

## Recovery of copper from a surface altered chalcopyrite contained ball mill spillage through bio-hydrometallurgical route

Sandeep Panda<sup>\*,\*\*\*,†</sup>, Pradeep Chandra Rout<sup>\*\*\*\*</sup>, Chinmaya Kumar Sarangi<sup>\*\*\*</sup>,  
Srabani Mishra<sup>\*\*\*</sup>, Nilotpala Pradhan<sup>\*</sup>, Umaballav Mohapatra<sup>\*\*\*\*</sup>, Tondepu Subbaiah<sup>\*\*\*</sup>,  
Lala Behari Sukla<sup>\*</sup>, and Barada Kanta Mishra<sup>\*\*\*\*\*</sup>

\*Bioresources Engineering Department, CSIR - Institute of Minerals & Materials Technology (CSIR-IMMT),  
Bhubaneswar-751013, India

\*\*Academy of Scientific and Innovation, Research, CSIR - Institute of Minerals & Materials Technology (CSIR-IMMT),  
Bhubaneswar-751013, India

\*\*\*Hydro and Electrometallurgy Department, CSIR - Institute of Minerals & Materials Technology (CSIR-IMMT),  
Bhubaneswar-751013, India

\*\*\*\*North Orissa University (NOU), Baripada-757003, Orissa, India

(Received 7 May 2013 • accepted 1 December 2013)

**Abstract**—Bioleaching studies for chalcopyrite contained ball mill spillages are very scarce in the literature. We developed a process flow sheet for the recovery of copper metal from surface activated (600 °C, 15 min) ball mill spillage through bio-hydrometallurgical processing route. Bioleaching of the activated sample using a mixed meso-acidophilic bacterial consortium predominantly *A. ferrooxidans* strains was found to be effective at a lixiviant flow rate of 1.5 L/h, enabling a maximum 72.36% copper recovery in 20 days. Mineralogical as well as morphological changes over the sample surface were seen to trigger the bioleaching efficiency of meso-acidophiles, thereby contributing towards an enhanced copper recovery from the ball mill spillage. The bio-leach liquor containing 1.84 g/L Cu was purified through solvent extraction using LIX 84I in kerosene prior to the recovery of copper metal by electrowinning. Purity of the copper produced through this process was 99.99%.

Keywords: Spillage, Thermal Activation, *Acidithiobacillus ferrooxidans*, BACFOX, Solvent Extraction, Electrowinning

### INTRODUCTION

The majority of copper bearing minerals are sulfides of which chalcopyrite (CuFeS<sub>2</sub>), an economically important copper sulfide, accounts for about 70% of the total copper reserves [1]. Since high grade copper resources are being exhausted at an alarming rate, particular concern has been raised for processing the low-grade copper ores through bio-hydrometallurgical route of extraction [2-6]. As of the 21<sup>st</sup> century, it has been estimated that about 20% of world's total copper production is through bio-hydrometallurgy [7].

Complexities in the mineralogical organization and properties of copper sulfides often possess challenges during selective dissolution of the desired metal in water or acid solutions [8,9]. However, they can be made soluble under oxidizing conditions in the presence of acidophilic bacteria such as *A. ferrooxidans*, *L. ferrooxidans* and *A. thiooxidans* [10,11]. It has now been well documented that a mixed culture is rather more effective than a pure culture for bioleaching reactions [12-14]. Microbial leaching has thus become very attractive because of the process simplicity and environmental compatibility in comparison to the conventional acid leaching process [15]. Slowly, it is gaining momentum in the field of waste treatment [16].

India is blessed with larger deposits of copper, with M/s Hindustan Copper Limited (HCL) contributing more than 80% of India's total

copper production. Copper ore beneficiation plants that treat chalcopyrite, such as Malanjkhand Copper Project (MCP)—a unit of HCL, generate considerable amount of ball mill spillages from their grinding unit. At present, these spillages are dumped as waste that contains a considerable amount of copper values. However, piling up of such waste material may lead to environmental as well as space issues. If these wastes could be suitably treated to recover the metal values, it could solve the environmental problems in addition to the economic benefits for the industry.

Hydrometallurgical processing of chalcopyrite has limitations due to slow dissolution kinetics [3,17,18]. Thus, a rapid dissolution rate of chalcopyrite using acidophilic iron and sulphur oxidizing bacteria is the need of the day. On the other hand, Rao et al. [17] reported that the bacterial leaching phenomenon/action is limited to the material surface, which ultimately upshots poor copper recovery. If a suitable technique can be applied that can directly affect the material surface by altering the mineralogical as well as morphological structure, thereby allowing surface as well as interior leaching of the material, then recovery rates can be expected to improve.

Thermal surface modification/activation technique has been reported to improve the dissolution kinetics from nickel laterites as well as chalcopyrite using acidophilic microorganisms [19-22]. However, very few or no bench scale reports for such studies towards development of a process flow sheet are available in the literature. In addition, available information on bioleaching studies for ball mill spillages is very limited. Our previous study [22] involved an effort

<sup>†</sup>To whom correspondence should be addressed.

E-mail: panda.sandeep84@gmail.com

Copyright by The Korean Institute of Chemical Engineers.

to understand the underlying mineralogical and structural changes in ball mill spillage material through thermal surface activation/modification technique that resulted in enhanced copper recovery through bioleaching conducted in shake flasks.

Therefore, the present work was motivated to optimize the bench scale bioleaching conditions based on the different optimized parameters at shake flask level. Further, the study aims at gaining an insight into the copper recovery patterns of the thermally surface activated chalcopyrite under natural environmental conditions using percolation columns using bacterial film oxidation (BACFOX) bioreactor technology [4]. In addition, the optimal conditions for solvent extraction (SX) and electrowinning (EW) of copper have also been established to recover pure cathode copper from the Cu-loaded bacterial lixiviant.

## MATERIALS AND METHODS

### 1. Ball Mill Spillage and Pretreatment Conditions

Ball mill spillage containing Cu -0.26%, Fe- 1.8%, S- 0.48% and acid insoluble - 91.82% was obtained from the dump disposal site of HCL-MCP, India [22]. About 55 kg of the ore sample was subjected to thermal activation at 600 °C for 15 mins in a resistance-heating furnace (herein referred to as activated spillage throughout the text). A detailed mineralogical analysis of sample was reported in our previous study [22]. The elemental analysis of the sample pre- and post-bioleaching was carried out using X-ray fluorescence (Philip's model 120454/3).

