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Comparative study on the selective chalcopyrite bioleaching of a molybdenite concentrate with mesophilic and thermophilic bacteria

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Abstract

This study evaluates different bioleaching treatments of a molybdenite concentrate using mesophilic and thermophilic bacterial cultures. Further studies on the chemical leaching and the electrochemical behavior of the MoS_2 concentrate were carried out. Bioleaching tests showed a progressive removal of chalcopyrite from the molybdenite concentrate with an increase in temperature. Chemical leaching tests support the idea of an indirect attack of the concentrate. Electrochemical tests indicate that chalcopyrite dissolution is favored when molybdenite is present. Therefore, this type of bioleaching treatment could be applied to purify molybdenite flotation concentrates by selectively dissolving chalcopyrite.

Keywords: Chalcopyrite bioleaching; Molybdenite concentrate; Acidophilic bacterium; Galvanic interaction

1. Introduction

Mineral bioleaching research has been a great success for the mining industry. As a result of this work, a significant number of commercial applications have emerged and are able to compete with conventional processes. Furthermore, bioleaching treatments have the great advantage of being environmental friendly. Bioleaching is defined as the use of different types of bacteria (mesophiles, moderate thermophiles and extreme thermophiles) to dissolve valuable metals from mineral sulfides [1,2]. Recently, bioleaching has also been used as a pre-treatment process for minerals. Bioleaching has been used to degrade sulfides such as pyrite or arsenopyrite, which contain gold and silver particles in their matrix. This process is further useful to facilitate the contact between these particles and a suitable chemical agent [3].

The role of bacteria in bioleaching is to catalyze the oxidation of metal sulfides. Two mechanisms of bacterial action have been suggested: (a) a direct attack of the bacteria on the mineral surface and its oxidation through enzymatic reactions; and (b) an indirect attack, where the bacteria regenerate the oxidizing agent of the mineral by means of the oxidation of Fe(II) to Fe(III) via thiosulfate or polysulfide depending on the type of mineral [4,5].

Molybdenite (MoS_2) is the main source of molybdenum. Generally, molybdenite, which is frequently associated to copper sulfides, is a by-product in copper mining. At present, molybdenite flotation concentrates are obtained. The presence of chalcopyrite in a molybdenite concentrate drastically reduces its market value due to terms imposed by buyers.

The aim of the present work is to study the different possibilities that bioleaching offers when treating a molybdenite concentrate. For this purpose, a comparative study has been carried out using three different types of acidophilic bacteria: mesophiles at 35°C, moderate thermophiles at 45°C and extreme thermophiles at 68°C. In order to determine the role played by microorganisms, chemical leaching tests were performed at the different temperatures using ferric iron as a leaching agent. Finally, the electrochemical behavior of both the unattacked and the attacked mineral was examined.

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2. Materials and methods

2.1. Ore

The substance used was a molybdenite concentrate from Rio Blanco (Chile). The chemical composition was as follows: 47% Mo, 3.2% Cu and 2.7% Fe. X-ray diffraction showed molybdenite (MoS_2) and chalcopyrite ($CuFeS_2$) as the main mineral phases.

2.2. Bacterial cultures

Three different mixed cultures of acidophilic bacteria were used:

1. A mesophilic culture (at 35°C) was obtained from water used in the mining industry along the Tinto river (Huelva, Spain). This culture was grown on a specific medium in order to isolate the acidophilic bacteria [6]. *Acidithiobacillus* (formerly *Thiobacillus*) *ferrooxidans*, *Acidithiobacillus* (formerly *Thiobacillus*) *thiooxidans* and *Leptospirillum ferrooxidans* were identified as the main bacteria in the culture.
2. A moderately thermophilic culture (at 45°C) was also obtained from the drainage waters of the Rio Tinto mines (Huelva, Spain) [7]. This culture was mainly composed of sulfur-oxidizing bacteria with a lower proportion of iron(II) ion-oxidizing microorganisms.
3. A thermophilic culture (at 68°C), originally *Sulfolobus BC*, was obtained with the capacity to oxidize both sulfur and ferrous iron [8].

The cultures were originally grown on a chalcopyrite concentrate as an energy source. 9K medium without $FeSO_4$ at pH 1.8 was used in the case of the mesophilic culture [9] and Norris medium at pH 1.5 was applied for the thermophilic cultures [10]. Due to the high toxicity of molybdenum, cell cultures were adapted to grow on molybdenite. This involved a successive enrichment by increasing the molybdenite concentrations and by reducing the amount of chalcopyrite progressively.

