

A New Process for Cobalt – Nickel Separation

By

D.L. Jones¹, T.M. McCoy¹, K.E. Mayhew¹, C.Y. Cheng², K.R. Barnard², W. Zhang²

Presented by

David Jones

david.jones@teckcominco.com

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¹ CESL Limited, Richmond, BC, Canada

² Parker Centre/CSIRO Minerals Down Under, Perth, Australia

ABSTRACT

A new process has been developed jointly by CSIRO and CESL, for separating cobalt from nickel in an impure leach solution.

The process uses synergistic solvent extraction (SSX) with commercially available reagents, but in a novel and efficient manner using kinetic factors. It is applicable to dilute nickel leach liquors containing high levels of impurities such as magnesium and manganese. It therefore allows the separation of nickel from cobalt without the usual need for prior purification, such as the standard production of a mixed hydroxide precipitation and a subsequent re-leach.

The process is applicable to a wide range of nickel-cobalt leach liquors, derived from both laterites and sulphides, and should have attractive operating and capital costs.

The process is described with examples and some illustration given of the potential commercial advantages, compared to existing technology.

1 INTRODUCTION

The distribution of cobalt and nickel in most leaching processes is similar and thus leaching of either nickel laterites or sulphides usually results in a mixed solution of cobalt and nickel, as well as other impurities. Separation of cobalt from nickel is almost invariably required at some stage to obtain maximum payment for these metals, but the separation is frequently complicated by the presence of certain impurities, such as magnesium and manganese.

Historically, a number of processes have been used commercially for cobalt separation from nickel in liquor, but currently the favoured process is the selective solvent extraction of cobalt away from nickel, using phosphinic acid derivatives, e.g. Cyanex 272. Although this extractant works well in pure solutions, unfortunately it also extracts many other metals commonly found in leach solutions; economic methods of solution purification such as solvent extraction, sulphide precipitation or hydrolysis can readily eliminate some of these, such as copper, zinc and iron. Other impurities such as magnesium and manganese cannot be so easily separated, thus reducing the effectiveness of Cyanex 272.

Therefore, to use this extractant or any other cobalt separation process on primary leach solutions, it is necessary to first separate both nickel and cobalt from these impurities, e.g.:

- a) Nickel/cobalt precipitation as mixed hydroxides, followed by re-leach in acidic or ammoniacal solution. This route used very successfully on the Cawse and Ravensthorpe/YEP projects for instance.
- b) Nickel/cobalt precipitation as mixed sulphides, then re-leach in an oxidizing environment, either acidic or ammoniacal. This route is still used successfully at Murrin Murrin, at Moa Bay/Sherritt, and at Coral Bay/Niihama.

For laterite ores, these are the main routes used in the hydrometallurgical nickel processes. One notable exception in recent times was the Bulong project, which succeeded in achieving

excellent cobalt-nickel separation primary leach liquor by Cyanex 272. However, manganese extraction from the leach liquor along with cobalt could not be avoided, thus increasing the cost of the process.

For sulphide ores, there is another alternative; if the ore can be concentrated by flotation, matte smelting is used instead of leaching. This combination of flotation and smelting effectively removes most of the deleterious impurities, and thus produces a nickel-cobalt matte suitable for leaching and eventual Cyanex 272 separation of nickel and cobalt. Historically of course almost all nickel sulphide ores have been treated in this way; however, not all sulphide ores remaining today are suitable for this route.

All of such preliminary steps outlined above, (precipitation/releach or smelting), are quite costly, and there is a perceived need for a cobalt-nickel separation that can proceed on the primary leach liquor with said impurities still present.

2 EXISTING TECHNOLOGY FOR COBALT EXTRACTION

Cobalt is commonly extracted in commercial plants from nickel solutions using Phosphinic Acids (e.g. Cyanex 272), as this extractant is very selective for cobalt over nickel, and demonstrates many admirable qualities.

As noted above, however, this extractant is not so selective for cobalt compared to many common impurities found in leach liquors, such as copper, zinc, iron (II), cadmium, calcium, magnesium and manganese. To confirm this understanding, preliminary tests were carried out with simulated leach liquors derived from leaching a nickel laterite.

A synthetic leach, as shown in Table 1, was prepared from metal sulphate salts, and was intended to simulate leach liquor derived from leaching a typical nickel laterite. It was first extracted with Cyanex 272 at 10 vol/v% in Shellsol 2046AR as diluent.

The objective was to extract sufficient cobalt from the leach liquor so that the resultant nickel raffinate met the cobalt requirements for LME Grade Nickel, (Ni:Co ratio > 666:1). In effect this meant >98.6 % cobalt extraction was required, depending on the extent of nickel extraction.

Basic operating parameters were used; pH 5.1 – 5.5, temperature of 60°C, retention time of 5 minutes and organic continuous continuity at various organic to aqueous (O:A) ratios. Caustic was used for maintain the pH in the mixer.

This test was completed as a two stage series parallel test. The first stage consisted of first contacting fresh organic solution and pregnant leach solution (PLS); after 5 minutes under these conditions, the resulting emulsion was separated, producing raffinate and loaded organic streams.

The raffinate was not at the target Ni:Co ratio (666:1), so was then contacted again in a second stage with fresh organic under the same conditions, but with an O:A ratio of only 1:1.

Feed and product assays for both stages are presented in Table 1.

Table 1: Cyanex 272 Feed and Product Assays on Simulated Laterite Feed Liquor

Stage	O:A Ratio	Aqueous						
		Ni mg/L	Ca mg/L	Cl mg/L	Co mg/L	Mg mg/L	Mn mg/L	Na mg/L
PLS		7671	196	8610	726	12667	5216	565
1	5:1	7078	185	8410	69	8905	162	11451
2	1:1	7291	182	8480	10	6750	7	15460

The percent extraction of each element for each stage is presented below in Table 2.

