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EFFECTIVENESS OF BIOLEACHING OF LOW GRADE INDIAN CHALCOPYRITE ORE USING PURE AND MIXED CULTURE OF MESOPHILES

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Abstract
In this research, efforts were made to examine bioleaching behaviour of copper from a low grade Indian copper ore (0.3% Cu) containing chalcopyrite as the major mineral phase using enriched culture of *Acidithiobacillus ferrooxidans* and a mixed culture (4:1 ratio) containing *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*. The experiments were carried out in shake flasks with the inocula of bacteria obtained from source mine water of Malanjkhand Copper Project (MCP) after adaptation on the ore. Results showed that metal extraction employing a mixed culture of *Acidithiobacillus ferrooxidans (A.ferrooxidans)* and *Acidithiobacillus thiooxidans (At.t)* was higher of 88% copper than that of 75% copper dissolution with a bacterial culture viz. *A.ferrooxidans* at 2.0 pH, 35^{o}C temperature using <50µm size particles. The selection of the pH and effective particle size during the bioleaching process were found to influence metal dissolution. The paper also highlights the mechanism of bioleaching, the role of iron and its precipitation as jarosite, and the correlation of redox potential with copper recovery.

Keywords: - low grade ore, chalcopyrite, bioleaching, mixed culture, *Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans.*

1. Introduction
World wide reserves of high-grade ores are depleting at an alarming rate due to rapid increase in the demand of metals [1]. However, there are fairly large stock of lean grade and complex ores and to extract the metals from them using conventional techniques are very expensive because of high energy and capital inputs required. Furthermore, fines generated during mining, milling and other metallurgical operations are to be processed not only to recover the values but also to comply with the stringent environmental issues. In order to recover values from these low-grade ores and fines, an appropriate processing technology is required [2]. Production of base metals from lean and off-grade ores using bio-hydrometallurgical processes has been widely used all over the world. Apart from recovering copper from chalcopyrite, chalcocite and covellite minerals, bio-hydrometallurgical processes have also been commercially employed for recovering gold from arsenopyrites and uranium from oxidic ores.

It was understood that the Romans made use of bacteria to extract metals from sulfide ores long before the actual importance was understood. Commercial exploiters of copper-bearing ore bodies have almost certainly made use of microorganisms down the centuries, but it was only in the mid nineties that their contribution was recognized. The microbial action on sulfide minerals was explained with the isolation and characterization of the sulfur and iron oxidizing bacterium, *Acidithiobacillus ferrooxidans* [3]. Commercial application of bacterial leaching began in the late 1950s at the Kennecott Copper Company's Bingham Canyon Mine [4]. Since then, most use of these and other microorganisms has expanded worldwide applications particularly in copper dump and heap-leaching applications [5]. The application of biotechnology to the minerals industry came in light with the commercial success with the mesophilic oxidation of refractory gold ores via the BIOX® process, followed by the recovery of copper from chalcopyrite by thermophiles using the BioCOP™ process [6-8]. Various researchers have exploited the complex sulfide ore/bulk concentrates using single/mixed culture(s) of mesophilic micro-organisms (*Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans*, *Leptospirillum ferrooxidans*,etc..) in recent past [9,10]. Implications of acidophilic thermophile-*Acidianus brierleyi*, *Sulfolobus* etc. has off late gained importance for the recovery of copper from chalcopyrite concentrate in various parts of world [11,12]. In India, attempts were earlier made to treat MCP ores, particularly the overburden material which were essentially a mixed copper oxide-sulphide (chalcopyrite) and lean grade ore [13,14]. 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 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 [15], 13-15% in 30-40 days by MCP [16,17]. 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 [18].

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 [19]. In bench scale studies, shake flasks were used for the optimization of bio-leaching parameters [20]. Ferric iron is an important oxidizing agent in the bacterial leaching of sulfide minerals. Soluble iron species are the main determinants of redox potential, with active iron-oxidizing bacteria, 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 [21].

Malanjkhand Copper Project (MCP), an open pit mine has around 16.5 million tonnes of ~1% Cu which will not last long. In such a situation, new methods for extracting copper from the low grade ores (2.5 million tonnes) found adjacent to the rich grades requires attention [22]. As such the bio-leaching of the lean MCP ore requires serious efforts so as to arrive at the conditions suitable for exploitation. This paper illustrates the bioleaching of copper from a low grade granitic chalcopyrite ore of MCP using a pure culture of *Acidithiobacillus ferrooxidans* and mixed culture of *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*.

