International Seminar on Mineral Processing Technology (MPT-2008), April 22-24, 2008
Jointly Organized by Indian Institute of Mineral Engineers & National Institute for Interdisciplinary Science & Technology, CSIR, Trivandrum.

MICROBIAL DISSOLUTION OF A LOW GRADE INDIAN CHALCOPYRITE ORE USING MIXED CULTURE OF MESOPHILES

Anand Ram, S[2]., Abhilash[1], Mehta, K.D.[1], Pandey, B.D.[1]✉ and Mankhand, T.R.[2]
[1]National Metallurgical laboratory, Jamshedpur-831007, Jharkhand, India
[2]Dept. of Metallurgical Engineering, I.T.B.H.U, Varansai-221005, U.P., India
✉ Author for Correspondence [Email-bd_pandey@yahoo.co.uk/biometnml@gmail.com]

Abstract
An enriched culture of mesophiles namely, Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans derived from mine water of Malanjhkhand Copper Project (MCP), India in the ratio of 4:1, and adapted on 5%(w/v) ore at 35°C was used for the bioleaching of a low grade chalcopyrite ore (0.27% Cu). Optimum copper recovery of 91% was achieved at 1.5pH and 10% (w/v) pulp density in 30days using <50µm particles. Copper recovery decreased to 82% when pH was raised to 2.5 under similar conditions. Higher copper recovery at pH 1.5 may be attributed to the improved bacterial activity ($7.0x10^8$ cells/mL), higher redox potential (666mV) and formation of minimum amount of hydronium jarosite, which was prominent at higher pH. Copper recovery was 41.2% in sterile control leaching conditions at 1.5pH. However, unadapted bacterial consortium yielded copper recovery of 69.4% only in 30 days at pH 1.5 under the above conditions. Higher metal recovery with adapted mixed culture may be attributed to increased rate of iron bio-oxidation. The biorecovery of copper from the MCP lean grade ore appeared to follow direct as well as indirect mechanism.

INTRODUCTION

With the extraction of metals, the reserves of high-grade ores are diminishing causing imbalance in the supply-to-demand ratio of metals [1]. However, there are fairly large stock of lean grade and complex ores from which extraction of metals using conventional techniques is not very attractive. In order to recover values from these materials particularly sulfides, an appropriate processing technology such as bioleaching has been a great success [2,3]. Chalcopyrite ($CuFeS_2$) is the most common, abundant and economically the most important mineral among all other sulfides of copper. Bioleaching of chalcopyrite using mesophilic bacteria has been extensively studied [4-6]. The microbial action on sulfide minerals with *A.ferrooxidans*, iron and sulfur oxidizing bacterium is well understood. Commercial application of bacterial leaching began in copper dump and heap-leaching applications [7,8] and also for the recovery of copper from chalcopyrite by the BioCOP™ process [9]. Various researchers have exploited the complex sulfide ore/bulk concentrates using single/mixed culture(s) of mesophilic micro-organisms (*A.ferrooxidans*, *A.thiooxidans*, *Leptospirillum ferrooxidans* etc.) in recent past. In India, attempts were earlier made to treat Malanjkhand Copper Project (MCP) ores, particularly the overburden material which was essentially a mixed copper oxide-sulphide (chalcopyrite) and lean grade ore [10,11]. Although, the copper bio-recovery from the mixed ore was observed to be favourable (50-60%) in 60 days on bench scale and 40-50% in column, however the same could not be established for the lean ore 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 [11] and 13-15% in heap in 30-40 days by MCP [12]. The bio-leaching of lean grade MCP ore has also been investigated to a limited extent with 75% recovery in 40 days in shake flasks from the quartzitic ore [13]. Oxidation of chalcopyrite by *A.ferrooxidans* generates [14] intermediate phases such as ferrous sulfate, sulfur and copper sulfate, and the presence of *A.thiooxidans* is expected to boost the dissolution of copper. Therefore, a consortium of *A.ferrooxidans* and *A.thiooxidans* isolated from source mine water and adapted on the ore was used for bioleaching of the low grade copper ore of granitic nature, found adjacent to the main ore body; the details are presented in the paper.

