Bio-Assisted Leaching of Copper, Nickel and Cobalt from Copper Converter Slag

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Bioleaching of the converter slag was studied on bench scale using **Thiobacillus ferrooxidans**, an iron oxidising bacteria, for recovery of valuable metals at room temperature. Parameters such as particle size, pH, pulp density, Fe(II) /Fe(III) ratio and amount of Fe(II), additives etc. were optimised to treat the slag. The recoveries of metals from the slag under the sterile and bio-assisted leaching conditions were found as 80.0% and 99.0%Cu in 1920 h, 18.0% and 22.0% Ni in 1680 h and 16.0% and 30.0%Co in 1200 h respectively. The variance in leach recoveries was mainly due to association of valuable metals in the fayalite, magnetite and copper metal/oxide phase. Based on these studies, it may be concluded that the microorganism oxidised the iron available in the solution which accelerated the dissolution of the valuable metals by indirect mechanism.

I. Introduction

Indian Copper Complex, Ghatsila is producing about 15000 t/a converter slag which contains 1–4%Cu, 1–2% Ni, and 0.4–0.8%Co. At present this converter slag is charged to the smelter to recover copper and upto some extent nickel also but cobalt is totally lost in the slag[1]. After recovery of copper the final slag is dumped around the smelter. Dumped slag contains about 0.8–1.0%Cu, 0.1–0.15%Ni and 0.2–0.25%Co which also creates environmental problems. Recycling of the converter slag to the smelter charge increases the burden on the unit thereby decreasing the productivity due to higher charge to metal ratio. This was confirmed by a recent study[2][3] which shows that addition of converter slag to a reverberatory furnace charge increases the slag volume and copper loss. In view of loss of significant amount of metals particularly the strategic metals like Ni and Co, attention has been directed towards decreasing the metal losses in the slag and developing alternative routes for the recovery of metal values from the converter slag as well as dump slag.

Recovery of valuable metals from converter slag has been reported using several lixiviants that include leaching with ferric chloride[4] and pressure leaching with sulphuric acid[5]. In ferric chloride leaching of converter slag extraction of nickel and cobalt is very low as 28% nickel and 24% cobalt was recovered with above 90% copper recovery. Pressure leaching using sulphuric acid showed high recovery but it could be expensive due to the use of high pressure autoclaves. Some attempts were also made to recover the metals from converter slag at different institutes in India using different lixiviants[6][7] and pyrometallurgical-techniques[8]. These processes suffer from one drawback to other and any viable route is yet to emerge for processing such a resource. The converter slag becomes still more important from the point of non-availability of a cobalt reserve in India and therefore this slag may be cosidered the richest known source for the country.

The bioprocessing is considered a clean technology for processing of lean grade sulphide ores and is found suitable for pocket deposits[9]. The process has been industrially exploited[10] for recovery of different non-ferrous metals. As regards processing of oxidic ores, some attempts have been made to treat lateritic nickel ore by microorganisms like **Aspergillus niger**[11]–[13]. To treat cobalt-rich ferromanganese crust, **Thiobacillus ferrooxidans** (Tf) have been used with elemental sulphur or pyrite as substrate[14]. Leaching of copper and zinc from oxidised ores by fungi[15] have been also reported. The use of **Aspergillus niger** has resulted in dissolution of valuable metals from converter slag[16]. During the bioleaching of metals from oxide ores by fungi, it is very critical to maintain certain conditions and under varying environment the reaction may cease to proceed due to uncertainties associated with the behaviour of the microorganism. A recent study[17] shows that Tf can be used for bioleaching of zinc and manganese from a slag sample. Since ferric chloride[4] is a known lixiviant for dissolution of metals from converter slag, Fe(III) generated by bio-oxidation of dissolved Fe(II) with Tf, can be adequately applied for this purpose through the so-called indirect mechanism. The kinetics and biochemical mechanisms of ferrous oxidation process have been widely studied[18]–[21]. Imaizumi[21] reported the possible industrial application of microbial oxidation, whereas Rao *et al.*[22] proposed Tf to be an excellent oxidant for Fe(II) in acidic solution. The investigations by Wiertz[18] clearly demonstrated that the rate of bio-oxidation of Fe(II) with Tf was higher for ferrous sulphate without sulphur than in presence of sul-

phur. Taking into account the advantage of Fe(III) for leaching, the present study was undertaken for the bio-assisted leaching of valuable metals from converter slag using Tf, a proven iron oxidising microorganism. The results are discussed in this communication.

II. Materials and Methods

1. Converter slag

Converter slag obtained from the Indian Copper Complex, Hindustan Copper Limited, Ghatsila was used for these studies. Slag was ground and sieved to the various size fractions as shown in **Table 1**. A representative sample of slag obtained by coning and quartering was analysed by Atomic Absorbtion Spectrophotometer; the composition is shown in **Table 2**. The chemical analysis of various sieve fraction of converter slag is shown in **Table 3**. It may be seen that the amount of copper, nickel and cobalt remains the same in the coarser fraction. In the finer fraction below 75 µm, the amount of copper increases to 2.0% with decrease in cobalt content from 0.65% to 0.48%.

2. Phases in the converter slag

The converter slag is greenish black in appearance with brilliant lusture. Magnetic material is very high (85%) in the slag. X-ray Diffraction of the converter slag shows that the major phases are fayalite ($2FeO \cdot SiO_2$) and magnetite (Fe_3O_4) whereas copper silicate ($CuO \cdot SiO_2$) and

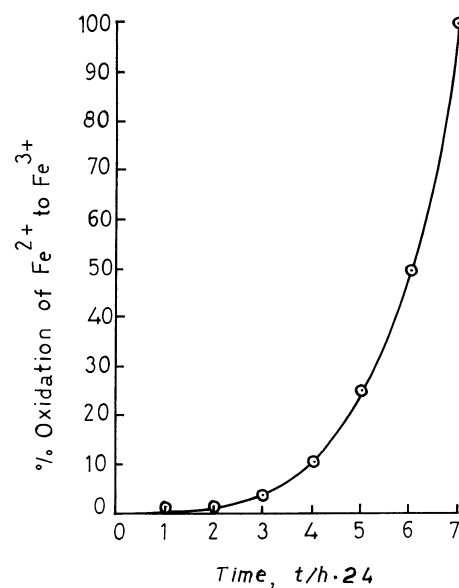
Fig. 1 Isolation of Thiobacillus ferrooxidans in 9 K medium. pH 2.0, Temp. 308 K, Shaker speed 80 min^{-1}.

wustite (FeO) are the minor phases. As regards morphology, sub-rounded to rounded grains of copper metal/oxide are reported[23] to be present in the converter slag. The metallic prill occurs either within crystals of magnetite or surrounded by the microlites of fayalite. Digenite (Cu–S) grains are also reported within the magnetite. Glassy/non-crystalline silicate phase has also been found.

