Solvent extraction test work to evaluate a Versatic 10/Nicksyn™ synergistic system for nickel-calcium separation

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Synopsis

Tati Nickel is currently operating a hydrometallurgical demonstration plant in Botswana, using the Activox® process developed by LionOre Technology to produce nickel cathode and a cobalt salt from a sulphide concentrate. Cobalt is extracted using Cyanex 272. This reagent also extracts all the iron, aluminium, copper, zinc, and manganese from the nickel stream. Versatic 10 carboxylic acid is then used as extractant to recover nickel from the stream, separating it from calcium and magnesium, and upgrading it to provide a suitable advance electrolyte for nickel electrowinning. However, the selectivity of Versatic 10 for nickel over calcium is limited, and gypsum formation in the extraction circuit is a problem when attempts are made to maximize the recovery of nickel.

Mintek has developed a synergistic system with Versatic 10 for improved separation of nickel from calcium and magnesium. Laboratory testwork was conducted on the raffinate of the cobalt solvent extraction circuit to optimize the Versatic 10/Nicksyn™ (Mintek synergist) system to be employed. Extraction and stripping parameters suitable for this stream were optimized in the laboratory and then applied on the demonstration plant. A commercial batch (0.5 tons) of Nicksyn™ reagent was produced for the demonstration plant.

The laboratory testwork results and the demonstration plant performance are discussed in detail in this paper.

Introduction

Nickel cathode and a cobalt salt are currently being produced by Tati Nickel in Botswana from a sulphide concentrate. The Activox® technology is employed for leaching, followed by oxidative precipitation of iron, precipitation of aluminium, cobalt solvent extraction using Cyanex 272, and finally nickel solvent extraction using Versatic 10 acid. Cobalt solvent extraction also removes residual iron, zinc, aluminium, manganese, and copper quantitatively from the solution. The Versatic 10 acid circuit primarily separates nickel from calcium and magnesium.

The Tati demonstration plant currently uses five stages in the nickel solvent extraction circuit, and the nickel loss to the raffinate is 0.08 g/L (from an 18 g/L feed, about 0.5% Ni loss). Although the Ni circuit has been performing on target for the last three years, recovery of nickel could be improved by increasing the pH profile across the extraction circuit, or increasing the number of extraction stages. The current circuit also relies on fresh water being added to the feed to the extraction circuit, which dilutes the calcium concentration from around 600 mg/L to 545 mg/L. This translates to an increase in the volumetric flowrate of about 10%, and hence a lower nickel throughput in the current plant. A plant 10% larger would be required for the full-scale operation of the current system.

To increase the pH profile across the extraction circuit would not result in an increase in capital costs, but it causes the formation of gypsum in the first and second extraction stages (even in the diluted feed). Additional extraction stages would increase the project's capital costs. It would be a major benefit in terms of capital and operating costs if the dilution of the feed were to be reduced or no longer required. Hence, Tati Nickel investigated the use of the Versatic 10/Nicksyn™ system for the separation of nickel and calcium from a stream saturated in calcium (around 600 mg/L, required no dilution of the cobalt solvent extraction raffinate).

Mintek has published numerous papers since the early 1990s about its development work on synergistic systems for the recovery of nickel and cobalt from leach liquors saturated in calcium.[1,2] More recently, Mintek secured a commercial producer of the Nicksyn™ reagent. Tati Nickel subsequently purchased a commercial batch of this reagent, which was evaluated on the demonstration plant.

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Experimental procedures

Analytical methods

All metal analyses were done by Mintek's Analytical Services Division. Aqueous samples were analysed for Ni, Co, Ca, Cu, Zn, Mn, Fe and Mg (detection limit 2 mg/L for all metals) using Inductively Coupled Plasma—Optical Emission Spectroscopy (ICP-OES). Organic samples were stripped with sulphuric acid (1 M) at an organic-to-aqueous (O:A) phase ratio of 0.5, after which the strip liquors were submitted for analysis.

The concentration of Versatic 10 (V10) in the organic phase was determined by potentiometric titration of a sample (4 mL) dissolved in ethanol (25 mL) and water (10 mL) against a standard sodium hydroxide solution (0.10 M, made up from Merck ampoule), using a calibrated combined glass-reference electrode.

Organic phases

Versatic 10 acid, V10 (a tertiary-branched carboxylic acid), was obtained from Chemquest (produced by Resolution Performance Products Ltd.), whilst Nicksyn™ was prepared for Mintek in a larger batch (30 kg) by an independent, reputable manufacturer. The chemical composition of, and technical information about Nicksyn™ remains the sole property of Mintek, and can therefore not be disclosed. Appropriate dilutions of V10 alone and V10 mixtures with Nicksyn™ were done using an aliphatic hydrocarbon diluent, Shellsol D70, which was obtained from Shell Chemicals. This diluent was used, as it was the diluent employed on the Tati Nickel demonstration plant. Organic phases were used as supplied, without any further purification.

Metal-distribution equilibria for extraction (pH vs. extraction)

Metal-distribution equilibria (pH vs. extraction isotherms) were determined by contacting the required organic phase (1.0 M V10 alone or mixed with 0.2–1.0 M Nicksyn™ in Shellsol D70) with Tati Co SX raffinate at an O:A phase ratio of 2, using rapid magnetic stirring and controlling the temperature at 35ºC in a water-jacketed glass vessel. The pH value of the aqueous phase was adjusted by the addition of ammonia solution (25 m/v%). Equilibrium was established between 10 to 15 minutes after alkali additions. Samples (15 mL aqueous and 30 mL organic) of each phase were taken after each adjustment of pH. Aqueous samples were submitted for analysis. No organic samples were stripped for analysis.

