Western Australian School of Mines
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Recovery of Nickel and Cobalt from Nitrate-Based Nickel Laterite Leach Solutions Using Direct Solvent Extraction

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DECLARATION

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material that has been accepted for the award of any other degree or diploma in any university.

Signed:

Michael Hutton-Ashkenny

Date: 2 November 2015

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LIST OF PUBLICATIONS

The following technical papers were written as a result of the work presented in this thesis:

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"The treatment of ores with nitric acid is not commonly resorted to even by the most daring of metallurgists. Occasionally, however, the exigencies of a situation cause the most cautious to look outside the boundaries of established practice, and sometimes a nitric acid process has seemed alluring. Very little has been published in connection with the quest of those who have departed from the beaten metallurgical track, and sought to utilise nitric acid in ore treatment. This is the story of perhaps one attempt out of many unrecorded ones."

George C. Westby, 1918.

ABSTRACT

Hydrometallurgical processing of nickel laterite is often carried out via pressure acid leaching (PAL) with sulfuric acid. Novel nitric acid-based processes such as the Direct Nickel (DNi) process, which involves atmospheric leaching with nitric acid, have recently become of interest as they promise to be cheaper alternatives that achieve comparable nickel and cobalt extractions. No single clear operation for purification and recovery of nickel and cobalt from commercial nickel laterite leach liquors exists. The use of direct solvent extraction (DSX) is attractive as it avoids the intermediate precipitation, solid-liquid separation and re-leaching steps required in other operations and additionally allows the production of high value separate nickel and cobalt products.

The present study attempted to develop a DSX process to purify nickel and cobalt in a nitrate-based pregnant leach solution (PLS). Specifically, it was aimed to (1) characterise the solvent extraction behaviour of relevant metals from a nitrate matrix, (2) identify promising solvent systems, (3) improve the performance of potential systems with respect to metal stripping and (4) phase transfer rates, (5) to determine the effect of reagent concentrations in any novel solvent systems, (6) compare the most promising solvent systems from the standpoint of commercial application, and (7) determine the chemical stability of the SX reagents used under expected operating conditions. These aims were pursued by carrying out a combination of extraction and stripping tests under systematically varied conditions, analysis of organic phase metal complexes using ultraviolet-visible (UV-Vis) spectroscopy, simulation and modelling of variables of interest, and long-term reagent stability studies.

In pursuing the first aim it was found that the selectivity of a solvent system for nickel and cobalt was preserved on moving from a sulfate to a nitrate-based matrix. Metal pH_{50} values generally shifted to a lower pH by 0.5 units, owing to the weaker complexing nature of the nitrate anion. Hence the results of a literature review in sulfate-based systems could be used as a guide to inform process development from a nitrate matrix. To address the second aim, pH isotherms generated under the same nitrate-based conditions were compared and the following promising solvent systems selected for further work: LIX 860 / Versatic 10, LIX 860 / sub-stoichiometric Cyanex 272, LIX 63 / Versatic 10, nonyl-4PC / Versatic 10, and Versatic 10 with tributyl phosphate (TBP) as a phase modifier.

In pursuing the third aim it was found that although Versatic 10 and Cyanex 272 reduced cobalt poisoning of LIX 860, cobalt poisoning was still too extensive for mixtures of LIX 860 with these organic acids to be considered prospective. Organic acids hindered cobalt poisoning of LIX 860 by forming a $Co(LIX\ 860)_2(Acid)_2$ complex in the bulk organic phase. Research into the fourth aim revealed that stripping and extraction of nickel using LIX 63 / Versatic 10 was greatly accelerated by the presence of nonyl-4-pyridine carboxylate (nonyl-4PC). Nonyl-4PC likely behaved as a phase-transfer catalyst, accelerating phase transfer of nickel without being involved in any metal–ligand associations in the organic phase. Pursuing the fifth aim revealed that the concentrations of LIX 63 and nonyl-4PC were the most important for determining nickel extraction and nickel stripping in LIX 63 / Versatic 10 / nonyl-4PC, whereas only LIX 63 concentrations determined cobalt extraction.

Research into the sixth aim compared the three promising solvent systems Versatic 10 / TBP, nonyl-4PC / Versatic 10, and LIX 63 / Versatic 10 / nonyl-4PC. Versatic 10 / TBP resulted in unacceptably high co-extraction of magnesium and required a high operational extraction pH. LIX 63 / Versatic 10 / nonyl-4PC resulted in high separation of nickel and cobalt from manganese and magnesium at a low pH, although nickel stripping was particularly difficult. Nonyl-4PC / Versatic 10 offered a compromise between separation of nickel and cobalt from impurities and ease of nickel stripping. LIX 63 / Versatic 10 / nonyl-4PC could, however, still be a viable option where high rejection of manganese is desirable.

Research into the seventh and final aim revealed that neither concentrated nitrate under extract conditions nor dilute nitrate in a sulfuric acid strip affected the stability of either hydroxyoxime or nonyl-4PC. Although nonyl-4PC did increase the rate of cobalt poisoning of LIX 63 / Versatic 10, to a point where a reductive strip bleed stream would have to be considered, it did not otherwise affect the stability of hydroxyoxime. These results are promising for the application of either LIX 63 / Versatic 10 / nonyl-4PC or nonyl-4PC / Versatic 10 to a potential DSX process for the extraction of nickel and cobalt from a nitrate-based PLS with stripping into sulfuric acid.

