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SEPARATION AND RECOVERY OF COPPER AND NICKEL FROM COPPER BLEED STREAM BY SOLVENT EXTRACTION ROUTE

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ABSTRACT

Bleed stream from electro refining step of copper smelter was processed to recover the metals as high value products such as copper and nickel powders or salts. The process consists of: partial decopperisation of the bleed stream followed by crystallisation of a mixed salt of copper and nickel sulphate, leaching of the mixed salt, removal of iron, solvent extraction separation of copper and nickel and winning the solution to produce metal powders.

With the partially decopperised bleed stream, the composite crystal was obtained by crystallisation which contained 8.4-12.5 % Cu and 13.7-14.38 % Ni with 1-2ppm Fe as impurity. This mixed salt was leached with water and was treated for iron precipitation. The purified solution was subjected to solvent extraction using LIX 84 and CYANEX 272. A 20% LIX 84 in kerosene extracted 99.88% copper and 0.059% nickel at a pH of 2.5 and 5% CYANEX 272 in kerosene extracted 98.06% copper and 0.51% nickel at a pH of 4.85. LIX 84 was used for metal separation in the mixer-settler unit. The pure solutions of copper and nickel sulphates obtained from stripping circuit were electrolysed to produce pure copper (99.9%) and nickel (99.8) powders; alternatively pure sulphate salts could also be crystallised.

Introduction

Copper bleed electrolyte is generated during the purification of impure anode copper in the electro-refining plant. Due to recycling of the electrolyte the impurities viz. arsenic, iron, bismuth, antimony, chloride etc get enriched in the solution. When the concentration of the impurities reaches their upper limit of tolerance it becomes deleterious for the cathode copper production. In order to control the purity of the cathodes during the continuous operation, a part of the solution is discarded as bleed stream periodically which contains 40-50g/L Cu, 170-200g/L H₂SO₄, 20g/L Ni and 1-2g/L Fe, and traces of other impurities like As, Sb, Bi, Cl etc.

The existing practice for the bleed electrolyte purification is removal of copper, arsenic and antimony by electrolytic stripping in the liberator cell, followed by liquor concentration to crystallise out salt of nickel and recycling of the black acid to the system. But the associated drawbacks are liberation of the arsine gas, high operation cost, poor grade NiSO_4 , and loss of acid (1).

Hence research in this area has been done on such bleed streams/electrolytes containing copper and other metals which could be treated by various processes such as hydrogen reduction, solvent extraction, cementation and electrowinning to produce copper as its sulphate salt which could be recycled back to the electrolysis tank or pure copper powder for P/M applications. Of these processes the solvent extraction is often in vogue in the copper industry and more than 1.5 million tons of copper are produced by this process annually from the lean grade ores/waste streams. Copper was recovered from motor scrap and other lean grade ores/waste streams by ammonia leaching, solvent extraction with LIX 84, and electrowinning of metal from the stripped solution [2,3]. Ritcey et al. [4] studied the solvent extraction separation of copper and zinc from chloride liquors using Acorga P5300 extractant for copper and TBP for zinc. PT-5050 is one of the Acorga products having the advantages of strong extraction, good stripping and high selectivity for copper [5,6]. Recovery of copper from HCl solution and its transfer into H_2SO_4 solution were reported using extractant mixtures such as trioctylamine-LIX 54 [7], and Alamine336-LIX 54 [8-10]. Recently some work by Kumar et al. [11] was done at NML for separating copper and zinc from sulphate solution in the presence of gangue metals like iron and manganese using LIX 84.

This paper describes a process developed at NML for the recovery of copper and nickel from copper bleed stream from an electro-refining unit. The process steps consists of partial de-copperisation of the bleed stream, concentration and crystallization of a mixed salt, leaching of the mixed crystal, iron purification, solvent extraction of the purified solution using LIX 84 and CYANEX 272, and electrolysis of the copper and nickel solutions to produce pure copper and nickel powders.