2.experimental procedure

2.1. Copper Ore: - Lean grade copper ore (containing 0.27%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 150µm sieve. Representative samples were then prepared by coning and quartering method for each fraction to get chemical analysis by using Atomic Absorption Spectrometer. The chemical analysis of the sieve fractions is given in Table-1.

Table 1: Chemical analysis of different sieve fractions of copper ore

Particle size (µm)	Fraction retained, %	Cumulative Fraction retained,%	Composition (%)		
			Cu	Ni	Fe
>150	26.87	26.87	0.17	0.14	4.41
150-75	23.13	50.00	0.27	0.22	4.47
75-50	13.63	63.63	0.29	0.12	3.34
<50	36.37	100.00	0.32	0..12	6.62

The low grade 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 indicated the presence of mineral chalcopyrite in the cracks and fissures in quartz vein. The microscopic study of a typical sample (bakelite mounted and polished section) was identified by Leitz Varian Orthomat Optical Microscope, microphotographs of typical sample of copper ore (Fig.1) showed the distribution of phases.

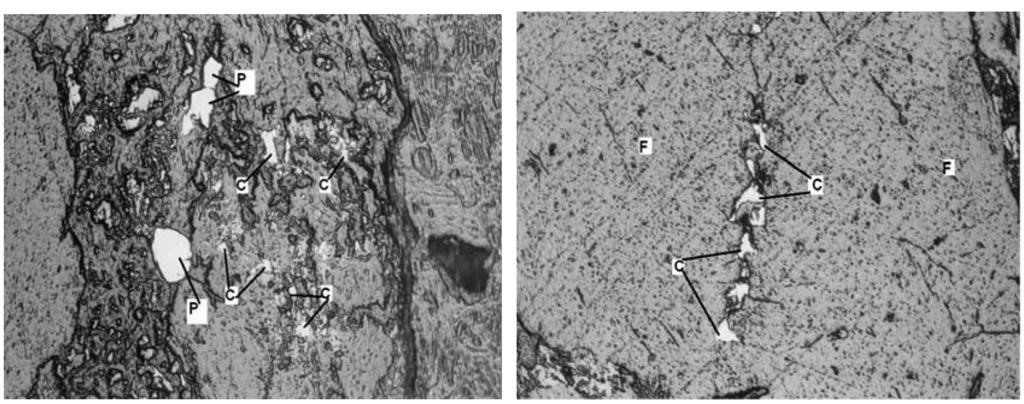


Fig.1: - Petrological micrograph of copper ore (100X) [C-Chalcopyrite, P- Pyrite, F-Feldspar]

Chalcopyrite is present in the form of irregular grains in the free form, in veins of quartz which is not continuous. Also, it reveals the presence of pyrite (brighter than chalcopyrite) and chalcopyrite on fractured, filling along fractured zone and within feldspar grains. The bulk ore is slightly pink in appearance; this is due to the high percentage of granite in the ore body. Silica is very high (38%) in the ore. Phase identified by XRD showed major phases as chalcopyrite ($CuFeS_2$), pyrite (FeS_2) and silica (SiO_2) whereas bornite was the minor phase.

