Enhanced Extraction of Nickel from a Concentrated Nitrate Aqueous Matrix Using LIX 63 / Versatic 10 / nonyl-4PC

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Recent development of nitrate-based leaching techniques for nickel laterite ores has sparked interest in the solvent extraction of nickel and cobalt from such leach solutions. Solvent extraction from concentrated magnesium nitrate-based aqueous phases using LIX 63/Versatic 10/nonyl-4PC at low pH results in a higher deportment of nickel to the organic phase compared to zinc and cobalt, offering a novel method to separate nickel from cobalt. The present investigation into this phenomenon found that increasing nitrate concentrations in the aqueous phase increased distribution of nickel to the organic phase at a given pH for a range of solvent extraction reagents. Co-extraction of nitrate with nickel was also found to increase with decreasing pH for LIX 63/Versatic 10/nonyl-4PC from near 0 at pH 3 to a NO_3:Ni ratio of 1.27 at pH 1. UV-Vis analysis demonstrated that the nickel complex extracted from a concentrated nitrate matrix using only LIX 63 was octahedral with a spectrum comparable to $[Ni(HL)_3]Cl_2$ where HL is hydroxyoxime. These results are consistent with additional nickel uptake occurring at lower operating pH due to extraction of a nickel-nitrate salt such as $[Ni(HL)_3](NO_3)_2$.

1. Introduction

The advent of nitric acid–based processes such as the Direct Nickel process [1] or the nitric acid pressure leach [2] has generated interest in the purification of nickel and cobalt from nitric acid leach solutions. Solvent extraction directly from a nitrate leach liquor, after iron and aluminium removal, is a potential alternative to mixed hydroxide or mixed sulfide precipitation that bypasses the generation of an intermediate solid.

Previous studies have shown that extraction of certain metals from nitrate-based aqueous feeds occurs at a lower pH than corresponding sulfate-based aqueous feeds [3-6]. A comparative investigation by the present authors showed that, in general, the extraction pH_{50} value of base metals by acidic solvent extraction reagents decreases by 0.5 units on moving from a moderate ionic strength (1 M) sulfate to comparable nitrate matrix [7].

The expected nitrate concentration in the Direct Nickel solvent extraction feed could be as high as 9 M [8]. The effect of this high ionic strength matrix on the extraction of base metals by common solvent extraction reagents is not well understood.

We have previously investigated metal extraction from a moderate ionic strength nitrate matrix

(1 M $NaNO_3$) using the combination of LIX 63/Versatic 10. Nonyl-4PC was additionally used to enhance nickel kinetics in place of tributyl phosphate [9]. Nickel was extracted preferentially over cobalt and zinc under these conditions [10], contrary to the sulfate system where nickel and cobalt are extracted at the same pH [11]. This result prompted the development of a process to separate nickel from cobalt and zinc in a nitrate matrix at low pH (pH 1.5 to 2) using LIX 63/Versatic 10/nonyl-4PC [9]. The present paper aimed to further investigate the effects of increasing the aqueous phase magnesium nitrate concentration on the solvent extraction of nickel as may be applicable to a Direct Nickel-type process.

2. Experimental

2.1 Aqueous and Organic Solutions

Organic solutions were prepared using technical grade reagents diluted with ShellSol D70 (Shell Chemicals). Extractants used were: Versatic 10 (iso-decanoic acid, 99%, Shell Chemicals), LIX®63 (5,8-diethyl-7-hydroxy-6-dodecanone oxime, 55%, BASF), and nonyl-4PC (nonyl-4-pyridinecarboxylate, 95%, China Central South University). LIX 63 concentration was determined by gas chromatography flame ionisation detection (GC-FID) using pure *anti*-hydroxyoxime standard as described elsewhere [12].

Pure *anti*-hydroxyoxime was prepared following the nickel method of Tammi [13]. The remaining reagents were used as supplied and the quoted purities were obtained from either the MSDS or the manufacturer.