Experimental

Synthetic copper bleed solution, similar to that available at ICC, Ghatsila containing 38.42g/L Cu, 19.37g/L Ni, 0.757g/L Fe, 0.2g/L Bi, 171g/L H_2SO_4 was prepared. 20% LIX84 and 5% CYANEX272 in kerosene were diluted for solvent extraction studies. In copper bleed stream, the copper concentration was very high and therefore, partial decopperisation of the bleed stream was carried out in a lead lined tank of 1L capacity to bring down the copper level similar to the concentration of nickel present. Subsequently, this solution was evaporated to crystallise out

mixed sulphate salt of copper and nickel in two stages. The first stage salt contained 21.7%Cu and 2.9%Ni. The second stage salt had 8.4%Cu and 15.6% Ni that was washed and leached with water to give an aqueous solution with a chemical composition: 8.4g/L Cu, 15.55g/L Ni, 15.68g/L H_2SO_4 , 0.1g/L Bi, and 0.52g/L Fe. Presence of iron is deleterious for solvent extraction and in electrolysis by decreasing the cathode current efficiency during electrowinning leading to high energy consumption and low production rates. Hence iron removal from the electrolyte is considered essential. Thus the mixed crystal leach solution containing iron was removed from the solution with the drop wise addition of NaOH solutions with a constant stirring to increase the pH of solution from 1.12 to 3.42 and aerated to precipitate the iron as ferric hydroxide thereby bringing down the iron content from 0.52 to 0.0041g/L. The iron free solution containing 8.39g/L Cu, 13.67g/L Ni was subjected to solvent extraction using LIX84 and CYANEX 272 to separate copper from nickel. Finally copper and nickel sulphate thus separated were subjected to electrolysis to give P/M grade copper and nickel powders. Various Parameters were optimized on bench scale and continuous operation for the separation of copper from nickel and are discussed briefly in the following text. The flow sheet shown in Fig. 1 depicts the steps followed.

RESULTS AND DISCUSSION

A Solvent extraction with 20% LIX 84.

Preliminary experiments (11) showed that 20% LIX84 diluted with kerosene oil is suitable for the extraction of copper from the concentrated aqueous feed solutions.

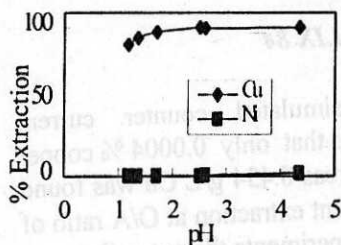


Fig2: copper extraction at different eq pH with LIX84, NO-1/2, Aq Soln- 8.39g/L Cu, 13.67g/L Ni, Time-1min

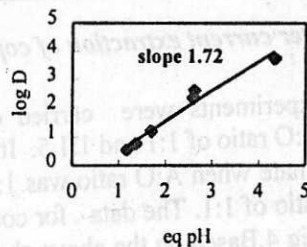


Fig 3: plot of log D vs eq pH on LIX 84

Hence all the experiments were conducted with 20% LIX84 diluted with kerosene. Effect of parameters for maximum metal recovery was studied and are given below.

Aqueous solution containing 8.39g/L Cu and 13.67g/L Ni was shaken with 20% LIX84 at O/A ratio of 2/1 for 10 min at different equilibrium pH varied from 1-5 as shown in Fig 2. At equilibrium pH of 2.5 copper extraction was 99.88% whereas nickel extraction was only 0.55%. Plot of logD for copper vs equilibrium pH (Fig 3) gives a slope of 1.72 indicating the extraction of the complex CuA_2 in the organic phase with the release of two H^+ with ions.

The loading capacity of 20 % LIX 84 was determined by repeated contact method and was found to be 7.94 g/L Cu at a pH of 2.73 in three contacts. The copper loaded organic was stirred with a strip solution containing 31.77 g/L Cu and 180 g/L H_2SO_4 . Stripping was done at different O: A ratios and at a ratio of 4:1 the stripped solution was found to contain 57.19 g/L Cu. Data on stripping of loaded copper from LIX84 are presented in Table 1.