### 2. Microorganisms and Bioleaching Conditions

A laboratory stock culture of mixed mesophilic acidophilic bacterial consortium, predominantly *A. ferrooxidans* along with *L. ferrooxidans* and *A. thiooxidans* strains, was used as inoculum for the present study [11]. For the growth of *A. ferrooxidans*, 9K<sup>+</sup> media containing 3 g/L (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 0.1 g/L KCl, 0.5 g/L MgSO<sub>4</sub>·7H<sub>2</sub>O, 0.5 g/L KH<sub>2</sub>PO<sub>4</sub>, and 44.2 g/L FeSO<sub>4</sub>·7H<sub>2</sub>O was used [23]. The strain was adapted to Cu of 1 g/L by incremental increase of the same. Further, the adapted bacteria were transferred to a BACFOX unit for the preparation of the lixiviant that was used for leaching. All the chemical reagents used were of analytical grade (Merck, Germany).

The activated spillage was bioleached using percolation column bioreactors since column bioleaching is considered as the simulation of heap bioleaching [11]. Five different columns (Col 1-Col 5) having dimensions of height-130 cm and internal diameter-7.5 cm were loaded with 10 kg each of thermally activated (-15+10 mm size) samples. Five BACFOX bioreactors containing bacterial lixiviant were placed at the bottom of each column operating under ambient temperature conditions (25-30 °C). The initial composition of bacterial lixiviant used for column leaching studies was pH-1.5, redox potential- 620 mV, Fe (II) - Nil, Fe (III) - 3.0 g/L and cell count of the inoculum - 3.92×10<sup>7</sup> cells mL<sup>-1</sup>. Bacterial lixiviant from the BACFOX bioreactors was supplied through a sprinkler (at top of each column) using a metering pump and the effluent solution was recirculated. Aeration to the column and BACFOX bioreactors was ensured initially. The flow rates (L/h) of the bacterial lixiviant to different columns were 0.5 (Col 1), 1.0 (Col 2), 1.5 (Col 3), 2.0 (Col 4) and 2.5 (Col 5). The leach liquor generated from the best-optimized column was subjected to downstream processing through SX-EW route. The column leaching setup is shown in Fig. 1.

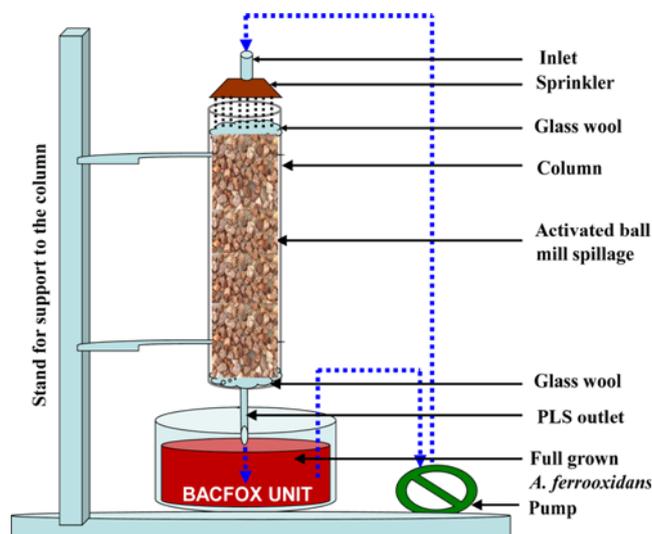


Fig. 1. Column leaching setup. Dotted lines indicate the direction of flow of bacterial lixiviant.

### 3. Downstream Processing (SX-EW)

The leach liquor generated from the best optimized column yielding maximum copper recovery was purified through solvent extraction using LIX 84I in kerosene as the extractant followed by activated carbon adsorption for the removal of any minute amount of solvent left in the solution after stripping. In the equilibrium studies, equal volumes of the aqueous phase bearing Cu and the organic phase containing the extractant were equilibrated manually for 5 minutes in a separatory funnel. After phase disengagement, the raffinate was separated and analyzed with AAS (Model-Perkin Elmer AA 200) after a suitable dilution. The loaded organic generated was stripped with 10% H<sub>2</sub>SO<sub>4</sub> solution. Parameters such as effect of equilibration time and extractant concentration were studied.

The pure solution obtained after purification of the bioleach liquor was subjected to electrowinning at ambient temperature for the recovery of copper metal in a glass cell using SS 304 and Pb - (7%) Sb sheets as cathode and anode, respectively. The electrolysis was carried out by applying direct current with the help of a rectifier from a regulated power supply unit. The purity level of the cathodic deposit was tested through chemical analysis method; the concentrations of various impurities were determined with an atomic absorption spectroscope (AAS). The surface morphology and elemental distribution of the deposit obtained from electrowinning were examined using field emission-scanning electron microscope coupled with energy dispersive X-ray spectroscopy (FESEM-EDS Zeiss Supra-55 model).

The process flow sheet for the bio-hydrometallurgical recovery of copper values from the activated ball mill spillage involving unit operations such as column leaching, solvent extraction and electrowinning is shown in Fig. 2.

