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Electrochemical behaviour of chalcopyrite in the presence of silver and *Sulfolobus* bacteria

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The electrochemical behaviour of massive chalcopyrite electrodes has been studied in an acid medium (pH 1.5) containing silver ions ($0.02\,\mathrm{g\,dm^{-3}}\,\mathrm{Ag^+}$) and thermophilic bacteria (68 °C). Preliminary tests on particulate electrodes made from graphite, elemental sulfur and $\mathrm{Ag_2S}$ were included to determine the electrochemical response of reactants ($\mathrm{Ag^+}$) and products ($\mathrm{S^\circ}$ and $\mathrm{Ag_2S}$) associated with the dissolution of chalcopyrite in the presence of silver. Massive chalcopyrite electrodes under potential scan showed a dependence on the dissolution of the $\mathrm{Ag_2S}$ film with both the time of contact with the silver solution and $[\mathrm{Ag^+}]$. As well as $\mathrm{Ag_2S}$, metallic silver was detected on the chalcopyrite surface. It has been demonstrated that $\mathrm{Fe^{3+}}$ and bacteria play an important role in the regeneration of the $\mathrm{Ag_2S}$ film. The breakdown of this film is a requirement for the further dissolution of chalcopyrite. The bioleaching of chalcopyrite with thermophilic microorganisms in the presence of silver decreased the decomposition potential of the electrode and favoured its electrodissolution. Bioleaching treatment in the presence of silver ions for periods of time longer than two weeks did not improve the surface reactivity. However, in the initial stages of the process, the lower reactivity of the bioleached electrodes was probably related to a toxic effect of silver on the microorganisms.

Keywords: *Chalcopyrite*, *Bioleaching*, *Thermophilic bacteria*, Sulfolobus, *Silver catalysis*, *Potentiodynamic polarization*, *Cyclic voltammetry*

1. Introduction

Different studies [1, 2] carried out on chalcopyrite leaching in acidic ferric sulfate have suggested that one of the main limiting steps regarding the kinetics control of this system is possibly the transport of electrons through a nonporous and protective layer of elemental sulfur formed during the dissolution process:

$$\mathrm{CuFeS_2} + 4\,\mathrm{Fe^{3+}} \rightleftharpoons \mathrm{Cu^{2+}} + 5\,\mathrm{Fe^{2+}} + 2\,\mathrm{S^\circ} \qquad (1)$$

In an attempt to overcome this problem several solutions have been proposed [3–5]:

(a) to increase the temperature to decompose the passive layer;
(b) to use microorganisms to accelerate the destruction of the passive layer;
(c) to add different ions, as $\mathrm{Ag^+}$, that permit a better electrical and ionic contact with the mineral and, therefore, a quicker electronic transport through the solid.

In the present investigation solution (c), in conjunction with the presence of thermophilic microorganisms, has been studied using electrochemical techniques.

The mechanism of silver behaviour during the chalcopyrite leaching has been widely studied [6, 7]. The catalytic effect of the silver has been attributed to the formation of a conducting $\mathrm{Ag_2S}$ film on the chalcopyrite surface. This film neutralizes the effect of the passive layer on the chalcopyrite as it acts as a channel for electrons generated during the anodic process and facilitates the cathodic reaction. The mechanism proposed by Miller and Portillo [6] establishes the following sequence of reactions:

$$\mathrm{CuFeS_2} + 4\,\mathrm{Ag^+} \rightleftharpoons 2\,\mathrm{Ag_2S} + \mathrm{Cu^{2+}} + \mathrm{Fe^{2+}} \qquad (2)$$

$$2\,\mathrm{Ag_2S} + \underbrace{4\,\mathrm{Fe^{3+}} \rightleftharpoons 4\,\mathrm{Ag^+} + 4\,\mathrm{Fe^{2+}}}_{\text{bacteria}} + 2\,\mathrm{S^\circ} \qquad (3)$$

giving the global reaction (Equation 1). Reaction 2 has been checked experimentally whereas Reaction 3 has not. The bacteria can affect the $\mathrm{Fe^{2+}}$ to $\mathrm{Fe^{3+}}$ oxidation, thus regenerating $\mathrm{Fe^{3+}}$.

The existence of the $\mathrm{Ag_2S}$ layer can be explained in terms of Eh–pH diagrams. The potential–pH diagrams for the Ag–S–$\mathrm{H_2O}$ and S–$\mathrm{H_2O}$ systems at 68 °C and 1 atm are given in Fig. 1(a) and 1(b). The Ag–S–$\mathrm{H_2O}$ diagram shows the existence of a $\mathrm{Ag_2S}$ zone in acid medium for a wide range of potentials,

