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Bio-hydrometallurgical processing of low grade chalcopyrite for the recovery of copper metal

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Abstract−A process flowsheet was developed to recover copper metal from the lean sulfide ore of copper available at Malanjkhand, Hindustan Copper Limited (HCL), India. Copper pregnant leach solution (PLS) obtained from bio-heap leaching of chalcopyrite containing 0.3% copper was purified through solvent extraction (SX) and the copper recovered by electrowinning (EW). The copper-free raffinate obtained from SX stripping unit was returned back to the bioleaching circuit. The purity of the electrolytic copper produced at pilot scale was found to be 99.96%. During electrowinning, the effect of flow rate of electrolyte on current efficiency and energy consumption was also studied.

Key words: Chalcopyrite, Bio-heap Leaching, Solvent Extraction, Electrowinning

INTRODUCTION

A large quantity of low-grade sulfide ore of copper exists throughout the world that cannot be treated through conventional extraction routes for the recovery of copper due to the high cost of production and environmental problems. Conventional pyrometallurgical processing followed by electrorefining is not found to be economical for such low grade copper resources. However, one of the most promising strategies developed for dissolution of copper from lower grade ores has been the utilization of acidophilic microorganisms as biological catalysts during leaching [1]. Thus, these low grade copper deposits can be effectively treated for extraction of metal values through bio-heap leaching followed by solvent extraction & electrowinning [2-7]. This process has specific advantages over the conventional route of copper extraction, such as short construction time, operational simplicity and insignificant environmental pollution. This process is slowly gaining importance in the field of waste treatment [8,9].

At present, a reserve of 2.75 million tons of low grade sulfide ore containing 0.3% Cu is available at Malanjkhand, India. This ore cannot be processed through the conventional route since the cut-off grade for treatment in concentrators is about 0.45% Cu. If an appropriate technology would be available for its commercial exploitation, then it would definitely contribute to India's total copper output and economy. Therefore, in the present work, based on the optimized process parameters developed at the Institute of Minerals and Materials Technology, Bhubaneswar, India [10], experiments were carried out at M/s Hindustan Copper Limited (HCL), Malanjkhand, India to establish the feasibility of the process at pilot scale in an industrial setting. An attempt was also made to study the effect of flow rate of electrolyte upon current efficiency and energy consumption.

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EXPERIMENTAL

1. Bioheap Leaching

A lean sulfide ore heap of 1,000 ton capacity was constructed at HCL, Malanjkhand, India. The schematic diagram of the heap is shown in Fig. 1. Chemical analysis of the ore sample from the heap showed the presence of copper mostly in the form of chalcopyrite about 80%. The concentration of copper in the heap was found to be about 0.34%. Prior to bacterial inoculation, the heap was acid conditioned and stacked on an impervious pad with proper network of pipeline at the bottom for the purpose of aeration. A BACFOX (bacterial film oxidation unit) tank of 120 m^3 capacity was built for the growth of micro-organisms. The heap was inoculated with a mixed culture of mesophilic acidophilic chemolithotrophic consortia and operated at ambient temperature. The initial volume of the bacterial solution was 30 m^3 with bacterial concentration of 1×10^9 cells/ml. Leach liquor was pumped at a rate of 1.5 $L\cdot min^{-1}\cdot m^{-2}$. The concentration of copper and other metals was analyzed using atomic absorption spectrophotometry (AAS, Perkin Elmer Model 3100).

2. Purification of Bacterial Leach Liquor

The leach liquor obtained from the bioheap leaching unit was subjected to solvent extraction using 5% LIX 622N in 95% kerosene. The loaded organic phase was stripped with the copper spent electrolyte (Cu-SE) in order to produce pure solution free from impurities, i.e., copper pregnant electrolyte (Cu-PE). The enriched Cu-PE was passed through an activated carbon column to remove the organic. The barren solution or raffinate obtained from the SX stripping unit after extraction of copper was sent back to BACFOX tanks for recycling in the leaching process.