## RESULTS AND DISCUSSION

### 1. Bacterial Oxidation Rate and Regeneration Time in the BACFOX Unit

Initially, 2 L of activated bacterial solution was inoculated in the

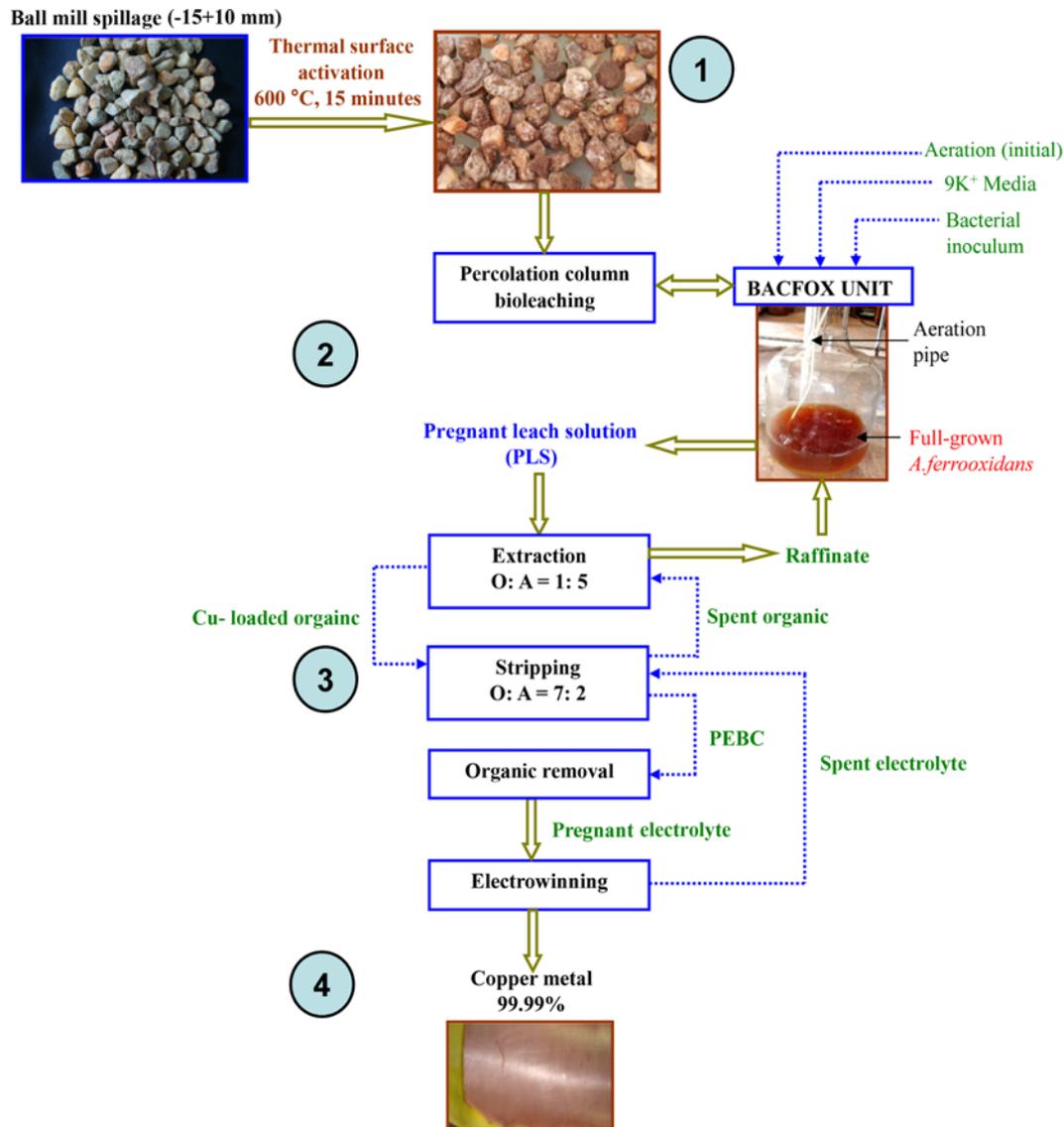


Fig. 2. Process flow sheet for recovery of copper from activated ball mill spillage. (1) Activation stage prior to bioleaching (2) Bioleaching (3) Solvent extraction (4) Electrowinning. PEBC- Pregnant electrolyte before activated carbon treatment.

BACFOX unit containing 8 L of 9K<sup>+</sup> media. The pH of the medium was adjusted to 1.5 [22]. The rate of bacterial oxidation was evaluated from the plot of Fe (II) concentration versus time (h), and the study continued till a steady state was achieved. Under steady state, the rate of iron oxidation was observed to be 501 mg/L/h (graph not shown). 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,  $t_g$ , was evaluated using the following relationship [24].

$$t_g = 0.693/\mu \quad (1)$$

From Eq. (1), regeneration time of the activated microorganism was calculated to be 16 h.

## 2. Column Leaching Tests for Activated Spillage

### 2-1. Acid Neutralization

Prior to the start of bioleaching experiments, the columns were

acid washed (pH-1.5 H<sub>2</sub>SO<sub>4</sub>) initially to neutralize the gangue minerals and provide an acidic environment for the growth of meso-acidophilic bacteria. During acid neutralization, a maximum of 17.28% copper was recovered in the solution from Col 3 in 2 days at a flow rate of 1.5 L/h. Copper recovery during this step from four other columns supplied with varying flow rates (discussed in section 2.2) were 7.38% (Col 1), 9.38% (Col 2), 16.54% (Col 4) and 16.98% (Col 5), respectively. Notice that at higher flow rates in Col 4 and Col 5, the recovery of copper was almost similar to Col 3. Higher recoveries initially during this neutralization step indicated that partially some copper have been oxidized during thermal activation [22]. This fact was also supported by the XRF studies as shown in Table 1. XRF studies indicated that most of the compounds present in the original ball mill spillage were converted to oxides after thermal activation. This clearly indicates that due to the conversion of some of the sulfide phase into oxides, a faster flow of the acidified solution into the columns (Col 3, Col 4 and Col 5) rapidly dissolved most of the entrapped copper in the oxide phase to the solution and vice

**Table 1. XRF analysis of ball mill spillage pre and post thermal activation**

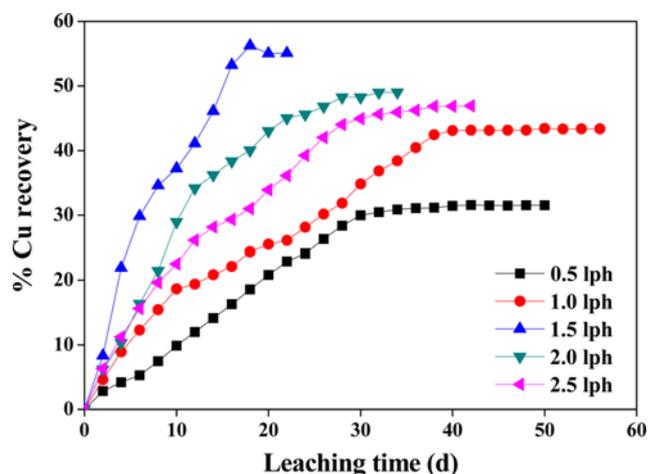
Analyte	Compound formula	Original spillage, concentration (%)	Activated spillage, concentration (%)
Na	Na <sub>2</sub> O	3.511	5.817
Mg	MgO	1.253	1.975
Al	Al <sub>2</sub> O <sub>3</sub>	8.685	9.224
Si	SiO <sub>2</sub>	77.637	67.786
P	P <sub>2</sub> O <sub>5</sub>	0.073	0.307
S	SO <sub>3</sub>	0.117	2.172
K	K <sub>2</sub> O	1.986	3.912
Ca	CaO	2.343	2.964
Cr	Cr <sub>2</sub> O <sub>3</sub>	-	0.049
Ti	TiO <sub>2</sub>	0.270	0.423
Mn	MnO	0.057	0.049
Fe	Fe <sub>2</sub> O <sub>3</sub>	3.950	4.946
Ni	NiO	0.007	0.015
Cu	CuO	0.040	0.047
Rb	Rb <sub>2</sub> O	0.004	0.005
Sr	SrO	0.018	0.023
Zr	ZrO <sub>2</sub>	0.010	0.076
Ba	BaO	0.040	0.047
Ce	CeO <sub>2</sub>	-	-
Y	Y <sub>2</sub> O <sub>3</sub>	-	0.011

