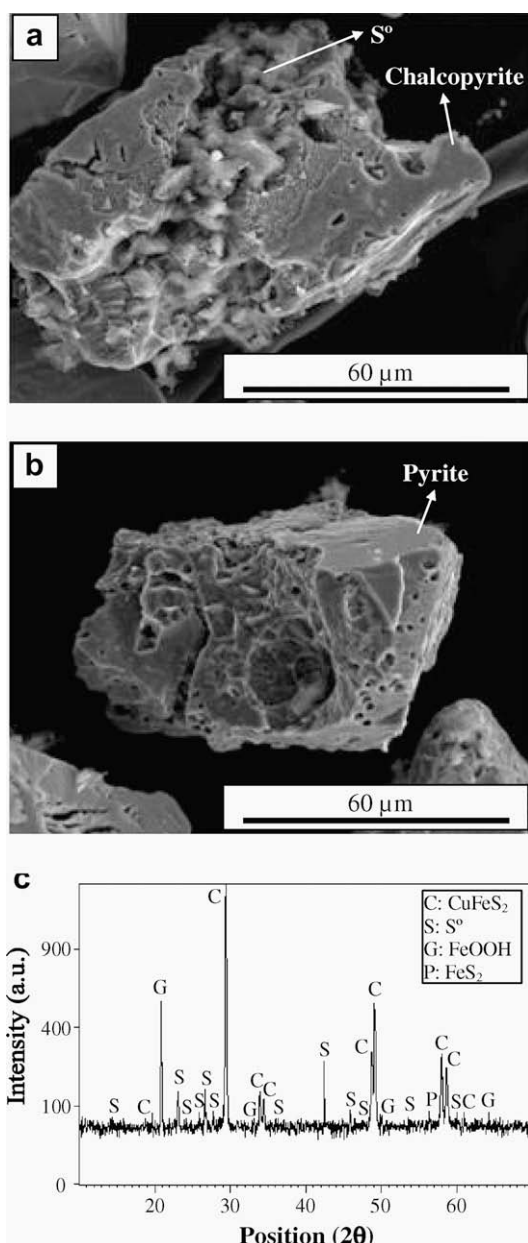


Fig. 2. SEM micrographs (a and b) and diffractogram (c) of the leaching residue at 68 °C, pH 0.5 and $[\text{Fe}^{3+}]_{\text{initial}} = 5 \text{ g/L}$.

attack but without reaction products on its surface (Fig. 2b). The X-ray diffractogram confirmed the presence of elemental sulphur and goethite in the leaching residue (Fig. 2c). The leaching behaviour of pyrite was similar to previous studies showing pitting attack that renders sulphate instead of elemental sulphur as the final product (Murr and Mehta, 1982; Lotens and Wesker, 1987).

Sand et al. (2001) reported that pyrite is not attacked at low pH by protons but, exclusively, by ferric ion. Then, the high attack of pyrite observed during the leaching at pH 0.5 would be related to the high redox potential reached. In fact, although the redox potential dropped in all tests (Fig. 1b), the final value was higher at pH 0.5 (approximately 530 mV) than at $\text{pH} \geq 1$ ($\leq 500 \text{ mV}$). Therefore, low pHs established oxidizing conditions of the leaching solution above the rest potential of pyrite, and that favoured its dissolution despite the presence of chalcopirite.

At pH 2, the nucleation and precipitation of a passivating layer of jarosite on mineral particles was very marked, as shown in the SEM micrograph of the leaching residue (Fig. 3a). X-ray diffraction analysis confirmed that jarosite was the main constituent in the leaching products (Fig. 3b). In the present study, the precipitation of jarosites was observed preferentially in tests at pH 1.5 and 2.0. Nevertheless, Lu et al. (2000) detected jarosite at pH as low as 0.9 in chloride media.

The negative effect of a decrease of pH observed during the chalcopirite leaching can be considered as unexpected. Since, as mentioned previously, hydrolysis and precipitation of ferric ion as jarosites seems to be responsible for the passivation of chalcopirite and that precipitation is related directly to pH.