2.2. Micro-organism and Bio-leaching experiments: - The source of bacteria was the mine water, which contained cultures of *Acidithiobacillus ferrooxidans (A.ferrooxidans)* and *Acidithiobacillus thiooxidans (A.thiooxidans).* The bacterium was isolated in 9K and $9K^-$ (*Silverman and Lundgren*) media respectively which provided sufficient nutrients for the growth. *Acidithiobacillus ferrooxidans (A.ferrooxidans)* required ferrous sulfate as an energy source for its growth, whereas sulfur was the energy source for *Acidithiobacillus thiooxidans (A.thiooxidans).* The oxidation of ferrous sulfate to ferric sulfate by *Acidithiobacillus ferrooxidans* at pH 2.0, 35^{o}C while shaking at 120 rpm was taken as an indication for the growth of *Acidithiobacillus ferrooxidans (A.ferrooxidans)*. *Acidithiobacillus ferrooxidans* was said to be fully grown, when the ferrous content of the solution became nil. The indication for growth of *Acidithiobacillus thiooxidans (A.thiooxidans)* was observed by its cell count and size. The constant readings of redox potential also gave the indication of its growth. The fully grown strain of *Acidithiobacillus ferrooxidans* contained 1.5×10^8 cells/mL and *Acidithiobacillus thiooxidans contained* 3.75×10^8 cells/mL after three times sub-culturing. The enriched culture thus derived from the source mine water were used as such for inoculation in subsequent bioleaching experiments.
Bioleaching experiments were performed in 500 mL Erlenmeyer conical flasks, fitted in an orbital motion incubator shaker. Leaching solutions were inoculated with 10% (v/v) of active and non-adapted *A.ferrooxidans* for pure culture based experiments. Whereas, *A.ferrooxidans* and *A.*thiooxidans in the ratio 4:1 as active and adapted consortia in all cases, except in sterile/control experimental sets, where mercuric chloride (0.02 g/L) was used as bactericide. General conditions like 35^{o}C temperature, pH 2 and 10% (w/v) pulp density with shaking at 120rpm were used unless otherwise stated. Sterilized distilled water was used for the experiments. The pH of the solution was maintained by using 10N sulfuric acid, and 2N NaOH. Along with the pH adjustment, redox potential (E_h) was measured against SCE and reported as such in the text which was mainly governed by the concentration of ferrous and ferric ions in the solution. During bioleaching experiments, cell counts were also obtained by Petroff Hauser Counter. Ferrous ion was estimated by titrating the sample against potassium dichromate with barium diphenylamine sulfonate as indicator. Samples were mostly taken at the interval of the five days unless stated otherwise to analyze metals and to compute the metal recovery by analyzing the solution by AAS. Solution losses due to titration and cell counting were made up by using distilled water. 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.

3. Results and discussion
For bioleaching of copper ore, a mesophilic bacterial species as pure culture and consortium was inoculated with the ore and various process parameters, viz., pH, pulp density, particle size and temperature were optimised. The details are presented in this section.

3.1. Bioleaching experiments using pure culture of *Acidithiobacillus ferrooxidans*

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.

3.1.1 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^{o}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.

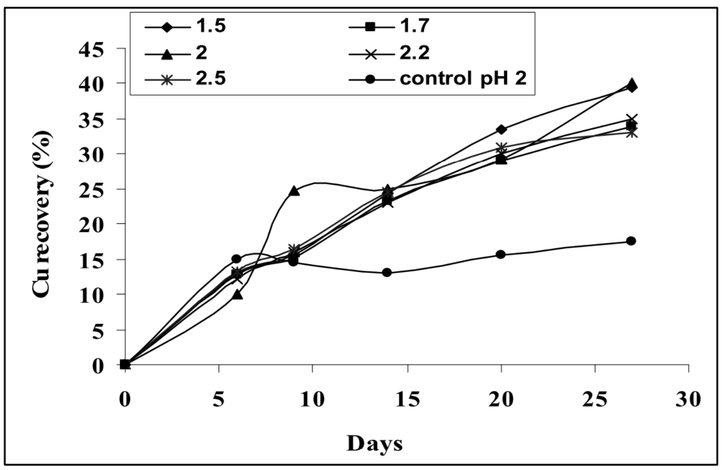


Fig.2: Recovery of copper at different pH in 30 days using *A.ferrooxidans* isolate from mine water without adaptation at 25^{o}C, 5%PD and particles of <50µm.

3.1.2. 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^{o}C with <50µm size particles using 10% (v/v) isolate of *A.ferrooxidans* 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.