Distribution isotherms for extraction

The required portions of organic phase (1.0–1.25 M V10 mixed with 0.25–0.50 M Nicksyn™ in Shellsol D70) and aqueous phase (Tati Co SX raffinate) were contacted at different O:A phase ratios (1:8 to 8:1) by means of rapid magnetic stirring and controlling the temperature at 35ºC, using a water-jacketed glass vessel. A contact time of 10 to 15 minutes was allowed to reach equilibrium. The pH values of the aqueous phases were controlled as required, using ammonia solution (25 m/v%). Samples of the aqueous phases were submitted for analysis. Samples of the organic phases were taken immediately after the aqueous samples to prevent possible re-equilibration, and stripped with sulphuric acid solution (1 M, O:A = 0.5). The strip liquors were submitted for analysis.

Distribution isotherms for stripping

Organic phase (1.25 M V10 mixed with 0.31 M Nicksyn™ in Shellsol D70) was batch-loaded by contacting a portion (500 mL) of fresh organic with Tati Co SX raffinate (555 mL, O:A = 0.9), controlling the pH at 6.0, using ammonia solution (25 m/v%) at ambient temperature. Samples (10 mL aqueous and 9 mL organic phase) were taken for analysis. The partially loaded organic phase was then contacted for a second and third time in the same manner, using a fresh portion of Tati Co SX raffinate each time. Samples of the organic phases were stripped with sulphuric acid (1 M, O:A = 0.5), and the strip liquors as well as the aqueous samples taken were tested for nickel by means of atomic absorption.

The batch-loaded organic phase obtained was then contacted with a synthetic spent electrolyte (61 g/L nickel in 40 g/L sulphuric acid solution) at different O:A phase ratios (1:8 to 8:1) at 35ºC by means of magnetic stirring in a water-jacketed glass vessel. A contact time of 10 to 15 minutes was allowed to reach equilibrium. Samples of the aqueous phases were submitted for analysis. Samples of the organic phases were taken immediately after the aqueous samples, to prevent possible re-equilibration, and restripped with sulphuric acid (1 M). The restrip liquors were submitted for analysis.

Acid extraction by organic phase

Aliquots of an aqueous phase (20 mL) consisting of 40 g/L sulphuric acid and 133 g/L sodium sulphate (simulating a typical spent electrolyte containing no nickel), were adjusted to the required pH value using a 10 M sodium hydroxide solution, and contacted with the appropriate organic phase (1.25 M V10 plus 0.31 M Nicksyn™ in Shellsol D70, 20 mL) at 35ºC. A sample of the organic phase (5 mL) was stripped with water (50 mL) and the resulting aqueous phase was separated and titrated against a 0.10 M sodium hydroxide solution to a bromothymol blue endpoint (pH ~ 8.5). The pH value of the raffinate was measured.

Stability of Nicksyn™

Stability tests were carried out by contacting a portion (500 mL) of organic phase (1.25 M V10 acid plus 0.31 M Nicksyn™ in Shellsol D70) with synthetic spent electrolyte (500 mL, containing 55 g/L nickel in 40 g/L sulphuric acid) by rapid magnetic stirring in a screw-top bottle of 1 litre capacity, thermostatted at 35°C, to simulate stripping conditions over a period of 90 days. The bottles were weighed periodically to check for possible evaporation losses, but none were detected. A similar set-up was done by contacting another portion (500 mL) of the same mixed organic phase with Tati Co SX raffinate (500 mL) and adjusting the pH value to 6.0 using ammonia solution (25 m/v%, 17.8 mL) in order to simulate extraction conditions. Samples of the organic phase (115 to 120 mL) of the experiment simulating stripping conditions were taken at suitable intervals, after which the aqueous phase was replaced with the appropriate volume of fresh synthetic spent electrolyte to maintain an O:A phase ratio of 1.

Metal-distribution equilibria (pH vs. extraction) were determined on a portion (100 mL) of these organic samples using Tati Co SX raffinate (50 ml) feed, as described in Section 2.4.

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## Results and discussion

Feed solution

The cobalt raffinate used as feed was obtained from the cobalt solvent extraction circuit (Tati Co SX raffinate) at Tati Nickel's demonstration plant and provided by Tati Nickel Mining Company. Four batches of about 20 L each were supplied. A typical composition of this feed solution to the nickel SX circuit is given in Table I.

Organic phase composition

The neutralization equivalent for V10 (supplied by Chemquest) was found to be 174.23 g/mol by potentiometric titration of a sample (169 g) of V10 against a standard 0.10 M sodium hydroxide solution. Detailed technical information concerning Nicksyn™ remains the sole property of Mintek and cannot be disclosed. The different V10 and Nicksyn™ concentration mixtures diluted with Shellsol D70 (molar and vol.%) used in this study are given in Table II.

Metal-distribution equilibria for extraction (pH vs. extraction)

The synergistic extraction of nickel by a carboxylic acid such as V10 (which exists in the form of dimers H_2A_2), with the addition of a synergistic compound (L) such as Nicksyn™, is given in Equation [1].[1]

$$Ni^{2+} + \overline{H_2A_2} + \overline{2L} = \overline{NiA_2L_2} + 2H^+ \qquad [1]$$
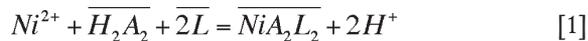
The bars denote the presence of the species in the organic phase.