2.3. Bioleaching and chemical leaching experiments

Bioleaching tests were performed in an orbital shaker at 150 rpm, with a pulp density of 20 g l^{-1}. The tests were inoculated with 5% (v/v) of a previous culture adapted to molybdenite. Measurements were taken to determine the cell number, pH, redox potential and copper and iron in solution.

Chemical leaching tests with ferric iron were carried out under the same conditions, at 35°, 45° and 68°C, by adding 10 g l^{-1} of Fe^{3+} (as $Fe_2(SO_4)_3$) instead of the bacterial culture.

Furthermore, control tests were performed with ore and nutrient medium under sterile conditions.

2.4. Electrochemical experiments

The electrodes were prepared from both the as-received molybdenite concentrate and the bioleaching and chemical leaching residues. In order to start with a compact electrode, 0.1 g of mineral sample was mixed with 0.9 g of a conductor material (graphite) in 5 ml of chloroform. Time was allowed for the chloroform to evaporate. Prior to the electrochemical test, the paste electrodes were softly polished with the appropriate paper.

The electrolyte used in the experiments at different temperatures was Norris medium without chlorides at 45° and 68°C. The remaining tests were carried out at room temperature applying a 9K medium which was diluted 10 times.

The electrochemical measurements were performed in a typical cell magnetically agitated with the following three electrodes: the working electrode (molybdenite concentrate), the counter electrode (Pt spiral wire) and the reference electrode (Ag/AgCl), which was provided with a Luggin capillary tip and placed as close as possible to the working electrode. Potential and current values were controlled with a potentiostat and a voltage scanner.

All the potential values in the text refer to the Ag/AgCl electrode (+207 mV vs. SHE at 25°C). The electrochemical experiments consisted of obtaining potentiodynamic polarization curves initiated from the rest potential of the working electrode in the nutrient medium.

3. Results and discussion

Fig. 1 shows the copper dissolution curves obtained for the different temperatures using the following tests: control, chemical leaching with Fe^{3+} and bioleaching. The copper dissolution process was almost negligible for the controls, increasing slightly with temperature.

At 35°C (Fig. 1a), chemical leaching levelled off at around 30% of extraction compared to 50% for bacterial leaching. From a practical point of view, it is more interesting to consider dissolution rates (the slope of the curves) which show that the bacterial kinetics were faster than the chemical ones. This is consistent with a redox potential jump around day 8 in the bioleaching test and a decrease of this variable during the first days for the chemical leaching test (Fig. 2a). In the case of the chemical test, an increase of the potential at the end of the experiment was due to bacterial contamination.

At 45°C (Fig. 1b), similar final copper extraction results (around 60%) were obtained for the chemical and bacterial leaching tests. However, it is to note that the dissolution in the chemical test levelled off, whereas the bacterial test continued to leach copper. The variation of the redox potential during the experiment was similar to that in the experiment carried out at 35°C, decreasing rapidly in the leaching test with Fe^{3+} and increasing in the bioleach-