However, the oxidizing action of Fe^{3+} species can be questioned considering the thermodynamic stability of the different ion species present in the leaching solutions tested. Fig. 4 shows the speciation diagram for the Fe(III) system at 70 °C in sulphate medium in the range of pH between 0 and 2 for the ferric and sulphate concentrations used in this study, 0.09 M Fe(III) and 0.2 M SO_4^{2-} . In that

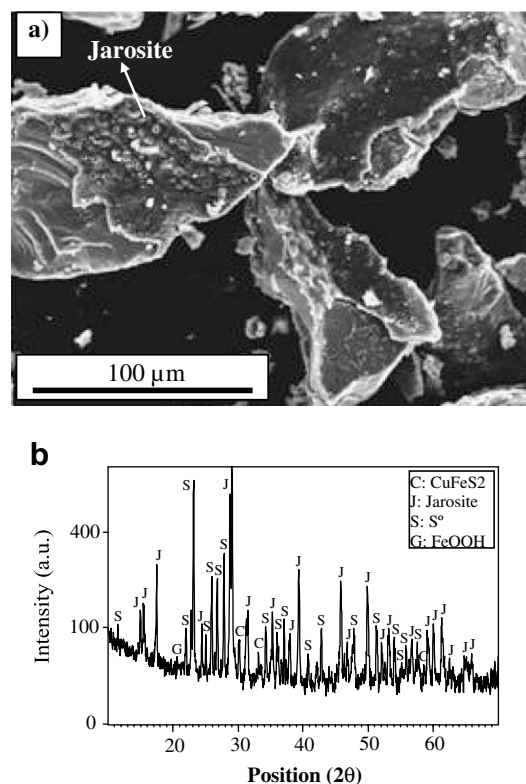


Fig. 3. SEM micrograph (a) and diffractogram (b) of the leaching residue at 68 °C, pH 2.0 and $[\text{Fe}^{3+}]_{\text{initial}} = 5 \text{ g/L}$.

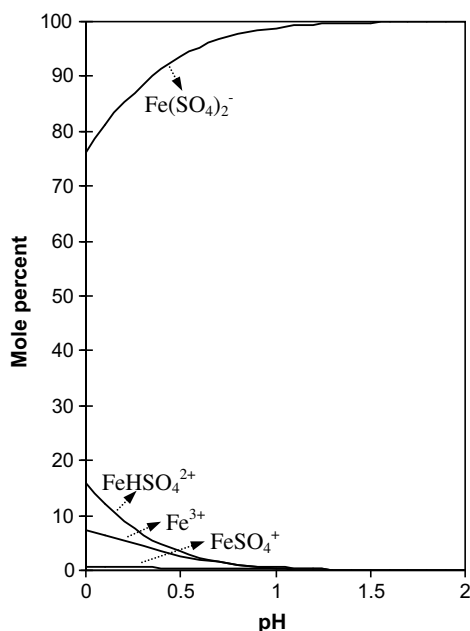
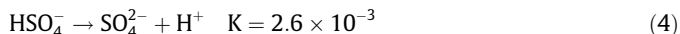
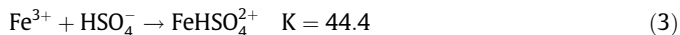
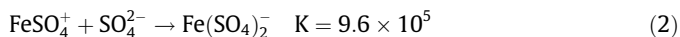
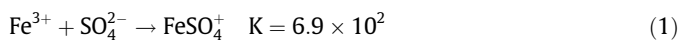


Fig. 4. Equilibrium iron species in a solution containing 0.09 M Fe(III) and 0.2 M SO_4^{2-} , at 70 °C.

diagram, the participation of hydroxide species is almost negligible.

