72 72

Copper Biodissolution from a Low Grade Chalcopyrite Ore by Unadapted/Adapted *Acidithiobacillus ferrooxidans*

S. C. Pal[2], K. D. Mehta[1], Abhilash[1], V. Kumar[1], B. D. Pandey[1] and T. R. Mankhand[2]*
[1] M.E.F. Division, National Metallurgical Laboratory, Jamshedpur - 831007
[2] Metallurgical Engineering Dept., I.T., B.H.U., Varanasi - 221005

ABSTRACT

The depletion of high-grade deposit of copper around the world has drawn attention for the utilisation of low-grade reserves. Malanjkhand Copper Project (MCP) in India is a low-grade ore containing ~0.3% Cu in which copper metal is found to be present as chalcopyrite associated with pyrite in quartz veins and granitic rocks. In order to extract copper from this material, an alternate processing option such as bioleaching has been followed. Bench scale bioleaching experiments were carried out using *Acidithiobacillus ferrooxidans* (*Ac.Tf*) isolated from mine water. On using unadapted *Ac.Tf* isolate directly at pH 2.0 and 35°C, the optimum leaching conditions in shake flask were found to be 5% pulp density (PD), 2.0pH, 35°C temperature for <50μm particles, yielding 72% Cu biorecovery in 35days. The *Tf* isolate when adapted to the ore and employed for the bioleaching of the ore at 5% PD (w/v), 2.0pH and 25°C with three particle sizes viz.150-76μm, 76-50μm and <50μm, resulted in recovery of 38.31%, 29.68% and 47.5% Cu respectively with a rise in E_h from 530 to 654 mV in 35 days. Under similar conditions, the unadapted strain gave maximum recovery of 44.0 % for <50μm ore size with rise in Eh from 525 to 650mV. Copper biorecovery increased to 75.3% with the adapted isolates at 35°C for the finer particles of <50μm at 2.0pH with a rise in cell count from $1x10^7$ cells/mL to $1.13x10^9$ cells/mL in 35 days. The biodissolution of copper from chalcopyrite with the involvement of adapted *Ac.Tf* species resulted in the improvement of iron oxidation rate (Fe^{2+} to Fe^{3+}) and consequently higher redox potential.

INTRODUCTION

With the depletion of high grade resources of ores, there is a need to process low grade discarded ores and tailings to meet the current demand of metals. The existing conventional processes are not suitable to recover the metals from such resources due to high energy consumption and cause environmental pollution. The biohydrometallurgy is one such approach which can recover metals economically without affecting environment with the application of microbes. The process has been initiated in isolation of a mesophilic and acidophilic bacteria from mine waters and its usage in bioleaching of copper ores. These bacteria have been used for dissolution of copper from different low grade ores and tailings and metal recovered [1-4]. Various researchers globally worked in elucidating the role of bacteria in bioleaching in catalyzing the oxidation of metal sulphides [5-10]. Two mechanisms of bacterial action have been suggested: (a) a direct attack of the bacteria on the mineral surface and its oxidation through enzymatic reactions; and (b) an indirect attack, where the bacteria regenerate the oxidizing agent of the mineral by means of the oxidation of Fe(II) to Fe(III) via thiosulphate or poly-sulphide depending on the type of mineral.

In India the demand for copper is also increasing with industrialisation and to meet the requirement of copper, low grade ores/ tailings located in Malanjkhand (M.P.), Khetri (Rajasthan) and Singhbhum (Jharkhand) regions can be important source. The Malanjkhand Copper Project (MCP) is the largest open-cast mine having copper deposits of 22 million T of low grade ores (~0.26%). Biohydrometallurgical processing can be an alternative route to recover copper from these low grade reserves [11, 12]. At NML, R & D studies have been carried out on bench scale for bio-leaching of lean MCP ore. This paper explains the optimizing of process parameters in bio-dissolution of copper metal from the ore using *Acidithiobacillus ferrooxidans* (*Ac.Tf*), initially derived from mine water of MCP. A series of experiments have been carried out using *Ac.Tf* unadapted and the adapted isolates to compare the efficiency of bio-leaching.