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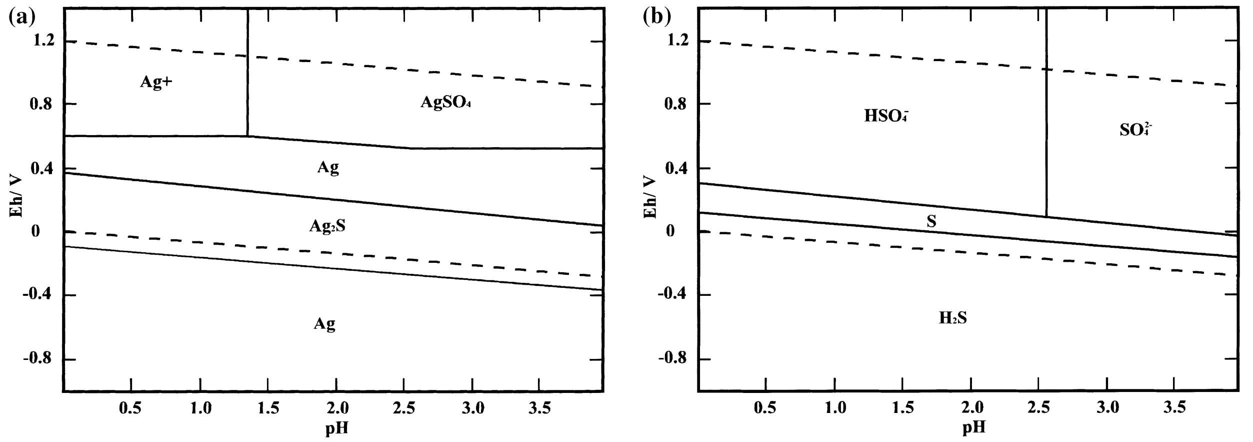

Fig. 1. Potential–pH diagrams for (a) Ag–S–H_2O and (b) S–H_2O systems at 68 °C and 1 atm ([Ag] = 10^{-2}M and [S] = 1 M). After HSC Chemistry Software. Version 1.11. Outokumpu Research Oy, Finland.

which would include the chalcopyrite leaching potential. An interesting point in Fig. 1(a) is that Ag_2S zone is surrounded by the stability zone of elemental silver, showing that metallic silver can appear by either silver sulfide reduction or oxidation. In fact, some researchers [8] have proposed that Ag° can nucleate on the chalcopyrite surface, improving its conductivity. The results of Price and Warren [9] show that both Ag_2S and Ag° can be identified on the chalcopyrite surface, although the quantity of elemental silver is always much smaller.

In addition, it has been established [6] that the S° formed in Reaction 3, unlike that of Reaction 1, forms a nonprotective porous layer and, therefore, favours the diffusion of the leaching reagents across it.

The role of the microorganisms in the silver-catalysed chalcopyrite leaching has been related to the regeneration of the oxidizing agent (reaction (3)) or the oxidation of the elemental sulfur [4, 10]. A negative aspect of the process is the toxic effect of silver on the bacterial metabolism, which is more marked for the case of thermophilic rather than mesophilic microorganisms. A concentration of about 0.03 g dm^{-3} Ag^+ produces an inhibitory effect on the growth of *Sulfolobus* species [11]. Nevertheless, the amount of silver necessary to catalyse the chalcopyrite dissolution is smaller than that for the inhibition of the microorganism because the majority of the silver remains, forming Ag_2S on the mineral surface [10].

However, for reasons not yet completely understood, the copper extraction in bioleaching systems with silver participation is much more favourable in the presence of mesophilic, rather than thermophilic, microorganisms [12]. On the other hand, the electrochemical studies on chalcopyrite samples in the presence of silver refer to abiotic systems at room temperature and 80 °C [6, 9]. In previous research we studied the electrochemical behaviour of the chalcopyrite with thermophilic microorganisms [13, 14]. In this study the electrochemical behaviour of chalcopyrite samples under silver-catalysed bioleaching attack at 68 °C was examined.

2. Experimental details

2.1. *Materials*

Massive samples of chalcopyrite from Transvaal (South Africa) were used for the electrochemical experiments. Chemical analysis (35.3% Cu, 30.1% Fe and 34.3%S), X-ray diffraction and scanning electron microscopy on the material revealed it to be a high purity chalcopyrite with small inclusions of silica. Graphite, elemental sulfur and Ag_2S of reagent grade were used in the particulate electrodes.

2.2. *Bacterial culture*

A thermophilic culture was used as inoculum for the electrochemical experiments in the presence of bacteria. The culture was grown in an orbital shaker at 68 °C in a 250 mL Erlenmeyer flask containing 95 mL of a nutrient medium (0.4 g $dm^{-3}(NH_4)_2SO_4$, 0.5 g $dm^{-3}MgSO_4.7H_2O$ and 0.2 g $dm^{-3}K_2HPO_4$) at pH 1.5, a chalcopyrite concentrate (1% w/v) and 5 mL of a bacterial culture of *Sulfolobus BC*.

2.3. *Preparation of the electrodes*

Two different kinds of electrodes were used in this study. Some experiments were performed with particulate electrodes. These electrodes were prepared under pressure and using a base conductor material (graphite) which was used alone or mixed with powdered materials (elemental sulfur or silver sulfide) in different proportions. Each electrochemical test was carried out with polished electrodes.

The other electrodes were made from massive chalcopyrite. These samples were cut to give a working surface of approximately 0.4 cm^2 with no visible imperfections. To make the electrode, the mineral sample was connected to a copper wire by a silver cement and isolated from the liquid medium by a methacrylate tube. This set was mounted in an epoxy matrix (Fig. 2).

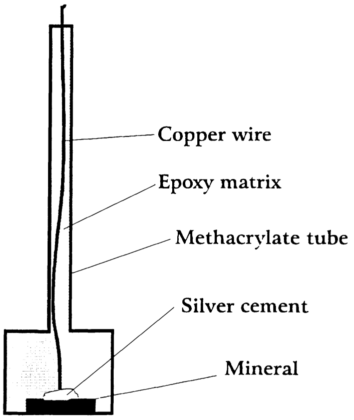

Fig. 2. Work electrode of massive chalcopyrite samples.

