Biomineral Processing for Extraction of Copper Metal from Lean Ore of Malanjkhand Copper Project

***Shyam Charan Pal, K.D. Mehta, B.D. Pandey and T.R. Mankhand*[1]**

Metal Extraction and Forming Division,
National Metallurgical Laboratory,
Jamshedpur - 831007

[1]Department of Mettalurgical Engineering,
I.T.B.H.U.,
Varanasi

Abstract

Bioprocessing for metal recovery from different oxidic and sulphidic ores and concentrates is considered very attractive in view of low energy consumption and environmentally benign option. The present work is carried out to recover copper from lean grade copper ore (0.3% Cu) of Malanjkhand Copper Project (MCP). In Malanjkhand Copper mine rich ore containing 0.9 to 1.0% Cu is currently beneficiated. Lean grade ore with 0.3-0.4% copper, which is adjacent to the rich grade ore, may be utilized to meet the growing demand of the country. The conventional processes are not suitable to treat this low grade ore as the desired grade with acceptable yield can not be achieved. Therefore bioleaching may be opted for recovery of copper along with some other valuable metals from the lean ore. Different parameters such as pH, temperature, pulp density, particle size, etc; were studied to optimise the process.

Bench scale experiments were carried out under incubator shaker by inoculating with the isolate of *Acidithiobacillus ferrooxidans (Tf)*, a mesophilic iron and sulphur oxidizing bacterium, initially derived from the source mine water. Copper bio-dissolution was initially rapid but slowed down after 30-35 days. The decrease in the metal dissolution rate could be ascribed to precipitation of jarosite on the mineral surface. Sterile sets were also run to assess the contribution of chemical leaching, during the bioleaching of copper. Leaching of copper in sterile controls was very poor. In inoculated sets, leaching of iron and nickel decreased due to the formation of solid phases like jarosite/Fe (III) oxide on the mineral surface, as revealed by XRD studies. The leaching of copper showed increasing trend with the dissolved ferric iron concentration in solution thus indicating the role of indirect leaching mechanism. A high redox potential (550-650mV) observed during the bioleaching may be attributed to the bacterial oxidation through direct mechanism leading to the higher concentration of dissolved ferric iron thereby resulting in increased copper dissolution. Using isolate strains of *Acidithiobacillus ferrooxidans*, 70% Cu recovery was obtained in 30 days at 35°C, pH 2, 5%PD and with <50μm ore particles. With the coarser size of the MCP ore, the copper recovery was comparatively lower under the similar conditions.

INTRODUCTION

Copper ore of Malanjkhand copper mine is basically of granitic origin with thin vein-lets of quartz (rock type), which may be to oxidative acid leaching. The ore of Malanjkhand copper project (MCP) mine, where mining is currently carried out by open cast method, has a complex mineralogy. The rich grade ore (0.9 – 1.0% Cu) being mined is concentrated by flotation to produce chalcopyrite concentrate which is the main feed-stock for HCL plants in the country. Adjacent to the main ore-body, the lean grade material containing 03-0.4% Cu is available, which is estimated to be 2.5-3.0 million tones and left out. This lean grade ore is generally not exploitable by conventional techniques. Biological leaching processes may therefore be considered as possible alternatives as it is an environmentally cleaner and energy efficient technique they are being used to treat several low-grade, complex and refractory ores. Earlier attempts were made [1-3] to treat MCP ores, particularly the overburden material which were essentially a mixed copper oxide-sulphide (chalcopyrite) and lean grade ore. Although, the copper bio-recovery from the mixed ore [1] was observed to be favourable - 50-60% in 60 days on bench scale and 40-50% in column, the same could not be established in large column and heap leaching experiments conducted at the dump site of MCP. In fact, copper dissolution was found to be 19% on tonnage scale by Agate [3], 13-15% in 30-40 days by MCP. The bio-leaching of lean grade MCP ore has also been investigated to a limited extent with 80% recovery in 40 days in shake flasks [2].