versa. Furthermore, no significant improvement in copper concentration was observed even after four days of recirculation, indicating the depletion of oxide phase. Acid consumed during washing for Col 3 was nearly 0.95 g/kg of ore. The acid consumption is mainly due to neutralization of acid-consuming gangue minerals as well as partial dissolution of the oxide phase.

#### 2-2. Effect of Bacterial Lixiviant Flow Rates on Copper Recovery Post Acid Neutralization

Lixiviant flow rates play a significant role in the leaching process [17]. With subsequent depletion of the oxide phase and exposure of the sulfides, it is very much necessary to optimize the best condition for lixiviant flow rates on copper recovery.

After acid neutralization of all the columns under observation, the acidified Fe (III) rich bacterial lixiviant from the BACFOX bioreactors was supplied to the top of each of the five columns at varying flow rates. At a flow rate of 1.5 L/h (Col 3), a maximum of 55.08% Cu was recovered in 18 days (Fig. 3). However, increasing the flow rates, i.e., 2.0 L/h in Col 4 and 2.5 L/h, in Col 5 resulted in slower copper recovery as compared to Col 3 post acid neutralization. This fact contradicts the recovery patterns as observed during the acid neutralization/washing of the sample prior to application of acidified bacterial lixiviant from the BACFOX bioreactors. In addition, slower flow rates in Col 1 and 2 resulted in lower percentage of copper

**Fig. 3. Effect of lixiviant flow rate on copper recovery from activated ball mill spillage. lph in the figure indicates liters per hour.**

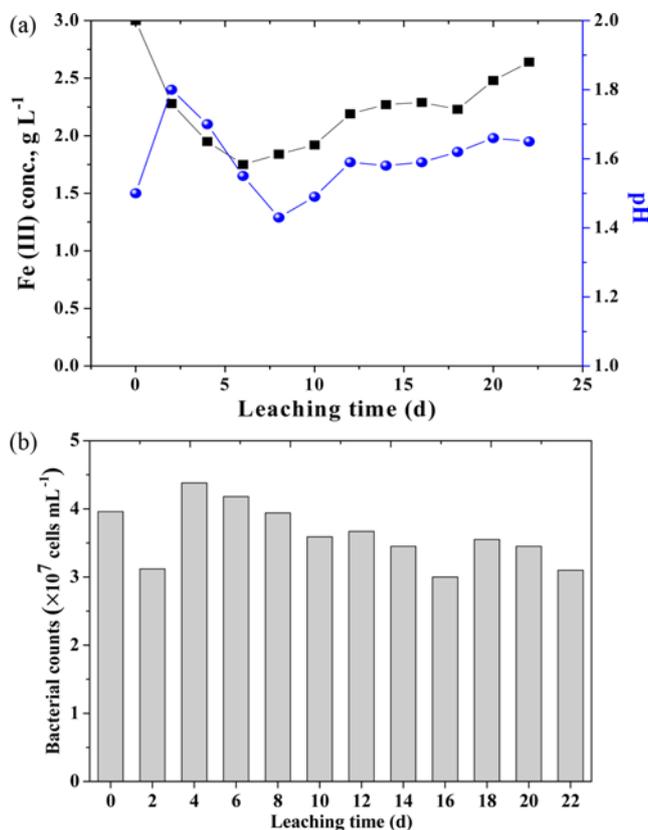
recovery when compared with the entire columns under observation. This observed phenomenon is in contradiction to the results obtained by Rao et al. [17] for column leaching studies with lean grade chalcopyrite ore of the same copper mine. They reported that the copper leaching rate is inversely proportional to the lixiviant flow rate, which is due to oxygen diffusion into the material and exposure of bacterial lixiviant for longer period onto the ore surfaces. However, in the present case, jarosite or iron precipitation in the columns was found to be lesser at higher flow rates such as 2.0 and 2.5 L/h, which agrees with Rao et al. [17]. The effect of different solution flow rates on copper recovery is shown in Fig. 3. In total, 72.38% copper was recovered in 20 days: 2 days of washing and 18 days of bacterial leaching. The results clearly demonstrated the enhanced rate of bioleaching to recover copper from ball mill spillage through thermal activation process, and that agrees with our earlier published studies [21,22]. The total output with acid consumption and Cu recovery figures from Col 3 is shown in Table 2.

#### 2-3. Monitoring the pH and Variation in Iron Concentration

Bacterial leaching of CuFeS<sub>2</sub> is dependent on acidic conditions, the acidity often being autonomously produced by the oxidation of pyrite (FeS<sub>2</sub>) and hydrolysis of the Fe (III) ions [4,25]. As is evident from the preliminary studies (discussed in section 2.2) that Col 3 yielded maximum recovery of copper, monitoring of the pH conditions and variation in the iron concentrations in the column becomes quite essential. Fig. 4(a) shows the changes in pH with time during bioleaching of the activated ore in Col 3. The initial increase in pH may be due to acid consumption by gangue minerals, iron oxidation, or both. A decrease in pH values was noticed from day 3 until day 8, indicating generation of acid due to bacterial activity because of iron hydrolysis that stabilized the bacterial leaching experiments. Thereafter, steady pH values were noticed from day 12 onwards

**Table 2. Output of column bioleaching (Col 3) with activated ball mill spillage**

Sample	Acid consumption (g/10 kg ore)			Cu leached (g)			Total Cu recovery (%)
	During washing	During bioleaching	Total	During washing	During bioleaching	Total	
Activated spillage	9.562	5.23	14.792	4.49	14.32	18.82	72.38



**Fig. 4. (a) Variation in Fe (III) conc., g/L and pH vs. leaching period (days). (b) Bacterial counts vs. leaching period (days).**

until day 22, indicating utilization and subsequent generation of acid during bacterial leaching with the activated ball mill spillage. It can be inferred that due to the development of cracks on the surface of the ball mill spillage (discussed in section 3.1), acidified bacterial solution was able to penetrate into its interior. This led to higher oxidation of pyrite ( $\text{FeS}_2$ ) and sulfur ( $\text{S}^0$ ), thereby generating more acid and maintaining an acidic environment required for bacterial leaching process, which subsequently facilitated faster dissolution of copper.