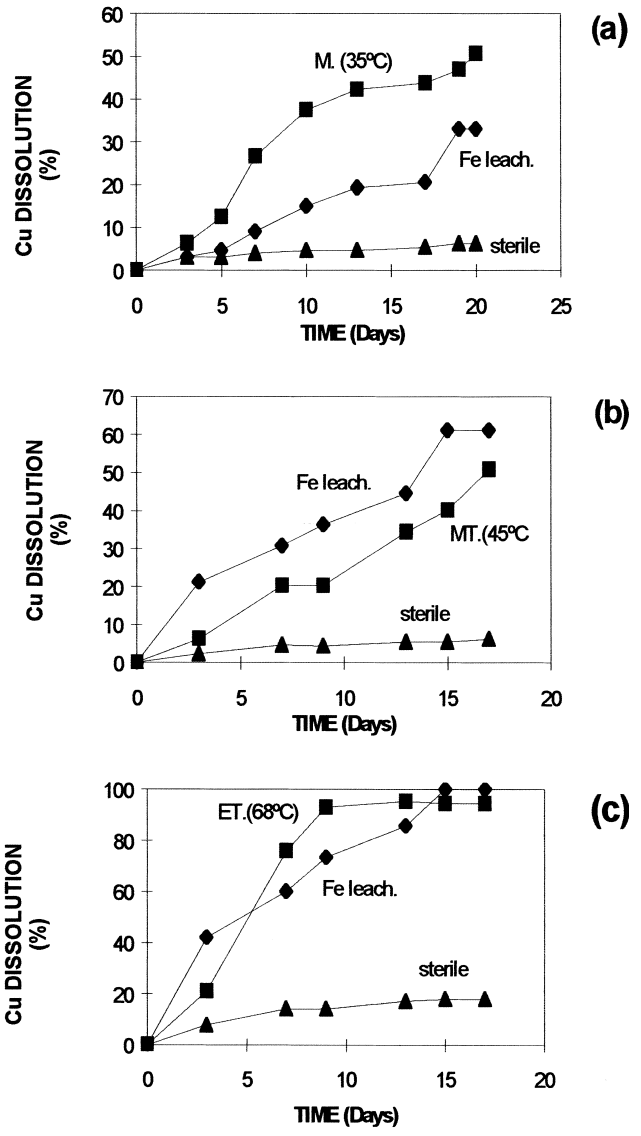

Fig. 1. Comparative copper dissolution using chemical leaching (Fe^{3+}), sterile medium and microorganisms at different temperatures: (a) mesophiles (M) at 35°C, (b) moderate thermophiles (MT) at 45°C, and (c) extreme thermophiles (ET) at 68°C.

ing test with moderate thermophiles. Nevertheless, a slower upsurge in the redox potential in this experiment was attributed to a smaller population of ferrous-oxidizing bacteria compared to sulfur-oxidizing bacteria in this culture.

At 68°C (Fig. 1c), a 100% copper dissolution was reached for both chemical and bacterial leaching tests. The main difference was related to the dissolution rate, which was faster in the bioleaching process. There is a clear relationship between the copper dissolved during the process (Fig. 1c) and the variation of the redox potential (Fig. 2c). The increase of the potential is directly related to the bacterial activity in the process, and more precisely to the presence of ferrous-oxidizing microorganisms, which enable the regeneration of Fe^{3+} and an increase of the ratio Fe^{3+}/Fe^{2+}.

The bacterial population was counted at the end of the chemical leaching tests with Fe^{3+}. This confirmed the contamination of the tests with mesophiles and moderate thermophiles, but extreme thermophiles were not observed. It is not unusual that bacterial growth takes place on mineral concentrates without inoculation under non-sterile conditions.

In addition to copper and iron analysis, concentrations of molybdenum were determined. The amount of molybdenum in solution remained very low. Molybdenum dissolution in the tests with mesophiles at 35°C and with moderate thermophiles at 45°C was lower than 1%, and with extreme thermophiles at 68°C lower than 0.5%. The same results were obtained for the chemical leaching tests

