Bioleaching of a Copper Sulphide Concentrate by Two Different Strains of Acidophilic Bacteria

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Abstract Two strains of acidophilic Thiobacillus genera, one isolated from the water of a copper mine and another, a pure culture have been used for the processing of a sulphidic copper concentrate with 14.13% Cu, 10.04% Ni, 0.33% Co, 0.71% Mo, 2.28% Fe, 36.4% S and 1.72% SiO₂ generated at UCIL Jaduguda, India. The concentrate has chalcopyrite and pentlandite as the major phases along with pyrite, pyrrhotite, violarite, millerite and molybdenite as the minor phases. The unadapted isolated culture of Acidithiobacillus ferrooxidans dissolved 41% Ni and 35% Co at 308K and pH 2.0 in 60 days from the mixed size (<200 μm) particles. Pyrite (10 wt%) was found to be an effective additive resulting in bioleaching of 81% Ni and 45% Co under above condition; biorecovery being high (90% Ni and 61% Co) from the finest size particles (<50 μm). A. ferrooxidans strains of another source (OU, Hyderabad) adapted over copper concentrate serially for four times at 2.3 pH and used for leaching, improved the kinetics showing biorecovery of 83% Ni and 88% Co in 30 days only with the mixed size particles.

Keywords Pyrite, Complex Sulphide Concentrate, Bioleaching, Bacteria, Redox Potential, Galvanic Interaction

1. Introduction

Ore of uranium at Jaduguda Mines contain significant amount of valuable metals[1] such as copper (0.1%), nickel (0.1%), cobalt (0.006%) and molybdenum (0.02%), besides other ingredients such as apatite (3-4%), rare earths (0.1% including yttrium) and magnete (5.5%). The by-product recovery plant (BRP) of the mill at Jaduguda, has been producing about 1200 t/y complex sulphide concentrate, out of which 600 t/y is a copper concentrate with almost equal amount of a low grade Cu-Ni-silicate tails, besides a saleable moly concentrate. The copper concentrate is not accepted by Hindustan Copper Limited, Ghatila because of high nickel content and therefore, it is stockpiled for want of a suitable processing option.

Galvanic interaction and surface properties of minerals play important role in dissolution of metals from sulphides with more than one mineral. Galvanic effect occurring between conducting and semiconducting minerals in aqueous system is critical in the aqueous processing of ores as in flotation and leaching. For semiconducting minerals such as sulphides, direct contact of different minerals with dissimilar rest potential initiates galvanic effect. These interactions occurring between sulphides involve the flow of electrons from grains with higher potential to grains with lower potential, modifying the Fermi level of both minerals [2],[3]. The mineral or the region with the highest rest potential will act as the cathode of galvanic cell and is protected, whereas that with the lowest rest potential will serve as anode, and its rate of dissolution increase[4-8]. Pyrite addition has a major catalytic effect on the chalcopyrite leaching due to the formation of a galvanic cell between the minerals because of difference in the rest potential[9]; leaching rate of this mineral increased up to a certain level above which further pyrite additions did not improve the leaching[3],[10-12]. Preferential dissolution of nickel over copper from nickel-copper bearing minerals in presence of A. ferrooxidans is reported[13]. Such a leaching behaviour is of practical significance in the selective oxidation of mixed sulphides. In order to turn the complex concentrate of UCIL an economically attractive product, it was considered worthwhile to selectively remove nickel through bioleaching thereby rendering copper concentrate for its conventional processing; results are presented in this paper.