Table 2: Cyanex 272 Extraction Results on Simulated Laterite Feed Liquor (cumulative)

Stage	O:A Ratio	Ni:Co Ratio	Ni %	Ca %	Co %	Mg %	Mn %	g NaOH:g Co
1	5:1	103	0.1	5.6	90.5	29.7	96.9	36.2
2	1:1	729	0.2	7.1	98.6	46.7	99.9	

All extractions are based on the aqueous solutions with the exception of nickel which is based on organic assay, (7 mg/L and 16 mg/L nickel in Stage 1 and 2 respectively).

Cobalt was extracted preferentially over nickel, but two stages and only with a large excess of organic did the raffinate finally meet the required target for Ni:Co ratio. However, virtually all of the manganese and a significant quantity of magnesium were also loaded at this point. Reagent consumption during this test was calculated (from sodium assays) at 36.2 g of NaOH / g Co which is very high, and indicates the difficulty with use of this reagent for such laterite leach liquors. Of this 36.2 g NaOH, about 25 g (or 70% of total) is due to the observed 46.7% magnesium extraction. However, it is understood that magnesium can largely be scrubbed off by cobalt in this situation, given sufficient stages, as per Bulong practice (Donegan 2006)¹; so the caustic consumption attributed to magnesium is unrealistically high. Reducing the magnesium extraction to say 1/10 of the above test result or 4.7%, the caustic consumption with Cyanex 272 from this solution would be about 13 g NaOH/g Co, based on the above test.

3 PROCESS DESCRIPTION

3.1 Basic Process for Cobalt Separation from Nickel

CSIRO have developed a number of solvent extraction processes to separate nickel and cobalt (together) from other elements present in solution such as zinc and manganese. This technology uses a synergistic combination of two or more extractants, and is thus known as SSX.

The new process developed by CESL and CSIRO uses SSX for the selective extraction of cobalt from a mixed nickel/cobalt solution containing other impurities. The resulting raffinate has

¹ Note that the reference quoted above on Bulong mentioned an actual NH₃ consumption of 1.6 t NH₃/t Ni. This is equivalent to 30 t NaOH/t Co, assuming a Ni:Co ratio of 13.3 in PLS.

a high Ni:Co ratio, sufficient to satisfy cobalt purity requirements for LME Grade Nickel. This extraction is achieved using a synergistic mixture of Versatic 10 and LIX 63.

There are two basic steps involved, as in any solvent extraction process: extraction and stripping. A third step, scrubbing, may be needed where the manganese impurity levels in feed solution are particularly high.

Prior to the solvent extraction process, it is necessary to remove certain metals, namely copper, zinc, cadmium and iron, which otherwise interfere with the process. Figure 1 shows the overall process flowsheet into which the new separation process is inserted. After the initial leaching process of the nickel ore or concentrate, and subsequent liquid/solid separation, purification is needed to remove:

- Copper, if present in commercial quantities, by solvent extraction.
- Iron and aluminum by hydrolysis with limestone or lime, and filtering.
- Last traces of copper, plus any zinc or cadmium present, by H_2S precipitation and filtering.

The resultant solution containing nickel, cobalt, and remaining impurities such as magnesium, manganese and calcium is now ready for the new cobalt separation process.

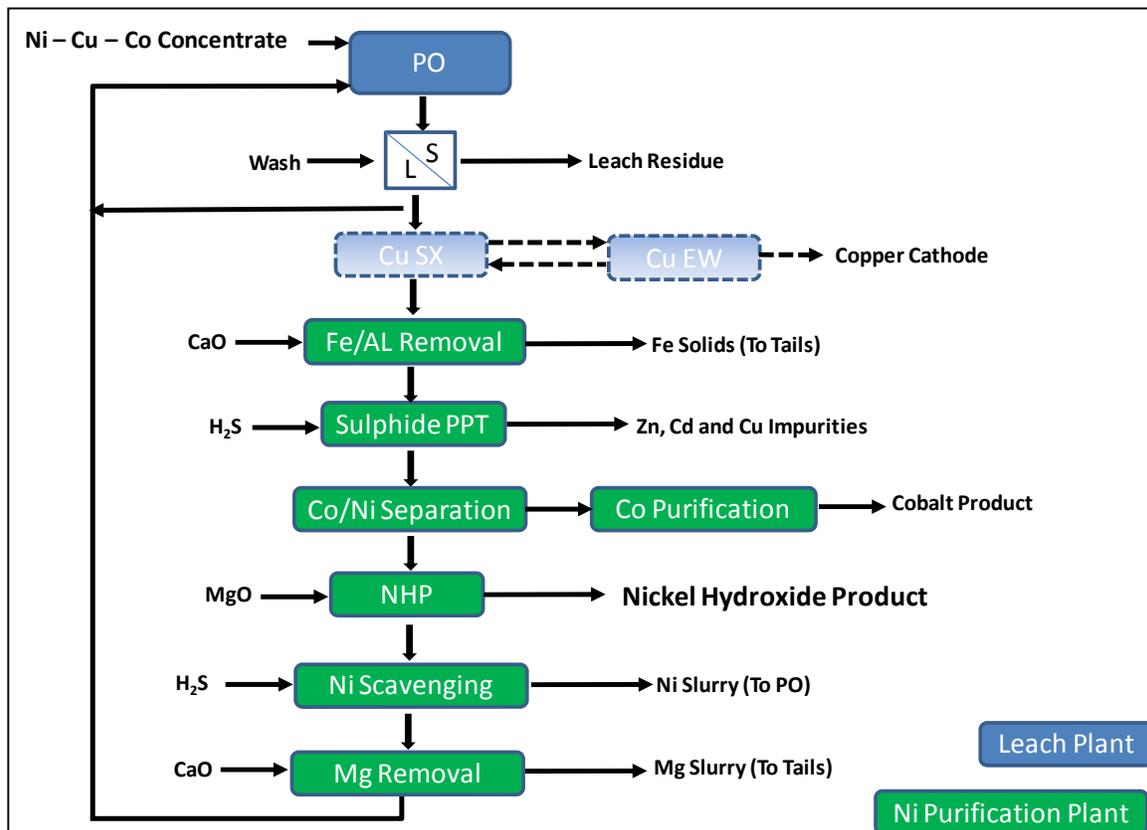
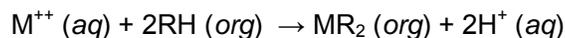


Figure 1: Nickel Recovery Flowsheet

3.1.1 Extraction

The extraction process works best in a fairly narrow pH range, about pH 4 – pH 5. As is usual with solvent extraction processes, the organic extractants produce H⁺ ions during extraction:



Since it is imperative to maintain an optimum pH during extraction, this can be achieved by:

- a) Adding a neutralizing agent to the emulsion *during extraction* to match acid production, or by:
- b) Pre-neutralizing the organic phase *before extraction*, to reach the pre-determined desired pH of the emulsion at the end of extraction. This is called saponification.