Solutions of nickel nitrate (AR) were made up in various matrices containing combinations of reagent grade magnesium nitrate or magnesium sulfate. Adjustment of pH was carried out using solutions of either sodium hydroxide (AR), sulfuric acid (AR), or nitric acid (AR).

2.2 Determination of metal extraction from varying matrix compositions

For slope analysis work, equilibrium nickel extraction (1.0 mM as nitrate) using LIX 63, Versatic 10, LIX 63/Versatic 10, Versatic 10/nonyl-4PC, and LIX 63/Versatic 10/nonyl-4PC all diluted to 0.35 M in ShellSol D70 was determined at various pH values depending on the organic composition used. The extraction tests were carried out from four different aqueous matrices of varying nitrate concentration but constant ionic strength assuming full dissociation of ions.

Further test work attempting to determine the extraction of nitrate via analytical methods was carried out from a 6 M magnesium nitrate solution containing 18 mM of nickel nitrate. Higher nickel concentrations were used for this work to allow greater extraction of nitrate and so improve the analytical resolution of the experiment.

All extraction tests were carried out in a water bath at 40 °C at an organic to aqueous ratio (O:A) of 1:1 using an overhead mixer (40 mm diameter impeller) at 900 rpm (tip speed 1.88 m/s) in a square stainless steel mixing box. The dispersion pH was measured using a pH probe (Ionode, IJ44-A). Samples of the dispersion were taken with a glass syringe and filtered through Whatman 1PS paper. The pH was adjusted using sodium hydroxide (10 g/L or 100 g/L) or sulfuric acid (100 g/L or 350 g/L). Sampled organic phases were stripped (50 g/L sulfuric acid, O:A 1:3, 40 °C, 40 minutes, or 62.5 g/L sulfuric acid, O:A = 1:4, 60 °C, 60 minutes for LIX 63 only) in a shaker-incubator operating at

250 rpm to allow calculation of mass balances and determination of organic phase nitrate concentrations.

2.3 Analytical Methods

Nickel, cobalt, and zinc were determined using atomic absorption spectroscopy (AAS) on an Agilent 240 FS spectrophotometer. Ultraviolet–visible (UV-Vis) spectroscopy was carried out on a Varian Cary 1C spectrophotometer.

Nitrate concentrations in the aqueous strip solutions were determined using a colorimetric method measuring UV-Vis absorbance at 410 nm after formation of a salicylic acid complex [14] with standards generated using potassium nitrate. Nitrate results were referenced against selected samples analysed using capillary electrophoresis (Beckman-Coulter, MDQ model).

3. Results and Discussion

3.1 Slope analysis for nickel extraction

Nickel extraction was carried out from aqueous phases of variable nitrate concentration but constant Ni concentration (1 mM) and ionic strength. The ionic strength was maintained using magnesium sulfate. The resulting log nickel distribution versus the log nitrate concentration is given in Figure 1.

