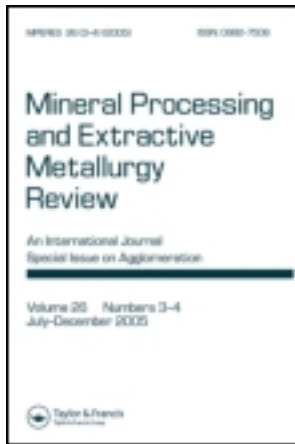


This article was downloaded by: [National Metallurgical Laboratory]

On: 28 June 2012, At: 21:22

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Mineral Processing and Extractive Metallurgy Review: An International Journal

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmpr20>

Exploitation of Copper Bleed Stream for the Extraction and Recovery of Copper and Nickel by Bis(2,4,4-trimethylpentyl)phosphinic Acid

Archana Agrawal^a, S. Kumari^a, M. Parveen^a & K. K. Sahu^a

^a Metal Extraction and Processing Division, National Metallurgical Laboratory, Jamshedpur, India

Version of record first published: 15 May 2012

To cite this article: Archana Agrawal, S. Kumari, M. Parveen & K. K. Sahu (2012): Exploitation of Copper Bleed Stream for the Extraction and Recovery of Copper and Nickel by Bis(2,4,4-trimethylpentyl)phosphinic Acid, Mineral Processing and Extractive Metallurgy Review: An International Journal, 33:5, 339-351

To link to this article: <http://dx.doi.org/10.1080/08827508.2011.601481>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

EXPLOITATION OF COPPER BLEED STREAM FOR THE EXTRACTION AND RECOVERY OF COPPER AND NICKEL BY BIS(2,4,4-TRIMETHYLPENTYL)PHOSPHINIC ACID

Archana Agrawal, S. Kumari, M. Parveen, and K. K. Sahu

Metal Extraction and Processing Division, National Metallurgical Laboratory, Jamshedpur, India

Bleed streams from copper electrolysis/electrowinning processes potentially contain high amounts of acid, copper, and nickel which need an effective treatment before disposal. A systematic study was carried out to optimize the parameters for the extraction and recovery of metal values using bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) diluted with kerosene. Since pH has a major role to play in the separation of Cu from Ni, a 60% saponified solvent was used for extraction studies. With an increase in equilibrium pH from 3.32 to 5.48 and extractant concentration from 5 to 20%, there is an increase in the percentage extraction of metal ions. With a solvent concentration of 20%, the separation factor for Cu with respect to Ni (α_{Ni}^{Cu}) increases from 39.1 to 118.8 with the increase in pH from 3.3 to 5.5. Loading capacity of 20% Cyanex 272 was found to be 30.8 g/L Cu and 0.024 g/L Ni. After scrubbing of coextracted Ni(II) with 15 g/L H_2SO_4 , the loaded organic containing 30.59 g/L Cu(II) and 4 ppm Ni(II) was stripped with 75 g/L sulfuric acid. A McCabe-Thiele plot shows the requirement of two counter-current stages at an O:A ratio of 1:1 for extraction and two counter-current stages at O:A ratio of 2:1 for the stripping of copper. Results of the present investigation indicate the possibility of the use of saponified Cyanex 272 for the extraction, separation, and recovery of copper and nickel from the actual spent copper bleed streams.

Keywords: bis(2,4,4-trimethylpentyl)phosphinic acid, copper(II), extraction, nickel(II), saponification, solvent extraction

INTRODUCTION

Today, any waste generated (solid or liquid) in an industry is tried to be used as a secondary source of the metals present in it. Copper bleed solution (CBS) is one of the metal-rich waste streams generated from the copper smelter during the electro-purification of impure copper anode to produce pure copper cathode. This solution contains high concentrations of copper, nickel, sulfuric acid, and traces of several other impurities such as Fe, As, etc. Classical methods such as precipitation, oxidation, and crystallization are unsuitable for the separation of copper and nickel from CBS in a simple and economical way. However, Cu and Ni separation is

Address correspondence to Archana Agrawal, Metal Extraction and Processing Division, National Metallurgical Laboratory, Jamshedpur-831007, India. E-mail: archana_nml03@yahoo.com

possible by solvent extraction. Commercial availability of copper-selective extractants has proposed a particular stimulus to the use of solvent extraction as a hydrometallurgical unit operation in processing of copper-containing leach liquor (Merigold, Agers, and House 1971; Ritcey and Ashbrook 1979; Ritcey and Ashbrook 1984a; Szymanowski 1993). These leach liquors arise through the hydrometallurgical processing of raw materials such as lean grade ores, spent catalysts, scrap, complex sulfides, etc. Presently, more than 30% of total world production of copper is achieved through the solvent extraction route (Fisher and Notebaart 1983).