Two stages of extraction are generally sufficient to extract 97-99% of the cobalt from the initial PLS. A series parallel arrangement was found to work best as shown later in the paper in Figure 9.

In the first stage of extraction, the PLS solution from the sulphide precipitation circuit (Figure 1) is contacted briefly with saponified (stripped) organic in a pre-mix tank and the resulting emulsion is sent through a pipe reactor, to gain additional retention time, utilizing an in-line mixer.

In the second stage of extraction the raffinate from the first stage is contacted with further saponified organic in the same fashion as the first stage. The raffinate produced from the second stage has a high Ni:Co ratio which is then ready for subsequent precipitation, or other refining steps.

The loaded organic from both extraction stages is combined for stripping.

Approximately 99% of the cobalt can be extracted from typical leach liquors with about 12 % of the nickel. With a typical PLS of 10:1 Ni:Co ratio (laterites), the resultant loaded organic has a Ni:Co ratio of approximately 2:1.

3.1.2 Stripping

Stripping can be done in several ways, depending on whether the cobalt is selectively stripped first, or both cobalt and nickel are stripped together.

Various stripping configurations were tested throughout the different scales of batch, semi-continuous and continuous testwork. The two main configurations were: (1) Bulk Stripping and (2) Selective Stripping.

As depicted in Figure 2, the bulk stripping option has three stages of stripping to remove >99% of the cobalt from the loaded organic, together with about 80 - 90% of the nickel, using dilute acid. It is not essential to strip all the nickel, and leaving some nickel on the stripped organic is more economic overall. The stripping stages are run counter-current with enough free acid in

the strip feed solution to produce a strip product solution which contains a free acid of about 3 - 10g/L at an external O:A ratio of 15-20:1. Temperature is a key operating parameter in stripping of the loaded organic due to the slow stripping kinetics for nickel; temperature for the stripping stage is best maintained at 45-50°C.

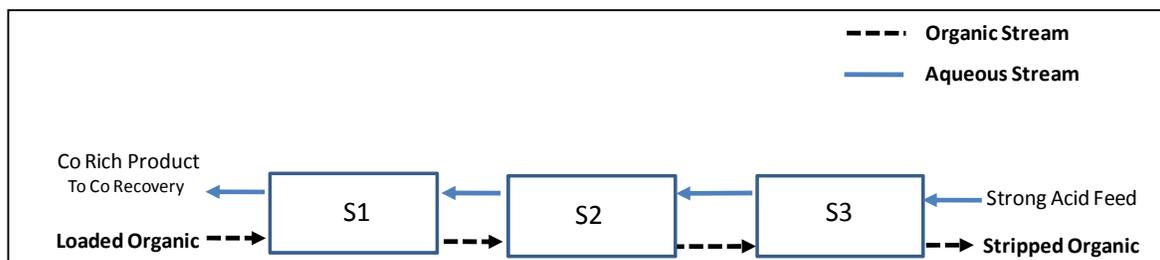


Figure 2: Bulk Stripping Option

In the selective stripping option (Figure 3), the loaded organic is contacted with a dilute aqueous stream in a counter-current arrangement. In order to selectively strip the cobalt from the loaded organic stream and leave the majority of the nickel, lower temperature, lower acid concentrations and shorter retention times are used. The second stage of stripping removes ~90% of the nickel from the organic by contacting the stream with a stronger acid in a counter current arrangement. This portion of the circuit operates at higher temperatures and retention times due to the slow stripping kinetics of the nickel.

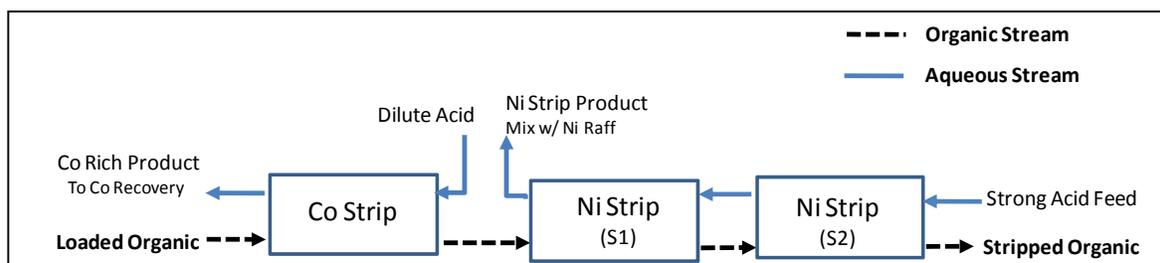


Figure 3: Selective Stripping Option

3.1.3 Manganese Scrub

A scrub stage to remove the manganese from the loaded organic is required in a laterite configuration of the SSX flowsheet, since these types of ore are usually high in manganese impurities. The combined loaded organic and a slip stream of the cobalt rich product is mixed; the nickel and cobalt are preferentially extracted onto the organic and the manganese is scrubbed off. The solution produced from this stage is recycled back to the PLS tank and the organic is forwarded to the stripping stages.

