

Separation of cobalt and zinc from concentrated nickel sulfate solutions with Cyanex 272

Zhaowu Zhu, Yoko Pranolo, Wensheng Zhang and Chu Yong Cheng*

Abstract

BACKGROUND: Removal of cobalt and zinc from concentrated nickel solutions separately using two Cyanex 272 circuits has been practised in the nickel industry. However, no detailed study has been conducted and data are scarce for further improvement. This study aims to optimise the operating conditions and to simplify the process flowsheet.

RESULTS: With a synthetic solution containing 100 g L^{-1} Ni, 1.4 g L^{-1} Co and 0.8 g L^{-1} Zn and the organic solution containing Cyanex 272 and TBP in Shellsol D70, the operating conditions of extraction, scrubbing and stripping were optimised. McCabe–Thiele diagrams were constructed to determine the theoretical extraction and stripping stages and a flowsheet to separate cobalt and zinc from nickel was proposed. With this flowsheet, more than 99% cobalt and zinc could be separated, resulting in a pure nickel solution with less than 10 mg L^{-1} of cobalt and zinc.

CONCLUSIONS: The current study shows that Cyanex 272 can be used to separate cobalt and zinc in one Cyanex 272 circuit effectively from concentrated nickel solutions to obtain very pure nickel solutions suitable for nickel electrowinning or hydrogen reduction. The cobalt and zinc in the loaded strip liquor were concentrated over 10 times and can be separated readily in another much smaller solvent extraction circuit.

© 2010 Society of Chemical Industry

Keywords: Cyanex 272; nickel; cobalt; zinc; solvent extraction

INTRODUCTION

Laterite ores are the main resource of nickel and cobalt and provide 70% of their resources in the world.¹ In recent years, high pressure acid leach (HPAL) has been widely investigated and commercially practised to dissolve nickel and cobalt from laterite ores into solutions.^{2–5} In the downstream process, nickel and cobalt may be separated and recovered by three main processes: precipitation of nickel and cobalt as a mixed sulfide product (MSP) or a mixed hydroxide product (MHP) and direct solvent extraction (DSX).^{6–10} In the Murrin Murrin process,⁸ after re-leaching the MSP intermediate product, Cyanex 272 (bis(2,4,4-trimethylpentyl)phosphinic acid) is used to separate zinc from nickel (up to 120 g L^{-1}) and cobalt (up to 10 g L^{-1}) in solvent extraction (SX) circuit 1, and to separate from nickel in SX circuit 2. Both nickel and cobalt are recovered by hydrogen reduction (HR).

Cyanex 272 is the preferred extractant for separating cobalt and zinc from nickel due to its high selectivity. The separation factor for cobalt over nickel with Cyanex 272 is at least an order of magnitude higher than that with EHEHPA (2-ethylhexyl-phosphonic acid mono-2-ethylhexyl ester, PC 88-A or Ionquest 801) and D2EHPA (di-2-ethylhexylphosphoric acid).¹¹ The separation of cobalt from nickel with Cyanex 272 has well documented in the literature,^{2,12–16} however, no research work has been reported on the simultaneous separation of Co and Zn from concentrated nickel solutions.

This paper presents and discusses the test results and proposed flowsheet for separating cobalt and zinc together from nickel in the concentrated nickel solution with Cyanex 272.

EXPERIMENTAL

Reagents and solution preparation

Cyanex 272 was provided by Cytec Australia, Shellsol D70 (an aliphatic diluent) by Shell Chemicals Australia, and TBP (tributylphosphate) was purchased from Sigma-Aldrich (St. Louis, USA). All the organic reagents were used without further purification.

A synthetic feed solution was prepared by dissolving $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (both chemical grade) and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (analytical grade) in de-ionised water. Its composition by ICP analysis is given in Table 1.

Batch test procedures for extraction, scrubbing and stripping

All the tests were carried out in 0.5 or 1 L stainless steel rectangular vessels immersed in a temperature controlled water bath. A

* Correspondence to: Chu Yong Cheng, Parker Centre/CSIRO Process Science and Engineering/CSIRO Minerals Down Under National Research Flagship, PO Box 7229, Karawara, WA Australia 6152. E-mail: chu.cheng@csiro.au

Parker Centre/CSIRO Process Science and Engineering/CSIRO Minerals Down Under National Research Flagship, PO Box 7229, Karawara, WA Australia 6152

Table 1. Composition of the synthetic feed solution

Elements	Ni ²⁺	Co ²⁺	Zn ²⁺
Concentration (g L ⁻¹)	100	1.44	0.80

Eurostar digital overhead stirrer and a 40 mm diameter impeller were used for mixing. The solution temperature was maintained at $40 \pm 1^\circ\text{C}$ during testing. The solution pH was continuously monitored using a Ross Sure Flow electrode (model 8172BN, Woonsocket, USA) coupled with a Hanna portable pH meter (model HI9025, Woonsocket, USA) and adjusted by addition of diluted ammonia or sulfuric acid solutions as required. Samples were taken using a syringe, and the organic and aqueous phases were immediately separated using Whatman 1 PS filter papers.