LIST OF ABBREVIATIONS AND DEFINITIONS

AAS	Atomic absorption spectroscopy
ACORGA CLX50	Di-isodecyl-3,5-pyridine carboxylate-based reagent
CSIRO	Commonwealth Scientific and Industrial Research Organisation (Australia)
Cyanex®272[1]	Bis-2,4,4(trimethyl pentyl)phosphinic acid-based reagent
Cyanex®301	Bis-2,4,4(trimethyl pentyl)dithiophosphinic acid-based reagent
Cyanex®302	Bis-2,4,4(trimethyl pentyl)monothiophosphinic acid-based reagent
D2EHPA	Di-2(ethylhexyl)phosphoric acid
decyl-4PC	Decyl-4-pyridine carboxylate
DNi	Direct Nickel Ltd. (Australia)
DNNSA	Di-nonylnaphthalenesulfonic acid
DSX	Direct solvent extraction
GC-FID	Gas chromatography with flame ionisation detection
GC-MS	Gas chromatography with mass spectrometry
HEH(EHP)	Mono(2-ethylhexyl)2-ethylhexylphosphonate
HL	A protonated general chelating ligand for metal complexation
HPAL	High pressure acid leaching
HPLC	High performance liquid chromatography
HR	A protonated general organic acid for metal complexation
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
ITD	*iso*-Tridecanol
Kelex 100	7-Undecyl-8-hydroxyquinoline-based reagent
LIX®63	5,8-Diethyl-7-hydroxy-dodecan-6-oxime-based reagent
LIX®64	Reagent containing LIX 65 with catalytic concentrations of LIX 63
LIX®65	5-Nonylbenzophenoneoxime-based reagent
LIX®84-I /	5-Nonylacetophenoneoxime-based reagent

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[1] *LIX is a registered trademark of BASF. ACORGA is a registered trademark of Cytec. Versatic is a trademark of Shell. Trademark symbols will not be repeated throughout the main body of this thesis.*

SME 529	
LIX®860N-I / ACORGA®P50 / ACORGA®M5640	5-Nonylsalicylaldoxime-based reagent
M	Molar
MHP	Mixed hydroxide precipitation / precipitate
MSP	Mixed sulfide precipitation / precipitate
Nicksyn™	Unknown synergist, expected to be a pyridine carboxylate
nonyl-4PC	Nonyl-4-pyridinecarboxylate
NPAL	Nitric acid pressure leach
ORP	Oxidation reduction potential
PC	Pyridine carboxylate
pH_{50}	pH required for 50% metal extraction
pH_{50}(A-B)	The pH_{50} difference between metals A and B using a given reagent
PHREEQC	pH, redox, equilibrium modelling software written in C
PLS	Pregnant leach solution
PTFE	polytetraflouroethylene
Poisoning	A phenomenon where a metal loaded into an organic phase cannot be stripped via conventional acid stripping
SSX	Synergistic solvent extraction
SX	Solvent extraction
TBP	Tributylphosphate
TXIB	2,2,4-Trimethyl-1,3-pentanedioldiisobutyrate
USGS	United States Geological Survey
UV-Vis	Ultraviolet-visible spectroscopy
Versatic™10	*iso*-Decanoic acid–based reagent
Versatic™911	Reagent containing mixtures of C_9 to C_{11} branched carboxylic acids
WEEE	Waste electronic and electrical equipment
$\Delta pH_{50(N-S)}$	pH_{50} difference for a given metal extracted with a given reagent between nitrate and sulfate matrices
ε	Molar attenuation coefficient

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CHAPTER 1
An overview of nickel laterite processing and solution treatment

1.1 Introduction to processing of nickel laterite ores

Nickel in ferrous and non-ferrous alloys used, for example, in construction and transportation industries accounts for 88% of total nickel consumption (Kuck, 2015). Demand for nickel has therefore continued to increase as the economies of India, China and South-East Asia become increasingly industrialised. Nickel has traditionally been sourced from sulfide deposits as it is relatively simple to generate a rich nickel concentrate via flotation. Nickel reserves held in sulfide deposits are, however, decreasing and the other primary source of nickel, nickel laterite deposits, is therefore becoming more important to meet this increased demand. In 2017, over half of primary nickel production (54%) is forecast to come from laterites (Kuck, 2015).

The early resistance to exploitation of nickel laterite ores can be attributed to their geology (Figure 1-1), which makes them difficult to process. Nickel laterites are highly weathered ore bodies where mobile elements have been preferentially leached over time, leading to the zoning profile shown in Figure 1-1. There are two potentially economic zones for nickel concentration, namely limonite and saprolite. Limonite is high in iron and contains economic levels of cobalt, a high value by-product used primarily in batteries and superalloys. Saprolite is low in iron, but high in acid-consuming magnesia. Hence, most commercial processes can only treat one horizon. This is seen as wasteful.

	Ni	Co	MgO	SiO_2	Fe_2O_3	Cr_2O_3	Al_2O_3
Iron oxide cap	0.5%	0.01%	1%	2%	75%	4%	6%
Limonite and nontorite	1%	0.15%	1%	3%	70%	3%	5%
Saprolite	3%	0.05%	30%	40%	15%	0.5%	0.5%
Fresh peridotite with garnierite veinlets	0.5%	0.01%	40%	40%	10%	0.5%	0.5%

Figure 1-1: Typical laterite profile giving indicative metal concentrations. Adapted from Troly *et al.* (1979)

1.1.1 Commercialised process options for nickel laterite ores

Three major processing routes exist for treating nickel laterite ores. These are smelting, ammoniacal leaching (Caron process), and high pressure acid leaching (HPAL). Atmospheric leaching using sulfuric acid has also been considered, but only as an auxiliary process for PAL. The industry standard for many years was smelting via reductive kilning to produce a ferro-nickel alloy. Smelting is, however, increasingly seen as a poor choice for new projects. It is energy intensive and so requires a source of low cost electricity, is limited to high-grade saprolite ore bodies with low iron concentrations, and ferro-nickel is only useful to the steel industry and cannot be used for the production of non-ferrous alloys.

The Caron process employs a reductive roast to convert nickel and cobalt to metals and the majority of iron to magnetite. The calcine is leached using ammonia / ammonium carbonate to dissolve nickel and cobalt and to reject the majority of iron. Nickel recoveries of only 78 – 85% are obtained and cobalt recovery is particularly low at only 54% (Reid and Fittock, 2004). Other disadvantages of the Caron process include high energy requirements for drying the ore before roasting, and sensitivity to iron concentrations in the ore above 35%, requiring careful mining and ore blending. The Caron process is therefore rarely considered as a processing option for new nickel laterite projects.