As such the bio-leaching of the lean MCP ore requires serious efforts so as to arrive at the conditions suitable for exploitation. Therefore, the present study has been taken up as a part of CSIR (New Delhi) network project by involving different organizations in India. In this direction, some aspects of R&D work being carried out at National Metallurgical Laboratory are presented in this paper. Microbiological, chemical and physical factors influencing the bio-leaching are include in the text. In the bio-leaching process, the proper contact of ore with the leach liquor is essential for fluxes of reactants and products, such as bacteria, dissolved gases (O_2 and CO_2), solubilized metals and sulfur species. In bench scale studies, shake flasks were used for the optimization of bio-leaching parameters.

Ferric iron is an important oxidizing agent in the bacterial leaching of sulfide minerals[4-8]. Soluble iron species are the main determinants of redox potential, with active iron-oxidizing bacteria (*Acidithiobacillus ferrooxidans*) contributing to high Fe^{3+}/Fe^{2+} ratio. Precipitation of ferric iron in the leaching system may suppress the metal solubilizaton by preventing the contact between the leaching agent and the mineral. The bacterial leaching process requires acidic conditions, the acidity often being produced by the oxidation of pyrite and hydrolysis of ferric iron. The acid may, however, be neutralized in various acid-consuming reactions; for example, the leaching of silicate minerals. Details on optimisation of process parameters in the bio-leaching of copper are presented in the text.

MATERIALS AND METHODS

Lean grade copper ore (containing 0.32%Cu) was collected in the form of lumps from Malanjkhand copper mine (located in Balaghat, Madhya Pradesh, India). The ore was crushed, ground and passed through a sieve of 50μm size. The bio-leaching experiments were carried out with this material (75μ) unless stated otherwise. A representative sample was then prepared by coning and quartering for chemical analysis by atomic absorption spectrometer. A known amount of ore was also passed through different screens to get sieve analysis. The chemical analysis of the sieve fractions is given in Table-1. The phase identification by XRD showed that $CuFeS_2$, FeS and silica were the major mineral phases and Cu_5FeS_4 (bornite) as a minor mineral phase in the ore.

Micro-organism and Bio-leaching experiments

The micro-organism used in this study was a strain of *Acidithiobacillus ferrooxidans (Tf)*, derived by successive enrichment of mine water sample using $FeSO_4.{}_7H_2O$ as a substrate in 9K nutrient medium for 30 days. Analytical Reagent Grade chemicals such as $FeSO_4.7H_2O$, $MgSO_4.7H_2O$, $Ca(NO_3)_2$, KCl, K_2HPO_4, and NH_4 (SO_4) were used for making 9K media. Other chemicals used were also of Analytical Reagent Grade. The culture thus derived was used for inoculation in subsequent bioleaching experiments. Unless otherwise stated, the bench scale leaching experiments were carried out in Erlenmeyer flasks in incubator shaker at $35\underline{+}2$°C. The bioleaching tests were carried out in 500 ml flasks with 200 ml of total solution, the flasks were inoculated with 10 %(v/v) of enriched liquid culture containing 1×10^8 cells/ml. General conditions like 35^o temperature, pH 2 and PD 5 % (w/v) were maintained unless otherwise stated. The flasks were incubated at a temperature of 35 ± 2^0C with 100 rpm orbital motion. 0.5 ml of the supernatant solution was taken for analysis of Cu, Ni and Fe by Atomic Absorption Spectrophotometer. The ferrous ion concentration in the solution was determined by titrating against standard potassium dichromate solution with barium diphenylamine sulfonate (BDAS) as indicator. Normal losses due to evaporation were periodically compensated by the addition of distilled water. All the inoculated sets had their corresponding sterile control sets prepared under the same conditions. During experiments samples were mostly taken at 5 days intervals for chemical analysis and other measurements like pH of the leach solution was maintained on alternate days. Upon termination of the leaching experiments, the solid residues were dried and samples were taken for chemical analysis and XRD phase identification. The solid residues were dissolved in $HCl-HNO_3$ mixture and analyzed by AAS. Redox potential (Eh) was measured with a Pt electrode using saturated calomel electrode (SCE) as a reference. The initial pH requirement was satisfied with $10N$ H_2SO_4.

Table 1: Chemical analysis of different sieve fractions of copper ore from Malanjkhand mine.