Metal distribution isotherms and McCabe-Thiele diagram

To determine metal extraction distribution isotherms, the organic solutions were mixed with the synthetic feed solution in a range of A/O ratios at 40°C at a given pH value. The McCabe–Thiele diagram was constructed based on the metal extraction equilibrium distribution at different A/O ratios. To determine metal stripping distribution isotherms, the loaded organic solution was mixed with a strip solution in a range of A/O ratios at 40°C . The McCabe–Thiele diagram was constructed based on metal stripping equilibrium distribution at different A/O ratios.

Phase disengagement

The organic and the synthetic solutions were pre-equilibrated at 40°C and an A/O ratio of 1 : 1. The phase disengagement time (PDT) was measured for both aqueous continuous (A/C) and organic continuous (O/C) modes. To achieve A/C mode, the aqueous solution (100 mL) was placed in the mixing vessel (7×7 cm base and 10 cm height) and stirred for 2 min at 1400 rpm. The organic solution (100 mL) was then added to the vessel within 3–5 s. Mixing was stopped after exactly 1 min. The emulsion was rapidly transferred to a 250 mL measuring cylinder and timing was started immediately. The separation of the two phases was monitored by recording the time required for every 10 mL increment of clear organic and aqueous phases. Timing was stopped when 90% of the clear organic and aqueous phases were achieved. For achieving O/C mode, the organic solution was stirred first. Each test was triplicated using fresh aqueous and organic solutions to achieve PDT readings within 10% relative standard deviation (RSD).

Chemical analysis

The separated organic samples were stripped with 100 g L^{-1} sulfuric acid at an A/O ratio of 1 : 1 and 40°C . The loaded strip liquids and aqueous samples were assayed for metals using ICP-AES.

RESULTS AND DISCUSSION

Metal extraction pH isotherms

The extraction pH isotherms of cobalt, zinc and nickel were determined (Fig. 1). Considering the cobalt and zinc concentrations in the feed solution and the organic capacity, an A/O ratio of 2 : 1 was chosen in the test work. It is shown that at pH 6.0 less than 1% Ni was extracted while almost 100% zinc and about 90% cobalt were

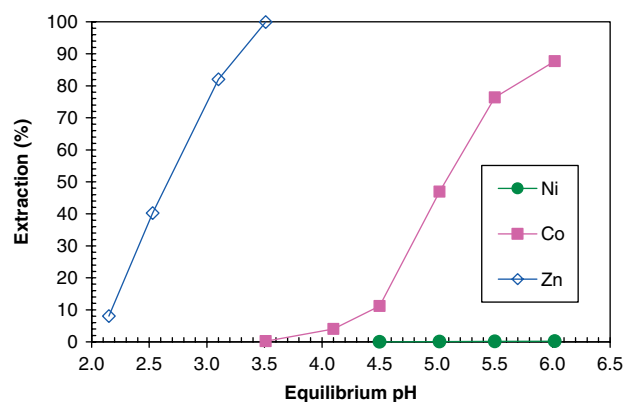


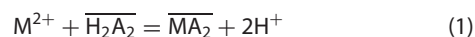
Figure 1. Metal extraction pH isotherms with 10% Cyanex 272 and 5% TBP (v/v) in Shellsol D70 at an A/O of 2 : 1 and 40°C .

Table 2. Separation factors of cobalt and zinc over nickel and the organic occupancies with 10% Cyanex 272 at an A/O of 2 : 1 and 40°C

Equilibrium pH	$\beta_{\text{Co/Ni}}$	$\beta_{\text{Zn/Ni}}$	Occupancy (%)
4.5	1390	>10 000	24.6
5.0	1157	>10 000	44.2
5.5	2448	>10 000	52.8
6.0	3081	>10 000	68.9

extracted. The results indicated that a good separation of cobalt and zinc from nickel at pH 6.0 can be achieved.

The cobalt and zinc separation factors over nickel and the organic occupancy (the percentage of the organic capacity occupied by metals) for various pH values were calculated and are shown in Table 2. Normally, Cyanex 272 exists as dimers, which may convert to monomers when it reacts with specific diluents or extracts particular metals.^{17,18} The organic occupancy was calculated based on the reaction of Equation (1).¹⁷



where M denotes Co^{2+} , Zn^{2+} and Ni^{2+} and $\overline{\text{H}_2\text{A}_2}$ the dimer of the active component of Cyanex 272 and $\overline{\text{MA}_2}$ the metal–organic complex.

The separation factors of zinc over nickel are greater than 10,000 at any tested pH values (Table 2) while that of cobalt over nickel were above 3000 at pH 6.0, indicating excellent separation of zinc and cobalt from nickel with Cyanex 272. As expected, the organic occupancy increased with increasing pH. However, when the pH was increased to 6.5, phase separation became difficult probably due to organic saturation or overloading. In order to achieve high cobalt extraction and its high separation factor over nickel, extraction in the pH range of 5.5–6.1 is preferred.^{17,19,20}

Effect of Cyanex 272 concentration on cobalt and zinc extraction

The extractions of cobalt, zinc and nickel at an A/O of 2 : 1, pH 5.5 and 6.0 with various Cyanex 272 concentrations are shown in Fig. 2. Zinc was extracted completely for all Cyanex 272 concentrations and any pH values tested. The extractions of cobalt and nickel increased with increasing Cyanex 272 concentrations and pH values. With 12% Cyanex 272, when the pH increased from 5.5 to