4 BATCH TESTS

All batch kinetics tests were carried out in a half litre stainless steel rectangular box immersed in a temperature controlled water bath. The two phases were mixed using an overhead stirrer at the appropriate A/O ratio and temperature. Solution mixture samples were taken at appropriate time intervals. The two phases of the mixture sample were separated through a Whatman 1PS

filter paper, and the aqueous phase of each sample was re-filtered through a 0.45 µm Supor membrane filter. A Cary-1C UV-visible Spectrometer was used to rapidly determine nickel and cobalt concentrations in the organic samples for test control. Some important organic samples were then stripped with 400 g/L sulphuric acid at 40°C. The loaded strip liquors were filtered through a 0.45 µm Supor membrane filter. The filtered aqueous samples were assayed by ICP-AES.

4.1 Batch Extraction Tests

The new process to separate cobalt from nickel is based on the differences in extraction and stripping kinetics of nickel and cobalt with some synergistic combinations of extractants, particularly Versatic 10 and LIX 63. The concentrations of the two extractants were varied to maximize the cobalt extraction at the expense of nickel; the optimal composition appeared to be 0.25 M V10 and 0.25 M LIX 63 (equivalent to 4.7 vol% V10 and 14.0 vol % LIX 63).

Batch tests were carried out with the synthetic solution is shown in Table 3; this solution simulated purified leach liquor from pressure oxidation of a low grade nickel sulphide concentrate, (by the CESL Nickel Process), produced in the Mesaba Cu-Ni project in USA. The synthetic solution was designed to match the purified nickel bleed stream from that project flowsheet, see Reference 2 for details. The CESL Nickel Process uses chloride as a catalyst in the pressure oxidation, hence the 11.7 g/L Cl. The Ni:Co ratio in this solution was approximately 20:1, fairly typical for a nickel sulphide concentrate. The main impurities of concern for cobalt SX were magnesium, manganese and calcium. Other metallic impurities, copper, zinc, and iron had been largely removed by prior purification. Magnesium was largely derived from magnesium recycled from magnesia precipitation stage downstream.

Table 3: Composition of the synthetic solution – from nickel sulphide leach

Element	Ni	Co	Mn	Mg	K	Al	Ca	Na	Si	Cl	Zn
(g/L)	20.3	1.06	0.44	11.3	0.25	0.021	0.564	0.21	0.035	11.7	0.032

Initial test results at pH 5 and an O:A ratio of 1:1 are shown in Figure 4. They indicate very fast extraction of both zinc and cobalt, but peaking at < 60 seconds at < 50 % extraction and then declining rapidly. Extraction of other metals were much slower, especially nickel, but increased steadily with time. Aluminum was an intermediate case, extracting fairly quickly after 60 seconds and not declining thereafter. Importantly, magnesium, manganese and calcium loading were negligible.

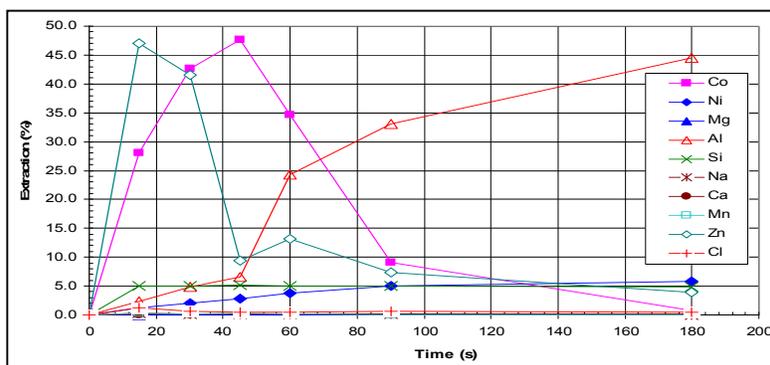


Figure 4: Metal Extraction Kinetics

A number of other variables were examined, including the effect of pH at 30°C and an O:A ratio of 0.5:1 as shown in Figures 5 and 6:

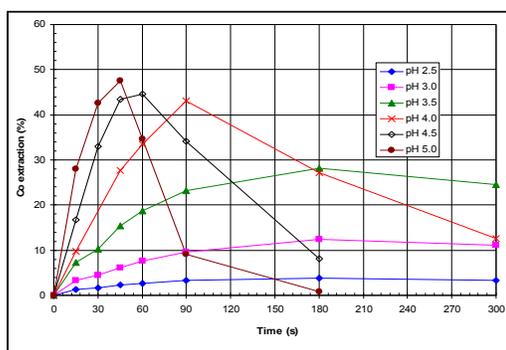


Figure 5: Cobalt Extraction vs. Time

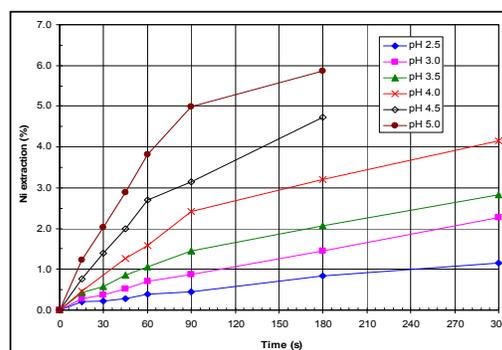


Figure 6: Nickel Extraction vs. Time

It was found that the best extraction pH for cobalt was in the range of 4.5 - 5.0. In this range, the extractions of the main impurities such as magnesium, manganese, calcium and chloride were very low and the cobalt extraction kinetics were much faster than nickel in the first 45-90 seconds.

At pH 4.5, cobalt extraction from the synthetic solution was 44 % after 60 seconds, compared to < 3 % of the nickel. This was for a single stage extraction with O:A of 1:1, demonstrating excellent selectivity with these conditions, but cobalt extraction peaked at 60 seconds and then declined thereafter, while nickel extraction continued to increase slowly. A cobalt extraction of 44% is insufficient to satisfy purity requirements for nickel, without further stages, or a higher O:A ratio.

A number of other variables were all tested; the effects of type of diluent, phase continuity and mixing speed were all minimal.

