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### Process for the Recovery of Cobalt and Nickel from Sulphate Leach Liquors with Saponified Cyanex 272 and D2EHPA

B. Ramachandra Reddy<sup>ab</sup>; Kyung Ho Park<sup>b</sup>

<sup>a</sup> Inorganic Chemistry Division, Indian Institute of Chemical Technology (CSIR), Hyderabad, India <sup>b</sup> Minerals and Materials Processing Division, Korea Institute of Geoscience and Mineral Resources (KIGAM), Daejeon, Korea

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## Process for the Recovery of Cobalt and Nickel from Sulphate Leach Liquors with Saponified Cyanex 272 and D2EHPA

**B. Ramachandra Reddy**

Inorganic Chemistry Division, Indian Institute of Chemical Technology (CSIR), Hyderabad, India and Minerals and Materials Processing Division, Korea Institute of Geoscience and Mineral Resources (KIGAM), Daejeon, Korea

**Kyung Ho Park**

Minerals and Materials Processing Division, Korea Institute of Geoscience and Mineral Resources (KIGAM), Daejeon, Korea

**Abstract:** In this paper, a process is reported for the recovery of cobalt and nickel from copper raffinate solutions using partially saponified Cyanex 272 and D2EHPA as the extractants. The aqueous feed contains 1.65 g/L cobalt and 16.42 g/L nickel. More than 99.9% cobalt separation was achieved with 0.13 M Cyanex 272 (60% neutralized with alkali) in two counter-current stages at an aqueous to organic phase ratio of 1.1:1. Co-extraction of nickel was 0.18% only. Stripping of cobalt from a loaded organic phase was carried out with synthetic spent electrolyte solution at an organic to aqueous phase ratio of 2.5 in two counter-current stages to generate a pregnant electrolyte solution to produce cobalt metal by electrowinning. Similarly, optimum conditions for nickel extraction with 60% neutralized 1 M D2EHPA at O/A ratio of 1.4 in 2 two stages and stripping of metal with synthetic spent electrolyte at O/A ratio of 1.6 in two stages were standardized. Extraction and stripping efficiencies were >99% and the flowsheet of the process is demonstrated.

**Keywords:** Cu-Ni-Co matte, cobalt, nickel, Cyanex 272, D2EHPA

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Address correspondence to B. Ramachandra Reddy, Inorganic Chemistry Division, Indian Institute of Chemical Technology (CSIR), Hyderabad 500 007, India. Fax: 91-40-27160921; E-mail: brcreddy\_iict@yahoo.com

## INTRODUCTION

Primary resources for the production of cobalt and nickel are the land based cobaltiferous pyrite concentrate/sulphide or oxide nickel ores. In addition to these, some secondaries such as spent catalysts, alloy scrap, sludge, dust etc., are being exploited for cobalt/nickel production. Further, manganese nodules found in the North and South Atlantic Ocean, the Indian Ocean, and the South Pacific Ocean are considered as potential futuristic resources for the production of nickel and cobalt (1).

The Minerals and Materials Division of the Korea Institute of Geosciences and Mineral Resources (KIGAM), Korea has been working for the last 10 years on the processing of Pacific Ocean manganese nodules for metal recovery. The processing methodology of nodules involve the pyrometallurgical smelting reduction -sulphidation route to produce Cu-Ni-Co rich matte and Mn slag from Pacific Ocean nodules (2) followed by dilute sulphuric acid pressure leaching of matte (3) to obtain Cu, Ni, Co metals in soluble form for further processing. Copper was separated and recovered selectively from sulphate leach liquor using 40 vol% LIX 84 (4). The copper raffinate contains Cu and Fe as impurities, which requires purification step prior to Co and Ni recovery.

