Copper Recovery from Chalcopyrite Concentrate by an Indigenous *Acidithiobacillus ferrooxidans* in Airlift Bioreactor

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Abstract: A mesophilic iron oxidizing bacterium, *Acidithiobacillus ferrooxidans* has been isolated from a typical chalcopyrite copper concentrate of the Sarcheshmeh Copper Mine in the region of Kerman located in the south of Iran. Effects of some variable parameters such as solid concentration, temperature, initial Fe^{2+} concentration and pH on bioleaching of sulfide mineral (chalcopyrite) that provided from mentioned mine were investigated. Bioleaching experiments were carried out in two batch air-lift bioreactors with recycling stream. One of the reactors was containing 2 liters of the medium and 10% (v/v) inoculum and in other reactors, sterile bioleaching testes were carried out with concentrate sterilized without inoculum. The results indicate that the efficiency of copper extraction is dependent on all of the mentioned variables. In addition, results show that the effects of solid concentration and temperature were more important than the effect of initial Fe^{2+} concentration in bioreactor.

Key-Words: Bioleaching; *Acidithiobacillus ferrooxidans*; Airlift bioreactor; Sulfide mineral; Copper extraction

1 Introduction

The supply of high grade ores in the world is becoming more and more scarce making the processing of more complex ores necessary. Conventional mineral possessing on complex sulfides ores carried out by differential flotation often produce high-grade concentrates but causes environmental pollutions and accompanying penalties, which make its marketing and pyrometallurgical processing difficult. Therefore, a lot of effort has been made in developing of hydrometallurgical process suitable for ores treatment, but most of the proposed methods are complex and expensive [1].

Among the hydrometallurgical processes, biohydrometallurgical techniques seem to be one of the best alternatives for treatment of these type of ores. These methods, which were applied industrially in copper and uranium productions, using bioassisted heap, dump and in situ technologies, are successfully used today in extraction of gold from refractory sulfide-bearing ores and concentrates [2-7]. However, for other metal concentrates, this technology remains as a promising alternative against conventional pyrometallurgical extraction processes. This is the case of the treatment of chalcopiritic concentrates, which represent a more complicated situation, due to the natural refractivity of chalcopyrite.

Several studies with mesophilic microorganisms such as *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* had showed very slow copper leaching rates [8,9]. However, when thermophilic microorganisms were used leaching rates were considerably enhanced due to high temperatures, higher metal tolerance capacity and metabolic characteristics of these type of microorganisms [10,11].

Many researchers have investigated the possibility of using thermophilic and mesophilic microorganisms to improve metal leaching rates. The use of these microorganisms for bioleaching of chalcopyrite implies the knowledge of the mechanisms involved in the process.

Initially, chalcopyrite can be oxidized by dissolved oxygen according to Eq. (1) which favored for acidic solution, and as it is recognized, two modes of bacterial attack (direct and indirect) have been distinguished [12]:

In indirect attack (Eq. (2)), the role of bacteria is to regenerate the oxidant ferric ion in the bulk phase, from the ferrous iron resulting from the chemical oxidation of the metal sulfide in the ore by ferric iron (Eq. (3)).

In the direct attack, the bacteria leach the metal sulfide by the attaching the mineral surface and oxidizing it enzymatically by conveying electrons from the reduced moiety of the mineral, [13].

$$CuFeS_2 + O_2 + 4H^+ = Cu^{2+} + Fe^{2+} + 2S^0 + 2H_2O \quad (1)$$

$$CuFeS_2 + 4Fe^{3+} = Cu^{2+} + 5Fe^{2+} + 2S^0 \quad (2)$$

$$4Fe^{2+} + 4H^{+} + O_2 = 4Fe^{3+} + 2H_2O \quad (3)$$

Sand [14] has suggested that because Fe^{3+} oxidizes metal sulfide with both the direct and indirect mechanisms, there is no difference between the two mechanisms. Their model emphasizes a similarity in the chemistry of attack of the sulfide moiety by iron, and makes no distinction between ferric iron in the bulk phase and ferric iron bound in the cell envelope.

Choosing a proper type of bioreactor is a key step in achieving successful bioleaching. Hence, the selection of reactor is an important subject. The propose of this study is to investigate the applicability of airlift bioreactors in bioleaching processes, which was found a suitable subject for research work, that least attention has been paid to it.