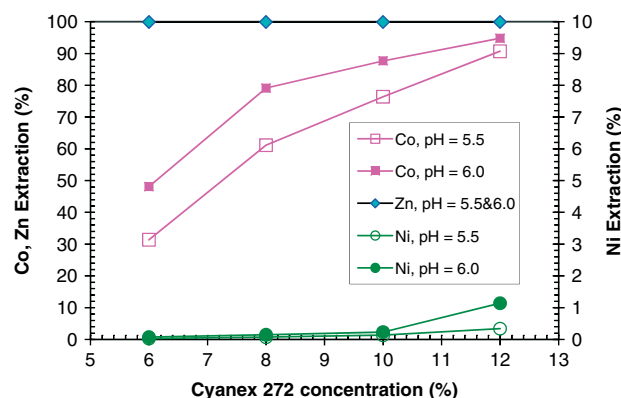


Figure 2. Effect of Cyanex 272 concentration on the extraction of cobalt, zinc and nickel at an A/O ratio of 2:1 and 40 °C.

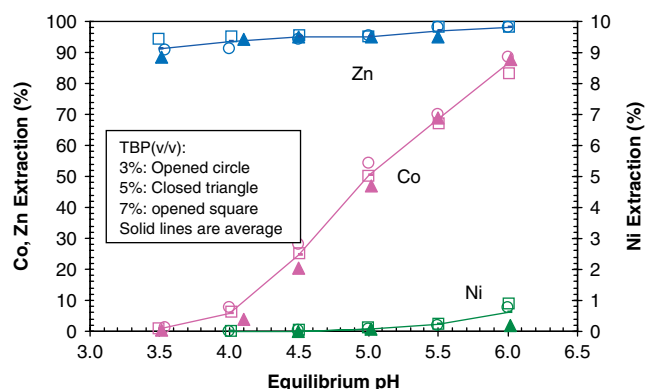


Figure 3. Metal extraction pH isotherms with 10% Cyanex 272 in Shellsol D 70 and various TBP concentrations at an A/O ratio of 2:1 and 40 °C.

Table 3. Organic occupancies and separation factors of cobalt over nickel at an A/O of 2:1 and 40 °C

Cyanex 272 (%)	pH 5.5		pH 6.0	
	Occupancy (%)	$\beta_{Co/Ni}$	Occupancy (%)	$\beta_{Co/Ni}$
6	55.1	1562	67.4	1293
8	58.5	2180	70.8	2583
10	52.8	2448	68.9	3081
12	52.6	2863	71.1	1575

6.0, the nickel extraction increased more significantly than that of cobalt, resulting in a decrease in separation factor of cobalt over nickel.

At a fixed pH, the organic occupancies were almost constant with averages of 55% and 70% at pH 5.5 and pH 6.0, respectively (Table 3). At pH 5.5, the separation factors increased with the increase in the Cyanex 272 concentration in the range tested due to more cobalt extraction than that of nickel. However, at pH 6.0, the separation factor of cobalt over nickel reached to a maximum of 3081 with 10% Cyanex 272 concentration and then it dropped quickly to 1575 when the Cyanex 272 concentration increased to 12% due to the increase in nickel extraction. This means that better separation can be achieved by optimising the extractant concentration at a fixed pH. In terms of organic occupancies and separation factor of cobalt over nickel, 10% Cyanex 272 at pH 6.0 and A/O of 2:1 are preferred.

Effect of TBP on metal extraction and phase disengagement

The effect of TBP on the metal extraction pH isotherms are shown in Fig. 3. When TBP concentrations were 3%, 5% and 7%, no significant changes in the extractions of cobalt, zinc and nickel were observed. Phase disengagement time (PDT) tests were carried out with different TBP concentrations in the organic phase and the results are shown in Fig. 4 for aqueous continuity and in Fig. 5 for organic continuity. For aqueous continuity, the shortest organic phase PDT of 280 s was obtained with 5% TBP compared with 350 s without TBP addition, indicating that 5% TBP is the optimised concentration to improve organic phase disengagement in an aqueous continuity mode (Fig. 4). No noticeable effect was observed on the phase disengagement time when the operation was in an organic continuity mode (Fig. 5).

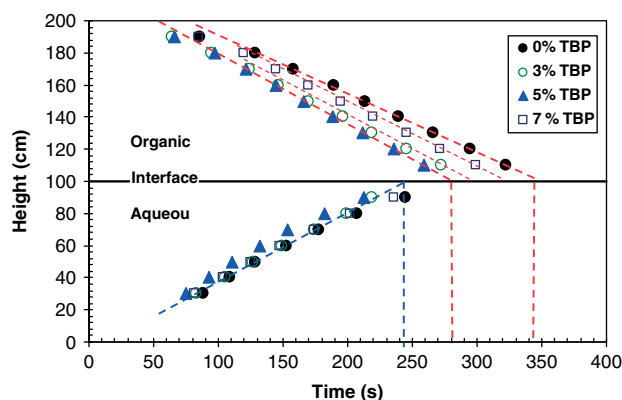


Figure 4. Effect of TBP concentration on phase disengagement time in extraction with 10% Cyanex 272 at an A/O ratio of 1:1 in aqueous continuity.