The PAL process leaches nickel laterite at high sulfuric acid concentrations (350 kg acid/tonne ore) under high temperature (245 °C) and high pressure (3500 kPa) in a titanium-clad autoclave. The high capital cost of the autoclave can be a significant drawback for project commercialisation. In addition, the high acid concentrations are not recycled, contributing to high operating costs. Temperatures above 200 °C cause leached iron to precipitate as haematite in the autoclave, regenerating acid and removing iron as major processing benefits. Aluminium in solution will also precipitate with the iron as either hydronium/sodium alunite or basic aluminium sulfate. Magnesium is therefore the major acid consuming element in nickel laterite ores and as a result PAL plants are unsuitable to processing high magnesium bearing saprolite ores and instead are often restricted to the limonite zone. Importantly, there is no industry standard route for treatment of the pregnant leach solution (PLS) to generate marketable nickel and cobalt products.

1.1.2 The Direct Nickel process

The Direct Nickel (DNi) process (Figure 1-2) is a novel, atmospheric nitric acid leach for nickel laterite ores. It is based around a nitric acid recycling process developed by Drinkard and Woerner (2011). This nitric acid recycle allows the DNi process to decouple the operational expense of the process from the price of nitric acid, and so enables the economic use of high concentrations (>55 wt-%) of nitric acid in the leach train. High dissolution of the target metals, nickel (>95%) and cobalt (>85%), can therefore be obtained under these aggressive leaching conditions. Magnesium nitrate formed during leaching is thermally decomposed, generating magnesium oxide, reused as a neutralisation reagent, and NO_x (a mixture of oxides of nitrogen) gases used to regenerate nitric acid. Therefore, unlike other technologies, the DNi process can economically treat the entire laterite profile from limonite to magnesium rich saprolite (Marsh and Anderson, 2011; McCarthy and Brock, 2011).

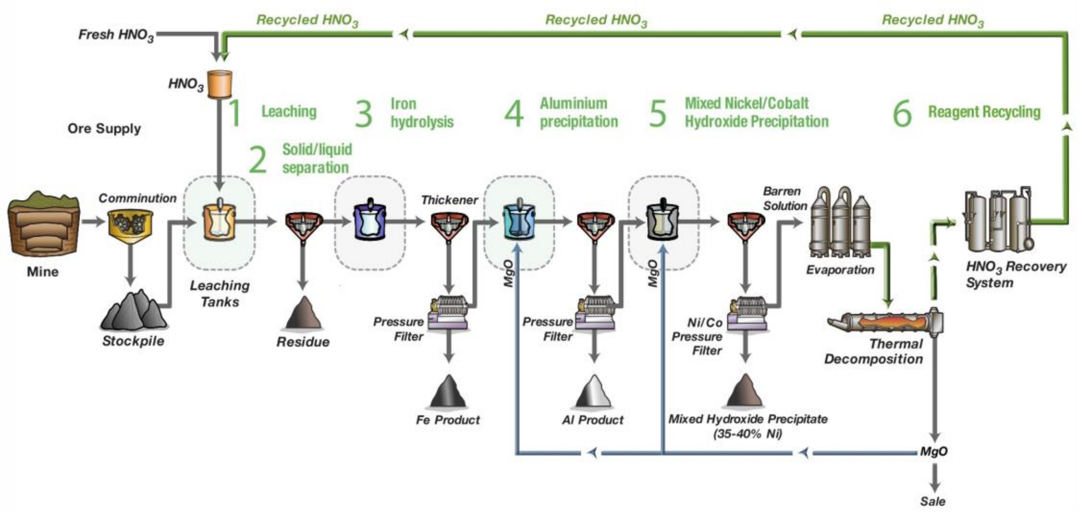

Figure 1-2: Direct Nickel process diagram (McCarthy and Brock, 2014)

The DNi flowsheet in Figure 1-2 differs from typical PAL flowsheets in the following key ways: nitric acid is used as the lixiviant at 110 °C in Figure 1-2(1) in place of the sulfuric acid pressure leach, iron is removed via thermal hydrolysis at 165 °C in Figure 1-2(3) as a separate unit operation from aluminium, which is removed via precipitation with magnesia in Figure 1-2(4), and the lixiviant is mostly recycled (>95%) in Figure 1-2(6). An analysis of a recent pilot plant purified PLS after iron and aluminium removal as in Figure 1-2(5) and a comparison with an equivalent sulfate-based liquor (Ravensthorpe) is shown in Table 1-1. The major difference is the high magnesium concentration in the DNi PLS, over twice that of the sulfate PLS. In the DNi process the balancing anion is nitrate (~500 g/L) rather than sulfate. Aluminium concentrations are particularly high in the DNi PLS in Table 1-1. During the pilot plant operation, removal of aluminium was not optimised and in future operations it is expected that aluminium will be removed to levels more closely matching sulfate-based processes (McCarthy, 2014)[2].

Table 1-1: MHP feed liquor analysis (mg/L) at pH 2.5 for Direct Nickel (McCarthy and Brock, 2014) and Ravensthorpe Nickel (White *et al.*, 2006)

	Ni	Co	Al	Fe	Mg	Ca	Cr	Mn	Si
Direct Nickel	4 843	183	847	43	9 3039	2 042	6	688	3
Ravensthorpe	5 200	210	1.4	1.5	4 1000	440	<10	1 200	30

The DNi process is particularly attractive as it can treat the entire nickel laterite ore profile under low temperature (atmospheric) conditions with high lixiviant recoveries without a capital intensive titanium-clad autoclave. The recent success of the DNi process has also triggered research into similar nitric acid-based leaching processes for nickel laterite ores with lixiviant recycling, such as nitric acid pressure leaching or NPAL (Ma *et al.*, 2015). As there is no single accepted route for solution treatment of sulfate-based PAL liquors, solution treatment of a nitrate-based PLS to generate marketable nickel and cobalt products cannot be informed from existing operations. In the current DNi and NPAL processes, nickel and cobalt are precipitated together as hydroxide salts (unit 5, Figure 1-2). Generation of separate high purity nickel and cobalt products directly from the nitrate PLS would be economically more appealing.

