High Purity Nickel Recovery from an Industrial Sidestream Using Concentration and Liquid–Liquid Extraction Techniques

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This article outlines an alternative flowsheet for the purification of a multi-metal industrial sidestream (16.3 g/l Ni, 0.7 g/l Co, 0.6 g/l Ca and 1.6 g/l Mg) to allow high-purity nickel recovery. The methodology comprises an initial evaporation step to achieve Ca removal followed by impurity (Ca, Mg) and valuable (Co, Ni) element separation via two-step solvent extraction with organophosphorus extractants. Results indicate that > 80% of Ca is selectively removed as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ by evaporation with a concentration degree > 6. In the following treatment, ~ 90% of residual Ca (0.6 g/l) can be selectively extracted with $\text{Na-D}_2\text{EHPA}$. The subsequent solvent extraction step with Na-Cyanex 272 separates Co (> 99%) and Mg (> 95%). The resultant nickel sulfate solution (61.7 g/l Ni, 0.3 g/l Mg and Co 0.007 g/l) of > 99.5% purity can be directly integrated into state-of-the-art nickel recovery processes.

INTRODUCTION

Nickel and cobalt production is essential to ensure the smooth functionality of industrial material supply chains that range from stainless steel to batteries. Consequently, the ability to efficiently recover nickel and cobalt from industrial hydrometallurgical sidestreams, for example, can have a significant impact on the related process economics and the future sustainability of these valuable resources.^{1–3} Nevertheless, in such process solutions impurities such as Ca, Cu, Mg, Al, Mn and Fe are often present. As a result, it is desirable that the most valuable elements—Ni and Co—are efficiently separated from these impurities to meet the required purity demands.

It has been previously reported that nickel recovery from industrial sidestreams can be achieved by a number of hydrometallurgical-based routes such as chemical precipitation,^{4,5} ion exchange,^{6,7} membrane technology,⁸ solvent extraction,^{9,10} cooling crystallization^{11,12} and electrowinning.^{13,14} Of

these, solvent extraction (SX) has become established as a commercially viable industrial-scale unit process that allows nickel capture.^{15–17} For example, in the Cawse plant (Australia), after re-leaching of the nickel/cobalt hydroxide precipitate with ammonia-ammonium carbonate medium, the SX step was used to separate Ni with 2-hydroxy-5-nonylacetophenone oxime (LIX84-I) in preference to Ca, Co, Mg, Mn and Zn.¹⁸ The Bulong process involved the direct extraction of Ni with neodecanoic acid (Versatic 10) after extraction of Co with bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), while impurities—Cu, Zn, Mn, Mg and Ca—remained in the raffinates.¹⁹ More recently, Guimaraes et al. investigated the purification of nickel sulfate solution from synthetic Ni-rich solutions by SX with Cyanex 272 and mixtures of Cyanex 272 and Versatic 10.²⁰ It was found that impurities such as Zn, Co, Cu and Mn could be selectively extracted using Cyanex 272, whereas preferential extraction of Ca and Mg was achieved by mixtures of Cyanex 272 and Versatic 10. The

same authors also evaluated the separation of Ca and Mg vs. Ni using bis(2-ethylhexyl) phosphate acid (D₂EHPA) and Cyanex 272.²¹ In general, for complex industrial solutions, the choice of suitable process depends on how effectively and efficiently impurities can be removed while concurrently maximizing the yield and purity of the desired final products.