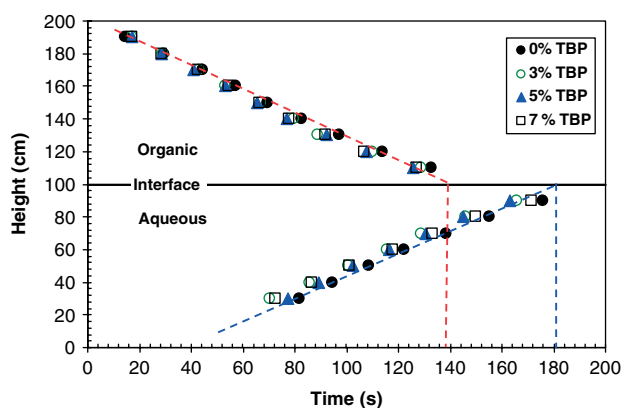


Figure 5. Effect of TBP concentration on phase disengagement time in extraction with 10% Cyanex 272 at an A/O ratio of 1:1 in organic continuity.

Determination of number of extraction stages

As zinc was more easily extracted than cobalt by Cyanex 272 at the same pH (Fig. 1), the number of stages required for cobalt extraction should be adequate for extraction of zinc. Therefore, only cobalt extraction was taken into consideration in the determination of the number of extraction stages by construction of its McCabe–Thiele diagram. The McCabe–Thiele diagram constructed for cobalt extraction is shown in Fig. 6. It is

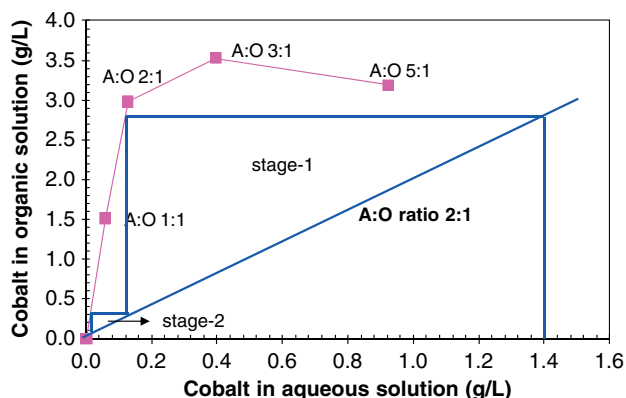


Figure 6. The McCabe–Thiele diagram for cobalt extraction with organic solution containing 10% Cyanex 272 and 5% TBP in Shellsol D70 at an A/O ratio of 2:1, 40 °C and pH 6.0.

Table 4. Nickel scrubbing efficiencies and metal concentrations in various solutions

Metal in scrub solution (g L ⁻¹)			Metal in scrubbed organic (g L ⁻¹)			Metal in loaded scrub liquor (g L ⁻¹)			Ni scrubbing efficiency (%)
Co	Zn	pH	Ni	Co	Zn	Ni	Co	Zn	
3.00	2.00	5.6	0.12	3.54	2.21	3.32	0.03	0.29	83.1
1.50	1.25	5.6	0.11	3.18	1.98	3.37	0.24	0.01	85.4
3.00	2.00	5.2	0.05	3.34	2.20	3.62	1.45	0.02	92.9
1.50	1.25	5.2	0.07	3.06	1.97	3.38	0.78	0.01	90.6

seen that for 1.44 g L⁻¹ Co in the feed solution, two stages are required to reduce its concentration to less than 10 mg L⁻¹ in the raffinate. The cobalt recovery would be more than 99%, and the Ni/Co ratio in the raffinate would be greater than 10⁴, which meets the requirement for nickel electrowinning.

Nickel scrubbing from loaded organic solution

Although nickel extraction was very low with Cyanex 272 under optimum conditions, a noticeable amount of nickel was co-extracted due to its high concentration of over 100 g L⁻¹. Therefore, scrubbing is needed to ensure its high recovery in the raffinate and the purity of the cobalt final product. Batch tests were carried out with the organic solution consisting of 10% Cyanex 272 and 5% TBP in Shellsol D70. The organic solution was loaded at an A/O ratio of 2:1, pH 6.0 and 40 °C and contained 2.85 g L⁻¹ Co, 1.79 g L⁻¹ Zn and 0.72 g L⁻¹ Ni. Two synthetic scrubbing solutions containing 3.0 g L⁻¹ Co and 2.0 g L⁻¹ Zn, and 1.5 g L⁻¹ Co and 1.25 g L⁻¹ Zn were employed at two pH values of 5.2 and 5.5. The four scrubbing tests were carried out at an A/O ratio of 1:5 and 40 °C. The nickel scrubbing efficiencies and the metal concentrations in the scrubbed organic solutions and the loaded scrub liquors are given in Table 4.

Obviously, a higher nickel scrubbing efficiency can be obtained at relatively lower pH. For example, when the scrub pH decreased from 5.6 to 5.2, the nickel scrubbing efficiency increased from 83% to 93% with the scrub solution containing 3.0 g L⁻¹ Co and 2.0 g L⁻¹ Zn, and from 85% to 91% with the scrub solution containing 1.5 g L⁻¹ Co and 1.25 g L⁻¹ Zn. The concentrations of cobalt and zinc in the scrubbing solution showed no significant

Table 5. Calculated percentage of cobalt and zinc to replace nickel and percentage of cobalt and zinc recycled