MATERIALS AND METHODS

Copper ore was procured in the form of lumps from the mine of Malanjkhand Copper Project, Balaghat, Madhya Pradesh, India. The ore was crushed, ground and passed through 150µm sieve to obtain different size fractions of the particles. 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 Spectrometer as discussed elsewhere [13]. Chemical analysis of the ore is: 0.27% Cu, 0.14% Ni, 8.91% Fe, 0.002% Co and 56.3% SiO_2. The low grade Malanjkhand copper ore is a granitic rock with disseminated sulfides. As regards morphology, sporadic bright patches were seen on the surface of the feldspar matrix of the bulk ore and the preliminary mineralogical study indicates the presence of mineral chalcopyrite in the cracks and fissures in quartz vein. Phases identified by XRD are chalcopyrite ($CuFeS_2$), pyrite (FeS) and silica (SiO_2) as the major phases whereas bornite is the minor phase.

The mine water was the source of *A.ferrooxidans* and *A.thiooxidans*. The bacterium was isolated in 9K and $9K^-$ (*Silverman and Lundgren*) media respectively which provided sufficient nutrients for the growth. *A.ferrooxidans* requires ferrous sulfate as an energy source for its growth and sulfur is the energy source for *A.thiooxidans.* Besides cell count, the oxidation of ferrous sulfate to ferric sulfate by *A.ferrooxidans* at pH 2.0, 35^oC while shaking at 120 rpm was taken as an indication for its growth. The enriched culture from the source with adaptation on 5% ore at 35^oC and without adaptation, and mixed in the ratio of 4:1 for *A.ferrooxidans* to *A.thiooxidans* were used as consortium for bioleaching.

Bioleaching experiments were performed in 500 ml Erlenmeyer conical flasks, fitted in an orbital motion incubator shaker with temperature control. Leaching solutions were inoculated with 10% (v/v) of enriched adapted consortium of *A.ferrooxidans* and *A.thiooxidans* in the ratio 4:1 in all cases except in sterile/control experimental sets, where mercuric chloride (0.02 g/L) was used as bactericide. The three times adapted consortium with a cell count of 6 $x10^8$ cells/mL were employed to examine the biodissolution of copper at pH 2.0, 35^oC temperature and 10% PD, unless otherwise stated. The pH of the solution was maintained by using 10N sulfuric acid, and 2N NaOH. Along with the pH adjustment, samples were mostly taken at the interval of the five days to analyze metals by AAS and to compute the metal recovery. During bioleaching, cell counts were also performed using Petroff Hauser Counter under Leica Biological Microscope. Ferrous ion was estimated by titrating the sample against potassium dichromate and redox potential (Eh) was measured and reported against SCE.

RESULTS AND DISCUSSION

Bioleaching of copper was examined at varying pH in the range 1.5-2.5 at 10%(w/v) pulp density, 35^oC for the ore of <50 µm size using the adapted consortia of enriched culture. The plot in Fig.2 showed maximum copper bio-recovery of 91% at pH 1.5 in 30 days. Copper recovery at this pH could be governed by both direct and indirect mechanism involving attachment of bacteria on the surface of sulfide mineral and also by oxidation with Fe(III) ions. The jarosite precipitation was also minimum at this pH. The bio-recovery was found to be 88% and 82% at pH 2.0 and pH 2.5 respectively, whereas it was 41%, 32.5% and 20.8% at pH 1.5, 2.0 and 2.5 in chemical leaching respectively. Lower recovery at a higher pH (2.0-2.5) may be attributed to the increased jarosite formation on the ore particles. The high bacterial population (7 $x10^8$ cells/mL) and redox potential (666mV) may be further correlated with high copper recovery at 1.5 pH.

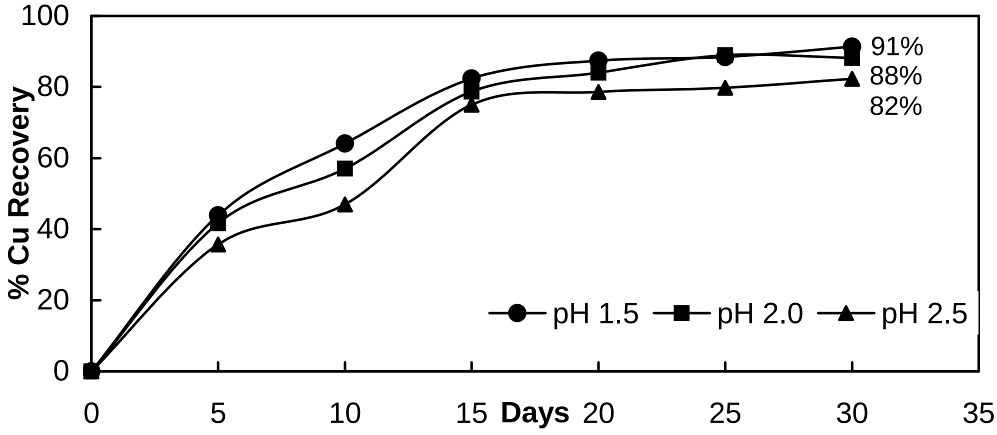

Fig.2:- Effect of pH on bioleaching of copper by bacterial consortium at 35^{o}C, 120 rpm, 10% w/v PD, <50 µm size

