Shake flask and column bioleaching of a pyritic porphyry copper sulphide ore

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A B S T R A C T

The purpose of this study was to test the feasibility of using bacterial leaching to solubilise copper from a pyritic sulphide ore, a part of the Sarcheshmeh Copper Complex. The bulk ore sample contained 18% pyrite and 0.8% Cu mostly as secondary chalcocite and Cu oxides. Mineral microscopy showed that pyrite grains in this porphyry ore were coated by chalcocite. Conventional flotation could not be used for ore beneficiation because Cu-sulphide could not be selectively separated from pyrite and consequently the flotation concentrate contained too much Fe and less Cu. Hence bioleaching was tested as an alternative process for this ore. The bioleaching was tested with a consortium of mesophilic acidophiles comprising Acidithiobacillus arcticus, Acidithiobacillus thiooxidans and Acidithiobacillus caldus, originally enriched from the Sarcheshmeh site. Several mineral salt formulations were tested in shake flask bioleaching experiments. These experiments resulted in 89–92% Cu yields with no discernible differences between the different formulations. Sterile controls representing chemical acid leaching resulted in about 60% Cu solubilization. For column bioleaching experiments, ore samples (~40 kg each; 75% – 12 mm) were agglomerated and treated with a schedule of 4 days of irrigation and 4 days of rest period. The column bioleaching tests yielded Cu recoveries of about 90%. The abiotic control had 50% Cu recovery. Thus the test results were favorable for using the bioleaching approach for this Cu-ore material.

1. Introduction

Bioheap leaching processes are commercially used especially for the recovery of copper. These processes involve acidophilic microorganisms that grow at pH-values < 3 and oxidize sulphur compounds and ferrous iron to generate solutions with relatively high redox potential values (Rawlings, 2005; Donati and Sand, 2007). Acidophilic, iron- and sulphur-oxidizing bacteria have been isolated from numerous sulphide mine sites and include of Leptospirillum ferrooxidans, L. ferriphilum, Acidithiobacillus ferrooxidans, A. thiooxidans and A. caldus (Demergasso et al., 2005; Lavalle et al., 2008; Zeng et al., 2010). Copper bioheap leaching processes are limited mostly to secondary sulphides and oxides because their leaching rates are much more favorable than those of the primary Cu-sulphide, chalcopyrite (CuFeS2). Most secondary Cu-sulphides such as chalcocite (Cu2S), digenite (Cu9S5), bornite (Cu5FeS4), and covellite (CuS) can be leached by mesophilic iron- and sulphur-oxidizing acidophiles (Donati and Sand, 2007). Among the most important bacteria in the biooxidation of minerals are those responsible for producing ferric iron and sulphuric acid required for the bioleaching reactions. Acidic ferric sulphate, a powerful oxidizing agent, chemically oxidizes Cu-sulphides, and sulphuric acid is responsible for proton attack and dissolution of minerals (Koleini et al., 2011). In the bioleaching process ferric iron is chemically reduced by reaction with the sulphide mineral matrix, and iron-oxidizing bacteria re-oxidize the iron to the ferric form. In most acidic bioleaching systems, the oxidation-reduction potential predominantly reflects the Fe3+/Fe2+ ratio and thus the activity of iron-oxidizing bacteria.

The purpose of this study was to test the bioleaching of a Cu-sulphide ore from Sarcheshmeh Copper Complex with a relatively high pyrite content using a mixed culture of A. ferrooxidans, A. thiooxidans and L. ferrooxidans. The Sarcheshmeh porphyry copper deposit in Kerman province, Iran is an open-pit mine of Cu-ore (0.8% average grade), which is processed by pyrometallurgical methods (Sarcheshmehpour et al., 2005b). The mine produces a low-grade Cu-ore (about 0.5% grade) as a by-product. In addition, the Sarcheshmeh Copper Complex has a deposit of low-grade Cu-sulphides. These low-grade Cu-ores are potential targets for bioheap leaching as Cu occurs mostly as secondary Cu-sulphides with lesser amount of chalcocryptite. Mineral alterations in oxidized zones have involved partial weathering, with chalcocite and covellite as secondary minerals which have formed layers on pyrite grains in this porphyry deposit. Chalcocite coating of pyrite surfaces and fractures has rendered the ore unsuitable for flotation because of the loss of selectivity due to altered surface characteristics and mixed potential of pyrite. The grade is also too low to warrant conventional mineral dressing–roast–leach–electrowin route.

