# Mini-Plant Trials on the Recovery of Nickel by Solvent Extraction

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## ABSTRACT

Several extraction systems for nickel have been evaluated in mini-plant trials to compare their efficiencies and relative selectivity for nickel over other elements under continuous counter-current conditions. The aqueous feed solution was a sulphate liquor derived from the biologically assisted leaching of low-grade sulphide ore, and contained ~9 $g/dm^3$ nickel, 0.5 $g/dm^3$ calcium, 0.2 $g/dm^3$ cobalt, 1.6 $g/dm^3$ magnesium, and 0.5 $g/dm^3$ manganese. The extractants tested were Versatic acid, Versatic acid in a synergistic mixture with 4-nonylpyridine, and di(2-ethylhexyl)phosphoric acid in synergistic combination with isodecyl 4-pyridine carboxylate. An aliphatic hydrocarbon diluent was employed.

*Keywords*: nickel, calcium, Versatic acid, D2EPHA, synergism, alkylpyridine, alkylpyridine carboxylic ester.

## INTRODUCTION

Biologically assisted processes are currently being developed for the extraction of nickel from low-grade sulphide ores.[1] Extractants need to be selective for nickel over other impurities present in the leach solutions.[2] This is particularly true with regards to calcium, as the solubility of this sulphate limits the upgrading ratio to a value below that which produces gypsum-saturated strip liquor.

Previous testwork at Mintek investigated the influence of a nitrogen-donor synergist in mixtures with either di(2-ethylhexyl)phosphoric acid (D2EPHA) or a carboxylic acid (Versatic acid) on the separation achievable between nickel and calcium.[2,3] This work identified appropriate mixtures for further continuous counter-current testwork.

Mini-plant trials were conducted using these extractant systems, together with Versatic acid on its own, using a typical bio-leach solution. The extraction efficiencies for nickel and relative selectivity for nickel over other metals were tested under continuous counter-current conditions. Stripping efficiencies, pH of operation, and consumption of NaOH as a neutralising agent were also monitored. The results obtained from the mini-plant runs are discussed in this paper.

## PROCESS DESCRIPTON

Mixtures of pyridine derivatives (L) and acid extractants (HA) extract nickel[4] according to Reaction 1

$$Ni^{2+}_{(Aq)} + 2\, HA_{(Org)} + n\, L_{(Org)} \Leftrightarrow NiA_2L_{n(Org)} + 2\, H^+_{(Aq)} \qquad (1)$$
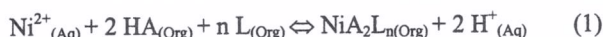
Because protons are released during extraction, the reaction is pH dependent. The appropriate pH was maintained by the addition of base to the mixers in the extraction stages. In the mini-plant trials, NaOH was used. Industrial practice is to pre-load the organic phase with sodium or ammonium ions in a separate stage, before extraction of the metal, to prevent excessive dilution of the aqueous phase. This practice is not favoured for the Versatic systems because of the high aqueous solubility of the sodium Versatic salt.

Nickel is stripped from the loaded organic phase by contacting it counter-currently with aqueous solution containing sulphuric acid, to effect the reverse of Reaction 1. By employing nickel-containing anolyte from nickel electrowinning as the aqueous strip liquor, the net consumption of acid is minimised.

## EXPERIMENTAL

### Aqueous solutions

The aqueous feed solution was a leach liquor derived from a biologically assisted process, which had been treated for the removal of iron. The composition is given in Table 1. The strip liquor was a synthetic solution made up from chemically pure grade nickel sulphate, and contained 50 g/dm$^3$ H$_2$SO$_4$, 65 g/dm$^3$ nickel, 0.1 g/dm$^3$ magnesium and traces of other metal impurities.

| Element | Concentration (g/dm$^3$) | Element | Concentration (g/dm$^3$) |
|---------|--------------------------|---------|--------------------------|
| Ni | 9.0 | Fe | < 0.002 |
| Co | 0.175 | Zn | 0.001 |
| Cu | 0.062 | Ca | 0.480 |
| Mn | 0.475 | Mg | 1.6 |

**Table 1.** Composition of the aqueous feed solution.

### Organic reagents

The various components of the organic phase systems tested are listed in Table 2. Isodecanol (Henkel) was used as a phase modifier where appropriate, and C$_{12}$-C$_{13}$ n-paraffin (SasolChem) was used as the diluent in all cases.

| Reagent | Supplier |
|---------|----------|
| D$_2$EHPA | Bayer |
| Versatic acid | Shell SA |
| 4-nonylpyridine *(SYN1)* | Aldrich |
| Isodecyl 4-pyridine carboxylate *(SYN2)* [*] | Mintek |

[*] Prepared as described in Reference 3.

