# **Recovery of copper values from bio-heap leaching of low grade Malanjkhand chalcopyrite ore**

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**Abstract**−M/S Hindustan Copper Limited (HCL), India generates large amounts of lean sulfide ores of copper. The current production of lean copper ores in India is 0.55 million tons with ~0.3% average copper content. Heap-bioleaching of the lean copper ores in 15 and 30 ton scales was undertaken at IMMT, Bhubaneswar. The leaching study showed 0.09% dissolution of copper from the ore body per day. The leach liquor was processed through solvent extraction and electrowinning. Extraction of copper from the actual leach liquor was carried out with 1.5% LIX 622N in kerosene with zero co-extraction of iron. The copper-free raffinate was fed back to the leaching unit. Stripping of copper from the loaded organic was carried out with 180 kg/m<sup>3</sup> H<sub>2</sub>SO<sub>4</sub>. The copper pregnant electrolyte was passed through a carbon column to make it free from entrained organic and was fed to the electrowinning unit. The increase in current efficiency was due to the increase in the concentration of electrolyte. The energy consumption was 1.7 kWh/kg at a flow rate of 4.5 L/h. Smooth and bright sheets of copper of 99.99% purity were obtained.

Key words: Lean Copper Ore, Bio-heap Leaching, Solvent Extraction and Electrowinning

#### **INTRODUCTION**

Bio-mineral processing is an alternative technology to recover metal values from low-grade ores and minerals. The technique dramatically reduces the fixed capital costs, as well as environmental pollution. As a result, this technique is slowly gaining importance in the field of waste treatment [1]. A substantial number of heap leaching processes leading to metal recovery are in operation [2,3]. Most of these processes are targeted for extraction of metals from marginal ores unsuitable for production of concentrates or undergo smelting. The development of heap leaching technology has been largely engineering focused rather than microbiology focused.

Large quantities of low-grade ore deposits such as copper, nickel, zinc, uranium, etc. available throughout the world are effectively treated through bio-heap leaching practices. India is in short supply of copper and the demand for copper minerals for primary production is met through two sources: from copper ores mined from indigenous mines, and from the imported concentrates. India has copper ore reserves of 1,690 million tons containing about 15 million tons of copper metal. There are 250 known deposits of copper in India, of which nearly 90% deposits are confined to Singhbhum (Bihar), Malanjkhand (Madhya Pradesh) and Khetri (Rajasthan), including about 17 more working copper mines. The copper demand of 31,000 tons in 1970-71 has been currently raised to 5 lakh tons per annum because of rapid industrial growth. With the current level of production and use, the ore will last a maximum of 30 years.

The available lean ores in India with an average copper content

concentrators, would definitely contribute considerably to the country's copper output, if appropriate technology would be available for its commercial exploitation. IMMT, Bhubaneswar has carried out the bioleaching studies on low-grade Malanjkhand copper ore at various scales from shake flasks to 15 and 30 tons heaps [4]. The sulfidic ores, typically chalcopyrite, contain copper in intimate association with sulfide minerals. Sulfide-oxidizing bacteria, namely *Acidithiobacillus ferrooxidans*, solubilize the host minerals for conventional recovery. Although heap bioleaching is an established costeffective technology for secondary copper sulfides, its application to primary chalcopyrite ores is not straightforward. Three technologies, namely roasting, pressure oxidation and bioleaching, are used commercially to treat the sulfide ores and concentrates. The run-of-mine ore is piled up in regular layers called 'lifts' on appropriately prepared areas to form heaps. The top of these heaps is regularly irrigated with solutions bearing microorganisms. These solutions percolating through the broken mass of rock are regularly recycled to solubilize the metal values in solution, and the pregnant solution is pumped to the solvent extraction unit. The raffinate collected after solvent extraction is fed to the bacterial leaching tank, and the enriched pregnant electrolyte from the SX unit is fed to the electro winning unit for metal recovery.

of ~0.3%, which is well below the cut-off grade of 0.45% Cu for

The majority of copper minerals are sulfides, of which chalcopyrite  $(CuFeS<sub>2</sub>)$  is most abundant and economically most important. Other copper minerals of economic importance are bornite  $(Cu<sub>5</sub>FeS<sub>4</sub>)$ ,  $chalcocite (Cu, S)$  and covellite (CuS). The sulfide minerals of copper are insoluble in water and acid solutions, but are only soluble under oxidizing conditions in the presence of *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*; the former catalyzes

