

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

Ores 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 magnetite (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 the Hindustan Copper

Limited, Ghatsila 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 potentials initiates galvanic effect. These interactions occurring between sulphides involve the flow of electrons from grains

with higher potential to grains with lower potentials, 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* was 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 form ($\leq 200 \mu\text{m}$) 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% SiO_2 . Phases present in the concentrate identified by XRD and petrology showed the presence of chalcopyrite - CuFeS_2 and pentlandite - $(\text{FeNi})\text{S}_8$ as the major phases whereas pyrite - FeS_2 , pyrrhotite- FeS_x , violarite- $(\text{FeNi})_3\text{S}_4$, millerite-NiS and molybdenite- MoS_2 as the minor phases. Petrology of copper concentrate (Fig.1(a)) also indicates that chalcopyrite and pentlandite are the major phases. The pyrite (Amjmore Pyrite Mines, Bihar) used in the experiments as additive had 13.4% Fe and

6.7% S. Wild strains of *Acidithobacillus ferrooxidans* (At.f) and *Acidithobacillus thiooxidans* (At.t) were isolated and cultured from copper mine water in 9K media in presence of ferrous sulphate and sulphur respectively.

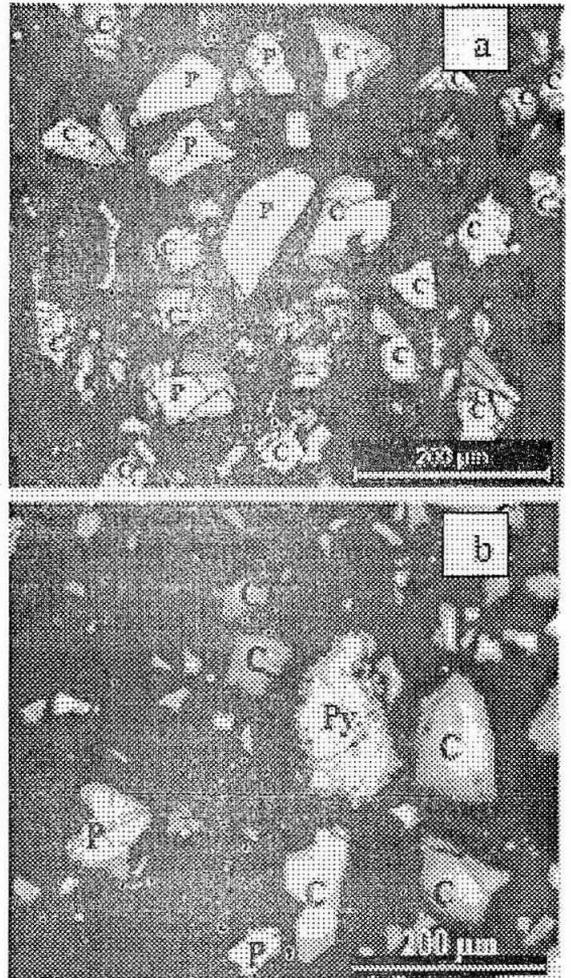


Fig.1. Micrograph of concentrate (a) & bio-leach residue in presence of pyrite (b) [C: Chalcopyrite, P: Pentlandite, Py-Pyrite]

3. Experimental Procedure

The bioleaching experiment was carried out in 1L conical flask at a scale of 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 At.f (40ml) and At.t (10ml) in presence of pyrite and without pyrite. Wild strains of

At.f and At.t were isolated and cultured from the copper mine water [14, 15]. The progress of leaching under sterile (control) condition and in presence of bacteria was monitored by determining the Fe^{2+} and Fe^{3+} levels and E measurements against SCE. Bacteria (At f) 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 for bioleaching at 308K. 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].

4. Results and Discussion

4.1. Bioleaching without shaking: The concentrate containing chalcopyrite and pentlandite as the major phases has adequate energy source such as iron and sulphur for the growth and sustenance of At.f and At.t. Initial experiments were carried out without shaking at 2.0 pH, 5% pulp density (PD) and 308K with particle size of $\leq 200 \mu\text{m}$. The recovery of copper, nickel and cobalt was 0.5%, 13% and 7% respectively in sterile condition, 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 and chemical leaching from the concentrate ($\leq 200 \mu\text{m}$ size) was carried out with shaking without additive (data not shown). Copper recovery was very low in sterile (4%) experiment as well as in the bio-leaching (4.8%). The recovery of nickel and cobalt improved with shaking at 100 rpm as compared to non-shaking condition. About 27% Ni and 24% Co were recovered in sterile experiment in 60 days which increased to 43% for nickel

and 35% for cobalt at pH 2.0 in bioleaching at 308K. Clearly dissolution of the metals has improved by shaking. The improvement in selective nickel dissolution under control and bacterial oxidation conditions 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 Fe^{3+} content (0.05 g/L) in 60 days in sterile experiment was responsible for lower recovery of nickel and cobalt. Very high $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio and higher E value (425 mV) during bioleaching yielded higher 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: Experiments were carried out at different temperatures (293–308K) and results are shown in Table 1. Higher growth and activities of the mesophilic organism viz. *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* at 308K favoured maximum dissolution of metals. The recovery of copper was no higher than 5% even at 303K and 308K in 60 days with additive, and biodissolution was not very different with that under sterile conditions at lower temperature. Temperature played important role in bioleaching of nickel from the concentrate as Ni recovery was 81% with pyrite at 308K as compared to the leaching of 27% in control experiment. 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-chemical 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. Petrology of bioleach residue of copper concentrate in presence of pyrite is shown in Fig.1(b) which reflects the presence of chalcopyrite as the major phase while pentlandite being the minor phase. This is corroborated by the XRD of bioleached residue shown later on. Externally added pyrite remains undissolved and can be seen as powdery structure in Fig.1(b).