**Table 2.** Organic reagents.

### Laboratory batch procedures

The operating pH values for each extractant, pH$_{90}$ (defined as the pH at which 90% of the nickel present in the feed solution was extracted), were determined by plotting the fractional extraction as a function of pH at an organic-to-aqueous phase ratio (O:A) of 3. The number of extraction stages required for continuous counter-current operation was determined from extraction equilibrium isotherms generated at appropriate pH$_{90}$ values at different O:A ratios. Stripping equilibrium isotherms were generated in a similar manner, but without pH control.

The batch tests were carried out by contacting the two phases in the appropriate O:A ratio using magnetic stirring. Where applicable, pH was controlled by the drop-wise addition of 100 g/dm$^3$ NaOH solution.

Aqueous- and organic-phase samples were taken for the analysis of the elements of interest. The organic-phase samples were stripped with 100 g/dm$^3$ H$_2$SO$_4$ and the acid solutions analysed, together with the aqueous samples, by inductively coupled plasma emission spectroscopy.

The relative phase-separation characteristics of the various extractant systems were tested by contacting equal volumes of the aqueous and organic phases in a beaker and noting the time required for separation.

### Continuous counter-current trials

The mini-plant comprised a series of conventional box-type mixer-settler units, each with a 100 cm$^3$ mixer and 400 cm$^3$ settler (settling area of 110 cm$^2$), constructed of clear PVC. Electrically driven pump-mix impellers accomplished mixing and inter-stage transfer of the

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The pH in the mixers of the extraction stages was controlled by the addition of an 80 to 100 g/dm$^3$ NaOH solution. A loaded organic reservoir was used to minimise carry-over of the aqueous phase with the loaded organic phase to the stripping circuit.

The general layout for a plant with three extraction and two stripping stages is shown in Figure 1. Aqueous and organic samples were taken at regular intervals from each stage. The samples were analysed in the same manner as for the laboratory batch procedures.
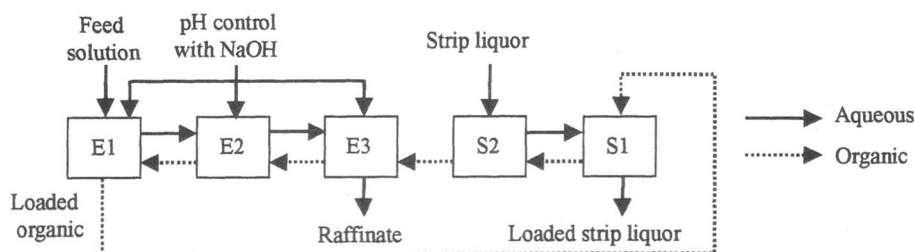


**Figure 1.** General layout of the continuous counter-current mini-plant.

## RESULTS

### Laboratory batch experiments

The different extractant systems tested are shown in Table 3. From plots of pH versus fractional extraction, and the extraction and stripping equilibrium isotherms, the operating conditions and plant layout for each extractant system were determined as shown in Table 4.

| System | Composition |
|---|---|
| 1 | 0.5 mol/dm$^3$ versatic acid |
| 2 | 0.25 mol/dm$^3$ versatic acid, 0.25 mol/dm$^3$ SYN1, 10 volume % isodecanol |
| 3 | 0.25 mol/dm$^3$ D2EHPA, 0.25 mol/dm$^3$ SYN2 |

**Table 3.** Composition of extractant systems tested in mini-plant trials.

The criteria applied to the McCabe-Thiele constructions were a nickel raffinate concentration below 0.1 g/dm$^3$, approximately 80 percent utilisation of the capacity on the organic phase, and a stage efficiency of 90 percent.

| System | No. of extraction Stages | No. of stripping Stages | Operating pH (pH$_{90}$) | Extraction O:A | Stripping O:A |
|---|---|---|---|---|---|
| 1 | 4 | 2* | 6.5 | 2 | 3.3 |
| 2 | 4 | 2 | 5.5 | 2.5 | 8.6 |
| 3 | 3** | 2 | 3 | 3 | 9.2 |

\*      McCabe-Thiele construction predicted 1 stage required.

\*\*     McCabe-Thiele constructions predicted 2 stages required.

**Table 4.** Plant layout and operating conditions for the different extractant systems.

Figure 2 shows the nickel/calcium separations achievable with systems 1 and 2. It can clearly be seen that system 2 exhibits better separation of nickel from calcium compared with system 1. The

extraction isotherms for systems 1 and 2 are shown in Figures 3 (a) and (b), respectively. System 1 has better nickel extraction properties than system 2.

It is interesting to note that the loading on the organic phase achieved with system 2 was similar to system 1, even with the reduced Versatic acid concentration.