The electrochemical behaviour of the bioleached chalcopyrite was studied on electrodes previously treated in an orbital shaker at 68 °C with the above mentioned nutrient medium, a bacterial inoculum and 0.02 g dm^{-3} Ag^+ as Ag_2SO_4. Then the electrodes were removed from the bioreactor at different intervals and tested in the corresponding electrochemical experiment. The electrochemical experiments with massive chalcopyrite in the absence of bacteria were performed with ground surface electrodes.

2.4. *Electrochemical measurements*

In the potentiodynamic polarization and cyclic voltammetry experiments a device consisting of a Wenking potentiostast (model MB81M) from Bank Electronic and a Wenking MVS87 wave generator were used. Data were collected into a computer by an analog board. The 150 mL electrochemical cell was provided with a water jacket connected to a recirculation pump to maintain the desired temperature during the test. Electrochemical measurements were made using a typical three-electrode system: a working electrode (chalcopyrite or any other substance under study), an auxiliary electrode (Pt) and a reference electrode (Ag/AgCl). The potential of the working electrode was measured against the reference electrode coupled to a Luggin capillary filled with a saturated solution of K_2SO_4, instead of KCl to avoid AgCl precipitation. Electrochemical experiments were carried out in 120 mL of electrolyte, of the same composition as the nutrient medium used for bacterial growth, in the presence of 0.02 g dm^{-3} Ag^+, but without microorganisms, and previously deoxygenated for 20 min with nitrogen, at pH 1.5 and 68 °C. The potential values are referred to the Ag/AgCl reference electrode (+ 207 mV vs SHE).

3. Results and discussion

3.1. *Experiments with particulate electrodes: graphite, elemental sulfur and silver sulfide*

The first consideration in this study was to understand the electrochemical behaviour of silver in an acid solution (pH 1.5) at 68 °C. To this end, a potentiodynamic test with a particulate graphite electrode in the presence of 0.02 g dm^{-3} Ag^+ was carried out (Fig. 3). The system response was initiated in the anodic direction from the rest potential (+ 334 mV). Between the potentials tested (−500 and + 1000 mV), the silver was electroactive showing two reverse peaks (A and A′) corresponding to the reversibility of the following reaction:

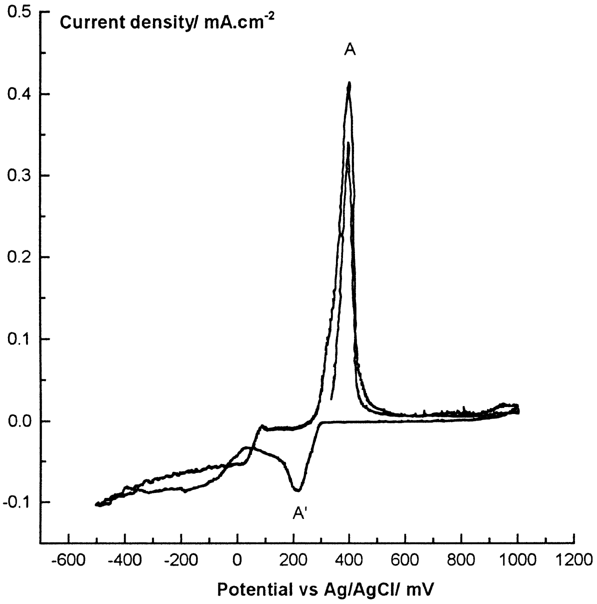

Fig. 3. Cyclic voltammograms for a particulate graphite electrode in a solution containing 0.02 g dm^{-3} Ag^+, at pH 1.5 and 68 °C (scan rate 5 mV s^{-1}).

$$Ag \rightleftharpoons Ag^+ + e^- \qquad (4)$$

in accordance with the Eh–pH diagram (Fig. 1(a)).

A similar experiment was performed with powdered elemental sulfur (10% in graphite) as the electrode (Fig. 4). No peaks were detected during the

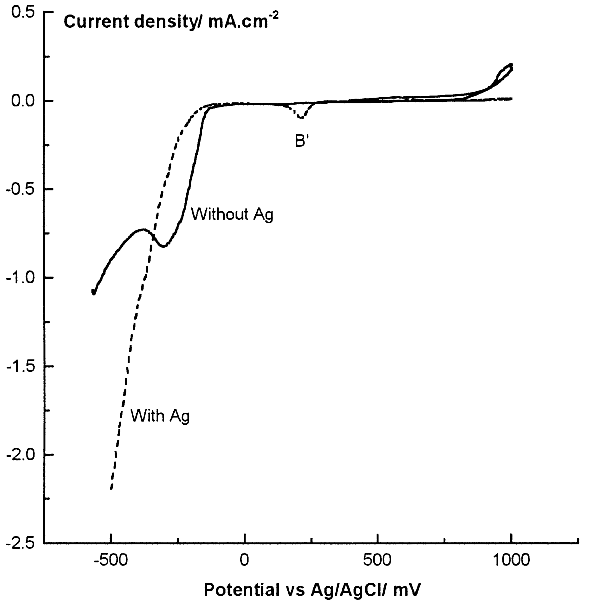

Fig. 4. Cyclic voltammograms for particulate elemental sulfur electrodes in the absence and in the presence of silver (0.02 g dm^{-3} Ag^+), at pH 1.5 and 68 °C (scan rate 5 mV s^{-1}).

anodic scan. In this case, the test with 0.02 g dm^{-3} Ag^{+} established a rest potential of +466 mV, higher than that required for Reaction 4. Nevertheless, during the cathodic scan, the reverse peak (B′) was detected. When the potential continued to diminish, a new peak appeared due to the reaction:

$$S^{\circ} + 2\,H^{+} + 2e^{-} \rightleftharpoons H_2S \qquad (5)$$

This reaction, predicted from the Eh–pH diagram (Fig. 1(b)), is remarkably affected by the presence of silver. The presence of metallic silver on the electrode enhances the conductive properties of S° producing a continuous current flow without reaching a limiting value in contrast to the same type of electrode without silver (Fig. 4). Figure 5 shows the voltammogram corresponding to the sulfur electrode treated with silver after being cycled in Fig. 4. The presence of two peaks in reduction (A′ and B′), with their homologous in oxidation, have been associated with the reduction of Ag^{+} on two different surfaces: graphite and elemental sulfur, respectively, in accordance with Figs 3 and 4. On the other hand, peak D is due to the dissolution of Ag_2S formed in a previous cathodic scan.