1.2 Recovery of nickel and cobalt products from nickel laterite PLS

Three general routes have been used commercially for recovery of nickel and cobalt from an acidic nickel laterite PLS, namely mixed hydroxide precipitation (MHP), mixed sulfide precipitation (MSP), and direct solvent extraction (DSX). The MHP route, using magnesia to generate a fine hydroxide precipitate, is applied in the current DNi and NPAL processes. MHP is only partially selective for nickel and cobalt (White *et al.*, 2006), and the product is often contaminated with high (3%) concentrations of manganese. Solid–liquid separation of this fine precipitate is difficult and results in a bulky product with a high moisture

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[2] McCarthy, F., Project Manager at Direct Nickel, personal email (2014)

content (60%). High energy input is then required to dry the product before it can be packaged for transport. The hydroxide product must then be further refined to generate nickel and cobalt products for ultimate sale to steelmaking or alloy making industries.

MSP selectively precipitates nickel and cobalt as sulfides using hydrogen sulfide gas, with very little contamination from impurity metals (Molina, 2009). Although a mixed product of high purity can be produced via MSP, the reagent gas is toxic and requires careful materials handling and on-site production. Solution treatment after generation of the intermediate product is often required to either meet discharge limits or to enable recycle of the barren liquor as process water. As with MHP, the mixed sulfide product is not directly useful to consumers and requires further refining.

The only other method currently used commercially for the recovery of nickel and cobalt from nickel laterite PLS is DSX. Solvent extraction (SX), also known as liquid–liquid extraction, is a process by which metals are transferred between two immiscible liquid phases with the aim of purifying specific metals. SX is already used to purify cobalt and nickel from solutions obtained after re-leaching both MHP and MSP. Compared with SX, DSX has the advantage of generating separate nickel and cobalt products directly from the PLS whilst bypassing requirements of precipitation, solid–liquid separation, and re-leaching. As such, DSX is a more efficient process option than either MHP or MSP and generates higher value products.

DSX in the nickel laterite industry is carried out after removal of nearly all the iron, aluminium and chromium in the PLS via neutralisation and subsequent precipitation, as these metals are strongly extracted by common SX reagents. To accommodate the particular nature of the DNi PLS (Table 1-1), any selected solvent system must also satisfy the following criteria: (1) high rejection of magnesium, (2) reagent stability in the presence of high (~500 g/L) nitrate concentrations at moderate pH (approximately pH 2), and (3) low operational pH (as close to 2.5 as possible) to both ease the requirements for upstream iron and aluminium removal and to minimise neutralisation requirements.

Two DSX processes have been used commercially for the recovery of nickel and cobalt from a sulfate-based pre-neutralised PLS, at Bulong Nickel (Donegan,

2006) and Goro Nickel (Mihaylov *et al.*, 2000). These processes were designed and tested on traditional sulfate-based liquors and it is not currently known whether they can be applied to a high magnesium nitrate bearing PLS. In order to develop a process for the recovery of nickel and cobalt from a nitrate-based PLS, it may be necessary to apply a commercially unproven or novel solvent system.

There is little prior knowledge or experience to aid in developing a suitable DSX process applicable to a nitrate-based PLS. It is not known, for example, how the nitrate matrix will affect the distribution of metals between the aqueous and organic phases, or how it will affect the stability of selected SX reagents. In addition, other general process difficulties that have been noted in the SX of nickel and cobalt may have to be overcome. In the nickel-cobalt laterite industry, these difficulties specifically include poor phase transfer kinetics for nickel, cobalt poisoning when cobalt loaded into the organic phase cannot be recovered using conventional acid stripping, and reagent stability.

1.3 Project objectives and limitations

1.3.1 Statement of the research problem

Nitric acid leaching is an attractive alternative to PAL for dissolution of nickel laterite ores, but it still suffers from the issue of product recovery from the PLS. The product recovery route proposed by DNi and NPAL (MHP) is inefficient as it requires numerous unit operations to generate an impure mixed product.

Development of a DSX option for recovery of nickel and cobalt directly from a nitrate-based PLS will allow the generation of separate, higher value products without the extra requirements of precipitation, solid–liquid separation, and re-leaching. DSX from nitrate-based PLS matrices is, however, poorly understood and research into this area is essential if a successful process is to be developed. The research within this thesis includes investigating the following: the effect of nitrate on metal distribution between the aqueous and organic phases, identification of prospective DSX organic systems, and various operational challenges associated with these prospective DSX solvent systems including nickel phase transfer kinetics, cobalt poisoning, and the chemical stability of the prospective solvent systems in contact with concentrated nitrate PLS.

1.3.2 Aims of the thesis

To address a gap in the scientific literature regarding commercial application of DSX to a nitrate-based nickel laterite PLS, this study was aimed at developing an SX method for the recovery of nickel and cobalt from a solution relevant to DNi. Specifically, the aims of this thesis were to:

- explore the literature for possible reagents that are suited to the separation of nickel and cobalt from magnesium and that are chemically stable under expected nitrate-based operating conditions (Chapter 2);
- determine if the results from the literature survey of SX options for metal extraction from sulfate-based leach liquors can be used as a useful guide for nitrate-based leach liquors (Chapter 3);
- select promising solvent systems for nickel and cobalt separation from magnesium at low pH by using the literature review as a guide and by determining the metal extraction characteristics of any novel reagent mixtures identified (Chapter 4);
- assess the potential to reduce or prevent cobalt poisoning of any solvent systems identified by the literature to be susceptible to this phenomenon (Chapter 5);
- investigate methods to accelerate the phase transfer of nickel for any potentially promising solvent systems identified that suffer from slow nickel extraction or stripping rates (Chapter 6);
- determine optimal reagent concentrations for any novel solvent systems suited to separation of nickel and cobalt from magnesium (Chapter 7);
- compare any promising solvent systems for separation of nickel and cobalt from magnesium in a nitrate-based PLS from the standpoint of a potential industrial application (Chapter 8); and
- investigate the chemical stability of the reagents in promising solvent systems with respect to expected operating conditions relevant to nickel and cobalt recovery from a nitrate-based PLS (Chapter 9).