Nickel and cobalt do not form independent mineral phases. Nickel occurs in solid solution in magnetite and metallic copper. Iron in the slag is present as both magnetite and fayalite. Silicate in the slag is contributed by both fayalite and the glassy phase.

3. Bacteria

Thiobacillus ferrooxidans (Tf) and **Thiobacillus thiooxidans (Tt)** were used in the experiments. The source of bacteria was mine water which contains Tf and Tt[24]–[27]. Mine water was collected from Mosaboni mines of Indian Copper Complex, Ghatsila. Bacteria were isolated in 9 K media using ferrous sulphate and elemental sulphur as energy source for Tf and Tt respectively. The oxidation of ferrous sulphate to ferric sulphate by Tf at 2.0 pH, 308 K and shaking speed 80 min^{-1}, is depicted in **Fig. 1** which represents indirectly the growth of the Tf.

4. Mechanism of bioleaching

The most obvious organisms used for leaching of metals from ore are **Thiobacillus ferrooxidans (Tf)** and **Thiobacillus thiooxidans (Tt)**. In case of sulphide ores, Tf directly attach on sulphide mineral and form metal sulphate. It can also generate a lixiviant in the form of ferric sulphate for solubilising copper sulphide through indirect mechanism. Tt attach directly on sulphur in the presence of water and oxygen to form sulphuric acid. During bioleaching of converter slag which is mostly

Table 1 Fractional size analysis of converter slag.

Size in µm	Percentage retained	Cumm.%age retained
+200	0.28	0.28
−200+150	40.51	40.79
−150+100	17.26	58.05
−100+75	11.48	69.53
−75	30.47	100.00

Table 2 Chemical analysis of converter slag.

Percentage of the elements					
Cu	Ni	Co	Fe	S	C
1.80	0.95	0.60	48.00	0.36	0.23

Table 3 Chemical analysis of different size fraction of converter slag.

Size in µm	Percentage of the elements			
	Cu	Ni	Co	Fe
−425+200	1.75	0.97	0.67	48.90
−200+150	1.70	0.95	0.65	48.90
−150+100	1.70	0.97	0.64	48.00
−100+75	1.70	0.96	0.65	48.00
−75	2.00	0.95	0.48	46.00

oxidic/silicious material, the possibility of direct attack of microorganism may not be prominent and the dissolution of the metals is expected to follow indirect mechanism. The expected reaction mechanism[28][29] can be represented as below.

In presence of air the minor amount of copper sulphide present as digenite reacts biologically to dissolve the metal.

$$CuS + 2O_2 \xrightarrow{\text{Bact.}} CuSO_4. \qquad (1)$$
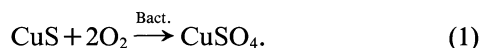
Magnetite/wustite present in the slag reacts with sulphuric acid and forms ferrous sulphate.

$$Fe_3O_4 + 4H_2SO_4 \rightarrow FeSO_4 + Fe_2(SO_4)_3 + 4H_2O. \qquad (2)$$

$$FeO + H_2SO_4 \rightarrow FeSO_4 + H_2O. \qquad (3)$$
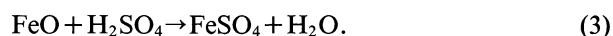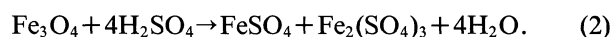
Thiobacillus ferrooxidans, an iron oxidising bactaria then oxidise dissolved ferrous sulphate of the solution to ferric sulphate

$$4FeSO_4 + 2H_2SO_4 + O_2 \xrightarrow{\text{Bact.}} 2Fe_2(SO_4)_3 + 2H_2O. \qquad (4)$$
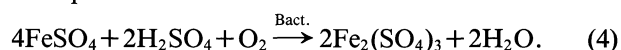
Ferric sulphate available in the solution reacts chemically with small amount of metallic sulphide to produce metal sulphate.

$$MS + Fe_2(SO_4)_3 \rightarrow MSO_4 + 2FeSO_4 + S^0$$

$$(M: Cu, Ni, Co). \qquad (5)$$
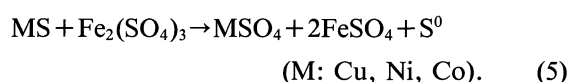
Sulphur is oxidised by **Thiobacillus thiooxidans** to sulphuric acid[27].

$$2S^0 + 2H_2O + 3O_2 \xrightarrow{\text{Bact.}} 2H_2SO_4. \qquad (6)$$
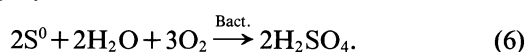
Metallic (M) copper, nickel and cobalt of the slag react chemically with ferric sulphate and form metal sulphate.

$$M + Fe_2(SO_4)_3 \rightarrow MSO_4 + 2FeSO_4. \qquad (7)$$
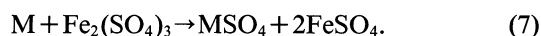
The high amount of ferric sulphate is continuously produced in the biological oxidation of ferrous sulphate from aqueous solution as reported[18][22] recently. The bacterial oxidation of Fe(II) has been reported to be comparable to chemical oxidation using strong oxidants. Thus, ferric sulphate formed *in-situ* in the system takes part appreciably in the dissolution of metal oxides of Cu, Ni and Co of the slag in acidic medium.

$$MO + Fe_2(SO_4)_3 + 2H^+ \rightarrow MSO_4 + 2FeSO_4 + H_2O. \qquad (8)$$

Thus, initial dissolution of iron in the chemical process and the generation of ferric sulphate in the biological oxidation, enhances the leaching of valuable metals by indirect mechanism. The dissolution process is thus bio-assisted to recover copper, nickel and cobalt from the converter slag.

