

# Role of Pyrite in Selective Bioleaching of Metals from a Complex Sulphide Concentrate

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*Keywords: Pyrite; Complex sulphide concentrate; Bioleaching; Bacteria; Redox potential; Galvanic Interaction*

## Abstract

The copper concentrate is a kind of complex sulphide material containing minerals such as chalcopyrite, pyrite, pentlandite, pyrrhotite, etc. with valuable metals like 14% Cu, 10% Ni, 0.33% Co and 0.71% Mo. Bioleaching of copper concentrate was carried out in presence of *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* isolated from the copper mine water to optimise the parameters. In order to understand the role of pyrite, selective bioleaching of 90% Ni and 61% Co was observed in presence of 10% pyrite in 60 days at 308K and 2pH with the particles of size < 50  $\mu\text{m}$  with unadapted culture. While recovery of 81% Ni, 45% Co and 5% Cu were achieved with the mixed size particles of  $\leq 200 \mu\text{m}$  in 60 days time under the above conditions. The selective bacterial dissolution of nickel and cobalt as compared to copper is governed by galvanic interaction between chalcopyrite and pentlandite/pyrrhotite which is accelerated by the addition of pyrite in the concentrate.

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## 1. Introduction

Ores of Uranium Corporation of India Limited, 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 important ingredients in appreciable amounts 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 no more processed 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 played an important role in dissolution of metals from sulphides with more than one mineral. Galvanic effect occurring between conducting and semiconducting minerals in aqueous systems, play an important role in the aqueous processing of ores and minerals such as in flotation and leaching. For semiconductive minerals, such as sulphides, direct contact of different minerals with dissimilar rest potentials initiates the galvanic effect. These interactions occur between sulphides, involving the flow of electrons from grains with higher potential to grains with lower potentials, modifying the Fermi level of both minerals [2], [3]. In nature, most of the metal sulphide minerals have semiconductor properties. The mineral or the region, with the highest rest potential will act as the cathode of the galvanic cell and is protected whereas that with the lowest rest potential will serve as anode, and its rate of dissolution will be increased [4]-[8]. Pyrite addition has a major catalytic effect on the chalcopyrite leaching due to the formation of a galvanic cell between the minerals which is caused by their difference in rest potential [9]. It was observed that as the amount of pyrite in contact with another mineral increases, the leaching rate of this mineral increases 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 At f 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; the results are presented in this paper.

## 2. Materials and Methods

Copper concentrate was obtained in powder form (below 200  $\mu\text{m}$ ) from UCIL Jaduguda. A representative sample obtained by coning and quartering was analysed by AAS Thermo Jarrell Ash: Smith Hieltje – 8000. It contains 14.13% Cu, 10.04% Ni, 0.33% Co, 2.28% Fe, 0.71% Mo, 36.4% S and 1.72%  $\text{SiO}_2$  whereas analysis of size fraction is given in Table 1. Phases present in the concentrate identified by XRD showed the presence of chalcopyrite –  $\text{CuFeS}_2$  and pentlandite –  $(\text{FeNi})\text{S}_8$  as the major phases whereas pyrite –  $\text{FeS}_2$ , pyrrhotite –  $\text{FeS}_x$  and violarite –  $(\text{FeNi})_3\text{S}_4$  as the minor phases. The pyrite used in the experiments as additive was obtained from Amjhore Pyrite Mines, Bihar and contained 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<sup>-</sup> media in present of ferrous sulphate and sulphur respectively.

Table 1: Sieve analysis of copper concentrate

Size in $\mu\text{m}$	% retained	Cumm. % retained
200- 100	12.17	12.17
100- 75	19.16	31.33
75- 50	28.84	60.17
<50	39.83	100.00

### 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). 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  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  levels and Eh measurements against SCE. Bacteria (At f) were also adapted for four times on the concentrate at 2pH under the shaking conditions and adapted strains were aseptically transferred in conical flask, containing the concentrate for bioleaching studies at 308K temperature. The effect of particle size on biorecovery of the metals was investigated with the size fractions as given in Table3. Samples were collected at an interval of 10 days for chemical analyses. The iron (II) content was determined by titrimetric method [16]. No extra nutrient in the leaching stage was added except those available from 9K medium. Mercuric chloride (0.2g/L) was used used in control experiment as a bactericide [17].