In the present work, a comprehensive study for purification of an industrial sidestream was explored. To allow the recovery of high-purity nickel products (rather than low-value mixed metal precipitate), the current investigation addresses issues related to the dilute and impure nature of the investigated solution as follows: (1) concentration and Ca removal by evaporation from the sidestream (PLS1); (2) residual Ca removal from the concentrated nickel-rich solution (PLS2) by the first SX step with saponified D₂EHPA (Na-D₂EHPA); (3) extraction of Co and Mg over Ni from a mixed solution (PLS5)—which is composed of the Ca-free solution (PLS3) and the scrubbing solution of the loaded D₂EHPA (PLS4)—through a second SX step with saponified Cyanex 272 (Na-Cyanex 272); (4) production of a purified solution (PLS6), which can be fully integrated into state-of-the-art processes for high-purity nickel recovery. The schematic flowsheet for these various process steps is outlined in Fig. 1. Moreover, a systematic evaluation of the precipitation and separation behaviors of the metal ions at each step of the process was performed.

MATERIALS AND METHODS

Materials

The process solution (PLS1) comprised an industrial sidestream with a composition of 16.3 g/l Ni, 0.7 g/l Co, 0.6 g/l Ca and 1.6 g/l Mg and a pH value of approximately 4.2. The extractants D₂EHPA (97%, Sigma-Aldrich, Germany) and Cyanex 272 (97%, Cytec, USA) were used as reagents for the SX processes, while kerosene (97%, Sigma-Aldrich, Germany) was used as a diluent. Sodium hydroxide (97%, Sigma-Aldrich, Germany) and sulfuric acid (96%, Merck, France) were used to prepare the saponification solution and the scrubbing solution, respectively. Deionized water (resistivity ≤ 18.2 M Ω .cm, Merck Millipore, Germany) was used throughout for all experiments.

Concentration Studies

Evaporation studies were conducted to remove Ca and concentrate the solution in preparation for the subsequent SX steps. PLS1 with an initial volume of 400 ml was heated in a 500-ml open glass beaker at $100 \pm 1^\circ\text{C}$ and stirred with a magnetic stirrer apparatus (MR Hei-Connect, Heidolph Instruments, Germany) at a speed of 350 rpm. A focused beam reflectance measurement (FBRM) Particle Track system (Mettler Toledo G400, USA) that allowed the continuous in situ monitoring of chord length sizes of particles, total count rates or count rates of the different chord length fractions was used to monitor precipitation of calcium sulfate during the

Fig. 1. Schematic flowsheet for the purification of the industrial sidestream.

evaporation period. The probe-based Particle Track was immersed into the solution such that the particles could flow freely through the probe window. A focused laser was then utilized to produce a beam spot with a fixed rotation speed of 2 m/s at the sapphire window to detect the presence of particles via laser light backscatter. The pulses of backscattered light were counted, and the duration of each pulse multiplied by the scan speed was used for the chord length determination. A balance (572 Kern & Sohn GmbH, Germany, $d = 0.01$ g) was used to determine the mass of the PLS1 and the concentrated solutions. The volume of the concentrated solutions, V_r , could then be calculated as follows:

$$V_r = V_i - \frac{m_i - m_r}{\rho} \quad (1)$$

The concentration degree, $X_{Vi/Vr}$, was determined according to Eq. 2:

$$X_{Vi/Vr} = \frac{V_i}{V_r} \quad (2)$$

And the removal efficiency of Ca (R_{Ca}) was calculated by Eq. 3:

$$R_{Ca} = \left(1 - \frac{C_r \times V_r}{C_i \times V_i}\right) \times 100\% \quad (3)$$

where V_i and V_r (l) represent the volume of the PLS1 and the PLS2, respectively; m_i and m_r (g) are the corresponding mass of the PLS1 and the PLS2. ρ is the density of water (1.0 g/ml); C_i and C_r (g/l) are the concentration of Ca in the PLS1 and the PLS2, respectively.

Solvent Extraction Studies

The extractants D₂EHPA and Cyanex 272 were first diluted with kerosene and then correspondingly saponified by 10 M and 5 M NaOH solutions prior to their use as extractants.^{22,23} Extraction experiments were carried out in an incubator shaker (Model KS 3000i, IKA, Germany). Equal volumes (10 ml) of the organic and aqueous solutions were mixed in the funnels and then shaken for 10 min with a fixed shaking speed of 250 rpm at $25 \pm 1^\circ\text{C}$. After phase disengagement, the concentrations of Ni, Co, Ca and Mg in the aqueous solutions were analyzed, and the concentrations of the metal ions in the loaded organic phases were determined by mass balance.