Solvent extraction separation and recovery of cobalt and nickel from sulphate solutions using organophosphorus compounds was extensively studied. The first commercial process for the separation of cobalt and nickel was developed using di(2-ethylhexyl) phosphoric acid (D2EHPA) (5), while a similar process using D2EHPA was used by Matthey Rustenburg Mining (6). The main drawbacks of the process were the poor selectivity at high Ni:Co ratios and high temperature used ( $>50^{\circ}\text{C}$ ). As a result, many efforts were made to synthesize more selective compounds such as phosphonic (PC 88A/Ionquest 801) and phosphinic acids (Cyanex 272), which led to successful Co/Ni separations on commercial scale. The Co/Ni separation factor increases in the order: Phosphoric < phosphonic < phosphinic acid (7). In our previous studies, organophosphorus extractants such as D2EHPA (TOPS 99 an Indian reagent equivalent to D2EHPA), PC 88A, and Cyanex 272 were exploited for the solvent extraction studies of Co and Ni from chloride/sulphate solutions (8–15).

The aim of the present study is to optimize conditions on a laboratory scale for the solvent extraction separation and recovery of cobalt and nickel from copper raffinate solutions of synthetic Cu-Ni-Co-Fe matte employing Cyanex 272 and D2EHPA as the extractants diluted in kerosene. Stripping of cobalt and nickel from loaded extractants were optimized with spent electrolyte (SE) to generate pregnant electrolyte (PE) solutions suitable for producing metals by electrowinning. Process parameters such as impurities removal, extractant concentration, and percentage neutralization, organic to aqueous phase ratio, counter-current extraction simulation, scrubbing, and counter-current stripping simulation were carried out. Based on the results, a flowsheet of the process is proposed.

## EXPERIMENTAL

### Apparatus

A Varian model SpectrAA 400 Atomic Absorption Spectrophotometer (AAS) and an Orion expandable ion analyzer EA 920 equipments were used for the determination of metal concentrations and pH of the aqueous phase.

### Reagents

Commercial extractants such as D2EHPA (di-2-ethylhexyl phosphoric acid) supplied by Sigma Chemical Company, USA and Cyanex 272 (bis (2,4,4-trimethyl pentyl phosphinic acid)) supplied by Cytec Inc., Canada, were used as received. The sodium salts of the extractants (60–80% neutralized) were prepared by adding the requisite quantity of NaOH solution to the extractant diluted in kerosene and mixing thoroughly to obtain a single phase. 5 vol% TBP was used as phase modifier through out the experiments. Extra pure kerosene supplied by Junsei Chemical Co, Japan was used as the diluent. All the other chemicals used were of Analar grade.

### Solvent Extraction Procedure

Suitable volumes of aqueous feed and organic phase (sodium salt of Cyanex 272/D2EHPA of desired concentrations) were contacted for 5 min in separating funnels (initial experiments showed that equilibrium reached within 1 min). After phase disengagement, the aqueous phase was separated and its pH was measured and analyzed for metal concentrations in the aqueous phase by AAS after suitable dilutions. The loaded organic (LO) phases were stripped three times with 2 M HCl wherever necessary, and the combined strip solutions were analyzed for metal values by AAS. All the experiments were carried out at room temperature ( $\sim 25^\circ\text{C}$ ). The distribution ratio, D, was calculated as the concentration of metal present in the organic phase to that part in the aqueous phase at equilibrium. From the D values, the percentage extraction (%E) and separation factor ( $\beta$ ) were calculated using the equations:

$$\text{Percentage extraction } (\%) = D \times 100 / (D + (V_{\text{aq}}/V_{\text{org}}))$$

Where  $V_{\text{aq}}$  and  $V_{\text{org}}$  are the volumes of aqueous and organic phases, respectively, and

$$\text{Separation factor } (\beta) = D_{\text{Co}}/D_{\text{Ni}} = \frac{[\text{Co}]_{\text{org}}}{[\text{Co}]_{\text{aq}}} / \frac{[\text{Ni}]_{\text{org}}}{[\text{Ni}]_{\text{aq}}}$$

