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Solvothermal synthesis of high value copper powder from copper bleed solution of an Indian copper smelter

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ABSTRACT

Recovery of copper powder from copper bleed solution (CBS) of a copper smelter by solvothermal route has been investigated. After removing sulphuric acid by solvent extraction with tri-iso-octyl-amine, copper from the acid depleted CBS was recovered by using Versatic 10 acid as an extractant in kerosene. In 1.5 M Versatic 10 acid 29.8 g/L copper was loaded at an equilibrium pH of 4.25. During the hydrogen stripping, a 97% copper powder was recovered from the loaded Versatic 10 acid solution at 20 bar hydrogen pressure and 403 K temperature. The solvothermal synthesis of copper powder followed nucleation and growth kinetic model with activation energy value of 145 kJ/mol. Stripping of copper powder could also follow the chemical control kinetic model with lower value of activation energy (66 kJ/mol). The copper powder as characterized by SEM exhibited globular particles of 0.25–0.5 μm size and was found to be suitable for P/M applications.

1. Introduction

Copper bleed solution (CBS) generated during the electrorefining of copper anode is a rich source of copper and nickel. This constitutes a perpetual toxic threat to the environment and represents a waste of valuable resources. The recovery of metals from this stream coincides with the goals of the waste management strategy since that could provide some useful revenue and mitigate the environmental problem.

There are many methods for recovery of heavy metals from industrial wastes and effluents [1–6]. Many of these are based on the solvent extraction of heavy metal ions from solutions. In solvent extraction process the desired metal is extracted into an organic phase, which is stripped by a suitable aqueous solution. The metal must be recovered by a separate operation such as electrowinning or precipitation.

Extraction and separation of copper, nickel and cobalt by solvent extraction have been studied for the processing of sulphate leach solutions of various low grade materials or wastes such as brass ash, converter slag, complex sulphide ores etc. using different organic extractants [7,8]. The extraction of copper and nickel are usually done with oximes and sometimes β-diketones have also been used [9,10]. At the National Metallurgical Laboratory (NML), India leaching-solvent extraction-electrowinning based processes have been developed to recover copper and nickel from polymetallic sea nodules [11–14]. Kumar et al. [15] have reported the recovery of copper and nickel from copper bleed solution by solvent extraction using LIX 84 as an extractant. Kathryn et al. [16] have successfully produced copper cathode from the leach liquor of flotation tailing following solvent extraction-electrowinning route. They used LIX 984N as an extractant to separate copper from the leach liquor.

A number of processes have been developed by Japanese researchers [17,18] for the recovery of metals from copper bleed solution using solvent extraction and ion exchange and implemented in some plants. Buttinelli et al. [19], Abhishev et al. [20] and De Schepper [21] have also studied solvent extraction and separation of acid and metal values from the copper bleed solution of copper refineries. The process used by SEC, Corporation at El Paso, USA described by Ritcey et al. [22] is based on solvent extraction-electrowinning of nickel from the decopperised copper bleed stream. At NML [15,23] a different approach was followed for the recovery of acid and metal values from the CBS of copper refinery. In this process, copper from the CBS is partially recovered by electrowinning. The partially decopperised CBS is then treated for the recovery of acid and metal values by crystallization of a mixed salt – redissolution of mixed crystal with water-solution purification with respect to iron by precipitation – solvent extraction separation of copper and nickel using LIX 84 – electrowinning of copper and nickel powder.

Recovery of metal powders directly from the loaded organic by hydrogen precipitation/stripping replacing aqueous stripping and electrowinning process steps is designated as solvothermal process. Hydrogen stripping of organic phase was first employed in the 1960s by Burkin and Burgees [24] and Van der Zeeuw and Gandon [25]. These researchers successfully stripped base metals from Versatic 10 acid (carboxylic acid)

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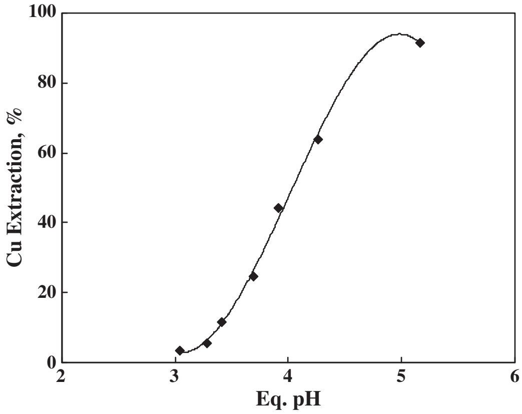

Fig. 1. Effect of pH on the extraction of copper from CBS with Versatic 10 acid. Aq. feed: 38.7 g/L Cu, 0.5 g/L Ni, organic phase: 1.5 M Versatic 10 acid in kerosene, O/A = 1:1, equilibration time: 15 min.