2 Material and methods

2.1 Ore concentrates

A copper sulfide concentrate supplied by Sarcheshmeh Copper Mine (Kerman, Iran) was used. Chemical analysis of the sample was: 24.74% Cu; 26.39% Fe; 0.68% Mo; and 35% S. X-ray diffraction analysis of the ore showed chalcopyrite ($CuFeS_2$) as the major component (57.1%), pyrite (FeS_2)(19.3%) as the minor one, and small amounts of chalcocite (Cu_2S), covellite (CuS) and molybdenite (MoS_2). Over 90% of the ore had a size less than 45 μm.

2.2 Microorganism and medium

The strain used in this work has been isolated from the heap of the Sarcheshmeh Copper Mine in Kerman region and it was identified by the department of microbiology in IROST (Iranian Research Organization of Science and Technology). According to the report of IROST the strain was identified *Acidithiobacillus ferrooxidans*.

The bacteria were grown on a medium containing $FeSO_4.7H_2O$: 33.4g/l, $(NH_4)_2SO_4$: 0.4g/l, $MgSO_4.7H_2O$: 0.4 g/l, and K_2HPO_4: 0.4g/l [15]. The cultures of *Acidithiobacillus ferrooxidans* were incubated in 500 ml Erlenmeyer flasks each containing of 200 ml of the medium and 10% (v/v) inoculum, at a constant temperature of 33°C on a rotary shaker at 180 rpm. The initial pH of the cultures was adjusted to 1.5 using 1N H_2SO_4. The stock and pre-inoculum cultures were maintained in the same medium under similar conditions. The stock cultures were subcultured every two weeks.

2.3 Bioleaching experiments

Bioleaching experiments were carried out in two batch air-lift bioreactors with recycling stream consisting of three parts: top part, main column with water jacket and bottom part with an air diffuser. Fig. 1 shows a schematic diagram of the experimental setup. The main column consisted of an internal tube of 3.5 cm internal diameter, an external tube of 7 cm diameter and 55 cm height and a total working volume of 2 l. Compressed air was sparged from the bottom of the column into the internal tube, which produced a recirculation flow pattern of the concentrate slurry in the column. The top part of the reactor had a 10 cm diameter and 20 cm height and was employed to prevent the overflow of slurry from the reactor. In order to the investigation of temperature reactors were maintained at different temperatures using a water jacket. One of the reactors contained 2 liters of medium and 10% (v/v) inoculum. At start-up variation amounts of concentrate was added to the medium. In the other reactor control bioleaching tests were also carried out, using sterilized concentrate by autoclaving at 121 ºC for 30 min under 1 atm pressure, without inoculum and 40 ml of 0.5% (v/v) formaline in ethanol was added to keep sterile control experiment after start-up.

For investigation of effect of initial Fe^{2+} concentration some medium with various amounts of $FeSO_4$ was made. During the experiments, the pH was kept at 1.5 by addition of 1N H_2SO_4 when were necessary. Variations of pH versus time in presence of bacteria were investigated. Cell number, pH, amounts of copper, total iron in solution, ferrous and ferric ion were measured every day. Water was added to the reactors to compensate for evaporation losses.

2.4 Analysis

Free bacteria in solution were determined by direct counting using a Thoma chamber of 0.1 mm depth and 0.0025 mm^2 area with an optical microscope (×1000). Copper and total iron concentration in solution were measured by atomic absorption spectrophotometer (model AAS 5EA). The ferric iron concentrations in the solution were determined by sulfosalicylic acid spectroscopy method (Varian Techtron UV-VIS spectrophotometer, model 635) [16] and the ferrous iron concentration was analysed by a volumetric method by titration with potassium dichromate [17]. The pH of the supernatant at room temperature was also measured with a pH meter (Metrohm, model 691).

3 Results and Discussion

In Fig. 2 the percentage copper recovery at different pulp densities as a function of time is shown. As it can be observed, the results show that at low pulp densities (1% and 5% w/v) almost all of the copper was extracted (about 94% and 90% respectively) from chalcopyrite in 5^{th} and 8^{th} days respectively, because in these pulp densities we don't have high viscosity in solution and consequently air contribution dose not limit. At the highest pulp density (20% w/v) copper extraction was reached to 65% after 15 days. The main reason for inefficient bioleaching at high pulp densities is that the rate of oxygen demand outstrips the oxygen supply limited by gas-liquid mass transfer rates. For this reason 10% (w/v) of pulp density was selected as the best level. Control is the medium containing chalcopyrite without microorganism and it has these conditions, namely pH=1.5; initial Fe^{2+} concentration =7 g/l; T=33ºC and pulp density =10% (w/v).