The different behaviour of nickel and calcium, magnesium, and manganese in this type of synergistic system is illustrated in the results for the extraction of metals from Tati Co SX raffinate by 1.0 M V10 alone and mixed with 0.50 M Nicksyn™ in Shellsol D70, as shown in Figure 1. Percentage extraction is calculated by the difference between the feed and raffinate solutions.

The pH_{50} value (the pH at which 50% of the metal originally present in the aqueous phase is extracted under a given set of conditions) of nickel shifted from 5.80 (using 1.0 M V10 alone) to 4.48 (1.0 M V10 plus 0.50 M Nicksyn™), which relates to a synergistic shift (ΔpH_{50}) of 1.32 pH units. Only a small synergistic shift ($\Delta pH_{50} = 0.17$) for calcium occurred for this feed solution, which contained about 18 g/L nickel and 0.6 g/L calcium.

Various concentration mixtures of V10 and Nicksyn™ were evaluated in order to obtain a reasonable nickel-calcium separation, whilst minimizing the volume (or mass) requirement and hence the costs of using Nicksyn™. The results are summarized in Table III. The separation between the extraction curves for nickel and calcium is indicated by pH_{50}^{Ca-Ni}.

Synergistic shifts in the pH_{50} values for the extraction of nickel increased from 0.90 to 1.45 units when Nicksyn™ addition was increased from 0.20 to 1.00 M respectively, whilst the extraction of calcium was largely unaffected. The separation between nickel and calcium (pH_{50}^{Ca-Ni}) increased from 1.32 pH units (V10 alone) to 2.83 pH units (1.0 M V10 plus 1.00 M Nicksyn™). Considering the additional costs of increasing the Nicksyn™ concentration beyond a ratio of 5:1

Table I

Typical composition of nickel SX feed solution

Metal	Concentration, g/L
Ni	18
Co	0.002–0.005
Ca	600
Mn	<0.002
Cu	<0.002
Mg	0.54
Zn	<0.002
Fe	<0.002

Table II

Different concentration mixtures of V10 and Nicksyn™ used in experimental test work

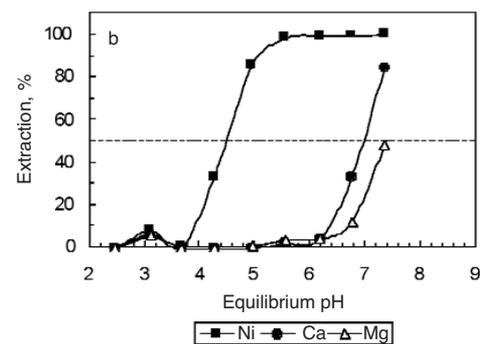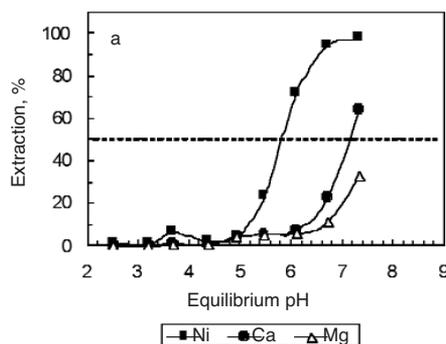| Organic phase	Concentration, M	Concentration, Vol.%
Versatic10	1.00	19.15
	1.25	23.93
	1.30	24.89
Nicksyn™	0.20	7.35
	0.25	9.19
	0.26	9.56
	0.31	11.40
	0.50	18.38
	0.75	27.57
	1.00	36.76

Figure 1—Metal-distribution equilibria for the extraction of metals from Tati Co SX raffinate by 1.0 M V10 alone (a) and 1.0 M V10 plus 0.50 M Nicksyn™ (b) in Shellsol D70 at 35ºC

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Extraction of nickel and calcium from Tati Co SX raffinate by mixtures of V10 (1.0 M) and Nicksyn™ (0.20-1.0 M) in Shellsol D70 at 35ºC

Organic phase		pH_{50}^{Ni}	pH_{50}^{Ca}	pH_{50}^{Ca-Ni}	
V10, M	**Nicksyn™, M**				
1.0	-	5.80	7.12	1.32	
1.0	0.20	4.90	6.89	1.99	
1.0	0.25	4.84	6.94	2.10	
1.0	0.50	4.48	6.95	2.47	
1.0	0.75	4.43	7.00	2.57	
1.0	1.00	4.35	7.18	2.83	

(pH_{50}^{Ca-Ni} of 2 pH units) to improve nickel-calcium separation incrementally with another pH unit (final ratio of 1:1), it was decided to consider only molar ratios of V10:Nicksyn™ of 5:1 and 4:1 for the demonstration plant.

A pH vs. extraction isotherm was done (Figure 2) using Tati Nickel cobalt pregnant leach solution (Tati Co PLS) and 1.25 M V10 plus 0.31 M Nicksyn™ at 35ºC to gauge the possibility of separating nickel, cobalt, zinc and copper from calcium, manganese and magnesium from Tati Nickel cobalt SX feed. This would allow the Ni SX to be done first, followed by Co SX to remove Co and other impurities from the Ni electrolyte. This would be especially beneficial if the PLS were diluted and upgrading of nickel takes place across the Ni SX circuit, because the Co SX can be done on a smaller volumetric flow.