3. Electrowinning

The organic-free PE thus generated was then subjected to electrowinning for copper metal recovery. An electrolytic cell having dimensions of length 1,100 mm, width 215 mm and height 175 mm with a provision for an inlet and outlet of 7 mm diameter was used in the present study. Stainless steel sheet (SS 304 grade) and lead -

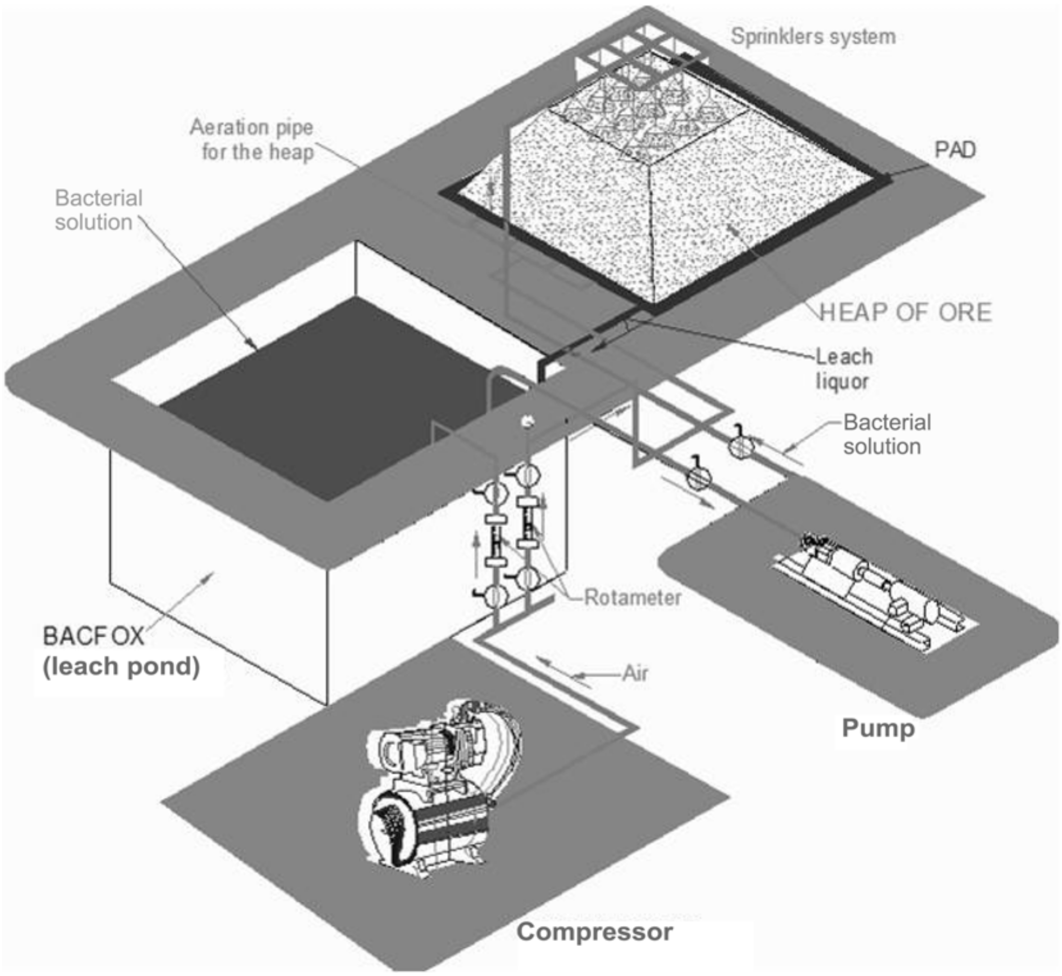

Fig. 1. Bioheap leaching set up at Malanjkhand copper project.

antimony (Pb - 7% Sb) were used as cathode and anode materials, respectively. Eight anodes and seven cathodes which are similar in shape and size were used. The dimensions of the electrodes used for electrowinning operation were: length 200 mm, breadth 170 mm and thickness 3 mm. A Watson-Marlow peristaltic pump was used for controlling the flow of the electrolyte into the electrolytic cell. The electrolysis was carried out at ambient temperature by applying DC with the help of a rectifier from a regulated power supply unit.