All systems except for system 2 (without the addition of isodecanol) exhibited acceptable phase-separation characteristics. With the addition of 10 vol. % isodecanol, the time required for complete phase separation of system 2 was comparable to those of the other systems.
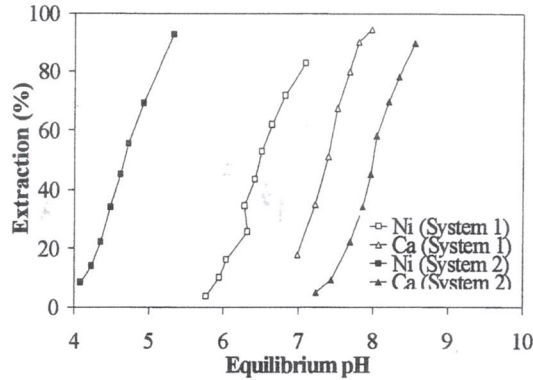


**Figure 2**. pH *vs.* extraction for system 1 and 2
(0.5 mol/dm³ of each constituent - system 2)[4].
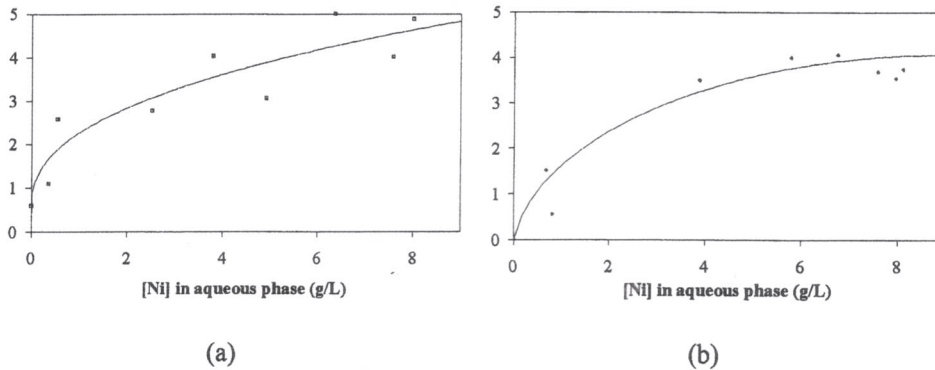


| (a) | (b) |

**Figure 3.** Equilibrium extraction isotherms (a) system 1 and (b) system 2 using feed solution.
([Ni] in organic phase (g/L) versus [Ni] in aqueous phase (g/L))

## Mini-plant trials

For systems 1 and 2 (see Table 5), an additional extraction stage would have reduced the nickel concentration of the raffinate significantly, and raffinate concentrations of less than 0.1 g/dm³ should be readily attainable with a slight increase in the operating pH of the extraction section. For circuits in which it is desirable to co-extract a large portion of the cobalt along with the nickel, systems 1 and 2 could be employed, operated at higher pH values. Both systems would be successful, but system 1 would co-extract more calcium and other impurities than system 2. This could be overcome by scrubbing the loaded organic phase of system 1 with loaded strip liquor. System 2 should co-extract significantly less calcium and other impurities, and the addition of scrubbing stages may not be required.

The excessive NaOH consumption experienced with system 2 was thought to be caused by the protonation of the synergist component. This will be investigated further. The soluble Versatic salt lost to the aqueous phase for system 1 can be recovered into the plant organic phase by contacting the raffinate with the stripped organic phase at pH 3 in one stage. For system 3, the quantity of nickel extracted was higher than for systems 1 and 2 but so was the co-extraction of impurities. This system would not be used in practice.

| Parameter | | System 1 | System 2 | System 3 |
|---|---|---|---|---|
| Raffinate [Ni] ($mg/dm^3$) | | 250 | 600 | 100 |
| pH profile ( E1 – last stage) | | 6.3 – 6.8 | 5.8 – 6.0 | 3 |
| Extraction efficiency (%): | Co | 78 | 40 | > 80 |
| | Cu | 100 | 100 | 100 |
| | Mn | 50 | < 20 | > 90 |
| | Ca | 1 | Negligible | > 80 |
| | Mg | 4 | Negligible | < 20 |
| NaOH consumption (g NaOH/g Ni extracted) | | 1.5 | 1.9 | 2 |
| Ni stripping efficiency (%) | | > 98 | > 95 | > 80 |
| Versatic acid lost ($g/dm^3$ aqueous phase) | | 1.4 | Negligible | NA |
| Residence time in extraction mixers (min) | | 3 | 5 | 3 |

**Table 5.** Summary of results obtained from mini-plant trials.

## CONCLUSIONS

Under the conditions employed, systems 1 and 2 were identified as likely extractant systems for the selective extraction of nickel and cobalt from bioleach liquors. System 3 exhibited unfavourable selectivity characteristics and excessive NaOH consumption.

The high operating pH value required for acceptable cobalt recovery, and the possible high co-extraction of calcium for system 1, can be overcome by an increase in the extractant concentration and the introduction of scrubbing stages.

Further testwork is required on system 2 to quantify the high NaOH consumption and long-term stability of 4-nonylpyridine. The relationship between operating pH and nickel, cobalt and calcium extractions will be interesting, as this system has the potential to eliminate the need for scrubbing stages for any co-extracted calcium and impurities.

## ACKNOWLEDGEMENTS

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