MATERIALS AND METHODS

Copper Ore

Lean copper ore (~ 0.3-0.4% Cu) obtained as lumps from the mine of Malanjkhand Copper Project, M.P was crushed, ground and sieved to obtain different size fractions. Representative samples were then prepared by coning and quartering method for each fraction to get sieve analysis and respective chemical analysis by using atomic absorption spectrophotometer. Chemical analysis of the ore is given in Table-1 whereas chemical analysis of sieve fractions is given in Table-2. It may be seen that the composition of the different fractions are almost same.

Table-1: Chemical analysis of copper ore from MCP (%)

Cu	Ni	Fe	Co	Zn	S	TiO_2	SiO_2
0.32	0.23	3.91	0.05	0.05	2.8	0.60	68.2

Table-2: Chemical analysis of different sieve fractions of copper ore

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

Phases in the copper ore

Malanjkhand copper ore is a granite rock with the preliminary mineralogical studies indicating the presence of chalcopyrite in the cracks and fishers of veins of quartz. The petrologic analysis for distribution of phase as in Fig.1 shows chalcopyrite *(yellowish)* is present in the form of irregular grains and pyrite *(brighter than chalcopyrite)* was observed within feldspar grains. The bulk ore is slightly pink in appearance due to high percentage of granite in the ore body.

XRD analysis of the ore shows that the major phases identified are chalcopyrite ($CuFeS_2$), pyrite (FeS) and silica (SiO_2) whereas bornite is the minor phase.

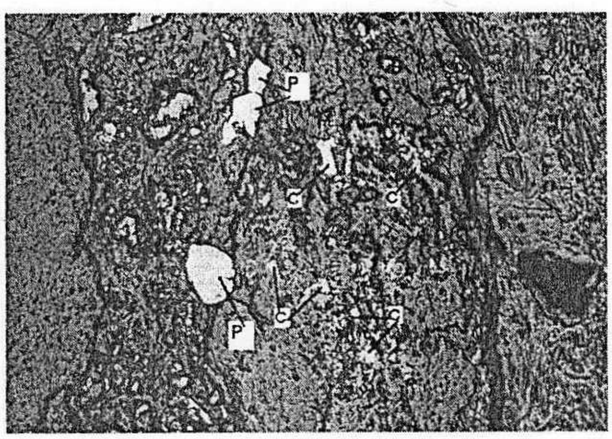

Fig.1: Petrological micrograph of copper ore (at 100X) [C-chalcopyrite, P-pyrite]

Bacteria Used and Bioleaching Experiments

The micro-organism used in this study was a strain of *Acidithiobacillus ferrooxidans (Ac.Tf)*, derived by successive enrichment of mine water sample using $FeSO_4.7H_2O$ as a substrate in 9K nutrient media for 30 days. The culture thus derived was used in subsequent bioleaching experiments. In general, bioleaching tests were carried out in 500 ml conical flasks with 200 ml of total solution, inoculated with 10%(v/v) of enriched liquid culture. The flasks were incubated at a temperature of 35±2°C, 2.0pH in incubator shaker with orbital motion at 100rpm. During experiments, samples were mostly taken at 5 days intervals for chemical analysis and pH of the leach solution was maintained on alternate days (initial pH maintained with 10N H_2SO_4. A quantity of 0.5 ml of the supernatant solution was taken for analysis of Cu, Ni and Fe by AAS (Model: GBC-980BT). The iron (II) concentration was determined by titrating against 0.05N potassium dichromate solution. All the inoculated sets had their corresponding sterile control sets prepared under the same conditions. Upon termination of the leaching experiments, the solid residues were dried and samples were taken for chemical analysis and XRD phase identification. Cell count was done using Petroff Hauser's Counting Chamber and enumerated using biological microscope.

Separate series of experiments were carried out using unadapted and adapted isolates. Leaching solutions were inoculated with 10% (v/v) of active and unadapted *Ac.Tf* except in case of sterile/control experimental sets, where mercuric chloride (0.2 g/l) was used as bactericide. In case of experiments with adapted isolates, *Ac.Tf* was initially adapted on 5%(w/v) pulp density of ore at 2.0pH and 35° C, and the resultant solution was grown in large volume to be used for further experiments.

RESULTS AND DISCUSSION

In the present work, extensive bench scale bioleaching work is cited for optimisation of the critical parameters for bioleaching of copper from lean grade copper ore of Malanjkhand Copper Project. The details presented and discussed below.