5. Experimental procedure

Bioleaching of converter slag was done initially to study the feasibility of the process. A sample of −200 μm was selected for bioleaching. 0.025 kg of each samples was placed in the conical flask. 450 mL of water and 40 mL of Tf as well as 10 mL of Tt fully grown and active culture were added in each flask. No extra nutrient in the

leaching stage was added except those available from 9 K medium. The effect of addition of ammonium sulphate on leaching was separately studied. The initial pH was adjusted to 2.0 and it was maintained from time to time by (10 N) sulphuric acid addition unless stated otherwise at room temperature (305 K). The experiments were carried out under non-agitated aerobic condition. Sample was collected at the interval of about 240 h for complete metal analysis by Atomic Absorption Spectrophotometer (AAS). In order to know the amount of Fe(II) in the leaching vessel, it was analysed volumetrically against standard solution of potassium dichromate using diphenylamine as the indicator. The amount of Fe(III) was deduced by difference of this value and that obtained by AAS. The pH of leaching media was varied from 1.0 to 3.5 and maintained during the entire period of leaching study. Volume of the leach slurry was maintained by water to account for losses in sampling for analysis.

Under the similar conditions of leaching viz. the culture, solid-liquid ratio and pH, experiments were also carried out with the addition of ammonium sulphate and sodium chloride to study their effect on recovery of the metals. The solid-liquid ratio was varied from 1:10 to 1:30 keeping other conditions same as mentioned above. Particle size of converter slag was varied from −425 + 200 to −75 μm, each size fraction was placed in the separate conical flask at solid-liquid ratio 1:20. For growing and isolation of the culture and chemical analysis, AnalaR grade reagents were used.

III. Results and Discussion

The powder sample was initially subjected to leaching in presence of bacteria. The sterile experiments were also carried out under the similar conditions without any microorganism. The results shown in **Fig. 2** indicate almost complete leaching of copper with bacteria within 1920 h whereas 80%Cu was dissolved out in the same period of leaching without bacteria. 22% Nickel with bacteria and 18% nickel without bacteria were leached out in 1680 h. In case of cobalt, 30% metal dissolution was observed under bio-assisted leaching in 1200 h as compared to recovery of 16% in the same period under sterile condition. Results from Fig. 2 also indicate that the bio-action during initial 240 h was insignificant and the dissolution of copper, nickel and cobalt was mainly governed by chemical leaching. The leaching of copper in presence and absence of Tf in 720 h was 75% and 22% respectively and bio-assisted dissolution of the metal was appreciable. Dissolution of nickel in sterile and bio-assisted leaching conditions improved beyond 480 h. The bioaction was also prominent for dissolution of cobalt from 480 h onwards. In 960 h, the enhanced recovery of cobalt was observed from 17 to 30% due to bioaction resulting in presence of higher ferric ions.

The Fe(II)/Fe(III) and Fe(II) concentration profiles given in **Fig. 3** show the progress of bioleaching. It may be noted that the ratio Fe(II)/Fe(III) and Fe(II) content were lower under bioaction as compared to the leaching
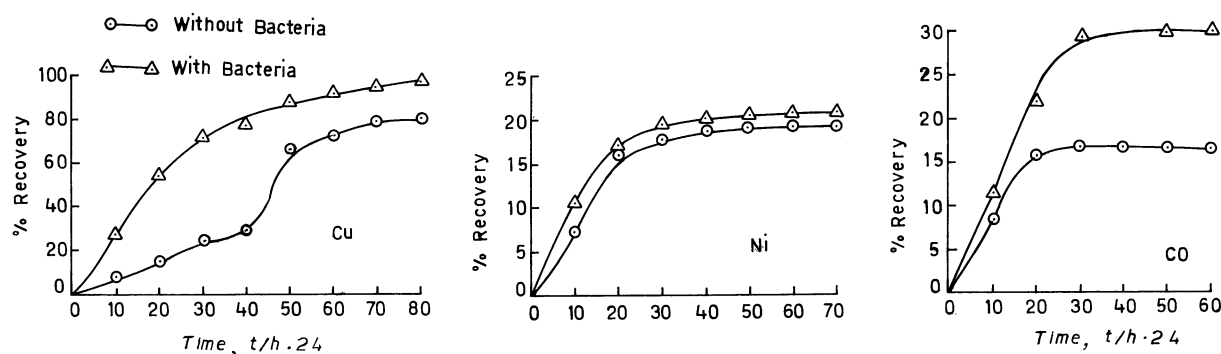
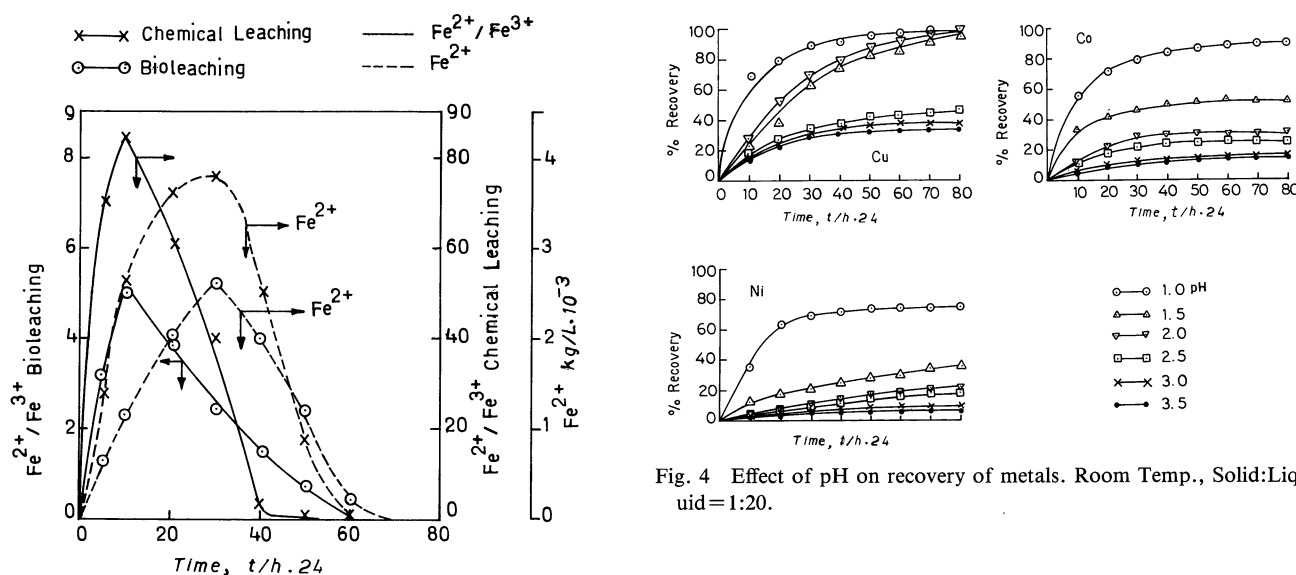Fig. 2 Chemical leaching and bioleaching of converter slag. 2.0 pH, Room Temperature, Solid:Liquid=1:20.