## RESULTS AND DISCUSSION

### Purification of Copper Raffinate

The typical composition of copper raffinate used for the present study contains: Cu: 0.35 g/L, Ni: 16.88 g/L, Co: 1.69 g/L and Fe: 0.07 g/L with a pH of 1.0. The removal of impurities such as copper and iron were carried out in the pH range from 5.3 to 7.7 using a 50% alkali solution. Iron removal was quantitative at pH 5.3, whereas the copper removal starts around pH 5.7 and reaches quantitative at pH  $\sim$ 7.5. The loss of cobalt and nickel at pH 7.5 was about 2.2 and 2.7%, respectively. Above pH 7.5, the loss of cobalt and nickel was almost 3- 4-fold (Fig. 1). As a result, the pH of 7.5 was selected to generate copper and iron free raffinate containing 1.65 g/L Co and 16.42 g/L Ni for further studies.

### SEPARATION OF COBALT AND NICKEL USING CYANEX 272

It is well-reported in the literature that the separation of cobalt from nickel using organophosphorus based extractants increase in the order D2EHPA < PC 88A < Cyanex 272 (7). In the present investigation on the separation of cobalt and nickel from copper raffinate was studied using Cyanex 272 dissolved in kerosene. The extraction of cobalt with a cation exchange type extractant such as Cyanex 272 is pH dependent and involves the release of  $H^+$  ions from the extractant during metal transfer from the

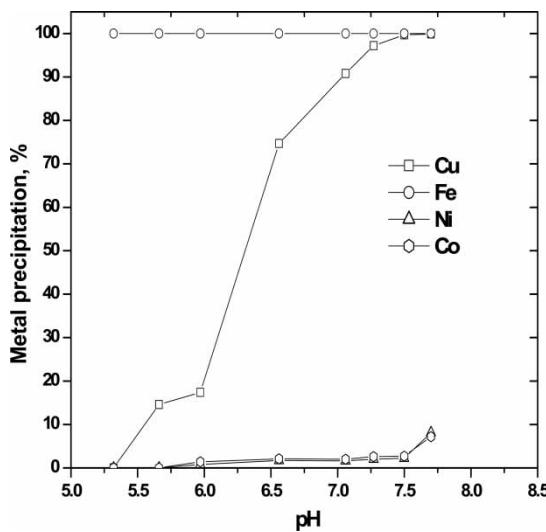


Figure 1. Effect of pH on metal precipitation.

aqueous phase to the organic phase. As a result, the pH of the aqueous phase decreases and needs to be maintained around pH 5–6.5 by the addition of alkali solution or by using saponified Cyanex 272 for metal extraction. In the present study, the later methodology of partial saponification of Cyanex 272 for cobalt- nickel separation was adopted.

