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VALUE ADDITION IN THE PROCESSING OF COPPER BLEED SOLUTION BY SOLVENT EXTRACTION PROCESS

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Copper bleed solution generated during the electrorefining of anode copper has been used for the recovery of metals as value added products viz. metal powders following partial decopperisation, solvent extraction and electrowinning. In this process, a mixed crystal containing copper and nickel sulphates is produced from the partially decopperised bleed solution by crystallization. The mixed crystal is dissolved and iron is removed by precipitation. The copper is extracted from the purified solution using LIX84 diluted in kerosene leaving nickel in the aqueous raffinate. Bench scale simulation study for the separation of copper and nickel is further confirmed by extracting copper in a mixer settler unit. The purified solution has been used for producing copper and nickel powders by electrolysis.

INTRODUCTION

Copper bleed solution is generated during the purification of impure copper in the electro-refining plant. Due to recycling of the electrolyte the impurities viz. nickel, arsenic, iron, bismuth, antimony, chloride etc are enriched in the solution [1]. When the concentration of the impurities increases above their upper limit of tolerance during recycling with time it becomes deleterious for the electro-refining. In order to control the purity of deposited cathode copper during refining, the solution is discarded as copper bleed stream (CBS). This discarded solution contains high concentration of copper and nickel. Various methods are employed to recover the valuable metals depending on the composition of the CBS. In conventional practice a portion of the electrolyte between the electrolytic cell and circulation tank is bled from the circulation tank to the liberator cell [1, 2]. The major operations followed are decopperisation, purification and crystallisation. In the decopperisation operation copper present in the electrolyte is deposited on the cathode up to a concentration level of 10 g/L of copper left in the solution. The decopperised solution containing other impurities is sent to the purification section, where the impurities co-deposit on the cathode with remaining copper. The purified solution is then crystallised to recover $NiS0_4.xH20$ and black acid thus generated is recycled to the circulation tank. The process is difficult to operate due to higher cost as reported by Shibata et al [3]. Purification of crude nickel sulphate by precipitation method has recently been reported by Havlik et al (4) involving cumbersome procedure.

At SNCR (Sumitomo Nihama Copper Refinery), a process (5) has been developed for purifying the impurities like arsenic, antimony, bismuth and nickel which contaminate the electrolyte thus making it unsuitable for further processing. Shibasaki et al(6) reported a process for the treatment of copper bleed electrolyte at Naoshima Smelter and Refinery, Japan following decopperisation, neutralization and solvent extraction steps. A number of processes have been developed by Japanese researchers(3) for the recovery of metals from bleed solution following SX and ion exchange and implemented in some plants. Other reports by different groups particularly Buttinelli et al(7) have also studied the treatment of CBS using SX techniques. SEC process (8) is based on SX - EW of Ni from the decopperised copper bleed stream at El Paso, USA. A process is also being developed at NML, India for the recovery of acid from the copper bleed solution followed by metal separation using SX(9).

The Sheritt process could be used for the separation of Cu and Ni from the solution. The process treated Cu & Ni from the metal amine sulphate solution obtained from the pressure leaching of sulphide concentrate and nickel matte at Sheritt Nickel Refinery at Fort Saskatchewan. The process of nickel powder preparation has mostly been adopted(10) from the work of Schaufelberger(11). Hydrogen reduction of aqueous metal salts at elevated temperature and pressure in autoclave from the leach liquors of ores/concentrates has been reported for producing metal powders in batch(12) and continuous mode(13). Tagashi and Nagai(14) reported hydrogen reduction of copper from CBS at 190°C temperature and 20 atmosphere pressure. Major drawbacks of the process are the requirement of incomplete reduction of copper for producing acceptable grade of powder, and material of construction with high acid present in the solution. A new approach on selective hydrogen reduction of copper and nickel powder is being developed at NML to obtain value added products from such solutions. In the present studies, the value added products viz copper and nickel powder has been produced following partial dccopperisation, crystallisation, dissolution, solvent extraction and electrolysis steps.