Metal in scrub solution (g L ⁻¹)					
Co	Zn	pH	P _{Ni/(Co,Zn)} (%)	R _{Co} (%)	R _{Zn} (%)
3.00	2.00	5.6	56.51	2.00	0.39
1.50	1.25	5.6	122.4*	1.66	0.12
3.00	2.00	5.2	77.98	10.2	0.17
1.50	1.25	5.2	176.3*	5.48	0.06

* More than 100% means that some nickel was scrubbed out by the acid, and not replaced by cobalt and zinc.

effect on the nickel scrubbing. However, lower pH would lead to higher cobalt concentrations in the loaded scrub solution and would result in more cobalt recycling to the extraction stages in a continuous process. For instance, at a scrub pH of 5.2, when the cobalt and zinc concentrations in the scrub solution increased from 1.5 and 1.25 g L⁻¹ to 3.0 and 2.0 g L⁻¹, respectively, the cobalt concentration in the loaded scrub liquor was almost doubled, increasing from 0.78 g L⁻¹ to 1.45 g L⁻¹ (Table 4). Equations (2), (3) and (4) are used to calculate the percentages of cobalt and zinc replacing nickel in the organic solution during scrubbing and the percentages of cobalt and zinc in the loaded scrub liquor which would be recycled to extraction stages in a continuous process, respectively. The calculated results are shown in Table 5.

$$P_{Ni/(Co,Zn)} = \frac{[\overline{Ni}_L] - [\overline{Ni}_S]}{([\overline{Co}_S] - [\overline{Co}_L]) + ([\overline{Zn}_S] - [\overline{Zn}_L])} \times 100 \quad (2)$$

$$R_{Co} = \frac{[\overline{Co}_S]}{5[\overline{Co}_L]} \times 100 \quad (3)$$

and

$$R_{Zn} = \frac{[\overline{Zn}_S]}{5[\overline{Zn}_L]} \times 100 \quad (4)$$

In Equation (2), $P_{Ni/(Co,Zn)}$ represents the percentage of cobalt and zinc replacing nickel in the organic solution during scrubbing. $[\overline{Ni}_L]$, $[\overline{Co}_L]$ and $[\overline{Zn}_L]$ denote the concentrations (mol L⁻¹) of nickel, cobalt and zinc in the loaded organic solution, respectively, and $[\overline{Ni}_S]$, $[\overline{Co}_S]$ and $[\overline{Zn}_S]$ the concentrations (mol L⁻¹) of nickel, cobalt and zinc in the scrubbed organic solution, respectively. In Equations (3) and (4), R_{Co} and R_{Zn} represent the percentage of cobalt and zinc in the loaded scrub solution which would be recycled to the extraction stage in a continuous process. $[\overline{Co}_L]$ and $[\overline{Zn}_L]$ denote the Co and Zn concentrations (mol L⁻¹) in the loaded organic solution, respectively and Co_S and Zn_S the cobalt and zinc concentrations (mol L⁻¹) in the loaded scrub liquor, respectively. The O/A ratio used in the experiment was 5.

By comparison of the calculated results with the two scrubbing solutions and the two scrubbing pH values (Table 5), it can be seen that at the lower pH of 5.2 with the scrubbing solution containing 3.0 g L⁻¹ Co and 2.0 g L⁻¹ Zn, the percentage of cobalt recycled was up to 10%. High cobalt recycling resulted in a decrease in throughput and an increase in base and acid consumption. With the lower pH of 5.2 and the scrub solution containing 1.5 g L⁻¹ Co and 1.25 g L⁻¹ Zn, the $P_{Ni/(Co,Zn)}$ reached 176.3%, indicating that a large part of the co-extracted nickel was scrubbed by acid, and not replaced by cobalt and zinc. This results in an increase in base and acid consumption, indicating higher operating costs. With

Table 6. Calculated nickel scrubbing efficiency (P_{Ni}) in each scrubbing stage and Co/Ni ratio (w/w) in the scrubbed organic solution from each scrubbing stage with the scrubbing solution containing 1.5 g L^{-1} Co and 1.25 g L^{-1} Zn at pH 5.6

Stage 1		Stage 2		Stage 3	
P_{Ni} (%)	Co/Ni ratio	P_{Ni} (%)	Co/Ni ratio	P_{Ni} (%)	Co/Ni ratio
86.9	27.1	97.9	191	99.7	1228

the higher pH of 5.6 and the scrub solution containing 3.0 g L^{-1} Co and 2.0 g L^{-1} Zn, the percentage of cobalt and zinc used for replacing nickel was only 54%, indicating that scrubbing efficiency of nickel by cobalt and zinc was low. Comparatively, with the higher scrub pH of 5.6 and scrubbing solution containing 1.5 g L^{-1} Co and 1.25 g L^{-1} , the $P_{Ni}/(\text{Co, Zn})$ value was 122.4%, indicating only 22.4% Ni was scrubbed by acid and less than 1.7% Co and Zn was recycled with a nickel scrubbing efficiency of 85.4% (Table 4). This suggests that with the higher scrub pH of 5.6 and the scrub solution containing lower concentrations of cobalt and zinc, both high nickel scrubbing efficiency and low cobalt recycling were obtained. Optimum scrub pH and concentrations of cobalt and zinc in the scrub solution can be obtained with additional tests.