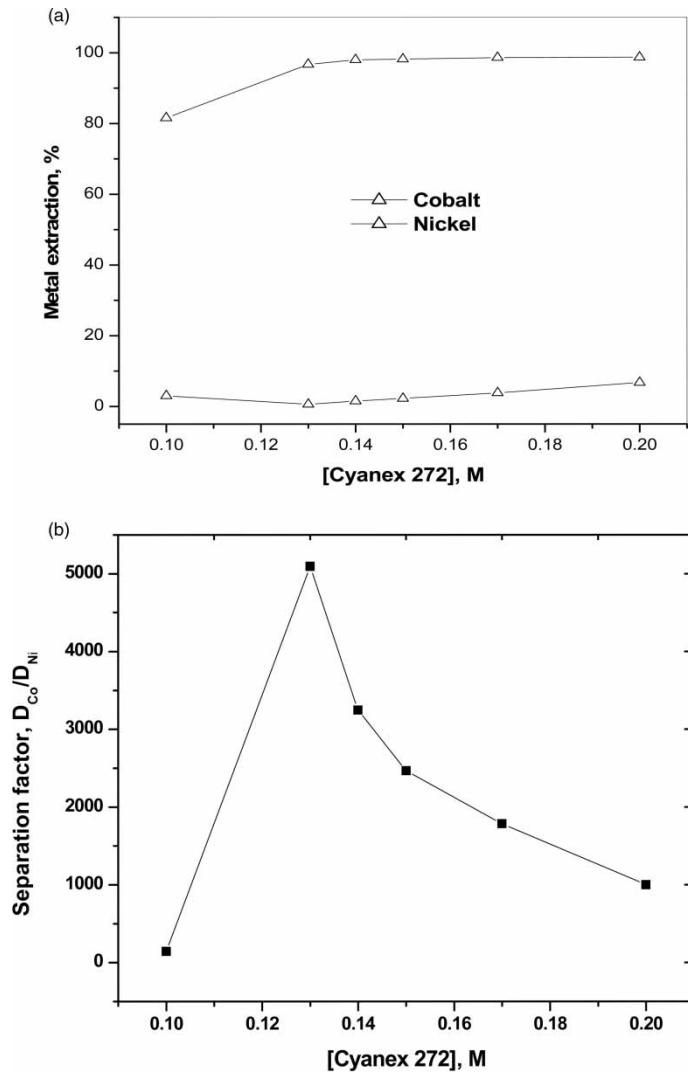
### Effect of Cyanex 272 Concentration

Cyanex 272 concentration has been varied from 0.1 to 0.2 M (60% neutralization with alkali) at unit phase ratio. The percentage extraction of cobalt increases with increase in extractant concentration whereas that of nickel depends on extractant concentration and cobalt percent extraction. Equilibrium pH of the aqueous phase was maintained around  $6.3 \pm 0.2$ . For example, with 0.1 M Cyanex 272, extraction of Co and Ni were 81.6 and 2.98% respectively, whereas that with 0.13 M Cyanex 272, Co and Ni extraction were 96.7 and 0.57% respectively. Further increase of extractant concentration to 0.2 M, Co and Ni extraction were 98.7 and 6.7% respectively (Fig. 2a). The results clearly demonstrated that 0.13 M extractant concentration is the best giving a high separation factor of about 5100 (Fig. 2b). The co-extraction of nickel was  $\sim 0.6$  % only. As a result, 0.13 M cyanex 272 was chosen for the determination of the number of stages and phase ratio to recover  $>99.9\%$  cobalt.

### Cobalt Extraction Isotherm

To determine the number of stages required at a chosen volume phase ratio for quantitative extraction of cobalt, the extraction isotherm was obtained by contacting the copper raffinate (pH: 7.5) with 0.13 M Cyanex 272 (60% neutralized) at different O/A phase ratios from 1 to 5 and A/O phase ratios from 1 to 3 (Fig. 3). The equilibrium pH of the aqueous phase was maintained around 6.5–6.6. The McCabe-Thiele plot indicates that complete cobalt extraction is possible in two counter-current stages at A/O phase ratio of unity. The co-extraction of Ni was 0.03–0.57%, which increased to 11.8–23.2% at higher O/A ratios greater than 1.

To confirm the extraction isotherm predictions, a two stage counter-current extraction simulation test was carried out at A/O phase ratio of 1, which resulted in 99.96% cobalt extraction efficiency. The co-extraction of nickel into the loaded organic (LO) phase was 0.57% (Table 1). In order to decrease the co-extraction of nickel into the loaded organic phase, further fine tuning of the process was carried out at A/O phase ratios of 1.05 and 1.1 and keeping the same extraction efficiency of cobalt. The results shown in Table 1, clearly indicated a decrease in Ni co-extraction from 0.57% to 0.18%, thereby reducing the load on the scrubbing circuit during continuous operations. The loaded organic obtained at A/O phase ratio of 1.1 (Co: 1.84 g/l, Ni: 0.03 g/L)