EXPERIMENTAL

For the development of a process on bench scale, a synthetic solution with chemical composition similar to the copper bleed generated in copper refinery (ICC, Ghatsila, India), comprising of 38.42 g/L Cu, 19.37 g/L Ni., 0.757 g/L Fe. 0,2 g/L Bi and 171 g/L H_2S0_4 was taken. Subsequently, actual copper bleed solution generated in the smelter was used. The solulion was decopperised at current density of 100 A/m^2 followed by cryslallisation to get the mixed crystals. The crystal so obtained were washed with water, neutralised with NaOH to bring down the pH to 3.5-4.0, aerated for 2-4 h to precipitate iron as hydroxide and filtered. The filtrate so obtained was subjected to solvent extraction using LIX 84 to separate copper from nickel. The loaded copper was stripped with sulphuric acid and electrolysed to give pure metal powder. Nickel powder was produced from the raffinate by electrolyis.

Analyses of the samples for low concentration of metallic values were carried out by an Atomic Absorption spectrometer. Solutions containing high metals were analysed by conventional method. All the chemicals used for the chemical analysis were Analar grade reagents.

RESULTS AND DISCUSSION

To recover copper and nickel from CBS in the most usable form such as metal powders or salts, partial decopperisation, crystallization, solvent extraction and electrolysis has been followed.

Partial decopperisation and crystallization of copper bleed solution

In order to recover the metallic values from the bleed solution, the solution was first decopperised by electrowinning at low current density (100 A/m^2) to bring copper concentration from 38.5 g/L to 17-18 g/L at room temperature. A good sheet deposit with a purity of 99.36 - 99.98% Cu was obtained in all the cases. The current efficiency and energy consumption for the metal deposition were 96.86 - 98.33 % and 1.64 - 1.82 kWh/kg respectively. The quality of deposited copper so produced was least affected for commercial application.

After decopperisation, crystallisation was carried out in two stages to see the possibility of getting the mixed crystals. The solution obtained in partial decopperisation had 17.96 g/L Cu, 20.39 g/L Ni, 206 g/L sulphuric acid. In a two-stage crystallisation, the mixed crystals obtained in the first stage had a composition 21.716 % Cu, 2.295 % Ni indicating that copper crystallised before nickel and it can further be used for making powder or can be recycled for make up. The fractional crystallisation as obtained in stage-1 was mainly due to solubility factor of different metal sulphates. In second stage of crystallisation mixed metal sulphates with high nickel (15.6%) and low copper (8.09%) were obtained. The crystal obtained from the single stage crystallisation had chemical composition as: 12.13% Cu, 13.48% Ni, 0.539% Fe, 0.046% Bi and 15.03% sulphuric acid.

The crystal obtained in second stage was leached in water to give aqueous solution with the composition as 8.39 g/L Cu, 13.67 g/L Ni, 0.5 g/L Fe and 20 g/L sulphuric acid. The presence of iron is deleterious for solvent extraction because of its transfer to organic phase and then to electrolyte which on electrolysis decreases the cathode current efficiency leading to high energy consumption. Hence iron removal from the electrolyte is essential to save energy and increase the production rate. Thus, leach solution obtained as above containing 0.5 g/L Fe was neutralised with NaOH solution to increase the pH of solution from 1.12 to 4.4. After adjustment of pH, air was passed for a period of 6-8 h at 80°C to precipitate iron as ferric hydroxide thereby bringing down the iron content from 0.5 to 0.004 g/L. The iron free solution was subjected to solvent extraction.

Solvent extraction using LIX 84

Initially, bench scale studies were carried out to optimise the process parameters for the separation of copper from nickel using LIX84. Aqueous solution generated by the dissolution of mixed crystal as mentioned above was shaken with 20% LIX84 at O/A ratio of 2/1 for 10 min at different equilibrium pH varying from 1-5 and the plot of percent extraction Vs equilibrium pH is shown in Figure 1. Thus, at an equilibrium pH of 2.5 copper extraction was 99.88% whereas nickel extraction was only 0.55%. Therefore, the equilibrium pH for further experiments was maintained around 2.5. A plot of copper distribution ratio (log D_{cu}) at different pH shows a straight line with a slope of 1.72 which indicates the release of $2H^+$ and extraction of copper as CuA_2 (HA: active organic hydroxyoxime species) in the organic phase. The loading capacity of 20% LIX84 determined by repeated contact method was found to be 7.94 g/L copper at O/A of 1 and equilibrium pH of 2.73. The loaded Cu was stripped with a solution containing 31.77 g/L Cu and 180 g/L H_2SO_4. Stripping was done at different O:A ratio and at O:A ratio of 4:1 the stripped solution was found to contain 57.18 g/L Cu, with low stripping efficiency of 80%. The stripping was maximum (96 %) at A/O ratio of 1.