Various concentrations for both Versatic 10 and LIX 63 were tested. Changing the organic composition from 4.7 vol% Versatic 10 and 14 vol% LIX 63 to 3.8 vol% Versatic 10 and 19.5 vol% LIX63 did not simultaneously increase both cobalt load and cobalt/nickel selectivity. It did however increase cobalt loading slightly for a given cobalt/nickel value, and delayed the onset of cobalt displacement by nickel, thereby increasing the operating window in which cobalt can

be extracted. Decreasing the Versatic 10 concentration to 2.8 vol% also appeared to be beneficial, but decreasing to 1.9 vol% had a clear, adverse effect on rates of metal uptake.

Both cobalt and nickel extraction kinetics increased with temperature and time. However, the cobalt extraction dropped with time due to quicker increase in extraction kinetics of nickel than that of cobalt. As a result, the cobalt was crowded out by the nickel, causing a decrease in cobalt extraction. It seems that temperature plays a bigger role for nickel extraction than that for cobalt and extraction at lower temperature is more favorable for cobalt than that for nickel. However, low temperatures (e.g. 20°C) may have their own problems with heat balance and settling rates. Therefore, a temperature of 30°C was chosen for the separation of cobalt from nickel as a reasonable compromise of extraction kinetics and ease of operation.

The effect of temperature on cobalt and nickel extraction is shown in Figures 7 and 8:

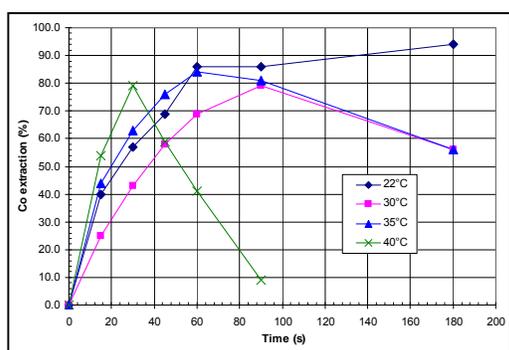


Figure 7: The effect of temperature on Co Ext.

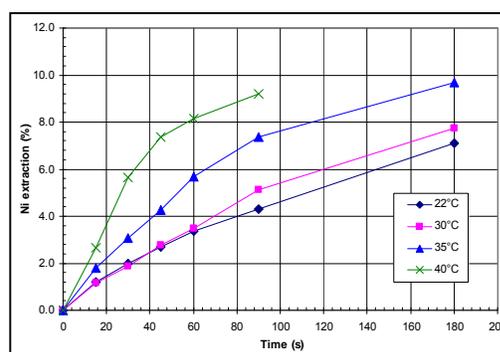


Figure 8: The effect of temperature on Ni Ext.

In order to achieve the target 97- 98% cobalt extraction it was clear however, that more than one stage of extraction would be required with any reasonable O:A ratio.

With a two-stage series/parallel extraction mode (Figure 9) at pH 4.5, 30°C and an O/A ratio of 1:1 in both stages, the cobalt extraction reached 97.8%, and the cobalt/nickel concentration ratio in the loaded organic solution 0.46 in average (Figure 10).

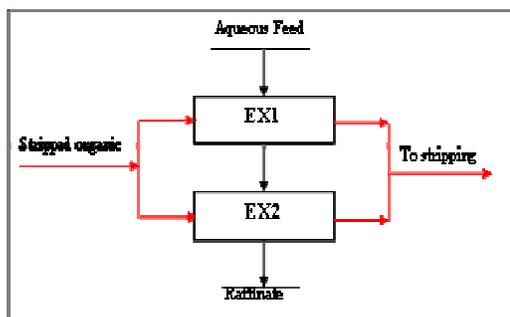


Figure 9: Extraction Flowsheet Schematic

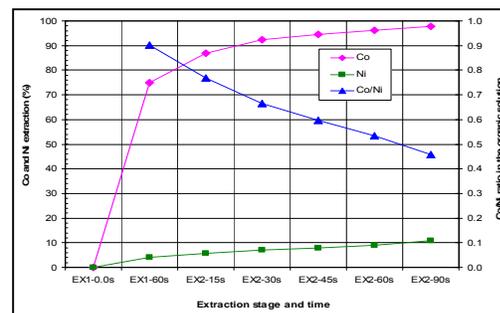


Figure 10: Co and Ni Extraction vs. Time

4.2 Batch Stripping Tests

Two stripping options were examined, either *selective* cobalt stripping followed by a 2nd strip for nickel, or a *bulk* strip of both cobalt and nickel. Batch testwork for the selective cobalt stripping is provided in the following section.

4.2.1 Cobalt Selective Stripping

The fresh organic solution was contacted with the aqueous solution at an A/O ratio of 1:1 at pH 4.5 and 30°C. The mixing was stopped at 60 seconds and a sample was taken. The two phases were separated. The loaded organic solution was mixed with a strip solution containing 5 g/L sulphuric acid and 0.2 M Na₂SO₄ at an A/O ratio of 1:1 and 30°C. Samples were taken at appropriate time intervals for assay.

With 5 g/L sulphuric acid at O:A of 1:1 and 30°C, nearly 95% cobalt was stripped in 60 seconds, indicating very fast cobalt stripping kinetics. The nickel stripping kinetics at this temperature were much slower with only 40% being stripped in 60 seconds. With 3 g/L sulphuric acid, the cobalt and nickel stripping kinetics was slower but more selective than with 5 g/L sulphuric acid, indicating that the cobalt/nickel ratio in the loaded strip liquor is higher when a lower acidity strip solution is used (Fig. 11). The only problem with this result is that the product strip liquor has very low [Co]. A more practical stripping regime using low O:A ratio confirmed that selective stripping was still possible, and consistent with producing a higher tenor cobalt product.