The concentrations of ferrous and ferric iron are important parameters in bioleaching and are useful as a measure of the biological activity. The variation in iron concentration is also shown in Fig. 4(a). The average oxidation rate of copper increased when soluble ferric iron was present in the leach solution at high concentrations.

#### 2-4. Bacterial Counts

Microscopic counts of bacterial cells from the effluent solution during column bioleaching (Col 3) operation are shown in Fig. 4(b). During day 2 of leaching there was a decrease in cell concentration from  $3.96$  to  $3.12 \times 10^7$  cells/mL. This can be attributed to the fact that some bacterial cells might have attached to the ore surface during recirculation of the bacterial lixiviant. From day 2 to day 4, bacterial counts were seen to increase, indicating activeness of the bacterial culture, which can be directly co-related to the availability of sufficient pyrite for oxidation and nutrients in the culture medium. A gradual fluctuation in the cell concentrations, i.e., from  $4.19$  to  $3.1 \times 10^7$  cells/mL, occurred, which might have been due to gradual depletion of ferrous ion in the medium until day 22.

### 3. Analytical Interpretation of Pre- and Post-activated Spillage

Activation at  $600^\circ\text{C}$  resulted in a phase change from  $\alpha\text{-SiO}_2$  (low quartz) to  $\beta\text{-SiO}_2$  (high quartz), which has been well explained in our previous study [22]. Silica ( $\alpha\text{-SiO}_2$  or low quartz) contributes to a higher percentage of all the minerals present in the sample. Due to activation the concentration of silica, i.e.,  $\beta\text{-SiO}_2$  was less as compared to the original sample (Table 1). The result could be explained based on the unstable nature of Beta Quartz at earth's surface temperature and pressure that quickly breaks down due to a distorted structural framework [26].

#### 3-1. Electron Microscopic (SEM, FESEM-EDS) Study

Analytical characterization of the pre- and post-activated spillage sample of MCP provided us with very interesting results. SEM (JOEL JSM-6510 model) characterization revealed that the sample surface was smooth prior to activation (Fig. 5(a) and (b)). However, post-activation, the sample showed striations with vein-like projections on the surface (Fig. 5(c)). The activated samples were rough where the surface was somewhat arranged in parallel layer fashion (see Fig. 4(d)). FESEM (Zeiss Supra-55 model) analysis of the activated sample showed similar striations. The sample was more compact with a massive fracture, parallel lines and bigger pits over the sample surface that confirmed the SEM results (Fig. 5(e) and (f)).

The changes as observed from the electron microscopic study could be a result of thermal effects on the sample. The striations with vein-like rough structures might be a result of rapid heating and cooling of the sample that might have affected some crystallographic changes in the sample. However, an accurate description for this phenomenon cannot be proposed with the information available.

The phase change of  $\alpha\text{-SiO}_2$  to  $\beta\text{-SiO}_2$  simultaneously resulted in volume expansion of the rock body, thereby creating micro and macro cracks as well as minute pores all over the material as was evident from the stereomicroscopic studies by Panda et al. [22] and in the present study through SEM, FE-SEM characterization. This fact facilitated the bacterial solution to penetrate the ore surfaces, resulting in an enhanced copper recovery. Owing to the optimized flow rate ( $1.5\text{ L/h}$ ) resulting a higher percentage of copper recovery from column 3 (Col 3), the bioleach liquor thus generated was subjected to downstream processing through solvent extraction (SX) and electrowinning (EW) for metal recovery.

### 4. Solvent Extraction

Extraction of Cu from the bioleach liquor containing  $1.848\text{ g/L}$  Cu was carried out using LIX 84I as extractant. In construction of McCabe-Thiele plots for extraction and stripping, the O : A ratio was kept within  $1 : 6$  to  $5 : 1$  and  $1 : 5$  to  $5 : 1$ , respectively, while keeping the total volume of phases constant. The McCabe-Thiele plot for extraction of Cu from the aqueous phase with 25% LIX 84I in kerosene was constructed to determine the O : A ratio and the number of stages, followed by the generation of Cu-loaded organic by the counter-current simulation method in 2-stages at O : A ratio of  $1 : 5$ .

#### 4-1. Effect of Contact Time

Equal volumes of bioleach liquor and the extractant (5% LIX84I) were equilibrated for 1, 2, 3, 5, 7 and 10 minutes and the raffinate were analyzed for copper. The extraction of copper gradually increased with the increase in equilibration time, i.e., up to five minutes, and then remained constant. Thus, an equilibration time of five