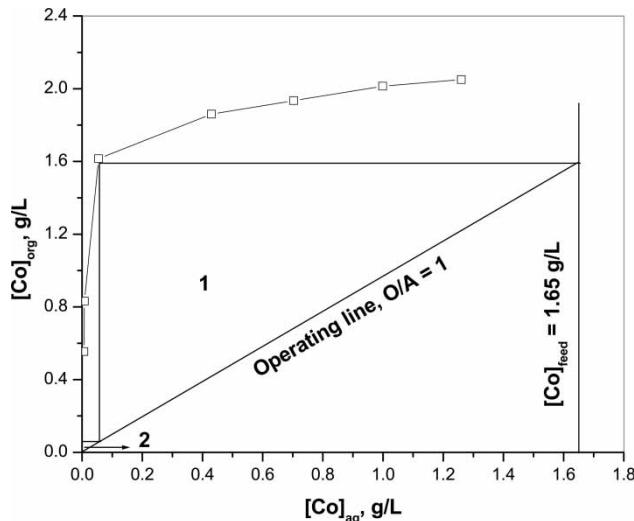


**Figure 2.** (a) Effect of extractant concentration on cobalt and nickel extraction; (b) Effect of extractant concentration vs. separation factor.

was selected for generating data on nickel scrubbing, cobalt stripping, and the raffinate to optimise conditions for nickel recovery.

#### Nickel Scrubbing from the Loaded Organic Phase

Nickel scrubbing from the loaded organic phase was carried out using a cobalt sulphate solution containing 0.06 to 0.48 g/L Co in the initial pH range from 3



**Figure 3.** McCabe-Thiele plot for cobalt extraction using partially saponified 0.13 M Cyanex 272.

to 4.5 (Table 2). Initial tests with 0.06 g/L CoSO<sub>4</sub> scrub feed indicated slow phase separation and the raffinate was not clear. Addition of 0.1 M Na<sub>2</sub>SO<sub>4</sub> to the scrub feed improved phase separation to <1 min and the scrub raffinate was clear. Using 0.06 g/L CoSO<sub>4</sub>, it was possible to achieve about 80% Ni scrubbing, whereas with 0.21 g/L CoSO<sub>4</sub> about 90% Ni scrubbing efficiency was achieved, and a further increase of concentration to 0.48 g/L CoSO<sub>4</sub> did not improve stripping efficiency.

#### Stripping of Cobalt from Loaded Organic Phase with Spent Electrolyte

Stripping of cobalt from the loaded organic phase was carried out in a single stage at unit phase ratio with a synthetic spent electrolyte (SE) solution (SE:

**Table 1.** Results of two stage counter-current extraction of cobalt at different phase ratios

Phase ratio (A:O)	Co in LO <sup>a</sup> , g/L	Co extraction, %	Ni in LO, mg/L	Ni co-extraction, %
1:1	1.7993	99.96	94	0.56
1.05:1	1.799	99.94	74.5	0.46
1.1:1	1.7986	99.92	30	0.18

<sup>a</sup>LO = Loaded organic.

36 g/L Co; 70 g/L Na<sub>2</sub>SO<sub>4</sub>; 5 g/L H<sub>3</sub>BO<sub>3</sub>) in the initial pH range from 0.99 to 2.46 (Table 3). The results indicated that >98% cobalt stripping is possible with SE pH of 1.5 and below.

### Stripping Isotherm of Cobalt from the Loaded Organic Phase

Considering cobalt enrichment of about 4–5 g/L in pregnant electrolyte (PE) with final PE pH of about 4 during stripping, which is reported to be the best condition for cobalt electrowinning to produce metal, the cobalt from the scrubbed loaded organic (SLO) was stripped with SE having initial pH of 1.3 at different O/A ratios with a view to determine possible enrichment of cobalt and number of stages needed for quantitative stripping of Co from LO (Fig. 4). The McCabe-Thiele plot indicates that complete cobalt stripping is possible in two counter-current stages at an O/A ratio of 2.5. The results of the two-stage counter-current stripping simulation carried out under optimum conditions (O/A ratio-2.5 and strip feed pH-1.3) indicated >99.6% stripping efficiency of cobalt.