The pH_{50} values obtained for nickel (4.68), cobalt (5.40), manganese (6.01) and calcium (6.61) indicate that a separation between cobalt and manganese (pH_{50}^{Mn-Co}) of only 0.61 units was achieved for this feed solution, which would probably require a large number of stages and tight pH control to facilitate efficient separation of nickel, cobalt, zinc and copper from calcium, manganese and magnesium. This separation between cobalt and manganese would be improved with a higher concentration of Nicksyn™ in the organic mixture.

Distribution isotherms for extraction of nickel

The distribution isotherm and McCabe–Thiele construction for the extraction of nickel from Tati Co SX raffinate generated using 1.0 M V10 plus 0.50 M Nicksyn™ in Shellsol D70, at pH 5.5 and controlling the temperature at 35ºC, is shown in Figure 3.

The results (based on calculations done based on the difference between the feed and raffinate solutions, as well as that derived by stripping the organic phases and analysing the strip liquors) and McCabe-Thiele construction on the extraction isotherm, indicate that a loading of about 18 g/L nickel could be achieved in three countercurrent extraction stages at an O:A phase ratio of 1. The calcium co-extraction under these conditions was about 2.3% (14 mg/L on the loaded organic).

The distribution isotherms for extraction of nickel using 1.0 M V10 together with a lower (0.25 M) concentration of Nicksyn™ at pH values 5.4 and 5.8, are shown in Figures 4 and 5 respectively.

The McCabe-Thiele constructions shown in Figures 4 and 5 predict nickel loadings of about 11 and 14 g/L at pH 5.4 and 5.8 respectively. Although an appreciable selectivity for nickel was shown by the limited co-loading of calcium on

the organic phases (about 12 mg/L and 20 mg/L at pH 5.4 and 5.8 respectively), optimum plant operation would require higher nickel loading on the organic phase to operate closer to an O:A phase ratio of unity in extraction.

Maximum loading experiments indicated that about 20 g/L nickel loading could be achieved using 1.25 M V10 plus 0.31 M Nicksyn™ in Shellsol D70 (V10:Nicksyn™ = 4) at pH 6.0 and 35ºC. These conditions were applied in generating the extraction isotherm shown in Figure 6.

The McCabe-Thiele construction confirmed that a nickel loading of about 20 g/L could be achieved in three counter-current extraction stages at an O:A phase ratio of 0.9, with calcium loading on the organic phase below detection limit (< 4 mg/L in strip liquor analyses). These operating conditions were therefore recommended for the extraction circuit on the demonstration plant.

Distribution isotherms for the stripping of nickel

The distribution isotherm generated for the stripping of nickel from batch-loaded 1.25 M V10 plus 0.31 M Nicksyn™ in Shellsol D70 (containing about 20 g/L nickel) at 35ºC, using synthetic spent electrolyte containing 61 g/L nickel and 40 g/L sulphuric acid as strip solution, is shown in Figure 7.

The McCabe-Thiele construction predicts that loaded organic phase containing about 21.5 g/L nickel could be stripped with synthetic spent electrolyte in two countercurrent
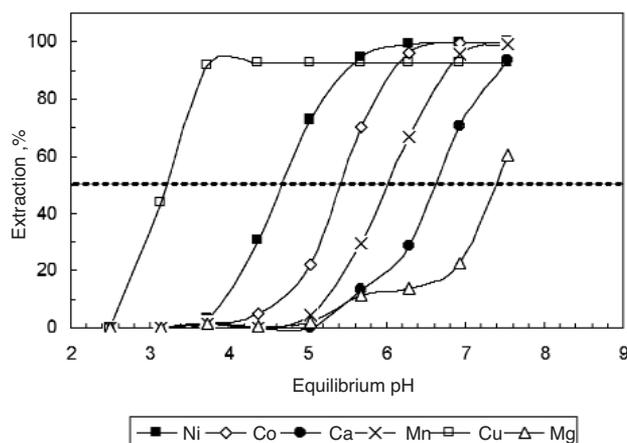

Figure 2—Metal-distribution equilibria for the extraction of metals from Tati Co PLS by 1.25 M V10 plus 0.31 M Nicksyn™ in Shellsol D70 at 35ºC(O:A = 2)
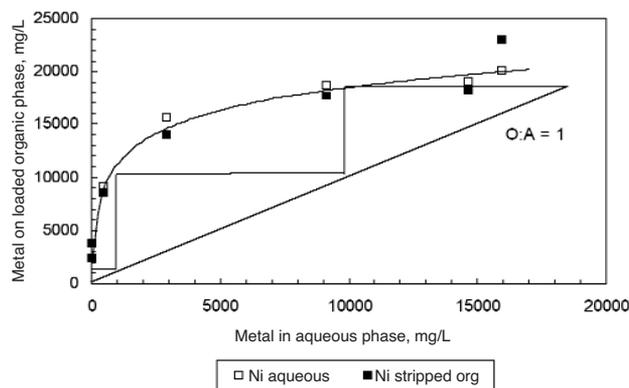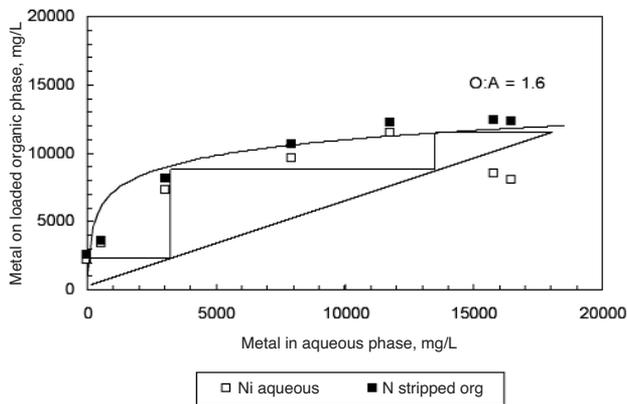

