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The effects of clay particles on the efficiency of bioleaching process

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ABSTRACT

In this study, the influence of clay particles on bioleaching process of Sarcheshmeh Copper Mine in the south of Iran was investigated. Shake flasks experiment was carried out in a completely randomized design with six treatments including washed (T1), sieved (T2), and untreated (T3) of low-grade ore particles <2 mm, all inoculated with a mixture of sulfur and iron oxidizing bacteria and non-inoculated treatments (T4, T5 and T6) with the same ore particle sizes and three replications. The results showed that bacteria number in T3 treatment decreased significantly compared to T1 and T2 treatments. oxidation–reduction potential (ORP) decreased in T3 and T6 treatments due to the presence of clay particles. The highest concentration of extracted copper (50 mg/L) was obtained in the inoculated washed and sieved treatments (T1 and T2) and the least copper concentrations was measured in those treatments with high level of clay particles (T3 and T6). It was concluded that copper extraction was increased significantly by removing the clay particles from low-grade ore and this was pronounced when clay particles were washed by water.

1. Introduction

Sarcheshmeh mine is one of the largest copper mines in Iran, located in Kerman province. It is an open-pit mining using 20 million tons of copper ore (containing 0.8% grade) per year for conventional extraction of copper (Pyrometallurgical methods). The by-product of Sarcheshmeh mine is about 1 million tons of low-grade copper ore per year. In addition, 83 million tons of a sulphide resource with a low-grade of copper (about 0.5%) has been estimated in Darrehzar area located in the southeast of Sarcheshmeh Copper Complex. These low-grade copper ores not only create environmental problems but also huge amounts of copper become unusable. While the Sarcheshmeh's high-grade copper diminishes, the recovery costs of copper from low-grade ores becomes a serious challenge. It is an economical idea to find low cost processing methods to extract copper from low-grade ores.

Heap bioleaching of low-grade copper sulphides is a developing technology that has been applied successfully to extract copper from secondary sulphide minerals such as chalcocite (Brierley and Brierley, 2001; Rawlings et al., 2003). However, heap bioleaching of the refractory primary copper sulphide, chalcopyrite, has yet to be implemented at commercial scale (Watling, 2006). Currently, the National Iranian Copper Industries Company (NICIC) is undertaking a large-scale pilot test by Mintek Company (heap bioleaching) for Darrehzar chalcopyrite ore at the Sarcheshmeh Copper Complex (van Staden et al., 2005). In a heap bioleaching process, a heap of crushed ore is treated with sulfuric acid/ferric sulphate solution that contains iron and sulfur oxidizing bacteria, which colonize the heap and catalyze the leaching reactions (Palencia et al., 2002). Good infiltration and conductivity with high porosity are required to allow leaching solution to percolate through the heap due to its direct effect on oxygen availability for bacterial growth. Therefore, the heap must be aerated continuously because of the huge demand for oxygen by the microbes. Another reason why good solution percolation is important is to transport metals solubilized by the ferric iron oxidizing the sulfide minerals. For example, the presence of excessive fine particles (especially clay particles) is challenging in bioleaching because fine particles may accompany with leach solution to the bottom of the heap and restrict water and oxygen flows (Olson et al., 2003).

Primary observations on Darrehzar (with low-grade ore samples) showed that low-grade copper ore has lots of clay particles. Therefore, this study was designed to investigate the role of clay particles on bacterial activity during bioleaching process in Sarcheshmeh Copper Complex.

2. Materials and methods

2.1. Ore sampling

The low-grade copper ore originally collected from Darrehzar was supplied by Sarcheshmeh Copper Complex. Darrehzar's ore sample

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Table 1
Treatments in shake flasks experiment.