Particle size (µm)	*Fraction retained, %*	*Cumulative Fraction retained,%*	*Composition (%)*		
			Cu	*Ni*	*Fe*
150-76	**3.33**	**3.33**	**0.321**	**0.228**	**3.90**
76-50	**34.92**	**38.25**	**0.316**	**0.225**	**3.92**
<50	**61.75**	**100**	**0.320**	**0.230**	**3.91**

RESULTS AND DISCUSSION

In the present work an extensive bench scale study was performed to optimize the critical parameters for bioleaching of copper from lean grade copper ore of Malanjkhand Copper Project. The details are presented and discussed below. The growth of bacteria was monitored by estimating the oxidation of Fe^{+2} with time. Total iron was oxidized in 7 days indicating the full growth of the bacteria. In subsequent sub-culturing, the growth was completed in 3-4 days. This sub-cultured Tf was used in the experiments for bio-leaching.

Effect of pH

pH is one of the important parameters which affects the bioleaching process. Bioleaching of copper ore was done at different pH i.e. 1.5, 1.7, 2, 2.2 and 2.5 at a solid-liquid ratio of 1:20(w/v) and a temperature of 25^0C. Data plotted in Fig 1 showed that recovery was maximum at pH 2.0. Copper recoveries at pH 1.5 and 1.7 were mainly governed by increase in bacterial oxidation by direct mechanism involving attachment of Tf on the surface of sulphide mineral. At pH 2.0 the bio-action was maximum [9-12]. The copper recoveries of 40% were almost same in the pH 1.5 to 2.0. Thereafter, copper recoveries decreased with increasing pH. At a higher pH of 2.5 the recovery of copper decreased due to the formation of jarosite on the ore particles, which was identified by XRD phase analysis.

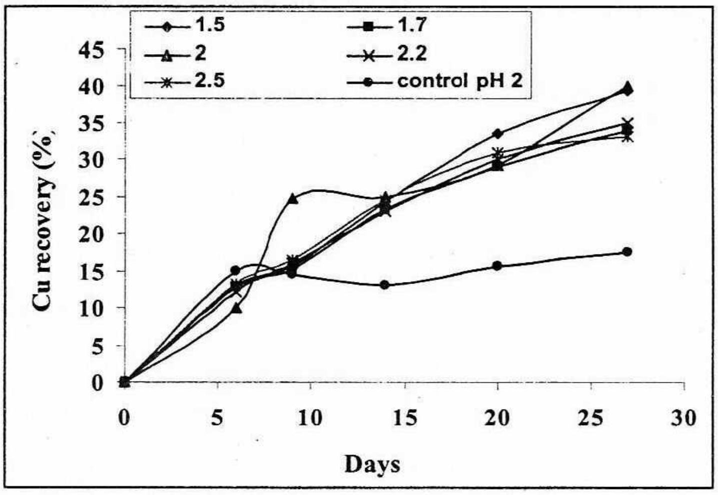

Fig.1: Recovery of copper at different pH in 27 days using Tf isolate from mine water at 25°C, 5%PD and particles of <50µm.

Acid consumption during leaching

Acidithiobacillus ferrooxidans produces acid from sulphide minerals but some acid must be present initially for driving the leaching in forward direction. As the amount of sulphur in the copper ore is 2.83%, auto-generation of acid is expected to be quite lesser. Consumption of sulphuric acid (10N) during bioleaching of copper ore is shown in Fig. 2. It is clear that initial acid requirement for leaching was sufficiently high which were 4.23 ml at pH 1.5 and 2.12 ml at pH 1.7. The acid requirement at pH 2.0 and above was moderately lower. Due to higher activity of bacteria at pH 2.0 more acid was produced and acid consumed was about 1.18 ml for 10 g of copper ore. The sterile control experiment carried out at pH 2.0 showed that 75% more acid was consumed in chemical leaching than bioleaching of copper ore.