With O:A mixing ratios as low as 40:1 at 30 °C resulted in a cobalt product solution containing a positive cobalt/nickel ratio. Cobalt stripping tests at O:A 1:1 mixing ratios but using high cobalt concentration aqueous solutions (13.5 g/L Co, 1.0 g/L Ni) to simulate O:A 40:1 flow ratios with aqueous recycle led to improved cobalt strip efficiency and maintained high cobalt/nickel selectivity ($\Delta\text{Co}/\Delta\text{Ni} > 10$) as well as resulting in a cobalt electrolyte with a high cobalt tenor.

4.2.2 Nickel Stripping

The organic solution was pre-loaded and then mixed with a stripping solution containing 3 or 5 g/L H₂SO₄ for cobalt selective stripping. The mixing was stopped at 60 seconds and a sample was taken. The cobalt-selectively stripped organic solution was contacted with different strip solutions at different temperatures at an O:A ratio of 1:1. Solution mixture samples (30 mL) were taken for assay at appropriate time intervals for assay.

The effect of temperature on nickel stripping was found to be substantial. After stripping the cobalt-selectively stripped organic solution with 50 g/L H₂SO₄ for 8 minutes at 40°C, the nickel stripping efficiency increased 40% (from 52 to 94%) compared to stripping at 30°C (Fig. 12). It seems that a higher stripping temperature (45-50°C) is necessary for stripping nickel from the organic solution.

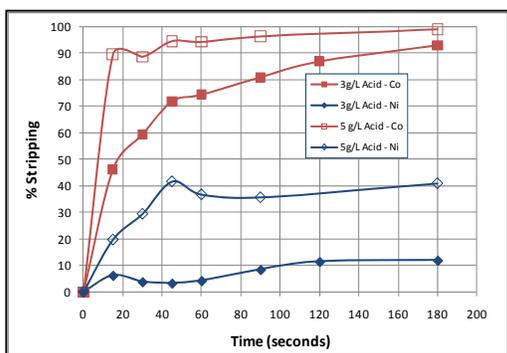


Figure 11: Stripping kinetics of Co and Ni

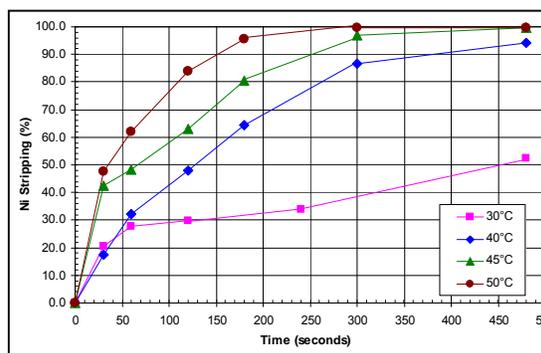


Figure 12: The effect of temperature on Ni stripping

Studies to optimize nickel stripping from the organic phase at 50 °C found that stripping efficiency was poor when low O:A ratios (5:1 to 20:1) were used, and left high (>0.4 g/L) residual nickel on the organic phase. Nickel stripping tests at O:A 1:1 mixing ratios using high nickel concentration aqueous solutions (up to 16 g/L) and 10 g/L sulfuric acid to simulate O:A 20:1 flow ratios with aqueous recycle enabled residual nickel levels of less than 0.2 g/L to be obtained after mixing for 10 minutes at 50 °C.

5 CONTINUOUS TESTS

Following the successful batch testing phase, continuous testing was carried out, first in semi-continuous mode and then in a fully continuous pilot plant.

These tests were completed at both CSIRO (Parker Centre) and at CESL (Demo plant in Richmond, B.C). The data presented in the following section are mostly those obtained from operations at the CESL pilot facility while the circuit was fully integrated with the CESL Cu-Ni Process.

Initially, tests were carried out in conventional mixer-settlers in semi-continuous mode, and the expectation was that results would largely follow those obtained in the Batch mode above, as it usually does. Unfortunately this was not the case here.

Continuous extraction tests with mixer-settler equipment gave significantly poorer results than batch tests with much less cobalt extraction and consequently a significantly lower Ni:Co ratio in final raffinate.

A number of experimental conditions were tried including pH control methods, different organic compositions, varying target pH, and 3 mixers in series, but none were successful. In a mixer, the organic and aqueous streams are continually added as the product emulsion is removed (by overflow); this leads to some degree of back mixing. The tentative conclusion was that *plugged flow of the emulsion* was necessary to achieve selective cobalt extraction; therefore testing was done with a pipe reactor, which proved to be a successful mode of operation.

5.1 Continuous Extraction Tests with Pipe Reactors

The extraction system consisted of two trains in a series-parallel configuration where the PLS flowed through each of the two mixers/pipe reactors/settlers in series, and the organic flowed through in parallel. That is, freshly saponified organic entered each of the two trains independently, and after a single pass through an extraction stage, recombined in the Loaded Organic Tank. The two trains were designed using the same design criteria except for differences in retention time.

The stripping system consisted of three conventional mixer settlers. The entire strip cells were fitted with steam heating coils controlled by solenoid valves.

5.2 Metal Extraction for Sulphide Feed

Continuous testing was completed using the synergistic organic system consisting of 19.5v/v% LIX 63, 3.8v/v% Versatic 10 in Shellsol D80 diluent. The extraction stages were completed at pH ranges of 3.9 – 4.1 and 4.1 – 4.3 for E1 and E2 respectively at 30°C. The feed solution tenors are presented in Table 4.

Table 4: PLS Solution Tenors

Feed	Nickel mg/L	Cobalt mg/L	Manganese mg/L	Magnesium mg/L	Calcium mg/L
Sulphide	21211	780	109	4252	603

The first stage of extraction averaged 5.3% nickel and 71.5% cobalt extraction with no impurity extraction. The second stage of extraction was 8.9% nickel and 89.7% cobalt. Overall extraction results are presented in Table 5 below.

Table 5: Overall Extraction Results

Stream	Ni %	Co %	Mn %	Mg %	Ca %
E1	5.3	71.5	<0.1	<0.1	<0.1
E2	8.9	89.7	<0.1	<0.1	<0.1
Overall	14.2	96.9	<0.1	<0.1	<0.1

The overall nickel and cobalt extractions achieved were 14.2% and 96.9% with a Ni:Co ratio of 734 in the final raffinate

Overall extractions for all elements with the exception of nickel were calculated based on aqueous assays; nickel extraction was based on organic assays

As represented in the table above there was no detectable extraction of magnesium, manganese or calcium.