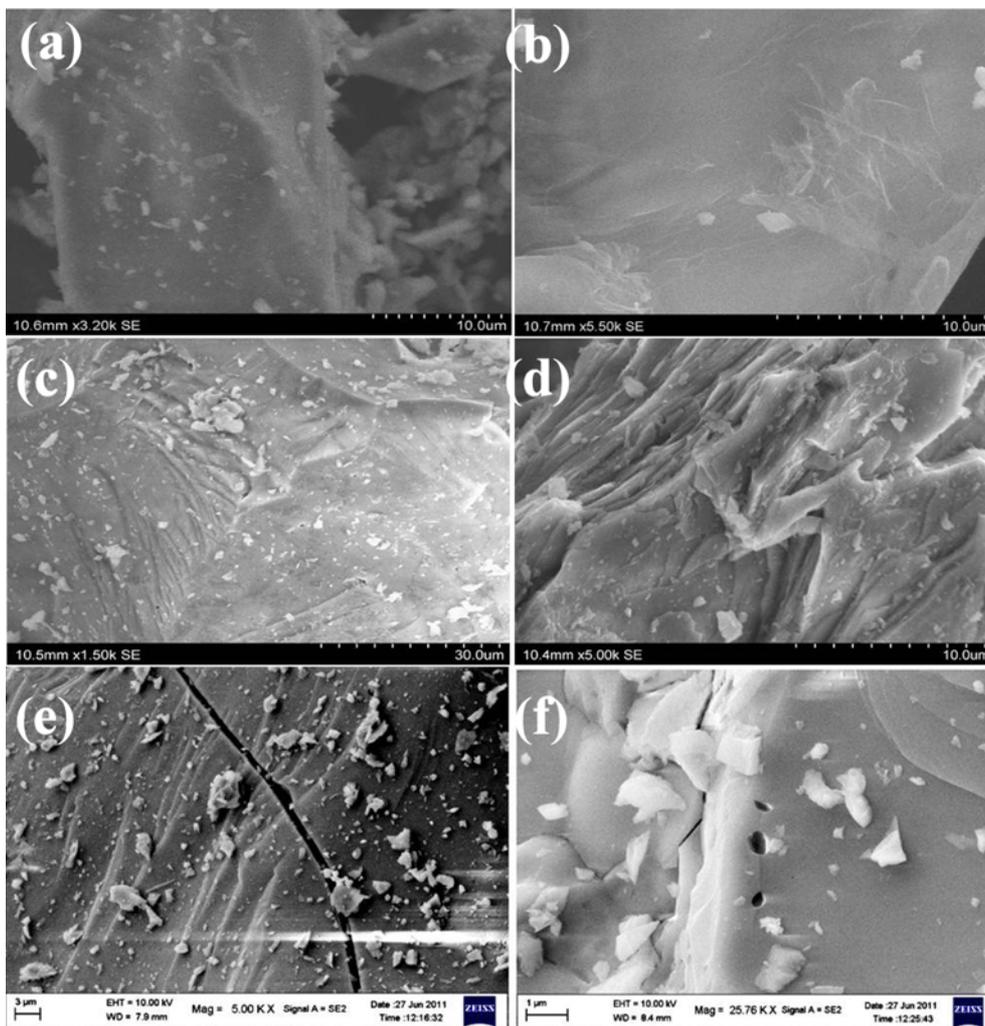


Fig. 5. SEM photographs of the ball mill spillage (a) and (b) pre-activation showing a smooth surface appearance (c) and (d) post activation showing striations, vein-like appearance with a compact rough surface arranged in parallels. FE-SEM photographs confirming SEM (e) and (f) showing massive cracks with compact rough surface and pits on the smooth surface.

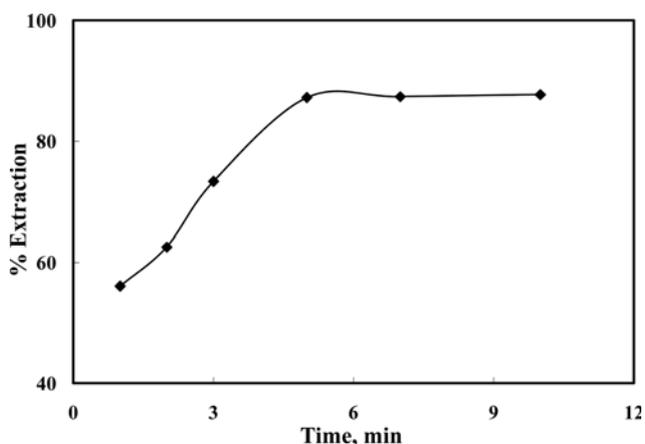


Fig. 6. Effect of contact time on extraction of Cu; Conditions:  $[Cu]_{LL}$ : 1.848 g/L, 5% LIX 84I, O : A=1, Room temperature.

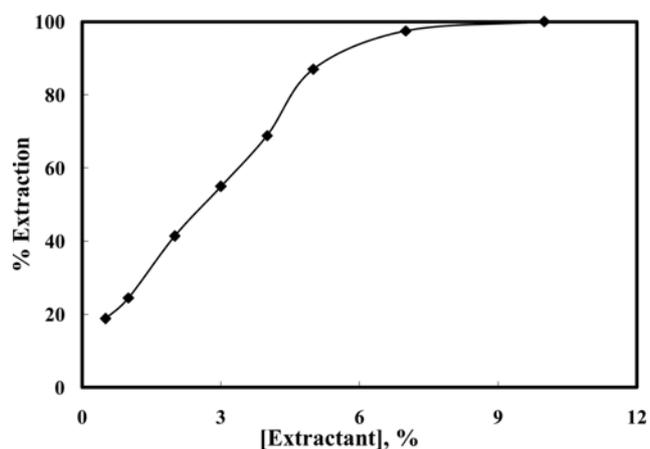


Fig. 7. Effect of [Extractant] on extraction of Cu; Conditions:  $[Cu]_{LL}$ : 1.848 g/L, O : A=1, Contact time=5 min, Room temperature.

minutes was adopted for further extraction studies. The experimental data is shown in Fig. 6.

#### 4-2. Effect of Extractant Concentration

The extraction of copper increased from 18.77 to 99.99% with

**Table 3. Effect of variation of LIX 84I concentration keeping O : A ratio 1 : 5**

[LIX 84I], %	[Cu] <sub>raff</sub> , g L <sup>-1</sup>	[Cu] <sub>org</sub> , g L <sup>-1</sup>
10	1.063	3.925
15	0.644	6.02
20	0.348	7.5
25	0.123	8.625
30	0.076	8.86