Fig. 3 Fe^{2+}/Fe^{3+} ratio and Fe^{2+} (kg/L·10^{-3}) during the leaching of converter slag. 2.0 pH, Room Temperature, Solid:Liquid=1:20.

Fig. 4 Effect of pH on recovery of metals. Room Temp., Solid:Liquid=1:20.

without bacteria upto 960 h. As a result, the higher recovery of the metals was observed. In 1440 h, the ferrous level dropped due to the covering of the slag surface by jarosite. This may be responsible for poor dissolution in the longer duration. These data confirm the bioassistance in metal leaching by oxidising ferrous ion to ferric ion which subsequently dissolved the valuable metals through indirect mechanism. The recovery of nickel and cobalt in presence of bacteria was quite low as compared to the recovery of copper. This may be attributed to association of these metals in the slag sample. Based on the results it appears that nickel and cobalt are associated with magnetite/fayalite matrix as reported earlier. Therefore, these metals are only partially attacked during leaching resulting in lesser recovery. The association of these metals are primarily governed by the condition in furnace operation during the converting stage. For an instance, slower cooling, higher settling time and lower viscosity of the slag provide lesser copper loss[3].

1. Effect of pH on recovery of metals

pH is one of the most important parameters which affects the bioleaching process. Bioleaching of converter slag was done in the pH range 1.0–3.5 at solid-liquid ra-

tio 1:20 and room temperature. The amount of Tf culture was same in all the experiments. Data plotted in **Fig. 4** show that bio-action was maximum at pH 2.0. Copper recoveries at pH 1.0 and 1.5 were mainly governed by chemical dissolution with almost no bacterial oxidation due to decreased bacterial activity[30] and at pH 2.0 it was bioassisted leaching, thus the recoveries were almost same (98–99%) in the pH range 1.0–2.0. Thereafter, the copper recovery decreased with increasing pH. At pH 2.0 bacterial action is reported to be very fast and at lower pH viz. 1.5 and 1.0 bacterial population is significantly lowered and chemical reaction becomes predominant. Similarly, the higher recoveries (Fig. 4) of nickel and cobalt at pH 1.0 and 1.5 are mainly due to chemical reaction and at pH 2.0, it is the bioassisted leaching. At higher pH of 2.5–3.5, the recoveries decreased due to jarosite formation on the slag particles, which is identified by XRD analysis.

2. Acid consumption during leaching

Thiobacillus thiooxidans produce acid from sulphide minerals but some acid must be present initially for maintaining pH of leach liquor. As the amount of sulphur in the converter slag is 0.4–0.5%, autogeneration of acid is expected to be quite lesser. Consumption of sulphuric acid (36 N) during bioleaching of converter slag is shown in **Fig. 5**. It is clear that initial acid requirement for leaching was sufficiently high which was 15 mL at pH 1.0 and
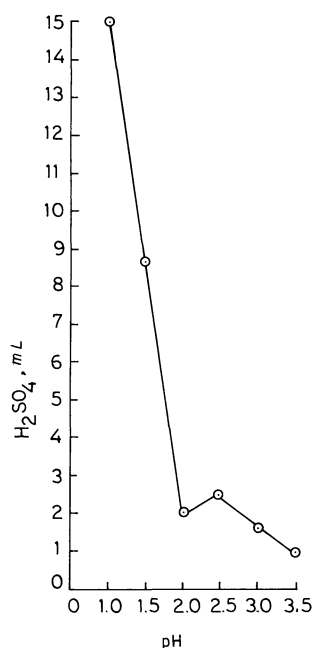
Fig. 5   Consumption of H_2SO_4 in maintaining pH of leach liquor at room temperature and solid:liquid = 1:20. Time: 1920 h, Acid: 36 N H_2SO_4.

Fig. 6   Effect of ammonium sulphate on recovery of metals. pH = 2.0, Temp. = Room temp.

8.6 mL at pH 1.5. The acid requirement at pH 2.0 and above was appreciably lower. Due to higher activity of bacteria at pH 2.0 more acid is produced. The sterile control experiments carried out at 2.0 pH show that 75% more acid was consumed in chemical leaching than bioassisted leaching of converter slag.

3.   Effect of ammonium sulphate on recovery of metals

Experiments were also carried out using ammonium sulphate as an additive. The amount of ammonium sulphate was varied from 1–5% of the amount of converter slag at 2.0 pH and room temperature. Results are shown in **Fig. 6**. Ammonium sulphate is known to be one of the most important nutrients of bacteria. It is apparent from the plot that copper recovery varied in the range 92–99% and nickel 17–22% in 1680 h. Cobalt varied from 30 to 40% in 1200 h. It is also clear that recoveries of nickel and cobalt were slightly more in presence of 4% ammonium sulphate but in case of copper the recovery was marginally higher with 1 or 2% ammonium sulphate.