### PROCESSING OF COBALT-FREE RAFFINATE FOR NICKEL RECOVERY

The objective of carrying out nickel extraction from raffinate is to produce pregnant electrolyte solution of pH~3 with Ni enrichment of about 20 g/L during stripping of metal from LO using synthetic spent electrolyte containing Ni: 50 g/L, Na<sub>2</sub>SO<sub>4</sub>: 100 g/L, H<sub>3</sub>BO<sub>3</sub>: 15 g/L, H<sub>2</sub>SO<sub>4</sub>: 40 g/L. The raffinate from the cobalt extraction circuit, containing 16.39 g/L of nickel with a pH of

**Table 2.** Scrubbing of Ni from loaded organic

Scrub feed, CoSO <sub>4</sub> (g/L)	Initial pH	Equilibrium pH	Ni in LO, mg/L	Ni scrubbing efficiency, %	Co loss, %
0.066	3.0	6.21	10.6	80.7	6.7
	3.51	6.13	10.0	81.9	6.6
	4.0	6.1	10.6	80.8	6.9
	4.53	6.23	10.1	81.7	7.6
0.21	3.01	5.69	6.8	87.6	9.5
	3.49	5.74	6.4	88.3	8.1
	3.99	5.74	5.5	90.0	7.7
	4.53	5.77	6.3	88.6	7.0
0.48	3.0	5.67	6.05	89.0	9.5
	3.51	5.63	6.5	88.2	7.6
	4.02	5.7	6.8	87.6	6.1
	4.53	5.66	6.8	87.6	6.5

**Table 3.** Effect of spent electrolyte pH on cobalt stripping

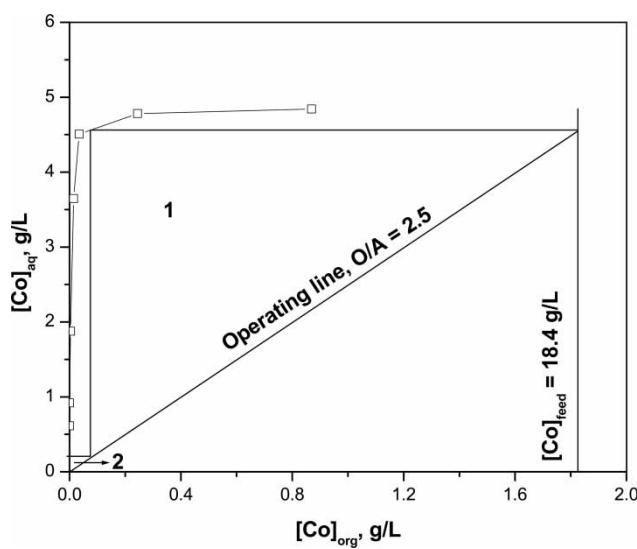
Initial pH	Final pH	Co in SO <sup>a</sup> left, g/L	% Co left in SO	% Stripping
0.99	1.17	0.00993	0.54	99.5
1.3	1.57	0.0202	1.1	98.9
1.5	2.03	0.0351	1.91	98.1
1.96	4.57	0.786	42.76	57.2
2.46	5.24	1.441	78.4	21.6

<sup>a</sup>SO = Stripped organic.

6.4, was used in optimizing conditions such as extractant and percentage neutralization, phase ratio and number of stages, for nickel recovery using partially saponified D2EHPA in kerosene as the extractant. 5 vol% TBP was used as phase modifier.

### Effect of Extractant Concentration on Nickel Extraction

From the cobalt raffinate, nickel extraction was carried out at unit phase ratio using D2EHPA concentration of 0.8 to 1 M and neutralization at 60, 70, and 80% (Table 4). The results show that neutralization of the extractant to >60% results slow phase separation (varied from 2.5 to 7 min) with an extraction efficiency of 81–92%. On the other hand, with 60% neutralization of extractant, it was 1–1.5 min with extraction efficiency of 63–76%, which