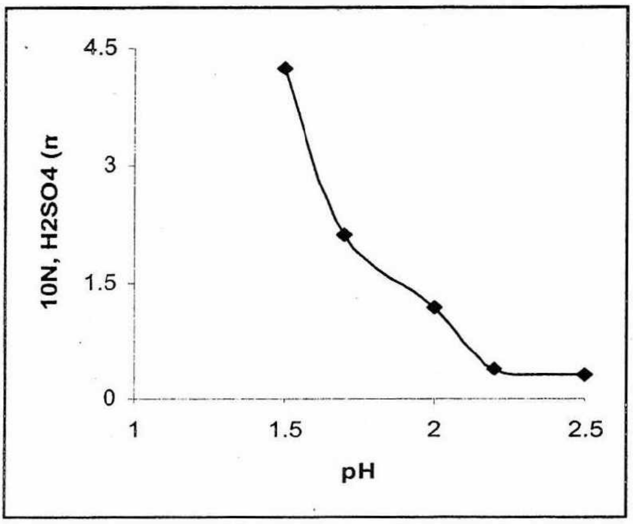

Fig.2: Consumption of H_2SO_4 (10N) in maintaining pH of leach liquor at different pH, 298K, 35days, 5%PDand 35°C.

The bioleaching of copper from chalcopyrite is reported [11-14] to involve both direct and indirect leaching mechanism. The direct mechanism proceeds through the attachment of Tf on the mineral surface to oxidize the metal.

$$4CuFeS_2 + 17O_2 + 2H_2SO_4 \longrightarrow 4CuSO_4 + 2\,Fe_2(SO_4)_3 + 2H_2O \ldots\ldots\ldots (1)$$

There is growing agreement that the biooxidation of sulphide minerals also involves oxidative ferric reaction with the mineral, which essentially represents indirect leaching mechanism represented as:

$$CuFeS_2 + 2O_2 + Fe_2(SO_4)_3 \longrightarrow CuSO_4 + FeSO_4 + S^{o} \ldots\ldots\ldots\ldots\ldots (2)$$

This apart from dissolution of the metal sulphide ions, produces ferrous iron and elemental sulfur (S^{o}). It is this ferrous iron and the elemental sulfur that form the substrate for microbial growth according to reaction:

$$4FeSO_4 + O_2 + 4H_2SO_4 \xrightarrow{Tf} 4Fe_2(SO_4)_3 + 2H_2O \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

And:

$$S^{o} + O_2 \xrightarrow{Tf} SO_4^{2-} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

The ferric iron thus formed is hydrolyzed in aqueous solution if pH is higher.

$$Fe^{+3} + H_2O \Longleftrightarrow FeOH^{+2} + H^+ \ldots\ldots (5)$$

$$Fe^{+3} + 2H_2O \Longleftrightarrow Fe(OH)_2^+ + 2H^+ \ldots\ldots (6)$$

Reaction (3) increases the pH, but the reaction (5) and (6) reduce and stabilizes it. So the extent of ferric iron hydrolysis is dependent on pH.

Effect of Pulp density (PD)

Effect of pulp density on biodissolution of metals was investigated with 5 - 20%(w/v) PD using 10% (v/v) isolate of *Tf* from Malanjkhand Cu-mine water (in 9K media) without adaptation in 200 ml leaching medium with <50µm size particles at pH 2 and 35°C while shaking at 100rpm. From the results shown in Fig.3, it is clear that recovery of copper is much higher at the lower pulp density of 5% (w/v) of the solution. The maximum copper bio-recovery was found to be 70.2 % with 5%PD in 35 days as shown in Fig.-3 as compared to 40% Cu recovery in chemical leaching. Copper recovery decreased with increase in pulp density; this may be attributed as to the lack of oxygen availability and increased concentration of metal ions causing toxicity to bacterial growth at higher pulp densities.