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the process of oxidation, whereas the latter catalyzes the oxidation of sulfur. The overall chemical reactions leading to the dissolution of chalcopyrite are represented as follows:

$$
\text{CuFeS}_2 + 2 \text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O} + 3\text{O}_2 \longrightarrow \text{CuSO}_4 + 5 \text{FeSO}_4 + 2\text{H}_2\text{SO}_4 \quad (1)
$$

Several steps leading to the dissolution of chalcopyrite are as follows:

$$
\text{CuFeS}_2 + 4\text{O}_2 \xrightarrow{\text{Bacteria}} \text{CuSO}_4 + \text{FeSO}_4 \tag{2}
$$

$$
2FeS_2+7O_2+2H_2O \xrightarrow{Bacteria} 2FeSO_4+2H_2SO_4 \tag{3}
$$

$$
4FeSO4+2 H2SO4+O2 \longrightarrow 2 Fe2(SO4)3+2 H2O
$$
\n(4)

$$
FeS_2+7Fe_2(SO_4)_3+8H_2O \longrightarrow 15 FeSO_4+8 H_2SO_4 \tag{5}
$$

$$
Cu2S + 2 Fe2(SO4)3 \longrightarrow 2CuSO4+4FeSO4+S
$$
 (6)

$$
2S+3O2+2H2OBacteria2H2SO4
$$
\n(7)

The hindrance in the leaching process is due to the formation of a passive layer of jarosite, i.e.,  $KFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>$ , and elemental sulfur particles around the unreacted ore body.

In bacterial leaching of sulfide minerals, ferric iron plays the important role of an oxidant. Decrease of Fe<sup>3+</sup> concentration in solution due to precipitation may suppress the dissolution of copper by preventing contact between the lixiviant and the ore. The solubility of iron is defined by the redox potential and pH of the solution. So optimization of these parameters largely influences the metal recovery. In this study, analyses of total iron and ferrous iron were done volumetrically, and the concentration of ferrous iron was found to be zero after a few runs.

This paper presents the experimental results obtained from the bioleaching of low grade copper ores obtained from M/S Hindustan Copper Limited at Malanjkhand through column and heap bioleaching, enrichment of copper values from the bioleach liquor by solvent extraction and electro winning of copper from the pregnant electrolyte leading to the production of 99.99% pure metal.

#### **ORE MINERALOGY**

About 45 tons of low-grade chalcopyrite ore procured from Malanjkhand copper mines was crushed. A representative sample of 122 kg ore was taken and sieved. The low-grade copper ore was analyzed with a high resolution synchrotron based X-ray diffractometer (XRD) and by optical microscopy to display the major and minor minerals.

The representative granite samples of Malanjkhand bearing copper minerals were collected and their surfaces were polished by the conventional polishing technique. Different ore mineral species were then identified under Leitz optical microscope. Elemental distributions in the feed granite sample and in the broken surfaces of the leach residue samples were studied with an electron microprobe (Joel, JXA 8100).

#### **METHODS**

#### **1. Preparation of Inoculum**

A mixed consortium of *Acidithiobacillus ferrooxidans* was used as the inoculum. To activate the strain, repeated sub culturing was done. During each set of sub-culturing, 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 lag 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<sup>3</sup>/h was achieved. This active bacterial culture was then finally inoculated to 1,800 L of 9 K media. On complete oxidation, the bacterial inoculum was used as the feed for heap leaching.