**Figure 4.** McCabe-Thiele plot for cobalt stripping with spent electrolyte.

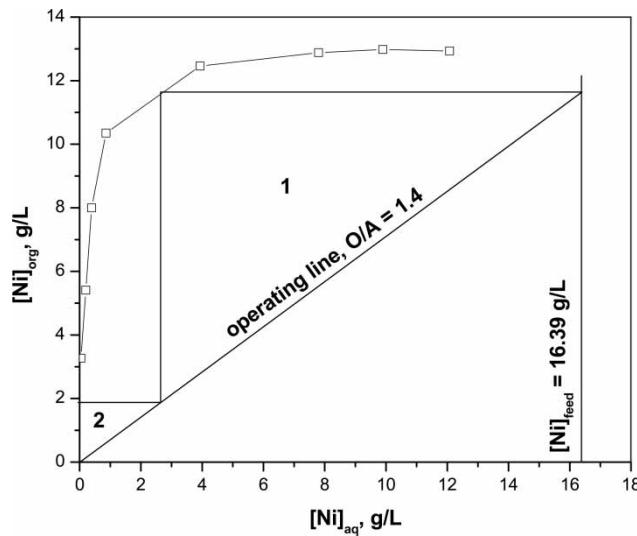
**Table 4.** Effect of extractant concentration and percent neutralisation on Ni extraction

D2EHPA, M	Neutralization, %	Eq. pH	[Ni] <sub>Aq</sub> , g/L	Ni Extraction, %	Phase separation, min
0.8	60	4.14	6.14	62.5	1.0
0.9	60	4.08	4.92	70.0	1.25
1.0	60	4.0	3.93	76.0	1.5
1.0	70	4.34	2.74	83.3	3.5
0.7	80	4.45	4.49	72.6	2.5
0.8	80	4.52	3.15	80.8	2.5
0.9	80	4.58	2.2	86.6	4.0
1.0	80	4.64	1.33	91.9	7.6

appears to be better for continuous operations using a mixer settler equipment. Further, the results suggest that O/A phase ratio of  $>1$  is necessary to extract Ni quantitatively in 2/3 stages.

### McCabe-Thiele Plot for Nickel Extraction

The extraction isotherm was obtained by contacting cobalt raffinate and 1M D2EHPA (with 60% neutralization) at different A:O phase ratios from 1 to 3 and vice versa (Fig. 5). The results show that about 99% Ni extraction