Bioleaching experiments using unadapted Ac.Tf

Acidithiobacillus ferrooxidans isolated from mine water of MCP was sub-cultured in presence of $FeSO_4.7H_2O$ and these sub-cultured isolates was used in the experiments for bio-leaching.

Effect of pH

Bioleaching of copper ore was carried at different pH in the range 1.5-2.5 at a pulp ratio of 1:20(w/v) and temperature of 25°C. Fig. 2 shows the bio-recovery being maximum (40%) at pH 2.0 which was mainly governed by increase in bacterial oxidation. With a rise in pH to 2.5, the recovery of copper decreased due to hydronium-jarosite precipitation which was identified by XRD phase analysis. Acid requirement is also an important aspect to be taken in consideration which was at a minimum level at 2.0pH due to higher bacterial activity, whereas it was 75% higher in control experiments at same pH.

Effect of Pulp density (PD)

Bio-dissolution of copper was investigated by varying pulp density in the range 5- 20%(w/v) at pH 2 and 35°C with <50μm size particles using 10% (v/v) isolate of *Ac.Tf* from Cu-mine water without adaptation in 200 ml leaching medium while shaking at 100rpm. From the results shown in Fig.3, it was clear that bio-recovery of copper was much high (72 %) at lower pulp density of 5% (w/v) in 35 days as compared to ~ 38% Cu dissolved in chemical leaching. The bio-dissolution of copper decreased with increase in pulp density. This may be attributed to the deficiency of oxygen availability and increased concentration of metal ions causing toxicity to bacterial growth at higher pulp densities. At 5% PD, redox potential varied from 522mV to 661mV for bioleaching in 35 days whereas it varied from 312mV to 401mV in control leaching at this pulp density. These data signified that high metal dissolution was governed by high redox potential owing to the high ferric iron concentration in the solution.

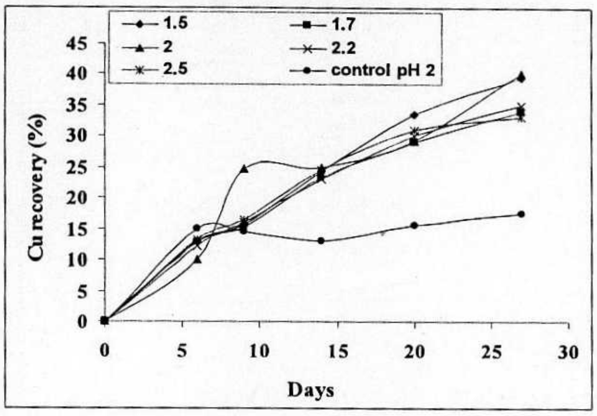

Fig.2: Recovery of copper at different pH in 30 days using *Ac.Tf* isolate from mine water without adaptation at 25°C, 5%PD and particles of <50μm.

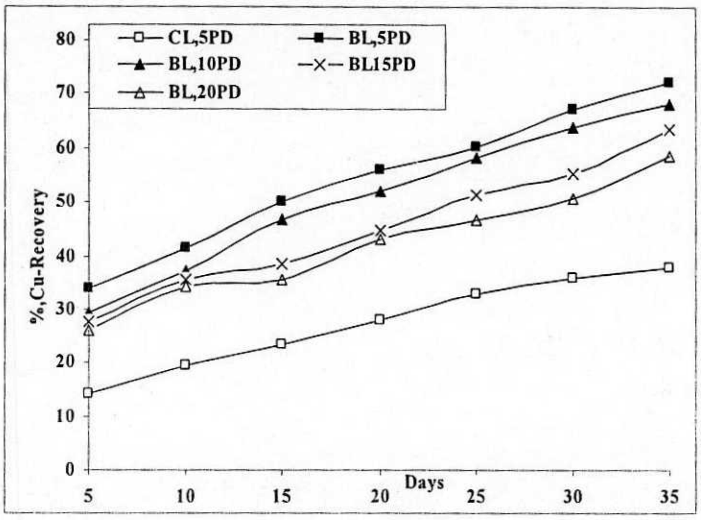

Fig.3: Copper recovery during bioleaching at different Pulp density using 10%(v/v) Ac.*Tf* without adaptation on ore at 35°C, <50μm particles and pH 2.