## **2. Bacterial Oxidation Rate and Regeneration Time**

Initially, 10 L of activated bacterial solution was inoculated in the BACFOX unit containing 90 L of 9 K media. The 9 K media contained 3 kg/m<sup>3</sup> (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 1.0 kg/m<sup>3</sup> KCl, 0.5 kg/m<sup>3</sup> MgSO<sub>4</sub>·7H<sub>2</sub>O,  $0.5 \text{ kg/m}^3 \text{ KH}_2\text{PO}_4$  and  $44.4 \text{ kg/m}^3 \text{ FeSO}_4 \cdot 7\text{H}_2\text{O}$ . The pH of the medium was adjusted at pH 1.5. The rate of bacterial oxidation was evaluated from the plot of Fe(II) concentration versus time (min), and the study continued till a steady state was obtained. Under steady state, the rate of iron oxidation was observed to be 500 kg/m<sup>3</sup>/h. Since the rate of bacterial growth is directly proportional to the rate of oxidation of ferrous iron, the specific growth rate constant of bacteria,  $\mu$ , was calculated as the slope of semi-logarithmic plots of ferric ion concentration against time for each set of data. The generation time,  $t_d$ , was evaluated by using the following relationship [5,6]:

$$
t_d=0.693/\mu\tag{8}
$$

From Eq. (8), the regeneration time of the activated microorganism was calculated to be 16 h.

#### **3. Bacterial Count of the Inoculum**

The bacterial counts of the inoculum were made by using a Petroff Hauser counting chamber at 10 days intervals to record the number of bacteria present per ml of solution.

## **4. Monitoring of pH**

The pH of the bioleach liquor was constantly monitored and adjusted to  $2.0$  with  $H_2SO_4$ . As bacterial leaching was pH dependent, addition of an acid or base was required to maintain the pH at 2.0. The pH of bacterial leach solution over a long range of time was within 1.54 to 2.22 during the course of progressive leaching.

#### **5. Heap Bioleaching**

A schematic drawing of the heap bioleaching facilities is shown in Fig. 1. The ore contained 0.3% copper and 3.9% total iron. As shown in Fig. 1, the first heap (15 tons) and second heap (30 tons) were made on the leach pads lined with FRP (bisphenol A resin). Two numbers of Kimline acid resistant pumps were used to circulate the solution at the rate of  $1 \text{ m}^3$ /h from the leach ponds on to the heaps. The solution from the first leach tank was sprinkled on the 30 tons heap by Pump (1) and collected back in the second leach pond through the pipe, and solution from second leach pond was sprinkled onto the 15 ton heap by Pump (2) and collected in the first leach pond. This was repeated. Compressed air at the rate of 40 L/h was supplied to the heaps and the Bacfox units during the spraying of leach liquor. Samples collected at the end of the day were analyzed for copper, ferrous iron and total iron. The pH of leach solution, its temperature, volume of leach liquor and the flow rates were measured. The leach solution was processed through solvent extraction by using LIX 622N and the copper pregnant electrolyte was fed to the electrowinning circuit.

**6. Analysis of Copper, Iron and Consumption of Free Acid**



**Fig. 1. Schematic drawing of heap leaching facilities at IMMT, Bhubaneswar.**

The concentration of copper in the leach liquor was analyzed by the Perkin Elmer Model 3100 atomic absorption spectrophotometer (AAS). Ferrous iron and total iron content in the bioleach liquor were estimated titrimetrically against a standard  $K_2Cr_2O_7$  solution using BDAS as the indicator.

## **7. Solvent Extraction**

Solution treatment was the final stage of heap leaching operations. The bacterial leach liquor was treated for separation of metal values by solvent extraction. Extraction of copper from the synthetic solution (pH 1.8) bearing  $0.5 \text{ kg/m}^3 \text{ Cu(II)}$  and  $3.64 \text{ kg/m}^3$ Fe(III), equal in concentration to that of the actual bacterial leach liquor, was carried out using LIX 622N in kerosene. All the experiments were performed in separating funnels at room temperature  $(35\pm1$  °C) and the aqueous and organic phases were equilibrated at equal phase ratio other than the McCabe-Thiele plots where the O: A ratio was within  $1:5$  to  $5:1$ . The aqueous and organic phases were equilibrated in separating funnels manually for 5 minutes and the phases were separated after complete phase disengagement. After separation of phases, the equilibrium pH of raffinate was measured and the samples were diluted as required with 1 M HCl for analysis by Perkin Elmer Model 3100 AAS. The metal-bearing organic phase was filtered through 1PS phase separating paper and a suitable aliquot of it was stripped with 20% HCl, diluted and analyzed. The extraction and stripping conditions generated in the study were applied to the actual bacterial leach liquor in a continuous run [7-10]. **8. Electrowinning**