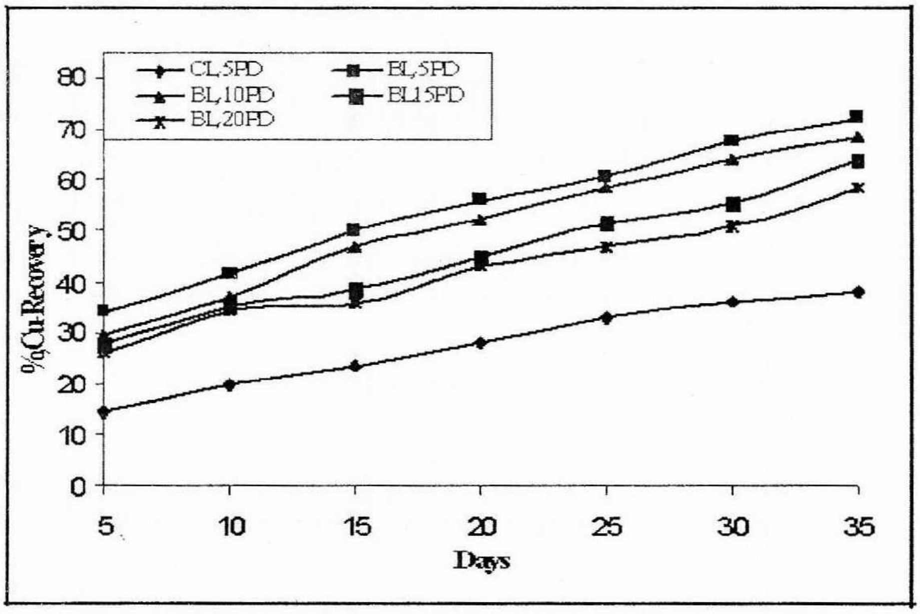

Fig 3: Effect of Pulp Density on bioleaching of copper ore with isolated Tf from Malanjkhand mine water without adaptation in 35 days at 35°C, pH 2 and <50µm size particles.

Effect of particle size

Studies on effect of particle size are shown in Fig.4. It may be seen that increased fineness to <50 µm decreased the recovery from 72% to 67.6%. This could be mainly due to better permeation of the leachant to oxidize the copper sulphide present in the ore and increased surface area. Finer particles were increasingly exposed to lixiviant that dissolved copper from the chalcopyrite phase. The concentration of ferric ions, oxidized by bacterial action on ferrous ions involved in chemically dissolving the metals was much higher in case of leaching of finer size than in case of coarser size.

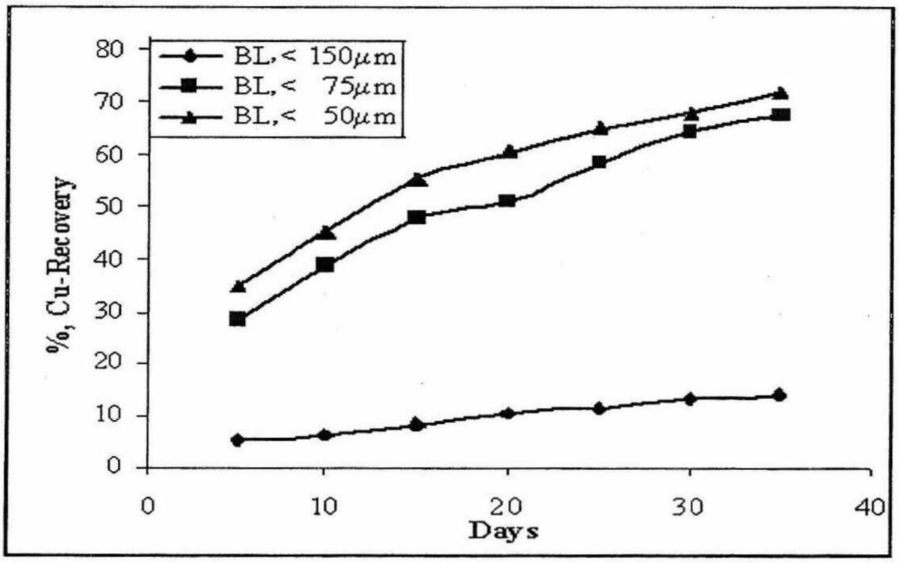

Fig 4: Effect of particle size on bioleaching of copper ore with isolated Tf from Malanjkhand mine water without adaptation at 35°C, pH 2 and 5% PD.

Effect of temperature

In general chemical reaction rate increases as the temperature increases, but the *Acidithiobacillus ferrooxidans* strains are mesophilic in nature and they can survive or thrive in the temperatures range 20-35°C. Influence of temperature variation on bioleaching, between 25 to 35°C at 5% PD and using 10% (v/v) isolate of *Tf* without adaptation at pH 2, while shaking at 100 rpm was studied. The maximum copper recovery was found to be 70.2 % at 35°C in 35 days as shown in Fig.5. At this temperature nickel recovery was 8.3% and Fe recovery was 7.1%. The changes in Eh (mV) values in 35 days at 35°C are reported in Fig.6. During bioleaching, redox potential varied from 316 to 674 mV in 35 days, whereas in control leaching it varied from 325 to 534mV.

