may precipitate on the electrode.

Table 3 - Time needed to reach the maximum potential value (t_{max}), growing time (t_g) and plateau potential (E_{pl}) reached for the galvanostatic growth of P-3-Meth.

j_g / mA cm^{-2}	t_{max} / s	t_g / s	E_{pl} / mV
0.4	30	150	1247
0.6	19	100	1254
0.8	12	75	1257
1.0	8	60	1265
1.2	2	50	1269

Although olygomers formation has been considered the path for conducting film formation [7], low oxidation rates must be avoided in order of obtaining a reasonable growth efficiency and electroactivity.

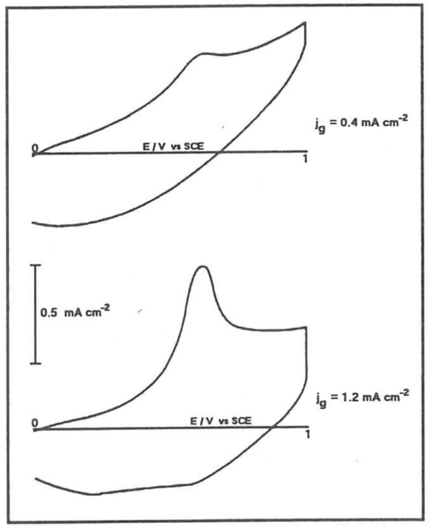

Fig. 5 - Redox behaviour of P-3-Meth films obtained galvanostatically.

References

1 – C. Lee, J. Kwak and A. J. Bard, *J. Electrochem. Soc.*, 136, 3720 (1989).

2 – A. G. MacDiarmid and A. J. Epstein, "Science and Applications of Conductive Polymers", W. R. Salaneck, D. T. Calrk and E. J. Samuelson Ed., Adam Hilger, pp. 117-127 (1991).

3 – B. Krische and M. Zagorska, *Mat. Science Forum*, 42, 79 (1989).

4 – See, for example, *Faraday Discussions of the Chemical Soc.* nº 88 "Charge Transfer in Polymeric Systems" (1989).

5 – F. Chao, M. Costa, E. Levant and L. M. Abrantes, *J. Chimie Physique et de Physico-Chimie Biologique*, 89, 1009 (1992).

6 – B. R. Scharifker, E. G. Pastoriza and W. Marino, *J. Electroanal. Chem.*, 300, 85 (1991).

7 – J. Hunze, *Synthetic Metals*, 41, 2805 (1991).

An electrochemical study of the behaviour of chalcopyrite in acid and alkaline solutions

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The refractory behaviour to hydro/electrometallurgical processing of metallic sulphides and the mineralogical complexity of the related ores have justified the study of surface chemical/electrochemical processes of the individual mineral entities [1-3]. Being the most important source for the extraction of copper, chalcopyrite ($CuFeS_2$) has received particular attention [3-5].

Unfortunately the use of both natural specimens from diverse origins and leaching solutions with different chemical composition makes difficult a correlation of published data in order of understanding the dissolution mechanism.Nevertheless, remarkable progress has been made in the knowledge of semiconductor properties of complex sulphides [6].

In the present work electrodes prepared from massive natural chalcopyrites were used to study their electrochemical behaviour under acidic and basic media (H_2SO_4 0.5 M and NaOH 0.5 M).

Cyclic voltammetry is able to show the chalcopyrite capacity to undergo reduction/oxidation reactions. The current response in sulphuric acid solution to a potential sweep starting anodically from the open circuit potential is shown in figure 1a. The mineral dissolution can be expressed by the reactions :

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$$CuFeS_2 \rightarrow Cu_{1-x}Fe_{1-y}S_{2-z} + xCu^{2+} + yFe^{2+} + zS + 2(x+y)e \qquad (1)$$

$$(x > y)$$

and

$$CuFeS_2 \rightarrow Cu^{2+} + Fe^{3+} + 2S^0 + 5e \qquad (2)$$

depending on the positive potential limit.