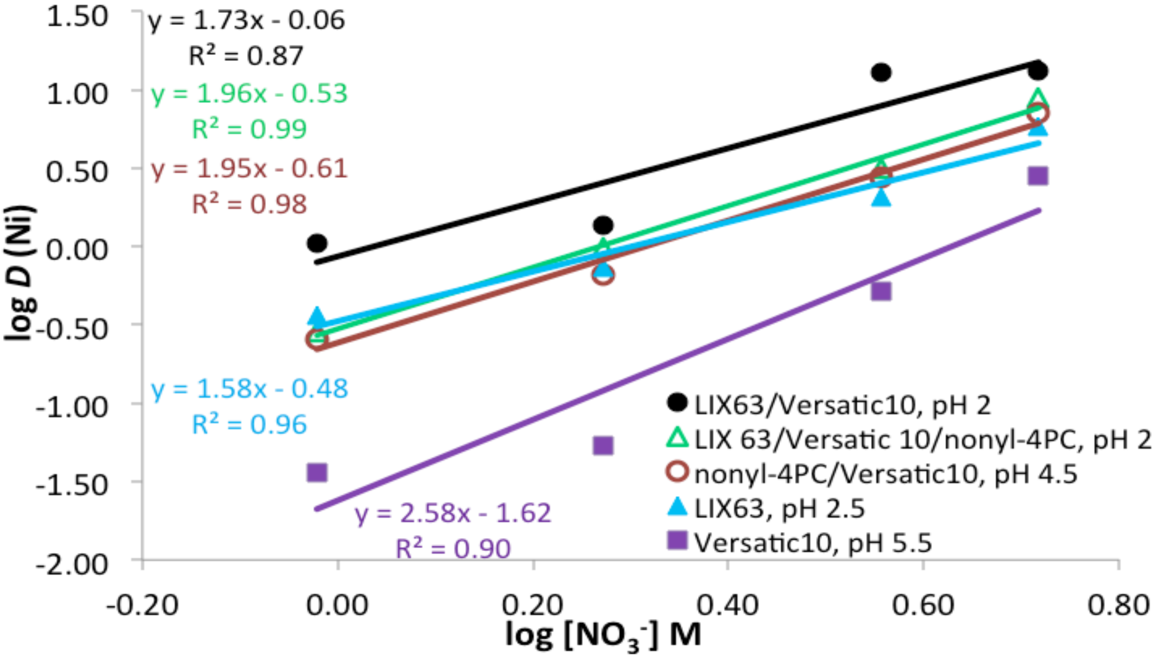

Figure 1. Effect of log nitrate concentration at constant ionic strength (9 M, balanced with magnesium sulfate) on log*D* of nickel extracted by various solvent extraction reagents in ShellSol D70.

The slopes of log*D* versus log[NO_3^-] in the five organic systems varied between 1.6 and 2.6 with a mean value of 1.96. R^2 values ranged from 0.87 to 0.99. Based on slope analysis techniques, the slope of the trend line in Figure 1 should represent the average number of nitrate anions extracted per nickel ion into the organic phase. The prediction of two nitrate anions extracted per nickel ion would be consistent with a solvating system extracting both nickel and nitrate into the organic phase, such as $[Ni(HL)_3](NO_3)_2$ or $Ni(HL)_2(NO_3)_2$ where HL represents the neutral hydroxyoxime extractant.

Results from slope analysis should always be treated with some caution. High reagent concentrations, like those used in the present study, lead to non-ideality. Altering the type of anion in the aqueous matrix can also have a substantial effect on aqueous phase activity coefficients despite constant calculated ionic strength [15]. Corrections for activity coefficients for nickel in the distribution ratio based on these considerations can make significant differences to the obtained slope [15]. In addition, at high concentrations, full dissociation of ions may not be an accurate assumption. Some uncertainties therefore exist in relation to the true ionic strength of the test solutions. Despite these concerns, an increase in nickel uptake with increased nitrate concentration is clear in Figure 1. Further work was therefore carried out to determine if nitrate was being extracted into an organic phase nickel complex.

3.2 Investigation of nitrate incorporation into an organic phase nickel complex

Slope analysis above indicated that nitrate may be extracted into the organic phase at a molar ratio of nitrate to nickel of 2:1. Analysis of nickel (18 mM) extraction from 6 M magnesium nitrate using a mixture of the three reagents tested (LIX 63/Versatic 10/nonyl-4PC), however, showed that the molar ratio of nitrate to nickel in the organic phase was well below 2 at the three pH points used (Table 1). Further, nitrate extraction into the organic phase decreased to near zero with increasing pH in Table 1, and therefore with increased nickel loading. The maximum nitrate to nickel ratio of 1.27 occurred at the lowest pH tested (pH 1), and was about half that expected from the slope analysis results in Figure 1.

