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Percolation bacterial leaching of low-grade chalcopyrite using acidophilic microorganisms

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Abstract−Bioleaching studies were carried out in percolation columns using low-grade copper containing rock (granite). The lixiviant consisted of acidified ferric sulfate containing acidophilic microorganisms. The iron oxidizing strain was isolated from Malanjkhand mine water and after adaptation the iron oxidation observed to be 500 mg/L/h. Leaching parameters studied were lixiviant flow rate, particle size and bed height. It was observed that leaching efficiency increased with decrease of particle size and lixiviant flow rate. The precipitation of iron during leaching observed to be low as pH was maintained at 2. Based on the leaching kinetics, a unified rate equation was developed and shown as $r\acute{\alpha}\ (d_p)^{-0.61}\ (F)^{-0.76}\ (H_b)^{0.97}$.

Key words: Bacterial Leaching, Columns, Lixiviant, *Thiobacillus ferrooxidans*, Particle Size

INTRODUCTION

Recovery of metal values through bioleaching is very common technique for the oxidation of gold-bearing pyrites, and commercial recovery of Uranium and copper in both heaps and tank reactors [1,2]. This technique is slowly gaining importance in the field of waste treatment [3]. In the year 1998, about 200,000 t/year of cathode copper was produced through bacterial leaching of agglomerated ore in heaps [4,5]. Renman et al. [6] described step by step progress made in setting up and operating bacterial heap leaching facilities to produce 300 to 10,000 t/year of cathode copper in the Zijinshan copper mine in China. In the bioleaching process, leaching studies are initially carried out in a shake flask, followed by percolation column and finally in pilot heap before going for commercial venture. The shake flask studies show the amenability of the ore towards bioleaching, percolation column leaching indicates the acid consumption and other leaching parameters which affect the leaching rate such as lixiviant flow rate, aeration rate, effect of rest period, and, finally, the precipitation of iron species during leaching. Therefore, the percolation leaching gives an important insight into the overall leaching process; and based on the same, further decisions are initiated regarding the fruitfulness of possible heap leaching. The heap leaching process helps in evaluating the techno-economics of the overall process. There are large numbers of publications related to bacterial percolation leaching [7-10]. Peterson and Dixon [7] used small scale columns to study bioleaching of pyrite and chalcopyrite ores at selected temperatures using bacterial consortia suited to those temperatures. They found that secondary copper sulfides would leach more rapidly than pyrite. Chalcopyrite, however, appeared to leach only in the presence of extremely thermophilic microbes. Bioleaching studies have also been carried out in percolation columns using thermophilic microorganisms [8]. Heat generated during the reaction was calculated based on the head and residue analyses. Column testing was also performed by Acar et al. [9] to compare bioleaching of covellite ore at ambient mesophilic temperature using *Acidithiobacillus/Leptospirillum/Sulfolobus* species and at elevated thermophilic temperature conditions with *Acidianus* and *Metallospheara.* They obtained only 12-20% copper extraction using mesophilic bacteria, whereas 62-65% of copper could be leached at elevated temperatures. Ahonen and Tuovinen [10] were interested in examining several variables in column bioleaching of complex sulfide ore material which contained chalcopyrite, pentlandite, pyrite, pyrrhotite and sphalerite. It was reported that in inoculated columns new solid phases (covellite, jarosite, Fe(III) oxide and elemental sulfur) were formed. Based on the leaching studies in a percolation column, a number of mathematical models have been developed [11-13]. Lizama [14] proposed shrinking core model for the dissolution of low grade ore in a percolation column, where bacteria initially attached to the sulfide moiety.

Although extensive works have been reported either with copper or copper-zinc ore, the literature is rather scanty regarding the effect of various parameters which actually determine the rate process. The biggest copper mine is located at Malanjkhand, in the central part of India under Hindustan Copper Limited, Government of India undertaking. It is excavating 2 million tones (MT)/annum of copper ore. During excavation, a large amount of waste (0.55 MT/annum) is generated which contains primarily chalcopyrite with traces of oxidized, semi-oxidized and secondary sulfides. In addition to this about 2 MT of low grade (<0.3% Cu) waste has accumulated near the mine site. Since there was no suitable viable process available to recovery copper from this waste as the waste contains mainly chalcopyrite which is resistant to hydrometallurgical processes [15]. Therefore, the Institute of Minerals and Material Technology, Bhubaneswar has initiated efforts to develop a new process to utilize the same. As part of this goal, the present communication reports the findings of studies carried on a low-grade chalcopyrite in columns using bacterial film oxidation (BACFOX) Unit.