Fig. 3 indicates that 33ºC is the best temperature for the bioleaching of chalcopyrite. Most growth of *Acidithiobacillus ferrooxidans* take place in 33ºC and it is the optimum temperature for this microorganism. In 20ºC and 40ºC the rate of bioleaching according to this figure was decreased because in these temperatures activity of bacteria was decreased. At higher temperature than 33ºC the solubility of Cu in solution increase but the growth of microorganism will be slowed.

Fig. 4 shows comparison of copper extraction in presence and absence of bacteria. At same conditions, namely pH=1.5; initial Fe^{2+} concentration =7 g/l; T=33ºC and pulp density =10% (w/v) in case of absence of bacteria, value of Cu extraction reached only to 10%, while Cu extraction in bioleaching was 70%.

Fig. 5 shows variation of Fe^{2+} and Fe^{3+} concentrations vs. time at pulp density of 10% (w/v) and T=33ºC. The changing of the values of Fe^{2+} and Fe^{3+} concentrations in solution indicates a microbial activity. As can be seen in this Figure while initial Fe^{2+} concentration decreases, Fe^{3+} concentration increases with respect to time.

Fig. 6 shows that the H^+ concentration decreased initially due to the consumption of acid during the protonic attack of the chalcopyrite according to the following reaction:

$$CuFeS_2 + O_2 + 4H^+ \rightarrow Cu^{2+} + Fe^{2+} + 2S^0 + 2H_2O$$

Later, acidity increased, because of the oxidation of elemental sulfur by sulfur-oxidizing microorganisms.

The effect of the initial ferrous ion concentration on the bioleaching kinetics was investigated. Five different media containing different quantities of Fe^{2+} as ferrous sulfate (0, 2, 4, 5.5, 7 and 9 g/l) were used. According to Fig. 7 at same conditions for all of the tests, copper extraction reached to 13%, 44%, 50%, 58%, 70% and 75% for media containing 0, 2, 4, 5.5, 7 and 9 g/l of initial Fe^{2+} concentration after 10 days respectively. These results indicate that increases in ferrous lead to enhanced activity and growth by bacteria and therefore higher copper recovery in airlift bioreactor was obtained.

4 Conclusion

The bioleaching ability an indigenous microorganisms which isolated from the soil of Sarcheshmeh mine near the city of Kerman in the south of Iran has been studied in an airlift bioreactor. The experimental results show that among the whole factors, temperature and solid concentration are more effective than other factors. In this way, high pulp densities decreased the copper extraction because of air distribution limiting. The optimum temperature has been determined 33°C and in this temperature the bacteria has the highest activity to copper recovery from chalcopyrite.

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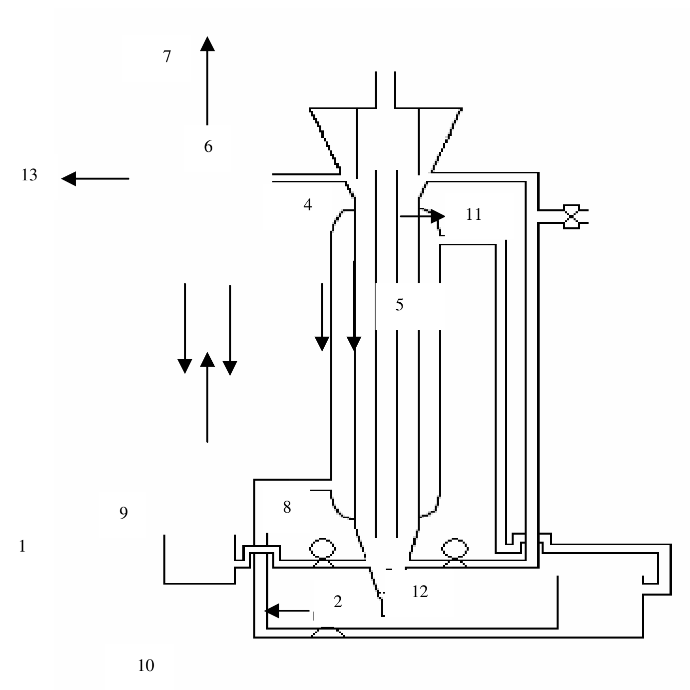