Extraction efficiency, E , was defined as:

$$E = \frac{[M]_o V_o}{[M]_o V_o + [M]_a V_a} \times 100\% \quad (4)$$

whereas the separation factor of Ca over Ni, $SF_{Ca/Ni}$, was calculated according to the distribution coefficient of the extracted components (D_M):

$$D_M = \frac{[M]_o}{[M]_a} \times \frac{V_o}{V_a} \quad (5)$$

$$SF_{Ca/Ni} = \frac{D_{Ca}}{D_{Ni}} \quad (6)$$

where $[M]_o$ and $[M]_a$ (g/l) are the concentrations of the respective metal ions in the loaded organic phase and the aqueous phase after equilibrium. V_o and V_a (l) are the corresponding volumes of the loaded organic phase and the aqueous phase.

In the scrubbing tests, the co-extracted metal ions were removed from the loaded organic phases using H₂SO₄ solutions with a range of concentrations at an aqueous-to-organic phase (A/O) ratio of 1:1 and a temperature of 25°C. All the systems were reacted for 10 min, and the results from preliminary experiments indicated that this duration was sufficient to establish equilibrium conditions.

Characterization Methods

The concentrations of the metal ions within the solid products (dissolved with aqua regia) and the aqueous solutions were determined using either inductively coupled plasma-optical emission spectroscopy (ICP-OES, PerkinElmer Optima 7100 DV, USA) or atomic adsorption spectroscopy (FAAS, Varian AA240). The solid products were also characterized by XRD (PANalytical X'Pert Pro Powder, The Netherlands) and SEM (LEO 1450, Carl Zeiss Microscopy GmbH, Germany).

RESULTS AND DISCUSSION

Concentration Behaviors of the Metal Ions

The plots in Fig. 2a–d display the concentration behaviors of the metal ions during evaporation. Figure 2a shows that the concentrations of Ni, Co and Mg increase exponentially as the solution becomes more concentrated, whereas, in contrast, the concentration of Ca is observed to continuously decrease, for example, the solution at $X_{Vi/Vr} = 6$ —comprised of 89.2 g/l Ni, 4.3 g/l Co, 0.6 g/l Ca and 7.7 g/l Mg—has an $\sim 80\%$ precipitation yield of Ca. Further concentration to an $X_{Vi/Vr}$ value of 8 results in a solution with 114.5 g/l Ni, 5.2 g/l Co, 0.6 g/l Ca and 9.0 g/l Mg and precipitation yield of Ca = 87% (as shown in Fig. 2b). These results indicate that Ca can be readily separated from the solution because of its low solubility.²⁴ Figure 2c presents the chord length counts recorded during the evaporation period, as determined by the Particle Track system. As can be observed, the counts of chord length $< 10 \mu\text{m}$ begin to increase at the $X_{Vi/Vr}$ of ca. ~ 2 after 1.6 h, which indicates the nucleation of solid particles. With longer experimental time, the counts of $< 10 \mu\text{m}$ and 10–100 μm

Fig. 2. (a) Concentration of the metal ions at different X_{Vi}/V_r ; (b) precipitation yield of Ca against Ni concentration; (c) particle counts against evaporation time; (d) XRD pattern and SEM image of the solid precipitate.

continue to rise rapidly, demonstrating that both nucleation and solid crystal growth increase during the evaporation period.