4.   Effect of sodium chloride on recovery of metals

Experiments were also done with sodium chloride which was varied from 1–5 mass% of converter slag at 2.0 pH, room temperature and 1:20 solid-liquid ratio in presence of Tf and results are shown in **Fig. 7**. These results indicate that 1%NaCl improved the rate of copper recovery and higher amount of the additive suppressed copper leaching. About 99% copper was recovered with 1%NaCl where as recovery dropped to 85% copper with 5% sodium chloride in 1680 h of leaching. But, in case of nickel and cobalt the effect of sodium chloride addition was favourable. A recovery of 30%Ni and 45%Co with
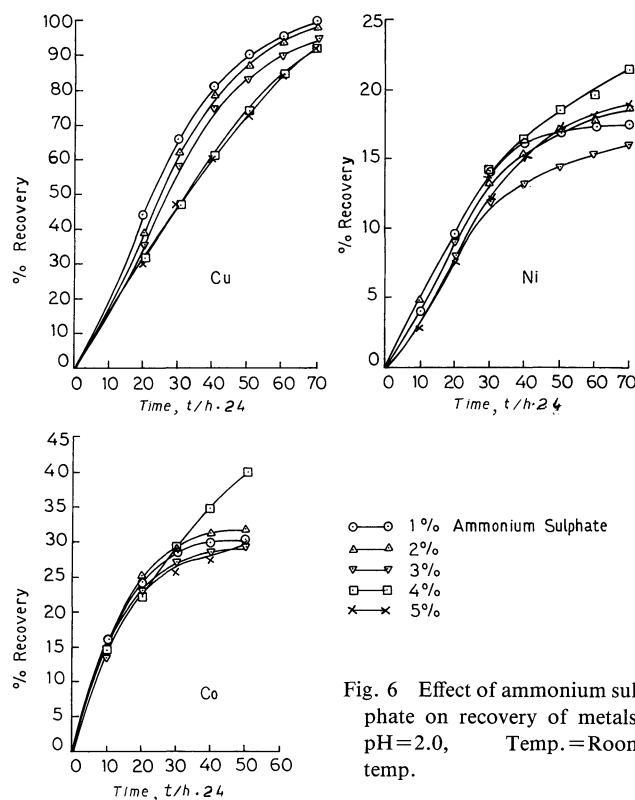
4–5%NaCl was obtained in 1920 h and 1200 h respectively. It may also be seen that addition of sodium chloride led to higher nickel and cobalt recovery as compared to the addition of ammonium sulphate. These results indicate the possibility of higher cobalt and nickel recovery along with copper from the slag. The improvement in these recoveries may be attributed to the effect of anions present in the solution.

Figure 8 indicates the plot of Fe(II)/Fe(III) and ferrous ion concentration in presence of ammonium sulphate and sodium chloride during bioprocessing of converter slag. It is interesting to note that Fe(II)/Fe(III) values in presence of ammonium sulphate and sodium chloride were 57.3 and 55.3 respectively in 240 h of leaching. The higher ratios with additives as compared to Fe(II)/Fe(III) without additive (5.0, Fig. 3) are attributed to lag period of the bacteria undergoing adaptation. Therefore metal recoveries were almost similar (Figs. 2, 6, 7). The value of Fe(II)/Fe(III) with ammonium sulphate and sodium chloride decreased sharply to zero in 960 h, indicated the improved biooxidation resulting in higher recoveries of valuable metals. The corresponding Fe(II)/Fe(III) was 1.5 in 960 h in case of bio-assisted leaching without any additive (Fig. 3). The lower ratio as mentioned above was responsible for improved bio-oxidation with additives. These results are similar to earlier studies reported by Vorreiter et al.[31] who indicated 6–8% higher copper recovery during bioleaching with Tf adapted to 8.2×10^{-3} kg/L sodium chloride medium. The results further show the lower concentration of Fe(II) in presence of sodium chloride as compared to the addition of ammonium sulphate which inferred the
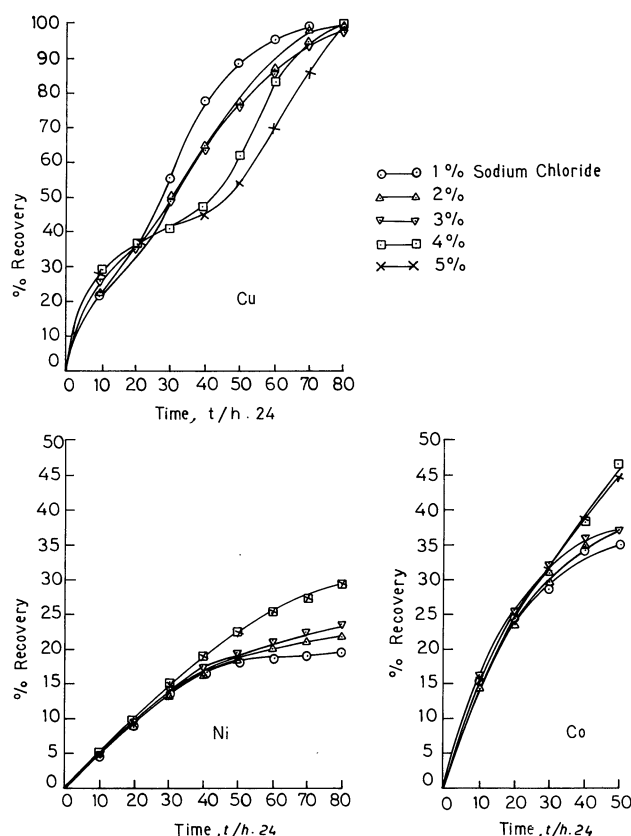
○——○ 1 % Sodium Chloride
△——△ 2%
▽——▽ 3%
□——□ 4%
✕——✕ 5%

Fig. 7   Effect of sodium chloride on recovery of metals. pH = 2.0, Temp. = Room temp., Solid:Liquid = 1:20.