Treatment		Particle size diameter, Φ (mm)
T_1	Inoculated	$0.075<\Phi<2$ (washed)
T_2		$0.075<\Phi<2$ (sieved)
T_3		$\Phi<2$ untreated
T_4	Non-inoculated	$0.075<\Phi<2$ (washed)
T_5		$0.075<\Phi<2$ (sieved)
T_6		$\Phi<2$ untreated

was crushed and passed through a 2-mm sieve (10 meshes) for this study.

2.2. Sample preparation for X-ray diffraction analysis

Some of the low-grade copper ore <2 mm was floated and washed in distilled water until the upper solution became clear (Zhang and Bogan, 1995). Floated fine particles was filtered by a Whatman No. 41 filter paper and dried in 110 °C and passed through a 0.075 mm (200 meshes) sieve. The crystal structure of the fine particles was determined by powder X-ray diffraction using a Jeol Model GDX-8030 diffractometer.

2.3. Bacterial cultures

A mixed culture of *Acidithiobacillus thiooxidans*, *Acidithiobacillus ferrooxidans*, and *Leptosprillum ferrooxidans* (in ratios of 2:4:4, respectively) from Sarcheshmeh copper mine drainage were prepared for bioleaching process (Seyed Bagheri and Hassani, 2001). The optimum temperature, pH, and culture medium for the strains were 32 °C, 1.8, and 9 K medium respectively (Salehi et al., 2002).

2.4. Bioleaching experiment

Shake flasks experiment was carried out in a completely randomized design with six different treatments and three replications (Table 1). The bioleaching experiment was performed in 500-mL Erlenmeyer flasks with 180 mL of 9 K medium (Silverman and Lundgren, 1959) containing K_2HPO_4 0.5 g/L, $(NH_4)_2SO_4$ 3 g/L, $MgSO_4\cdot7H_2O$ 0.5 g/L, KCl 0.1 g/L, and $Ca(NO_3)_2\cdot H_2O$ 0.01 g/L. Ten grams (5% w/v pulp density) of each ore treatment was added to the flasks. The ore flasks were inoculated with 20 mL (10% v/v) of the mixed bacterial culture (T1, T2, and T3 treatments). Another set of the same treatments were prepared without bacterial inoculation as the control samples (T4, T5, and T6 treatments). Ten milliliter (0.2% w/v) of thymol in methanol was added to the non-inoculated flasks to prevent microbial growth. The samples of control media were taken periodically and checked to ensure the absence of bacteria. pH was adjusted at 1.8 by adding concentrated H_2SO_4. All six treatments with three replications (18 samples) were incubated in a rotary shaker at 150 rpm and constant temperature of 32 °C for 23 days.

2.5. Analytical determination

The pH and oxidation–reduction potential (ORP) of the samples were monitored periodically (as an index of bacterial activity) by a pH/Eh meter (Metrohm model 826). The population of free bacteria in solution was determined by direct microscopic counting. Solution evaporation was compensated by addition of distilled water. Copper concentration was determined in the leached solutions by atomic absorption spectrometer (Varian 220 FS). The results were analyzed by using Minitab and Excel softwares.

Table 2
Chemical and mineral composition of sulfide copper ore collected from Darrehzar.

Element/mineral	Cu (total)	Cu[a]	Fe	FeS_2	CuS	Cu_2S	$CuFeS_2$	Fe_2O_3	Fe_3O_4
Weight (%)	0.47	0.02	3.89	7.10	0.06	0.15	0.83	0.03	0.07

[a] Acid soluble copper.

2.6. Cell growth experiment with clay particles

Five milliliter of a previous isolated adapted strain of *A. ferrooxidans* from Sarcheshmeh Copper mine at its exponential growth phase was added to 250 mL Erlenmeyer flask containing 95 mL of 9 K medium and pH was adjusted to 1.8 with H_2SO_4. The initial bacterial cell numbers in the flask was determined using direct count technique. Two grams of clay fraction (particles less than 75 µm) was added to the flask culture (Flask A). After 6 h, 4.4 g of $FeSO_4\cdot7H_2O$ as energy source was added to the culture medium. A second flask was set up containing the same culture and no clay particles was added (Flask B). Two flasks were incubated at 32 °C in a rotary shaker at 150 rpm. The free bacterial cell number and the ferrous iron concentration in slurry were monitored periodically in two flasks separately. The bacterial cell numbers in slurry was determined by direct counting using an optical microscope (Zeiss Standard 20). Ferrous iron concentration was measured by the *o*-phenanthroline colorimetric method (Muir and Anderson, 1977) using spectrophotometer (Varian Cary 50).