The solid precipitate obtained at $X_{Vi}/V_r = 8$ was separated and washed with the deionized water three times. Analysis of the washing water showed that it contained 5.9 g/l Ni, 0.3 g/l Co, 0.2 g/l Ca and 0.6 g/l Mg, which was slightly more dilute compared with the PLS1; however, it was possible to recycle this solution back to the evaporation stage. The contents of Ni, Mg and Co in the washed solid precipitate were determined to be 3.2% (g/g), 0.3% (g/g) and 0.7% (g/g), respectively, which implied that only 0.3% Ni, 0.3% Mg and 1.6% Co were lost within the calcium precipitate. Subsequent analysis of the solid precipitate by XRD and SEM (Fig. 2d) confirmed that the main phase present in the solid precipitate was composed of $CaSO_4 \cdot 2H_2O$.

Selective Extraction of Ca with Na-D₂EHPA

The concentrated solution (PLS2) that originated from evaporation up to $X_{Vi}/V_r = 6$ (89.2 g/l Ni, 4.3 g/l Co, 0.6 g/l Ca and 7.7 g/l Mg) was used for the investigation of residual Ca removal. The effects of the extraction parameters, including equilibrium

pH value (pH_{eq}) and the concentration of the extractant Na-D₂EHPA, were evaluated with an O/A ratio of 1:1 at 25°C. As shown in Fig. 3a, the extraction order of the metal ions follows $Ca > Mg > Co > Ni$, and these findings are consistent with results reported previously.^{25,26} At $pH_{eq} = 1.6$, the extraction efficiency of Ca with 20 vol.% Na-D₂EHPA was found to be 74%, and this was seen to increase until a maximum of 93% at $pH_{eq} = 3.0$. Over this same pH_{eq} range, the respective extraction efficiencies of Mg changed from 7% to 23% and Co from 1% to 13%, while the Ni extraction remained negligible (< 2%). When $pH_{eq} \geq 3$, the extraction of Ni, Co and Mg increased, whereas the extraction of Ca decreased slightly as a consequence of the crowding out effect of Ni.²⁷ The results in Fig. 3b reveal that after a single contact with 10 vol.% Na-D₂EHPA at a $pH_{eq} = 2.5$, > 89% of Ca can be extracted, while the extractions of Mg (10.5%), Co (7.2%) and Ni (0.6%) are much lower, leading to an associated $SF_{Ca/Ni}$ of 1267. With the increase of pH_{eq} to 3, approximately 91% Ca, 16% Mg, 8% Co and 1% Ni were extracted. Consequently, 10 vol.% Na-D₂EHPA and $pH_{eq} = 2.5$ were chosen as the optimum conditions. The resultant Ca-free solution (PLS 3)—with a composition of 88.7 g/l Ni, 0.06 g/l

Fig. 3. Effect of the equilibrium pH on the extraction efficiencies and $SF_{Ca/Mg}$ with (a) 20 vol.% and (b) 10 vol.% Na-D₂EHPA.

Fig. 4. Effect of $[Ni^{2+}]$ of the concentrated solutions on the selective extraction of Ca with 10 vol.% Na-D₂EHPA.

Ca, 4.0 g/l of Co and 7.0 g/l of Mg—was used in the subsequent experiments.

The concentrated solutions with different initial Ni concentrations (highlighted in Fig. 2b) were contacted with 10 vol.% Na-D₂EHPA at O/A = 1:1, $pH_{eq} \sim 2.5$ and $T = 25^\circ C$, and the corresponding extraction efficiencies of the metal ions are shown in Fig. 4. A slight decrease of the extraction efficiency of Ca from $\sim 92\%$ to $\sim 88\%$ can be observed as the initial Ni concentration increases from 16.3 g/l to 114.5 g/l. A similar outcome was obtained at $X_{Vi/Vr} = 8$, where 2% Ni, 8% Co and 11% Mg were co-extracted into the loaded D₂EHPA. The results suggested that the residual Ca could be selectively extracted, as after extraction, the raffinate was found to have only 60 mg/l to 70 mg/l Ca over the concentration range tested.