5.3 Metal Stripping for Sulphide Feed

Stripping of the loaded organic was required to produce a stripped organic containing <0.25g/L nickel, as well as a strip product solution with a Ni:Co ratio <3:1. The strip circuit operated in a three stage counter current arrangement at 40°C, an O:A ratio of 15 – 20:1 and an acid feed tenor of ~81 g/L in the aqueous strip feed solution. Average feed and product streams for the stripping of the loaded organic are presented in Table 6.

Table 6: Aqueous and Organic Data for Bulk Strip Data

Stage	Loaded Org.		Feed Aq.		Stripped Org.		Product Aq.		Strip Eff.	
	Ni mg/L	Co mg/L	Ni mg/L	Co mg/L	Ni mg/L	Co mg/L	Ni mg/L	Co mg/L	Ni %	Co %
S1	1940	534	19000	3660	1990	384	16800	6470	-1.6	28.1
S2	1990	384	12200	340	1130	33	19000	3660	30.7	91.4
S3	1130	33	0	0	178	3	12200	340	84.3	90.9
Overall	-	-	-	-	-	-	-	-	90.8	99.4

The overall nickel and cobalt strip efficiencies were 90.8% and 99.4% respectively with stripped organic nickel tenors being less than 200mg/L. The low nickel tenors in the stripped organic indicate that less acid or a higher O:A can be utilized.

Free acid tenors across the strip circuit are presented in Table 7 below.

Table 7: Aqueous Stream FA Tenors for 15:1 O:A Strip Tests

Stage	Aqueous Stream	Free Acid (g/L)
-	Acid Feed	81.0
S1	Cobalt PE	0.25
S2	S2 Product to S1	5.07
S3	S3 Product to S2	35.6

99.7% of the acid was utilized across the circuit with only 0.25g/L FA remaining on the cobalt rich product.

As a basis, calculations were completed to determine a theoretical quantity of acid (mass g) needed to theoretically strip a quantity of metal (1 g). Equation 1 below shows that theoretically 1.67 g of acid is needed to strip off one gram of metal (e.g. nickel & cobalt).

Equation 1

$$\Delta Ni(g) \times \frac{1}{MM Ni} \times \frac{1 \text{ mol } H_2SO_4}{1 \text{ mol } Ni} \times MM H_2SO_4 = g H_2SO_4$$

$$1 \times \frac{1}{58.71} \times \frac{1}{1} \times 98 = 1.67 \frac{g H_2SO_4}{g Ni}$$

When examining the typical feed tenors of the loaded organic entering the circuit, there was an average of 1.8 g/L nickel and 0.4 g/L cobalt with negligible amounts of impurities. Using the 1.67g FA/g metal with an average of 2.2 g of metal on the organic, a value of 3.7 g FA/L organic was calculated for the theoretical amount of acid needed to strip the organic.

5.4 Reagent Consumption for Sulphide Feed

The stripped organic solution is saponified (pre-neutralized) with 30% NaOH solution manually prior to entering the two extraction stages. Caustic consumption was calculated based on two variables. The first was the flow of caustic to the saponification tanks over a specific run time. The amount of 30% NaOH used to for the saponification in the first stage of extraction was 2.0 g per liter of organic and 2.1g per liter of organic for stage 2.

Another way to calculate the NaOH consumption is to take the Na assays and calculate the grams of caustic consumed per gram of cobalt extracted (as per the Cyanex 272 testwork). Assay results and calculations for this method are presented in Table 8.

Table 8: Caustic Utilization for New Process

Stream	O:A Ratio	Aqueous			Organic		g NaOH:g Co
		Ni:Co Ratio	Co mg/L	Na mg/L	Co mg/L	Na mg/L	
PLS/SO	1:1	27	780	862	3	BDL	8.2
Raff/LO		734	24	4419	229	BDL	

5.5 Metal Extraction for Laterite Feed

Testing of a synthetic laterite feed material commenced after the integrated sulphide feed testing was complete. Almost all of the conditions in the circuit stayed constant with respect to equipment and operating conditions with the exception of retention time, caustic consumption and the addition of a manganese scrub circuit. The overall nickel and cobalt extractions achieved were 11.7% and 98.9% with a Ni:Co ratio of 796 in the final raffinate.

Table 9: PLS Solution Tenors

Feed	Ni mg/L	Co mg/L	Mn mg/L	Mg mg/L	Ca mg/L
Laterite	6980	696	4980	12200	212

The first stage of extraction averaged 4.9% nickel and 85.5% cobalt extraction with minimal to no impurity extraction. The second stage of extraction was 6.7% nickel, 92.1% cobalt.

Overall extraction percentages are presented in Table 10 below.

Table 10: Overall Extraction Results

Stream	Ni %	Co %	Mn %	Mg %	Ca %
E1	4.9	85.5	2.0	<0.1	<0.1
E2	6.7	92.1	2.3	<0.1	<0.1
Overall	11.7	98.9	4.3	<0.1	<0.1

As shown in the table above only minor amounts of manganese was extracted, and virtually no calcium or magnesium extraction was found.

5.6 Manganese Scrub for Laterite Feed

The strip circuit also included a manganese scrub stage; the circuit set up is shown in Figure 13.