This series of experiments with particulate electrodes was concluded with a powdered synthetic Ag_2S electrode, containing 60% Ag_2S in graphite (Fig. 6). Experimental conditions were maintained constant as in the former experiments, with the addition of 0.02 g dm^{-3} Ag^{+}. The appearance of a first peak at +500 mV (peak C) due to Reaction 4 produces a similar response in the cathodic branch due to the reverse reaction (peak C′). This is followed by the oxidation of the silver sulfide at high potentials (peak D), according to the reaction:

$$Ag_2S \rightleftharpoons 2\,Ag^{+} + S^{\circ} + 2e^{-} \qquad (6)$$

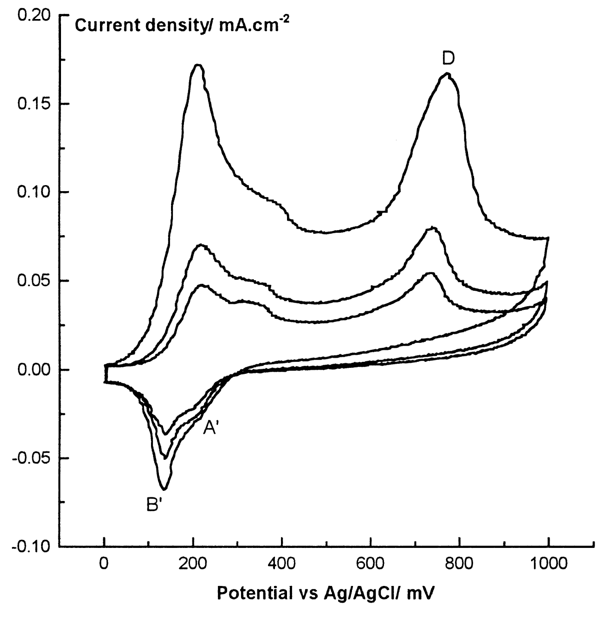

Fig. 5. Cyclic voltammograms of the particulate elemental sulfur electrodes in the presence of silver (0.02 g dm^{-3} Ag^{+}), at pH 1.5 and 68°C (scan rate 20 mV s^{-1}).

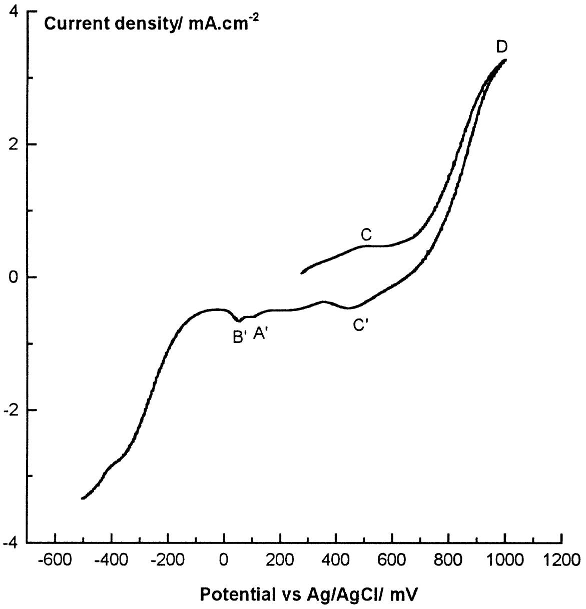

Fig. 6. Cyclic voltammograms for a particulate Ag_2S electrode in a solution containing 0.02 g dm^{-3} Ag^{+}, at pH 1.5 and 68 °C (scan rate 5 mV s^{-1}).

When the potential is shifted towards the cathodic direction, it is possible to observe the reduction of silver ions on three different surfaces: Ag_2S (peak C′), graphite (peak A′) and S° (peak B′). Elemental sulfur was produced in the last reaction. At lower potentials, the reduction of silver sulfide takes place according to

$$Ag_2S + 2\,H^{+} + 2e^{-} \rightleftharpoons 2\,Ag^{\circ} + H_2S \qquad (7)$$

Figure 7 shows the cyclic voltammogram corresponding to the Ag_2S particulate electrode. The scan was initiated from the end of the scan in Fig. 6 (−500 mV) up to +1000 mV. Then the electrode was