Scrubbing of the Loaded D₂EHPA

The scrubbing/stripping behavior of the metal ions from the loaded D₂EHPA—which contained 1.2 g/l Ni, 0.3 g/l Co, 0.6 g/l Ca and 0.7 g/l Mg—was studied by varying the H₂SO₄ concentration from 0 to 1 M at O/A = 1:1 and $T = 25^\circ C$. The scrubbing

efficiencies of both Ni and Co were enhanced as the concentration of H₂SO₄ was increased from 0.01 M to 0.05 M (49% to 95% for Ni and 48% to 84% for Co). These findings show that Ni and Co can be selectively scrubbed from the loaded D₂EHPA with low H₂SO₄ concentrations (Fig. 5a), i.e., using 0.025 M H₂SO₄, results in a solution with 1.0 g/l Ni, 0.25 g/l Co and 0.3 g/l Mg (PLS4). With higher concentrations of H₂SO₄, Ca can be also stripped, for example, 1.0 M H₂SO₄ is shown to increase Ca yield to $\sim 90\%$ (Fig. 5a). Use of more concentrated H₂SO₄ enhances Ca precipitation as gypsum, especially with higher O/A ratios ($> 2:1$). Therefore, based on the literature, the HCl solution can be suggested as an optional reagent for Ca stripping from the loaded organic phase and to regenerate the D₂EHPA.²¹

Selective Extraction of Co and Mg with Na-Cyanex 272

The scrubbing solution (PLS4) from the loaded D₂EHPA was integrated into the Ca-free solution (PLS3) for the recovery of Ni and Co.²¹ Nevertheless, the volume of the scrubbing solution that can be added is dependent on the Ni concentration of the feeding solutions used in the second extraction step. In the case detailed here, a combination of the PLS3 (~ 80 vol.%) and the PLS4 (~ 20 vol.%) resulted in a feedstock (PLS5) that contained approximately 67.5 g/l Ni, 3.8 g/l Co and 6.3 g/l Mg. The pH of PLS5 was adjusted to around 5.5 with 10 M NaOH before being treated with Na-Cyanex 272 to extract Co and Mg.²⁶ The effects of pH_{eq} and Na-Cyanex 272 concentration on the extraction efficiencies of Co, Mg and Ni were examined as detailed in Fig. 6. From Fig. 6a, the extraction efficiencies of Co and Mg gradually increase with the increase of pH_{eq} . When the pH_{eq} value is < 5.2 , the extraction efficiencies of Co and Mg are $< 95\%$ and 44% , respectively, whereas the Ni extraction is $< 2\%$. Mg appears to be difficult to extract compared with Co, which is in accordance with the relative order of extraction selectivity previously determined for

Fig. 5. Scrubbing of metals from the loaded D₂EHPA using H₂SO₄ solutions with concentrations of (a) 0–0.05 M and (b) 0.05–1.0 M.

Fig. 6. Effect of (a) pH_{eq} and (b) Na-Cyanex 272 concentration (at pH_{eq} ~ 5.5) on the extraction efficiencies of Ni, Co and Mg.

Cyanex 272.²⁸ A further increase in pH_{eq} to 5.6 gives rise to extraction efficiencies of ~ 97% Co and 51% Mg; however, crud begins to be observed when the pH_{eq} is > 6.3. The formation of crud within the solution at elevated pH_{eq} is believed to result from the formation of insoluble Ni(OH)₂, as proposed by both Cheng et al.²⁹ and Guimarães et al.^{21,30} In Fig. 6b, the increase in the concentration of Na-Cyanex 272 from 10 vol.% to 30 vol.% at pH_{eq} ~ 5.5 results in an increase in the extraction of all metal ions, especially Mg. Nevertheless, the extraction efficiency of Ni is relatively high at ~ 5% with 30 vol.% Na-Cyanex 272. Consequently, 20 vol.% Na-Cyanex 272 was determined to be the optimum level required to selectively extract Co and Mg.