In the process of developing extractants for copper recovery, various reagents with small variations in their structure and composition have been introduced into the industry under trade names such as LIX 64N, LIX 84 (Henkel) SME 529 (Shell), P17, P50, P5300 (Acorga), Kele \times 100 (Ashland). Among the various copper extraction reagents, LIX 64N was used on a commercial scale in a number of copper industries (Bart et al. 1990). Calligaro et al. (1983) studied the extraction of copper, nickel, cobalt, zinc, and iron from a solution using LIX 64N in kerosene. They reported the order of extractability as a function of pH as $\text{Cu(II)} < \text{Fe(III)} < \text{Ni(II)} < \text{Zn(II)} < \text{Co(II)}$. Ali, Daoud, and Ali (1996) established conditions for purification of copper-containing waste solution (on a plant scale employing mixer settlers) using LIX 84. In China (Jiayong 1993), LIX 84 is being used in four plants to produce copper from oxide ores. One of the new chelating extractants for Cu extraction is MOC 45 (oxime derivative) developed by ALLCO Chemical (Allied Chemical Corporation 1996). Amores, Coedo, and Alguacil (1997) have studied the application of MOC for copper extraction from sulfate solutions. The species extracted into the organic phase were reported to be CuR_2 and $\text{Cu}(\text{HR}_2)_2$. Rao, Devi, and Reddy (2000) have studied the extraction and recovery of copper from a solution containing 0.1 M each of copper and sodium sulfate using MOC 45 as the extractant. Increase in equilibrium pH and extractant concentration increases the percentage extraction of metal ion. The extracted species appear to CuR_2 .

Di(2-ethylhexyl)phosphoric acid (D2EHPA) and di(2-ethylhexyl)phosphonic acid (PC 88A) are considered to be suitable liquid cation exchangers for separation of Zn, Cu, Mn, Co, and Ni (Preston 1982; Preston 1983; Devi, Nathsarma, and Chakarvorty 1994; Thakur 1998; Thakur and Mishra 1998). Extraction of copper using D2EHPA has been shown to occur by an interfacial reaction mechanism. It was assumed that the extraction of metal ions took place mainly by reaction with extractant molecules adsorbed at interface and not by reaction in bulk liquid, on account of the high interfacial activity of D2EHPA and its low solubility in the aqueous solution. In addition, it was suggested that the overall extraction rate was mainly controlled by diffusional resistance in the immediate vicinity of the interface (Ihm, Lee, and Huilee 1988). Belkhouche, Didi, and Villemin (2005) studied the extraction of Cu(II) and Ni(II) from acetate media with D2EHPA under the optimal condition. Sarangi et al. (2007) studied the separation of iron(III), copper(II), and zinc(II) from a mixed sulfate/chloride leach liquor using tributylphosphate, LIX 84I, and Cyanex 923 in kerosene, respectively.

After removing sulfuric acid from CBS by some suitable acid extractant and further pH adjustment for the removal of iron present in the bleed stream, Cu(II) and Ni(II) can be separated from this acid-depleted CBS using a suitable solvent. In the present work, preneutralized Cyanex 272 was used as a solvent for Cu and

Ni separation. Although this extractant has mostly been used for the extraction and separation of cobalt from nickel, this work mainly focuses on a systematic study for the extraction and separation of Cu from Ni present in the CBS using the sodium salt of Cyanex 272. Various parameters, such as the effect of equilibrium pH, extractant concentration, and separation factor on the extraction system, were studied in addition to the use of McCabe-Thiele plots for extraction and stripping studies. Extracted copper was stripped with an appropriate concentration of sulfuric acid solution and this copper sulfate solution can further be electrolyzed to prepare pure Cu powder.

EXPERIMENTAL

Reagents and Solutions

CBS from a copper smelter was procured for the extraction studies. The chemical composition of the bleed stream was found to be 41.97 g/L Cu, 9.97 g/L Ni, 198 g/L H₂SO₄, and 0.300 g/L Fe. Arsenic was not present in this bleed solution. Since the acid concentration of the bleed stream is not suitable for solvent extraction of copper and nickel, it was first removed by solvent extraction using a tertiary amine with the objective to remove and recover acid and then extract and separate copper from nickel present in the acid-depleted solution. Thus, the solution used for extraction of copper and nickel contained 41.97 g/L Cu, 9.97 g/L Ni, 0.30 g/L Fe, and 40 g/L of H₂SO₄ acid. Since extraction of Cu and Ni is not possible in this acidity range, the solution was neutralized with NaOH to bring up the pH to 3.5–4.0, aerated for 24 h to precipitate iron as the hydroxide and filtered. The filtrate so obtained was subjected to solvent extraction using Cyanex 272 procured from Cytec Industries, which was used without further purification. It is a colorless liquid with a molecular mass of 290 and boiling point of 300°C and the specific gravity of the extractant is 0.92 g/cc at 24°C. Since copper and nickel extraction is pH sensitive, the solvent was saponified to 60% by NaOH. Analytical grade H₂SO₄ was used for scrubbing and stripping purposes.

Chemical Analysis

The aqueous phases were analyzed by an atomic absorption spectrophotometer (Thermo Solaar S2) before and after extraction. A Toshniwal pH meter with combined glass electrode was used to measure the pH of the aqueous solution at equilibrium, after extraction.