At lower pH, especially near pH 1, Versatic 10 proton dissociation will be unfavourable. Co-ordination of nitrate anions in place of a negatively charged organic acid [16, 17] may then be able to occur in the organic phase. This suggests that two competing nickel complexes were present in the organic phase, one charge balanced with nitrate and one with deprotonated Versatic 10. The increasing nitrate/nickel ratio further suggested that the relative concentration of the nitrate complex increased with decreasing pH. Extraction of nickel can therefore continue to occur at lower pH values by forming a nickel complex charge balanced with nitrate, such as $[Ni(HL)_3](NO_3)_2$ or $Ni(HL)_2(NO_3)_2$.

Table 1: Nickel and nitrate extractions of LIX 63/Versatic 10/nonyl-4PC. Nitrate extraction calculated by subtracting the nitrate obtained from contacting with a nickel-free aqueous.

pH	**Nickel Extracted mM**	**Net Nitrate Extracted mM**	**Molar Ratio of nitrate / nickel**
3	17.5	2.1	0.12
2	15.0	7.8	0.52
1	8.1	10.3	1.27

3.3 Ultraviolet-visible analysis of the organic phase nickel complex

UV-vis analysis was used as an investigative technique to further understand the different nickel complexes formed with the pure *anti*-hydroxyoxime in LIX 63. Synergistic extraction of nickel using mixtures of LIX 63 and organic acids such as Versatic 10 results in the formation of octahedral mixed reagent complexes [17]. The UV-Vis spectrum for such a nickel complex, with a major peak at 600 nm, is shown in Figure 2. Nickel extracted by LIX 63 as a single reagent from a sulfate-based matrix at low acidity forms a square planar orange NiL_2 complex [18], where L is the deprotonated hydroxyoxime. This NiL_2 complex has a UV-Vis spectrum with a major peak at 440 nm (Figure 2).

At high sulfuric acid concentrations, nickel extracted with LIX 63 hydroxyoxime (HL) can form an insoluble octahedral $[Ni(HL)_3]SO_4$ salt, which readily precipitates [19]. Although the analogous $[Ni(HL)_3](NO_3)_2$ salt does not readily precipitate at high acidity, a short chain analogue has been successfully isolated by Barnard *et al.* [19], indicating that this complex can also exist. It was further found that a stable nickel salt with a nickel:chloride ratio of 1:2 is extracted from hydrochloric acid solutions [19]. The UV-Vis spectrum of the resulting organic phase nickel-hydroxyoxime-chloride complex closely resembles that of the octahedral nickel-hydroxyoxime-Versatic 10 complex (Figure 2), suggesting that the nickel chloride complex is also octahedral. Additional unpublished work has established a 3:1 HL:Ni ratio in the extracted nickel complex, allowing the stoichiometry to be established as $[Ni(HL)_3]Cl_2$.