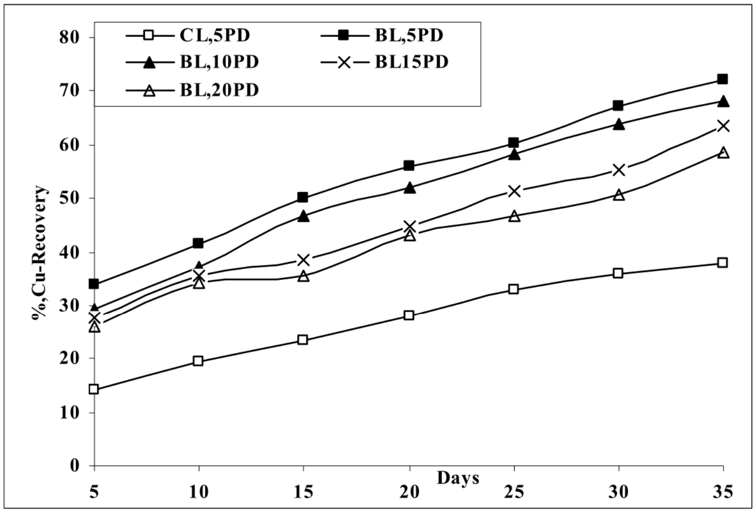


Fig.3: Copper recovery during bioleaching at different Pulp density using 10%(v/v) *A.ferrooxidans* without adaptation on ore at 35^{o}C, <50µm particles and pH 2.

3.1.3. 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.

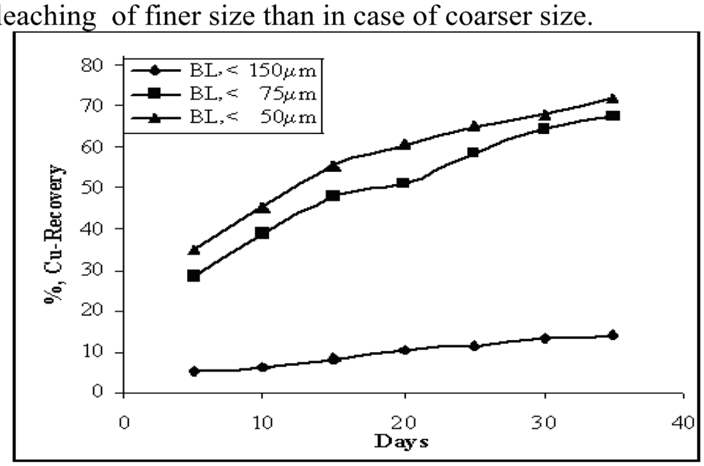


Fig.4: Effect of particle size on bioleaching of copper ore with isolated *A.ferrooxidans* from Malanjkhand mine water without adaptation at 35^{o}C, pH 2 and 5% PD.

3.1.4. 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^{o}C at 5% PD and using 10% (v/v) isolate of *A.ferrooxidans* at pH 2, while shaking at 100 rpm was studied**.** The maximum copper recovery was found to be 70.2 % at 35^{o}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.

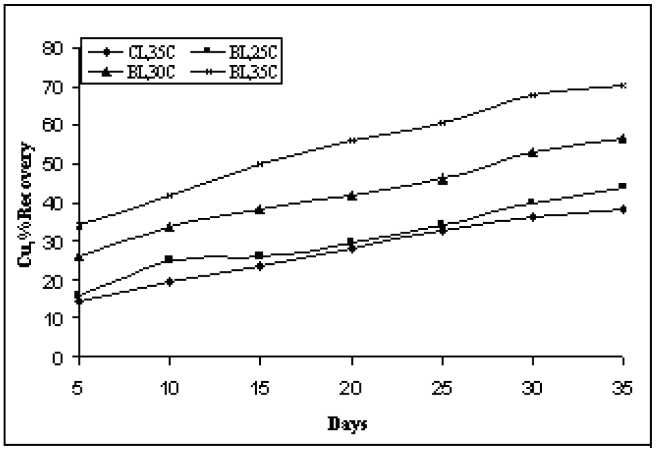


Fig.5: Effect of temperature on bioleaching of copper ore with isolated *A.ferrooxidans* from Malanjkhand mine water without adaptation at PD 5% w/v, pH 2 and <50µm size.

3.2. Bioleaching experiments using adapted culture of *Acidithiobacillus ferrooxidans*

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

3.2.1 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^{0}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.