The following reactions were considered:



The equilibrium constants of these reactions were calculated from the thermodynamic data obtained using the Outokumpu HSC Chemistry® for Windows database (Roine, 2002). Except for the values of free energy of Gibbs for $\text{Fe}(\text{SO}_4)_2^-$ and FeHSO_4^{2+} species which were determined from Casas et al. (2007).

In the speciation diagram, the predominant species in the range of pH between 0 and 2 is $\text{Fe}(\text{SO}_4)_2^-$. Conversely, the participation of Fe^{3+} and other species could be considered irrelevant. For instance, at pH 0.5, the concentration of Fe(III) as Fe^{3+} is approximately 3% and nil at pH 2.0. Therefore, the main species responsible for the dissolution of chalcopyrite seems to be not Fe^{3+} but $\text{Fe}(\text{SO}_4)_2^-$, since that is the only species that increases its concentration with pH.

Antonijević and Bogdanović (2004) also reported the negative effect of a decrease of pH on the chalcopyrite dissolution. They concluded that, in very acidic media, chalcopyrite is iron deficient causing its passivation.

In addition, Ruitenberg et al. (1999) found the same negative effect of a decrease of pH on the arsenopyrite dissolution. They suggested that the differences of the leaching kinetics at different pH values are due, mainly, to differences in the oxidizing capability of the ferric complexes formed.

Therefore, the slow chalcopyrite dissolution rate cannot be improved by decreasing the pH of the solution. As pointed out by Dutrizac et al. (1969), the role of acidity in this process seems to be to control the hydrolysis of ferric ion.

3.2. Influence of pulp density

The chalcopyrite leaching at 68 °C with different percentages of solids was investigated in solutions at two different initial redox potentials (400 and 600 mV vs. Ag/AgCl).

The effect of this variable at low potential, 400 mV, is shown in Fig. 5. *A priori*, the copper extraction should be higher for a lower pulp density. However, the results obtained indicate that an increase of the pulp density improves the dissolution of chalcopyrite (Fig. 5a), which seems to be related to a low redox potential main-