### 4. Results and Discussion

#### 4.1 Bioleaching with unadapted culture without shaking

The complex sulphide 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 temperature 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 leaching 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 and unadapted culture in absence of additive

Bioleaching and chemical leaching from the mixed size particles of the concentrate ( $\leq 200 \mu\text{m}$ ) was carried out with shaking without additive. 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 35% for cobalt at 2.0 pH in bioleaching at 308K. It is clear that dissolution of the metals is 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, the concentration of ferrous iron at 308K was higher in bioleaching as compared to chemical leaching in control experiment but it was oxidised to ferric iron by bacterial action in 20 days. Beyond 20 days, ferric ion became almost constant at 1.7 – 1.8 g/L resulting in continuous increase in bio-dissolution of nickel and cobalt. Low  $\text{Fe}^{3+}$  content of 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 development of high Eh of 425 mV in bioleaching led to higher recovery of nickel and cobalt in 60 days. Redox potential was low at 370 mV in chemical leaching for control experiments in 60 days signifying lower metal dissolution.

#### **4.3 Bioleaching at different pH with shaking in presence of additive**

An additive such as pyrite was introduced in the bioleaching experiments as At f and At t may attach preferentially on these as compared to pyrite and other sulphides that were available in the associated form. Also improved/aggressive galvanic interaction with pyrite may result in still higher selectivity for nickel dissolution. The effect of pH (1-2.5) on the biodissolution of metals from copper concentrate in presence of 10 wt% pyrite is shown in Fig 1. Low recovery (4-5%) of copper was observed at 1-2.5 pH in presence of pyrite in 60 days. A 81% Ni recovery was achieved at 2.0 pH and 308K in 60 days in presence of 10wt% pyrite. At a pH of 1.0 when bioaction was much lesser, nickel recovery with pyrite was 74% because of aggressive galvanic interaction. It was due to the galvanic interaction that bioleaching of nickel at pH 2.5 in 60 days was 78% with pyrite. Cobalt dissolution was in the range 39–50 % for the pH of 1-2.5 in presence of pyrite in 60 days at 308K. The dissolution of metals at 308K may further be explained by analysing the  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  concentration and Eh measurement. High recovery of nickel and cobalt was accompanied by higher concentration of  $\text{Fe}^{3+}$  (0.89) and  $\text{Fe}^{3+}/\text{Fe}^{2+}$  (1.45) with Eh value of 429 mV in 60 days.

#### **4.4 Effect of temperature**

Experiments were carried out at different temperatures (293–308K) and results are shown in Table 2. Above this range of temperature bacterial decay starts and below this the bacterial activities are very low for all practical purposes. As the growth and activities of the mesophilic organism viz. *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* were high at 308K, maximum dissolution of the metals was achieved at 308K. It may be seen from Table 2 that the recovery of copper was no higher than 5% even at 303K and 308K in 60 days with additive, whereas the biodissolution was not very different with those under sterile conditions at lower temperature. As mentioned earlier, temperature played important role in bioleaching of nickel from the sulphide concentrate. Nickel biorecovery was 81% with pyrite at 308K as

compared to the chemical dissolution of 27% in control experiment. With low bacterial activity at the low temperature of 293K the nickel biorecovery was very low of 23%. A 12-13% nickel recovery in chemical leaching at the low temperature was observed. Cobalt dissolution pattern shown at different temperatures in Table 2 was similar to nickel. Here also high metal recovery was achieved at high temperature (308K). The cobalt recovery figure was 45% in 60 days at 308K under bio-oxidation in presence of pyrite as compared to 24% metal recovery under the sterile conditions. The bio-chemical recovery with pyrite and chemical recovery were found as 41% and 14% at 303K and very low recovery of 11% and 1% Co respectively at 293K.