Extraction Experiments

Equilibrium bench scale experiments were carried out at 30°C in order to assess favorable operating conditions for the extraction and separation of copper and nickel present in the aqueous solution using Cyanex 272 as extractant. The solvent phase consisted of Cyanex 272 procured from Cytec Industries dissolved in distilled kerosene (160–200°C fraction). In the extraction experiment 10 mL of the aqueous phase was contacted with 10 mL of the organic phase in a separatory funnel and

mixed by mechanical shaking for 5 min (as determined in preliminary tests). The pH of the aqueous phase was monitored using a pH-meter (Toshniwal model) and was adjusted by adding NaOH or H₂SO₄ solutions (analytical grade reagents). The equilibrium concentration of Cu and Ni in the raffinate was determined by atomic absorption spectrophotometry while that in the organic phase (extract) was calculated by mass balance difference. No third phase formation was observed for the experimental conditions studied.

The following variables were investigated in the extraction tests: concentration of extractant (5–20%, w/w) and aqueous/organic volumetric phase ratio (0.33–3), pH of the aqueous phase (0.76–5.55). After deciding the equilibrium pH for the maximum extraction and separation of Cu and Ni, the pH was maintained by varying the saponification (preneutralization) of the solvent with NaOH. In the stripping tests, the organic/aqueous volumetric phase ratio (0.2–5) was investigated by contacting a loaded organic phase (extract) with H₂SO₄. The concentration of the extractant was selected in such a way that the difference between the yields of extraction of each cation, taken separately, is largest (maximum for copper and minimum for nickel).

RESULTS AND DISCUSSION

Effect of Extractant Concentration on Extraction of Copper From CBS

The effect of initial Cyanex 272 concentration on the extraction of copper from CBS was studied (Figure 1) in the range of 5–20% (v/v) at O:A ratio of 1 at 30°C. It was observed from these results that the percentage extraction of copper increases from 15.35 to 89.8% with an increase of extractant concentration, whereas the loading of Cu in the organic phase increases from 6.44 to 37.29 g/L in a single contact. The log D for Cu and Ni vs. log [Cyanex 272] plot (Figure 1) is linear.

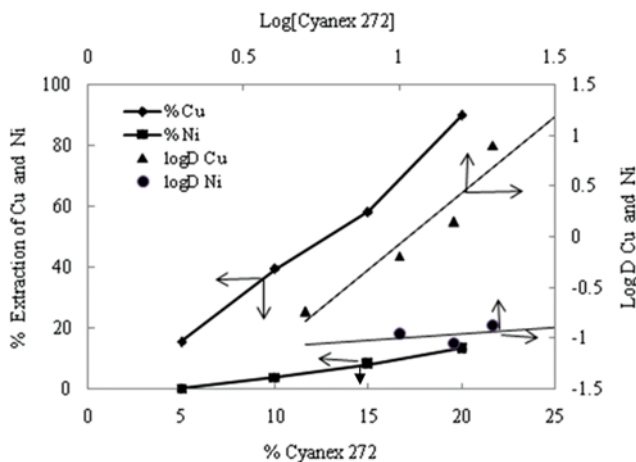


Figure 1 Effect of solvent concentration on extraction of Cu(II) from CBS and plot of log [Cyanex 272] vs. log D. Aq. Feed: 41.97 g/L Cu and 9.97 g/L Ni(II), Org. Feed: Cyanex 272 in kerosene, O:A—1, t —5 min, T —30°C (color figure available online).

Thus, for Cu extraction

$$y = 2.517x - 2.597 \quad y = 1.83x - 1.9 \quad \text{with } R = 0.9143 \quad (1)$$

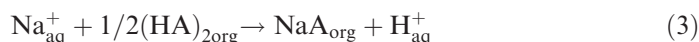
and for Ni extraction

$$y = 0.211x - 1.211 \quad \text{with } R = 0.125. \quad (2)$$

The slope of 2.51 for Cu^{2+} indicates the association of 2 mol of the extractant with 1 mol of the extracted metal species. However, the regression coefficient value for Ni is only 0.125 indicating a lower extraction of Ni by Cyanex 272.

Effect of Equilibrium Ph on Extraction of Copper From CBS

Since the extractions of copper and nickel were found to be very sensitive to pH, this parameter was varied in the range of 0.76 to 5.55. The maximum extraction was observed at an equilibrium pH of 5.48. Maintaining this pH by the addition of an acid or an alkali while performing the experiments with the unsaponified 20% Cyanex 272 has several problems such as increase in the volume of aqueous phase; a slight variation in pH will affect the extraction of copper and nickel, hence 20% Cyanex 272 was saponified to 60% by adding a stoichiometric amount of NaOH and the neutralization reaction can be written as



Thus, in such a case the solvent exists as monomer when it is in the neutral form and as dimers when it is in the acidic form (Ritcey and Ashbrook 1984b) and both the forms take part in the extraction. Assuming that the extracting species of Cu(II) and Ni(II) in the organic phase exist as $[\text{MA}_2 \cdot 3\text{AH}]_{\text{org}}$ and in the aqueous phase as M^{2+} , the extraction mechanism for M^{2+} (M is Cu and Ni) extraction by saponified Cyanex 272 can be written as (Devi, Nathsarma, and Chakravorty 1998)



The equilibrium constant can, thus, be written as

$$\text{K}_{\text{ext}} = \frac{[\text{MA}_2 \cdot 3\text{HA}]_{\text{org}} [\text{H}^{+}]_{\text{aq}}}{[\text{M}^{2+}]_{\text{aq}} [\text{A}^{-}]_{\text{org}} [(\text{HA})_2]_{\text{org}}^2} \quad (5)$$

$$\text{Since } D = \frac{[\text{MA}_2 \cdot 3\text{HA}]_{\text{org}}}{[\text{M}^{2+}]_{\text{aq}}} \quad (6)$$