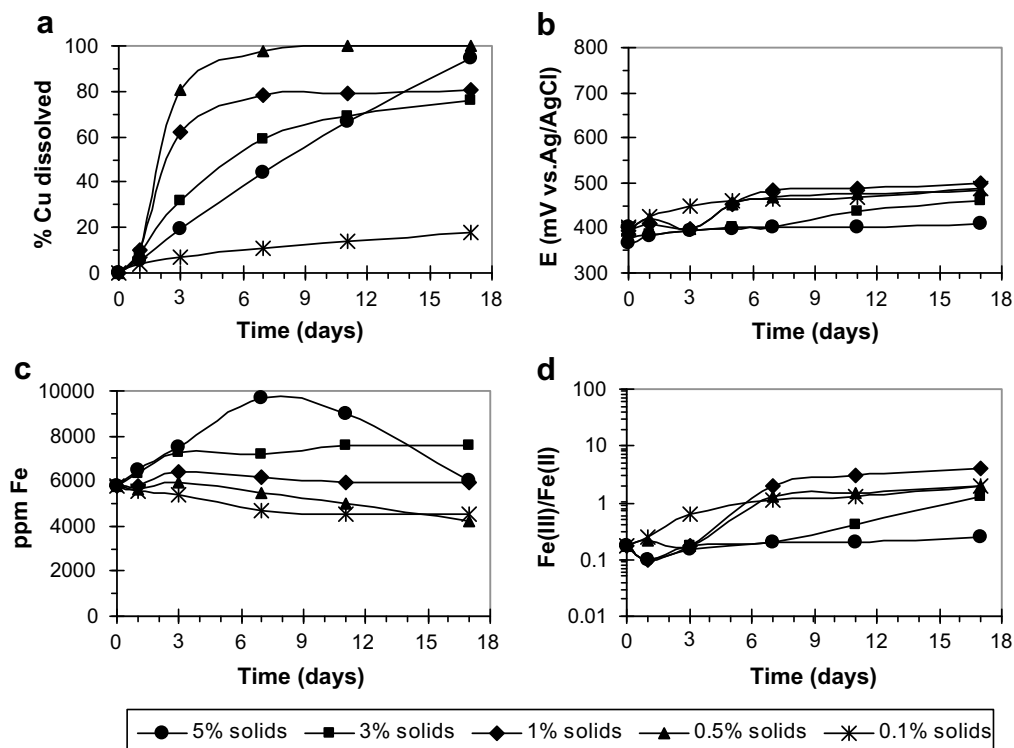


Fig. 5. Influence of pulp density on the chalcopyrite leaching at 68 °C, pH 1.8 and $E_{\text{initial}} = 400$ mV.

tained for a longer time (Fig. 5b). The complete dissolution of chalcopryrite, with a linear kinetic relatively acceptable, was achieved with a pulp density of 5%.

These results could be explained considering the indirect relationship between the pulp density and the redox potential of the solution. For a given volume of leach solution, the concentration of the reaction product of chalcopryrite, Fe^{2+} , increases with increasing the percentage of solids and, at the same time, the redox potential of the solution decreases.

The previous assumption, however, is true only if precipitation of iron compounds is avoided, since those products favour the formation of passivating films on the chalcopryrite surface. For instance, the test with 5% of solids reached a maximum iron concentration of 9.8 g/L (Fig. 5c), which practically doubled the initial concentration (5 g/L). That sharp increase of iron in solution can be followed by its massive precipitation. Thus, the risk of jarosite formation and later passivation of the mineral surfaces is high.

The fastest kinetics was obtained with a pulp density of 0.5%, that is, when the experimental conditions establish a good solid/liquid contact compatible with a low redox potential. For a lower pulp density, 0.1%, the redox potential is above a critical value (≈ 450 mV vs. Ag/AgCl) from the beginning and the chalcopryrite leaching stops. Pulp density values higher than 0.5% show an initial fast leaching kinetics, which slows down above a critical potential.

The diffractograms of the leaching residues with 5% and 0.1% of solids are shown in Figs. 6a and 6b, respectively. The reaction products formed were similar to previous tests: elemental sulphur, jarosite, covellite and goethite. Nevertheless, the relative intensity of the peaks would indicate that high pulp densities, which establish a lower redox potential than the critical, favour the formation of goethite besides jarosite; whereas low pulp densities, which establish a redox potential higher than the critical, promote the precipitation of iron as jarosite. Similarly, Kandori et al. (2004) found that goethite is preferentially formed at low concentrations of ferric sulphate (0.01 M) whereas jarosite preferentially forms at high concentrations of ferric sulphate (0.1 M).

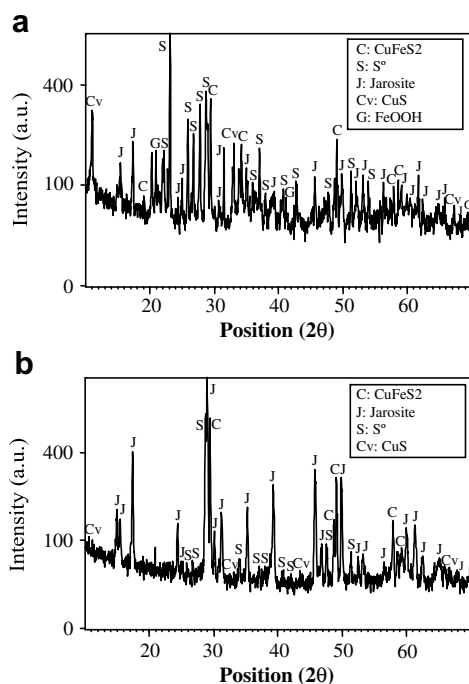


Fig. 6. Diffractograms of the leaching residues at 68 °C, pH 1.8, $E_{\text{initial}} = 400$ mV and $[\text{Fe}^{3+}]_{\text{Total}} = 5$ g/L, at a pulp density of: (a) 5% and (b) 0.1%.