Figure 3—Distribution isotherm for the extraction of nickel from Tati Co SX raffinate by 1.0 M V10 plus 0.50 M Nicksyn™ in Shellsol D70 at pH 5.5 and 35ºC

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Figure 4—Distribution isotherm for the extraction of nickel from Tati Co SX raffinate by 1.0 M V10 plus 0.25 M Nicksyn™ in Shellsol D70 at pH 5.4 and 35ºC
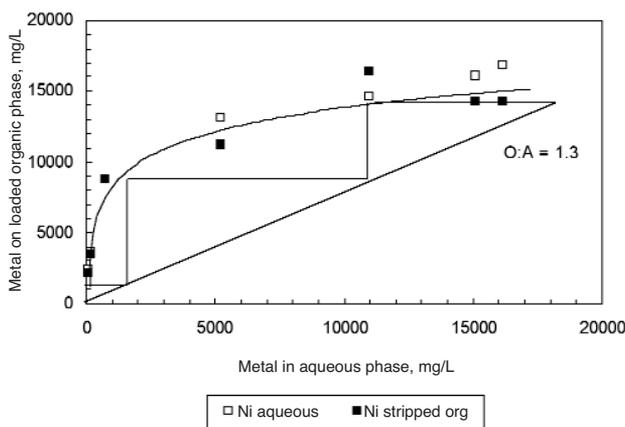

Figure 5—Distribution isotherm for the extraction of nickel from Tati Co SX raffinate by 1.0 M V10 plus 0.25 M Nicksyn™ in Shellsol D70 at pH 5.8 and 35ºC
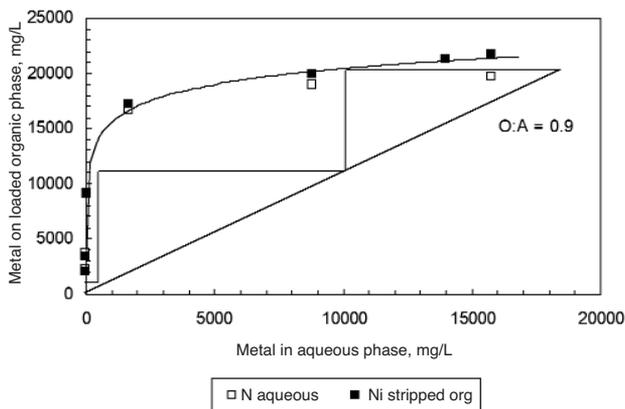

Figure 6—Distribution isotherm for the extraction of nickel from Tati Co SX raffinate by 1.25 M V10 plus 0.31 M Nicksyn™ in Shellsol D70 at pH 6.0 and 35ºC

stripping stages at an O:A phase ratio of 1.2 and at 35ºC. Loaded strip liquor containing about 86 g/L nickel was obtained, as would be expected because of the acid content of the synthetic strip liquor.

Strip liquor pH values measured for stripping done at O:A phase ratios of 0.125, 0.20, 0.5 and 1.0 were 0.75, 0.76, 1.06 and 1.43, respectively, which indicates that enough (or even excess) sulphuric acid was available for complete stripping of nickel. Stripping done at O:A phase ratios of 2, 5 and 8 resulted in strip liquors exhibiting pH values of 5.2, 5.7 and 5.8 respectively, which indicates unfavourable stripping conditions for nickel. If plant operation required these operating conditions, pH control coulde be employed (at about 3) in order to facilitate efficient stripping of nickel in the minimum number of stages.

Acid extraction by organic phase

The acid uptake as a function of the equilibrium pH of the aqueous phase (40 g/L sulphuric acid plus 133 g/L sodium sulphate), using an organic phase containing 1.25 M V10 mixed with 0.31 M Nicksyn™ in Shellsol D70, is shown in Figure 8.

The extraction of acid by Nicksyn™ from aqueous solutions between pH 0.7 and 0.9 was 8 mM, while the average extraction of acid by Nicksyn™ from aqueous solutions between pH 1.4 and 3.3 was 6.1 mM, which is negligible.
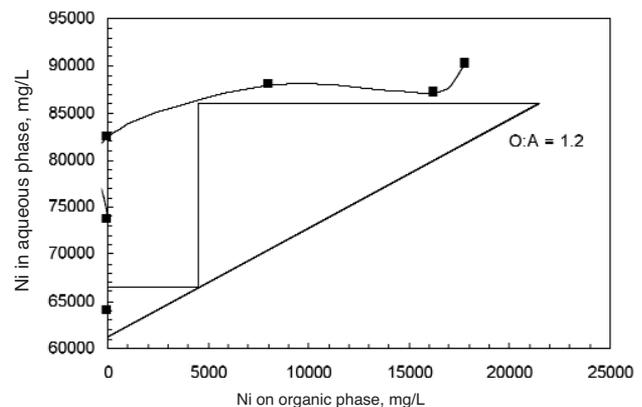