Solid : Liquid
○——○ 1 : 10
△——△ 1 : 15
▽——▽ 1 : 20
□——□ 1 : 25
✕——✕ 1 : 30

Fig. 9   Effect of solid-liquid ratio on recovery of metals. pH = 2.0, Room Temperature.

△——△ $(NH_4)_2 SO_4$ 1% OF SLAG
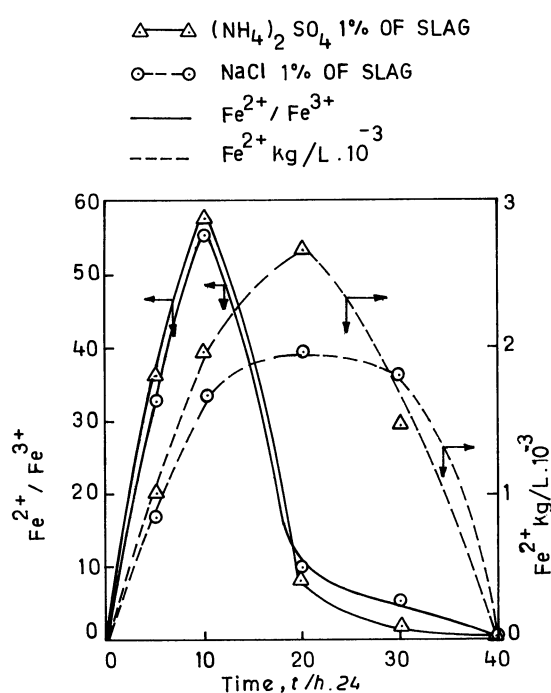
○- - -○ NaCl 1% OF SLAG

———— Fe^{2+}/Fe^{3+}

- - - - Fe^{2+} kg/L . 10^{-3}

Fig. 8 Fe^{2+}/Fe^{3+} ratio and Fe^{2+} (kg/L·10^{-3}) during bioleaching of converter slag with addition of $(NH_4)_2SO_4$ and NaCl. 2.0 pH, Room Temperature, Solid:Liquid = 1:20.

○——○ -425 + 200 μ m
△——△ -200 + 150
▽——▽ -150 + 100
□——□ -100 + 75
✕——✕ - 75

Fig. 10   Effect of particle size on recovery of metals. pH = 2.0, Room Temperature, Solid:Liquid = 1:20.

higher rate of bio-oxidation of Fe(II) with NaCl.

5.   Effect of solid-liquid ratio

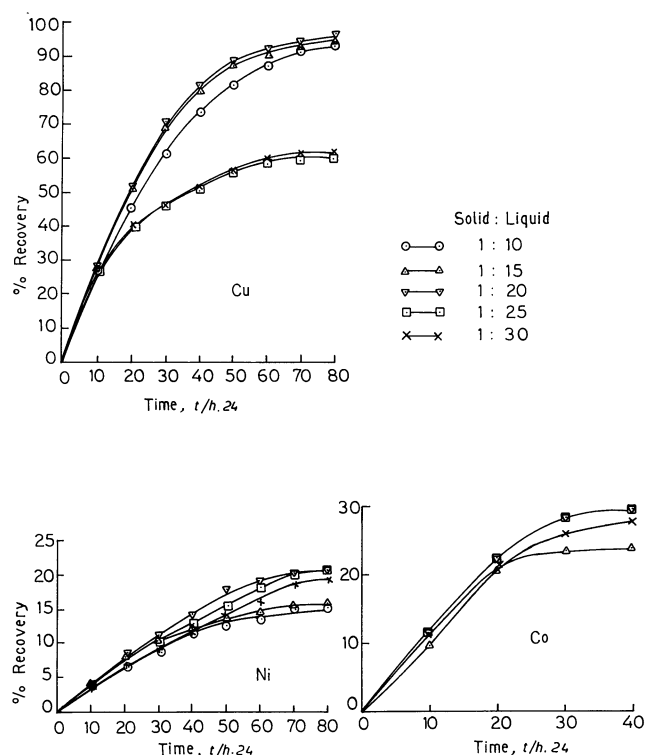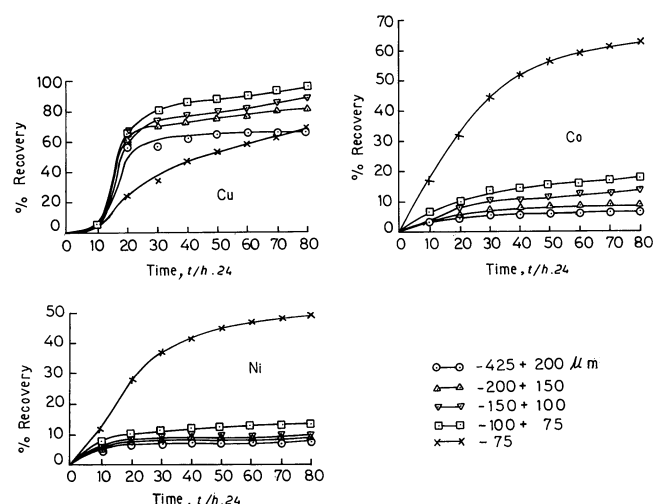From **Fig. 9** it is clear that recovery of copper is much higher for the solid-liquid ratio of 1:10 to 1:20 but in case of nickel and cobalt the recovery was higher at higher solid-liquid ratio of 1:20 to 1:25. Therefore, most suitable solid-liquid ratio for uniformly good recoveries of copper, nickel and cobalt was 1:20 and this ratio was used for further experiments.