MECHANISM OF BACTERIAL LEACHING

The following reactions were proposed [16,17] to take place dur-

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ing the dissolution process of copper bearing sulfide minerals with bacteria. In pyrite oxidation, acid forms as a result of the following two reactions:

$$FeS_2+7/2\ O_2+H_2O\rightarrow Fe^{2+}+2H^{+}+2\ SO_4^{2-}+2e^{-} \quad (1)$$

$$FeS_2+14\ Fe^{3+}+8H_2O\rightarrow 15\ Fe^{2+}+16H^{+}+2SO_4^{2-} \quad (2)$$

In chalcopyrite, both the oxidizable metal moiety and sulfide moiety are simultaneously attacked.

$$4\ CuFeS_2+17O_2+10\ H_2O\rightarrow 4\ Cu^{2+}+4\ Fe\ (OH)_3+8\ H^{+}+8\ SO_4^{2-} \quad (3)$$

MATERIALS AND METHODS

1. SEM Studies

Representative granite sample containing copper minerals were collected from Malanjkhand and their surfaces were polished by conventional polishing technique. Different ore mineral species were then identified under Leitz optical microscope. Element distribution of the feed granite and broken surface of leached samples was studied during different stages of column leaching studies by using an electron microprobe (Jeol, JXA 8100).

2. Leaching Studies

The acidophilic microorganisms (*Thiobacillus ferrooxidans*) were isolated from the mine site. Initially the strains were grown in 9 K medium. After activation by repeated sub-culturing, the most suitable strain was selected for leaching purpose based on iron oxidation rate. The strain was adapted to Cu (1 g/L) by incremental increase of the same. Adapted strain was transferred to BACFOX and lixiviant being supplied for leaching purpose during the entire period. Percolation leaching studies were carried out in PVC columns having an internal diameter of 7.5 cm. In total 10 nos. of columns were installed to study leaching parameters like flow rate, particle size and bed height. The leaching conditions and other operating parameters are shown in Table 1. The bacterial lixiviant composition is shown in Table 2A. The columns were operated in lock-day fashion; that is the effluent, or intermediate leach solution (ILS), was reapplied to the top surface of the ore in the column. The percolation leaching studies were carried out in ambient temperature. Each column was percolated with 10 liters of lixiviant. The concentrations of Fe(II) and Fe(T) were analyzed by volumetric method using dichromate as standard solution and Barium diphenyl ammonium sulfate (BDAS) [18] as indicator. Other metal ions were analyzed by Perkin Elmer-372 model atomic absorption spectrophotometer.

RESULT AND DISCUSSION

1. Characterization of Malanjkhand Copper-containing Rock Sample

The ore sample is pink colored granites irregularly traversed by quartz vein. The granite is constituted of both feldspar (aluminum silicate mineral) and quartz (silica mineral) as major phases. Copper minerals are sparsely distributed (<1%) within granite. The major copper-bearing minerals present are chalcopyrite (Fig. 1) and covellite. The former mineral occurs as minute disseminated grains in-

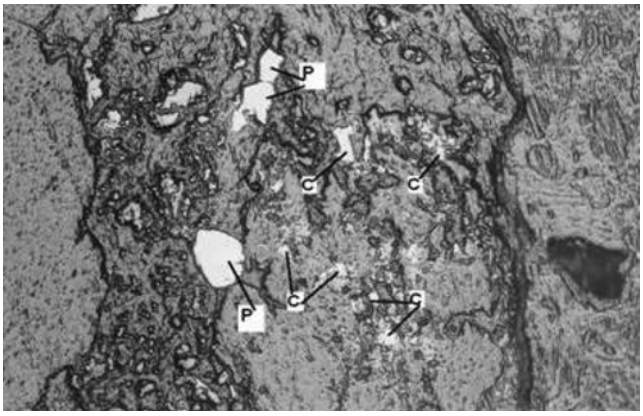

Fig. 1. Optical photomicrograph of Chalcopyrite (C) and Pyrite (P) within silicate matrix (F) ×100.