If the distribution ratio of nickel in each scrub stage is the same, the nickel scrubbing efficiency in each theoretical stage calculated²¹ based on Equation (5) is shown in Table 6.

$$P_{Ni} = \bar{N}_{iL} \left[1 - \left(\frac{V_A}{V_O D_{Ni}^n} - 1 \right) \left(\frac{V_A}{V_O D_{Ni}^{n+1}} - 1 \right) \right] 100 \quad (5)$$

where P_{Ni} represents the percentage of nickel scrubbed from the loaded organic solution, \bar{N}_{iL} the nickel concentration (g L^{-1}) in the loaded organic solution, V_A and V_O the aqueous and organic flowrate (L min^{-1}), respectively, and D_{Ni}^n and D_{Ni}^{n+1} the nickel distribution coefficient in scrubbing stage n and $n+1$, respectively.

Under optimum conditions, more than 99% Ni could be scrubbed from the loaded organic solution and the Co/Ni concentration ratio in the loaded strip liquor could reach more than 1000 theoretically after three stages of scrubbing. Based on the requirement for Co/Ni ratio of 700 for cobalt electrowinning,²² three scrubbing stages would be required.

Cobalt and zinc stripping

After nickel scrubbing, cobalt and zinc in the scrubbed organic solution would be purified. The stripping pH isotherms of cobalt and zinc are shown in Fig. 7.

From Fig. 7, it can be seen that at a pH of approximately 3.5, almost 99% Co could be stripped with only about 1% Zn co-stripped to the cobalt loaded strip liquor. The separation factor of zinc over cobalt was ~ 7000 , indicating that selective stripping of cobalt¹⁵ to separate it from zinc could be employed in the pH range 3.0–3.5. A pure zinc product solution could be obtained with scrub stages and a pure cobalt product solution with scavenging stages using a small portion of the same organic solution. In the current paper, cobalt and zinc were stripped together using 105 g L^{-1} H_2SO_4 with various A/O ratios at 40°C (Table 7).

More than 99.9% Co and 96% Zn were stripped in a single contact with the strip solution at an A/O ratio of 1 : 10. The equilibrium pH was 0.90, indicating a small amount of acid remaining in the loaded strip liquor. One stage is enough to almost completely strip cobalt,

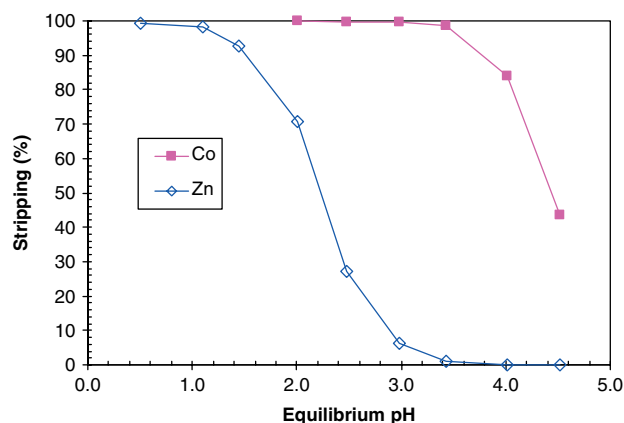


Figure 7. Stripping pH isotherms of cobalt and zinc with organic solution containing 10% Cyanex 272 and 5% TBP in Shellsol D70 at an A/O ratio of 1 : 1 and 40°C .

Table 7. Stripping of cobalt and zinc using 105 g L^{-1} H_2SO_4 with different A/O ratios at 40°C

A/O ratio	Co (g L^{-1})		Zn (g L^{-1})		Equilibrium pH	Strip efficiency (%)	
	* Aq.	** Org.	* Aq.	** Org.		Co	Zn
1 : 1	2.93	0.001	1.68	0.012	–	99.96	99.35
1 : 5	14.8	0.001	8.74	0.052	–	99.98	97.20
1 : 10	30.2	0.001	16.64	0.068	0.90	99.98	96.33
1 : 15	45.4	0.001	4.94	1.338	1.88	99.96	27.30

* Aq. = loaded strip liquor and
** Org. = stripped organic solution.

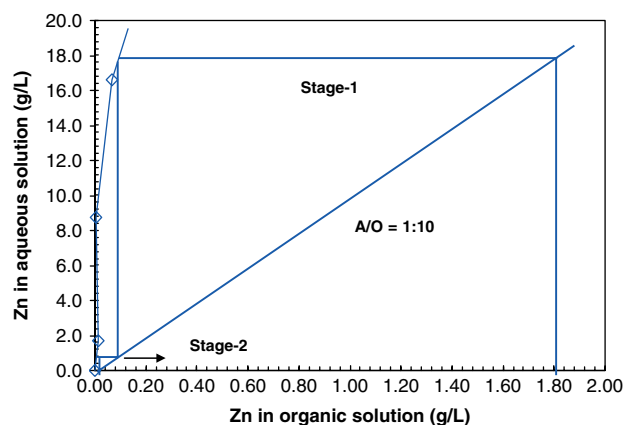


Figure 8. A McCabe–Thiele diagram for Zn stripping with organic solution containing 10% Cyanex 272 and 5% TBP in Shellsol D70 and 105 g L^{-1} H_2SO_4 strip solution at 40°C .

with only 1 mg L^{-1} left in the organic phase. The McCabe–Thiele diagram was constructed for zinc stripping with the same organic solution at an A/O ratio of 1 : 10 (Fig. 8), indicating that less than 10 mg L^{-1} Zn would be left in the organic solution with two theoretical stripping stages. Both cobalt and zinc recoveries could be more than 99%. In the loaded strip liquor, the concentrations of cobalt and zinc would be increased by 10 times that in the feed solution.