In general, chalcocite as a single mineral can be floated efficiently with ethyl xanthate as a function of its electrode potential and distinctly separately from pyrite flotation. With a mixture of pyrite and...
chalcocite, as is the case here, the selectivity conferred by the difference in the potentials of the two minerals is decreased (Woods, 2003). While the flotation recovery is a function of the potential also for mixtures of sulphide minerals, chalcocite activates pyrite and pyrite depresses chalcocite in the flotation. Thus the flotation is not efficient as the Cu-concentrate contains too much Fe, and the selectivity is no longer predictable from single mineral studies. Pyrite activated with chalcocite rim also acts as a galvanic couple that enhances Cu dissolution from chalcocite.

Both shake flask and column leaching techniques were used to assess the bioleaching of Cu from the ore in this work. Several mineral salt formulations were also evaluated for the bioleaching process in an effort to rank them in relation to the Cu bioleaching yields.

2. Materials and methods

2.1. Ore sample

A bulk sample of 500 kg of copper bearing ore was taken from the Sarcheshmeh Copper Mine. The ore was crushed and screened to 75% − 12 mm for column leaching and to − 100 μm for shake flask experiments. Partial elemental analysis of the sample used in the column leaching is listed in Table 1. The total Cu content was 0.8% and the H2SO4-soluble Cu-content was 0.2%. The ore sample also contained minor and trace amounts Pb, Ag, Ni, Co and Bi (not analyzed for this study).

Roll bottle tests performed on the ore sample showed a net acid consumption of about 8 kg H2SO4/t. The main copper bearing minerals were chalcocite and, in minor amounts, chalcopyrite and covellite. The sample contained 18.4% pyrite. Mineral microscopy showed that pyrite grains were coated with secondary Cu-bearing minerals, especially chalcocite.

2.2. Bacteria and culture conditions

A mixed culture of mesophilic bacteria, including A. ferrooxidans, A. thiooxidans and L. ferrooxidans was previously enriched from the Sarcheshmeh Copper Mine site (Seyyed Bagheri and Hassani, 2001) and used in bioleaching tests in this study. Bacteria were cultured in 9K mineral salt media in shake flasks with 10% (wt/wt) Cu-bearing sulphide ore, 8.4 g Fe2+ (added as FeSO4∙7H2O), and 2 g elemental S as energy sources per liter. Cultures (10% inocula) were incubated on a shaker at 150 rpm at 32 °C.

2.3. Bioleaching experiments

The mineral salt media used in the bioleaching experiments are listed in Table 2. The formulations were pooled and modified from

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Column 1</th>
<th>Column 2</th>
<th>Column 3</th>
<th>Column 4</th>
<th>Column 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore sample (kg dry wt.)</td>
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<td>39</td>
<td>37</td>
<td>39.5</td>
<td>44.5</td>
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<tr>
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<td>312</td>
<td>296</td>
<td>316</td>
<td>356</td>
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<tr>
<td>Antimicrobial reagent</td>
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<td>No</td>
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<tr>
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<td>9K</td>
<td>E</td>
<td>9K</td>
<td>Dist. H2O</td>
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<td>Closed</td>
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<tr>
<td>Irrigation type</td>
<td>Four days irrigation followed by a four days rest period</td>
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</tbody>
</table>

* Leach solution from the column was passed to solvent extraction for Cu extraction, and the resultant raffinate solution was returned to the column.