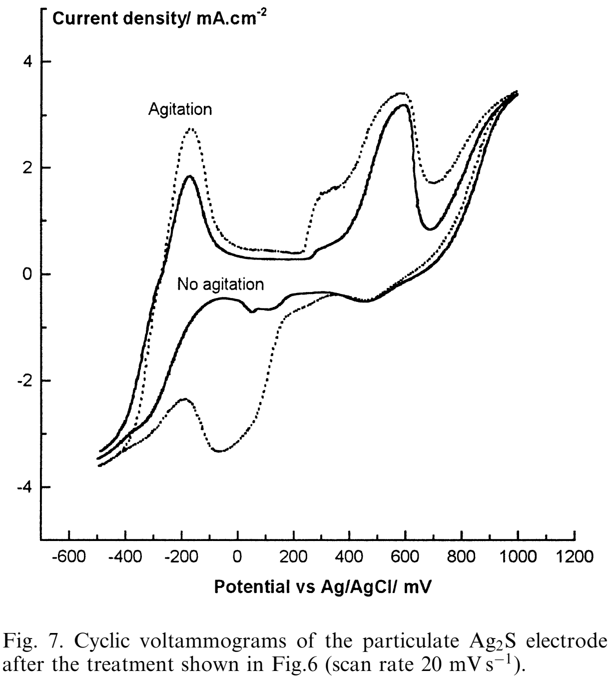

Fig. 7. Cyclic voltammograms of the particulate Ag_2S electrode after the treatment shown in Fig.6 (scan rate 20 mV s^{-1}).

cycled twice between those limits, first without agitation and, later with nitrogen gas agitation. After the introduction of agitation in to the system, there was an enhancement in the intensity of the peaks (particularly due to the deposition of metallic silver on graphite and S°), suggesting a relevant effect of stirring on the Ag_2S dissolution.

3.2. *Experiments with massive electrodes: chalcopyrite*

The particulate electrodes provided information about the electrochemical response that can be expected from the reactants (e.g., Ag^+) or the products of reaction (such as S° or Ag_2S) in the silver-catalysed leaching of the chalcopyrite. To gain further details on the silver-catalysed bioleaching, experiments with massive chalcopyrite electrodes were carried out.

When a chalcopyrite sample is submerged in an acid solution containing Ag^+, its surface is rapidly covered by a greyish layer of Ag_2S. In addition, the rest potential (+350 mV) increases in relation to the same potential in the absence of silver (+150 mV). As Miller *et al.* [7] pointed out this potential is the result of a Ag_2S film, which completely coats the chalcopyrite surface.

The mechanism of silver catalysis in the dissolution of chalcopyrite has been considered under a wide range of experimental conditions [2, 4, 6, 9, 10]. Therefore, a modification of the system conditions (pH, temperature, bacteria) may change the characteristics of the attack. The experiments described later were carried out at pH 1.5 and 68 °C.

Several experiments were performed to study the influence of the contact time of the electrode with the silver solution. Similar experiments have been carried out by other researchers at 25 °C [6]. The same massive electrode was used in all experiments, in the presence of a solution containing $0.02\,g\,dm^{-3}$ Ag^+. The time of contact of the electrode with the solution varied between 1 min and 13 h. Figure 8 gives the anodic polarization curves corresponding to 1 min, 30 min and 13 h.

The results show that when the contact time increases, the characteristics of the Ag_2S layer change since a change in the electrochemical response is obtained. The growth of the Ag_2S film takes place for a certain period of time (30 min) until a steady state is reached. As a result, the anodic polarization curves show a lower decomposition potential for 1 min than for 30 min or 13 h of contact. The significance of the contact time in the silver-catalysed process of the chalcopyrite can be seen as a measure of the bonding with the Ag_2S film which is formed.

After 1 min and after 13 h of contact (Fig. 8), although in this last case the phenomenon is less important, the oxidation of the sulfide layer is accompanied by a decrease in the current density. This behaviour is related to the saturation of the surface electrode in Ag^+ and SO_4^{2-}, leading to the formation of a porous layer of silver sulfate on the S° produced in Reaction 6, according to the following reaction:

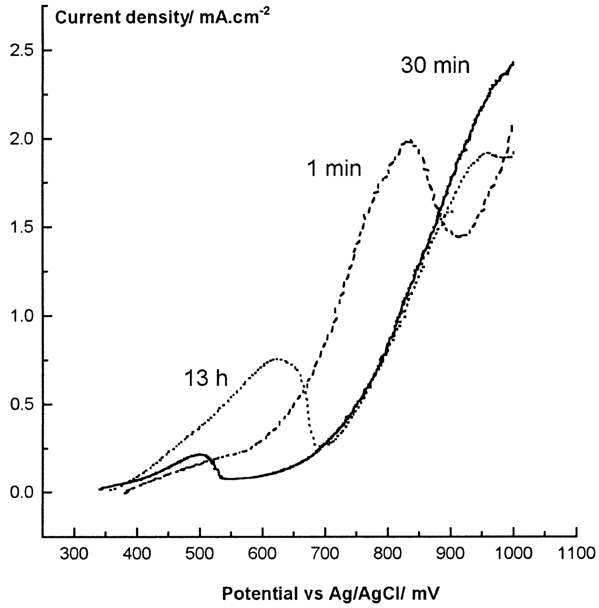

Fig. 8. Anodic polarization curves of a massive chalcopyrite electrode after different time of contact with a solution containing 0.02 g $dm^{-3}Ag^+$, at pH 1.5 and 68 °C (scan rate 5 $mV\,s^{-1}$).

$$2\,Ag^+ + SO_4^{2-} \rightleftharpoons Ag_2SO_4 \qquad (8)$$

This Ag_2SO_4 does not form a totally protective layer because significant current values are still observed.

The appearance of a peak at +500 mV after 30 min of contact can be related to the deposition of metallic silver after contact with chalcopyrite, as predicted by the Eh–pH diagram (Fig. 1(a)):

$$CuFeS_2 + 2\,Ag^+ \rightleftharpoons Cu^{2+} + Fe^{2+} + 4\,Ag^\circ + 2\,S^\circ \qquad (9)$$

and its later oxidation according to Reaction 4. When the contact time is increased to 13 h, the peak is more pronounced, suggesting a more significant participation of Reaction 9. This would affect the later appearance of the Ag_2SO_4 layer, as noted previously.

