Study of local electrochemical behavior of Cu-containing minerals by means of electrochemical micro-cell

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Introduction

Chalcopyrite is a strongly refractory¹ Cu-based mineral employed mainly in pyrometallurgy, but also in hydro- and bio-hydrometallurgy in order to recover metallic Cu. Chalcopyrite dissolution is a complex process since intermediate compounds (chalcocite and /or covellite) were detected during bioleaching^{2,3,4,5,6,7,8}. Sulfur can be oxidized to sulfuric acid in several steps, and other complex sulfur species such as thiosulfate, sulfite, hydrosulfate and sulfate were detected in solution and elemental sulfur and jarosite were found in the residues during bioleaching process^{3,4,7,8,9,10,11}.

The chalcopyrite dissolution processes can involve chlorides, which are known to enhance the chemical leaching of chalcopyrite. During the leaching of chalcopyrite in cupric chloride solutions the composition of the reaction product layer on solid stationary chalcopyrite were a fragile more resistive elemental sulfur layer at pH 1 and a porous less resistive FeOOH layer at pH 3^{12,13}. In chloride-containing media, the chalcopyrite dissolution rate is higher than in sulfate-containing media^{14,15}. The activation energy for chalcopyrite dissolution in chloride solution was 42 kJ/mol, while in sulfate-containing solution was 75 kJ/mol¹⁶. It was found that Cl⁻ ions increase the surface area and porosity of solid products and promote the formation of crystalline and porous elemental S layers on the mineral increasing the chalcopyrite dissolution^{14,15,17}.

Several works were developed using concentrates of chalcopyrite in chloride-copper(II)containing medium¹⁸⁻²⁰. It was demonstrated that the chalcopyrite dissolution rate was linear and strongly dependent on the potential of the solution in 0.2 M HCl and 0.5 g L⁻¹ Cu(II) at 35 °C¹⁸, and the rates increase in the potential region from 550 to 620 mV/SHE and the oxygen is essential for this increase, but an excessive oxidation can increase the potential into a region where inhibition of the dissolution may occur. Below 540 mV/SHE the copper dissolution decreases and above 580 mV/SHE increases. The rates of dissolution at constant potential (580–600 mV/SHE) by control of the oxygen supplied to the reactor are approximately constant for up to 80% dissolution for sized fractions of the concentrates, and are highly independent of the pulp density, iron and copper ion concentrations, the acidity and the chloride ion concentration¹⁹. Chalcopyrite dissolution under heap leach conditions seems to involve an initial step in which a non-oxidative dissolution to form H₂S and either cupric ions or a covellite-like surface as the initial products takes place; finally copper ions catalyzes the H₂S oxidation by oxygen²⁰.

The chloride effect on chalcopyrite leaching has also been investigated by performing batch leaching tests with different leaching solutions, and considering that a zone of rapid leaching exists between the critical potential E_c , equilibrium redox potential for the reduction of CuFeS₂ to Cu₂S and the oxidation potential E_{ox} , equilibrium redox potential for the oxidation of Cu₂S. The results showed that the leaching rate in HCl solution is the highest and the relationship between the Cu leaching rate and oxidation–reduction potential (ORP) follows Hiroyoshi's model. Thermodynamically, an increase in the Cl⁻ concentration forms chlorocuprate(I) complex ions, and the contribution of Cu(I) ions to the E_c value is greater than that of Cu(II) ions, even considering that [Cu(I)] < [Cu(II)] ions. So, the formation of

chlorocuprate(I) ions in a chloride solution may improve the chalcopyrite leaching rate by increasing the E_c value²¹. Chalcopyrite leaching in H₂SO₄–NaCl–O₂ media depends largely on the temperature, and the linear kinetics model represents the copper dissolution well; the activation energy was 91.2 kJ/mol between 80 and 100 °C²². The addition of Cl⁻ ions in heap leaching of sulfide minerals represents a problem to regenerate copper (II) and iron(III) ions via bacteria oxidation of iron (II) due to their sensitivity to high Cl⁻ concentrations. This problem can be overcame by chemical reaction of Cu(I) with dissolved oxygen in chloride systems, via a second order in relation to Cu(I)²³. Recently, the NaCl influence on chalcopyrite dissolution and surface sulfur speciation during chalcopyrite bioleaching with the mineral dissolution and diminishing the surface elemental sulfur accumulation, resulting in an increase of copper ions in solution²⁴. Similar results were obtained in shake flasks experiments of chalcopyrite bioleaching by Acidithiobacillus ferrooxidans strain LR²⁵.

Despite the grate number of studies on chalcopyrite dissolution under different conditions, as the best knowledge of the authors, there is no working where the different phases present on a chalcopyrite mineral had been investigated. Chalcopyrite-based minerals contain different phases, which might exhibit different leaching behavior mainly in the presence of chlorides. This work investigates by electrochemical micro-cell the electrochemical behavior of the phases detected in three different minerals usually found in Cu-containing ores: chalcopyrite, pyrite and bornite.

Experimental

The Vale chalcopyrite concentrate sample contained 23.0% Cu, 27.3% Fe, 22.9% S, 3.2% Si and 7.0% Ca and comprised chalcopyrite as the only sulfide phase and minor amounts of quartz and Ca-apatite. The morphology of the minerals was investigated by optical and scanning electron microscopy. The chemical composition of the phases was analyzed by energy dispersive X-ray spectroscopy. The electrochemical behavior of the phases detected in the minerals was studied by potentiodynamic polarization and cyclic voltammetry using an electrochemical micro-cell. The electrochemical measurements were carried out in 0.1 M NaCl neutral aqueous solution. Glass capillaries with internal diameter of 100 μ m were employed to perform the electrochemical measurements on the different phases found in the two Cu-containing minerals and in the pyrite.

Results and Discussion

The chalcopyrite exhibits a heterogeneous microstructure with a Cu-Fe-S matrix (CuFeS₂) and at least seven phases with different Fe, Si, S, Co and Ni content. Al, Ti, Ca and Mg might be also detected in some phases. The bornite (Cu₅FeS₄) shows a Cu-Fe-S matrix with at least four phases containing Fe, Si, Al, Ca, P and Sn. The phases detected in the chalcopyrite and in the bornite might be oxidized. The pyrite exhibits a more homogeneous structure and chemical composition mainly constituted by Fe and S.

Figure 1 illustrates the surface of chalcopyrite mineral with different secondary phases where the marks indicate the regions where the polarization curves were obtained.



Figure 1. Polarization curves for chalcopyrite, at different regions, obtained in neutral and naturally aerated 0.1 M NaCl solution (1-10) at 2 mV/s and 25 °C.

As can be seen the polarization curves present mixed potential and current at this potential which depend on the area of the electrode surface examined, that means the sites present different chemical composition. Polarization curves and cyclic voltammograms were also obtained for bornite and pyrite samples (data not shown).

Conclusions

The use of micro-cell with glass capillaries of 100 μ m diameter allowed to access different secondary phases of copper-containing minerals. The second phases exhibit different electrochemical behavior in the potentiodynamic polarization and cyclic voltammetry measurements depending on their electrochemical composition. Moreover, the behavior of the phases is different than that of the Cu-Fe-S matrix for the chalcopyrite and the bornite. In contrast, the pyrite exhibits a homogeneous electrochemical behavior, which is similar to that of the Cu-Fe-S matrix of the chalcopyrite and bornite.

Acknowledgements

The authors A.V.B. thank CNPq (Proc. 305890/2010-7) for scholarship, D.B. FAPESP (2012/19865-9) for financial support, and, also thank University of Udine for the facilities and cooperation.

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