Table 1. Leaching parameters

Column no	Column height cm	Screen size, mm	d_p, mm	Flow rate L/h	Amount of ore, kg	Acid consumed during washing (g)	Cu leached during acid washing (%)	Acid consumed during leaching (Acid, g/Cu)
C1	131	−18 +15	16.5	1.0	10	4.23	0.1575	13.802
C2		−15 +10	12.5			9.2	0.2893	5.868
C3		−10 +6	8			10.8	0.7381	4.702
C4		−6 +3	4.5			12.08	0.9158	6.2
C5		−18 +15	16.5	0.5		11.57	0.2014	5.586
C6		−18 +15		1.5		6.28	0.1192	6.983
C7		−18 +15		2		12.9	0.1986	9.575
C8	105	−18 +15		1.0	7	10.58	0.2544	7.533
C9	70	−18 +15			5	6.55	0.7534	12.47
C10	47	−18 +15			3	5.32	0.9269	16.132

Table 2A. Composition of bacterial Lixiviant

pH	Eh	Fe(II),g/L	Fe(III), g/L	Cu, mg/L	Cell count,10^5 cells/mL	Temp, °C	Iron Oxidation rate, mg/L/h
2	700 mV	0.25	8.5	10	2.5	30± 2	500

dependently or as inclusion within pyrite or as secondary vein in the contact of pyrite and quartz. The covellite appears as veins/veinlets traversing magnetite. The other associated ore minerals are iron-bearing phases like magnetite (Fe_3O_4) and pyrite (FeS_2). Chalcopyrite grains are usually smaller than both pyrite and magnetite.

Selective samples were also studied under electron microscope. X-ray image map of Cu, Fe, S elements confirmed the presence of the phases recognized under optical microscope. Fig. 2 illustrates the occurrence of chalcopyrite both as inclusion within pyrite and as veins. After a period of eight months no further leaching of copper value was recorded. When this sample was studied under electron microprobe a thin layer covering the mineral surface was observed (product layer, Fig. 3) which prevented further leaching. Sometimes, inclusion of chalcopyrite specks within magnetite is recorded, which is difficult to liberate.

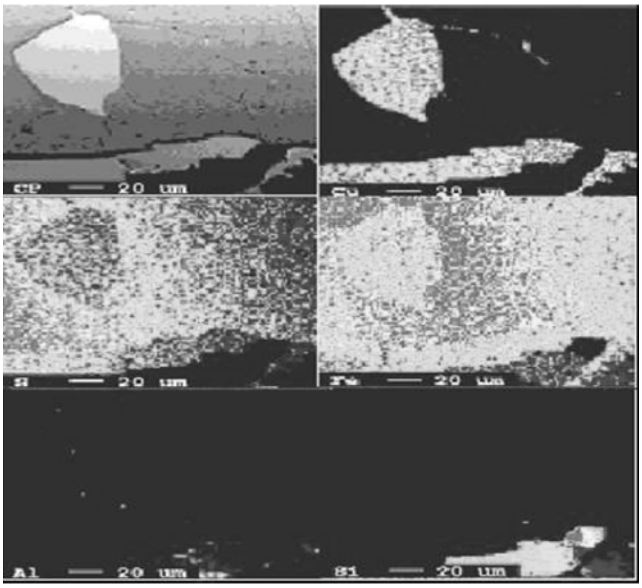

Fig. 2. Tiny chalcopyrite ($CuFeS_2$) grain within pyrite (FeS_2). A small vein of chalcopyrite is traversing along the contact of pyrite and quartz. X-ray image of Fe, S, Cu, confirm the presence of chalcopyrite and pyrite.

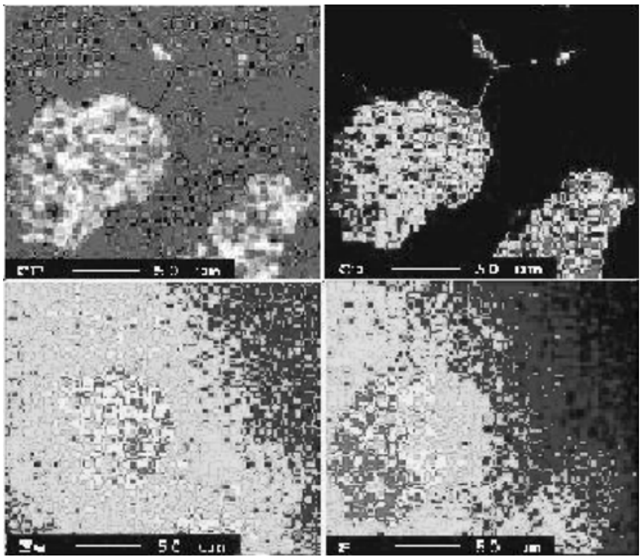

Fig. 3. Thin product layer that blankets both sulfide and silicate mineral phases of a granite sample exposed to bioleaching in a column. cp: back scattered electron image. X-ray image map of Cu, Fe, S show the distribution of three elements in the layer.