It is obvious that one of the most important parameters in the silver-catalysed bioleaching of chalcopyrite is the amount of silver which is added. The silver concentration has been examined using the same massive electrode (Fig. 9(a) and (b)). The electrode was maintained in contact with a solution containing 0.02, 0.1 and $0.2\,g\,dm^{-3}Ag^+$ for 30 min.

The response of the chalcopyrite electrode is clearly dependent on the silver concentration in the electrolyte. At low silver concentration, the electrode shows better electrochemical dissolution. When the silver concentration rises to $0.1\,g\,dm^{-3}$, a very important passivation of the electrode takes place. This fact is related to an excessive growth of the Ag_2S film, preventing the occurrence of Reaction 2 and, the dissolution of Ag_2S through Reaction 3. This decrease in current must also be due to formation of Ag_2SO_4 as the silver concentration increases. This Ag_2SO_4 would decrease the chalcopyrite surface

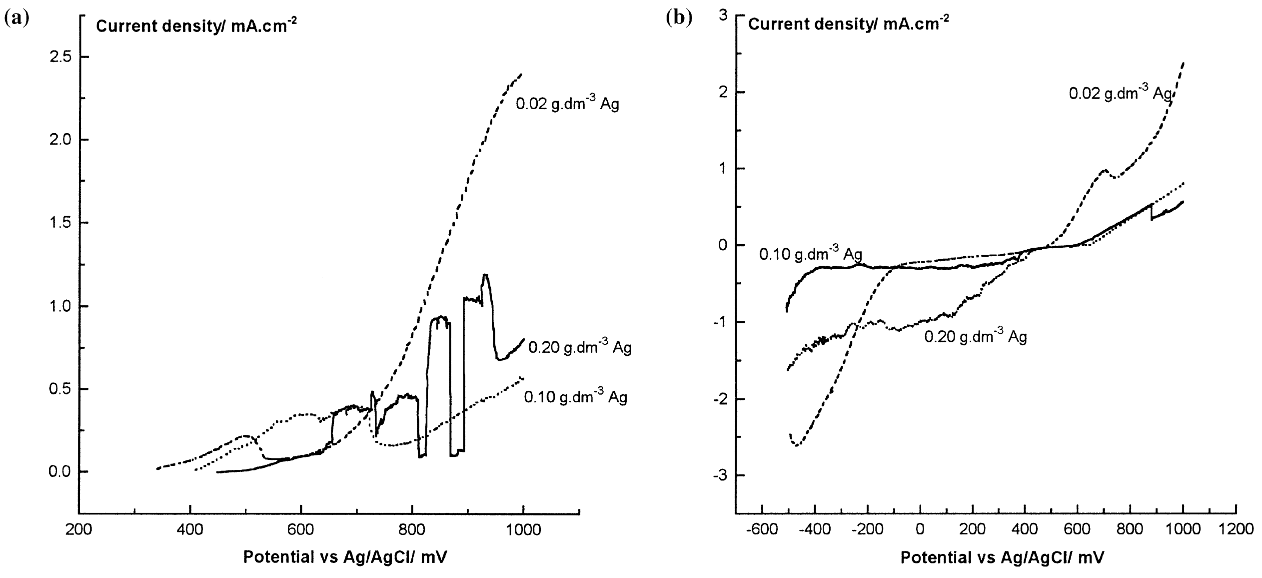

Fig. 9. Polarization curves of a massive chalcopyrite electrode after 30 min of contact with different silver concentrations, at pH 1.5 and 68 °C (scan rate 5 mV s^{-1}): (a) anodic scan, and (b) cathodic scan.

exposed to the attack and, therefore, the effectiveness of its dissolution.

When the concentration was increased up to 0.2 g dm^{-3}Ag, the breakdown of the layer was more significant than at 0.1 g dm^{-3}. This indicates a more limited adherence of the Ag_2S film to the chalcopyrite surface as a result of a thicker layer. Thus, the values of current obtained during the cathodic scan were higher in the presence of 0.20 g dm^{-3}Ag$^+$ than with 0.10 g dm^{-3}Ag$^+$ (Fig. 9(b)).

From a chemical point of view, the dissolution of the silver sulfide takes place in the presence of ferric ions according to the Reaction 3. Therefore, the addition of ferric ions assists the electrochemical dissolution of chalcopyrite in the presence of silver. To confirm this point, an experiment similar to that carried out in the presence of 0.1 g dm^{-3}Ag$^+$ was performed with the addition of 0.5 g dm^{-3}Fe^{3+}. These tests are compared in Fig. 10. The presence of ferric ions was decisive in the decomposition of the Ag_2S film and in the subsequent dissolution of the chalcopyrite, overcoming the problems associated with a surface film. These results agree with the proposals of Miller and Portillo [6] who claim that the chalcopyrite dissolution with silver ions (Reaction 2) is controlled by Reaction 3, i.e., the oxidation of Ag_2S.

Following the results already presented in this investigation, the effect of the silver on the electrochemical behaviour of chalcopyrite in the presence of thermophilic microorganisms was studied. It was considered that the oxidizing ability of these microorganisms which transform Fe^{2+} to Fe^{3+}, could be used to advantage in bioleaching systems involving silver catalysis.