3. Results and discussion

3.1. Chemical and mineralogical analysis of the ore sample

The chemical composition of sulfide copper ore collected from Darrehzar is shown in Table 2. The physical analysis of the ore sample

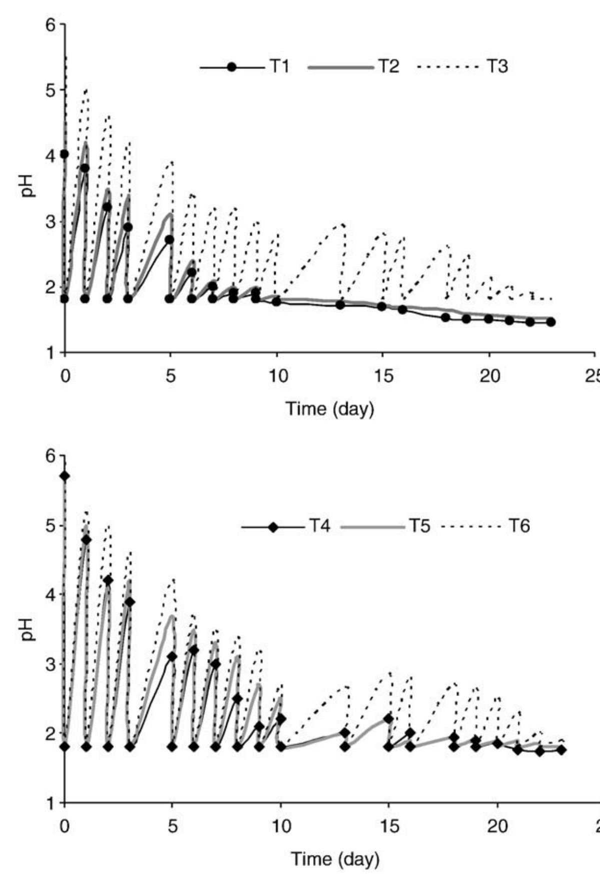

Fig. 1. pH variations in the inoculated (above) and non-inoculated (bottom) treatments.

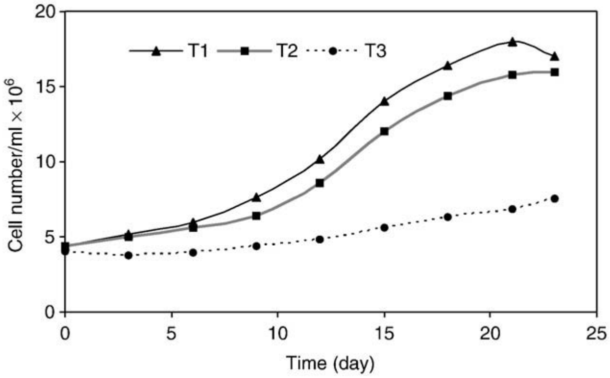

Fig. 2. Growth cure of sulfur and iron oxidizing bacteria in T1, T2 and T3 treatments.