The isotherms of Co and Mg extractions were evaluated at varying A/O ratios (2:1, 1:1, 1:2, 1:3, 1:4 and 1:5) by exposing the mixed solution (PLS5) to a single contact with 20 vol.% Na-Cyanex 272. The extraction distribution isotherms and their McCabe-

Thiele diagrams are displayed in Fig. 7a and b. The results in Fig. 7a show that at the A/O ratio of 1:1, two theoretical stages are required to extract ~ 100% Co, whereas Fig. 7b highlights that two theoretical extraction stages at the A/O ratio of 1:2 are needed to extract ~ 95% Mg. It is worth noting that with the increase in the O/A ratio, the co-extraction of Ni becomes significantly higher as more extraction sites are freely available. Therefore, for the successful separation of Co and Mg vs. Ni, the O/A ratio plays a crucial role.³² A lower O/A ratio (1:1) with an additional extraction stage can be used to suppress Ni co-extraction and ensure efficient Mg separation. Use of an O/A ratio of 2:1 in the first stage, followed by two subsequent stages at an O/A ratio of 1:1, resulted in a raffinate (PLS6) that contained 61.7 g/l Ni, 0.007 g/l Co and 0.3 g/l Mg, which is of an acceptable purity and concentration to be used as a feedstock for state-of-the-art hydrometallurgical high-purity Ni recovery processes.^{31,32}

Fig. 7. McCabe-Thiele diagrams for (a) Co and (b) Mg extractions with 20 vol.% Na-Cyanex 272.

Fig. 8. Scrubbing of Ni, Co and Mg from the loaded Cyanex 272 using H_2SO_4 solutions with concentrations of 0–0.1 M.

Scrubbing of the Loaded Cyanex 272

The scrubbing behavior of Ni, Co and Mg from the loaded Cyanex 272—which contained 1.4 g/l Ni, 3.5 g/l Co and 2.8 g/l Mg—were studied with different concentrations (0–0.1 M) of H₂SO₄ solution. As shown in Fig. 8, with a 0.025 M H₂SO₄ solution, approximately 91% Ni and 13% Mg can be selectively scrubbed, while only 1% Co is removed from the loaded Cyanex 272. When 0.05 M H₂SO₄ is used, the scrubbing efficiency of Mg increases significantly to around 50%, whereas the associated efficiencies of Ni and Co increase to 97% and 3%, respectively. Accordingly, the H₂SO₄ concentration for the selective scrubbing Ni from the loaded Cyanex 272 was chosen as 0.025 M to minimize impurities in the resultant Ni solution. After the selective scrubbing of Ni, the loaded Cyanex 272 can be further scrubbed to produce a relatively Co-rich strip solution that can then be treated via sulfide precipitation to recover the Co.^{33,34}

CONCLUSION

To enhance the purity and increase the value of an underutilized industrial sidestream, a combined evaporation and solution purification method was investigated. Results showed that when the concentration degree was $X_{Vi}/V_r \geq 6$, at least 80% of Ca impurities could be precipitated as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with minimal associated losses (0.3% Ni, 0.3% Mg and 1.6% Co). Residual impurities were then effectively removed by solvent extraction with $\text{Na-D}_2\text{EHPA}$ (10 vol.% $\text{Na-D}_2\text{EHPA}$, O/A ratio of 1:1 and pH_{eq} of 2.5 at 25°C), and any co-extracted Ni and Co were recovered by selective scrubbing (0.025 M H_2SO_4) before being re-integrated back into the process. Finally, the use of a three-stage solvent extraction by Na-Cyanex 272 (20 vol.% Na-Cyanex 272 , first stage at an O/A ratio of 2:1 and two further stages at an O/A ratio of 1:1, $\text{pH}_{eq} \sim 5.7$ at 25°C) demonstrated that a high-purity Ni-rich solution could be produced from the initial sidestream. As a result, the application of a concentration and multi-step solvent extraction combination has the potential to simultaneously valorize low-grade solutions, reduce waste and enhance the metal's circular economy.

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