Several massive chalcopyrite electrodes were maintained under silver-catalysed bioleaching attack for different periods of time. Each of the electrodes was studied for electrochemical behaviour in the absence of bacteria.

Figure 11 shows typical anodic polarization curves obtained with different electrodes in the absence of bacteria without silver or in the presence of bacteria and silver. It is clear that the presence of bacteria modifies the original surface, decreasing the decomposition potential of the electrode and favouring the electrodissolution of the electrode. At the same time, an increase in the rest potential was observed from +150 mV (in the absence of bacteria and silver) to +460 mV (in the presence of bacteria and silver).

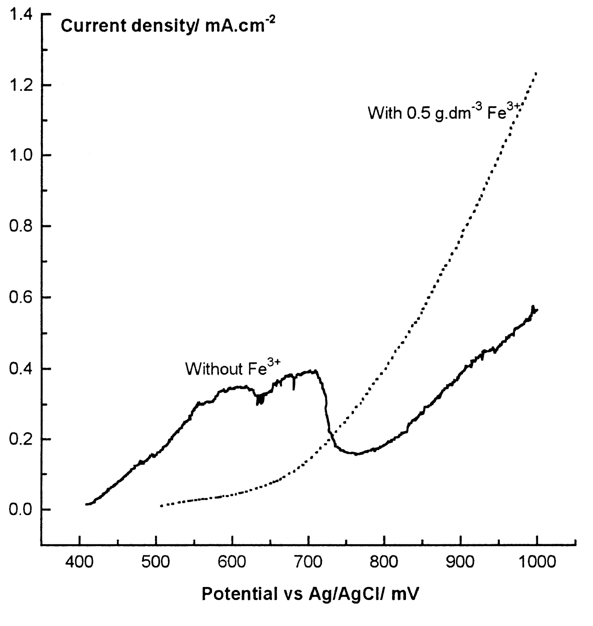

Fig. 10. Anodic polarization curves of a massive chalcopyrite electrode in the presence and in the absence of Fe^{3+} with a solution containing 0.10 g dm^{-3} Ag$^+$, at pH 1.5 and 68 °C (scan rate 5 mV s^{-1}).

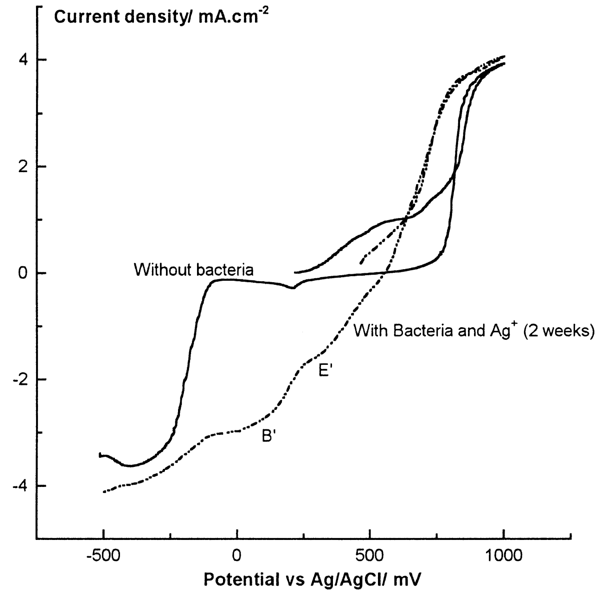

Fig. 11. Cyclic voltammograms of massive chalcopyrite electrodes in the absence of bacteria and silver and in the presence of bacteria and 0.02 g dm^{-3} Ag$^+$, at pH 1.5 and 68 °C (scan rate 20 mV s^{-1}).

The effect of the bioleaching time in the presence of silver was also tested (Fig. 12(a) and (b)). An increase in the bioleaching time reduces the decomposition potential at which the electrode dissolves significantly. Appreciable differences can be observed between the tests after 1 day/1 week and 2 weeks/4 weeks of bioleaching, in the anodic and in the cathodic polarization curves (Fig. 12(a) and (b)). This behaviour is likely related to a toxic effect of silver on the thermophilic population during the first stages of the bioleaching. In this way, a higher capability of mesophilic microorganisms to adapt to silver has been demonstrated [11]. After two weeks of bioleaching, the reactivity of the electrode surface did not improve appreciably.

Figure 13 presents further evidence of the high reactivity of the bioleached surfaces since, as time proceeds, zones of zero current tend to disappear. On the other hand, the apparent similarity of this voltammogram with that one shown in Fig. 7 reveals an important aspect of the participation of Ag_2S in this electrode.

The results obtained in the presence of silver show that to accelerate the chalcopyrite dissolution it is not sufficient to form a Ag_2S film. In addition, it is necessary to cause its decomposition to avoid the inhibition of the process. In this sense, Reaction 3 plays a very important role. There is some evidence showing that the presence of thermophilic bacteria can cause cracks on the Ag_2S film [12]. In the absence of bacteria a continuous layer appears which limits the attack on the chalcopyrite. Thus, the bacteria could be producing a Fe^{3+} concentration gradient close to the ore surface causing dissolution of the layer through Reaction 3.

4. Conclusions

The electrochemical behaviour of chalcopyrite in an acidic medium containing silver ions and thermophilic bacteria has been studied. Initially, particulate electrodes were studied to determine the electrochemical response of reactants and products involved in the silver-catalysed bioleaching process. It was demonstrated that the electrodeposition of metallic silver on an elemental sulfur surface enhances the conductive properties of sulfur. Besides, this electrodeposition takes place at lower potentials on S° than on Ag_2S. On the other hand, the dissolution of Ag_2S produces a decrease in the current due to the formation of a poorly conductive Ag_2SO_4 layer on the electrode surface, this effect being more marked with an increasing of the silver concentration.