Hence, Eq. (5) can be written as

$$\text{K}_{\text{ext}} = \frac{D[\text{H}^{+}]_{\text{aq}}}{[\text{A}^{-}]_{\text{org}} [(\text{HA})_2]_{\text{org}}^2} \quad (7)$$

log of both the sides in Eq. (7) can be written as

$$\log D = \log K + \text{pH} + \log[A^-]_{\text{org}} + 2 \log[(\text{HA})_2]_{\text{org}} \quad (8)$$

Where M^{2+} is the bivalent metal ion which is exchanged and here it is Cu^{2+} and Ni^{2+} .

The slope analysis from Figures 1 and 3 supports this mechanism.

The extraction of copper from aqueous sulfate medium was studied using this sodium salt of Cyanex 272 within the initial pH range 0.76–5.55 for solvent concentrations varying from 10–20%. It was found that the equilibrium pH varied differently with different concentration of the solvent, thus, for 10% solvent the equilibrium pH varied from 1.6 to 4.1, for 15% Cyanex 272 it varied from 2.9 to 4.7, and for 20% Cyanex 272 it varied from 2.53 to 5.48. Percentage extraction of copper increases from 7.6 to 39.4, 13.6 to 58.5, and 13.64 to 98.47% for the solvent concentration varying from 10, 15, and 20% respectively, whereas percentage extraction of Ni(II) increases from 0 to 35.21% with an increase in the equilibrium pH of the aqueous phase with 20% Cyanex 272. However, in cases of 10 and 15% Cyanex 272, Ni extraction is possible only when the equilibrium pH is more than 4 (Figure 2). Figure 3 shows the plot of log D (distribution coefficient) for Cu and Ni vs. equilibrium pH. The plot is linear for both the metal ions with the best fit equation as

$$y = 0.8538x - 2.9666, R^2 = 0.9863 \text{ for Cu extraction and} \quad (9)$$

$$y = 0.6132x - 3.6841, R^2 = 0.949 \text{ for Ni extraction.} \quad (10)$$

A slope of 0.8549 for copper and 0.61 for Ni indicates the exchange of one mole of H^+ with one mole of the extracted metal species. The separation factor ($\alpha_{\text{Ni}}^{\text{Cu}}$) for the separation of Cu from Ni using Na-Cyanex 272 also increases with the increasing extractant concentration from 10 to 20% (v/v) (Table 1). The highest separation

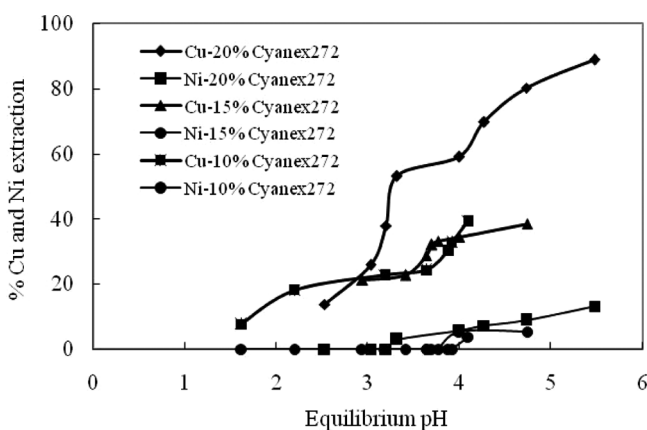


Figure 2 Effect of equilibrium pH on percentage extraction of Cu and Ni from CBS with different concentration of Cyanex 272. Aq. Feed: 41.97 g/L Cu and 9.97 g/L Ni(II), Org. Feed: $x\%$ Cyanex 272 in kerosene, O:A—1, t —5 min, T —30°C.

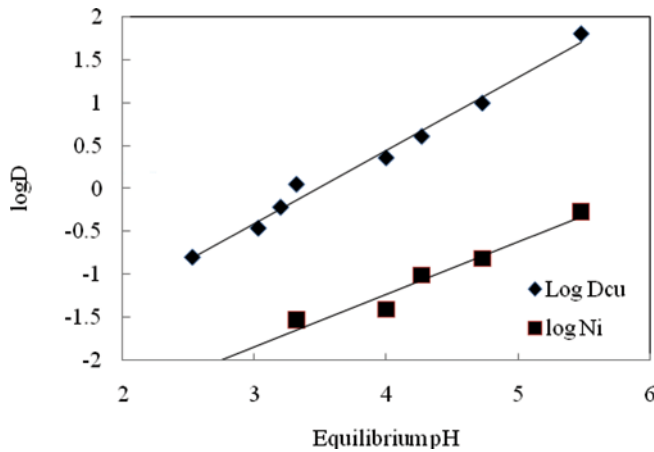


Figure 3 Plot of equilibrium pH of the aqueous feed vs. Log D. Aq. Feed: 41.97 g/L Cu and 9.97 g/L Ni(II), Org. Feed: 20% Cyanex 272 in kerosene, O:A—1, t —5 min, T —30°C (color figure available online).