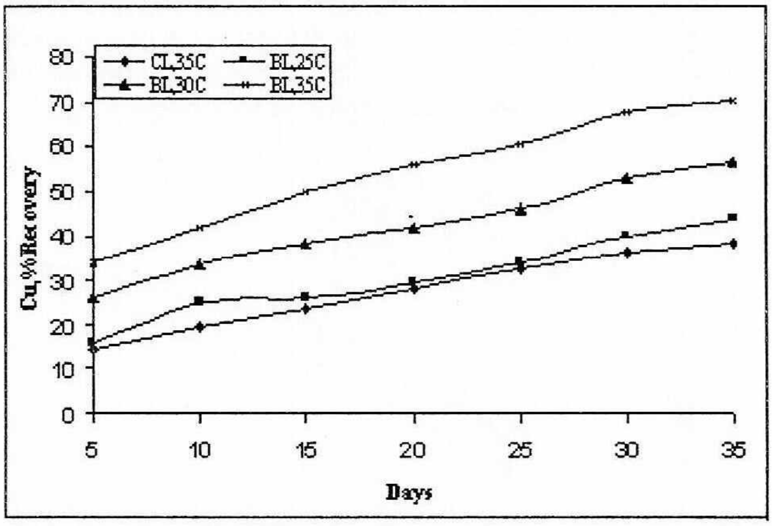

Fig 5: Effect of temperature on bioleaching of copper ore with isolated Tf from Malanjkhand mine water without adaptation at PD 5% w/v, pH 2 and 50µm size.

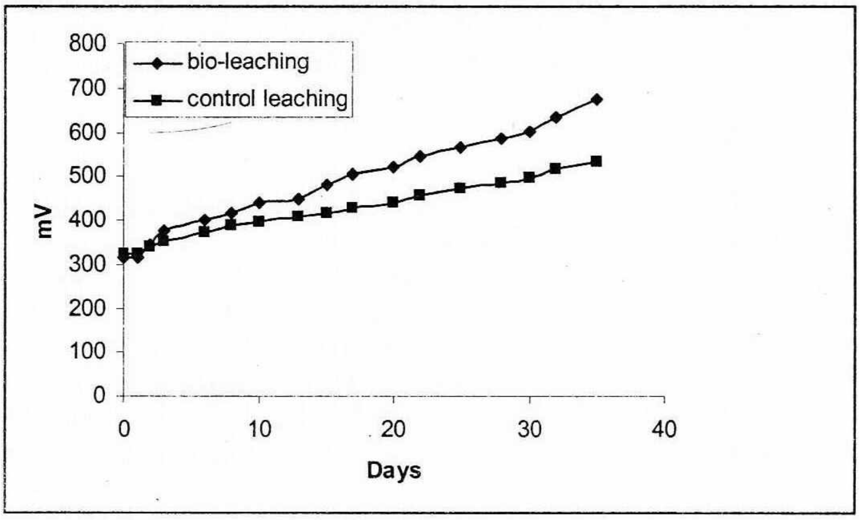

Fig 6: Redox potential during bio-leaching of copper pH: 2, temp. 35°C, particle size :< 50µm, PD: 5%.

The XRD identification of the phases can be seen from Table 2. The leach residues obtained the bio-leaching contained chalcopyrite and pyrite as the minor phases and bornite as the minor phase that were also present in the ore sample. Besides these, residue contained hydronium jarosite [$H_3OFe_3(SO_4)_2\ (OH)_6$] in major amount which was formed during the leaching process. Jarosite precipitation can be indicated by general equation:

$$3Fe^{3+}+2SO_4{}^{2-}+X^{+}+6H_2O \Longleftrightarrow X\,[Fe_3(SO_4)_2(OH)_6]+6H^{+} \ldots\ldots\ldots\ldots\ldots\ldots \text{(7)}$$

where X+ is a monovalent cation (generally K^+, Na^+, $NH_4{}^+$ or H_3O^+). Precipitation of jarosite was lower at pH 2, but at pH 2.5 increased precipitation of the same was observed.

Table2. XRD phase identification of copper ore before and after bioleaching at 25°C, 35 days, pH 2 and <50 µm particle size.