An electrolytic cell having dimensions of 13.0 cm length, 6.0 cm width and 10.0 cm height with provisions for inlet and outlet diameter of 0.5 cm was used in the present study. A lead-antimony (Sb-7%) anode having the dimensions of 10 cm length, 5.8 cm width and 0.3 cm thickness was used. The cathode was a stainless steel sheet having the dimensions of 10 cm length and 5 cm width. In general, two anodes and two cathodes were used, but depending upon the current density, the number of electrodes was changed. The electrolysis was carried out by applying DC voltage from a regulated power supply unit. A 3'' diameter column of polypropylene containing activated carbon granules was used to remove the

entrained organic from the pregnant electrolyte. The electrolyte was circulated by metering pumps.

For solutions bearing 1 to  $2 \text{ kg/m}^3$  of metal ions, the conventional electrowinning process becomes very inefficient. The rate at which the metal ions can be recovered from the pregnant solution depends on several factors such as concentration of metal ions in the electrolyte, current density, temperature, additives and impurities [11-15].

#### **RESULTS AND DISCUSSION**

## **1. Chemical Analysis, Sieve Analysis and Mineral Phase Analysis of Malanjkhand Copper Ore**

The low-grade Malanjkhand copper ore contained 0.3% Cu, 0.03% Ni, 0.05% each of Co and Zn, 3.9% Fe, 2.83% S and 0.6% TiO<sub>2</sub> with 91.2% acid insolubles. The sieve analysis of the copper ore contained 49.2% of  $+10$  mm size, 11.5% of  $+6$  mm size, 12.3% of  $+3$ mm size, 14.8% of +1 mm size and 12.3% of −1 mm size. The mineral phase analyses of the copper ore and the heap leach residue were done with XRD and TEM studies. The XRD study of the ore identified the presence of chalcopyrite, feldspar and quartz, but the TEM study confirmed the presence of CuS in addition to chalcopyrite, feldspar and quartz. The XRD study of heap leach residue identified quartz, goethite,  $Cu<sub>8</sub>S$ , digenite and  $Na<sub>2</sub>SiO<sub>3</sub>$ , and the TEM study identified quartz, goethite, digenite and silicate.

## **2. Characterization of Malanjkhand Copper-bearing Rock Sample**

The ore samples were pink colored granites irregularly traversed by quartz vein. Granite is constituted of both feldspar (aluminum silicate mineral) and quartz (silica mineral) as the major phases. Copper minerals were sparsely distributed (<1%) within the granites. The major copper-bearing minerals present were chalcopyrite and covellite. The former mineral occurred as minute disseminated grains independently, or as inclusion within pyrite, or as secondary vein in contact with pyrite and quartz. The covellite appeared as veins/ vein let's traversing magnetite. The other associated ore minerals were iron-bearing phases like magnetite  $(Fe<sub>3</sub>O<sub>4</sub>)$  and pyrite  $(FeS<sub>2</sub>)$ . Chalcopyrite grains were usually smaller than both pyrite and mag-

#### netite.

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

## **3. Bacterial Count**

The bacterial count of the inoculum was done at 10 days intervals to find the number of bacteria per ml of solution. The bacterial count ranged within  $6.58 \times 10^5$  to  $2.76 \times 10^9$  within 75 days of progressive leaching.

#### **4. Bioleaching of Malanjkhand Copper Ore**

In this study, the concentration of iron in the solution was 1.95 kg/m<sup>3</sup> on the first day and was increased to  $2.0 \text{ kg/m}^3$  on the sixth day, and since then the concentration remained between 1.68 to 1.96 kg/m<sup>3</sup> as seen from the plot of pH of solution and [Fe], kg/m<sup>3</sup> vs. No. of days in Fig. 2. The pH of the solution on the first day was







Fig. 3. The plot of pH of solution and [Fe], kg/m<sup>3</sup> vs. No. of days.  $\qquad \qquad 622N$  in kerosene.