factor of 183.3 for the separation Cu from Ni was achieved with 20% (v/v) Na-Cyanex 272 at an equilibrium pH of 5.48. One more interesting observation from the separation factor data is that for 10% Na-Cyanex 272 only Cu is extracted up to an equilibrium pH of 3.9 with no extraction of Ni at all. At a pH of 4.2, Ni shows some extraction but the separation factor is 4.9 showing a possibility of separation, but as the percentage extraction of Cu is very low, hence, this composition of solvent will not be suitable for Cu and Ni separation. In case of 15% Na-Cyanex 272, separation factor is infinite up to an equilibrium pH of 3.6 but again the percentage Cu extraction is only about 25%, and beyond this pH, i.e., up to a pH of 4.74 the separation factor is about 11.53. In case of 20% Na-Cyanex 272, the separation factor is infinite up to an equilibrium pH of 3.32. As the pH increases from 3.3 to 5.5 the separation factor increases from 39.10 to 183.3. It was found that in this case the

Table 1 Effect of equilibrium pH on the separation factor of Cu and Ni at different concentration of 60% saponified Cyanex 272 (Cu—41.97 g/L, Ni—9.97 g/L, O:A—1, t —5 min, T —30°C)

60% saponified Cyanex 272											
10%				15%				20%			
pH eq	D_{Cu}	D_{Ni}	α_{Ni}^{Cu}	pH eq	D_{Cu}	D_{Ni}	α_{Ni}^{Cu}	pH eq	D_{Cu}	D_{Ni}	α_{Ni}^{Cu}
1.62	0.082	0	∞	2.94	0.158	0	∞	2.53	0.158	0	∞
3.19	0.222	0	∞	3.41	0.269	0	∞	3.03	0.346	0	∞
3.64	0.294	0	∞	3.64	0.320	0	∞	3.2	0.609	0	∞
3.88	0.320	0	∞	3.7	0.404	0	∞	3.32	1.13	0.029	39.1
3.86	0.434	0	∞	3.77	0.434	0	∞	4	2.3	0.038	32.2
3.92	0.434	0	∞	4	0.626	0.056	11.15	4.27	4.08	0.097	46.2
4.1	0.650	0.133	4.89	4.77	1.53	0.186	8.21	4.73	10.0	0.151	61.03
—	—	—	—	—	—	—	—	5.48	64.53	0.543	183.3

percentage extraction of Cu increases from 13.7 to 98.5% with the increase in equilibrium pH from 2.5 to 5.5. Thus, at an equilibrium pH of 5.5 separation of Cu and Ni is possible with 60% saponified 20% Cyanex 272. This analysis also clearly shows the impact of pH variation and its sensitivity on metal separation.

Effect of Phase Contact Time on Extraction of Copper From CBS

The aqueous phase containing 41.97 g/L Cu and 9.97 g/L Ni was shaken with 20% (v/v) Cyanex 272 (60% saponified) for a period ranging from 0.5 to 15 min at an O:A ratio of 1 and initial pH 5.55. Percentage extraction of copper increased from 93.94 to 98.47 with increase of shaking time from 0.5 to 5 min. Beyond 5 min of shaking, there is no further increase in the extraction of copper into the organic phase in a single contact. Therefore, in all the other experiments a shaking time of 5 min was maintained to ensure achievement of equilibrium.

Determination of Loading Capacity of Cyanex 272

Saturation loading capacity of 60% saponified 20% (v/v) Cyanex 272 was achieved by a multiple contact method. The fresh aqueous feed containing 41.97 g/L Cu and 9.97 g/L Ni was contacted with same loaded organic each time at O/A ratio of 1 at initial aqueous feed pH of 5.55 at 30°C. Thus after three contacts, the loaded organic contains 30.80 g/L Cu and 0.024 g/L Ni. It was also seen that with the repeated contact, the copper from aqueous feed continuously gets extracted in the organic phase. However, beyond certain concentration of copper loaded into the organic (approximately 40 g/L), the loaded copper gets precipitated and remains in the interface of the aqueous-organic phases. Once the precipitation starts, the copper in the organic decreases to about 30 g/L. Hence, the phase ratio and the saponification of the organic has to be maintained to such an extent that maximum loading of copper in the organic will be restricted to about 30 g/L.

Effect of O:A Ratio Variation on Extraction of Copper End Extraction Isotherm

Extraction of Cu(II) from CBS containing 41.97 g/L Cu and 9.97 g/L Ni was carried out at different O:A ratios using 60% saponified 20% (v/v) Cyanex 272 at initial pH 5.55 at 30°C for the possibility to extract maximum amount of Cu in single contact. It was observed from the result (Figure 4) that on increasing the O:A ratio from 0.33 to 3, the percentage extraction of Cu increases from 46.97 to 100%, however, at lower O/A ratios of 0.33 and 0.5 the loaded organic becomes turbid and after few hours a light blue color precipitate settles at the interface. Therefore, to avoid precipitation the extraction of copper has to be done at higher O/A ratio with minimum saponification.

To determine the number of stages required at a chosen volume phase ratio, an extraction isotherm (McCabe-Thiele plot) was plotted between the amount of copper extracted by the solvent and copper left unextracted in the raffinate at different O/A ratios. As can be seen from Figure 5 that 100% extraction of copper was possible in two counter-current stages at an O:A ratio of unity.