Figure 7—Distribution isotherm for the stripping of nickel from batch loaded 1.25 M V10 plus 0.31 M Nicksyn™ in Shellsol D70 with synthetic spent electrolyte (61 g/L nickel in 40 g/L sulphuric acid solution) at 35ºC
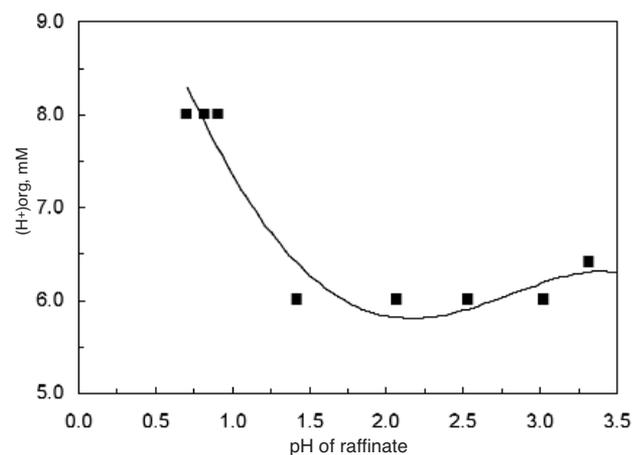

Figure 8—Extraction of acid (as H+) from a simulated spent electrolyte (40 g/L H_2SO_4 + 133 g/L Na_2SO_4, no Ni) by 1.25 M V10 plus 0.31 M Nicksyn™ in Shellsol D70 at 35ºC

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Stability tests

Stability tests were carried out using organic phases containing 1.25 M V10 mixed with 0.31 M Nicksyn™, simulating extraction and stripping conditions. Samples taken of the organic phases at chosen time intervals (15, 29, 45 and 90 days for stability tests representing stripping conditions and 90 days for a stability test representing extraction conditions) were then used (separately) to determine the pH vs. extraction curves for nickel and calcium from Tati Co SX raffinate at 35°C. These are shown in Figure 9. No intermittent samples were taken for the test-simulating extraction conditions. A portion of the organic phase (250 mL) was stripped batch-wise (three times) with 1 M sulphuric acid (500 mL) after 90 days to ensure complete stripping of nickel, after which it was used to determine pH vs. extraction data (shown in Figure 9). The pH_{50} values, as well as pH_{50}^{Ca-Ni} obtained for nickel and calcium, are given in Table IV together with those obtained using the fresh organic phase.

It can be seen from Figure 9 and Table IV that variations in pH_{50} values of nickel (4.57 to 4.63) and calcium (6.55 to 6.67), and therefore variations in pH_{50}^{Ca-Ni} (1.97 to 2.05) are insignificantly small over the 90-day period of the stability tests, representing stripping as well as extraction conditions.

All phases were clear during stability tests done simulating stripping conditions. White crud accumulated at the interface of the phases of the stability test simulating extraction conditions.

It can be concluded that the organic phase mixture containing 1.25 M V10 plus 0.31 M Nicksyn™ in Shellsol D70 was stable under the given conditions tested for a period of 90 days.

Demonstration plant data

Tati Nickel acquired 0.5 tons of Nicksyn™ from the manufacturer appointed by Mintek. The quality of the Nicksyn™ product was evaluated at Mintek prior to shipment to the Tati Nickel site, and the results confirmed that it was of a quality equivalent to that of the laboratory-scale product. Nicksyn™ was introduced into the plant during October 2006, and has been in operation since then. The operating conditions applied to the V10 and V10 plus Nicksyn™ trials are compared in Table V.

The nickel profiles across the extraction circuit for V10 alone and V10 plus Nicksyn™ are given in Figure 10.

The more efficient extraction of nickel by V10 plus Nicksyn™ system is clear, although it was done at a lower pH profile (albeit a higher O:A phase ratio). As mentioned earlier, the maximum nickel loading of 20 g/L was obtained in the laboratory testwork using a 1.25 M V10 plus 0.31 M Nicksyn™ mixture (see Section 3.4). The loading of nickel could therefore be increased by increasing the Nicksyn™ concentration or lifting the pH values slightly over the extraction circuit.

The calcium organic loading profiles across the extraction circuit are given in Figure 11.

The profile for V10 plus Nicksyn™ system is rather flat, which demonstrates the advantage of the synergistic system. With V10 alone, a significant amount of calcium was co-loaded on the organic phase at the tail end of the extraction circuit, which was then displaced by nickel as the organic advanced towards the front end of the circuit. This clearly demonstrates the problem in the V10 circuit, as any calcium that is displaced from the organic could result in gypsum formation in the extraction circuit if the feed contains calcium at saturation. Previously Tati Nickel minimized the problem

of gypsum by diluting the feed stream with fresh water. This, however, will increase the size of the plant by 10% (higher flow rates for similar nickel production). With the synergistic system, no dilution of the feed is required, as gypsum formation can be completely avoided.

Figure 12 shows the nickel relative recoveries obtained over a period. With V10 alone, an average recovery of about 99.3% was achieved, while that of the V10 plus Nicksyn™ was 99.7%. With the extraction circuit containing V10 alone, the pH of extraction cannot be increased, as this causes higher calcium loading, and hence an increased likelihood of gypsum formation in the extraction circuit. Hence, to improve extraction efficiency, more stages would be required. The V10 alone circuit already employed five extraction stages. The V10 plus Nicksyn™ operation achieved higher nickel recoveries using four stages only, and with very little risk of gypsum formation. The recovery of nickel can be improved in this circuit by increasing the pH profile somewhat, whilst still avoiding additional calcium loading.