Table 1: Effect of O/A ratio on stripping of copper from loaded copper from LIX84
Loaded organic (20% LIX84)-7.94g/L Cu; Strip solution: 31.77g/L Cu; 180g/L H_2SO_4 ;
stirring time-10min.

Stripping stage	O/A ratio	[Cu] g/L	[Cu] _{org} /L	Stripping (%)
1	4:1	1.59	57.19	80.0
2	2:1	1.87	43.85	76.4
3	1.33:1	0.31	41.94	96.1
4	1:1	0.29	39.41	96.3

Simulation of counter current extraction of copper with LIX 84

Two shake out experiments were carried out in a simulated counter current extraction mode at A:O ratio of 1:1 and 1:1.5. It was found that only 0.0004 % copper remained in the raffinate when A:O ratio was 1:1.5, Whereas 0.434 g/L Cu was found in raffinate at A:O ratio of 1:1. The data for counter current extraction at O/A ratio of 1/1.5 are shown in Fig 4. Based on the above shake out experiments the extraction was carried out in mixer settler unit where extraction was done in four stages, scrubbing and stripping in two stages each (Fig 5). A 25% LIX 84 was used for separation of copper and nickel.

An attempt was made to produce pure copper powder from the stripped copper solution obtained in running the mixer settler unit. The composition of solution used for copper powder preparation was 37.75g/L Cu and 0.57g/L Ni. Thus at different current densities from 600-1000A/m² copper powder of the purity varying from 99.5-99.98% was produced. Nickel powder of 99.8% purity was also produced by electrowinning of

raffinate on copper extraction. Thus pure metal powders for P/M application could be produced by electrowinning.

B. Solvent extraction using CYANEX272.

Initially the extraction of copper from the aqueous feed solution with 8.26g/L Cu and 13.67g/L Ni was carried out at different pH using 20% CYANEX 272 and 4% isodecanol in kerosene. Aqueous solution was stirred with 20% CYANEX 272 at O/A ratio of 1/1 for 10min. Plot of equilibrium pH vs % extraction as shown in Fig 6 shows 98.05% extraction of Cu and 0.51%Ni at a pH of 4.85. Plot of logD for Cu at different eq. PH (Fig. 7) shows a straight line with a slope of 1.75 indicating the extraction of the complex CuA_2 in the organic phase.

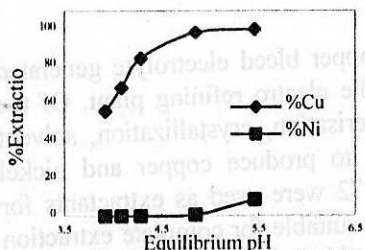


Fig 6 : Effect of eq pH on Cu, Ni extraction with 20% CYANEX272. A/O-1/1, Aq. Soln. - 8.39 g/L Cu, 13.67g/L Ni

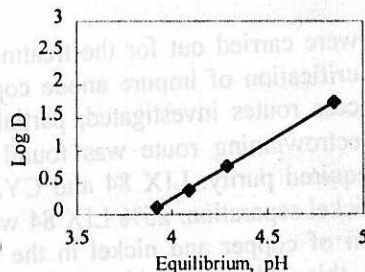


Fig 7 : Plot of logD vs eq pH with CYANEX272.

Table 2: Scrubbing and stripping of loaded copper from the organic phase.

Sl. No.	Conc. of H_2SO_4 (g/l.) for scrubbing	Composition of scrubbed solution(ppm)		Conc of H_2SO_4 (%) for stripping	Composition of stripped solution (g/L)	
		Cu	Ni		Cu	Ni
1	0.9	0.572	2.16	0.5	4.193	NF
2	1.8	1.271	1.18	2.0	4.193	NF
3	2.7	1.779	2.23	4.0	4.193	NF
4	3.6	2.288	1.39	10.0	4.193	NF