6.   Effect of particle size

Study of particle size effect is shown in **Fig. 10**. In case of copper when fineness increased −75 μm its recovery decreased drastically from 96% to 66%. This could be mainly due to poor permeation of the leachant to oxidise the copper present in the fine size. Nickel and cobalt
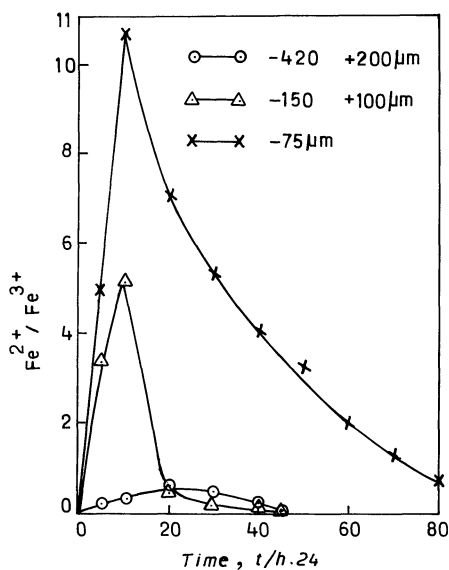
Fig. 11 Fe^{2+}/Fe^{3+} ratio during bioleaching of different particle size of converter slag. 2.0 pH, Room Temperature, Solid:Liquid=1:20.

Table 5   XRD phase analysis in slag.

Phase	ASTM peaks		Observed peaks	
	d	I/I_0	d	I/I_0
Fayalite	3.556	55	3.5463	28.9
	2.829	86	2.8195	100.0
	2.565	45	2.5606	34
	2.500	100	2.496	46.3
	1.7781	79	1.7751	21.8
Magnetite	2.967	30	2.956	21
	2.532	100	2.5216	45.3
	2.0993	20	2.0927	17.8
	1.6158	30	1.6121	19.7
	1.4845	40	1.4802	20.7
Copper silicate	4.870	60	4.8267	15.2
	2.431	50	2.4026	20.9
	2.583	90	2.5606	34
	2.100	35	2.0927	17.8
Wustite	2.490	80	2.496	46.3
	2.153	100	2.1858	13.0
	1.523	60	1.5203	16.9
	1.299	25	1.3088	16.1

Major phases: Fayalite and Magnetite.
Minor phases: Copper silicate and Wustite.

recoveries show increasing trend with fineness of the particles. 14% Recoveries of nickel and cobalt were observed when particle size was +75 µm but below 75 µm, recoveries of nickel and cobalt increased drastically to 50% and 64% respectively. This is due to the fact that finer particles were increasingly exposed to lixiviant that dissolved nickel and cobalt oxides/metals found in the magnetite phase. In the leaching of coarser size fraction, the ferrous ion concentrations as shown in **Table 4** and **Fig. 11** were much lesser and in 1200 h Fe(II) was absent. Therefore, dissolution of cobalt and nickel became insignificant after 1200 h. However, the ferrous ion with finer fraction (−75 µm) of the slag continued to maintain higher profile upto 1920 h indicating the enhanced leaching of the two metals. The ferric ions oxidized by bacterial action on ferrous ions, were involved in chemically dissolving the metals.

The XRD identification of the phases can be seen from **Tables 5** and **6**. The leach residues obtained from slag contained fayalite and magnetite as the major phases that were also present in the slag sample. Besides these, residues contained goethite (FeO·OH) and hydronium

jarosite [$H_3OFe_3(SO_4)_2(OH)_6$] in smaller amounts which were formed during the leaching process. The wustite phase present in the slag disappeared in the leach residue as it chemically dissolved as per reaction (3) given earlier.

IV. Conclusion

Based on the work carried out for the processing of the converter slag through bio-assisted leaching, the following conclusions are drawn.

(1) The dissolution of copper, nickel and cobalt from the slag was initially governed by the chemical leaching. In the presence of Thiobacillus ferrooxidans, the dissolved ferrous ions were oxidised to ferric state by bio-action. The ferric ions were responsible for enhanced recovery of copper, nickel and cobalt from the slag. The indirect mechanism appears to be mainly responsible for bio-assisted leaching of the metals.

(2) The lower concentration of Fe(II) and Fe(II)/

Table 4   Amount of Fe(II) and Fe(III) ions during bioleaching of different size fraction of slag.

Time h	−420+200 µm		−150+100 µm		−75 µm	
	Fe(II) $kg/L \cdot 10^{-3}$	Fe(III) $kg/L \cdot 10^{-3}$	Fe(II) $kg/L \cdot 10^{-3}$	Fe(III) $kg/L \cdot 10^{-3}$	Fe(II) $kg/L \cdot 10^{-3}$	Fe(III) $kg/L \cdot 10^{-3}$
120	0.202	0.840	0.802	0.240	1.004	0.200
240	0.280	1.070	1.676	0.324	2.514	0.236
480	0.558	0.942	0.838	1.812	7.400	1.040
720	0.418	0.842	0.280	1.920	9.216	1.744
960	0.280	1.200	0.280	2.400	9.774	2.402
1200	0.000	1.452	0.000	2.000	10.612	2.242
1440	—	—	—	—	9.774	4.762
1680	—	—	—	—	8.024	6.204
1920	—	—	—	—	4.306	7.212

Table 6   XRD phase analysis in the leach residue.

Phases	ASTM peaks		Observed peaks	
	d	I/I_0	d	I/I_0
Fayalite	3.556	55	3.553	26.5
	2.829	86	2.8233	36.3
	2.565	45	2.5653	21.9
	2.500	100	2.4993	42.7
	1.7735	65	1.7721	25.0
Magnetite	2.967	30	2.9620	29.3
	2.532	100	2.5256	58.2
	2.0993	20	2.0947	36.5
	1.6158	30	1.6131	30.0
	1.4845	40	1.4819	25.9
Goethite	4.183	100	3.9629	17.1
	2.4890	10	2.4993	42.7
	2.450	50	—	—
	2.253	14	2.2495	17.3
	1.7192	20	1.7114	18.2
	1.5614	8	1.560	16.5
Hydronium jarosite	5.100	100	5.1372	43.3
	3.13	90	3.1102	48.2
	3.090	65	3.1102	48.2
	1.839	30	1.8309	24.8

Major phases: Fayalite and Magnetite.
Minor phases: Goethite and Hydronium jarosite.

Fe(III) ratio in the bio-assisted leaching experiments as compared to chemical leaching under sterile conditions further suggested the role of microorganism during metal dissolution process.

(3)   The recoveries under identical conditions without and with microorganism were 80% and 99% for Cu in 1920 h, 18% and 22% for Ni in 1680 h, and 16% and 30% for Co in 1200 h.