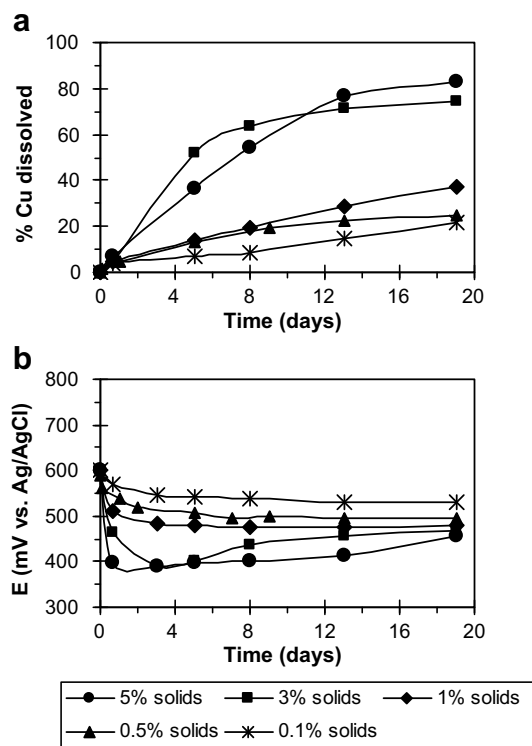


Fig. 7. Influence of pulp density on the chalcopryrite leaching at 68 °C, pH 1.8 and $E_{\text{initial}} = 600$ mV.

The effect of pulp density at a high initial redox potential (600 mV vs. Ag/AgCl) is shown in Fig. 7. Again, an increase of the pulp density decreases the redox potential of the solution (Fig. 7b) and, at the same time, improves the chalcopryrite dissolution rate (Fig. 7a). It is clear that when the redox potential is above the critical value, 450 mV vs. Ag/AgCl, the copper dissolution rate slows down, for the whole range of pulp density studied. This suggests that the redox potential of the solution is, besides temperature, one of the most important factors in controlling the chalcopryrite dissolution kinetics.

Considering the copper rate obtained at low (Fig. 5) and high (Fig. 7) initial potential, low redox potentials improve the chalcopryrite dissolution indistinctly of the percentage of solids used.

3.3. Influence of oxygen

Fig. 8 shows the results obtained during the chalcopryrite leaching at 68 °C and at an initial redox potential of 400 mV under aerobic and anaerobic conditions.

The presence of oxygen in the leaching medium remarkably improved the copper dissolution rate (Fig. 8a). Several authors have pointed out that the role of oxygen in this process seems to be as direct oxidizing agent whether of chalcopryrite or of Fe^{2+} in solution (Dutrizac and MacDonald, 1974; Antonijević and Bogdanović, 2004). The first option is very improbable, given the incapacity of oxygen to oxidize directly chalcopryrite under atmospheric pressure. Therefore, the most probable action of oxygen in the chalcopryrite leaching is to regenerate Fe^{3+} . Lu et al. (2000) reported that the copper dissolution rate from chalcopryrite at 95 °C in acid solution remarkably improved after increasing the oxygen partial pressure. They concluded that the importance of oxygen in this process resides in the oxidation of ferrous to ferric ion.

In addition, the variation of the redox potential (Fig. 8b) and the Fe(III)/Fe(II) molar ratio (Fig. 8c) was almost negligible in the absence of oxygen in the medium. Conversely, under aerobic condi-