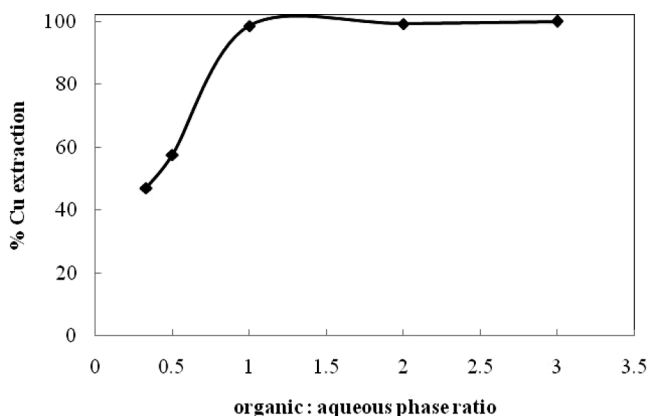


Figure 4 Effect of organic:aqueous phase ratio on the extraction of Cu and Ni from the Aq. Feed: 41.97 g/L Cu and 9.97 g/L Ni(II), Org. Feed: 20% Cyanex 272 in kerosene, $t=5$ min, $T=30^{\circ}\text{C}$.

Scrubbing of Ni and Stripping of Cu From Loaded Organic

Sufficient quantity of 60% saponified 20% Cyanex 272 was saturated loaded with Cu by repeated contact of same loaded organic with fresh aqueous feed each time. As already discussed that with the repeated contact of the organic and aqueous phases, the loaded organic turned hazy which was allowed to settle and filtered through a phase separation paper to obtain a clear and a uniform loaded organic for further study. Due to precipitation, the metal concentration in the loaded organic was analyzed to be 30.9 g/L copper and 0.024 g/L Ni. For scrubbing the coextracted nickel, the loaded organic was contacted with different concentrations of sulfuric

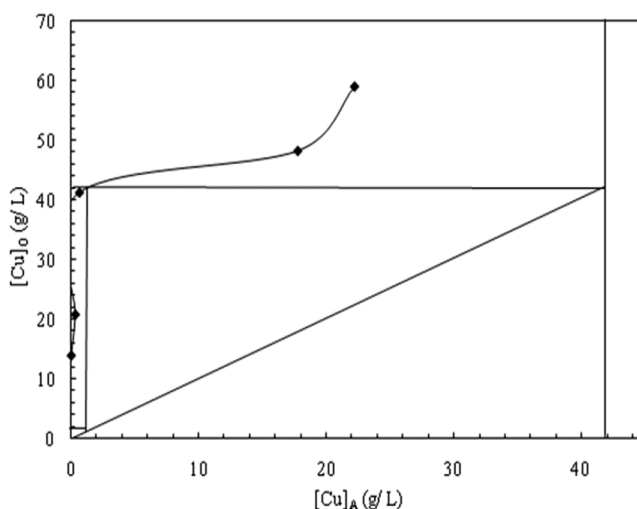


Figure 5 McCabe-Thiele plot for extraction of copper by 20% Cyanex 272. Aq. Feed: 41.97 g/L Cu and 9.97 g/L Ni(II), Org. Feed: 20% Cyanex 272 in kerosene, $t=5$ min, $T=30^{\circ}\text{C}$.

acid (5–20 g/L) at O:A ratio of 5. Since the scrubbed solution is usually recycled into the main stream, the ratio of organic:scrub feed is maintained at 5:1. It was observed that 15 g/L H_2SO_4 was suitable for scrubbing of Ni in one stage leaving 4 ppm of Ni in the organic phase. The mixture was shaken for 2–3 min which was found sufficient for the removal of coextracted nickel from the loaded organic. The scrubbed loaded organic was used for stripping studies.

Effect of Concentration of H_2SO_4 on Stripping of Copper From Loaded Organic

Stripping studies were carried out to strip out all the copper from the loaded organic to the aqueous phase at varying concentrations of sulfuric acid ranging from 50 to 125 g/L keeping an O/A of 2. As can be seen from Figure 6, the percentage stripping of copper increases from 87.9 to 100% with an increase in acid concentration and reaches quantitative stripping at 100 g/L (Figure 6). However, stripping with 75 g/L of H_2SO_4 was about 95.5%, hence, further stripping studies were performed with 75 g/L H_2SO_4 .

Effect of O:A Ratio Variation on Stripping of Copper From Loaded Organic and Stripping Isotherm

Stripping of loaded organic (60% saponified 20% Cyanex 272 containing 30.4 g/L Cu and 0.024 g/L Ni) was carried out using 75 g/L sulfuric acid at different O:A ratios and the plot of O/A vs. % Cu stripped at 30°C is plotted (Figure 6). It can be seen from the result that with increase in O:A ratio from 0.2 to 5, the concentration of stripped copper decreases from 100 to 66.67%.