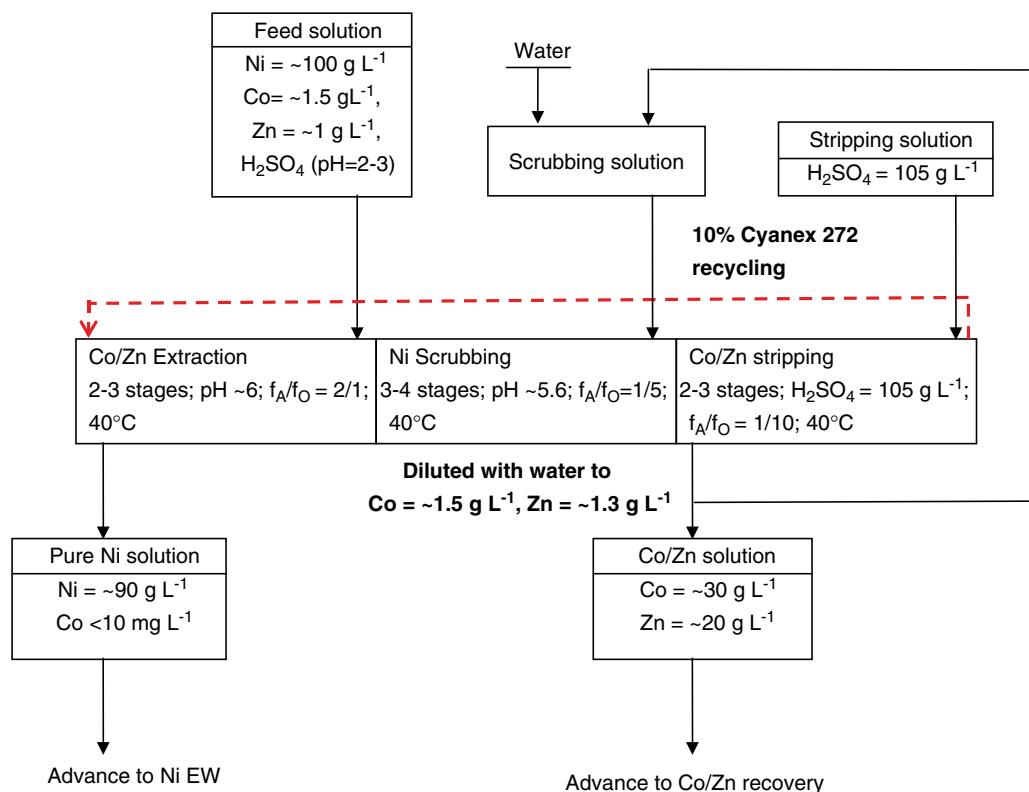


Figure 9. A proposed process flowsheet for the separation of cobalt and zinc from high nickel concentration solution with Cyanex 272.

Proposed flowsheet for the separation of cobalt and zinc from nickel

Summarising the above optimum conditions, the flowsheet for nickel purification and cobalt and zinc recovery with the synthetic feed solution is proposed in Fig. 9. The feature of this flowsheet is that pure nickel solution can be obtained in a single SX circuit instead of two consecutive SX circuits using Cyanex 272, resulting in capital and operating cost savings. The cobalt could be separated from the zinc in the much concentrated loaded strip liquor using another much smaller SX circuit with Cyanex 272, Ionquest 801 or D2EHPA.

Generally, in an industrial nickel purification process, metal impurities such as Fe(III), Al(III), Cu(II), Mn(II), Mg(II), and Ca(II) are removed before the separation of cobalt and zinc from nickel. If the above minor metal impurities are present in the feed solution, Fe(III), Al(III), Cu(II) and Mn(II) could enter the Co–Zn stream and most of the Mg(II) and all the Ca(II), together with all the nickel, could report to the raffinate.^{14,23}

CONCLUSIONS

Cyanex 272 is an effective extractant for the separation of cobalt and zinc from concentrated nickel sulfate solutions. It was found that for a feed solution containing about 1.4 g L^{-1} Co, 0.8 g L^{-1} Zn and 100 g L^{-1} Ni, an organic solution containing 10% Cyanex 272 and 5% TBP in Shellsol D70 at A/O ratio of 2:1 was the preferred. Two theoretical extraction stages would be needed to extract more than 99% Co and Zn, resulting in a Ni/Co ratio of over 10^4 in the raffinate. The co-extracted nickel could be scrubbed with a scrub solution containing about 1.5 g L^{-1} Co and 1.25 g L^{-1} Zn at pH 5.6. The scrub solution could be obtained by diluting the loaded cobalt and zinc strip liquor. Theoretically, three scrubbing

stages could achieve a Co/Ni ratio of greater than 700 in the Co product solution. In batch stripping tests, it was found that with a strip solution containing 105 g L^{-1} H_2SO_4 at an A/O of 1:10, more than 99% Zn and Co was stripped into the loaded strip liquor with a final pH of about 0.9. A McCabe–Thiele diagram for zinc stripping showed that two theoretical strip stages would be required to almost completely strip the cobalt and zinc from the loaded organic solution.