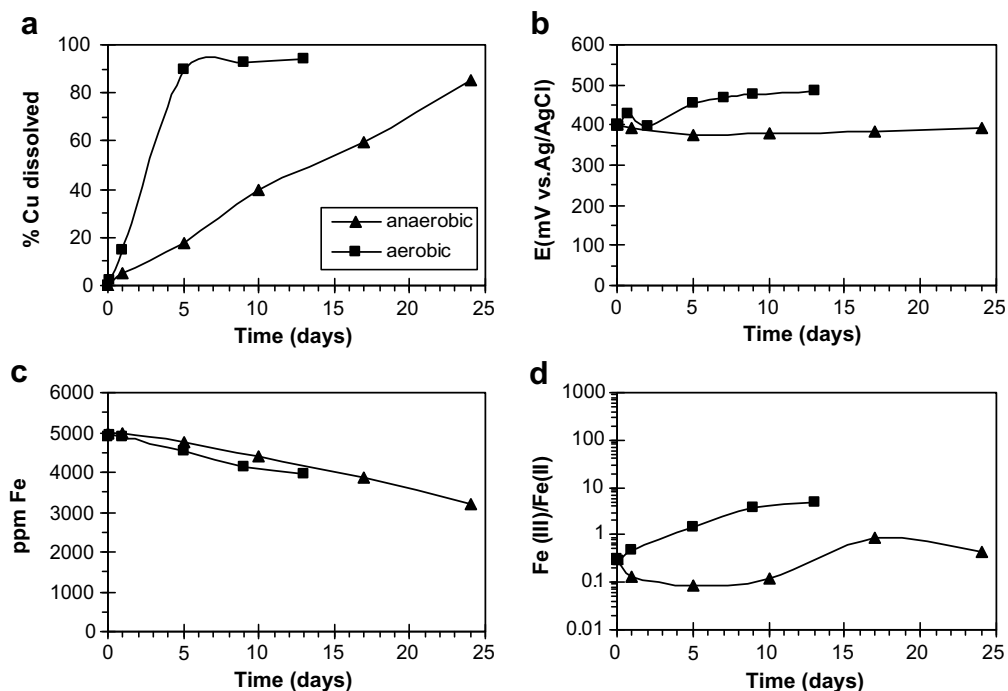


Fig. 8. Influence of the presence of oxygen on the chalcopyrite leaching at 68 °C, pH 1.8 and $E_{\text{initial}} = 400$ mV.

