EFFECT OF CATALYTIC IONS ADDITION ON THE BIOOXIDATION OF CHALCOPYRITE

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RESUMO

A influência de ions Cl⁻ e Ag⁺ na dissolução química e bacteriana da calcopirita foi avaliada por meio da análise de ruídos eletroquímicos (ENA). ENA é um termo genérico que descreve o fenômeno das flutuações espontâneas de potencial ou de corrente de sistemas eletroquímicos. Esta técnica fornece uma condição não destrutiva para a investigação de processos de corrosão e pode ser usada para o entendimento da oxidação do mineral. A dissolução da calcopirita foi investigada imediatamente após a imersão (0 h) e após 24 horas, em meio ácido, na ausência e na presença da espécie bacteriana *Acidithiobacillus ferrooxidans*. Observou-se que a adição de íons prata não aumentou a taxa de dissolução da calcopirita, seja no ataque químico ou bacteriano. Isto pode ser explicado pela formação de um filme passivo de sulfato de prata, que modifica a interface mineral / solução. Entretanto, no meio contendo íons cloreto, as flutuações de corrente foram significativamente maiores. Como conseqüência, a resistência do ruído, R_n, calculada a partir da amplitude e das freqüências destas oscilações, foi aproximadamente cinco vezes menor na presença de *A. ferrooxidans*, indicando que os íons cloreto aceleraram o ataque bacteriano na superfície do mineral, uma vez que aumentaram a força iônica do meio, diminuindo a repulsão eletrostática entre a bactéria e a superfície do eletrodo e facilitam a degradação do filme de óxidos, enxofre e/ou sulfeto na superfície do mineral.

PALAVRAS-CHAVE: calcopirita, *Acidithiobacillus ferrooxidans*, análise de ruídos eletroquímicos, biolixiviação.

ABSTRACT

The influence of Cl⁻ and Ag⁺ ions on the bacterial and chemical dissolution of chalcopyrite was evaluated by means of the electrochemical noise analysis (ENA). ENA is a generic term describing the phenomenon of spontaneous fluctuations of potential or current noise of electrochemical systems. It provides a non-destructive condition for investigating corrosion processes and can be useful to understand the electrochemical oxidation of mineral. The dissolution of chalcopyrite electrode was evaluated at 0 and 24 hours contact time, in acidic medium and in the presence or absence of bacterium. It was observed that the addition of silver ions does not improve the chalcopyrite dissolution rate during the course of the experiment, in chemical or bacterial attack. It can be explained by formation of a passive silver sulfate film that modifies the mineral / solution interphase. However, the current noise fluctuations were much higher in the medium containing chloride ions. As a consequence, noise resistance, R_n, calculated from amplitude and frequencies of these oscillations, was about five times lower in the presence of *A. ferrooxidans*. It indicates that Cl⁻ ions improve the bacterial attack on the mineral sulfide, once increased the ionic strength of the leaching medium decreasing the electrostatic repulsion between bacteria and electrode surface and facilitate the oxide, sulfur and/or sulfide passive film degradation.

KEY-WORDS: chalcopyrite, *Acidithiobacillus ferrooxidans*, electrochemical noise analysis, bioleaching.

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1. INTRODUCTION

The knowledge of the mechanisms of bacterial dissolution of sulfides has been focused on several copper minerals to improve the efficiency of the bioleaching operations. The dissolution of metals from mineral sulfides can be accelerated by the addition of catalytic ions that modify the electrochemical reactions, in order to avoid the formation of a passive layer that limits the oxidation rate of the mineral sulfide in the acidic medium.

The utilization of chloride solutions in chalcopyrite leaching can be advantageous due to the aggressive nature of the leaching and to the stability of cuprous and cupric ions by the formation of the chloro-complexes (Lundstrom, 2005). It is believed that the role of chloride is to promote the formation of a more porous sulfur product, thus permitting the dissolution reactions of the mineral sulfides.

Lu and co-workers (2000) demonstrated by scanning electron microscopy (SEM) that the leaching of the chalcopyrite performed in the presence of chloride ions, the sulfur layer formed is more crystalline and porous, while in the absence of chloride, the chalcopyrite surface was coated by an amorphous film of sulfur.