Reagent make-up for the V10 and V10 plus Nicksyn™ systems was compared over a period of four months. Indicative results are given in Table VI. The lower reagent loss experienced using the V10 plus Nicksyn™ was ascribed to the much lower pH of operation and the reduction in crud formation. The diluent and Versatic 10 acid make-up were 21% and 30% higher respectively for the V10 alone system.
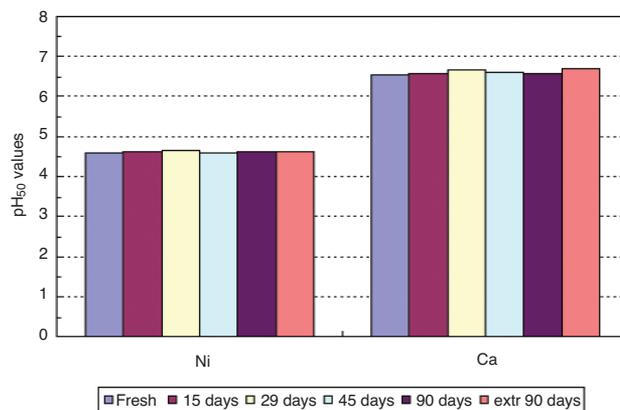

Figure 9—pH_{50} values for nickel and calcium extraction by 1.25 M V10 plus 0.31 M Nicksyn™ in Shellsol D70 (fresh and after use in stability tests) at 35°C

Table IV

pH_{50} and pH_{50}Ca-Ni values for nickel and calcium extraction by 1.25 M V10 plus 0.31 M Nicksyn™ in Shellsol D70 (fresh and after use in stability tests) at 35°C

Sample of 1.25 M V10 + 0.31 M Nicksyn™	pH_{50}		pH_{50}^{Ca-Ni}
	Ni	Ca	
Stripping conditions:			
Fresh	4.57	6.55	1.98
15 days	4.61	6.58	1.97
29 days	4.63	6.66	2.03
45 days	4.59	6.60	2.01
90 days	4.60	6.58	1.98
Extraction conditions:			
90 days	4.62	6.67	2.05

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Table V

Comparison of operating conditions

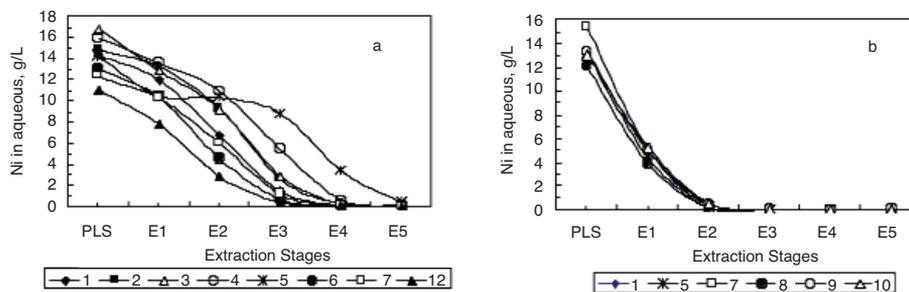|	V10	V10 + Nicksyn™	
Versatic 10 acid concentration, M	1.57	1.31	
Nicksyn™ concentration, M	0	0.27	
Ni maximum loading, g/L	21	14	
Number of stages			
Extraction	5		4
Scrubbing	2		1
Stripping	2		2
Washing	0		1
Versatic 10 recovery (VR)	1		1
Total	10		9
O:A phase ratio			
Extraction	0.7		1.4
Scrubbing	4.4		35.5
Stripping	0.96		1.54
pH profile across extraction			
E1	6.95		5.5
E2	6.65		5.5
E3	6.40		5.4
E4	6.35		5.4
E5	6.35		Not in use
Phase disengagement time, s			
Extraction	53		82
Scrubbing	96		116
Stripping	51		94
Ni concentration across extraction, g/L			
Feed	13.3		13.4
E1	10.9		3.7
E2	6.7		0.25
E3	2.4		0.03
E4	0.5		0.007
E5	0.1		Not in use
Ca concentration in organic across extraction, g/L			
E1	0.011		0.005
E2	0.012		0.006
E3	0.063		0.005
E4	0.149		0.006
E5	0.149		Not in use

Figure 10—Nickel aqueous concentration profile across extraction circuit (V10 alone (a) and V10 plus Nicksyn™(b))
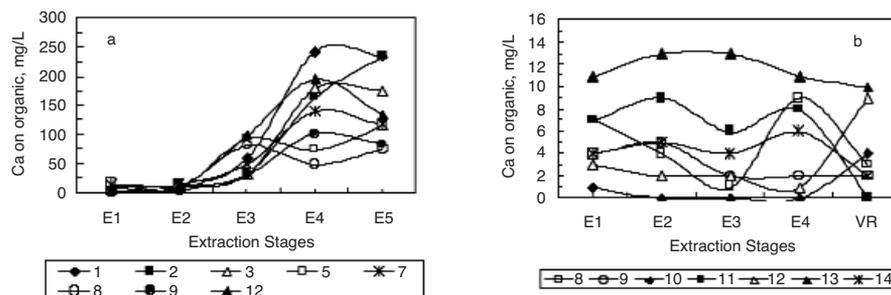

Figure 11—Calcium organic concentration profile across extraction circuit (V10 alone (a) and V10 plus Nicksyn™(b))