RESULTS AND DISCUSSION

1. Observations in Bioheap Leaching

Chemical analysis reveals that low grade ore contains 0.34% Cu. Sulfide minerals in the sample are shown in Table 1. XRD and SEM (data not shown) suggest that it contains chalcopyrite as the major sulfide mineral along with other minerals as minor phases. A mixed culture of acidophilic bacteria predominantly of *Acidithiobacillus ferrooxidans* was used as the inoculum. A method of repeated sub-culturing was used to activate the strain. During each set of subculturing, 2 L of the full-grown media was centrifuged, to collect the total biomass used as the inoculum for the next set of experiment. Subsequently, the bacterial lag phase was reduced and the growth phase was initiated immediately after inoculation of the strains in fresh media. After six sets of sub-culturing, a stable iron oxidation rate of 500 kg/m^3/h was achieved. This active bacterial culture was then finally inoculated to 1 m^3 of 9K$^+$ media. On complete oxidation, the bacterial inoculum was used as the feed for both the heaps. This bacterial solution was prepared in a specially designed BACFOX tank and was sprinkled onto the heap surface with the help of an anticorrosive pump, and the effluent solution loaded with copper metal values from the heap was directed to the BACFOX tank from where it was recirculated for increasing the copper concentration in the leach liquor. The initial composition of the prepared bacterial solution is given in Table 2. Fig. 2 shows the variation in concentration of copper with time in the bioleach liquor over a period of 12 days. The concentration of copper in the BACFOX tank gradually increased over a period of ten days, and after that there was no significant increase in copper concentration for the next two to three days. This phenomenon can be attributed to the fact that initially

Table 1. Sulphide minerals in lean grade Malanjkhand Copper ore

Composition	Chalcopyrite	Bornite	Pyrite	Chalcocite	Malachite
Percentage	85	4	8	3	Trace

Table 2. Composition of Bacterial Lixiviant

pH	Eh (mV)	Fe(II), gpl	Fe(III), gpl	Cell count, 10^9 cells/ml	Temp. ºC
1.75	680	0.3	1.68	1.0	22

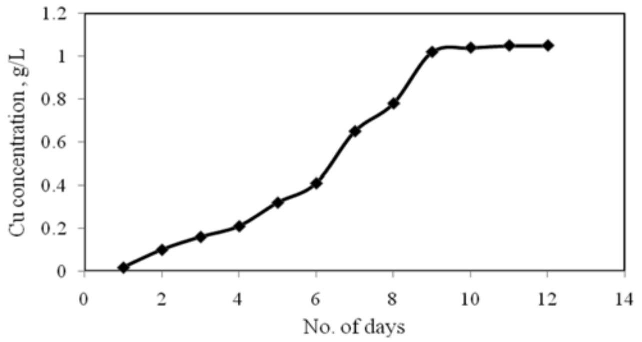

Fig. 2. Concentration of Cu in heap bioleach liquor used for SX studies.

the particle surfaces were available to bacterial solution and the precipitation of jarosite was also less. With time a thin layer of jarosite coating developed which retarded the rate of dissolution. Since there was no increase in copper concentration after 10 days of heap leaching, the solution was shifted to storage tanks for further purification of the liquor (Pregnant leach solution-PLS) after attaining a concentration of 1 g/L copper (Fig. 2) in the BACFOX tank. To remove any entrapped copper over the particle surface and coating of jarosite over it, a fresh new solution was prepared and recirculated as mentioned earlier. It was clear from the above results that the solution in the BACFOX tank needed to be transferred and fresh new solution had to be prepared for bioheap leaching.

2. Solvent Extraction of Heap Leach Liquor

The pregnant leach solution was purified by solvent extraction. The analysis of leach liquor and the raffinate coming out of the solvent extraction unit is shown in Table 3. On the basis of previous laboratory studies at IMMT, Bhubaneswar, purification of the bioleach liquor was achieved through three stages of extraction, two stages of stripping and one stage of washing [10]. The copper spent electrolyte (Cu-SE) and the loaded organic (LO) were taken within A : O ratios of 1 : 6 to 6 : 1 while keeping the total volume of phases constant. Extraction efficiency during purification of heap leach liquor was found to be about 95%. Entrained solvent present in the purified solution was removed through adsorption method using activated carbon (specification shown in Table 4).

3. Electrowinning

Impurity-free solution containing 43 g/L copper and 182 g/L H_2SO_4 was subjected to electrowinning in a continuous mode at a current density of 100 A/m^2 and depletion rate of 4 g/L copper in order to produce copper sheets of good morphology. During this campaign about 35 m^3 of electrolytic solution was processed for electrodeposition of copper. Cell voltage was found to be about 2.2 V. The amount of copper deposited in the continuous run of 3,515 h was 65.824 kg. By chemical analysis the purity of the metal produced during this campaign was found to be 99.96%. The chemical composition of copper metal deposit is given in Table 5. The morphologies of the copper deposits obtained under described conditions are shown in Fig. 3(a) and (b). Analysis of these SEM images revealed that it consisted of agglomerates of copper grains. The aggregates are spheroid and the deposit appeared to be bright, smooth and compact consisting of coarser grains.