Effect of particle size

Studies on effect of particle sizes on bio-leaching of copper are shown in Fig.4. It may be seen that increasing fineness to <50 μm increased the recovery to 72%. This could be mainly due to better permeation of leachant to oxidize the copper sulphide present in 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.

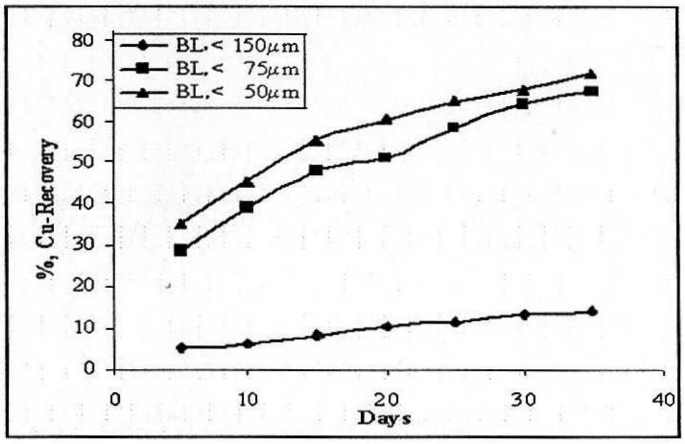

Fig.4: Effect of particle size on bioleaching of copper ore with isolated *Ac.Tf* from Malanjkhand mine water without adaptation at 35°C, pH 2 and 5% PD.

Effect of temperature

In general chemical reaction rate increases as the temperature increases, but the *Acidithiobacillus ferrooxidans* strains are mesophilic in nature. Effect of temperature variation on bioleaching in temperature range between 25 to 35°C at 5% PD and using 10% (v/v) isolate of *Ac.Tf* 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. During bioleaching, redox potential varied from 316 to 674 mV in 35 days, whereas in control leaching it varied from 325 to 534 mV.

Bioleaching experiments using adapted Ac.Tf

The bacteria isolated from mine water was adapted on 5% (w/v) ore of <50μm particle size at 2.0pH and 25°C. These adapted isolates were further sub-cultured and used in bio-leaching experiments.

Effect of pH

Bioleaching of copper ore was carried using adapted isolates at pH ranging from 1.5-2.5 at a pulp density of 5%(w/v) and 25°C. The bio-recovery was found maximum at pH 2.0 which was mainly governed by increase in bacterial oxidation (Fig.6). With a rise in pH above 2.0, the recovery of copper decreased due to the jarosite precipitation.

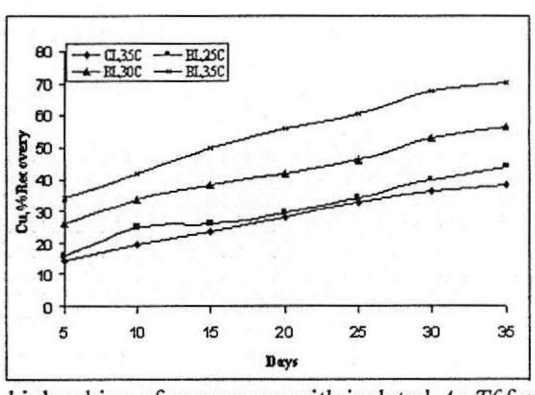

Fig.5: Effect of temperature on bioleaching of copper ore with isolated *Ac.Tf* from Malanjkhand mine water without adaptation at PD 5% w/v, pH 2 and <50μm size.

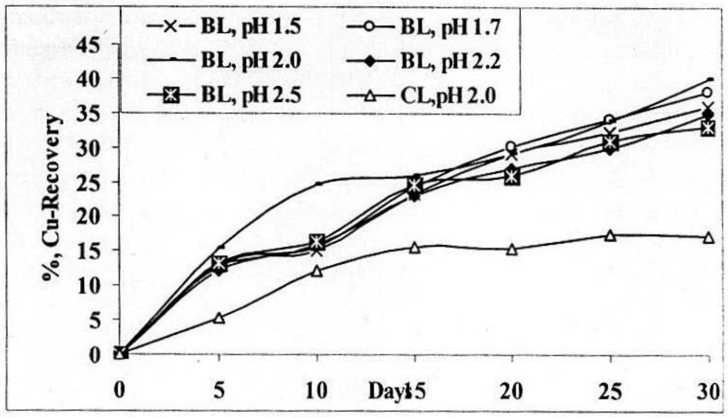

Fig.6: Recovery of copper during bioleaching with adapted *Ac.Tf* at different pH with adapted *Ac.Tf* at 5% (w/v) PD, 25°C using <50μm particles.