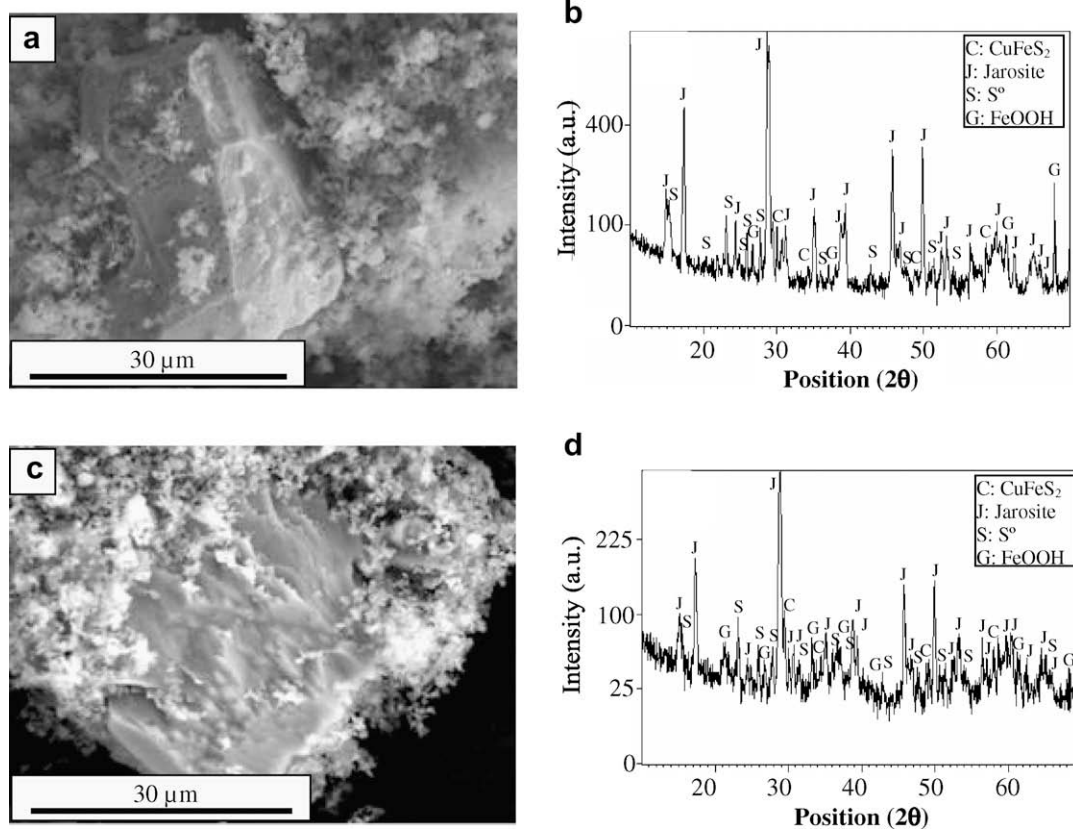


Fig. 9. SEM micrographs and X-ray diffractograms of the leaching residues at 68 °C, $E_{\text{initial}} = 400$ mV, $[\text{Fe}]_{\text{Total}} = 5$ g/L and aerobic (a and b) or anaerobic (c and d) mediums.

tions, the increase observed in the concentration of Fe(III) and, thus, in the potential, could be considered as an evidence of the oxidation of ferrous ion by oxygen.

Another interesting observation in the anaerobic test was a large iron precipitation (Fig. 8c), in spite that the potential remained at low values. It seems that, under those conditions (low

potential and absence of oxygen), hydrolysis and precipitation of non-crystalline compounds of Fe^{2+} are favoured.

Fig. 9 shows the SEM micrographs and XRD diffractograms of the leaching residues obtained in aerobic and anaerobic conditions. The morphology of the reaction products (Fig. 9a and c), apparently porous, is very similar in both cases and the layer formed on the mineral surfaces is apparently non-passivating. That is in accordance with the linear copper kinetics observed in both tests (Fig. 8a).

The XRD diffractograms of the residues (Fig. 9b and d) do not show large differences between the leaching products formed under both conditions (aerobic and anaerobic). Again, the main reaction products were: elemental sulphur, potassium jarosite and goethite.

Although in the diffractogram of the anaerobic test residue (Fig. 9d) jarosite and goethite were the only iron hydrolysis products detected, the formation of non-crystalline ferrous hydroxyl-complexes could explain the extensive iron precipitation observed in that test.

Therefore, the positive effect of oxygen during the chalcopryrite leaching would be related to the regeneration of the oxidizing agent.

4. Conclusions

1. Low pH values ($\text{pH} \leq 1.0$) of the leach solution have a negative effect on the chalcopryrite dissolution rate with ferric ion, compared with the high pH (1.5 and 2.0) that favours its dissolution.
2. According to the diagram of speciation for Fe(III) at 68°C , the only species with an increase of its concentration in the range of pH studied (0.5–2.0) is $\text{Fe(SO}_4)_2$. Therefore, that species could be responsible for the dissolution of chalcopryrite.
3. The role of pH in the chalcopryrite leaching with ferric sulphate is exclusively related to control the hydrolysis of ferric species more than to oxidize that sulphide.
4. In the range of pulp density studied (between 0.5 and 5%), higher values of this variable improve the copper dissolution rate. An increase of the percentage of solids increases the amount of ferrous ion in solution resulting in low redox potentials of the solution, which avoids ferric hydrolysis and, in turn, chalcopryrite passivation.
5. The absence of oxygen in the leaching medium remarkably slows down the chalcopryrite dissolution. Oxygen plays a key role in the regeneration of ferric ion as the oxidizing agent of the sulphide.
6. The hydrolysis products of ferric ion, mainly jarosites, seem to be responsible for the passivation of chalcopryrite. Conversely, the elemental sulphur formed during chalcopryrite dissolution is porous and does not contribute to the passivation of the chalcopryrite surface.

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