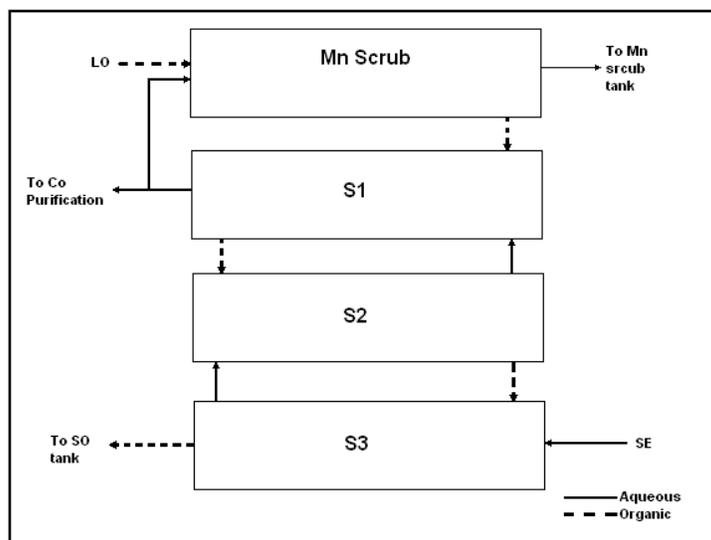


Figure 13: Strip Circuit Flowsheet with added Manganese Scrub Stage

The manganese scrub solution feed rate was calculated using Equation 2 to maintain a 1:1 Co:Mn ratio in the mixer.

Equation 2

i.e. Mn in Org = 0.2 g/L at 0.850 ml/min; Co in Aq = 5.0 g/L at 0.02 ml/min

$$\frac{0.2 \text{ g Mn}}{\text{L}} \times \frac{0.850 \text{ L}}{\text{min}} = \frac{0.17 \text{ g Mn}}{\text{min}}$$

$$\frac{5.0 \text{ g Co}}{\text{L}} \times y = \frac{0.17 \text{ g Mn}}{\text{min}}$$

$$y = 0.034 \text{ L/min}$$

Table 11: Manganese Scrub Operating Conditions

LO feed mL/min	Scrub Feed mL/min	Mixer Rt min	Temperature °C	Overall O:A	Overall Co:Mn
850	20	5.3	30	43:1	0.88

The assay results from the pilot plant manganese scrub testwork are presented below in Table 12; with results high-lighting that the manganese scrub efficiency was >99%.

Table 12: Manganese Scrub Pilot Tests - Aqueous/Organic Feed Assays

<i>Streams</i>	<i>Aqueous</i>			<i>Organic</i>		
	Ni (mg/L)	Co (mg/L)	Mn (mg/L)	Ni (mg/L)	Co (mg/L)	Mn (mg/L)
Cobalt Prod / LO	16000	6140	75	686	628	163
Scrub Prod / LO	3650	1410	387	904	582	1

5.7 Reagent Consumption for Laterite Feed

Both of the organic extractants used produce H⁺ ions during extraction, as a result of the basic reaction: $M^{++} (aq) + 2RH (org) = MR_2 (org) + 2H^+ (aq)$.

Thus the aqueous phase becomes more acidic as extraction proceeds, which constitutes a problem as extraction efficiency is pH-dependent; thus it is imperative to maintain an optimum pH (or rather a constant pH), during extraction. To maintain the optimum pH during extraction the organic was pre-neutralized (saponified) with caustic to reach the pre-determined desired pH of the emulsion at the end of extraction

Caustic consumption was calculated based on the Na and cobalt assays and determined to be 3.4 g NaOH/ g of cobalt extracted. Assay results and calculated values are presented in Table 13.

Table 13: Caustic Utilization for New Process

		Aqueous			Organic		
Stream	O:A Ratio	Ni:Co Ratio	Co mg/L	Na mg/L	Co mg/L	Na mg/L	g NaOH:g Co
PLS/SO	1:1	20:1	696	491	4	BDL	3.4
Raff/LO		805:1	8	1878	365	74	

6 CONCLUSIONS

A new solvent extraction process has been developed for separating cobalt from nickel that is applicable to typical leach solutions without the usual recourse to precipitation and re-leach of nickel/cobalt values.

The process is different from the usual solvent extraction process (which is based on thermodynamic or equilibrium differences in extraction chemistry); this process is based on *kinetic differences* in extraction and stripping between cobalt and nickel. The extractant used so far is a synergistic combination of two extractants, Versatic 10 and LIX 63, although other combinations may be possible.

The process is suitable mainly for solutions that are essentially free of copper, zinc, and iron, as these interfere with the separation process. However, the process is practically immune to other important impurities, such as manganese, magnesium and calcium, which pose difficulties with existing cobalt-nickel separation processes.

It can be applied to solutions derived from both sulphide concentrates and laterite ores. It is intended to be an addition to many hydrometallurgical processes for nickel ores or

concentrates, which will hopefully reduce costs overall and enhance revenue, partly by producing a purified cobalt stream at an early stage.

The process has been demonstrated on a small pilot plant in continuous mode, but has not yet been tested commercially.

The process is relatively simple, with few operating steps, and is capable of >97% cobalt extraction in two stages from a typical leach solution, which produces a nickel raffinate with a Ni:Co ratio > 700:1. Nickel co-extraction is about 15% so the strip product contains both nickel and cobalt typically in a ratio of between 2:1 and 4:1. This strip product, free of manganese and magnesium, can be further refined by known technology (Cyanex 272) to produce a refined cobalt stream and return nickel values to the nickel raffinate.

Stripping of the loaded organic occurs easily with dilute acid, and the cobalt strips more easily than the nickel, leading to possibilities of separate strip products.

Reagent consumption for neutralization was about 3.5 g NaOH/g Co extracted for laterite-derived leach liquors; this is equivalent to about 1.5 t NH₃/t Co, or 0.15 t NH₃/t Ni which is far less than a commercial plant would use with existing technology for cobalt extraction from an impure leach liquor. For leach liquors derived from nickel sulphide concentrates (which have higher Ni:Co ratios) the reagent consumption is about double that for laterites.

The extraction process works well in a pipe reactor, with short retention times and modest pressures, but not so well in a conventional mixer settler, evidently due to the requirement for plugged flow. Stripping works well in conventional mixers.

A very minor amount of manganese co-extracts with cobalt, (<5%) but is easily scrubbed off by a slip stream of cobalt strip product.

7 REFERENCES

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