Fig. 1:
Schematic diagram of airlift bioreactor (1: fresh feed; 2: input air; 3: air sparger; 4: circulation of water in jacket; 5: recycling stream; 6: draft tube; 7: output air; 8,9,10: peristaltic pump; 11: sampling port; 12: thermostatic bath; 13: effluent solution)

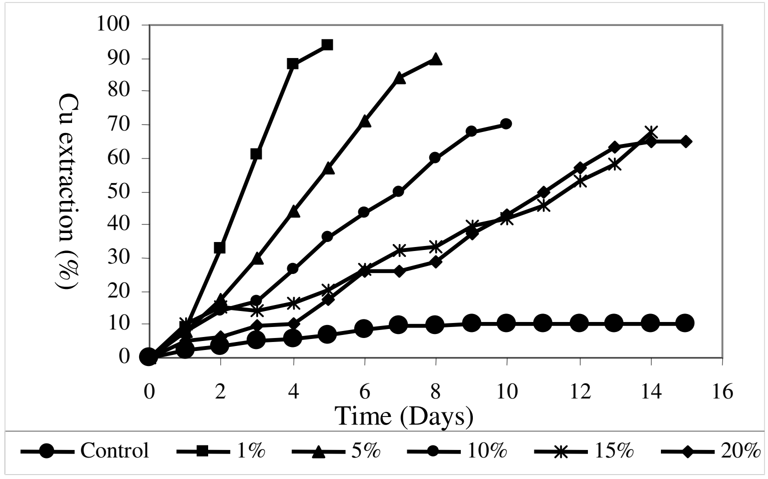

Fig. 2: Effect of pulp density on Cu extraction; pH=1.5; initial Fe^{2+} concentration = 7 g/l; T=33 °C

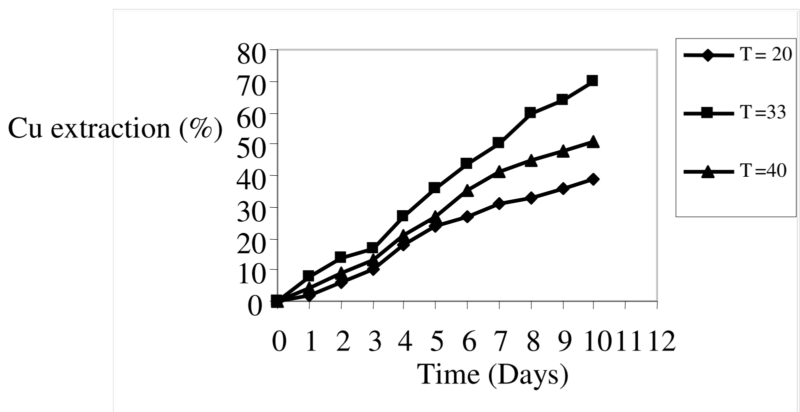

Fig. 3: Cu extraction at different temperatures in airlift bioreactor; pH=1.5; initial Fe^{2+} concentration=7 g/l; pulp density = 10% (w/v)

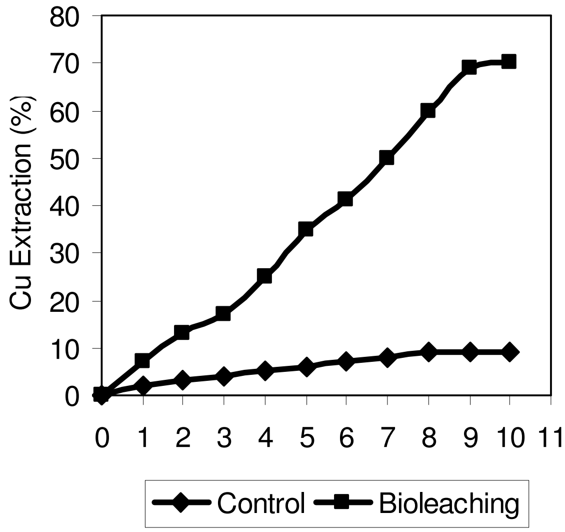

Fig. 4: Cu extraction in presence and absence of bacteria in airlift bioreactor; pH=1.5; initial Fe^{2+} concentration=7 g/l; pulp density = 10% (w/v); T=33 °C