The spent electrolyte (SE) containing 39 g/L copper and 187 g/L H_2SO_4 was recycled back to the solvent extraction circuit. The flow rate of electrolyte was maintained at 10 L/h based on the previous laboratory scale studies at one liter scale carried out at IMMT, Bhubaneswar. Figs. 4 and 5 show the effect of flow rate of electrolyte on current efficiency and energy consumption at one liter scale. It is clear that with the variation in flow rate from 2 L/h to 4 L/h, the current efficiency increases significantly due to agitation assisting the rate of deposition. The current efficiency varied from 92.12% to 96.746%, whereas energy consumption varied from 1.676 to 2.1 kWh/kg, which is near the literature value of 2 kWh/kg [11]. Beyond 4 L/h, the effect of increase in flow rate on both current efficiency

Table 4. Specifications of the activated carbon granules used (Sorbonorit B4)

Apparent bulk density	430 gpl
Pellet dia.	3.8 mm
Moisture wt%	2%
Total ash content wt%	5%
Abrasion resistance, ASTM	99%
BET specific surface area	110-120 m^2/g
Voids packed bed cm^3/cm^3	0.4
Ignition temperature, 0 ºC	450

Table 5. Purity of electrodeposited copper at Malanjkhand copper project

Metal	Impurity (%)
Fe	0.02
Ni	0.008
Co	0.003
Cr	0.004
Total impurity	0.035
Purity of copper cathode	99.965

Table 3. Analysis of bioleach liquor & Raffinate produced from SX studies

Solution	Cu (g·L^{-1})	Fe (g·L^{-1})	Free acid (g·L^{-1})	Ni (mg·L^{-1})	Mn (mg·L^{-1})	Pb (mg·L^{-1})
PLS	1.05	1.12	2.74	0.03	0.03	0.03
Raffinate	0.03	0.99	5.88	0.01	0.02	0.015

*Note: PLS - pregnant leach solution

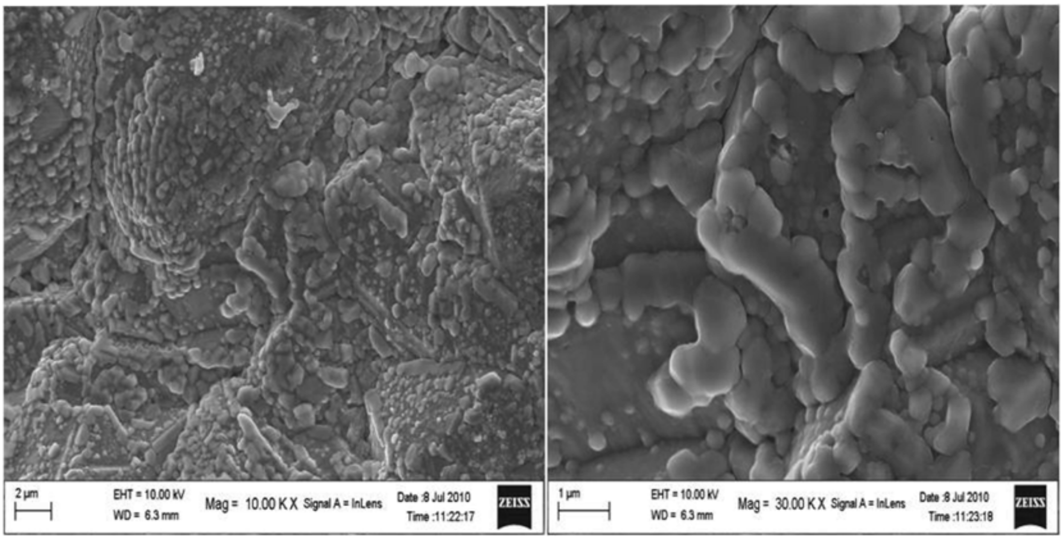

Fig. 3. SEM micrographs (a) and (b) of copper electrodeposit showing agglomerated spheroids at scale bar 2 µm and 1 µm, respectively.