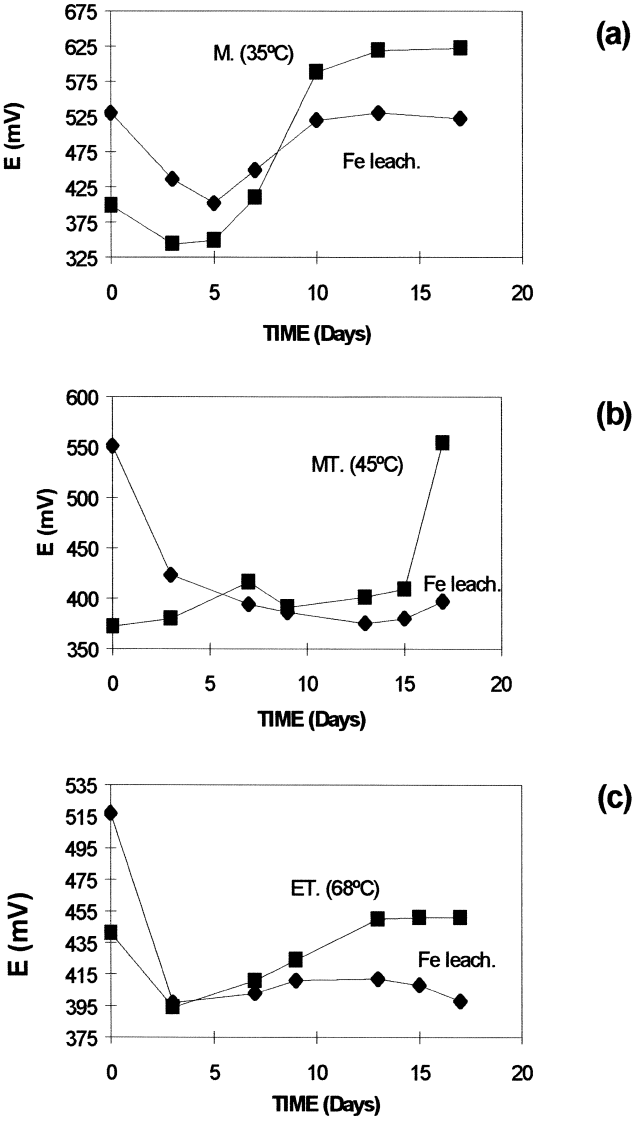

Fig. 2. Variation of the redox potential for the chemical leaching and bioleaching tests at different temperatures: (a) 35°C, (b) 45°C, and (c) 68°C.

confirming that ferric iron is not oxidizing enough to dissolve molybdenite.

According to these results it could be concluded that Fe^{3+} is responsible for chalcopyrite dissolution. This would mean that the bacteria act in an indirect way regenerating the oxidizing agent and maintaining a high oxidizing potential, which allows an improvement of the kinetics.

Therefore, the bioleaching of the molybdenite concentrate at the different temperatures applied leads only to the dissolution of chalcopyrite, which is favored by the presence of molybdenite. Based on an electrochemical mechanism, molybdenite, with a higher rest potential, should behave cathodically against chalcopyrite, with a lower rest potential. This has been confirmed by measuring the rest potentials of samples of high-purity chalcopyrite and the as-received molybdenite concentrate under the same conditions (1/10 of 9K medium at pH 1.5 and at room temperature) in powder electrodes. The measured rest potentials were about +200 mV for the chalcopyrite electrode and +500 mV for the molybdenite electrode. The latter value was similar to the as-received molybdenite concentrate after extracting the chalcopyrite.

Electrochemical tests were carried out in order to establish the mechanism, by which oxidation of the molybdenite concentrate was taking place and, at the same time, to justify the formation of a galvanic couple chalcopyrite–molybdenite with chalcopyrite dissolving anodically.

In this study, different anodic polarization tests at room temperature were performed on the following samples: as-received concentrate and bacterial and chemical leaching residues. Additionally, anodic polarization was carried out on the as-received ore at different temperatures (room temperature, 45° and 68°C) in order to determine the influence of such a variable in the molybdenite dissolution mechanism. Finally, an anodic scan was applied consecutively to the as-received concentrate to characterize the possible formation of passive layers.

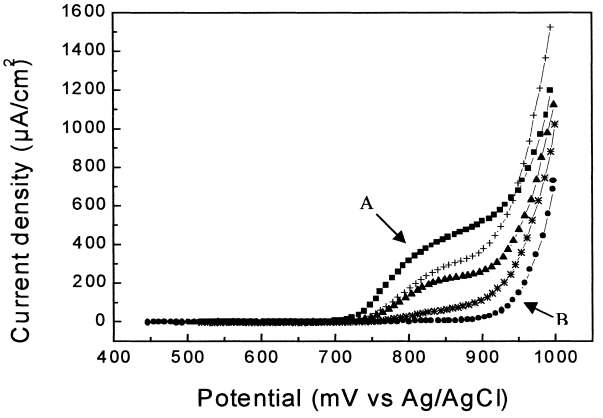

Fig. 3. Anodic polarization curves at room temperature for the different treatments carried out at a scan rate of 5 mV s^{-1}. ■, as-received (the molybdenite concentrate without attack); *, chemical leaching (a residue of the molybdenite concentrate attacked with 5 ml of 50% H_2SO_4-HNO_3 for 72 h, chalcopyrite dissolution reached 80%); ▲, mesophiles (a residue of the molybdenite concentrate attacked with mesophilic bacteria at 35°C, chalcopyrite dissolution reached 25%); ×, moderate thermophiles (a residue of the molybdenite concentrate attacked with thermophilic bacteria at 45°C, chalcopyrite dissolution reached 30%); ●, extreme thermophiles (a residue of the molybdenite concentrate attacked with thermophilic bacteria at 68°C, chalcopyrite dissolution reached 100%).