2. Materials and Methods

Copper concentrate was obtained in powder from (≤200 μm) from UCIL Jaduguda. A representative sample analysed by AAS Thermo Jarrell Ash: Smith Hieftje – 8000, contains 14.13% Cu, 10.04% Ni, 0.33% Co, 2.28% Fe, 0.71% Mo, 36.4% S and 1.72% SiO₂. XRD and petrology analysis of concentrate showed the presence of chalcopyrite – CuFeS₂ and pentlandite–(FeNi) S₈ as the major phases, whereas
pyrite–FeS2, pyrrhotite–FeSx, violarite–(FeNi)3S4, millerite-NiS and molybdenite-MoS2 as the minor phases. Petrology of copper concentrate (Figure 1(a)) also indicates that chalcopyrite and pentlandite are the major phases. The pyrite (Amjhore Pyrite Mines, Bihar) used in the experiments as additive had 13.4% Fe and 6.7% S. Wild strains of Acidithobacillus ferrooxidans (A. ferrooxidans) and Acidithobacillus thiooxidans (A. thiooxidans) were isolated and cultured from copper mine water in 9K media in presence of ferrous sulphate and sulphur respectively. The bacterial count of the fully grown culture determined in Petrof-hauser counter was found as 2.0x10⁸ and 1.4x10⁸ cells per ml for A. ferrooxidans and A. thiooxidans respectively.

3. Experimental Procedure

The bioleaching experiment was carried out in 1L conical flask using 25g sample in an orbital motion incubator shaker as reported elsewhere[14]. The experiments were conducted under non-shaking and shaking aerobic conditions with fully grown and unadapted culture of A. ferrooxidans (40mL) and A. thiooxidans (10mL) in presence of pyrite and without pyrite. Wild strains of A. ferrooxidans and A. thiooxidans were isolated and cultured from the copper mine water[14],[15]. During the leaching (control/bioleaching) Fe²⁺ and Fe³⁺ levels were determined and Eh measured against SCE. Bacteria (A. ferrooxidans) were also adapted for four times on the concentrate at pH 2 under the shaking conditions and adapted strains were aseptically transferred in conical flask containing the concentrate at desired temperature. Samples were withdrawn at an interval of 10 days for chemical analyses. Fe(II) content was determined by titrimetric method[16]. Mercuric chloride (0.2g/L) was used in control experiment as a bactericide[17]. At the end of the experiment the slurry was filtered over Whatman (No 41) paper and leach solution and residue were analysed by AAS. The data reported in the text are from the average of duplicate experiments with ±2% variation.

4. Results and Discussion

4.1. Bioleaching without Shaking

Initial experiments were carried out without shaking at 2.0 pH, 5% pulp density (PD) and 308K with particle size of ≤200 µm. The recovery of copper, nickel and cobalt was 0.5%, 13% and 7% respectively in sterile conditions, whereas it was 2.2%, 28% and 20% respectively in 60 days of in presence of bacteria. Results further showed minor dissolution of copper in chemical as well as bio-leaching, but there was some effect of bacterial oxidation on leaching of nickel and cobalt.

4.2. Bioleaching with Shaking

Bioleaching of concentrate (≤200 µm size) was carried out with shaking without additive (data not shown). Copper recovery was very low in sterile (4%) as well as in the bio-leaching (4.8%). The recovery of nickel and cobalt improved with shaking at 100 rpm. About 27% Ni and 24% Co were recovered in control leaching which increased to 43% and 35% respectively 308K in 60 days at pH 2.0 in bioleaching. The improvement in selective nickel dissolution under control and bioleaching may be attributed to galvanic interaction of pentlandite and pyrrhotite minerals with chalcopyrite present in the concentrate.

In initial 10 days, concentration of Fe(II) at 308K was higher in bioleaching as compared to control experiment, but it was oxidised to Fe(III) by bacterial action in 20 days. Beyond 20 days, Fe(III) became almost constant (1.7–1.8 g/L) resulting in continuous increase in bio-dissolution of nickel and cobalt. Low Fe³+/Fe²⁺ ratio and higher E value (425 mV) during bioleaching improved recovery of nickel and cobalt in 60 days. Redox potential was low at 370 mV in control experiments in 60 days signifying lower metal dissolution.