The catalytic effect of silver ion in the leaching of chalcopyrite by ferric sulfate is explained by precipitation of Ag_2S film on the surface of chalcopyrite (Sato, 2000; Ballester, 2006) which neutralizes the effect of the sulfur layer facilitating the cathodic reaction described by reactions:

$$CuFeS_2 + 4 Ag^+ \rightarrow 2 Ag_2S + Cu^{2+} + Fe^{2+} \tag{1}$$

$$Ag_2S + 2 Fe^{3+} \rightarrow 2 Ag^+ + S^0 + 2 Fe^{2+} \tag{2}$$

In accordance whit the reactions (1) and (2), ferric ions oxidize Ag_2S regenerating Ag^+ ions that will again react with chalcopyrite. Sato and co-workers (2000) stated that the elemental sulfur formed in reaction (2) is more porous, thus the oxidative dissolution of the chalcopyrite proceeds continuously.

In the bioleaching of the chalcopyrite catalyzed by silver, the role of the bacteria is maintain a favorable rate of Fe^{3+}/Fe^{2+} to promote the oxidation of the Ag_2S. In this mechanism, Ballester and co-workers (2006) considered that the discontinuous film formed by Ag_2S behaviors as cathode and the chalcopyrite as an anode, constituting a galvanic couple. However, the formation of Ag^0 or Ag_2SO_4 is also possible, resulting in a controversial effect due to the increase of the layer thickness onto the electrode with the increase of the immersion time, leaving a decreasing in the kinetic dissolution of the chalcopyrite.

According to contradictory nature on chalcopyrite dissolution in different experimental conditions a deeper study is necessary in order to examine its electrochemical reactivity in several media. The purpose of this work is to investigate the oxidative dissolution of the chalcopyrite in different experimental conditions, using electrochemical noise analysis (ENA). ENA is a generic term describing the phenomenon of spontaneous fluctuations of potential or current noise of electrochemical systems. It provides a non-destructive condition for investigating corrosion processes and can be useful to understand the electrochemical oxidation of mineral sulfides comparing two conditions: the presence and absence of bacteria, besides the influence of Cl^- and Ag^+ ions.

2. MATERIALS AND METHODS

Research-grade chalcopyrite ($CuFeS_2$) used in this study was obtained from Ward's Natural Science Establishment (Rochester, NY).

2.1 Bacterium and growth conditions

A. ferrooxidans strain LR was used in this work (Garcia Jr., 1991). The culture was grown in a mineral salts medium: 0.5 g of $(NH_4)_2SO_4$, 0.5 g of K_2HPO_4 and 0.5 g of $MgSO_4*7H_2O$, pH 1.8 adjusted with H_2SO_4 plus

ferrous sulfate as energy source (Tuovinen and Kelly, 1973). The cells for electrochemical analysis were obtained after growth for 48 hours in a shaker (150 rpm and 30 °C) by successive washing and centrifugation (5000 × *g*) to eliminate residual ferric ion from the medium. The washed suspension was centrifuged at 12000 × *g* for 25 min, washed twice in a Milli-Q water of 18 M ohm cm and finally suspended in 10 mL of the mineral salts medium, using pro analysis purity grade chemicals and Milli-Q water. The cell suspension was standardized by the modified Lowry protein determination method (Hartree, 1973).

2.2 Carbon paste electrode (CPE)

A total of 0.4 g of graphite (Aldrich), 0.1 g of chalcopyrite (< 400 mesh) was mixed with chloroform to obtain a homogenous paste which was preserved under oxygen-free atmosphere. This paste was placed in a cavity in the electrode body, in contact with a platinum disk of geometric area of 7.54 mm^2 constituting the working electrodes.

2.3 Electrochemical noise experiments

The simultaneous potential and current noise measurements were performed using a Potentiostat/Galvanostat model 273A (EG&G) controlled by the model 352 SoftCorr. The experimental arrangement for noise measurements required the use of two electrodes prepared as identical as possible.

Potential noise was measured between one of the two working electrodes and the reference electrode (Ag|AgCl|KCl$_{sat}$), which was connected to the auxiliary A/D input of the potentiostat. Potential and current noise data were collected simultaneously for a period of 1024 s with a sampling rate of two points per second in different experimental conditions.

The essay was carried out in three conditions: in a cell containing iron-free mineral salts solution of T&K medium (pH 1.8) and ionic strength 0.08 mol L^{-1} and others two containing 0.927 mmol L^{-1} of silver ions (Ag$_2$SO$_4$) or 400 mmol L^{-1} of chloride ions (NaCl) in the same condition. The tests were conducted in the presence and absence of bacteria. It was utilized 11,42 μg mL^{-1} of bacterial cells in the inoculated essays from protein analysis (Hartree, 1972). Electrochemical measurements were done at 0 and 24 hours of immersion in all conditions described above.