As this study was focused on developing a commercially viable option for DSX of both nickel and cobalt from a nitrate-based PLS, not all avenues of commercial or scientific interest could be followed. Specifically, this project did not aim to address:

- separation of nickel from cobalt and generation of separate nickel and cobalt products; and
- the mechanisms and fundamental chemistry behind phenomena observed during the course of the research project. Although attempts were made to explain and address these as succinctly as possible, time constraints for completing the defined objectives of the thesis often precluded exhaustive studies.

The hypothesis of the following thesis, developed after a review of the literature presented in Chapter 2, was as follows: *a solvent system can be developed to recover nickel and cobalt from a concentrated magnesium nitrate PLS that successfully rejects magnesium and is chemically stable under expected operating conditions.*

1.4 Structure of the thesis

Chapter 2 presents a review of the literature pertinent to the project aims. This chapter also identifies potential solvent systems that may be applicable to nickel and cobalt recovery from a nitrate-based PLS and discusses the potential operational difficulties that require consideration.

Chapter 3 compares the differences in metal extraction between similar nitrate and sulfate matrices. Any reasons for the differences noted are further explored using thermodynamic modelling and by studying organic phase metal complexes using ultraviolet-visible (UV-Vis) spectroscopy.

Chapter 4 investigates the metal extraction characteristics of some promising reagent mixtures that have not previously been presented in the literature. The results of this investigation are subsequently combined with those from nitrate matrices generated in Chapter 3 to identify promising solvent systems for DSX of nickel and cobalt from a concentrated magnesium nitrate matrix.

Chapter 5 assesses the effect of organic acids on the cobalt poisoning of a phenolic aldoxime. A number of investigations using different acids address the potential to use mixtures of the phenolic aldoxime with organic acids for the extraction of cobalt.

Chapter 6 studies the acceleration of slow rates of nickel extraction and stripping using a mixture of hydroxyoxime and carboxylic acid by adding different modifiers to the organic phase. The most promising additive is further investigated to explain the mechanism by which it accelerates the phase transfer reactions of nickel. This resulted in the development of a novel three-reagent solvent system to evaluate alongside other promising solvent systems.

Chapter 7 uses a statistical experimental design to model the effects of the three reagents in the novel solvent system developed on nickel and cobalt extraction and nickel stripping. The models are used to then optimise the three reagent concentrations and thus provide a solvent system for use in a comparative investigation.

Chapter 8 compares the solvent systems deemed promising for nickel and cobalt extraction and magnesium rejection in a nitrate matrix from the standpoint of industrial application. The comparison presented used industrially relevant operating conditions (reagent concentrations, temperature and strip acidity) informed by previously published optimisation studies for each solvent system.

Chapter 9 addresses the chemical stability of the SX reagents in the selected solvent systems under expected operational conditions. These are extraction from a concentrated magnesium nitrate matrix followed by stripping into sulfuric acid.

Chapter 10 summaries the conclusions from the research conducted to address the thesis aims presented in Section 1.3. Recommendations for further study are then presented to consolidate and progress the research already undertaken.

CHAPTER 2
Review of studies for solvent extraction of nickel and cobalt from a nitrate based nickel laterite leach liquor

2.1 Introduction

In order to learn from previous experience, and to avoid repeating past research, an in depth understanding of solvent extraction (SX) is essential when developing a solvent system for a novel application. With previous knowledge as a guide, informed decisions can be made to meet the goals of a SX process. For an SX process to treat the nitrate-based pregnant leach solution (PLS) generated by the DNi pilot plant, the following three major goals were identified in Section 1.2: (1) to completely reject magnesium, (2) to be stable to oxidative degradation from concentrated nitrate (~500 g/L) at moderate to low pH (approximately pH 2), and (3) to operate at low pH values near pH 2.5. The following chapter presents a review of the literature to inform the development of solvent systems able to meet these goals.

A review of SX of base metals from nitrate leach liquors is initially presented and any guide to compare data between sulfate and nitrate matrices is subsequently assessed (Section 2.2). Commercialised direct solvent extraction (DSX) processes for acid-sulfate leach liquors are reviewed and their drawbacks for application to a nitrate PLS are considered (Section 2.3). The use of modifiers to improve the performance of solvent systems is then summarised (Section 2.4) to inform an in depth discussion of promising solvent systems yet to be commercialised (Sections 2.5, 2.6 and 2.7). The potential degradation of SX reagents is finally discussed in detail (Section 2.8) before making conclusions as to the most appropriate research path to develop a successful solvent system for application to a nitrate-based PLS (Section 2.9).

2.2 Solvent extraction of base metals from nitrate matrices

2.2.1 Extraction of nickel and cobalt from nitrate matrices

Commercial SX of base metals traditionally takes place from sulfate, chloride or ammoniacal matrices. There is no known commercial SX application for base metals from a nitrate matrix, and much of the research into extraction of nickel and cobalt from a nitrate matrix focuses on fundamental chemistry rather than process development (Grimm and Kolařík, 1974; Zapatero *et al.*, 1987; Preston and du Preez, 2000; Andrade and Elizalde, 2005; Dey and Basu, 2011). In these past studies, the nitrate matrix was generally weak (0.5 – 1 M alkali metal nitrate) and chosen to minimise anion interferences with metal extraction, rather than to promote a potential nitric acid leach process. In addition, the organic diluent was generally a single pure chemical, such as toluene, xylene or tetrachloromethane, rather than a commercially relevant mixture of hydrocarbons. As these studies were designed to investigate the extraction mechanism and organic phase base metal complexes formed with various reagents, they are not directly relevant to process development.