Table 2B. Composition of 9 K media

$(NH_3)_4SO_4$, g/L	K_2HPO_4, g/L	KCl, g/L	$MgSO_4$, g/L	$FeSO_4$, g/L
3	0.5	0.1	0.5	45

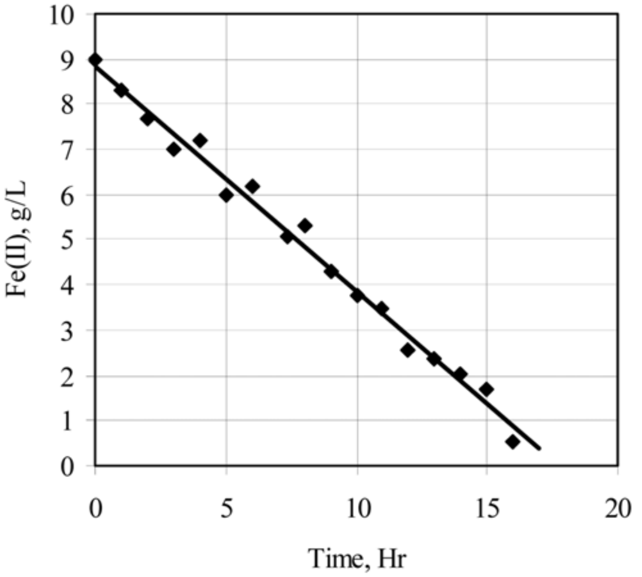

Fig. 4. Evaluation of iron oxidation rate using adapted bacteria.

2. Bacterial Oxidation Rate and Regeneration Time

Initially, 10 L of activated bacterial solution was inoculated in BACFOX unit containing 90 L of 9 K media. The composition of 9 K media is shown in Table 2B. Bacterial oxidation rate was evaluated by plotting between Fe (II) concentrations versus time (min). The study continued until a steady state was obtained. Under steady state the iron oxidation rate was observed to be 500 mg/L/h. as shown in Fig. 4. Since the rate of bacterial growth is directly proportional to ferrous iron oxidation rate, the specific growth rate constant of bacteria, μ, was calculated as the slope of semi-logarithmic plots of ferric ion concentration against time for each data set. The generation time, t_d, was evaluated by using the following relation [19],

$$t_d=0.693/\mu \qquad (4)$$

From Eq. (4), the regeneration time of the activated microorganism was calculated to be 16 hours.

3. Acid Washing

Initially, all the percolation columns containing ore were washed individually with dil. H_2SO_4 until the effluent solution pH attained a value of ~2. The acid consumption for various particle sizes was 0.42, 0.92, 1.08 and 1.21 g/kg of ore for particle size of 16.5, 12.5, 8 and 4.5 mm, respectively. The acid consumption decreased with the increase of particle size. This decrease may be attributed to the availability of surface area. The acid consumption is mainly due to neutralization acid consuming gangue minerals as well as partial dissolution of oxide ores. During acid neutralization about <1% of Cu could be leached out as shown in Table 1.

4. Leaching

After neutralization, the columns were percolated with acidified bacterial solution obtained from the bacterial film oxidation unit (BACFOX). BACFOX used in this study is a rectangular reactor of 50×60×70 cm in which bundles of 10 mm dia×200 mm length PVC tubes were placed. Air sparger arrangement was made at the bottom of the box and compressed air was fed to the solution through the sparger. In due course of time, jarosite coating was formed on the surface of these PVC pipes, which in turn provides ample surface area for the bacteria to grow, thus increasing the bacterial population. The advantages of using solution from BACFOX are:

a. The rate of iron oxidation would be high due to high bacterial concentration.

b. The lixiviant obtained from BACFOX would give higher leaching rate due to high concentration of Fe (III).

4-1. Variation of Particle Size

Particle size is an important parameter in determining the leaching kinetics. In the leaching process, the lixiviant has selectivity with respect to certain minerals or group of minerals. During leaching, the lixiviant penetrates through micro-fissures or micro-pores created in the ore body. Thus, the optimization of the leaching process requires quantitative information on the effect of grain size and the propagation of lixiviant inside the ore body.