Solvent extraction test work to evaluate a Versatic 10/Nicksyn™ synergistic system
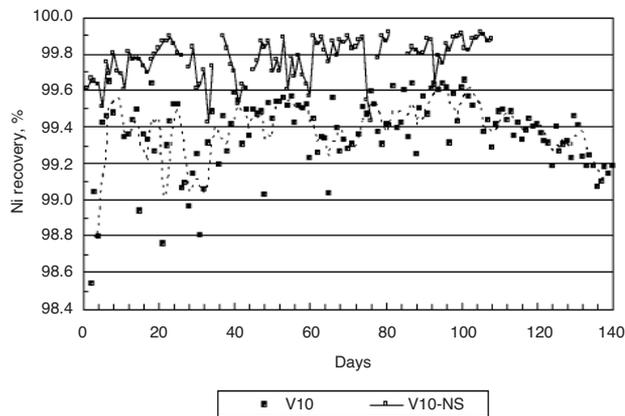

Figure 12—Nickel recoveries for V10 alone and V10 plus Nicksyn™ extraction systems

Table VI

Reagent make-up

Make-up (L/m³)	V10	V10 plus Nicksyn™
Diluent	1.84	1.5
V10	0.40	0.28
Nicksyn™	0	0.13

The results obtained during the demonstration plant run were used to make a techno- economic comparison between the V10 and V10 plus Nicksyn™ systems in order to quantify the capital and operating cost difference between the two technologies.

Conclusions

➤ The Mintek-developed synergist (Nicksyn™) in different combinations with V10 (a commercially available tertiary-branched carboxylic acid) and diluted with Shellsol D70 (aliphatic), was evaluated as optimizing nickel recovery and nickel-calcium separation from a cobalt solvent extraction raffinate stream at Tati Nickel. This stream typically contained about 20 g/L nickel, 500-600 mg/L calcium and 540 mg/L magnesium. Copper, zinc, manganese, iron and cobalt were <2 mg/L in solution as a result of their effective extraction in the upfront Cyanex 272 circuit

➤ Extraction vs. pH curves done with 1.0 M Versatic 10 alone and mixed with 0.20–1.00 M Nicksyn™ in Shellsol D70 at 35ºC showed that synergistic shifts in the pH_{50} (ΔpH_{50}) values for the extraction of nickel increased from 0.90 to 1.45 units when Nicksyn™ addition was increased from 0.20 to 1.00 M respectively. The extraction of calcium was insignificantly affected. The separation between nickel and calcium (pH_{50}^{Ca-Ni}) increased from 1.32 pH units (V10 alone) to 2.83 pH units (1.0 M V10 plus 1.00 M Nicksyn™). Considering the higher costs of adding Nicksyn™ to a molar ratio of unity to increase the separation by a further pH unit (from 2 to 3 pH units), molar ratios of V10:Nicksyn™ of 5:1 and 4:1 were considered for the demonstration plant

➤ A combination of 1.25 M V10 plus 0.31 M Nicksyn™ at 35ºC was used to gauge the possibility of separating nickel, cobalt, zinc and copper from calcium, manganese and magnesium in the Co SX feed (PLS). This would allow for the Ni extraction to be done first, followed by Co recovery and impurity removal on the Ni SX loaded strip liquor. The pH_{50} values obtained for nickel (4.68), cobalt (5.40), manganese (6.01) and calcium (6.61) indicate that a separation between cobalt and manganese (pH_{50}^{Mn-Co}) of only 0.61 units was achieved for this feed solution. It would probably require a large number of stages and tight pH control to facilitate efficient separation of nickel, cobalt, zinc and copper from calcium, manganese and magnesium. A higher proportion of Nicksyn™ would enhance the separation

➤ The use of 1.0 M V10 plus 0.50 M Nicksyn™ in Shellsol D70, at pH 5.5, indicated that a loading of about 18 g/L nickel could be achieved in three counter-current extraction stages at an O:A phase ratio of unity. The calcium co-extraction under these conditions was about 2.3% (14 mg/L on loaded organic phase)

➤ The testing of 1.0 M V10 together with a lower (0.25 M) concentration of Nicksyn™ at pH 5.4 and 5.8 predicted nickel loadings of about 11 and 14 g/L at pH 5.4 and 5.8, respectively

➤ The combination of 1.25 M V10 plus 0.31 M Nicksyn™ in Shellsol D70 resulted in a nickel loading of about 20 g/L in three countercurrent extraction stages at an O:A phase ratio of 0.9, with calcium co-loading on the organic phase below detection limit. These operating conditions were therefore recommended for the extraction circuit on the demonstration plant

➤ Two stripping stages were deemed adequate for complete stripping

➤ No meaningful acid loading, and hence carry-over to the extraction circuit, was determined for the reagent mixture

➤ Stability tests under extraction and stripping conditions over a period of 90 days indicated no change in the composition of the extraction mixture

➤ V10 alone and V10 plus Nicksyn™ systems were compared during a demonstration plant run at Tati Nickel. The recovery of nickel increased by 0.5% using the V10 plus Nicksyn™ mixture and four extraction stages. The co-loading of calcium was about 150 mg/L in E5 (using V10), which could form gypsum if displaced. The co-loading of calcium in E4 (using V10 plus Nicksyn™) was about 14 mg/L, with no risk of gypsum formation.

Acknowledgements

References

1. DU PREEZ, A.C. and PRESTON, J.S. Separation of nickel and cobalt from calcium, magnesium and manganese by solvent extraction with synergistic mixtures of carboxylic acids, SAIMM Journal, July 2004, pp. 333–338.

2. PRESTON, J.S. and DU PREEZ, A.C. Separation of nickel and calcium by solvent extraction using mixtures of carboxylic acids and alkylpyridines, Hydrometallurgy, vol. 58, 2000, pp. 239–250. ◆