The studies were also carried out to simulate counter current extraction of copper at A:O ratio of 1:1 and 1:1.5. It was found that only 0.0004 g/L copper remained in the raffinate at A:O ratio of 1:1.5, whereas 0.434 g/L Cu was left in the raffinate when A:O ratio was maintained at 1:1. Based on this the stages were fixed in the mixer

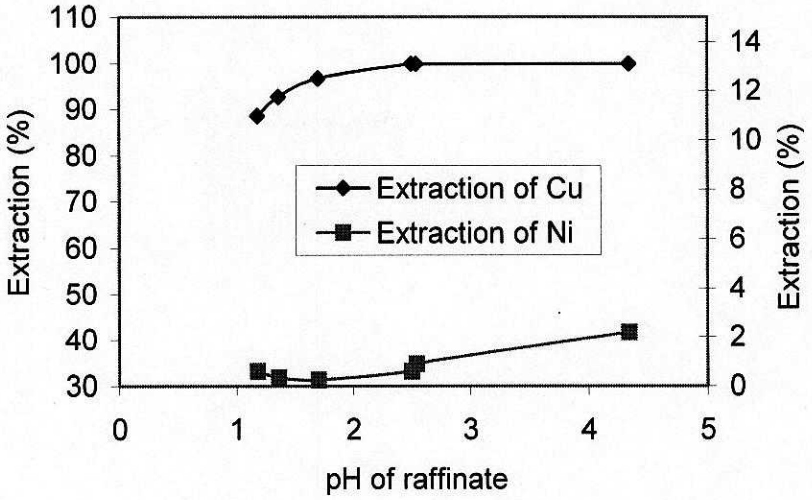

Figure 1. Extraction of metals with 20% LIX84 in kerosene [Organic = 20% LIX84 in kerosene, Aqueous feed (g/L) = 8.39 Cu, 13.67 Ni; A/O = 1/2 for extraction; t = 10 min]

settler (volume: 0.6 L mixer and 0.86 L settler) units as: extraction: 4; scrubbing: 2; stripping: 2. Data on counter current extraction of copper in mixer settler unit with 25 % LIX84 in kerosene are shown in Figure 2. The composition of raffinate obtained in the mixer settler operation under different conditions is given in Table 1.