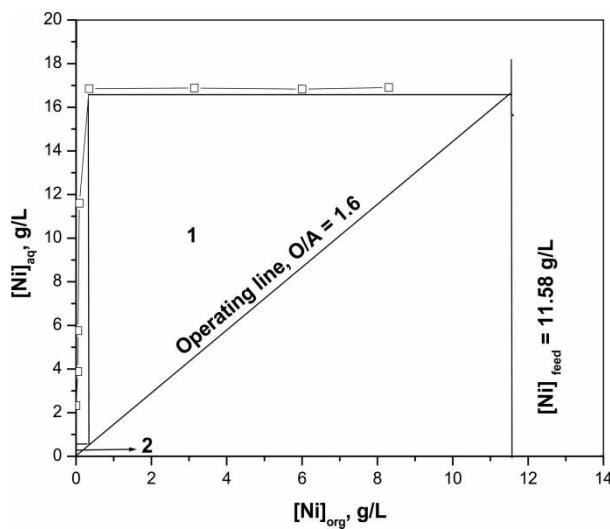


**Figure 5.** McCabe-Thiele plot for nickel extraction using partially saponified (60%) 1 M D2EHPA.

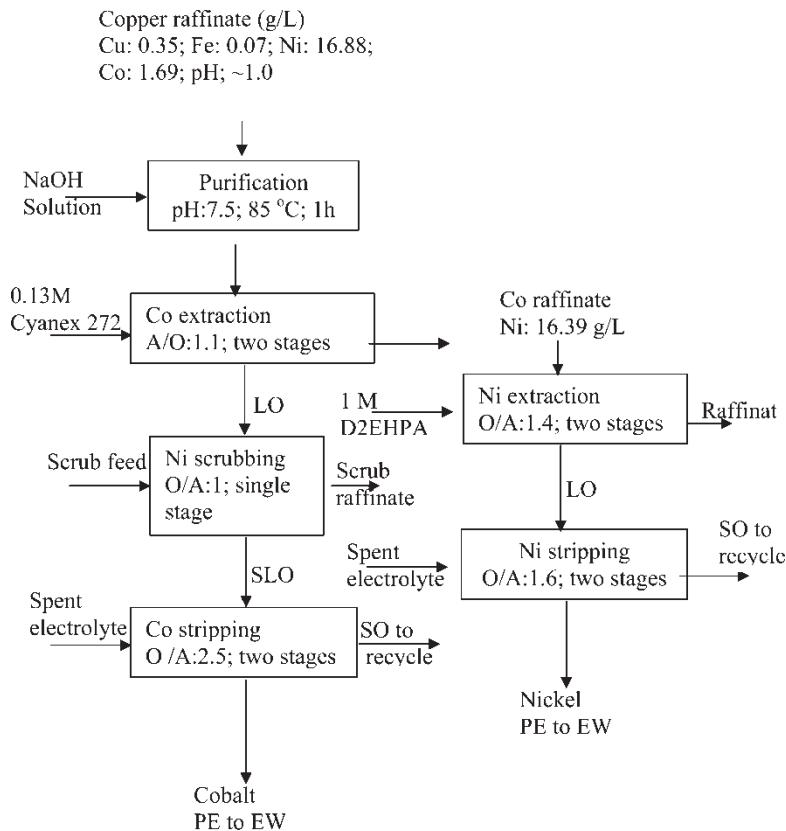
can be achieved if nickel extraction was carried for two counter-current stages at the O/A phase ratio of 1.4. Based on single stage extraction data, a two stage counter current extraction simulation test was carried out at O/A phase ratio of 1.4 and the representative raffinate showed the presence of 0.023 g/L of Ni, corresponding to an extraction efficiency of 98.9%. The LO phase contained 11.58 g/L Ni. Sufficient quantity of LO was generated under optimum conditions (using 1 M D2EHPA 60% neutralized, O/A ratio : 1.4) for carrying out nickel stripping studies.

### Stripping Isotherm of Nickel from Loaded Organic

A nickel stripping isotherm was obtained from LO containing 11.58 g/L metal with spent electrolyte (SE: Ni: 50 g/L,  $\text{Na}_2\text{SO}_4$ : 100 g/L,  $\text{H}_3\text{BO}_3$ : 15 g/L,  $\text{H}_2\text{SO}_4$ : 40 g/L) at A:O phase ratios from 1:1–5 and O:A from 1–5:1 (Fig. 6). The results clearly indicate an increase in percentage stripping with increase in acid concentration. Considering the better acid utilization, minimum number of stages, better stripping efficiency and enrichment of Ni, an O/A ratio of 1.6 was selected to carry out Ni stripping in two counter-current stages. The stripped organic contains 33 mg/L nickel, corresponding to a stripping efficiency of 99.7%. Enrichment of Ni in the pregnant electrolyte was  $\sim$ 18.5 g/L with a pH of 2.4, which can be further improved by adding one more stage. A complete flowsheet of the process is presented in (Fig. 7).



**Figure 6.** McCabe-Thiele plot for nickel stripping from loaded organic with synthetic spent electrolyte solution.



**Figure 7.** Process flowsheet for the recovery of Co and Ni from copper raffinate using saponified Cyanex 272 and D2EHPA extractants in kerosene.

## CONCLUSION

The present study demonstrated the development of a process flowsheet for the separation and recovery of cobalt and nickel from copper raffinate containing 1.65 g/L cobalt and 16.42 g/L nickel with saponified Cyanex 272 and D2EHPA diluted in kerosene. The conditions with respect to extractant concentration, phase ratio, number of stages for extraction, and stripping were optimized. Cobalt was selectively extracted with 0.13 M Cyanex 272 at O/A ratio of 1.1 in two stages and stripping Co from the loaded organic phase was affected with spent electrolyte to produce pregnant electrolyte suitable for electrowinning. Similarly conditions were established for Ni. In both the cases, the overall recovery of metals during extraction-stripping stages was >99.0%.

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