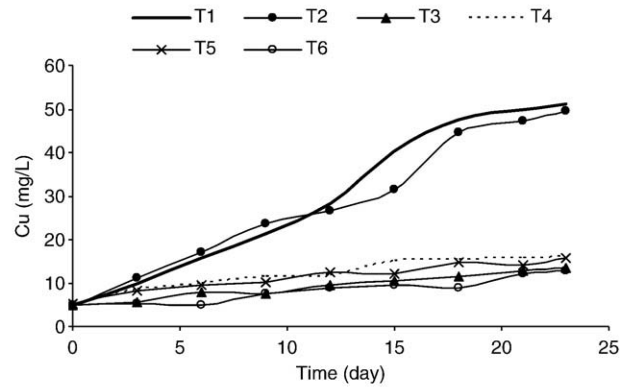

Fig. 4. Copper concentrations in T1, T2, T3, T4, T5 and T6 treatments during 23 days of shake flask experiment.

revealed that clay particles formed 35% (w/w) of the whole sample. X-ray diffraction analysis showed that sulfide copper ore of Darrehzar (<75 µm) contains montmorilonite, kaolonite and illite clay minerals.

3.2. Bioleaching experiment

Fig. 1 illustrates pH changes in inoculated and non-inoculated media during shake flasks experiment. Due to the acid consumption, pH changes in the first part of experiment were high for all treatments (T1 to T6). These results were in agreement with Seyed Bagheri (2003). In the middle of the experiment pH variations decreased considerably and at the end, pH was almost constant. The amount of acid consumed for control samples (T4, T5, and T6) was higher than inoculated treatments (T1, T2, and T3). Furthermore, inoculated treatments reached to the constant pH faster than non-inoculated treatments. Due to the bacterial activity, the amount of consumed acid for adjusting the pH of the media decreased in inoculated treatments compared with the non-inoculated treatments. After 10 days, no acid sulfuric was added to T1 and T2 treatments, while pH adjustment in T3 treatment was continued until the end of experiment in order to maintain the desired pH value. The presence of particles with less than 75 µm in diameter (clay particle) have a high cation exchange capacity and a considerable amount of H^+ can be adsorbed by their extended surface area of fine particles (Rinder, 1979; Manafi, 2002). In the fifth day of experiment, pH variations decreased in T1 and T2 treatments. Sulfur oxidation was occurred by bacterial activity and pH in the slurries decreased significantly and reached to 1.8 in the 10th day of the experiment. These results were in agreement with Rodríguez et al. (2003). Therefore, no acid was added to adjust pH of the slurries. pH variation in T4 and T5 was similar but it was different in T6 treatment. For pH adjustment, acid sulfuric was added in T6 treatment until the end of the experiment. Regarding Fig. 1, it can be concluded that microbial oxidation reaction has happened in inoculated treatments and pH variations in inoculated treatments were less than non-inoculated ones.

Fig. 2 depicts changes in the population of sulfur and iron oxidizing bacteria during the bioleaching process. The number of bacteria in T1 and T2 treatments were similar, but were different from T3 treatment. The number of bacterial cells in T1 and T2 treatments was higher compared with T3 treatment. Lag, exponential, and stationery phases were unambiguous in T1 and T2 treatments while they were not obvious in T3 treatment. The bacterial cells in T1 and T2 treatments reached to 1.8×10^7 and 1.58×10^7 cell/ mL after 21 days, respectively, while it reached to 6.8×10^6 cell / mL in T3. According to Rinder (1979), fine particles (especially clay minerals) can adsorb bacterial cells on their surfaces and consequently the number of bacteria decreased in solution.

Fig. 3 shows the variations of ORP in T1 to T6 treatments. ORP depends on the ferric to ferrous iron ratio. *A. ferrooxidans* and *L. ferrooxidans* oxidize ferrous iron to ferric iron. Therefore, ORP is used as an indirect value of bacterial activity in bioleaching processes (Weston et al., 1995). The results showed that in the first day of incubation, ORP rapidly decreased. There was a primary reaction between soluble redox species and sulfide minerals (Ahonen and Tuovinen, 1993). But from the second day ORP increased due to the microbial and chemical oxidation processes in all treatments because pH artificially or naturally was reduced to 1.8 during the bioleaching process. The highest value of ORP (600 mV) was observed in T1 and T2 treatments while T3 treatment had the least ORP value (560 mV) among inoculated treatments. The reason of minimum ORP values in T3 can be related to the less O_2 transfer from the gaseous to aqueous phase because of clay particles and higher viscosity of the solution. According to Brierley and Briggs (2002) small particles can increase