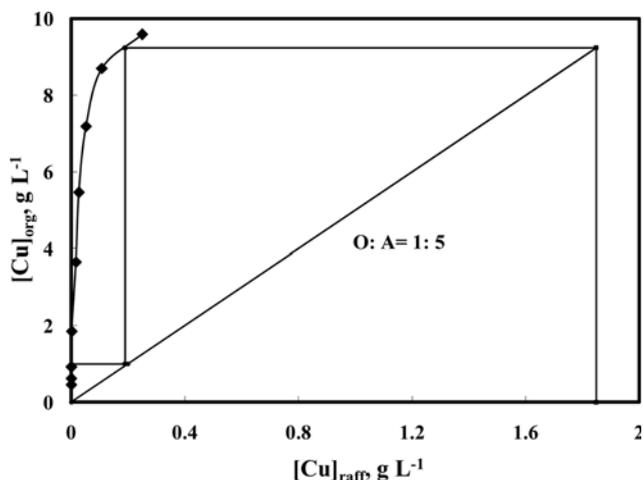
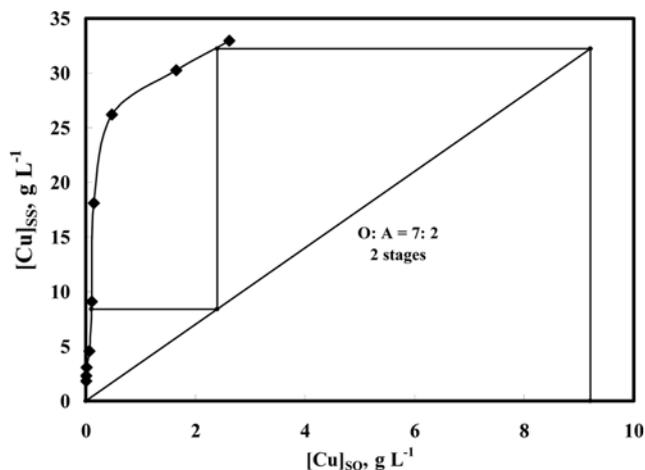
increase in concentration of LIX 84I in kerosene from 0.5 to 10% while keeping the O : A ratio 1 : 1 (Fig. 7). An additional set of experiments were conducted by varying the concentration of LIX 84I from 10 to 30% keeping O:A ratio 1 : 5. The concentrations of Cu in the organic and aqueous phases are shown in Table 3. The percentage of Cu extraction with 25% LIX 84I and 30% LIX 84I was 93.34 and 95.88%, respectively, in a single stage. Therefore, from an economical point of view, LIX 84I was selected for carrying out the extraction isotherm.

#### 4-3. Extraction Isotherm

The extraction isotherm was constructed to ensure the O : A ratio and the number of stages required for countercurrent study for quantitative extraction of a metal from its liquor at a chosen phase ratio. The bioleach liquor and 25% LIX 84I in kerosene were contacted at different O : A ratios within 1 : 6 to 5 : 1 for five minutes while keeping the total volume of phases constant, followed by phase separation and analysis of the raffinates. The McCabe-Thiele plot (Fig. 8) showed quantitative extraction of copper in two-stages at O : A ratio of 1 : 5 followed by the generation of Cu-loaded organic by countercurrent simulation method. The mixed loaded organic phase contained 9.21 g/L Cu and was used for the stripping studies.

#### 4-4. Stripping of Cu

Stripping studies ensure the O : A ratio and number of stages required for countercurrent study for quantitative stripping of copper. Fig. 9 shows the stripping isotherm for Cu from the loaded organic. The stripping of loaded organic containing 9.21 g/L copper was car-

**Fig. 8. McCabe-Thiele plot for extraction of Cu; Conditions: [Cu]<sub>LL</sub>: 1.848 g/L, 25% LIX 84I, Contact time=5 min, Room temperature.****Fig. 9. McCabe-Thiele plot for stripping of Cu-LO; Conditions: [Cu]<sub>LO</sub>: 9.21 g/L, 10% H<sub>2</sub>SO<sub>4</sub> as strip solution, Contact time=5 min, Room temperature.**

ried out with 10% H<sub>2</sub>SO<sub>4</sub>. In construction of McCabe-Thiele plot (Fig. 9) for stripping, the loaded organic was stripped at O : A ratios within 1 : 5 to 5 : 1 by keeping the total volume of phases constant to determine the O : A ratio and the number of stages for countercurrent simulation. It shows that Cu can be successfully stripped from the loaded organic by two-stage countercurrent simulation method at O : A ratio of 7 : 2. The stripping efficiency was found to be 99.35%, leading to the generation of an electrolyte containing about 32.03 g/L Cu.

#### 5. Electrowinning

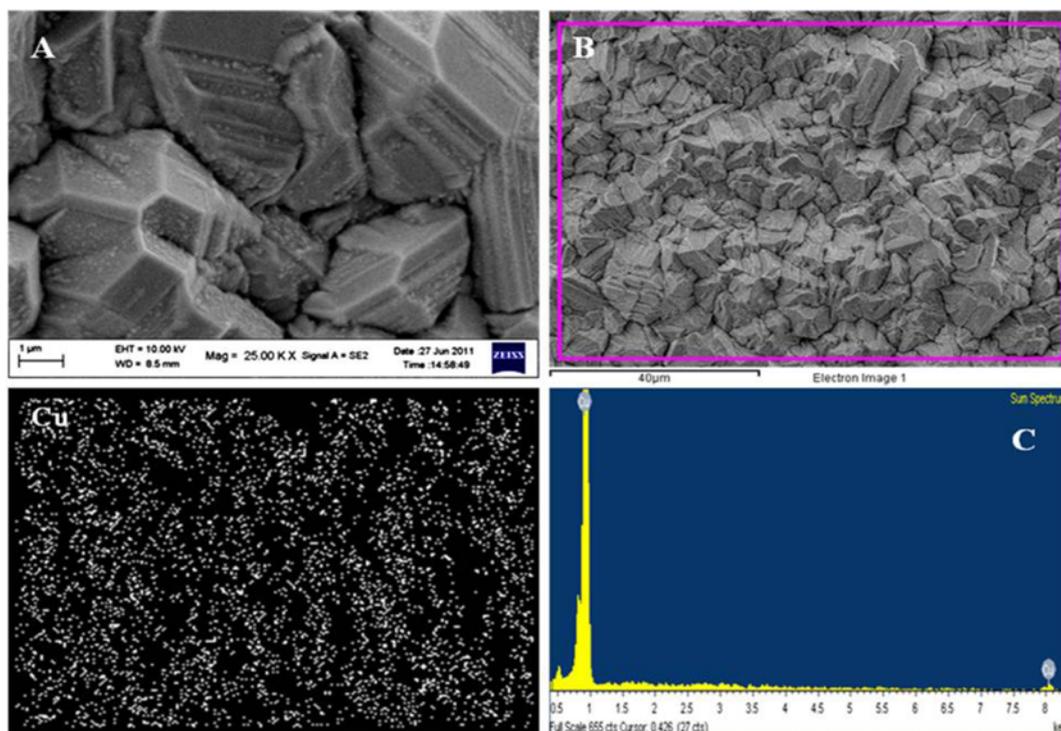
Electrodeposition of copper from organic- and impurity-free sulfate solution was carried out at cathodic current density of 200 A m<sup>-2</sup> for 3 h under ambient temperature conditions. A smooth, continuous and dense deposit was produced with 100% current efficiency and 1.5 kWh kg<sup>-1</sup> specific energy consumption. The composition of the cathodic deposit is given in Table 4, which indicates that the purity of the metal deposit is more than 99.99% or 4N grade. The SEM photograph shown in Fig. 10 confirms the compact and coarse-grained deposit formation during electrowinning of copper metal. EDS spectra (Fig. 9) characterize the deposit to be impurity-free copper.