Fig.3 showed recovery of copper at pH 2.0 for the particle size of 150-75µm to be 43.5% and 26.6% with adapted and non-adapted bacterial consortia in 30 days time at 5% PD whereas it was 9.2% Cu dissolved in chemical leaching. Biorecovery of 40.7%, 37.7% and 35.2% Cu was obtained using adapted culture at 10, 15 and 20% PD. The lower recovery at higher pulp density may be attributed to the deficiency of oxygen and CO_2 availability for growth of bacteria. The high ferrous ion in chemical leaching produced lower oxidation potential resulting in poor metal dissolution.

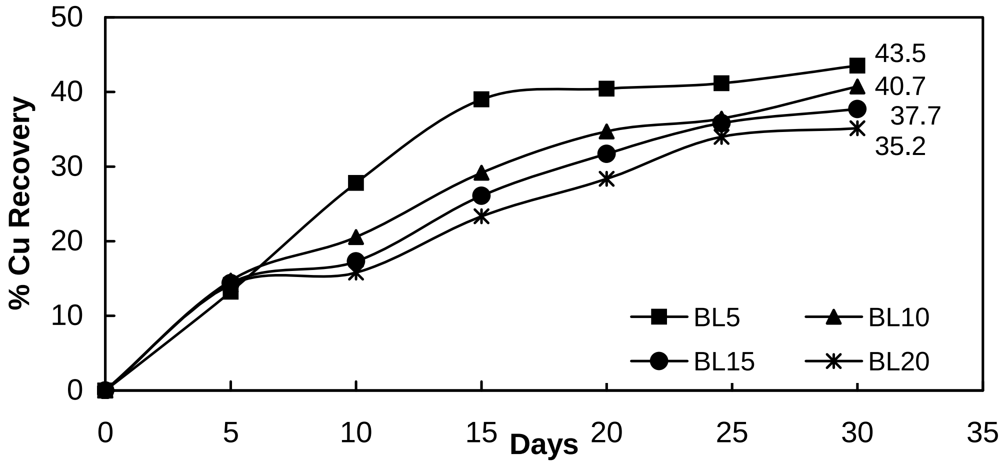

Fig. 3:-Effect of pulp density on bio-leaching of copper by bacterial consortium with particle size of

150-75 µm at 35^{o}C and pH 2.0

Recoveries of copper at different particle size in 30 days are reported in Fig.4. Copper recovery was 88% with <50µm size material using adapted consortium as compared to 69.5% recovery with non-adapted culture and 32.5% dissolution in control experiments. Copper biorecovery was found to 40.7% and 63.4% with 150-75µm, 75-50µm size ore particles in 30 days.

Fig.4:- Effect of particle size on bio-leaching of copper with bacterial consortium at 10% w/v PD, 35°C and pH 2.0

Copper recovery at different temperature in 30 days at 2.0 pH (Fig.5) showed maximum leaching at 35°C with adapted consortia. Biorecovery of copper increased from 51.6%-88% with increase in temperature from 25°C to 35°C. At 35°C, redox potential varied between 530 to 642 mV and 584 to 652mV in leaching experiments with unadapted and adapted strain whereas it varied between 305 to 378 mV in chemical leaching in 30 days. Maximum cell count of 5.6×10^8 cells/mL at 35°C was observed in 30 days time.