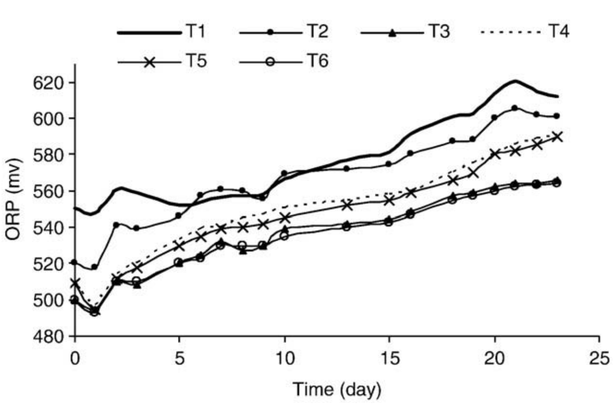

Fig. 3. Oxidation reduction potential (ORP) variations in all treatments.

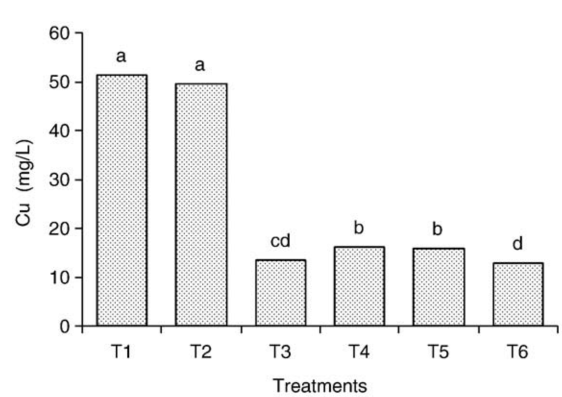

Fig. 5. Mean copper concentrations in leach solution of T1, T2, T3, T4, T5 and T6 treatments during 23 days of shake flask experiment. Different letters indicate significant differences at $P<0.01$.

the apparent viscosity of the slurries and decrease oxygen transfer rates. This would affect bacterial iron oxidation and consequently resulted in lower ORP. T1 and T2 treatments had no particles less than 75 µm in diameter and ORP in T1 treatment was higher than T2 treatment. As a result for removing fine particles, washing was more effective than sieving. The least ORP value observed among non-inoculated treatments belonged to T6. ORP values of T4 and T5 treatments were lower than T1 and T2 treatments. It is due to the lack of microbial oxidations which happened in non-inoculated treatments. ORP values for T4 were a few higher than T5 and it confirmed that washing was more effective than sieving technique in removing fine particles in bioleaching process. T6 treatment had the least value of ORP among all treatments that could be related to the absence of bacterial cells and the slurry with greater viscosity.

The rate of copper extraction during 23 days of shake flask experiment was higher in T1 and T2 treatments while T6 and T3 had the minimum rate of extraction (Fig. 4). At the end of the experiment, copper concentration was about 52 and 50 mg/L in T1 and T2 treatments, respectively, and the difference between these two treatments was not statistically different (Fig. 5). However, the efficiency of extracted copper in T1 was higher than T2 treatment. Copper concentration in T4 and T5 treatments was 3.5 times less than T1 and T2 treatments (~15 mg/L). Extracted copper in T5 and T6 treatments was 13.5 and 12.8 mg/L, respectively. There was statistically no difference between copper concentrations in T3 and T6 treatments. Manafi (2002) suggested that adsorbed copper cations on the fine particle surfaces are the main reason for reducing the copper concentration in solution. Hence, the insignificant leached copper from bacterial activity in T3 could be adsorbed with clay particles. In general, the finer particle size the more rapid the oxidation, because of the grater surface area (Brierley and Briggs, 2002). Nevertheless Shrihari et al. (1991 and 1995) also reported increasing the rate of chalcopyrite leaching with increasing the particle size. There are also some reports that show the rate and extend of loss viability of bacterial population increase with decreasing the particle size (Deveci, 2004). Also Soljanto et al. (1980) reported that finely ground particles inhibit bacterial oxidation, because the rock samples may contain of potentially inhibitory components which grinding release them faster into the leach solution.