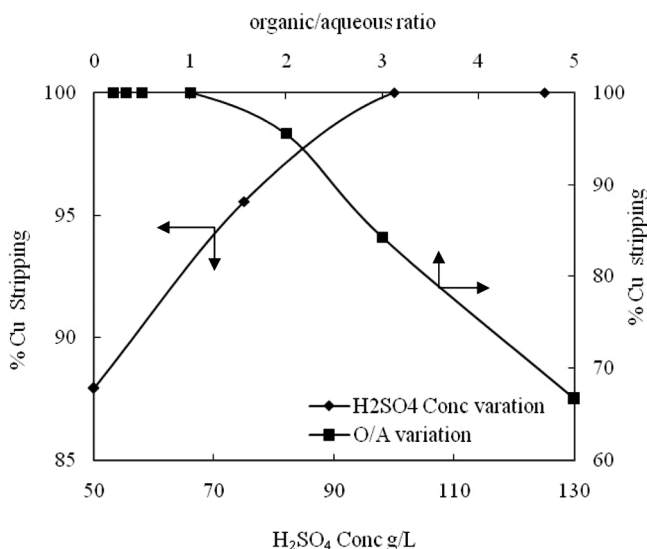


Figure 6 Effect of H_2SO_4 concentration and O/A ratio on the stripping of loaded Cu from 20% Cyanex 272.

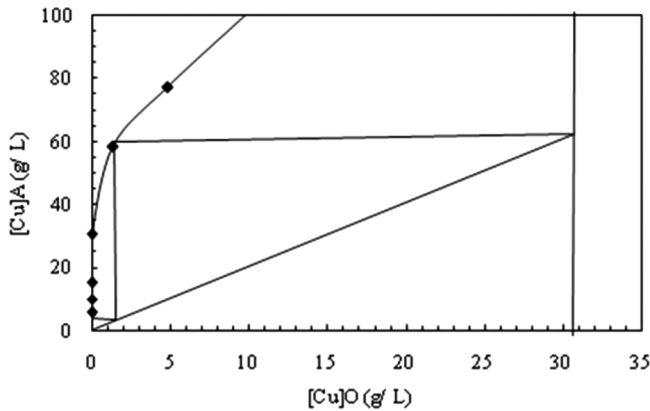


Figure 7 McCabe-Thiele plot for stripping of copper from the loaded organic by 75% H_2SO_4 .

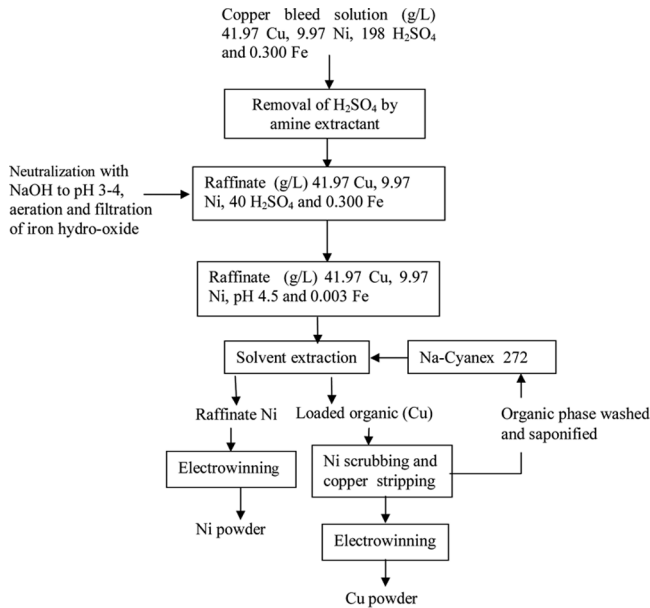


Figure 8 Flow diagram for the treatment of copper bleed stream by solvent extraction route.

A stripping isotherm was obtained by plotting the concentration of Cu in the organic phase vs. concentration of Cu stripped in the aqueous phase at O/A ratios varying from 5:1 to 1:5 (Figure 7). This figure shows that about 100% of copper was stripped in two counter-current stages at O:A ratio of 2:1.

Thus, an overall flow sheet for the separation of Cu and nickel from CBS after the extraction of acid is given in Figure 8. Acid and metal values can be reclaimed from the highly acidic solutions such as copper bleed stream.

CONCLUSION

Cyanex 272 (60% saponified) diluted in kerosene was used as a solvent for the separation and recovery of copper and nickel from CBS. The concentration of acid could be brought down from 198 to 40 g/L by an amine extractant. The pH of the solution was further brought up to 4 by alkali addition, iron was removed as hydroxide by aeration and the filtrate was used as a feed for Cu and Ni separation. With the increase in equilibrium pH and the extractant concentration, there is an increase in the percentage extraction of metal ion. The extracted species for copper was $\text{CuA}_2 \cdot 3\text{HA}$. Loading capacity of 60% saponified 20% (v/v) Cyanex 272 was determined to be 30.8 g/L Cu and 0.024 g/L Ni. The separation factor of Cu and Ni also increases from 39.11 to 183.3 with increase of pH from 3.32 to 5.48. Scrubbing of Ni(II) from loaded organic was done with 15 g/L sulfuric acid and after scrubbing only 4 ppm of Ni was left in the organic phase. Cu was then stripped with 75 g/L sulfuric acid. Extraction and stripping isotherms were obtained with 20% Cyanex 272 (60% saponified). Hundred percent copper extraction was achieved in two counter-current stages at O:A ratio of unity, whereas 100% stripping of copper was possible in two counter-current stages at O:A ratio of 2:1. Results of the present investigation indicate that Cyanex 272 could be used as a commercial extractant for copper extraction and recovery from copper bleed stream.