(4)   The optimum metal dissolution in presence of bacteria was observed at pH 2.0, pulp density (S/L) 1:20 and particle size -75 μm excepting copper where $-100+75$ μm fraction was more suitable. Maximum recovery of nickel and cobalt obtained was 50% and 64% respectively with -75 μm fraction in 1920 h. The marginal effect of addition of NaCl and $(NH_4)_2SO_4$ on metal recovery was noticed.

REFERENCES

(1) A. K. Biswas and W. G. Davenport: *Extractive Metallurgy of Copper*, Third Edition, Pergamon, Oxford, (1994), p. 194.

(2) Y. P. Kupryakov, F. V. Makarov and V. S. Chakhotin: Tsvetn. Met., **9** (1974), 6.

(3) V. N. Mashuryan, V. V. Mecher and L. N. Kovalenko: Tsvetn. Met., **10** (1974), 16.

(4) S. Anand, P. Kanta Rao and P. K. Jena: Hydrometallurgy, **5** (1980), 335.

(5) S. Anand, K. S. Rao and P. K. Jena: Hydrometallurgy, **10** (1983), 305.

(6) P. D. Sharma: Indian Patent No. 148741, March 1978.

(7) S. Anand, K. S. Rao and P. K. Jena: Trans. IIM, **33** (1980), 77.

(8) M. A. Pabalkar and S. Basu: Hydrometallurgy of cobalt, Proc. Research and practice in hydrometallurgy, Hydromet. 90, Udaipur, 6-7 Feb. (1990), 1.1.1-1.1.77.

(9) L. E. Murr, A. E. Torma and J. A. Brierley: *Metallurgical Application of Bacterial Leaching and Related Microbiological Phenomena*, Academic Press, New York, (1978), p. 491.

(10) T. Brewis: Mining Magazine, October (1995), p. 197.

(11) L. B. Sukla and V. Panchanadikar: Hydrometallurgy, **32** (1993), 373.

(12) L. B. Sukla, R. N. Kar and V. Panchanadikar: *Bioleaching of Sukinda lateritic nickel ore using a native fungal strain. In: Recent trends in Biotechnology*, ed. by C. Ayyanna, Tata Mc Graw Hill, New Delhi, (1993), p. 128.

(13) L. B. Sukla, K. M. Swamy, K. L. Narayana, R. N. Kar and V. Panchanadikar: Hydrometallurgy, **37** (1995), 387.

(14) H. Nakazawa and H. Sato: Int. J. Miner. Process, **43** (1995), 255.

(15) S. R. Dave and K. A. Natarajan: Hydrometallurgy, **7** (1981), 235.

(16) L. B. Sukla, R. N. Kar and V. Panchanadikar: Biometals, **5** (1992), 169.

(17) P. Fecko and P. Kucerova: Miner. Slovaca, **28**(5), (1996), 388.

(18) J. V. Wiertz: *Ferrous and sulphur oxidation by Thiobacillus ferrooxidans. Bio-hydrometallurgical Technologies*, Part II, ed. by A. E. Torma, M. L. Apel and C. L. Brierley. The Minerals, Metals and Materials Society, (1997), p. 463.

(19) W. J. Ingledew: Biochemica Biophysica Acta, **683** (1982), 89.

(20) R. Aguirre, J. V. Wiertz and R. Badilla-Ohlbaum: *An amperometric method for measuring iron oxidising activity of Thiobacillus ferrooxidans, Bioleaching: from molecular biology to industrial application*, ed. by R. Badilla-Ohlbaum, T. Vargas and L. Herrera, Santiago, Chile: University of Chile, (1991), p. 107.

(21) T. Imaizumi: Some industrial applications of inorganic microbial oxidation in Japan. Biotechnology and Bioengineering Symposium, No. 16 (1986), p. 363.

(22) S. R. Rao, J. A. Finch and N. Kuyucar: Minerals. Engg., **8**(8), (1995), 905.

(23) B. K. Mahapatra, B. D. Nayak and G. V. Rao: Trans. Inst. Min. Met. Sec C, **103** (1994), C 217.

(24) Olli H. Tuovinen and Ilona J. Fry: Bioleaching and mineral bioleaching. Current opinion in Biotechnology, **4** (1993), 344.

(25) Douglas E. Rawlings and Tomonobu Kusano: Molecular Genetics of Thiobacillus ferrooxidans. Microbiol. Reviews. Copyrite (C) 1994. American Society for Microbiology, Mar. (1994), p. 35.

(26) Ahonen Lasse and Olli H. Tuovinen: Hydrometallurgy, **37** (1995), 1.

(27) Kazutami Imai: *On the mechanism of bacterial leaching, In: Metallurgical Applications of Bacterial Leaching and Related Microbiological Phenomena*, ed. by Lawrence E. Murr, Arpad E. Torma and James A. Brierley, Academic Press, New York, (1978), p. 275.

(28) H. L. Ehrlich: Proc. National Science Foundation Symp. on Biochemistry of sulphur isotopes, Yale, New Haven, Connecticut, (1962), p. 154.

(29) V. K. Berry and L. E. Murr: *Direct observation of Bacterial and Quantitative studies of their catalytic role in the leaching of low grade, copper-bearing waste, In: Metallurgical Application of Bacterial Leaching and Related Microbiological Phenomena*, ed. by Lawrence E. Murr, Arpad E. Torma and James A. Brierley, Academic Press, New York, (1978), p. 103.

(30) J. C. Madgwick and B. S. Ralph: Proc. Australas. Inst. Min. Metall., **279** (1981), p. 33.

(31) B. J. Y. Leong, B. D. Dreisinger, M. Lo, R. Branion, R. P. Hackl, L. S. Gormely and D. R. Crombie: *Microbiological leaching of a sulphidic copper ore in a strongly saline medium (I)*: Shakeflask and column studies, In: Biohydrometallurgical technologies, ed. by A. E. Torma, J. E. Wey and V. I. Lakshmanan, The Minerals, Metals & Materials Society, (1993), p. 117.