Average particle size (d_p) of the ore varied from 4.5 to 16.5 mm. Results are shown in Fig. 5. The percentage of copper extraction in 80 days was observed to be 8, 15, 20 and 27% for d_p of 16.5, 12.5, 4.5 and 8, respectively. The leaching rate increased with a smaller particle size fraction. This trend is attributed to the increased solubility of Fe^{3+} and higher redox potential, which together with a geometric increase in available surface area, causes a positive rate effect. It can be observed that in all cases the leaching rate progressively increased up to initial 40 days and thereafter the rate decreased. The initial faster rate may be due to dissolution of secondary sulfides and oxides of copper which are prone to faster dissolution by acidified solution. The decrease in rate may be due to the formation of a film which builds up on the surface of the mineral and inhibits the electron transfer from chalcopyrite to ferric medium, necessary for the redox reaction. With regard to this passivating layer, there are two basic hypotheses: elemental sulfur [20] and an intermediate sulfide resulting from the transformation of the original chalcopyrite [21,22]. In this study also it was found by SEM studies that a layer was formed on the surface of the ore as shown in Fig. 3.

In the present studies the % of copper leached observed to be 27% in 80 days for a particle size of 8 mm. Ahonen and Tuovinen [10] reported that 13% of copper was leached in 550 days using similar type of ore. Renman et al. [6] reported recovery of 80% of copper in 167 days in percolation column using −12 mm copper ore containing chalcocite, covellite and enargite. Since these are secondary sulfides, the leaching rate was observed to be high.

It was also observed from Fig. 5 that the percentage of leaching increased with the decrease of d_p up to 8 mm and thereafter it decreased with decrease of the same. The decrease of leaching rate at the finer fraction (d_p 4.5 mm) may be either due to higher level of Fe precipitation thereby forming a diffusion barrier over the reactant which inhibits the diffusion of reactants and products or lower dissolution of pyrite. The formation of product layer was observed during SEM studies (Fig. 3). The formation of acid during leaching may be either due to the dissolution of pyrite or oxidation of elemental sulfur or both. Assuming the sulfur oxidation rate in all columns is the same, the difference of acid formation may be due to dissolution of pyrite. In Column-3, since the acid generation was more, therefore the dissolution of pyrite may be assumed to be more. The higher dissolution of pyrite would definitely increase the leaching rate of copper as a part of the same intruded to pyrite (Fig. 2).

If the leaching reaction rate follows 1^{st} order, then the graph between log (r) versus log (d_p) would give a straight line. For evaluation of leaching rate, initial 40 days of leaching were considered. The results are shown in Fig. 6. From the slope the rate equation can be written as:

$$r \,\alpha\, (d_p)^{-0.61} \tag{5}$$

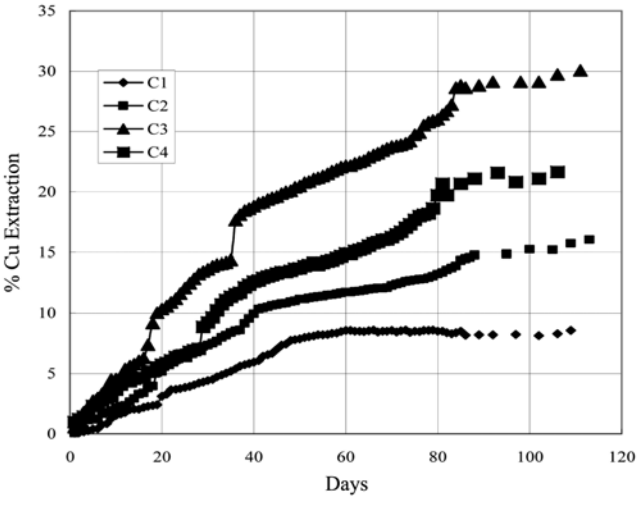

Fig. 5. Effect of particle size on copper extraction from chalcopyrite ore through bacterial leaching (H_b: 131 cm, F: 1 L/h).