3. RESULTS AND DISCUSSION

Figure 1 shows simultaneous records of the experimental current noise data obtained for chalcopyrite electrodes in different experimental conditions. Comparing the curves illustrated in absence of bacteria at 0 hours of immersion (Figure 1A), it can be observed that the current levels oscillate insight a narrow scale in the absence of bacteria. This is due to the refractory nature of the chalcopyrite.

In absence of bacteria it was observed that the oscillations increased significantly after 24 hours immersion (Figure 1B), especially in the medium containing chloride ions. This occurred probably due to the passive film breakdown leaving to the continuous dissolution of the mineral.

In the Figures 1C and 1D are represented the experiments in the presence of *A. ferrooxidans* at 0 and 24 hours of immersion respectively. It was observed that the frequency of the fluctuations characteristics of the chalcopyrite behavior in chloride medium appears only after 24 hours immersion. It can indicate that Cl$^-$ increasing the ionic strength of the leaching medium decrease the electrostatic repulsion between bacteria and electrode surface as stated by Flecther (1996). This fact contributed to improve the bacterial interaction with mineral sulfide. Also, the chloride ion can attack the passive film present on the mineral surface facilitating its dissolution (Sato, 2000; Ballester, 2006).

In the other side, the addition of silver ions does not improve the chalcopyrite dissolution rate during the course of the experiment, in the sterile or inoculated medium. The formation of a passive silver sulfide film

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that modifies the solution near mineral surface can be associated with this observation (Lu, 2000; Skrobian, 2005).

The statistical parameters values calculated from experimental records are shown in Table 1. The mean potential E_{coup} is the potential of the coupled electrodes versus the stable reference electrode, and I_{coup} is the mean coupling current flowing between the two minerals electrodes, measured by a zero resistance ammeter (ZRA). The negative values obtained for I_{coup} indicate changes in the direction of the flow of current imposed by the asymmetry between working electrodes (Acciari, 2005). The terms $\sigma[V(t)]$ and $\sigma[I(t)]$ correspond to the standard deviations of potential and current noise fluctuations, respectively. They are also used to compute R_n, the noise resistance, defined as the $\sigma[V(t)]/\sigma[I(t)]$ ratio.
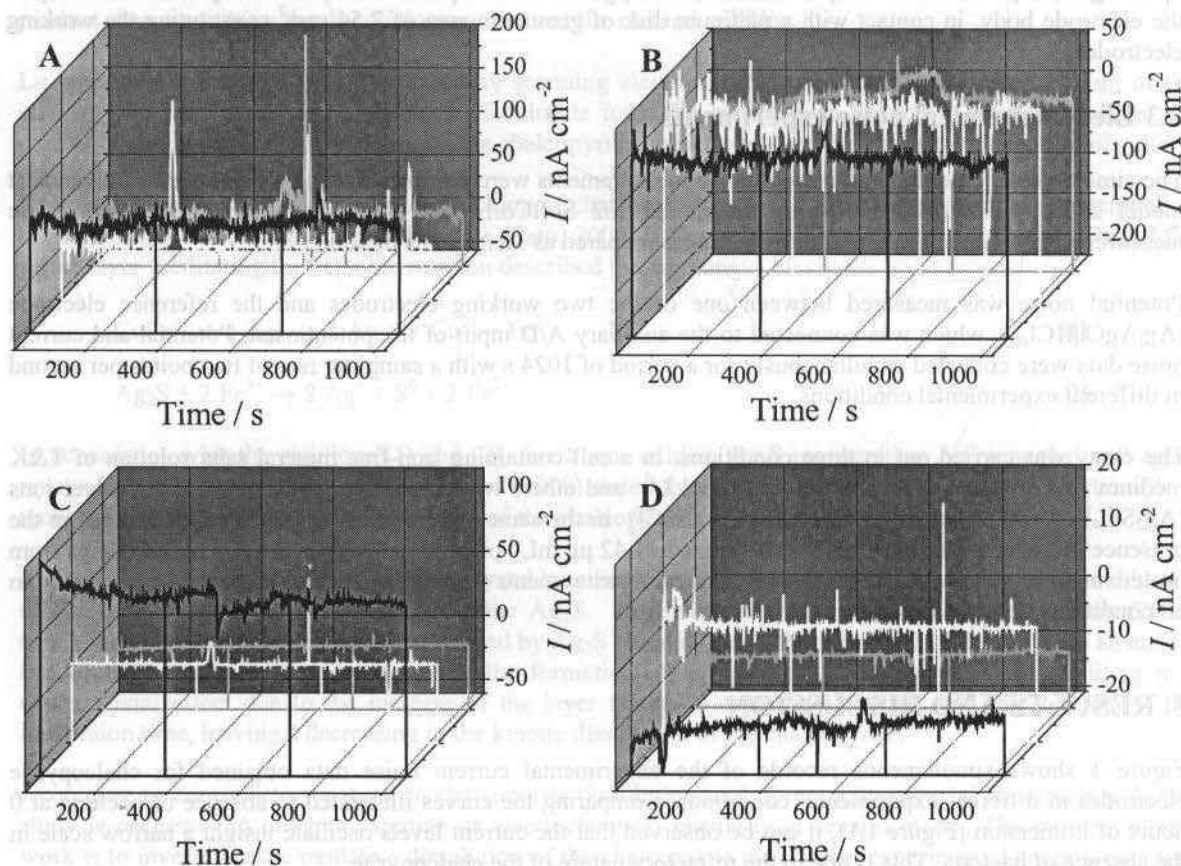