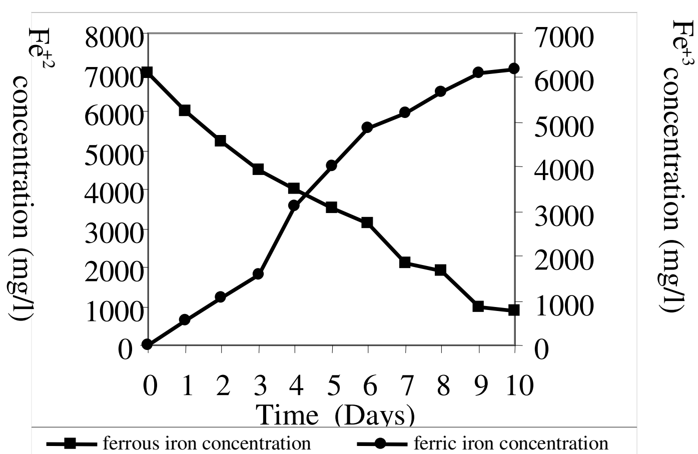

Fig. 5: Variation of ferrous and ferric concentration vs. Time in airlift bioreactor; pH=1.5; pulp density = 10% (w/v); T=33 °C

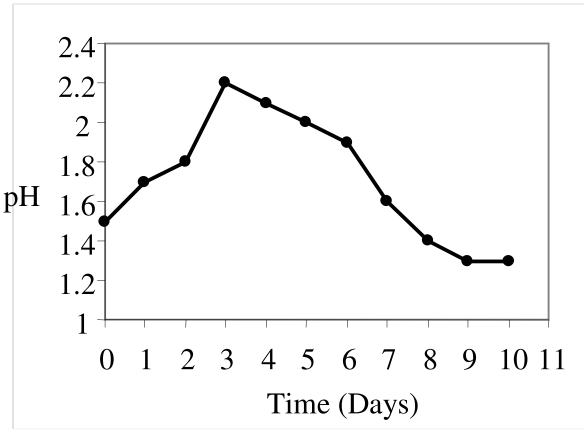

Fig. 6: Variation of pH vs. Time in airlift bioreactor; pulp density = 10% (w/v); T=33 °C; initial Fe^{2+} concentration = 7 g/l

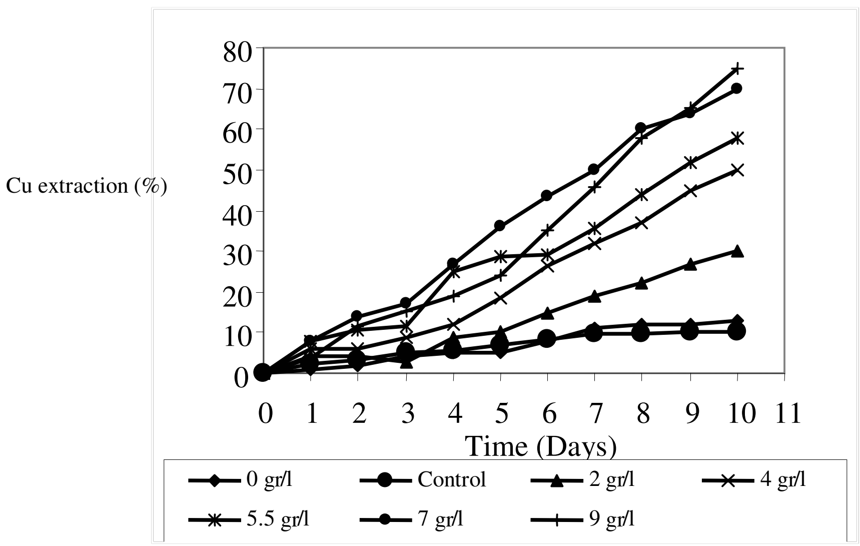

Fig. 7: Effect of initial Fe^{2+} concentration on Cu extraction; pH=1.5; pulp density =10% (w/v); T=33 °C