Fig. 1. Changes in pH (A), ORP (B), and planktonic cell counts (C) with time in shake flask bioleaching experiments.
various literature sources as indicated in Table 2. The formulation E was specifically designed for the column leaching, with phosphate supplied as H₃PO₄ instead of K-phosphate. Phosphoric acid is relatively inexpensive as a bulk chemical and its use may help reduce K-jarosite precipitation. The mineral salt formulations 9K through D2 (Table 2) were tested in shake flask bioleaching experiments with 10% (wt/wt) suspensions of finely ground (−100 μm) ore material. The cultures were incubated at 32 °C for 16 days and monitored by microscopic counts and measurements of pH and oxidation–reduction potential (ORP). Cell counts were determined using a Neubauer chamber counter with a depth of 0.02 mm and area of 1/400 mm² under a light microscope. Copper dissolution was monitored by daily analysis of the culture solution using atomic absorption spectroscopy.

Five columns (height 200 cm, ID 13.5 cm) were used for column bioleaching tests (Table 3). The columns 1, 2, 3 and 5 were filled with approx. 40 kg crushed ore (75% − 12 mm) which was agglomerated stepwise (50, 80, 120, and 150 g/l) of polyacrylamide and H₂SO₄ solutions using a rotating disc agglomerator at 16–17 rpm with adjustable gradient (set to 45°). Column 4 was filled with unagglomerated ore. Column 5 was used as a chemical control by adding thymol to the leach solution. Microscopic observations as well as ORP measurements were conducted to confirm that column 5 remained abiotic. Columns 1–4 were filled with 9K or E salt solution and inoculated with the mixed culture from the shake flask experiments. The irrigation was performed in closed circuit in columns 1 and 3–5. Each column effluent was passed to a solvent extraction stage in which copper was extracted and the resultant raffinate solution was returned to the specific column. Column 2 was operated in open circuit mode whereby the solution was replaced with 9K mineral salt solution acidified with H₂SO₄. The solution flow and pH of the irrigation solutions for all columns were initially set to 1 ml/min and 1.8, respectively. The leaching schedule was operated with 4 days of irrigation followed by 4 days of rest period. The column tests were run for 184 days. Column effluent solutions were analyzed for pH, acidity (titrimetrically with NaOH), ORP, cell counts, dissolved Cu, Fe²⁺, and dissolved Fe. Cumulative leaching curves for dissolved Cu and Fe were also constructed.

3. Results and discussion

3.1. Shake flask leaching experiments

The purpose of the shake flask experiments was to compare mineral salt formulations for the bioleaching of the −100 μm ore sample by the mixed culture. The ore sample was the only source energy in the shake flask cultures. The changes in pH, ORP, and cell counts over time are shown in Fig. 1A–C. The copper recoveries in the various mineral salt media varied between 89% and 92%, all within the same range. Copper solubilization reached 65% in the sterile control.

The increasing trend of ORP (ΔORP ~280–300 mV) and cell counts were most pronounced with the 9K and C mineral salt solutions and the least with formulation B. The ore material showed acid demand for the first two days before the reaction became acid producing. Changes in pH were clustered and relative differences reflected the buffering of the mineral salt media. The formulation 0.9K contained 1/10 of the mineral salts in 9K and supported less cell counts than the 9K medium. The lowest cell counts were associated with the B, D1 and D2 formulations, although the Cu yields were comparable across all inoculated media. In the sterile control, the pH was relatively constant after initial acid demand and the increase in ORP was <40 mV. Previously, a comparison of several media formulations produced...
3.2. Column leaching experiments

About 80% of the total Cu in the ore was present as sulphide minerals and the remainder as acid soluble Cu (Table 1). Chalcocite and pyrite represented the main Cu and Fe sulphide minerals in the ore. The results of agglomeration tests showed that stable agglomerates could be obtained by using polyacrylamide and H2SO4 as binders. In light of these agglomeration tests, sulphuric acid solution at 50 g/l was subsequently used for agglomeration of the ore.

The corresponding changes in ORP and pH were similar in all inoculated columns (Fig. 2A and B). The ORP increased from 360 mV to 700 mV in 60 days and remained constant thereafter. The pH changes indicated acid demand for the first three weeks before the overall reaction became acid producing and remained at pH 1.5 for the rest of the time course. In the sterile column, the ORP remained at -350 mV and the reaction did not produce net acid. The changes in acidity in column effluents are summarized in Fig. 2C and were consistent with the pH time course.