Effect of particle size

Effect of particle size on bio-leaching of copper was investigated for three size range at 5% (w/v) PD using 10% (v/v) isolate of adapted *Ac.Tf* in 200 ml leaching medium at pH 2 and 25°C while shaking at 100rpm. As shown in Fig.7, maximum copper recovery (47.5%) was obtained with *<50μm* size material using adapted *Ac.Tf* which is a little higher (44%) than that of non-adapted *Ac.Tf*. This may be attributed to the fact that metal ion tolerance of adapted strains contributes to the bioleaching of metals. Copper bio-recovery of 29.68% and 38.31% were obtained with 150-76μm, 76-50μm size ore particles in 35 days. In control experiment for *<50μm* size ore, recovery of copper was 20.5% in 35 days. Increase in Eh was noticed in the range 530 to 654 mV and 584 to 652 mV in bioleaching with adapted and non-adapted *Ac.Tf* respectively in 30 days with *<50μm* size particles which suggested high metal dissolution was obtained in case of adapted *Ac.Tf* strains.

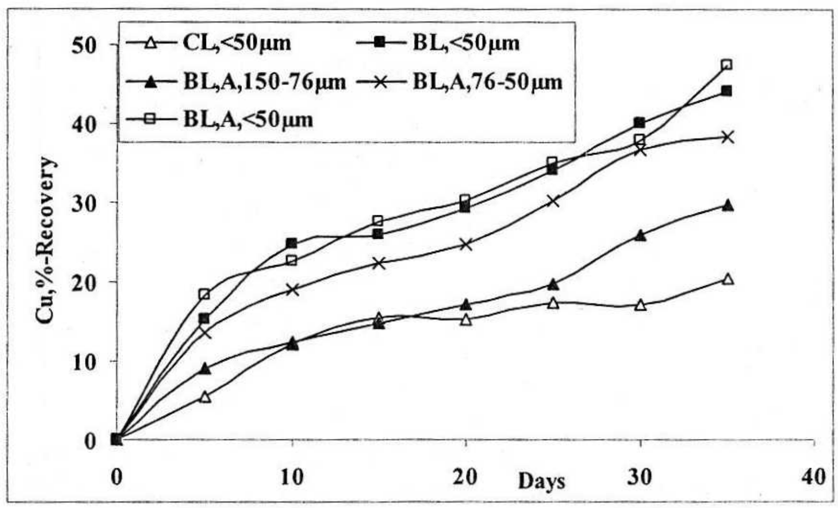

Fig.7: Cu recovery during bioleaching with adapted *Ac.Tf* at different particle size of ore, pH 2, 5% pulp density and 25°C.

Effect of pulp density

Recovery of copper at different pulp density along with the change in Eh (mV) values in 35 days has been presented in Figs.8-9. The influence of pulp density variation from 5-20% (w/v) using 10% (v/v) isolate of *Ac.Tf* (adapted on MCP Cu-ore) in 200 ml leaching medium at pH 2, while shaking at 100 rpm at 25°C was investigated. Control experiments were also run under similar conditions. The maximum copper recovery was found to be 47.5% and 44% with adapted and non-adapted strains of *Ac.Tf* as mentioned earlier whereas 20.5%Cu was leached out in control experiments at 5% (w/v) pulp density in 35 days. Bio-recovery of 38.5%, 33.04% and 31.19%Cu was obtained using adapted *Ac.Tf* at 10, 15 and 20% PD; this indicated that recovery decreased with increase in pulp density. At 5% (w/v) pulp density, maximum redox potential of the solutions was found to be 401, 652and 654mV with chemical leaching and for leaching with non-adapted *Ac.Tf* and *Ac.Tf* adapted on copper ore (Fig.8) respectively. This might be the reason for maximum recovery with adapted *Ac.Tf* at this pulp density as shown in Fig.8.