ACKNOWLEDGEMENTS

The authors would like to thank Dr Matthew Jeffrey for reviewing this paper and providing valuable comments. The support of the Parker CRC for Integrated Hydrometallurgy Solutions (established and supported under the Australian Government's Cooperative Research Centres Program) is gratefully acknowledged.

REFERENCES

- 1 Sudol S, The thunder from Down Under – everything you wanted to know about nickel laterites but were afraid to ask. *Can Mining J* **126**:8–12 (2005).
- 2 Moskalyk RR and Alfantazi AM, Nickel laterite processing and electrowinning practice. *Min Eng* **15**:593–605 (2002).
- 3 Cheng CY and Urbani MD, Purification of laterite leach solutions by direct solvent extraction. in *Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies, Aqueous and Electrochemical Processing*, ed by Kongoli F, Itagaki K, Yamauchi C and Sohn HY. TMS, Warrendale, **3**: 251–265 (2003).
- 4 Dalvi AD, Bacon WG and Osborne RC, The past and the future of nickel laterites. *PDAC 2004 International Convention, Trade Show & Investors Exchange*, Ontario, Canada, March 7–10 (2004).
- 5 Scarlett NVY, Madsen IC and Whittington BI, Time-resolved diffraction studies into the pressure acid leaching of nickel laterite ores:

- a comparison of laboratory and synchrotron X-ray experiments. *J Appl Crystal* **41**:572–583 (2008).
- 6 Cheng CY, Boddy G., Zhang W, Godfrey M, Robinson D, Pranolo Y, *et al*, Direct solvent extraction for recovery of nickel and cobalt from Rio Tinto laterite leach solutions. *COM' 09/Hydrometallurgy of Nickel-Cobalt*, August 23–26, Sudbury, Canada, pp. 243–254 (2009).
 - 7 Eberhard K and Derek K, Nickel processing techniques and the next millennium. *1999 Parker Centre Hydrometallurgy Conference*, October 10–12, Perth, Australia (1999).
 - 8 Motteram G., RyanBerezowsky MR and Raudsepp R, Murrin Murrin nickel and cobalt project: Project development overview. Nickel and Cobalt Pressure Leaching and Hydrometallurgy Forum, May, 1996, Perth, Western Australia, Alta Metallurgical Service (1996).
 - 9 Cheng CY and Urbani MD, Solvent extraction process for separation cobalt and/or nickel from impurities. Patent No. WO 2005/073416 A1 (2005).
 - 10 Cheng CY, Solvent extraction of nickel and cobalt with synergistic systems consisting of carboxylic acid and aliphatic hydroxyoxime. *Hydrometallurgy* **84**:109–117 (2006).
 - 11 Flett DS, Solvent extraction in hydrometallurgy: the role of organophosphorus extractants. *J Organomet Chem* **690**:2426–2438 (2005).
 - 12 Parhi PK, Panigrahi S, Sarangi K and Nathsarma KC, Separation of cobalt and nickel from ammoniacal sulfate solution using Cyanex 272. *Sep Purif Technol* **59**:310–317 (2008).
 - 13 Rickelton WA, Flett DS and West DW, Cobalt-nickel separation by solvent extraction with bis(2,4,4-trimethylpentyl)phosphinic acid. *Solv Extr Ion Exch* **2**:815–838 (1984).
 - 14 Senapati D, Chaudhury GR and Sarma PVR Bhaskara, Purification of nickel sulfate solutions containing iron, copper, cobalt, zinc and manganese. *J Chem Technol Biotechnol* **59**:335–339 (1994).
 - 15 Lerner O, Ilan Y and Kleinberger R, Cobalt extraction and stripping by Cyanex 272. *ALTA 2006 Conference*, May 14–17, Perth, Australia (2006).
 - 16 Park KH and Mohapatra D, Process for cobalt separation and recovery in the presence of nickel from sulfate solutions by Cyanex 272. *Met Mater Int* **12**:441–446 (2006).
 - 17 Zbigniew H and Halina H, Study on the extraction process of nickel (II) sulfate purification using Cyanex 272. *Hydrometallurgy* **40**:65–67 (1996).
 - 18 Biswas RK and Singha HP, Densities, viscosities and excess properties of bis-2,4,4-trimethylpentylphosphinic acid (Cyanex 272)+diluent binary mixtures at 298.15 K and atmospheric pressure. *J Mol Liquids* **135**:179–187 (2007).
 - 19 Chou EC and Beckstead LW, Separation of nickel and cobalt from sulfate solutions by solvent extraction. Patent No. US 4900522 (1990).
 - 20 O'Callaghan J and Chamberlain A, Solvent extraction of impurities from concentrated metal sulfate solutions. Patent No. US 2004/0052707 A1 (2004).
 - 21 Donegan S, Direct solvent extraction of nickel at Bulong operations. *Min Eng* **19**:1234–1245 (2006).
 - 22 Chopping G, Liljenzin JO and Rydberg J, *Radiochemistry and Nuclear Chemistry*, 3rd edn. Butterworth-Heinemann, Wildwood Avenue, Woburn, MA (2002).
 - 23 Tsakiridis PE and Agatzini-Leonardou S, Solvent extraction of aluminium in the presence of cobalt, nickel and magnesium from sulfate solutions by Cyanex 272. *Hydrometallurgy* **80**:90–97 (2005).