3.3. Effect of clay particles in cell growth experiment

Fig. 6 shows the number of bacterial cells in the presence and the absence of clay particles. The initial bacterial cell numbers in flask A (with clay particles) and in flask B (without clay particles) were 1.97×10^6 and 1.93×10^6 cell/ mL respectively. After 6 h incubation the free cell number in flask A reached to 1.25×10^6 while it was 1.95×10^6 cell/ mL in the flask B. It seems that the free bacterial cells in flask A decreased because of cell destructions or their adhesion to the clay surfaces. The number of bacterial cells in flask B was almost constant during 18 h of incubation. This part of growth cure shows the Lag phase.

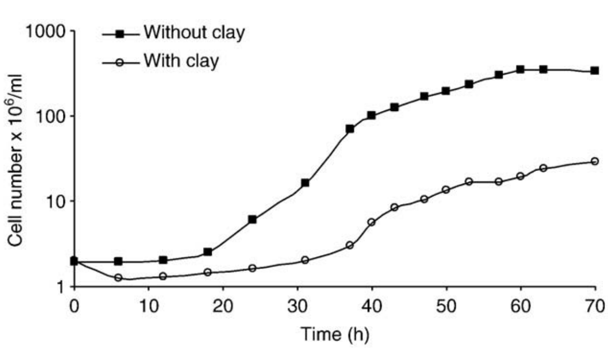

Fig. 6. Growth cure of sulfur and iron oxidizing bacteria in the presence and absences of clay particles.

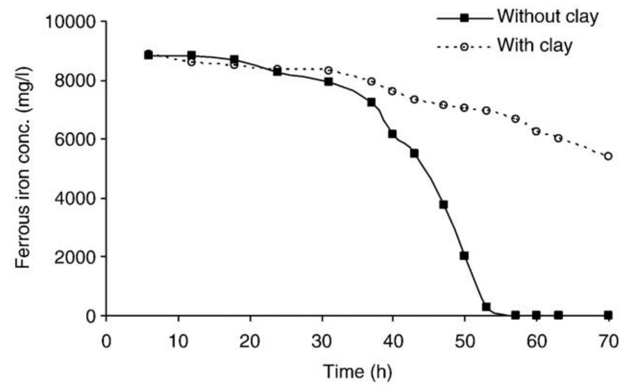

Fig. 7. Oxidation of ferrous iron in the presence and absences of clay particles.

Exponential phase started after 18 h and growth cure reached to the stationery phase after 42 h of incubation. Final bacterial cells in flasks A and B were 3.35×10^8 and 2.85×10^7 cell/ mL respectively. The bacterial cell number was diminished about 11.7 times in flask A compared to flask B.

Ferrous iron concentration in both treatments (with and without clay particles) after 24 h of incubation was almost constant (8800 mg/L) and then biological oxidation process started with different rate in flask A (with clay particles) and flask B (without clay) (Fig. 7). After 57 h of incubation, the entire ferrous iron was oxidized in flask B. While even after 70 h of incubation, the ferrous iron concentration in flask A was 5400 mg/L. These results exposed that bacterial cells and consequently biological oxidation of ferrous iron was reduced in the presence of clay particles.

4. Conclusion

A higher recovery of copper in bioleaching process was achieved by removing clay particles from low-grade copper ore originated from Darrehzar. The results also discovered that washing by water was more effective than sieving process in removing the clay particles in bioleaching process.

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