Only one process promoting SX of nickel or cobalt from a nitric acid leach solution was found in the literature. The patent for this process by Ritcey and Ashbrook (1968) describes the separation of cobalt from nickel and arsenic in a nitric acid leach using D2EHPA (di-2(ethyl-hexyl)phosphoric acid) at pH 5.5. The process was successfully piloted at 12 L/h using a nitric acid leach feed solution and stripping with 1.6 M nitric acid. The deportment of magnesium and the chemical stability of D2EHPA and the diluent with respect to nitric acid were not reported in this study. As such, the referenced patent is not directly useful for generating a nickel-cobalt extraction process for a nitrate-based nickel laterite PLS.

Although research into SX of nickel or cobalt from nitric acid has been limited, there has been some research into SX from nitric acid liquors outside the nickel industry. Examples of this are leaching of refractory copper sulfides (Prater *et al.*, 1973) and leaching of metals from waste electrical and electronic equipment (WEEE). Le *et al.* (2011) and Kinoshita *et al.* (2003) both describe similar processes for the recovery of copper from WEEE via SX using LIX 984, a 1:1 mixture of the phenolic aldoxime LIX 860 and the phenolic ketoxime LIX 84. Both studies state that copper can be successfully extracted at pH 1.5 from nitric acid and stripped using either 4 M nitric acid (Kinoshita *et al.*, 2003) or 3.7 M sulfuric acid (Le *et al.*, 2011).

In summary, there are few studies promoting the extraction of base metals from nitrate matrices. Where studies do exist they are generally focused on fundamental chemistry and explore the nature of the extracted metalloorganic species, rather than developing a commercially viable process. Only one study promoted the SX of nickel or cobalt from a nitric acid leach. In this case, the deportment of magnesium and the oxidative stability of the organic phase were not discussed.

2.2.2 Comparison of solvent extraction of base metals from sulfate and nitrate-based matrices

The few studies that compare the pH of extraction between sulfate and nitrate matrices all point towards a common trend of decreasing extraction pH from nitrate matrices compared with sulfate. Lanagan and Ibana (2003) investigated the change in extraction pH for 0.01 M chromium(III) using the phosphinic acid Cyanex 272 (0.3 M) by altering the aqueous matrix. The pH extraction curves for chromium(III) from a 0.1 M chloride or nitrate matrix were almost identical. Extraction from a 0.1 M sulfate matrix occurred with a pH_{50} (the pH at which 50% of a metal is extracted) 0.4 units higher than the nitrate or chloride matrices. Lanagan and Ibana (2003) explained this phenomenon by suggesting that sulfate anions are more likely to complex chromium in the aqueous phase than nitrate, thereby hindering chromium extraction into the organic phase.

El-Hefny and Daoud (2007) found that the pH_{50} for copper extracted by the thiophosphinic acid Cyanex 302 (0.08 M) decreased in the following order: 0.1 M sulfate (4.22) > 0.1 M nitrate (3.81) > 0.1 M chloride (3.53). Grigorieva and Fleitlikh (2013) added to this research by combining data from two studies to also demonstrate that the extraction pH_{50} of copper using the dithiophosphinic acid Cyanex 301 is smaller from a nitrate than a sulfate matrix. The explanation given in both cases was the same as that previously used by Lanagan and Ibana (2003); nitrate anions are weaker complexing agents than sulfate anions. El-Hefny and Daoud (2007) used thermodynamic modelling software (Medusa, Royal Institute of Technology, Sweden) to justify this explanation. An unanswered question regarding this work is that aqueous copper nitrate and copper sulfate species are not included in the default Medusa database, and no mention of adding them was made. As such, there is some uncertainty surrounding the results from this thermodynamic model.

This trend of decreasing extraction pH_{50} from a sulfate to nitrate matrix persists when the ionic strength of the matrix is kept constant, rather than the anion concentration. Research by du Preez and Preston (1992) showed that at 1 M ionic strength all lanthanide metals are extracted at 0.5 pH units lower from a nitrate matrix using Versatic 10 (*iso*-decanoic acid). A decrease in pH_{50} of 0.5 units on moving from sodium sulfate to sodium nitrate, both at 1 M ionic strength, was also calculated for nickel extraction using 4-(5-nonyl)pyridine / Versatic 10 (Preston and du Preez, 2000). In this case, changing the sodium sulfate concentration to give the same anion concentration as the nitrate matrix (1 M) resulted in a similar pH_{50} decrease (0.6 units).

Although limited, the discussed studies all point towards a general trend where extraction of a given metal from a nitrate matrix occurs at a lower pH than from a comparable sulfate matrix. The pH_{50} decrease on moving from a sulfate to a nitrate matrix in the literature was consistently around 0.5 units for all metals, regardless of the reagent type or aqueous ionic strength. It is therefore hypothesised that this trend will persist for extraction of all base metals from these two matrices. This further suggests that the order of metal extraction, and therefore metal separations, will remain consistent between sulfate and nitrate matrices. A systematic investigation into the differences between extraction of base metals from nitrate and sulfate matrices under comparable conditions will determine if this hypothesis is correct.

2.3 Established solvent extraction processes in the nickel and cobalt industry

2.3.1 Direct solvent extraction of nickel and cobalt from HPAL liquors

The literature suggests that the order of metal extraction between nitrate and sulfate matrices will be consistent. Commercial practices in the sulfate-based nickel and cobalt industry may therefore be applicable to a nitrate-based solution. Two DSX processes have been used commercially for the recovery of nickel and cobalt from sulfate-based HPAL liquors: the Bulong process and the Goro process.

The first nickel laterite DSX process (now decommissioned) operated at Bulong Nickel in Western Australia and relied on two separate SX circuits. In the first circuit Cyanex 272 recovered cobalt, zinc, manganese and 19% of the available magnesium in the PLS at pH 5.7, separating them from nickel remaining in the raffinate. Nickel was then extracted from the raffinate in a second circuit using

Versatic 10 at pH 6.5 – 6.8, separating it from calcium and the remaining magnesium.

The poor rejection of magnesium by Cyanex 272 in the Bulong process resulted in high neutralisation requirements, consuming 39% of the total ammonia in the process, and a large reagent holdup – comprising 66% of the loaded strip liquor (Donegan, 2006). The magnesium concentration in the DNi PLS (93 g/L) is six times higher than the typical Bulong PLS (16 g/L). For the DNi PLS, the co-extraction of magnesium with Cyanex 272 would be so extensive as to make this process option highly unattractive.