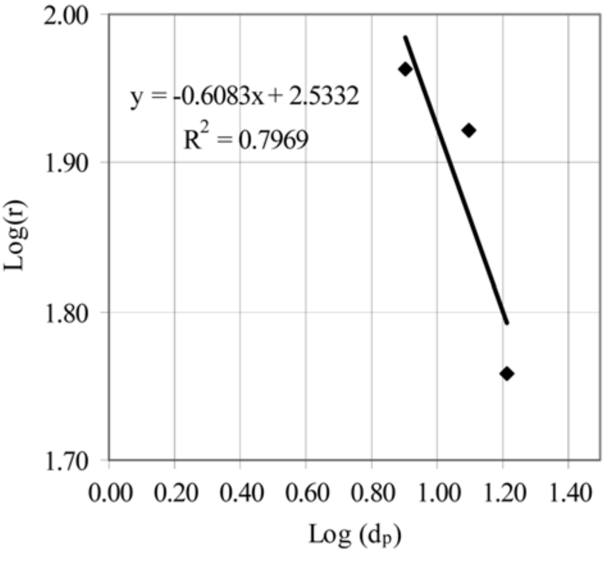

Fig. 6. 1st order copper dissolution rate plot with respect to particle size.

The negative slope indicates that the rate of leaching is inversely proportional to the particle size; in other words, the decrease of particle size would increase the surface area which would eventually help in attacking the lixiviant to the sulfide moiety.

4-2. Effect of Solution Feed Rate

The flow rate (F) was varied from 0.5 to 2 L/h in the various columns (C1, C5, C7) to evaluate the effect of the same on the efficiency of copper leaching at a d_p of 16.5 mm. Results are shown in Fig. 7. The copper leaching rate was observed to vary inversely, as the lixiviant flow rate may be due to longer contact time between lixiviant and ore particle as well as diffusion of more oxygen from the ambient air. The extent of iron preciptation decreased with the increase of lixiviant flow rate.

Fig. 8 shows the log (r) versus log (F). The slope of the graph was found to be −0.76. So rate equation can be written as:

$$r \alpha (F)^{-0.76} \quad (6)$$

Here too the slope was found to be negative, which indicates that at higher flow rate the contact between the ore particle and the lixiviant decreased, thereby decreasing the reaction rate.

4-3. Effect of Bed Height

Bed height (H_b) in the column was varied from 135 to 47 cm (C1, C8, C9, C10) keeping d_p and F at 16.5 mm and 1 L/h, respectively. Results are shown in Fig. 8. The amount of copper extracted increased with the bed height. The increase of copper extraction with the bed height is due to the availability of higher amount of ore and also

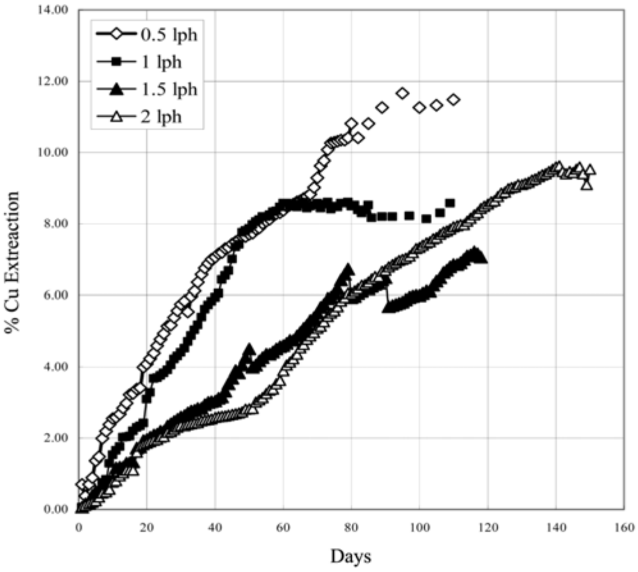

Fig. 7. Effect of lixiviant flow rate on copper leaching from chalcopyrite ore through bacterial leaching (d_p 16.5 mm, H_b 131 cm).

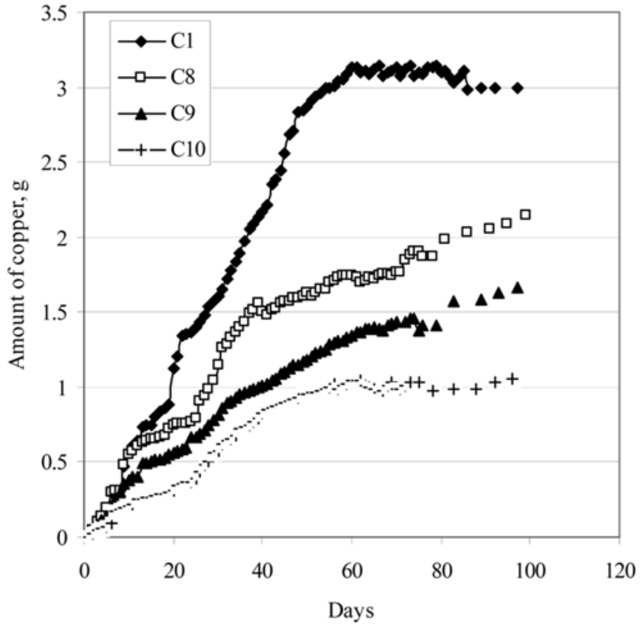

Fig. 9. Effect of bed height on copper leaching from chalcopyrite ore through bacterial leaching (d_p 16.5 mm, F 1 L/h).