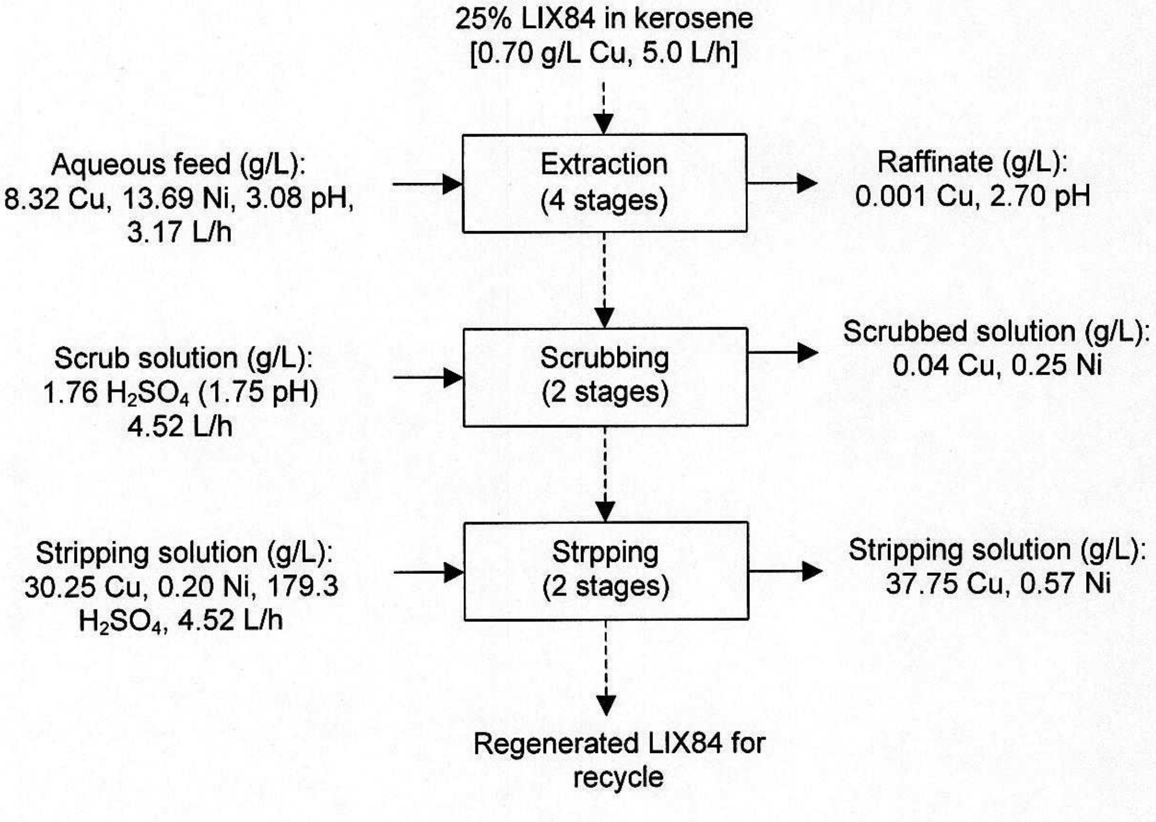

Figure 2. Extraction of copper in mixer settler unit from copper bleed solution

Table 1. Extraction of copper at different pH in the mixer-settler

Aqueous feed (g/L): 8.37 Cu, 13.69 Ni, 3.08 pH
Organic: 25% LIX 84 in kerosene, No. of stages in extraction: 4

pH of the raffinate	Aqueous feed flow rate (L/h)	O/A ratio	Copper in raffinate (g/L)
1.57	3.90	1.10	0.87
2.13	3.90	1.10	0.25
2.68	3.17	1.60	0.001

A raffinate free of copper was obtained at O/A ratio of 1.6 and equilibrium pH of 2.68. The composition of raffinate, scrubbed solution and stripped solution showed the performance of the circuit (Figure 2). The stripped solution rich in copper was used for producing copper powder.

Electrolytic grade metal powder

An attempt was made to produce copper powder at the current density in the range 600-1000 A/m^2 from the pregnant solution containing 37.75 g/L Cu and 166 g/L H_2SO_4. Thus, at different current densities copper powder of the purity varying from 99.50-99.98 % was produced. Decrease in time of electrolysis from 3.5 h to 2.0 h increased current efficiency from 98.36 to 99.70, but at 1000 A/m^2 the current efficiency dropped to 85 %. The purity of copper powder was found to be 99.93%. The raffinate produced in the counter-current mixer-settler operation was taken to recover nickel powder. The composition of the nickel electrolyte was adjusted to: 10 g/L Ni, 40 g/L $(NH_4)_2SO_4$, 10 g/L H_3BO_3, O.2 g/L thiourea, pH 4.5. The solution was electrolysed at 65-70° C at the current density ranging from 4000-10,000 A/m^2 with current efficiency varying between 40-53 %. The energy consumption was 19.5kWh/kg of nickel powder at 5000 A/m^2 current density. The copper and nickel powders for P/M application can thus be produced.

CONCLUSIONS

The studies were carried out for the treatment of copper bleed electrolyte generated in the electrorefining of copper. Since this solution contains high concentrations of copper and nickel, various possibilities were worked out to augment the overall recovery of copper and nickel and produce value added products. Of the different process routes investigated, partial decopperisation, crystallisation, solvent extraction-electrowinning route was found suitable to produce copper and nickel powders of required purity.

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