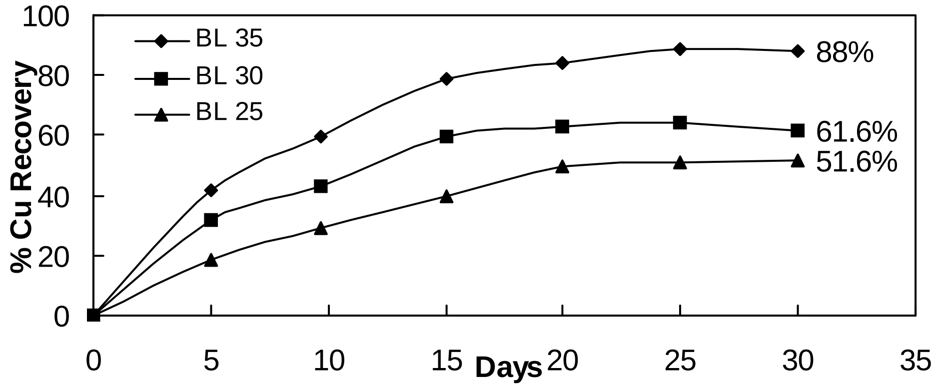

Fig. 5:- Effect of temperature on bioleaching of <50 µm size particle using adapted bacterial consortium at 10% w/v PD and pH 2.0

CONCLUSIONS

i) By using adapted bacterial consortium containing enriched culture of *A.ferrooxidans* and *A.thioooxidans* in 4:1 ratio, the biorecovery of copper increases by increasing the temperature from 25 to 35°C and decreasing the particle size from 150-75 to <50 µm. The metal recovery decreases at higher pulp densities with the adapted culture.

ii) Copper bio-recovery is maximum of 91% at 1.5 pH with the adapted bacterial consortium. Copper recovery decreases from 91% to 82% when pH is raised from 1.5-2.5 at 35°C, 10% (w/v) pulp density with particles of <50 µm size. Higher copper recoveries at low pH of 1.5 may be attributed to the improved bacterial activity and formation of minimum amount of hydronium jarosite as against larger amount of hydronium jarosite formation at high pH. The higher copper recovery may be correlated with oxidation of Fe (II) to Fe (III) with corresponding increase in redox potential and cell count. At 1.5 pH and 35°C temperature, the increase in redox potential and bacterial population is recorded as 340 to 666 mV and 1.5×10^7 to 7×10^8 cells/mL respectively in 30 days of bio-leaching.

iii) Treatment of MCP lean grade ore in the presence of native bacterial consortia shows the possibility of achieving high copper recovery.

REFERENCES

1. J.A. Brierley and C.L. Brierley, Hydromet. 2001, Vol. 59, pp. 233-239.
2. D.E. Rawlings and D.B.Johnson, Microbiol. 2007, Vol. 153, pp. 315–324.
3. L.C. Bryner and A.K. Jameson, Appl. Environ. Microbiol. 1958 Vol. 6, pp.281–287.
4. D. Bevilaqua, A.L.L.C. Leite, O. García and O.H. Tuovinen, Proc. Biochem. 2002, Vol. 38, pp. 587–592.
5. N.Okibe, M.Gericke, K.B.Hallberg, and D.B.Johnson, Appl. Environ. Microbiol. 2003, Vol.69, pp.1936-1943.
6. K.A. Third, R. Cord-Ruwisch and H.R. Watling, Hydromet, 2000, Vol. 55, pp. 225– 233.
7. M.B. Stott, H.R. Watling, P.D. Franzmann and D. Sutton, Min. Engg. 2000, Vol.13, pp. 1117–1127.
8. M.Qiu, S.Xiong, W.Zhang and G.Whang, Min. Engg. 2005, Vol.18,pp.989-990.
9. M.E. Clark, J.D. Batty, C.B. van Buuren, D.W. Dew and M.A. Eamon, Hydromet. 2006, Vol. 83, pp. 3–9.

10. K.A. Natarajan and Narayanmoorty, Trans. Ind Inst. Met., 1980, Vol. 35(5), pp. 353-358.

11. A.D. Agate, K.M. Panikar and N.J. Khinvasara, In Proc. “Biohydrometallurgy’89”, CANMET, 1989, (Eds. J. Salley, R.G.L. Mcready & P.L. Wichlaez,), pp. 577-589.

12. M.M. Nandi, R.C. Gupta and B.R.Sant, Met.Mat.Rev.,1978, pp. 238-240.

13. S.C. Pal, Abhilash, K.D. Mehta, V. Kumar, B.D. Pandey and T.R. Mankhand, In. Proc. Int. Sem. Min. Proc. Tech. (MPT-2007),Feb.22-24, Mumbai (Eds. N.K.Khosala & G.N.Jadhav), pp.524-527.

14. A.E. Torma, Adv. Biochem. Engg., 1977, Vol. 3, pp. 1-37.