4.3. Bioleaching at Different Temperature in Presence of Pyrite

Higher growth and activities of A. ferrooxidans and A. thiooxidans at higher temperature (308K) favoured dissolution of metals (Table 1). The recovery of copper was no higher than 5% even at 303K and 308K in 60 days with additive, and bioleaching was not very different with that of
control leaching at lower temperature. At 308K bioleaching of nickel was 81% with pyrite as compared to the leaching of 27% in control. With low bacterial activity at the low temperature (293K) nickel biorecovery was very low (23%). A 12-13% nickel recovery in chemical leaching at the low temperature was observed.

Cobalt dissolution pattern (Table 1) was similar to that of nickel. High Co bio-recovery (45%) was achieved at 308K in 60 days in presence of pyrite as compared to 24% metal recovery under the sterile conditions. The bio-recovery with pyrite and chemical leaching were found as 41% and 14% at 303K and very low of 11% and 1% Co, respectively at 293K. Micrograph(Figure 1(b)) of bioleach residue in presence of pyrite reflects the presence of chalcopyrite as the major phase and pentlandite as the minor phase which is corroborated by the XRD study also. Externally added pyrite remains undissolved and can be seen as powdery structure in Figure 1(b).

**Table 1.** Biorecovery of metals at different temperatures, pH 2, 100 rpm, 60 day and ≤200 µm particle size

<table>
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<tr>
<th>Condition</th>
<th>Metal</th>
<th>293 K</th>
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<td></td>
<td>Co</td>
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<td>6</td>
<td>14</td>
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<tr>
<td>Bioleaching with pyrite</td>
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<td>Co</td>
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<td>21</td>
<td>41</td>
<td>45</td>
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### 4.4. Effect of Particle Size

High recovery of metals was achieved with finer size of the particles at 308K. In the presence of pyrite recovery of copper was 7.7% with <50 µm size particles and 3.5% with 200 - 100 µm size particles, whereas nickel recovery was 90% and 86% with <50 µm and 75 - 50 µm size particles, respectively. From the coarser fraction (200 - 100 µm), 36% Ni was dissolved. Similar trend was observed for the recovery of cobalt as 61% metal dissolved with finer size fraction (<50 µm) and only 21% Co was leached out from coarser fraction (200 - 100 µm) in 60 days. About 81% Ni, 45% Co and 5% Cu were leached from the particles of ≤200 µm size in 60 days.

### 4.5. Bioleaching with Adapted Culture

*A. ferrooxidans* of OU, Hyderabad was adapted four times in the 9K media over sterilized concentrate (PD = 10% wt/vol.) in an incubator at 2.3 pH, 308K and 100 rpm. Experiments in presence of adapted *A. ferrooxidans* (Fig. 2) showed the biorecovery of 5% Cu, 83% Ni, 88% Co and 26% Fe in 30 days. In control experiment metal recovery was very low. Higher (559 mV) redox potential in bioleaching (Fig. 3) accounts for high Ni and Co recovery as compared to chemical leaching with low Eh value (366 mV).

Petrological micrograph (Figure 4) of leach residue in presence of concentrate tolerant bacteria shows that chalcopyrite remains the major phase and pentlandite being the minor phase similar to that of Figure 1(b). XRD pattern (Figure 5), shows the absence of millerite and molybdenite in the residue that was leached with pyrite, whereas molybdenite remained intact with concentrate tolerant bacteria. Hydronium jarosite formed during the bioleaching (Figure 5) hindered the dissolution of nickel.
5. Conclusions

Selective dissolution of nickel from copper concentrate is governed by galvanic interaction between minerals phases such as [pentlandite & pyrrhotite (anodic): chalcopyrite & pyrite (cathodic)] and accelerated by bacteria. As a result, high recovery of nickel and low recovery of copper was observed; Cu leaching may increase once most of nickel is leached out. Pyrite (10 wt%) was an effective additive for the biorecovery of metals. This may be attributed to aggressive galvanic interaction of pentlandite/cobaltite with pyrite. Metal dissolution increased with temperature from 293 to 308K because of enhanced bacterial action.

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REFERENCES