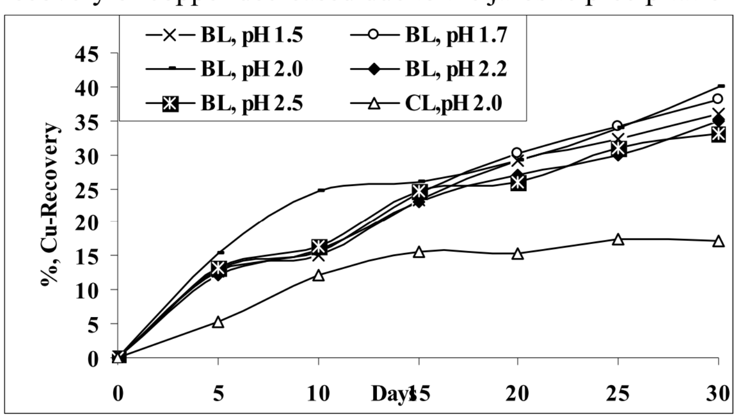


Fig.6: Recovery of copper during bioleaching with adapted *A.ferrooxidans* at different pH at 5% (w/v) PD, 25°C using <50µm particles.

3.2.2 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 *A.ferrooxidans* in 200 ml leaching medium at pH 2 and 25^{o}C while shaking at 100rpm. As shown in Fig.7, maximum copper recovery (47.5%) was obtained with *<50µm* size material using adapted *A.ferrooxidans* which is a little higher (44%) than that of non-adapted *A.ferrooxidans*. 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 *A.ferrooxidans* respectively in 30 days with <*50µm* size particles which suggested high metal dissolution was obtained in case of adapted *A.ferrooxidans* strains.

3.2.3 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 *A.ferrooxidans* (adapted on MCP Cu-ore) in 200 ml leaching medium at pH 2, while shaking at 100 rpm at 25^{o}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 *A.ferrooxidans* 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 *A.ferrooxidans* 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 *A.ferrooxidans* and *A.ferrooxidans* adapted on copper ore (Fig.8) respectively. This might be the reason for maximum recovery with adapted *A.ferrooxidans* at this pulp density as shown in Fig.8.

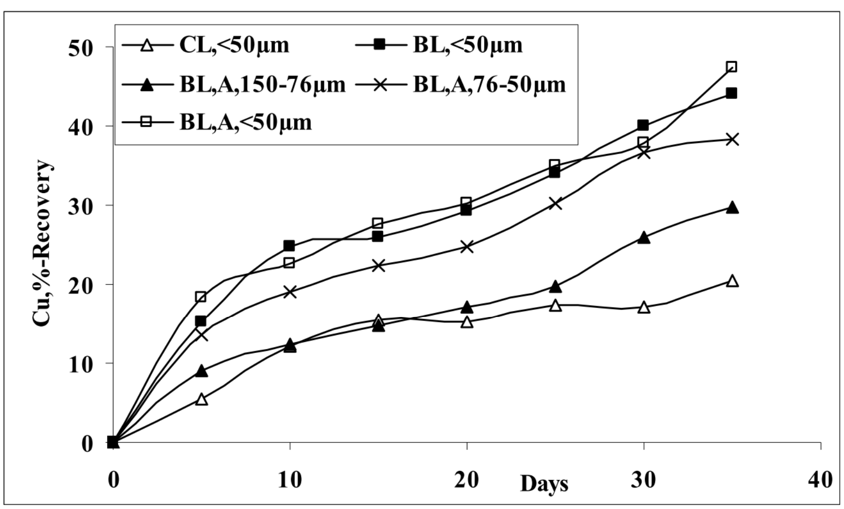


Fig.7: Cu recovery during bioleaching with adapted *A.ferrooxidans* at different particle size of ore, pH 2, 5% pulp density and 25°C.