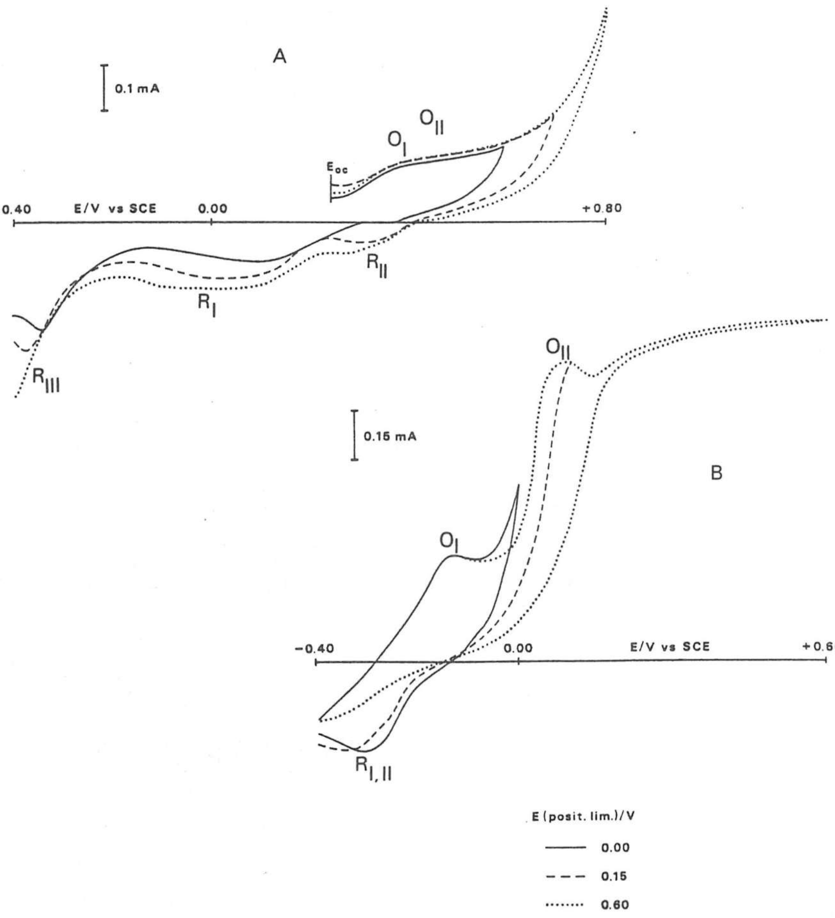

Fig. 1 : Cyclic voltammograms of chalcopyrite mineral electrode : a in 0.5 mol dm^{-3} H_2SO_4
b in 0.5 mol dm^{-3} NaOH

During the reverse sweep it can be seen that the intermediate sulphide undergoes reduction at potential ≅ + 0.20 V (R_I); when reaction (2) takes place, R_{II} reflects the conversion of Fe^{3+} to Fe^{2+}. At further negative potentials, the reduction of the elemental sulphur to H_2S originates other peak (R_{III}).

Figure 1b shows the cyclic voltammograms obtained in alkaline solution. The chalcopyrite dissolution denotated by O_I is

$$CuFeS_2 + 3OH^- \rightarrow CuS + Fe(OH)_3 + S^0 + 3e \qquad (3)$$

For more positive potentials other peak (O_{II}) can be observed due to

$$CuS + 2OH^- \rightarrow Cu(OH)_2 + S^0 + 2e \qquad (4)$$

In both cycles the reduction of S^0 to sulphide ions can be observed in the reverse potential sweep. However, if during the anodic scan, the oxidation of elemental sulphur to sulphate is promoted, that cathodic wave is no more detectable.

Potentiostatic studies were also carried out and figure 2 illustrates the current transient behaviour in both media.

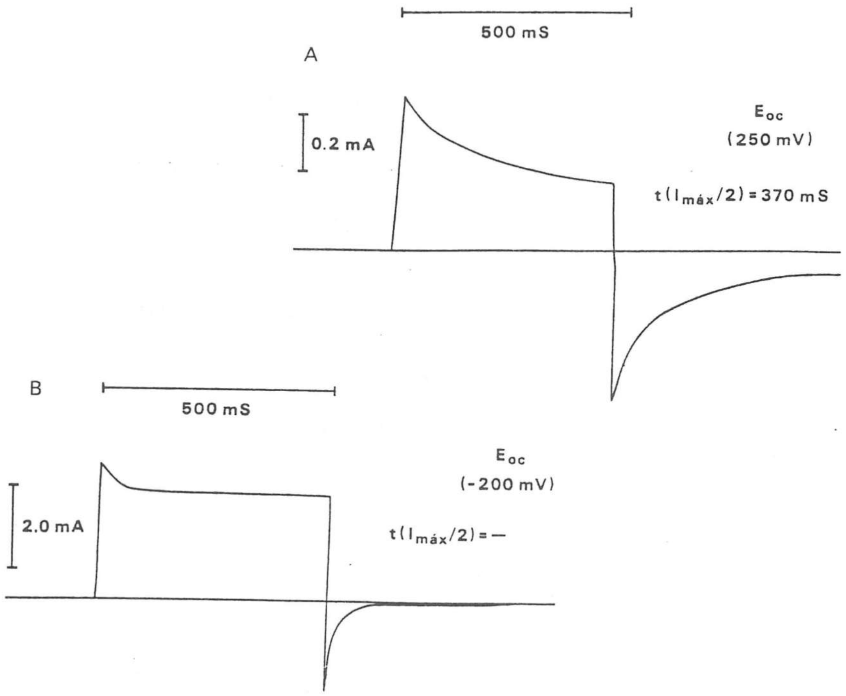

Fig. 2 : Potentiostatic transient for the oxidation of chalcopyrite : a in 0.5 mol dm^{-3} H_2SO_4
b in 0.5 mol dm^{-3} NaOH
(The potential was stepped from the open circuit potential to 600 mV (a) and to 250 mV (b) and back)

The transient features agree with the reactions suggested by the voltammetric results : strong surface modification caused by anodic polarization, in acid media (figure 2a); continuous dissolution with formation of soluble species when the solution is alkaline (figure 2b).

In order to establishing the particular mechanisms involved and the effect of initial apllied potential (or current) on the chalcopyrite dissolution yield, further work is in progress including the cathodic reduction process characterization.

References

1. M. D. Fritzer and R. H. Yoon, *Hydrometallurgy*, 23 (1990) 341-352.
2. V. M. Sanchez and J. B. Hiskey, *Minerals & Metallurgical Processing*, Feb. (1991) 1-6.
3. R. I. Holliday and W. R. Richmond, *J. Electroanal. Chem.*, 288 (1990) 83-98.
4. T. Biegler and M. D. Horne, *J. Electrochem. Soc.*, 6 (1985) 1363-1369.
5. G. W. Warren, H. J. Sohn, M. E. Wadsworth and T. G. Wang, *Hydrometallurgy*, 14 (1985) 133-149.
6. F. K. Crundwell, *Hydrometallurgy*, 21 (1988) 155-190.

Aknowledgment :

L. V. Araújo wishes to express thanks to JNICT by the financial support to his Ph.D. work.