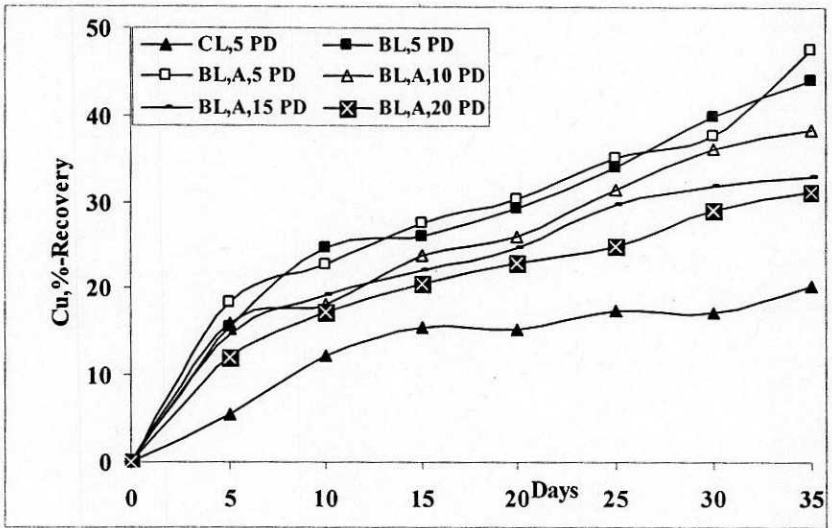

Fig.8: Recovery of copper during bioleaching with adapted *Ac.Tf* at different pulp densities with adapted *Ac.Tf*, 25°C, <50μm particles, pH 2.

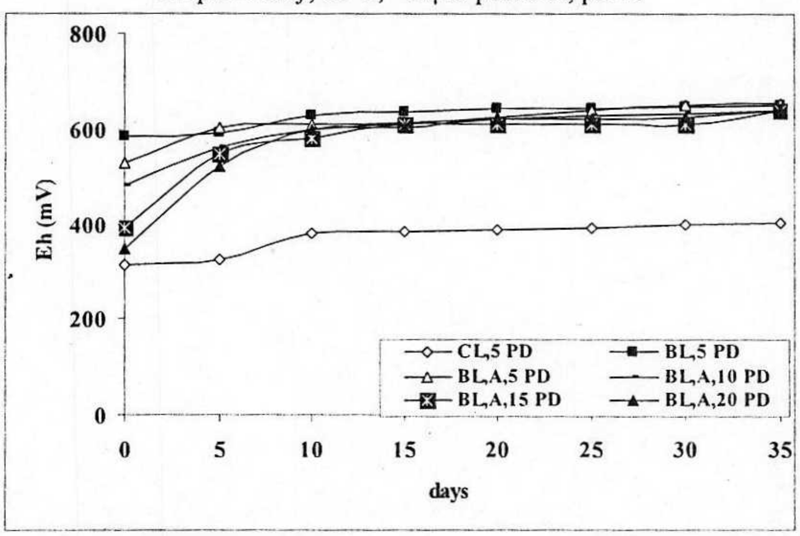

Fig.9: Change in redox potential of the solution during bioleaching with adapted *Ac.Tf* at different pulp densities, <50μm particles, pH 2 and 25°C.

Effect of temperature

Effect of temperature on bio-dissolution of copper using adapted *Ac.Tf* was investigated in the range 25-35°C at 5% (w/v) PD, pH 2 under shaking condition (100 rpm). As reported in Fig.10, Cu-recovery was maximum in leaching with adapted *Ac.Tf* (75.3%) as compared the recovery (72%) with non-adapted *Ac.Tf*; which is essentially due to the metal ion tolerance of the adapted strains. Bio-recovery of copper increased from 47.5-75.3% with increase in temperature from 25°C to 35°C. At 35°C redox potential varied between 602 to 661mV and 580 to 668 mV in leaching experiments with unadapted and adapted *Ac.Tf* whereas it varied between 312 to 401 mV in chemical leaching in 35 days. During bioleaching bacterial growth was found to be from 0.6 to 9.8×10^8 and 0.96 to 11.3×10^8 (cells/ml) with unadapted and adapted *Ac.Tf* strains respectively. It was interesting to see that the bacterial population increased with time resulting in improved metal bio-recovery. Apparently the higher cell population in case of leaching with adapted *Ac.Tf*, resulted in better metal bio-dissolution.