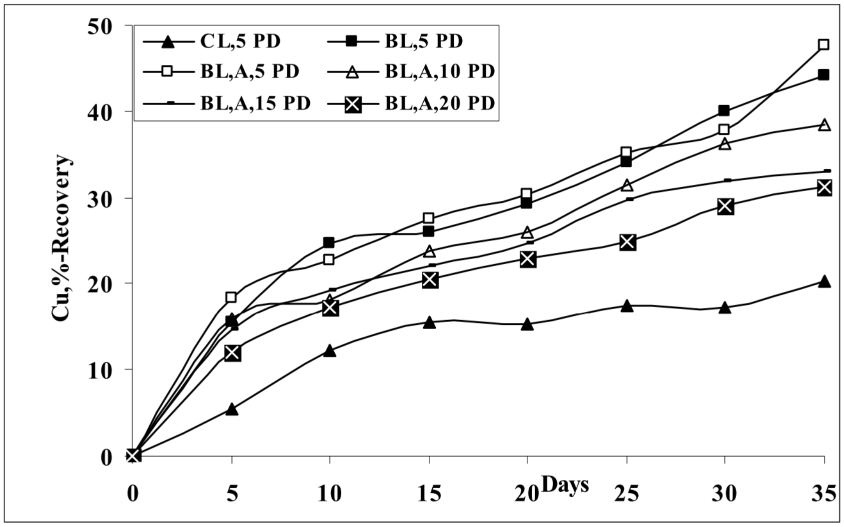


Fig.8: Recovery of copper during bioleaching with adapted *A.ferrooxidans* at different pulp densities and 25°C, <50µm particles, pH 2.

3.2.4 Effect of temperature

Effect of temperature on bio-dissolution of copper using adapted *A.ferrooxidans* was investigated in the range 25-35ºC 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 *A.ferrooxidans* (75.3%) as compared the recovery (72%) with non-adapted *A.ferrooxidans*; 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^{o}C to 35^{o}C. At 35^{o}C redox potential varied between 602 to 661mV and 580 to 668 mV in leaching experiments with unadapted and adapted *A.ferrooxidans* 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 *A.ferrooxidans* 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 *A.ferrooxidans*, resulted in better metal bio-dissolution.

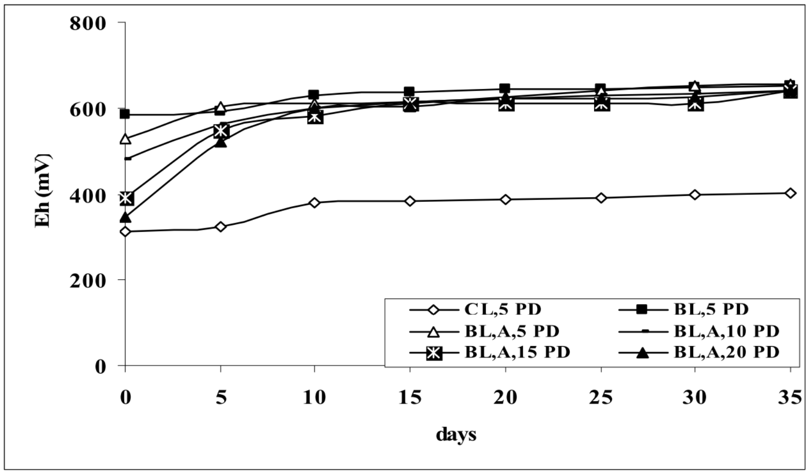


Fig.9: Change in redox potential of the solution during bioleaching with adapted *A.ferrooxidans* at different pulp densities, <50µm particles, pH 2 and 25°C.

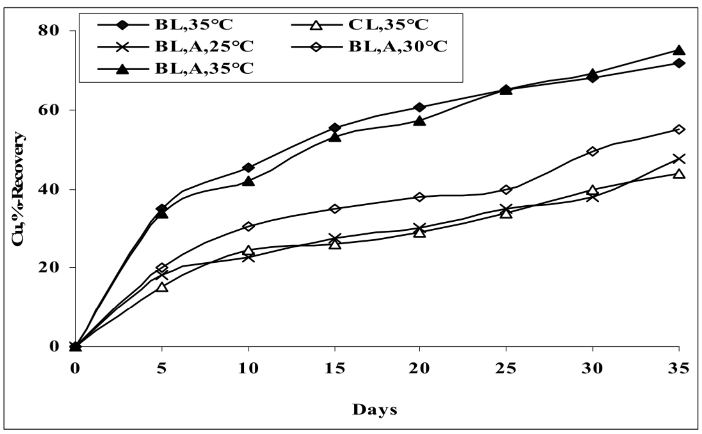
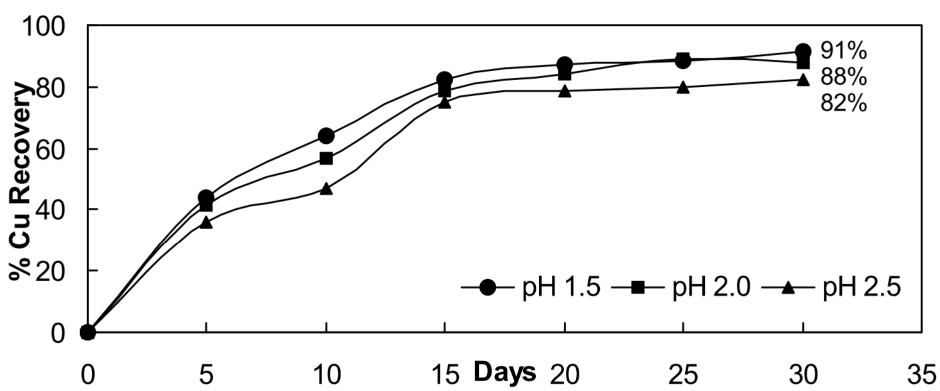