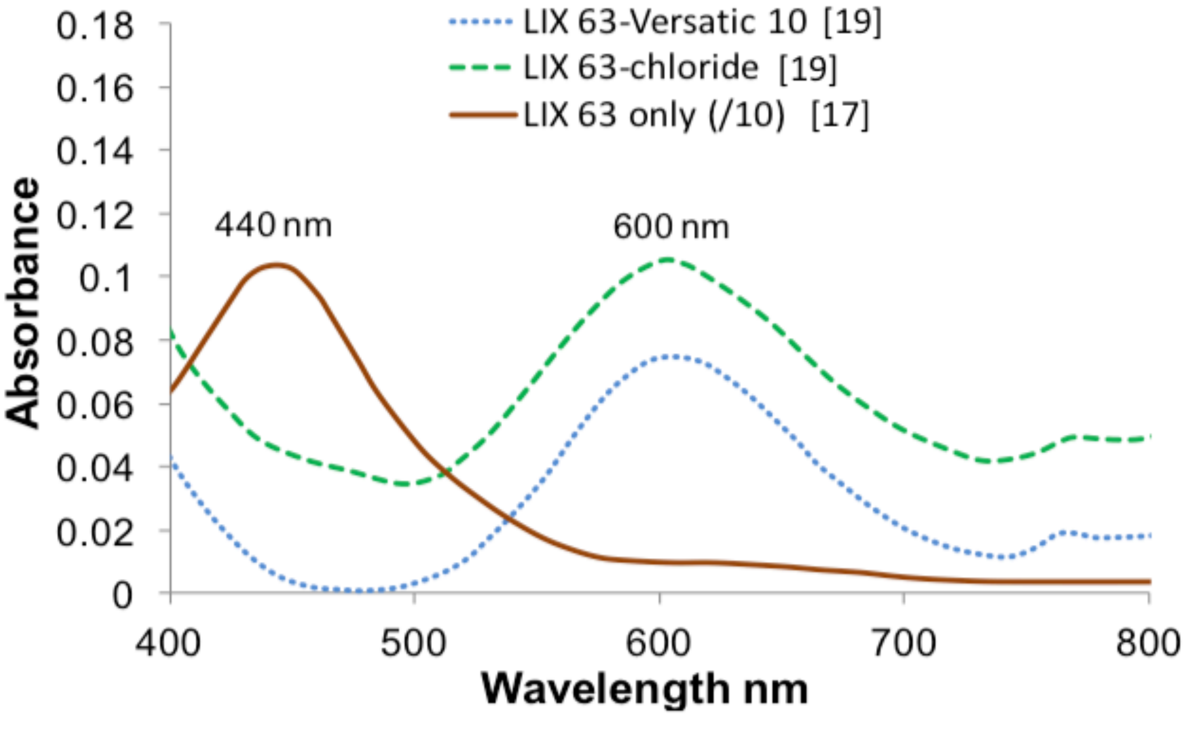

Figure 2: UV-Vis spectra for different nickel-LIX 63 complexes. Adapted from [17, 19]. Baseline of unloaded organic was manually subtracted in cited papers.

The UV-Vis spectrum of the nickel complex extracted from the concentrated nitrate matrix using *anti*-hydroxyoxime in the present investigation had a major peak at 613 nm (Figure 3) signifying that an octahedral nickel complex similar to that of nickel-hydroxyoxime-chloride, possibly of the form $[Ni(HL)_3](NO_3)_2$, had been generated in the organic phase. Contacting the organic phase with concentrated magnesium sulfate resulted in the pale blue organic solution turning brown. This is reflected in Figure 3 with the peak at 613 nm being suppressed and the appearance of a new peak at 430 nm, resembling that of the NiL_2 square planar complex in Figure 2. Two different coordination environments (octahedral and square planar) therefore existed for nickel between the nitrate extract organic and the sulfate washed organic.

The obtained UV-Vis spectra coupled with the absence of any $[Ni(HL)_3]SO_4$ precipitate are consistent with the sulfate matrix removing nitrate from the organic phase and concurrent deprotonation of hydroxyoxime to maintain charge neutrality. The small residual peak around 600 nm after the sulfate wash in Figure 3 indicated that some residual nitrate remained in the organic phase after a new equilibrium had been established with the sulfate aqueous wash solution.