As the 20% CYANEX 272 formed a viscous organic phase while determining the loading capacity, the maximum loading of the extractant was determined using 5% CYANEX 272 by repeated contact method at O/A ratio 1:1. The maximum loading of 4.19g/L Cu and 2.23ppm Ni was obtained in three contacts. The loaded organic was

scrubbed with 0.9 g/L to 3.6 g/L H_2SO_4 to remove the co extracted and entrapped nickel and then stripped with 0.5% to 10% H_2SO_4 (Table 2). It was observed that total copper present in loaded organic can be stripped even with 0.5% H_2SO_4 . Since the electrolysis of copper takes place at a very high acid concentration therefore stripping of copper from the scrubbed loaded organic was done with 10% acid. The A:O ratio in both scrubbing and stripping was 1:1. It was observed that almost all nickel and some copper was removed from loaded organic during scrubbing resulting a Ni free copper solution. Thus a maximum loading of copper was observed with 20% LIX 84 in kerosene oil as diluent at O/A ratio of 1.33/1 for a stirring time of 10 min at a pH of 2.5

CONCLUSION

The studies were carried out for the treatment of copper bleed electrolyte generated during the purification of impure anode copper in the electro refining plant. Of the different process routes investigated, partial decopperisation, crystallization, solvent extraction electrowinning route was found suitable to produce copper and nickel powder of required purity. LIX 84 and CYANEX 272 were used as extractants for copper and nickel separation. 25% LIX 84 was found suitable for complete extraction and separation of copper and nickel in the mixer settler unit. Direct electrolysis of copper from this solution yielded P/M grade powder of 99.9% purity. Nickel electrolysis from the raffinate of copper solution produced P/M grade nickel powder of 99.8% purity.

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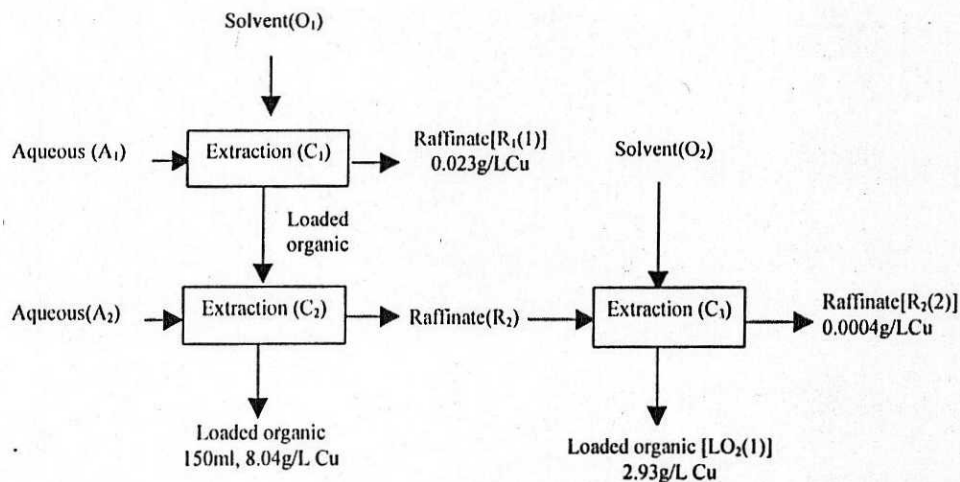


Fig.-4 : Simulation of counter current extraction using 20% LIX 84 at A/O of 1/1.5, in three stages. Aqueous phase(100ml) : 8.58g/L Cu & 13.67g/L Ni, Stripping solution: 10% H_2SO_4 , Stirring time: 10 min.