Fig.10: Cu recovery during bioleaching with adapted *A.ferrooxidans* at different temperatures, <50µm particles, pH 2, 5% pulp density.

3.3. ***Bioleaching experiments using consortia of Acidithiobacillus ferrooxidans: Acidithiobacillus thioooxidans***



3.3.1 Effect of pH

Bioleaching of copper was examined at varying pH in the range 1.5-2.5 at 10%(w/v) pulp density, 35^{o}C for the ore of <50 µm size using the adapted consortia of enriched culture. The plot in Fig.11 showed maximum biorecovery of copper was maximum 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.11:- Effect of pH on bioleaching of copper by bacterial consortium at 35^{o}C, 120 rpm, 10% w/v PD, <50 µm size

3.3.2 Effect of Pulp Density

Fig.12 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.

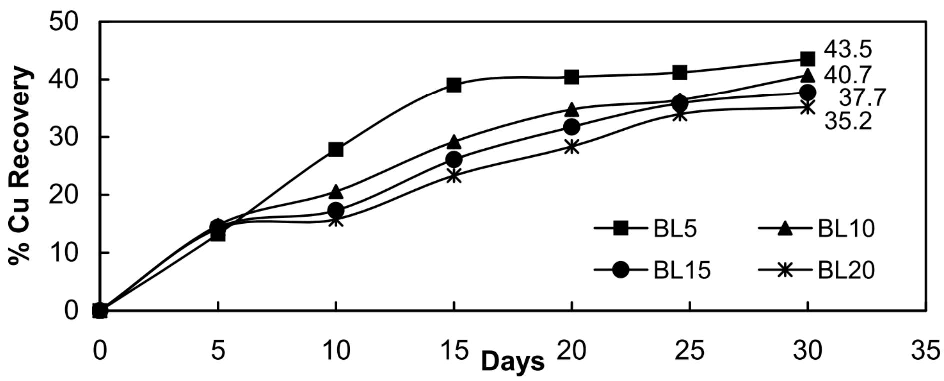


Fig.12:-Effect of pulp density on bio-leaching of copper by bacterial consortium with particle size of 150-75 µm at 35^{o}C and pH 2.0

3.3.3 Effect of Particle Size

Recoveries of copper at different particle size in 30 days are reported in Fig.13. 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.

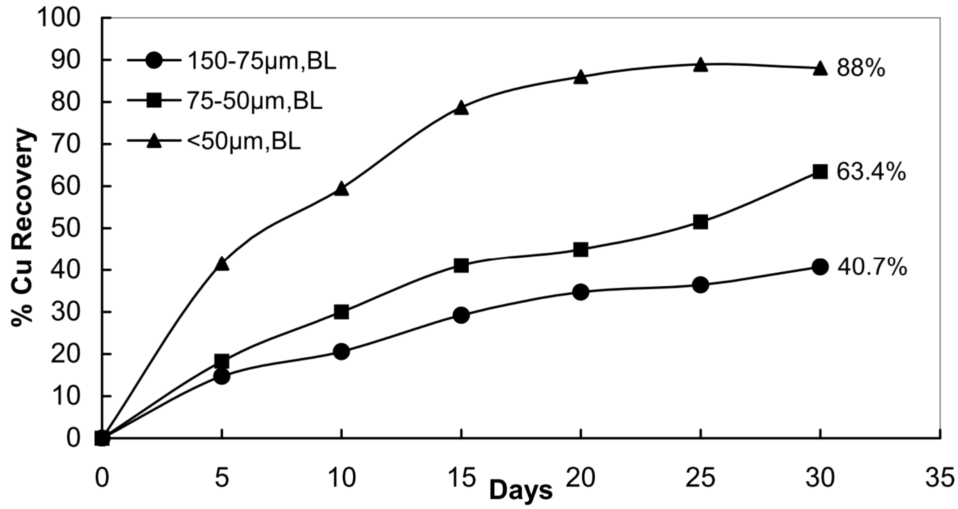


Fig.13:- Effect of particle size on bio-leaching of copper with bacterial consortium at 10% w/v PD, 35°C and pH 2.0

3.3.4 Effect of Temperature

Copper recovery at different temperature in 30 days at 2.0 pH (Fig.14) 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.