Figure 1: Experimental current noise recorded in the absence (A and B) and presence (C and D) of bacteria at 0 hour (A and C) and 24 hours (B and D). The color curves correspond to the chloride ions (white), silver ions (light gray) and control (black).

It can be observed in Table 1 that E_{coup} remained approximately constant during the 24 hours of immersion for all conditions evaluated in sterile medium. However, in the presence of bacteria a significant increase in the E_{coup} values was observed for the control and chloride conditions, probably due to fast oxidation of chemically formed Fe(II) to Fe(III) ions and anodic dissolution of the mineral, caused by the increase of oxidized species near the electrode.

It is possible to estimate the dissolution rate of the chalcopyrite from order of magnitude of the R_n values, calculated from changes of $\sigma[V(t)]$ and $\sigma[I(t)]$. The abrupt decrease in $\sigma[V(t)]$ values for 0 and 24 hours, calculated for chloride condition in the both sterile and inoculated media occasioned a significant decrease in the R_n values. As discussed above, the fluctuations profile observed in the Figure 1 reflected in the R_n values.

The R_n values determined in the solutions containing Ag^+ ions, indicated that the addition of silver ions does not improve the chalcopyrite dissolution rate during the course of the experiment, in chemical or bacterial attack. It can be explained by formation of a passive silver sulfate film that modifies the mineral / solution interphase.

Table 1: Electrochemical noise data calculated in the time domain for chalcopyrite at different experimental conditions.

Immersion Times / h		Sterile					Inoculated				
		E_{coup} / V	$\sigma[V(t)]$	I_{coup} / nA	$\sigma[I(t)]$ / 10^{-9}	R_n / $M\Omega$	E_{coup} / V	$\sigma[V(t)]$	I_{coup} / nA	$\sigma[I(t)]$ / 10^{-9}	R_n / $M\Omega$
Control	0	0.26	0.057	-0.62	17	3.31	0.43	0.0025	-14	12	0.21
	24	0.37	0.0011	-12	1.30	0.82	0.36	0.00080	-11	0.48	1.7
Cl^-	0	0.23	0.014	5.3	18	0.80	0.51	0.30	1.74	29	10
	24	0.29	0.0032	0.50	4.90	0.65	0.29	0.0020	0.046	1.5	1.37
Ag^+	0	0.49	0.0013	66	6.70	0.20	0.50	0.0038	-6.8	7.7	0.50
	24	0.47	0.0022	79	7.5	0.29	0.47	0.00074	-12	1.4	0.51

4. CONCLUSIONS

ENA is adequate for evaluating the oxidative dissolution of chalcopyrite in the absence and presence of *A. ferrooxidans* since it is simple and a non-destructive technique. However, comparing the different experimental conditions evaluated, a controversial behavior persisted from the electrochemical noise data.

The formation of the elemental sulfur on mineral surface, as product of chalcopyrite oxidation, limits the dissolution of this substrate. The period of 24 h of immersion was not enough for the bacterial action on this mineral. In a next step, a longer time of monitoring should be evaluated.

5. ACKNOWLEDGEMENTS

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