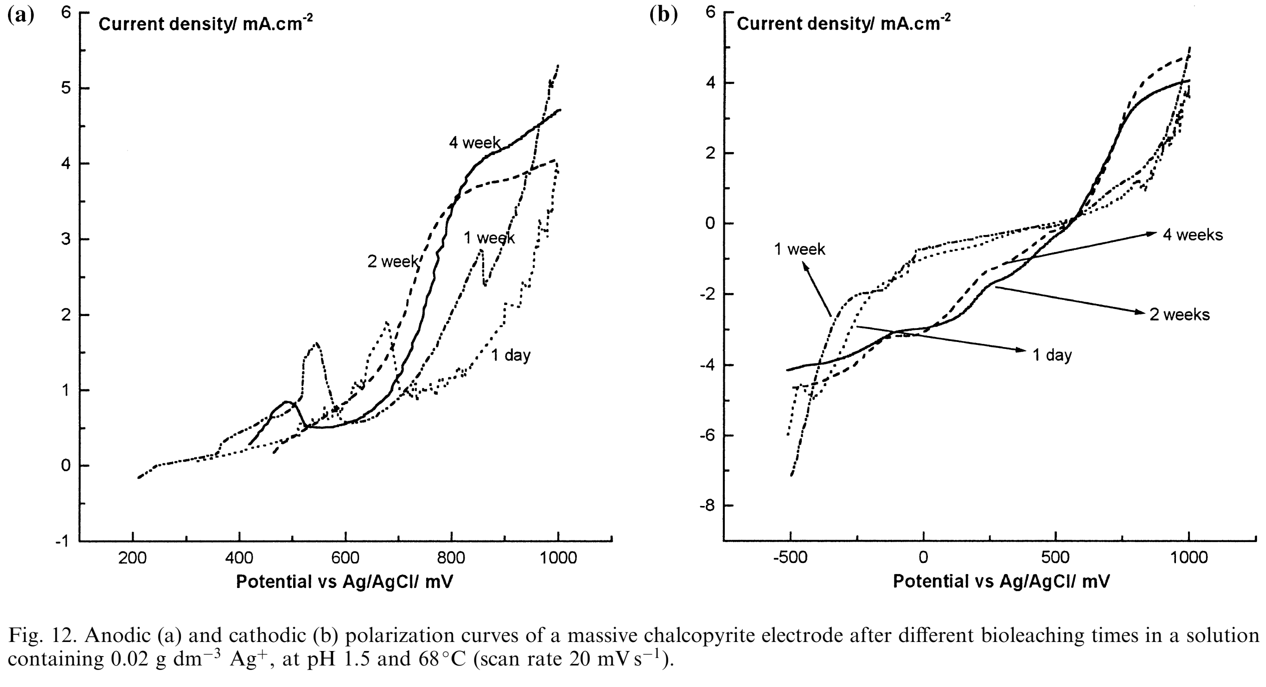

Fig. 12. Anodic (a) and cathodic (b) polarization curves of a massive chalcopyrite electrode after different bioleaching times in a solution containing 0.02 g dm^{-3} Ag$^+$, at pH 1.5 and 68 °C (scan rate 20 mV s^{-1}).

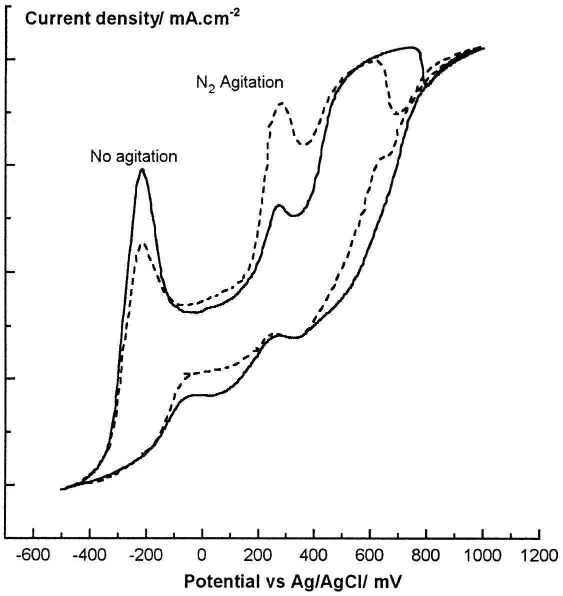

Fig. 13. Cyclic voltammetry of a massive chalcopyrite electrode, after two weeks of silver-catalysed bioleaching attack shown in Fig.11 (scan rate 20 mV s^{-1}).

The contact of silver solution with a chalcopyrite electrode produces a film of Ag_2S on the ore surface and metallic silver. When the time of contact between the solution and the ore increases, both the thickness of the Ag_2S film and the quantity of Ag° also increase.

An increase in silver concentration from 0.02 to 0.2 g dm^{-3} favours the growth of the Ag_2S layer and the Ag_2SO_4 precipitation increases producing passivation of the mineral. The addition of Fe^{3+} to the solution in the system Ag^+–chalcopyrite favours the ore attack as a consequence of the Ag_2S layer breakdown.

The presence of thermophilic bacteria improves the chalcopyrite oxidation in the presence of silver. However, bioleaching times longer than two weeks did not affect the behaviour of the chalcopyrite electrode. For shorter times, the surface reactivity is controlled by the toxic effect of silver ions on the bacterial population.

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