1.98 and was raised to 2.2 on the 10th day; it came down to 1.53 on the 24th day and to 1.73 on the 78th day, but on the 100th day the pH was 2.19. The leaching of copper with time is shown in the plot of %Cu recovery and [Free acid], kg/m<sup>3</sup> vs. No. of days in Fig. 3 indicating 1.75% recovery on first day to 10.48% on the 100th day, with the highest value of 10.57% attained on the 98th day. Copper recovery in Fig. 3 seems to be linear and the slope of the line, i.e., 0.0924 (not shown) indicates 0.09% copper leaching out per day. The [Free acid] in the leach solution was  $1.92 \text{ kg/m}^3$  on the first day and  $4.12 \text{ kg/m}^3$  on the 18th day. It remained almost the same up to the 74th day following which it increased to  $5.68 \text{ kg/m}^3$  on the 100th day.

#### **5. Solvent Extraction**

Before the treatment of actual leach liquor was taken up, solvent extraction of copper from a synthetic solution (pH 1.8) containing 0.5 kg/m<sup>3</sup> Cu(II) and 3.64 kg/m<sup>3</sup> Fe(III) was carried out with LIX622N in kerosene. There was only extraction of copper leaving Fe(III) and other impurities in the leach liquor.

## 5-1. Effect of pH

The effect of pH on extraction of copper from the solution was investigated with 2% LIX622N in kerosene within the initial pH range 0.46-2.24 (equilibrium pH range 0.37-2.12) at 1 : 1 phase ratio. Study at higher pH values was not possible since the raffinate of the 2.49 initial pH solution was not clear. The experimental data indicated increasing extraction of copper from 30.02-99.32% with increasing equilibrium pH. In this study of pH variation, there was no co-extraction of Fe(III).

## 5-2. Effect of Extractant Concentration

Various concentrations (0.5-5.0%) of LIX622N were used for the extraction of copper from the solution (pH  $1.80$ ) at  $1:1$  phase ratio. The plot of percentage copper extraction versus solvent concentration indicated an increase in extraction from 52.57 to 99.49% with extractant concentration. With 1.5% LIX 622N, the percentage extraction was 94.09%.

5-3. Extraction of Copper

A McCabe-Thiele plot, Fig. 4, for extraction of copper from the synthetic solution was developed with 1.5% LIX 622N in kero-



**Fig. 4. McCabe-Thiele plot for extraction of copper with 1.5% LIX**



**Fig. 5. McCabe-Thiele plot for stripping of copper with 180 kg/m3**  $H_2SO_4$ .

sene which predicted three stages at O : A ratio of 2 : 3, i.e., 36.27, 51.97 and 11.76% extraction in the first, second and third stages, respectively. To establish the prediction and generate copper loaded organic (Cu-LO) for further studies, a counter-current simulation (CCS) study in the above conditions was performed up to 13 cycles to extract 24.1, 58.74, and 16.67% in the first, second and third stages, respectively. During extraction, copper in the organic phase was concentrated 1.5 times more than that of the leach liquor.

5-4. Stripping of Copper with  $H_2SO_4$ 

The Cu-LO generated as above was stripped with different concentrations of  $H_2SO_4$  (0.5-185.41 kg/m<sup>3</sup>) solution at 1 : 1 phase ratio. The strip solution was analyzed. The plot of percentage copper stripping versus  $[H, SO_4]$  indicated an increase in copper stripping with increasing  $H_2SO_4$  concentration. In this study,  $100\%$  stripping of copper was achieved with  $140 \text{ kg/m}^3 \text{ H}_2\text{SO}_4$ ; however,  $180 \text{ kg/m}^3 \text{ H}_2\text{SO}_4$ was used for stripping.

## 5-5. McCabe-Thiele Plot for Stripping of Copper

Copper was stripped from the loaded organic phase with 180 kg/ m<sup>3</sup> H<sub>2</sub>SO<sub>4</sub>. The McCabe-Thiele plot in Fig. 5 reads 2-stages at O: A ratio of 9 : 2. The spent organic phase was analyzed for copper content. In  $H_2SO_4$  stripping, copper in the strip solution was enriched 4.5 times compared to the loaded organic.

A CCS study for the loaded organic with  $180 \text{ kg/m}^3 \text{ H}_2\text{SO}_4$  was done in the above conditions up to 10-cycles to confirm the predicted data. From the analysis of spent organic, the extent of stripping in the first and second stages was 96.32 and 99.96%, respectively. Finally, the concentration of copper in the strip solution was 3.37  $kg/m<sup>3</sup>$ .