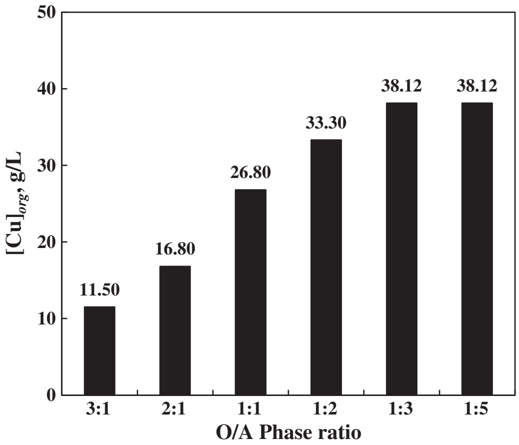

Fig. 3. Effect of O/A phase ratio on loading of copper in the organic phase. Aq. feed: 38.7 g/L Cu, 0.5 g/L Ni, org. phase: 1.5 M Versatic 10 acid in kerosene, eq. pH: 4.25, time: 15 min.

and organo-phosphoric extractants using hydrogen gas under pressure at elevated temperatures. Wu and Ding [26] reported the fine copper powder preparation by chemical reduction method. Various organic solvents such as Versatic 10 acid, Kelex 100 and LIX 65N loaded with metal ions have been tested on laboratory scale for the production of metal powders by pressure hydrogen stripping method [27–30]. Mamoory et al. [28] prepared copper powder by pressure hydrogen reduction from Cu-loaded Kelex 100-decanol-kerosene media. Different parameters such as temperature, pressure time and use of Versatic 10 as additive were studied and the copper powder produced was spheroidal in nature. They also studied the kinetics of the Cu-powder produced [29] and observed that the Avrami–Erafeer model for nucleation growth process showed best fit to this process.

Hydrogen stripping of copper from loaded LIX 65N was reported by Hernandez and Distin [30]. LIX 65N was mixed with decanol and kerosene. Hydrolytic stripping of single and mixed metal from the loaded Versatic 10 acid solution has been also reviewed [31]. Here metal ions were directly precipitated as oxides or hydroxides from loaded organic by hydrolysis with water typically in the temperature range 130–200 °C.

The present study deals with the extraction and separation of copper from a copper bleed solution obtained from ICC, Ghatsila using Versatic 10 acid followed by hydrolytic stripping of loaded organic to prepare high value copper powder suitable for powder metallurgical applications. This process may eventually result in developing an alternate method to produce high value copper powder as compared to the existing process in which impure copper metal is produced by electrowinning in the liberator cell at the expense of energy for recycling in the smelter while decreasing the plant productivity and producing poor grade nickel sulphate crystal. Results are presented and discussed in the text.

2. Experiment

Copper bleed solution obtained from ICC, copper refinery Ghatsila contained 207 g/L H_2SO_4, 39.5 g/L Cu, 0.6 g/L Ni, 0.5 g/L Fe, 0.5 g/L Bi, 0.15 g/L As and 0.4 g/L Sb. Nickel content of the above CBS was found to be very low as compared to the concentration of nickel in the typical CBS generated at any copper refinery because of the closure of the plant for some time and then use of Malanjkhand Copper concentrate with negligible nickel content as feed in the smelter. Prior to the recovery of copper, sulphuric acid from the CBS was recovered by solvent extraction with tri-iso-octyl amine and there after iron was removed by precipitation at pH 3.5. The results of solvent extraction of sulphuric acid are not included in this article. The purified CBS contained 38.7 g/L copper, 0.5 g/L Ni and trace amount of bismuth, arsenic and antimony.

Solvent extraction of copper from the purified CBS was studied using Versatic 10 acid in kerosene as extractant. Under optimized conditions a bulk amount of copper loaded Versatic 10 acid solution was generated to use for the study of hydrogen precipitation stripping of copper. In order to prepare copper powder, the autoclave was charged with 700 mL of copper loaded Versatic 10 acid (1.5 M) solution containing 30 g/L copper. One gram of copper powder was added as seed material

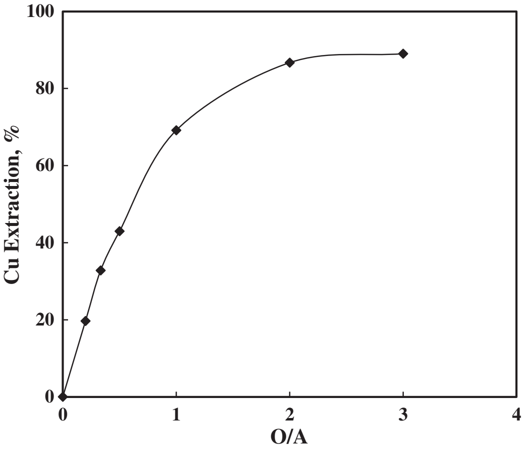

Fig. 2. Effect of O/A phase ratio on extraction of copper from CBS. Aq. feed: 38.7 g/L Cu, 0.5 g/L Ni, organic phase: 1.5 M Versatic 10 acid in kerosene, Eq. pH: 4.25, time = 15 min.

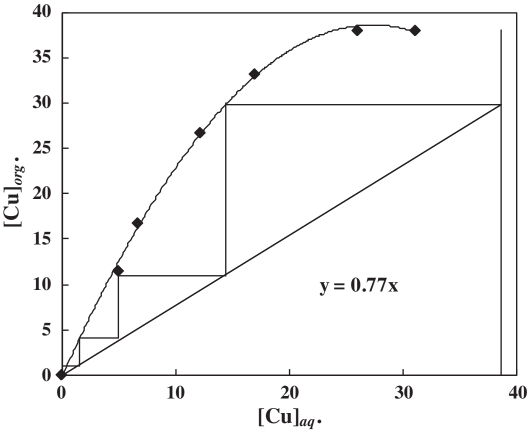

Fig. 4. McCabe Thiele plot for copper extraction from CBS with 1.5 M Versatic 10 acid at eq. pH 4.25.