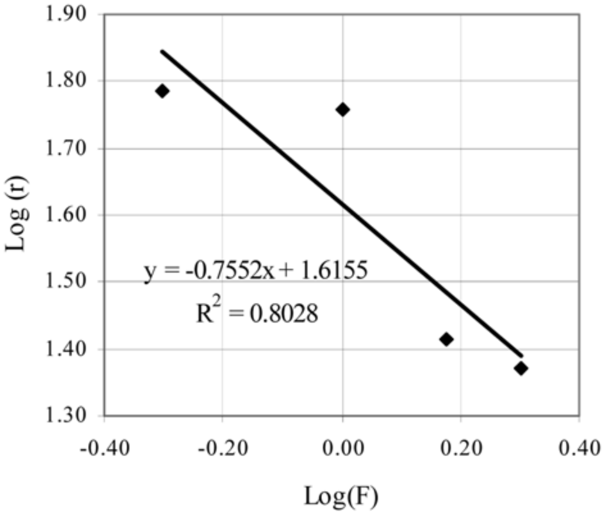

Fig. 8. 1st order copper dissolution rate plot with respect to lixiviant flow rate.

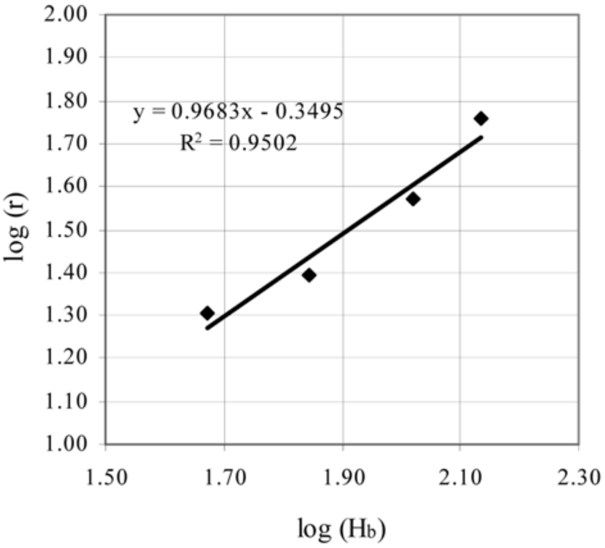

Fig. 10. 1st order copper dissolution rate plot with respect to bed height.

sufficient contact time between lixiviant and the ore particles.

Fig. 10 shows the log (r) versus log (H_b). The slope of the graph was found to be 0.97, so the rate equation can be written as:

$$r\,\alpha\,(H_b)^{0.97} \qquad (7)$$

4-5. Monitoring the pH

Bacterial leaching process is acid dependent and during leaching the acid is produced in situ by the oxidation of pyrite and hydrolysis of ferric iron [10]. Therefore, pH was constantly monitored as well as adjusted around 2 with acid or base until the 20^{th} day. Beyond the 20^{th} day the pH of the lixiviant was observed to be stable, as shown in Fig. 11. The initial increase of pH may be due to either iron oxidation or neutralization of acid consuming gangue minerals or both.

4-6. The Effect of Mass Transfer

The ore used in the present case was granitic based with small intrusion of silica. Therefore, it can be presumed that the raw material may not be very porous. The Cu leaching may be either surface or intra particle or both. A contact time experiment can be used to study the rate-determining step in the leaching process [23].

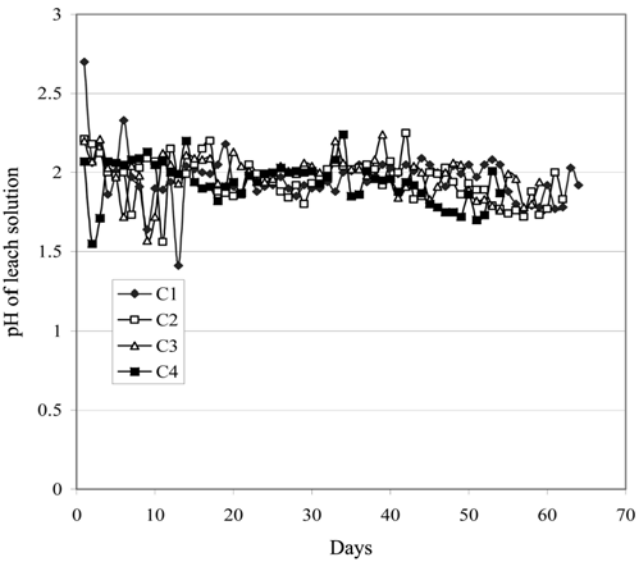

Fig. 11. Effect of variation of pH.