#### **6. Bench Scale Run for Recovery of Cu from the Leach Liquor**

Extraction of copper from the actual leach liquor and stripping of the loaded organic phase were carried out in mixer-settler units in the above conditions. The flow rates of leach liquor and extractant were 3 and 2 L/h, respectively, in the extraction stage. Copper was stripped from the LO with  $180 \text{ kg/m}^3 \text{ H}_2\text{SO}_4$  where the flow rates of LO and strip solution were 2 and 0.44 L/h, respectively. After the copper content in the pregnant solution attained 27.32 kg/ m<sup>3</sup>, coupling of electro winning with SX was started. The bench scale run was made at the rate of 8 h/day for 340.5 h, and the data are discussed here.

## 6-1. Leach Liquor

At the outset, the concentration of copper in the leach liquor was  $0.6944 \text{ kg/m}^3$ , which gradually increased to  $1.185 \text{ kg/m}^3$ . The high-



**Fig. 6. Variation of [Cu] in Cu-PE with time, h.**

est concentration of Mn, Zn and Ca in the leach liquor was 56, 88 and 53  $g/m<sup>3</sup>$ , respectively. The concentration of Ni, Co and Mg in the solution was 5, 7, and  $0.66$  g/m<sup>3</sup>, respectively. There was no extraction of Fe, Mn, Co, Ni, Zn, Ca, and Mg into the organic phase. 6-2. Raffinate

Initially, the concentration of copper in the raffinate was  $0.2 g$  $m<sup>3</sup>$  (99.76% extraction) up to 142.15 h. With the increase in concentration of copper in the leach liquor to  $1.185 \text{ kg/m}^3$  with time, the percentage extraction came down to 80 due to the use of the same extractant (1.5% LIX 622N). The copper-loading capacity of the extractant increased from  $0.5734$  to  $1.253$  kg/m<sup>3</sup>. 6-3. Copper Strip Solution

The loaded organic was stripped with  $180 \text{ kg/m}^3 \text{ H}_2\text{SO}_4$  for which the metal concentration in the acid solution increased from nil to 27.32 kg/m<sup>3</sup> after which electrowinning of copper was started. The plot of [Cu] in the strip solution vs. time, Fig. 6, shows a regular increase in metal concentration. The slope of the plot illustrates an increase in concentration 0.0971 kg/m<sup>3</sup> of copper per hour. 6-4. Copper Spent Organic (Cu-SO)

After the copper-loaded organic was stripped with  $180 \text{ kg/m}^3 \text{ H}_2$  $SO_4$ , the spent organic (Cu-SO) was washed with 5.5 pH Na<sub>2</sub>SO<sub>4</sub> solution at 1 : 1 phase ratio and was re-circulated for extraction. A suitable aliquot of the Cu-SO after filtration through 1PS phase separating paper was stripped and analyzed. The stripping of copper came down from 97.7% (17.25 h) to 62.7% (249.1 h), because the acid concentration in the strip solution came down to  $138.6 \text{ kg/m}^3$ . The stripping of copper was again increased to 86.07% (340.5 h) after the level of acid in the strip solution was adjusted to its original value.

#### **7. Electro Winning**

During solvent extraction, some minor quantities of impurities may enter into the pregnant electrolyte and interfere with the electrowinning process. In addition, the pregnant electrolyte mostly contaminated with the entrained solvent is purified by passing through the activated carbon column. Impurities like Fe, Al, Ca, Mg, suspended solids and gelatinous materials in the pregnant electrolyte do affect the quality of copper deposit and reduce the current efficiency. The presence of iron in the copper pregnant electrolyte reduces the current efficiency during electrowinning due to the oxidation and reduction reactions taking place. The bacterial leach liquor after being processed through solvent extraction and activated carbon contained 35 kg/m<sup>3</sup> Cu, 0.61 kg/m<sup>3</sup> Fe, 0.024 kg/m<sup>3</sup> Mn and 0.06 kg/m<sup>3</sup> Co. The following reactions took place during electrowinning of copper from the copper sulfate solution:

At cathode  
\n
$$
Cu^{2+}+2e \longrightarrow Cu^{\circ}, E_o=0.34 V
$$
 (9)

$$
2H_2O \longrightarrow O_2 + 4H^+ + 4e^-, E_o = 1.23 V \tag{10}
$$

The net electro winning reaction is:

At Anode

$$
Cu^{2+}+H_2O \longrightarrow Cu^{2+}V_2O_2+2H^+ \tag{11}
$$

The electrolyte flow rate was varied from 2 to 10.8 L/h. In total, 26 continuous experiments were carried out with 21 to 25 h duration. Nearly 565 hours of copper electrowinning was carried out, and about 1,251 g of copper metal was produced after enriching the copper concentration in the bacterial leach liquor through solvent extraction. The concentration of copper and  $H_2SO_4$  in the bath



**Fig. 7. Effect of flow rate on current efficiency and energy consumption.**





was about 35 kg/m<sup>3</sup> and 180 kg/m<sup>3</sup>, respectively. The current density varied from 120 A/m<sup>2</sup> to 240 A/m<sup>2</sup>. The cell voltage was observed from 1.8 to 2.2 V, depending upon the operating conditions. The current efficiency increased from 92 to 100% with increase of flow rate from 2 to 10.8 L/h Fig. 7, and the energy consumption during the campaign varied from 1.7 to 2.05 kWh/kg, which was comparable to the literature value of 2.0 kWh/kg. The acid concentration varied from 20 to 200 kg/m<sup>3</sup> and the current efficiency increased from 92 to 97.2% up to 100 kg/m<sup>3</sup> acid concentration; further increase in acid concentration did not affect the current efficiency. The optimum conditions for electrowinning of copper are given in Table 1. The acid and copper concentration in different experiments given in Table 2 show much variation in concentrations during the continuous SX-EW study. The purity of metal with two samples produced during this campaign was 99.996 and 99.999%, and the impurities present in the deposit are given in Table 3. The quality of deposit produced at different current densities of 240 A/

**Table 3. Purity of the electrodeposited copper**

| Metal                    | Impurity % | Impurity % |
|--------------------------|------------|------------|
| Fe                       | 0.0003     | 0.0002     |
| Zn                       | 0.0015     | 0.0007     |
| Pb                       | 0.0008     | 0.0004     |
| Ni                       | 0.0011     | 0.0004     |
| Co                       | 0.0001     | 0.0001     |
| Total impurity           | 0.0038     | 0.0014     |
| Purity of copper cathode | 99.996     | 99.999     |





**Table 2. Copper and acid concentrations during continuous campaigns**



m<sup>2</sup> and 120 A/m<sup>2</sup> was very good. A smooth copper deposit was obtained at lower current density, but nodular growth was observed at higher current density. A flow sheet for recovery of copper from the bacterial leach liquor involving solvent extraction and electrowinning is shown in Fig. 8.

## **CONCLUSIONS**

Heap bioleaching of low-grade copper ore was performed at IMMT, Bhubaneswar. The leaching study showed 0.09% dissolution of copper from the ore body per day. The leach liquor was processed through solvent extraction and electrowinning. Extraction of copper from the solution increased with pH and extractant concentration. The copper was extracted from the actual leach liquor with 1.5% LIX622N in kerosene in 3-stages at O : A ratio of 2 : 3. There was no co-extraction of iron with copper. Copper was stripped from the loaded organic with  $180 \text{ kg/m}^3 \text{ H}_2\text{SO}_4$  in two stages at O : A ratio of 9 : 2. With increase in copper concentration in the feed, the metal concentration in the raffinate was increased in the bench scale run. The concentration of copper in the strip solution increased at the rate of 0.0971 kg/m<sup>3</sup> per hour. The electrowinning circuit was coupled with the solvent extraction after the concentration of copper in the pregnant electrolyte was 27.32 kg/m<sup>3</sup>. Activated carbon was used to remove the entrained organic from the pregnant electrolyte. The amount of copper enriched during solvent extraction was deposited during electrowinning. Conditions were established to deposit smooth and bright sheets of copper of 99.99% purity by using a current density of 120 A/m<sup>2</sup>.

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