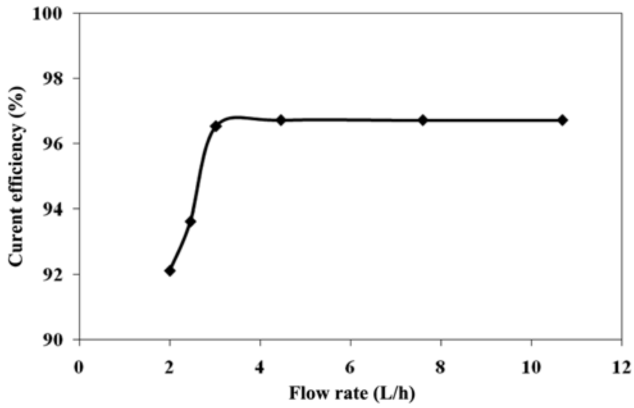

Fig. 4. Effect of flow rate on current efficiency.

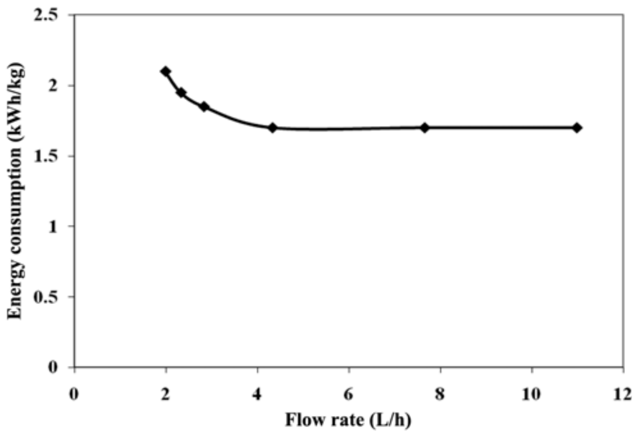

Fig. 5. Effect of flow rate on energy consumption.

and energy consumption was found to be negligible. Thus, for the campaign at HCL, Malanjkhand, India, the flow rate of electrolyte was fixed at 10 L/h.

A process flow sheet was developed for the recovery of copper metal values from low grade chalcopyrite as shown in Fig. 6.

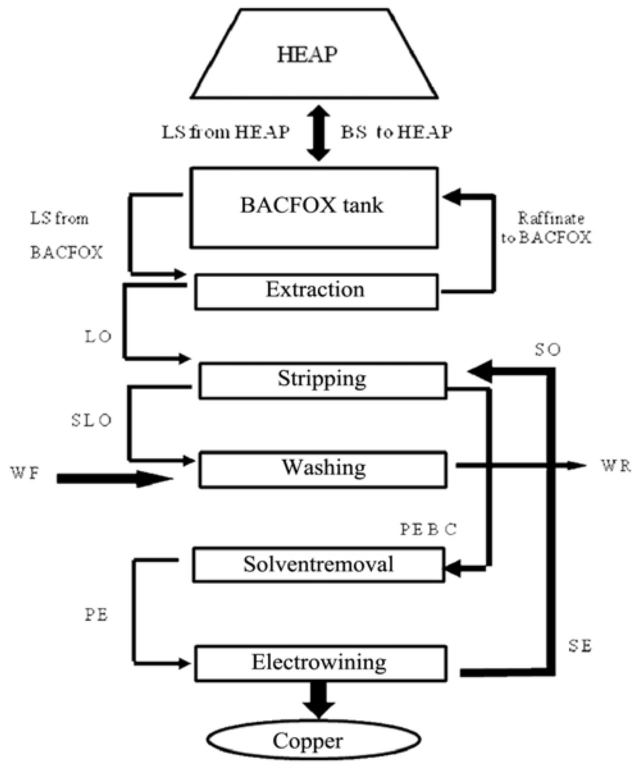

Fig. 6. Process flow sheet for recovery of copper from Malanjkhand bacterial leach liquor.

BS . Bacterial solution
LS . Leach solution
LO . Loaded organic
SE . Spent electrolyte
PE . Pregnant electrolyte
WR. Wash raffinate
PEBC. Pregnant electrolyte before carbon treatment
SO . Spent organic
WF . Wash solution feed
SLO . Spent loaded organic

CONCLUSIONS

Lean grade copper ores were treated through bio-heap leaching route. The leach liquor obtained from the heap was processed for purification through solvent extraction for removal of impurities and then passed through activated carbon column to produce organic-free solution suitable for copper electrowinning. Smooth copper sheets were deposited at the cathode during electrowinning with 99.96% purity. A process flow sheet was also developed for the recovery of copper metal values from low grade sulfide ores. This process route is found to be technically feasible and environment friendly. It has the potential to replace the conventional process, specifically for the treatment of lean copper sulfide ores.

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