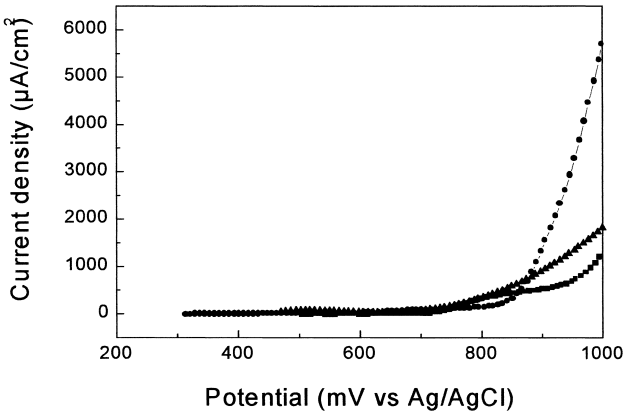

Fig. 4. Anodic polarization curves for the as-received molybdenite concentrate at different temperatures: ■, room temperature; ▲, 45°C; and ●, 68°C. Scan rate 5 mV s^{-1}.

Fig. 3 shows the anodic polarization curves obtained for the different electrodes starting from the rest potential. When comparing the electrochemical response of the as-received concentrate with the different residues, a decrease of the chalcopyrite peak (A) was observed with an increase in the degree of chalcopyrite dissolution. The greatest increase was obtained for the residue with the treatment using extremely thermophilic bacteria. The result is a gradual loss of chalcopyrite depending on the treatment applied (see dissolution percentages in Fig. 3). In the case of the acid leaching residue, the height of the chalcopyrite peak was lower than with the mesophiles but higher than with the extreme thermophiles. This is consistent with the degree of chalcopyrite dissolution reached in each test.

The polarization curves show clear differences among the residues attacked chemically or biologically. When chalcopyrite was completely dissolved, as shown for the treatment with extremely thermophilic bacteria, no peak corresponding to this compound appeared in the polarization curve. In this case, there was only molybdenite (peak B) present. Furthermore, when the chalcopyrite attack increases, the molybdenite decomposition potential shifts towards more positive values and its dissolution becomes even more difficult.

Fig. 4 shows polarization curves of the as-received concentrate at different temperatures. These curves point out that the molybdenite concentrate dissolution is very sensitive to temperature changes. A significant increase of the current density was obtained, when temperature was increased from 45°C to 68°C showing that chalcopyrite and molybdenite dissolution kinetics increase with temperature.

Products that are generated electrochemically at high potentials, which are above the molybdenite decomposition potential, do not exert any barrier effect on the dissolution process (data not shown). Thus, it is expected that in the molybdenite dissolution process a limiting effect due to the formation of a passive layer does not take place.

4. Conclusions

1. Chalcopyrite dissolution reached 50% with mesophiles and moderate thermophiles and 100% with extreme thermophiles after 3 weeks of treatment. Molybdenite dissolution was very low for all bioleaching tests. These results are closely related to the oxidizing potential reached during the tests: 675, 650 and 500 mV for the mesophilic, moderately thermophilic and extremely thermophilic microorganisms, respectively. In the latter case, a lower potential is required to reach a copper extraction of 100% in less than 10 days.
2. Chemical leaching tests with Fe^{3+} confirmed that the chalcopyrite dissolution mechanism in the presence of molybdenite is mainly indirect. According to this mechanism, ferric iron is the main oxidizing agent for the decomposition of the mineral sulfide and therefore, the regeneration of this agent is a function of the microorganisms.
3. Chalcopyrite is a refractory ore, but in the presence of molybdenite its dissolution is sped up due to the formation of a galvanic couple. According to the electrochemical tests carried out, the decomposition potential for chalcopyrite and molybdenite is +730 mV and +925 mV, respectively. The latter potential is very high and is virtually impossible to reach using the bioleaching processes. This is the reason why molybdenum concentrations in solution were very low.
4. Molybdenite dissolution is very sensitive to temperature changes and the dissolution rate increases with temperature (from room temperature to 68°C).
5. Bioleaching treatments would be a way to purify molybdenite flotation concentrates by selectively dissolving chalcopyrite.

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