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Electrochemical study of enargite bioleaching by mesophilic and thermophilic microorganisms

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Abstract

The bioleaching effects of two microorganisms on two different enargite (Cu_3AsS_4) minerals have been followed by solution titration and rest potential measurements and studied by cyclic voltammetry. The investigation focused on the superficial modifications produced in the minerals by the activity of the mesophilic bacterium *Acidithiobacillus ferrooxidans* at 35 °C and the thermophilic archaeon *Sulfolobus* sp. at 68 °C after 3 and 12 days of attack, comparing the modified surfaces with that of untreated samples. The electrochemical characterization of all the electrodes was done by means of potentiometric assays performed under the same conditions: acidulated deionized water as electrolyte (pH 2.0), and temperature of 26 ± 2 °C. Additionally, a comparative SEM and EDX study of untreated and biotreated samples was carried out.

Keywords: Enargite; Bacterial attack; Mesophiles; Thermophiles; Electrochemical response

1. Introduction

Enargite (Cu_3AsS_4) is a sulphur mineral of not too common occurrence. Its principal deposits are located mainly in Yugoslavia and also in Argentine, Chile, Peru, the Philippines and the United States (Hurlbut, 1956). This sulphide is usually found together with pyrite, chalcocite, covellite and other copper sulphides, and in some locations associated with refractory gold minerals, as in the case of Chile (Acevedo et al., 1998). For the economical utilization of these types of gold deposits, biooxidation of the sulphide layer occluding gold microparticles has been proposed and implemented in several mines across the world. Enargite has proved to be very recalcitrant to the attack by the traditional mesophilic bacteria, but more sensitive to the action of thermophilic microorganisms (Acevedo et al., 1997; Ñancucheo et al., 2003; Astudillo et al., 2004).

Enargite has been less studied than other better-known sulphur minerals. Welham (2001) studied enargite oxidation at ambient temperature. Electrochemical studies of enargite under different conditions have been presented by Pauporté and Schuhmann (1996), Córdova et al. (1997), Ábsjörnsson et al. (2004), and Guo and Yen (2005). Detailed studies including electrochemical, SEM, EDX and EIS techniques were reported by Velásquez et al. (2000a,b).

Biooxidation of enargite minerals and concentrates has been discussed by Ehrlich (1964), Hao et al. (1972),

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Table 1
Experimental conditions for massive electrodes assays

Assay	Sampling time (d)	Temperature (°C)	Mineral *	Exposed area (cm^2)
A	3	35	I	0.30
B	3	35	II	0.18
C	3	68	I	0.13
D	3	68	II	0.06
E	12	35	II	0.21
F	12	35	I	0.24
G	12	68	II	0.08
H	12	68	I	0.49

* I: Peruvian mineral; II: Chilean mineral.

Escobar et al. (1997), Acevedo et al. (1997), Acevedo et al. (1998) and Canales et al. (2002). All these investigations were conducted using strains of *Acidithiobacillus ferrooxidans* or similar mesophilic bacteria and none of them included the study of the modification of the particle surface throughout the biooxidation process.

The objective of this work was to relate the behaviour of enargite biooxidation processes by mesophilic bacteria and thermophilic Archaea to surface changes of the particles.

2. Materials and methods

2.1. Minerals

Two different minerals were used. One of them (I) was kindly supplied by Professor Joan Viñals of the University of Barcelona, Spain. It consisted in fragments of an enargite single crystal coming from Huencavélica, Peru. Chemical analysis gave an elemental composition of 46% Cu, 31% S, 17% As, 1.8% Sb, and quartz inclusions. The other (II) was a concentrate supplied by Compañía Minera El Indio, IV Region, Chile, containing 16% enargite, 38% pyrite, 11% grey copper ($Cu_{12}As_4S_{13}$), 11% chalcopyrite, traces of chalcosite, covellite and bornite, and 23% gangue. Crystals of high purity enargite obtained from Minera El Indio were kindly supplied by Professor Ricardo Córdova (Institute of Chemistry, Catholic University of Valparaíso).

Both minerals were mineralogically characterized by X-ray diffraction (XRD) and by scanning electron microscopy (SEM), complemented with X-ray energy dispersive spectroscopy (X-EDS) microanalysis. The mineralogical characterization by XRD was done on dusty samples using a Philips PW 1877 difractometer and software for the identification of the phases. Enargite presents an orthorhombic crystal structure. The spectra that were obtained (results not shown) were very similar for both minerals, except for a very pronounced peak characteristic of silica only present in the Chilean sample. The SEM studies for the original and biotreated samples were carried out with a JEOL JSM 6400 electron microscope at 20 kV and the Inca Analyser software. For this purpose, the samples were covered with a thin layer of graphite using a vaporiser.

2.2. Biooxidation kinetics

The biooxidation runs were performed with the concentrate mineral II at the School of Biochemical Engineering in Valparaíso. Flask experiments with *A. ferrooxidans* were carried out using 9K medium (Silverman and Lundgren, 1959) with 1% w/v concentrate of particle size in the range of 38 to 75 μm as energy source. The 500 ml flasks containing 40 ml of liquid suspension were incubated at 33 °C in an orbital shaker at 220 rpm. Initial pH and Eh (Ag/AgCl reference electrode) were 1.8 and 500 mV, respectively. In the case of *Sulfolobus metallicus* similar conditions were used, except temperature was 68 °C and pulp density 10% w/v. Evaporation was compensated by daily water addition.

Solubilised iron was measured by the *o*-phenanthroline method of Herrera et al. (1989), copper by iodometry according to Vogel (1969), sulphate by turbidity (Instituto de Hidrología de España, 1980) and arsenic by reduction with hydrazine followed by iodometry (Brescia et al., 1970). Total cell population was estimated from protein determinations (Lowry et al., 1951) after alkaline hydrolysis (Stickland, 1951), assuming a cell protein content of 37% (Torma, 1977).

2.3. Electrochemical assays

These tests were performed at the Department of Materials Science and Metallurgical Engineering in

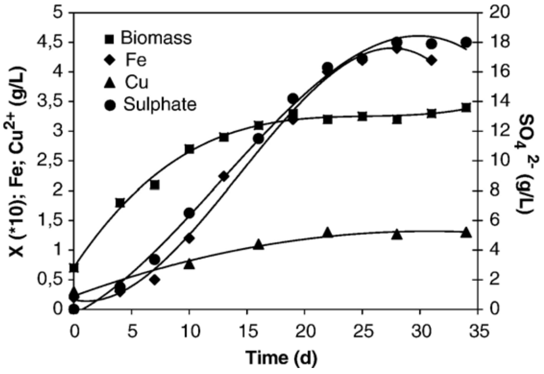

Fig. 1. Biooxidation kinetics of mineral II by *Acidithiobacillus ferrooxidans* in shake flasks. The experimental conditions were: 4% w/v pulp density, 33 °C, 220 rpm and initial pH 1.8.