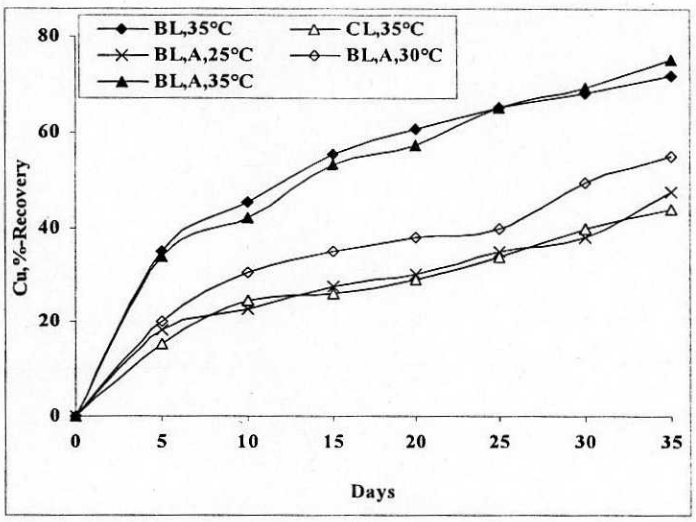

Fig.10: Cu recovery during bioleaching with adapted *Ac.Tf* at different temperatures, <50μm particles, pH 2, 5% pulp density.

XRD Phase Analysis

The XRD phase analysis of the residue shows that hydronium jarosite $[H_3OFe_3(SO_4)_2(OH)_6]$ and silica were present as major phases and chalcopyrite and pyrite as minor whereas chalcopyrite and pyrite were found as major phases in the ore. During bioleaching jarosite was formed as in equation:

$$3Fe^{3+} + 2SO_4^{2-} + X^+ + 6H_2O \Leftrightarrow [Fe_3(SO_4)_2(OH)_6] + 6H^+$$

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.

Mechanism Involved

The bioleaching of copper from chalcopyrite is reported to involve both direct and indirect leaching mechanism. The direct mechanism proceeds through the attachment of *Ac.Tf* on the mineral surface to oxidize the metal.

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

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

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

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:

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

And:

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

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

$$Fe^{3+} + H_2O \Longleftrightarrow FeOH^{2+} + H^+ \quad (5)$$
$$Fe^{3+} + 2H_2O \Longleftrightarrow Fe(OH)_2^+ + 2H^+ \quad (6)$$

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.

CONCLUSIONS

The recovery under conditions at 25°C, pH 2, 5% PD and <50μm particles of ore, with and without microorganism were 40% and 17.2% Cu in 30 days respectively. This showed that bioleaching of the ore (MCP) using *Acidithiobacillus ferrooxidans* is quite amenable. During leaching, bacterial growth on the ore was observed which confirms the applicability of bio-assisted leaching of this lean grade ore from MCP.

The optimum metal dissolution in presence of bacteria (non-adapted) was observed at pH 2.0 pulp density 5% (w/v) and particle size <50 μm with a maximum recovery of copper being 72%Cu in 35 days. In presence of *Ac.Tf* adapted on copper ore, bioleaching of copper was found to be 75.3%Cu under the optimum conditions. Thus, the introduction of adapted *Ac.Tf* markedly improved the metals recovery.

ACKNOWLEDGEMENTS

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.

REFERENCES

1. Rossi, G., *Biohydrometallurgy*, Mc Graw-Hill, Hamburg (1990).
2. 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.
3. Natarajan, K.A., Proc. *Biohydrometallurgy*, Theory & Practice, 131-134 & 697-718, 1994.
4. 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.
5. Silverman, M.P., Mechanism of bacterial pyrite oxidation, *J. Bacteriol.*, 94, 1046-1051, 1967.
6. 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.
7. Schippers, A. and 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.
8. Patnaik, L., 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.
9. Hansford, G.S., Vargas, T., Chemical and electrochemical basis of bioleaching processes, *Hydrometallurgy*, 59, 135-145, 2001.

10. Sand, W., Gehrke, T.J. and Schippers, A., (Bio)chemistry of bacterial leaching— direct vs. indirect bioleaching, *Hydrometallurgy*, 59, 159-175, 2001.
11. 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.
12. Pal,S.C., Mehta,K.D., Pandey,B.D. and Mankhand, T.R, Biomineral processing for extraction of copper metal from lean ore of Malanjkhand Copper Project, In. Proc. ICME-2005,Bhubanewar,246-255.