Sample	*Phases Identified*
Copper ore	**Major: chalcopyrite and pyrite (associated with copper ore), silica**
	Minor: bornite
Bioleach residue	**Major: hydronium jarosite, silica**
	Minor: chalcopyrite, pyrite

CONCLUSIONS

The studies on bio-leaching of copper from lean grade MCP ore showed that the dissolution rate is significantly enhanced by the presence of species of *Acidithiobacillus ferrooxidans* at pH 2 and 35°C temperature. The results demonstrate that the bacterial leaching of chalcopyrite follows both direct and indirect leaching mechanism. Low leaching rates is accompanied by acid consuming gangue minerals. The high redox potential in the range 316-674 mV in the presence of Tf indicates oxidizing conditions prevailing in the system as compared to chemical leaching under sterile conditions. The maximum copper bio-recovery is 72% at pH2 and 35°C with the ore particles of <50 µm size in 35 days interval.

Acknowledgement

The authors are thankful to the Director, NML Jamshedpur for giving permission to present the paper, to the Hindustan Copper Limited for providing the sample and to Shri A.K.Giri for chemical analysis. Help received from Dr. (Mrs.) C.Das and Mr. Abhilash for their unflinching support rendered during preparation of this paper is acknowledged.

References

[1] Natrajan, K.A., Proc. Biohydrometallurgy, Theory & Practice, pp.131-134 & pp. 697-718, Jan 10-16, 1994.

[2] Sukla, L.B., Roy Chaudhary, G., and Das, R.P., Recovery of copper from Malanjkhand oxide and sulphide ores through column leaching-SX-EW. Report submitted to HCL, Jnue, 1991.

[3] Agate,A.D., Panikar, K.M. and Khinvasara, N.J., In Proc. Biohydrometallurgy'89, Ed. J. Salley, R.G.L. Mcready & P.L. Wichlaez, CANMET, 577-589, 1989.

[4] Rossi, G., Biohydrometallurgy, Mc Graw-Hill, Hamburg (1990).

[5] Patnaik Lipika, Kar R.N, and Sukla L.B., Influence of pH on bioleaching of copper and zinc from complex sulphide concentrate using Thiobacillus Ferrooxidans, Trans Indian Inst Met 54(4),139-144, 2001.

[6] Schippers A, Sand W. Bacterial Leaching of metal sulfides proceeds by two indirect mechanisms via thiosulfate or via polysulfides and sulfur. Appl Environ Microbiol 65, 319-21, 1999.

[7] Silverman, M.P., Mechanism of bacterial pyrite oxidation, J. Bacteriol., 94, 1046-1051, 1967.

[8] Use of Microorganisms in Hydrometallurgy, ed., Anonymous, Pecs, Hungarian Academy of Science, Hungary, 1, 220, 1980.

[9] Natarajan, K.A., Electrochemical aspects of bioleaching of base-metal sulphides, In: Microbial Mineral Recovery, eds., Ehrlich, H.L. and Brierley, C.L., McGraw-Hill Publishing Company, New York, 79-106, 1990.

[10] Das, A., Modak, J.M. and Natarajan, K.A., Studies on Multi-metal ion tolerance of Thiobacillus ferrooxidans, Miner. Engg. 10(7), 743-749, 1997.

[11] Natarajan, K.A., Biotechnological innovations in nonferrous extraction, In: Proc. Nonferrous Extractive Metallurgy in the New Millennium, eds. Rao, P.R., Kumar, R., Srikanth, S. and Goswami, N.G., NML, Jamshedpur, 1-20, 1999.

[12] Hansford, G.S., Vargas, T., Chemical and electrochemical basis of bioleaching processes, Hydrometallurgy 59, 135-145, 2001.

[13] Sand, Wolfgang., Gehrke, Tilman., Jozsa, Peter-Georg., and Schippers, Axel., (Bio)chemistry of bacterial leaching—direct vs. indirect bioleaching, Hydrometallurgy 59, 159-175, 2001.

[14] Brickett, L.A., Hammack, R.W., and Edenborn H.M., Comparison of methods used to inhibit bacterial activity in sulfide ore bioleaching studies, Hydrometallurgy, 39, 293-305, 1995.