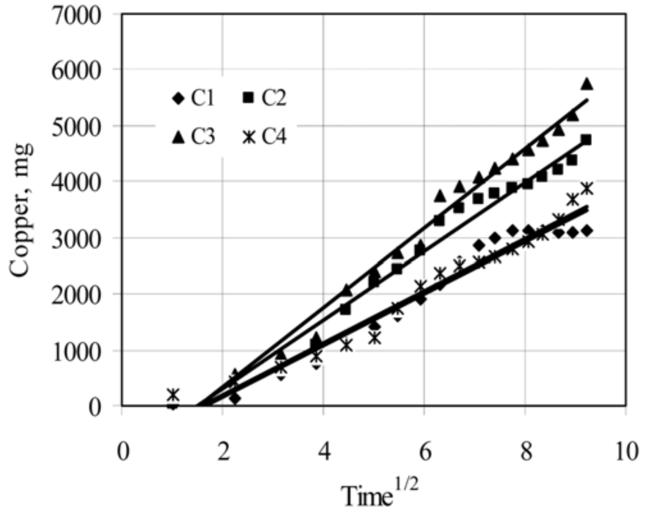

Fig. 12. Intra-particle diffusion of copper.

Since the leaching was carried out by gravitational flow of leach liquor, mass transfer from the bulk liquid to the particle external surface does not limit the rate. Therefore, the rate determining step may be either film or intra particle diffusion, as both the processes act in series the slower of the two will be the rate determining step. Rate constant for intra particle diffusion can be evaluated by using Eq. (8)

$$Q = k\,t^{0.5} \qquad (8)$$

The results are shown in Fig. 12. If the leaching follows both surface as well intra-particle one, then it would give two curves having different slopes. The initial and final one would represent the surface and intra-particle one, respectively. From Fig. 12, it was observed that a single slope was found in all cases (R^2 values >0.95), so it can be concluded that the reaction is limited to surface only. The results also corroborated the mineralogical studies which show the granitic nature of the waste ore.

CONCLUSIONS

Mineralogical studies of the waste ore showed that the copper minerals are present in locked state mostly associated with silicate and iron minerals. Cu leaching can only be possible after dissolution of these minerals; therefore, the ore is not very much amenable to leaching. The acid-consuming gangue minerals are less as the acid consumption during acid washing stages were very much less. The mineralogical studies further confirm the presence of oxidic ore from the acid washing stages as the extent of copper leaching was less than 1% of the total copper.

In order to improve the leaching rate, indigenous microflora were isolated. By repeated re-culture the iron oxidation rate could increase up to 500 mg/L/h. An active culture was used for leaching purposes. The leaching rate depends on lixiviant flow rate as well as particle size. The leaching rate increased with the decrease of particle size. Although column-4 contained finer particles (d_p 4.5 mm), it showed lower leaching rate compared to column-3 (d_p 8 mm). The difference of leaching rates between the said columns might be due to enhanced pyrite dissolution in column-3, thereby increasing the leaching rate. The leaching rate decreased with the increase of lixiviant flow rate may be due to less contact time between the lixiviant and ore particles. The leaching rate is also affected by the bed height. The amount of copper leached is proportional to the bed height. Based on the leaching rate, a unified leaching reaction kinetic equation developed based on the assumption that the copper leaching process followed first order kinetics. From the mass transfer equation, it was concluded that the leaching process is limited only to the surface.

NOMENCLATURE

d_p : average particle diameter of the ore [mm]
F : Lixiviant flow rate [L/h]
FeT : concentration of total iron in solution [g/L]
H_b : ore bed height in the percolation column [cm]

k : mass transfer coefficient [mg/day]
t : time [day]
t_d : generation time for bacteria [h]
r : rate of copper leaching [mg/day]
Q : amount of copper in solution [mg]
μ : specific bacterial growth rate [h^{-1}]

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