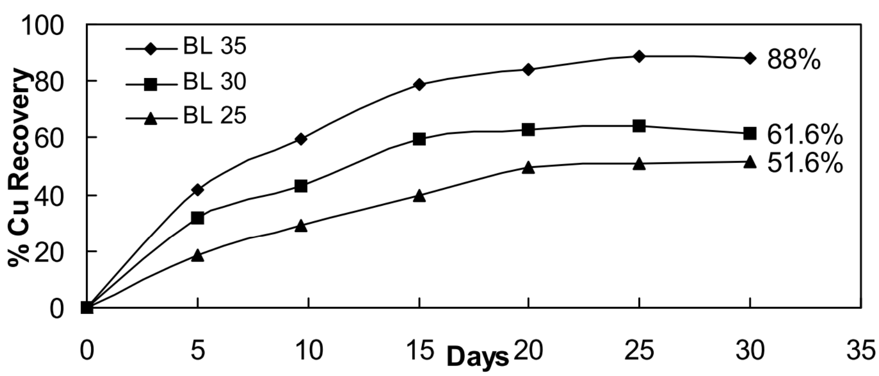


Fig.14:- Effect of temperature on bioleaching of <50 µm size particle using adapted bacterial consortium at 10% w/v PD and pH 2.0

4.0 XRD Phase Analysis & Mechanism of Bioleaching

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: -

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

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.

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

$$4CuFeS_2 + 17O_2 + 2H_2SO_4 \xrightarrow{A.ferrooxidans} 4CuSO_4 + 2\,Fe_2(SO_4)_3 + 2H_2O \ldots\ldots (1)$$

The bio-oxidation of chalcopyrite also involves oxidative ferric reaction, which represents indirect leaching mechanism as:

$$CuFeS_2 + 2O_2 + Fe_2(SO_4)_3 \xrightarrow{A.ferrooxidans} CuSO_4 + 3\,FeSO_4 + S^o \ldots\ldots (2)$$

This apart from dissolution of the metal sulfide 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 equations (3) and (4) respectively:

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

and:

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

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

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

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

Reaction (2) 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

Following conclusions may be derived from the present work on the bioleaching of copper ore of MCP:

1. 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.

2. With the use of pure culture of bacteria (non-adapted), the optimum metal dissolution of 72% copper was observed at pH 2.0, pulp density 5% (w/v) and particle size <50 μm in 35 days. In presence of *A.ferrooxidans* adapted on copper ore, bioleaching of copper was found to be 75.3% Cu under the optimum conditions. Thus, the introduction of adapted *A.ferrooxidans* markedly improved the metals recovery.

3. Use of enriched microbial culture in the ratio of 4:1(*Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*) for biodissolution of copper showed an increasing trend with rise in the temperature from 25-35^{o}C and increase in fineness of the ore particle. Increase in pH from 1.5-2.5 and pulp density from 5-20% (w/v) has decreased the copper biorecovery irrespective of the particle size of the ore.

4. 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^oC and decreasing the particle size from 150-75 to <50 µm. The metal recovery decreases at higher pulp densities with the adapted culture.

5. The optimum copper bio-recovery using adapted consortia was 91% against 69.4% recovery in 30 days using unadapted consortia at 35^oC temperature, 1.5 pH, 10% (w/v) pulp density using ore particles of <50µm size. The higher copper recovery may be again correlated with oxidation of Fe (II) to Fe (III) with corresponding increase in redox potential and cell count. At 1.5 pH and 35^oC temperature, the increase in redox potential and bacterial population is recorded as 340 to 666 mV and $1.5x10^7$ to$7x10^8$ cells/mL respectively in 30 days of bio-leaching.

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

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