#### CONCLUSIONS

Thermal surface activation at 600 °C of α-SiO<sub>2</sub> contained ball mill spillage sample of MCP resulted in a phase change to β-SiO<sub>2</sub>.

**Table 4. Purity of the electrodeposited copper metal**

Metal	%
Fe	0.0003
Zn	0.0013
Pb	0.0009
Ni	0.0010
Co	0.0001
Rest Cu	~99.996



**Fig. 10. (A) SEM photograph of copper deposit (B) Elemental map of the deposit showing Cu as white dots and (C) EDS spectra of the deposit showing only Cu peaks.**

The mineralogical change affected the morphology of the sample, resulting in volume expansion and thereby creating cracks, minute pores and pits all over the sample surface. Post activation of the sample by XRF analysis indicated a fraction of the sulfide phase to have been converted to oxides. Bioleaching of the activated spillage in a percolation column resulted in enhanced copper recovery as well as increased bioleaching efficiency by the meso-acidophilic bacterial consortium. Copper was preferentially extracted from the bioleach liquor using 25% LIX84I with two stages of extraction at O : A ratio of 1 : 5. Smooth copper deposit of 99.99% purity or 4N grade was produced at a current density of 200 A m<sup>-2</sup> under ambient temperature conditions with 100% efficiency. FE-SEM and EDS analysis of the deposit indicated a coarse and compact structure with 99.99% copper purity. Thermal surface activation technique is very attractive and has the potential to be a valid alternative for faster processing of low-grade chalcopyrite.

#### ACKNOWLEDGEMENTS

Authors are grateful to M/s Hindustan Copper Limited, Malankhand copper mines for providing ball mill spillage samples. The first author (S. Panda) is thankful to the Council of Scientific and Industrial Research, New Delhi, India for the award of Senior Research Fellowship. The authors are also grateful to the Director, CSIR-IMMT, for his kind permission to publish the paper.

#### REFERENCES

1. S. Wang, *J. Microbiol.*, **57**, 48 (2005).
2. P. A. Olubambi, S. Ndlovu, J. H. Potgieter and J. O. Borode, *Hydro-*
3. S. Panda, C. K. Sarangi, N. Pradhan, T. Subbaiah, L. B. Sukla, B. K. Mishra, G. L. Bhatia, M. S. R. Prasad and S. K. Ray, *Korean J. Chem. Eng.*, **26**, 781 (2012).
4. S. Panda, K. Sanjay, L. B. Sukla, N. Pradhan, T. Subbaiah, B. K. Mishra, M. S. R. Prasad and S. K. Ray, *Hydrometallurgy*, **125-126**, 157 (2012).
5. S. Panda, P. K. Parhi, N. Pradhan, U. B. Mohapatra, L. B. Sukla and K. H. Park, *Hydrometallurgy*, **121-124**, 116 (2012).
6. R. Renman, L. Xingyu, Z. Gang, C. Jinghe, W. Jiankang and W. Dianzuo, *Hydrometallurgy*, **108**, 130 (2011).
7. D. E. Rawlings and B. D. Johnson Eds., *Biomining*, Springer (2007).
8. F. K. Crundwell, *Hydrometallurgy*, **21**, 155 (1988).
9. F. Habashi, McGraw-Hill, New York (1978).
10. H. R. Watling, *Hydrometallurgy*, **84**, 81 (2006).
11. M. Qiu, S. Xiong, W. Zhang and G. Wang, *Min. Eng.*, **18**, 987 (2005).
12. J. Valdes, I. Pedroso, R. Quatrini, R. J. Dodson, H. Tettelin, R. Blake, J. A. Eisen and D. S. Holmes, *BMC Genomics*, **9**, 597 (2008).
13. A. A. Baba, F. A. Adekola, R. F. Atata, R. N. Ahmed and S. Panda, *Trans. Nonferrous Met. Soc. China*, **21**, 2535 (2011).
14. S. Acar, J. A. Brierley and R. Y. Wan., *Hydrometallurgy*, **77**, 239 (2005).
15. A. T. Bull., *Korean J. Chem. Eng.*, **18**, 137 (2001).
16. K. S. Rao, A. Mishra, D. Pradhan, G. R. Chaudhury, B. K. Mohapatra, T. Das, L. B. Sukla and B. K. Mishra, *Korean J. Chem. Eng.*, **25**, 524 (2008).
17. L. B. Sukla, K. C. Nathsarma, J. R. Mahanta, S. Singh, S. Behera, K. S. Rao, T. Subbaiah and B. K. Mishra, *Korean J. Chem. Eng.*, **26**, 1668 (2009).
18. S. Panda, P. K. Parhi, B. D. Nayak, N. Pradhan, U. B. Mohapatra

- and L. B. Sukla, *Bioresour. Technol.*, **130**, 332 (2013).
19. T. Norgate and S. Jahanshahi, *Min. Eng.*, **23**, 65 (2010).
20. S. Mohapatra, C. Sengupta, B. D. Nayak, L. B. Sukla and B. K. Mishra, *Korean J. Chem. Eng.*, **25**, 1070 (2008).
21. S. Panda, S. K. Panda, B. D. Nayak, D. S. Rao, N. Pradhan, L. B. Sukla and B. K. Mishra, *Proceedings of the XI international seminar on mineral processing technology*; NML Jamshedpur, India, 955 (2010).
22. S. Panda, N. Pradhan, U. B. Mohapatra, S. K. Panda, S. S. Rath, B. D. Nayak, D. S. Rao, L. B. Sukla and B. K. Mishra, *Front. Env. Sci. Eng.*, **7**, 281 (2013).
23. M. P. Silverman and D. G. Lundgren, *J. Bacteriol.*, **77**, 642 (1959).
24. J. M. Modaka, K. A. Natarajan and S. Mukhopadhyay, *Hydrometallurgy*, **42**, 51 (1996).
25. W. Sand, T. Gehrke, P. G. Jozsa and A. Schippers, *Hydrometallurgy*, **59**, 159 (2001).
26. Web reference: <http://www.minweb.co.uk/quartz/alphaquartz.html>, Accessed on 03.04.2013.