ACKNOWLEDGMENTS

The authors wish to thank the Director, National Metallurgical Laboratory, for his kind permission to publish this paper.

REFERENCES

- Ali, A. I., Daoud, J. A., and Ali, H. F., 1996, "Recovery of copper from sulphate medium by Lix-84 in kerosene." *Journal of Chemical Technology and Biotechnology*, 67(2), p. 137.
- Alguacil, F. J., 1988, "Modelling copper solvent extraction from acidic sulphate solutions using MOC 45." *Revista de Metalurgia (Madrid)*, 38, p. 381.
- Amores, M., Coedo, A. G., and Alguacil, F. J., 1997, "Extraction of copper from sulphate solutions by MOC 45: Application to Cu separation from leachates of a copper flue dust." *Hydrometallurgy*, 47, p. 99.
- Bart, H. J., Marr, R., Bauer, A., Schein, R., Marageter, E., 1990, "Copper extraction in nitrate media." *Hydrometallurgy*, 23(2-3), p. 281.
- Belkhouche, N. E., Didi, M. A., and Villemin, D., 2005, "Separation of nickel and copper by solvent extraction using di-2-ethylhexylphosphoric acid-based synergistic mixture." *Solvent Extraction and Ion Exchange*, 23(5), p. 677.
- Calligaro, L., Mantovani, A., Belluco, U., and Acampora, M., 1983, "Solvent extraction of copper(II), nickel(II), cobalt(II), zinc(II) and iron(II) by high molecular weight hydroxyoximes." *Polyhedron*, 2(11), p. 1189.
- Devi, N. B., Nathsarma, K. C., and Chakarvortty, V., 1994, "Sodium salt of D2EHPA, PC 88A and Cyanex 272 and their mixtures as extractants for cobalt(II)." *Hydrometallurgy*, 34(3), p. 331.
- Devi, N. B., Nathsarma, K. C., and Chakravortty, V., 1998, "Separation and recovery of cobalt(II) and nickel(II) from sulphate solutions using sodium salts of D2EHPA, P C 88A and Cyanex 272." *Hydrometallurgy*, 49(1-2), p. 47.

- Fisher, J. F. C. and Notebaart, C. W., 1983, "Commercial processes for copper." In *Handbook of Solvent Extraction* (T. C. Lo, M. H. I. Baird and C. Hanson Eds.), New York: Wiley, p. 649.
- Ihm, S. K., Lee, H. Y., and Huilee, D., 1988, "Kinetic study of the extraction of copper(II) by di(2 ethylhexyl) phosphonic acid in a Lewis type cell." *Journal of Membrane Science*, 37(2), p. 181.
- Jiayong, Y., 1993, "Development of copper extraction technology in China." *Proceedings of the International Solvent Extraction Conference, ISEC'93*, York, UK, September 9–15, p. 183.
- Merigold, C. R., Agers, D. W., and House, J. E., 1971, "The recovery of copper from ammoniacal leech solution." *Proceedings of the International Solvent Extraction Conference, ISEC' 71*, April 19–23, Vol. 2, London: Society of Chemical Industry, p. 1351.
- Preston, J. S., 1982, "Solvent extraction of cobalt and nickel by organophosphorous acids." *Hydrometallurgy*, 9(2), p. 115.
- Preston, J. S., 1983, "Solvent extraction of base metals by mixtures of organophosphoric acids and non chelating oximes." *Hydrometallurgy*, 10(2), p. 187.
- Rao, K. S., Devi, N. B., and Reddy, B. R., 2000, "Solvent extraction of copper from sulphate medium using MOC 45 as extractant." *Hydrometallurgy*, 57(3), p. 269.
- Ritcey, G. M. and Ashbrook, A. W., 1979, "*Solvent Extraction, Part II*", Amsterdam: Elsevier, p. 196.
- Ritcey, G. M. and Ashbrook, A. W., 1984a, "*Solvent Extraction, Part I*", Amsterdam: Elsevier, p. 87.
- Ritcey, G. M. and Ashbrook, A. W., 1984b, "*Solvent Extraction Principles and Applications to Process Metallurgy, Part-1*". Amsterdam: Elsevier Science Publishers B.V, pp. 15–20.
- Sarangi, K., Parhi, P. K., Padhan, E., Palai, A. K., Nathsarma, K. C., and Park, K. H., 2007, "Separation of iron(III), copper(II) and zinc(II) from a mixed sulphate/chloride solution using TBP, LIX841 and Cyanex 923." *Separation and Purification Technology*, 55, p. 44.
- Szymanowski, J., 1993, "*Hydroxyoximes in copper hydrometallurgy*", Boca Raton: CRC Press.
- Thakur, N. V., 1998, "Extraction of base metals (Mn, Cu, Co and Ni) using the extractant 2-ethylhexyl phosphonic acid, PC 88A." *Hydrometallurgy*, 48(1), p. 125.
- Thakur, N. V. and Mishra, S. L., 1998, "Separation of Co, Ni and Cu by solvent extraction using di(2 ethylhexyl) phosphonic acid, PC 88A." *Hydrometallurgy*, 48(3), p. 277.