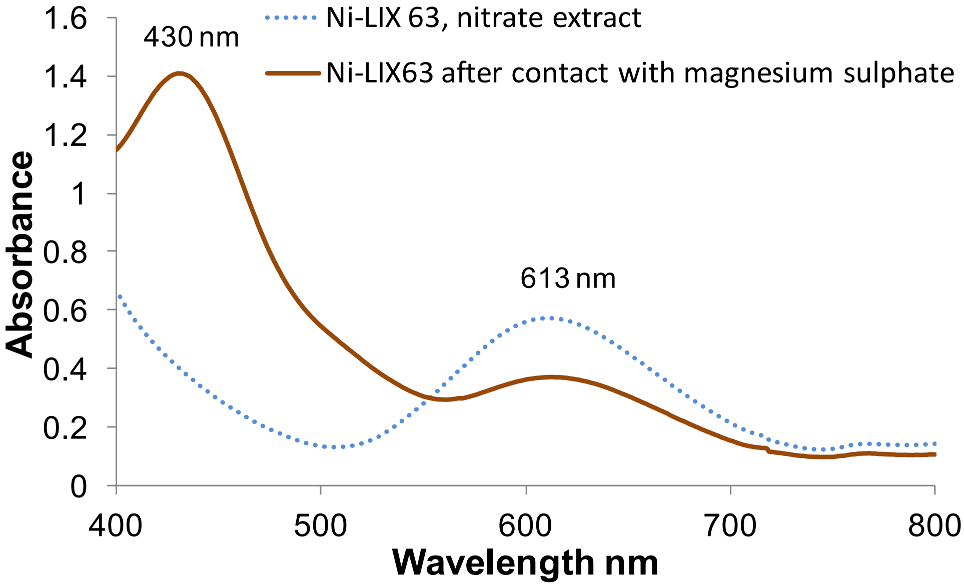

Figure 3: Change in UV-Vis spectrum of Ni-LIX 63 extracted from a nitrate matrix after washing with a concentrated sulfate solution ([Ni(II)] = 18 mM, [*anti*-hydroxyoxime] = 310 mM, magnesium salt concentrations = 2.5 M).

Nitrate anions in the aqueous phase can, therefore, potentially be co-extracted into organic systems containing LIX 63 at low to moderate pH to stabilise an octahedral nickel complex (either with or without Versatic 10 present) by forming an organic salt. This effect would be particularly promoted for nickel over other metals, which has a high octahedral ligand field stabilisation energy [20] and hence a preference for octahedral geometry. In the present study using LIX 63/Versatic 10/nonyl-4PC, co-ordination of a deprotonated Versatic 10 would take preference at higher pH values and nickel extraction would behave as expected using LIX 63/Versatic 10 in a sulphate matrix. As the pH decreases a new equilibrium between a nitrate counter-ion and a deprotonated Versatic 10 counter-ion will be established, increasing the nickel–nitrate ratio in the organic phase and thereby enhancing nickel extraction in the presence of high nitrate concentrations.

4. Conclusion

The present work has shown that nickel extraction using LIX 63 hydroxyoxime can occur via the use of both inorganic (nitrate) and organic (Versatic 10) counter-ions Operation at pH levels sufficiently high to encourage deprotonation of Versatic 10 favour its incorporation into a nickel-hydroxyoxime complex. At lower pH levels, where Versatic 10 deprotonation is not favored, nickel extraction can proceeed via incorporation of a suitable inorganic counter-ion, such as nitrate, into an organic phase complex. Increasing nitrate concentration in the aqueous phase therefore favoured increased nickel uptake via this mechanism for systems containing LIX 63.

UV-vis analysis of organic phase nickel complexes extracted using pure *anti*-hydroxyoxime revealed that an octahedral nickel complex, similar to the synergistic nickel complex formed using LIX 63/Versatic 10, was extracted from a concentrated nitrate matrix. The spectum obtained also aligned closely with $[Ni(HL)_3]Cl_2$ as presented in earlier work, suggesting that the nickel-nitrate complex formed was $[Ni(HL)_3](NO_3)_2$. This potential for some inorganic anions to co-ordinate with nickel-hydroxyoxime complexes at low pH values explains continued nickel extraction from a nitrate matrix with decreasing pH.

Practically, operation of a solvent extraction circuit from a concentrated nitrate aqueous phase at pH 1.5 will allow a greater separation of nickel from cobalt and zinc using LIX 63/Versatic 10/nonyl-4PC than from a comparable sulfate aqueous phase. This can be exploited to provide a novel method for separation of nickel from cobalt.

Acknowledgement

This study was supported by the Curtin University International Postgraduate Research Scholarship, the CSIRO Minerals Resources Flagship and Direct Nickel.

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