The Goro Nickel Project in New Caledonia is the only operating commercial plant using DSX for nickel and cobalt extraction from a sulfate-based nickel laterite PLS. The Goro process uses Cyanex 301 to extract nickel and cobalt together below pH 2 with complete rejection of magnesium, calcium and manganese. Nickel and cobalt must be stripped using 6 M hydrochloric acid due to very strong affinity for the reagent. Cobalt is separated from nickel in the chloride-based loaded strip liquor using anion-exchange SX (Mihaylov *et al.*, 2000). As Cyanex 301 is particularly susceptible to oxidation, ferric iron and copper are removed to less than 5 mg/L to avoid oxidation by redox coupling (Sole *et al.*, 1993), and the SX process is carried out under a nitrogen atmosphere to exclude atmospheric oxygen (Mackenzie, 2015).

The ultimate pH on extraction of nickel and cobalt from the DNi PLS would likely be well below 2.5 due to acid generated from the metal extraction reaction. In terms of potential application of the Goro process for nitrate-based PLS, the presence of concentrated nitrate anions at less than pH 2.5, and the potential for nitrate anions to be entrained into the highly acidic chloride-based strip circuit, would likely cause significant oxidation of Cyanex 301, and therefore significant reagent loss. This would occur even under anaerobic operation as nitric acid will act as an electron acceptor even in the absence of oxygen. The Goro process, in addition to the Bulong process, is therefore unattractive for application to nitrate-based leach liquors.

2.3.2 *Solvent extraction of nickel from Caron Process liquors*

SX of nickel from the ammoniacal leach liquors produced by the Caron process is currently carried out at the Yabulu Queensland Nickel refinery in Australia (Mackenzie *et al.*, 2005). As practiced at Queensland Nickel, nickel can be extracted from ammoniacal solutions using phenolic oximes (Figure 2-1). Altering the R group in Figure 2-1 increases the affinity of the reagent for metal ions in the following order (Watarai, 2001): phenyl (e.g., LIX 65N) < methyl (e.g. LIX 84-I) < hydrogen (e.g. LIX 860N-I). For all phenolic oximes two theoretical stereoisomers exist. Only the *anti* or E isomer of the reagent is able to chelate metals; the *syn* or Z isomers are inactive (Ashbrook, 1975; Szymanowski, 1993). For the commercially relevant oximes LIX 860 and LIX 84, the reagent is supplied as only the active *anti* isomer (Szymanowski, 1993).

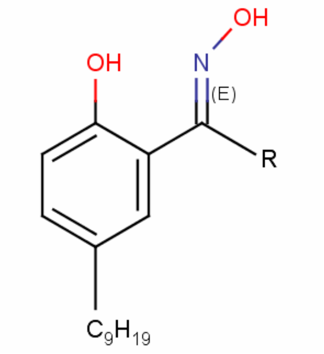

Figure 2-1: Chemical structure of 4-nonyl phenolic oximes, 4-dodecyl derivatives are also commercially available

Although nickel can be recovered using phenolic oximes, cobalt extracted by phenolic oximes cannot be stripped using conventional acid stripping. This decreases the net cobalt transfer to the loaded strip liquor and sequesters some of the reagent, resulting in cobalt poisoning. As cobalt(III) is not extracted by phenolic oximes, this phenomenon can be avoided in an ammoniacal phase by oxidising cobalt(II) to cobalt(III) prior to SX. Any residual cobalt(II) that is extracted can be removed using a reductive strip with either zinc or iron dust (Fittock, 1992). This ammoniacal process used by Queensland Nickel is therefore useful for separating nickel from cobalt.

Under acidic conditions, phenolic oximes are selective for copper over ferric iron and other base metals. Nickel and cobalt are extracted at slightly higher pH (Figure 2-2). Magnesium, manganese and calcium are not extracted by phenolic oximes, such as LIX 860, from acidic solutions (Dahl, 1968). There is therefore the potential to apply phenolic oximes to extraction of nickel and cobalt from acidic nitrate matrices with good rejection of magnesium. Unfortunately, cobalt(II) in an acidic aqueous phase cannot be oxidised to aqueous cobalt(III). Therefore, because of the phenomenon of cobalt poisoning, phenolic oximes cannot be used as the only reagent in a solvent system targeting nickel and cobalt. This would have to be addressed in future work if phenolic oximes were to be applied to nickel and cobalt extraction from a nitrate PLS.

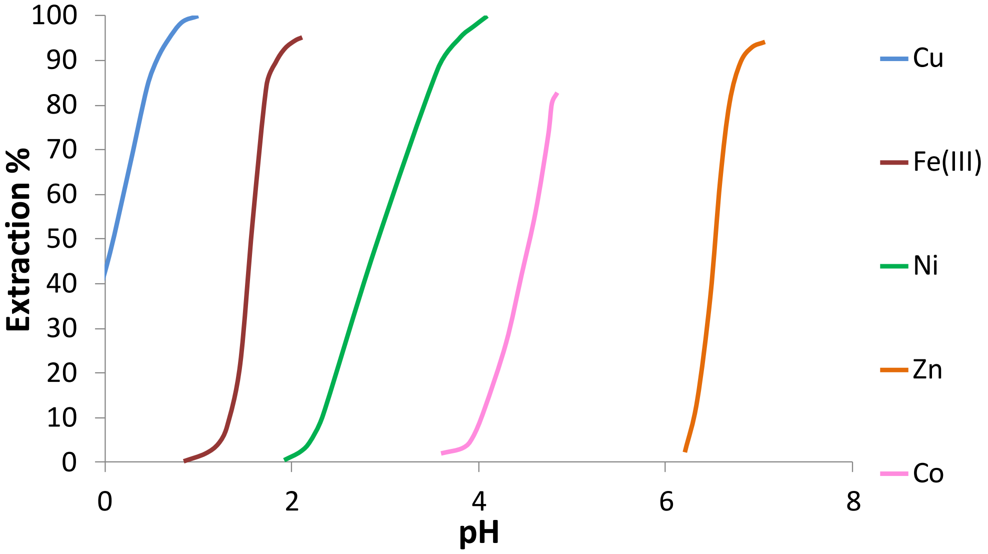

Figure 2-2: Example pH isotherms for ACORGA P50 (same active reagent as LIX 860N-I) adapted from Wilson *et al.* (2014) – conditions not disclosed