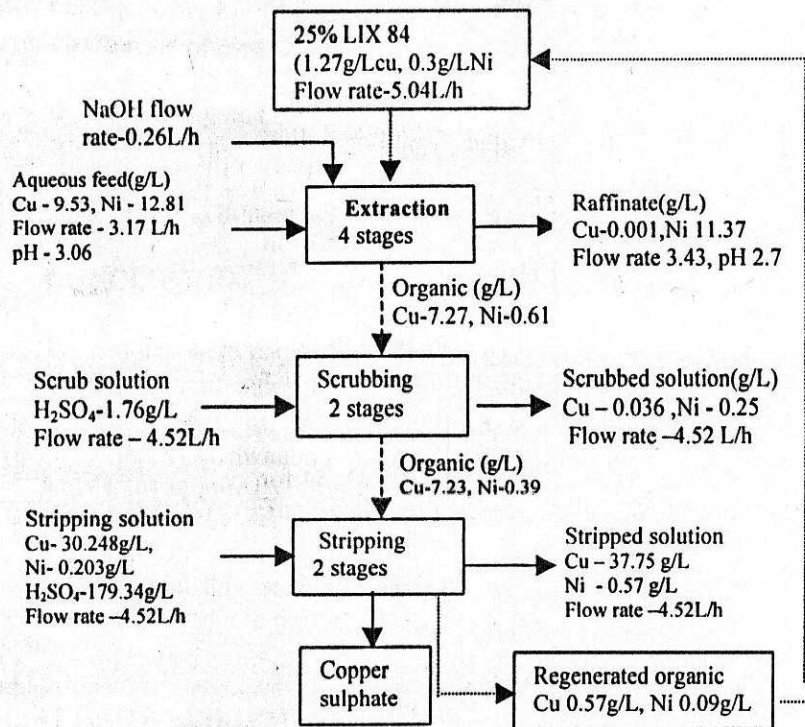


Fig 5 : Separation of copper and nickel in mixer settler unit

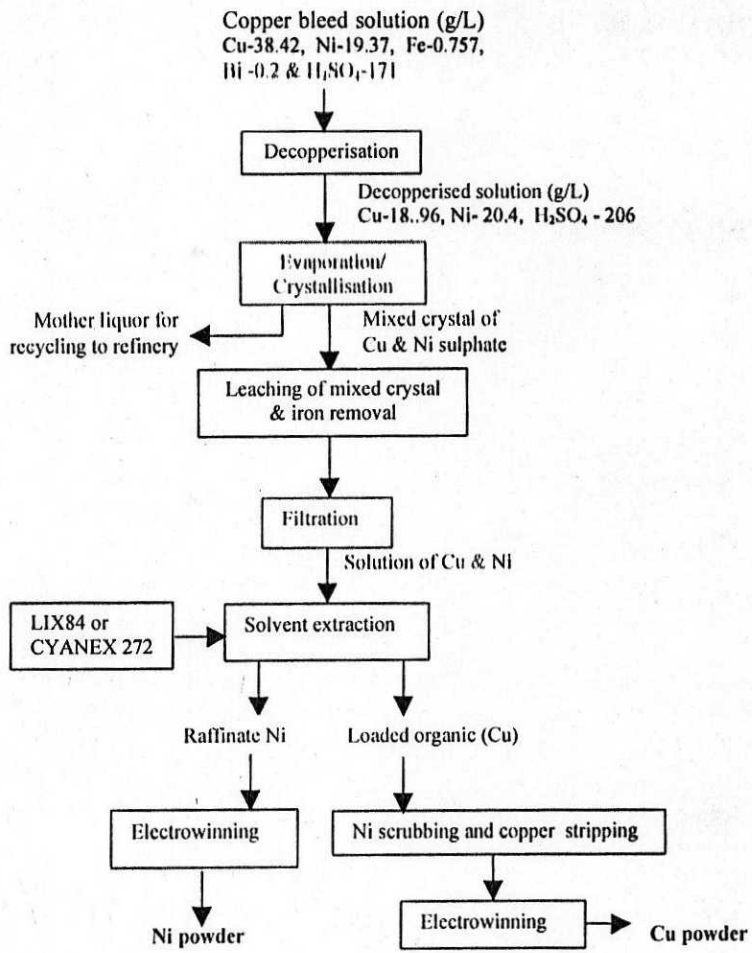


Fig. 1: Copper bleed solution treatment following Decopperisation-Crystallisation-Solvent extraction-Electrowinning