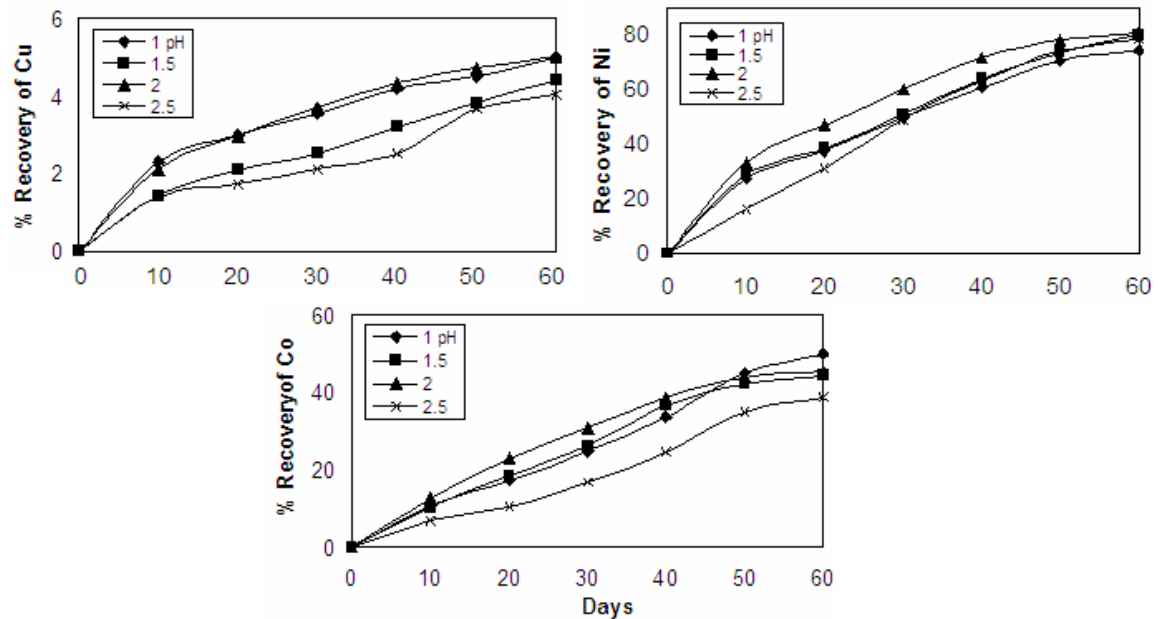


Fig 1: Biorecovery of metals at different pH with 10wt% Pyrite, 308K and  $\leq 200 \mu\text{m}$  particles

Table 2: Biorecovery of metals from copper concentrate at different temperatures, 2 pH, 100 rpm, 60 day and  $\leq 200 \mu\text{m}$  particle size

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

#### 4.5 Effect of particle size

High recovery of copper, nickel and cobalt was achieved with finer size of the particles at 308K. Recovery of copper was 7.7% with  $< 50 \mu\text{m}$  particles and 3.5% with 200 - 100  $\mu\text{m}$  size particles in the presence of pyrite. Nickel recovery was 90% and 86% with  $< 50 \mu\text{m}$  and 75 - 50  $\mu\text{m}$  size particles in presence of pyrite. With coarser size (200 - 100  $\mu\text{m}$ ) of the concentrate, 36% nickel was dissolved. Similar trend was observed for the recovery of cobalt as 61% metal dissolved with

finer size fraction (<50  $\mu\text{m}$ ) and only 21% cobalt recovery was achieved in coarser size fraction (200 - 100  $\mu\text{m}$ ) in 60 days. While recovery of 81% Ni, 45% Co and 5% Cu were achieved with the mixed size particles of  $\leq 200 \mu\text{m}$  in 60 days time under the above conditions. Phases in concentrate and leach residue were analysed by XRD, which showed the presence of chalcopyrite as the main phase in the residue. Hydronium jarosite formed during the bioleaching hindered the progress of reaction.

#### 4.6 Bioleaching with adapted culture under shaking

*Acidithiobacillus ferrooxidans* was adapted in the M9K<sup>-</sup> media over stabilized copper concentrate (PD = 10% wt/vol.) serially for four times under incubator at 2.3 pH, 308K and 100 rpm. Experiments with adapted strains were carried out under the same condition for 30 days each. The biorecovery of metals in presence of 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.

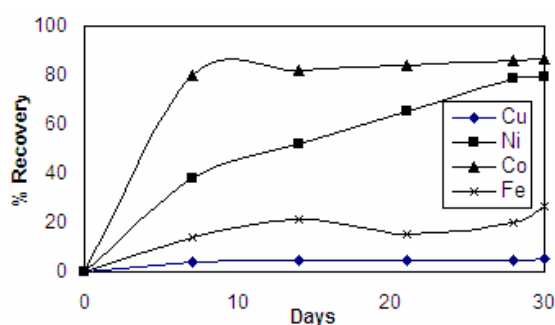


Fig 2: Biorecovery of metals with adapted at f strains 308K, 2pH, 10% PD, 100 rpm and  $\leq 200 \mu\text{m}$  size

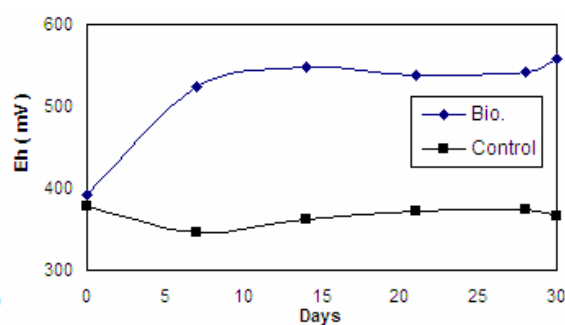


Fig 3: Redox Potential during bio and control leaching with adapted at f strains 308K, 2.3pH, 10% PD, 100rpm

### 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 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 and chemical action.

### 6. Acknowledgement

Authors are thankful to the Director, NML Jamshedpur, India for giving permission to publish the paper.

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