Bacterial counts showed a lag of 11 days before the counts increased 8 to 9 fold (Fig. 2D). The microscopic counts only represent planktonic cells. The extent of sessile bacterial association with mineral surfaces was not assessed in this study.

Fig. 3A shows the changes in effluent ferrous iron concentrations in each column. The concentration of Fe2+ decreased to negligible levels in the inoculated columns after day 70. Fig. 3B shows the time course of the dissolved Fe concentration in column effluents. After the initial acid consumption, the iron concentration increased considerably, indicating active bioleaching of pyrite. The abiotic control contained 0.02 g Fe2+/l throughout the test. Because of the oxidation of the high pyrite content, it was sometimes necessary to bleed some of the raffinate solution in order to minimize the precipitation of iron in the columns. The cumulative dissolved Fe concentration is shown in Fig. 3C. The cumulative concentration of dissolved Fe did not increase in column 5 effluents (sterile control).

Fig. 4A shows the changes in the dissolved Cu concentration over time in each column. Initially, the Cu levels were 7.5–9.3 g/l representing the acid soluble Cu. During the first three weeks of operation, the Cu concentrations decreased due to the acid demand and pH increases to as high as pH 5. After the acid demand was satisfied, the pH decreased and Cu concentrations increased in the inoculated column effluents. The low levels of Cu in the subsequent time course are due to the bleeding of the raffinate as a means of controlling dissolved Fe concentrations. The cumulative Cu concentrations (Fig. 4B) had the same profile as for cumulative Fe, but the Cu dissolution in the sterile control was

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Fig. 3. Changes in the concentration of Fe2+ (A), dissolved Fe (B), and cumulative dissolved Fe (C) with time in column bioleaching experiments.

Fig. 4. Changes in the concentration of dissolved Cu (A) and cumulative dissolved Cu (B) with time in column bioleaching experiments.
considerably higher than the corresponding Fe dissolution. The final Cu recoveries were 90–91% for columns 1–4 and 50% for column 5 (sterile control). Ore agglomeration (columns 1–3 vs. column 4) did not impact dissolved Fe or other leaching parameters. All inoculated columns displayed comparable recoveries including column 3 (minerals salt formulation E), which had phosphate supplied as phosphoric acid. These results indicated that H$_3$PO$_4$ is a suitable source of phosphate and may reduce Fe(III) precipitation as K-jarosite if used to replace K-phosphate. Similarly, ammonium addition leads to NH$_4$-jarosite formation in bioleaching systems (Niemelä et al., 1994), which may also be contributing to passivation of mineral surfaces.

It is debatable whether supplemental mineral salt formulations are needed in commercial operations. Phosphate and nitrogen sources are essential as they may not be available from the dissolution of the ore matrix. Recent bioleaching studies have shown that the alkali earth metals Ca and Mg and the alkali metal K are solubilized from gangue minerals due to acid attack during the bioleaching of sulphide ores (Dopson et al., 2008, 2009; Cameron et al., in press). While these three—Ca, Mg, and K—are necessary nutrient ions in liquid media for iron- and sulphur-oxidizers, their addition to heap bioleaching systems may be immaterial. Analysis of these ions in column and heap bioleaching solutions can give insightful information in this respect.

4. Conclusions

The Cu-ore sample with high pyrite content was amenable to Cu solubilization via bioleaching. Shake flask studies showed no differences in Cu recovery (89–92%) between different mineral salt formulations used to prepare leach solutions. Cell counts varied but could reflect differences in sessile and planktonic bacterial populations. Similar Cu-recoveries were obtained in the bioleaching columns. The residual Cu in the solids, about 10%, may represent recalcitrant chalcopyrite. Chemical leaching released between 50 and 60% Cu during comparable time courses, whereas the dissolution of Fe from pyrite was considerably more suppressed. The results suggested that agglomeration of the ore is not required for column leaching. Inhibitory substances were not detected in these experiments.

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