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. Phases in concentrate and leach residue were analysed by XRD, which showed the presence of chalcopyrite as the main phase.

4.5. Bioleaching with adapted culture: *A. ferrooxidans* (procured from Osmania University, Hyderabad) was adapted in the 9K media over sterilized concentrate (PD = 10% wt/vol.) serially for four times in an incubator at 2.3 pH, 308K and 100 rpm.

Experiments with adapted strains were carried out under the same condition for 30 days each. Biorecovery of metals in presence of adapted At.f is shown in Fig.2. In 30 days a recovery of 5% Cu, 83% Ni, 88% Co and 26% Fe was obtained. In control experiment recovery of metals was very low. Change in redox potential during the bioleaching is shown in Fig.3. Potential in bioleaching was very high (559 mV) which accounted for high nickel and cobalt recovery as compared to chemical leaching where maximum Eh was 366 mV.

Table-1: Biorecovery of metals from copper concentrate at different temperatures, pH 2, 100 rpm, 60 day and ≤ 200 μm particle size

Condition	Metal	% Recovery			
		293 K	298 K	303 K	308K
Sterile	Cu	2	2	4	4
	Ni	12	13	20	27
	Co	1	6	14	24
Bioleaching with pyrite	Cu	2	2	5	5
	Ni	23	25	73	81
	Co	11	21	41	45

Petrological micrograph of leach residue in presence of bacteria tolerant to copper concentrate is shown in Fig.4. Chalcopyrite remains the major phase and pentlandite became the minor phase very similar to that of Fig. 1(a). XRD pattern (Fig.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 as observed in Fig 5, hindered the dissolution of nickel.

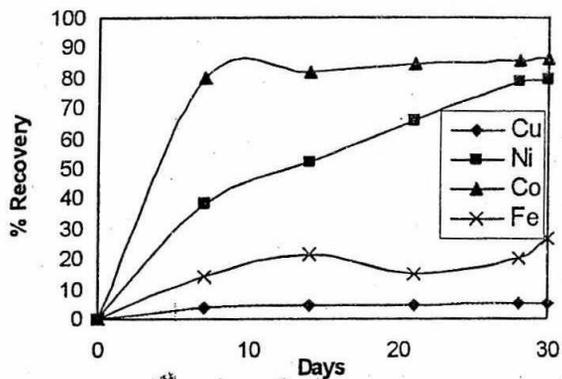


Fig.2: Biorecovery of metals with adapted At.f strains

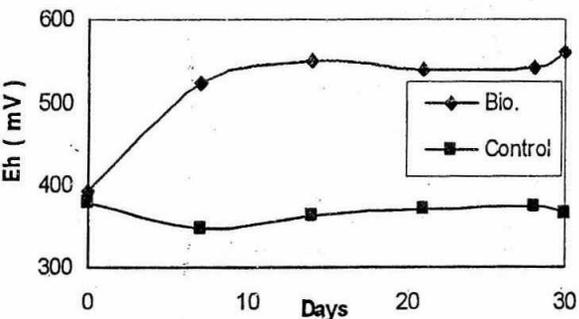


Fig.3: Redox Potential in bio and control leaching with adapted At.f strains 308K, 2.3pH, 10% PD, 100rpm

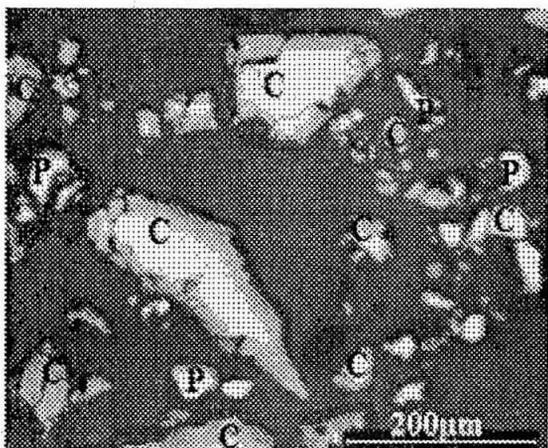


Fig.4: Petrology of leach residue in presence of copper concentrates tolerant bacteria [C-chalcopyrite, P-pentlandite]

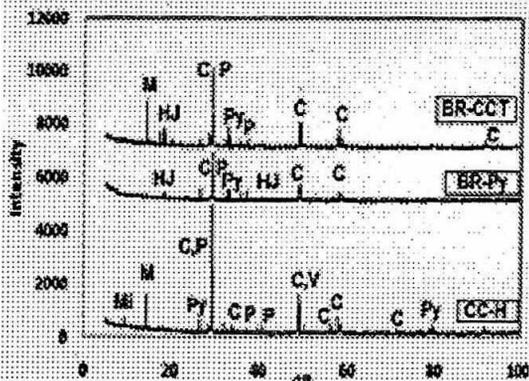


Fig.5. XRD of Cu-concentrate (CC-H), bioleach residue with pyrite (BR-Py) and bioleach residue with concentrate tolerant bacteria (BR-CCT) [C-Chalcopyrite, P-Pentlandite, V-Violarite, Py-pyrite, Mi-Millerite, M-Molybdenite, HJ-Hydronium Jarosite]

5. Conclusions

Selective dissolution of nickel from copper concentrate is governed by galvanic interaction between mineral 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 which may increase once most of the 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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