2.3.3 Versatic 10 for refining of nickel via solvent extraction

The carboxylic acid-based reagent Versatic 10 (Figure 2-3) has been used commercially to extract nickel and cobalt together from sulfate solutions, for example at Sumitomo's Niihama nickel refinery (Ritcey, 1996), and also historically at the Rustenburg refinery in South Africa (Bacon and Mihaylov, 2002; Lakshmanan *et al.*, 2016). A sample pH isotherm (Figure 2-4) suggests that Versatic 10 can be used to separate nickel and cobalt from magnesium and, to a lesser extent, calcium. Separation of nickel and cobalt from manganese and zinc is not possible using Versatic 10, and nickel and cobalt cannot be separated from each other. Versatic 10 operates at a high pH, full nickel extraction in Figure 2-4 only occurs at pH 7.

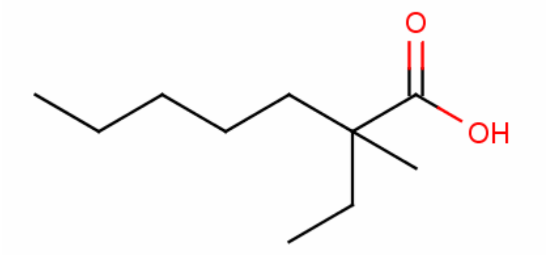

Figure 2-3: Chemical structure for one isomer of Versatic 10

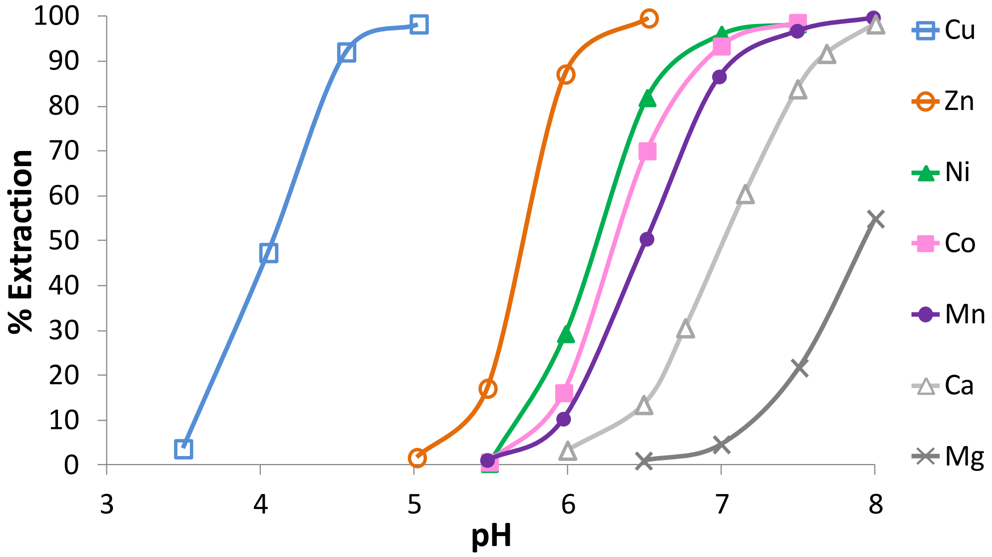

Figure 2-4: Example pH isotherm for 0.5 M Versatic 10 in ShellSol 2046 (0.5 M Versatic 10, 40 °C, sulfate laterite leach, aqueous to organic ratio A:O = 1:1) (Cheng, 2006)

Historically, nickel and cobalt were stripped from Versatic 10 into an acid chloride solution (Ritcey, 1996). Nickel–cobalt separation was then achieved via SX using an anion-exchange reagent. It is also possible to strip the loaded Versatic 10 into sulfuric acid and separately extract cobalt from nickel using Cyanex 272. This process idea was previously promoted by Tsakiridis and Agatzini (2004).

Carboxylic acids such as Versatic 10 are generally resistant to oxidation as the carboxylate group cannot undergo further oxidation (Wade, 2013). Accordingly, they have potential for use in oxidising matrices such as nitric acid. Although carboxylic acids are prone to acid catalysed esterification in the presence of alcohols, this reaction is reversible in the presence of water and has not been reported for Versatic 10. At the high pH required for full nickel and cobalt extraction, however, the solubility of Versatic 10 in the aqueous phase increases dramatically. The loss of the reagent to the aqueous phase can be substantial in operating circuits and has been cited by Rice (1978) and Ashbrook (1973) as a significant drawback to commercial applications of Versatic 10. At pH 4 the solubility of Versatic 10 in water is 0.41 mM. For the extraction of nickel at pH 7, as required from Figure 2-4, the solubility of a similar reagent to Versatic 10 (Versatic 911, a mixture of C_9 to C_{11} branched carboxylic acids) increases over 10 fold to 5.23 mM (Ashbrook, 1973).

In summary, from the reviewed methods of SX of nickel and cobalt in the nickel laterite industry, Versatic 10 appears the most promising reagent for separation of nickel and cobalt from magnesium. Cyanex 272 does not reject sufficient magnesium, Cyanex 301 is susceptible to oxidative degradation, and phenolic oximes are susceptible to cobalt poisoning. In contrast, Versatic 10 is expected to be stable to oxidative degradation in the presence of nitrates and is not prone to degradation. The high operational pH and high aqueous solubility of Versatic 10 at this pH are significant barriers to commercial application that would need to be addressed in future work for application of Versatic 10 to a nitrate-based PLS.

2.4 Mixing organic reagents to improve the solvent extraction process

In SX, chemicals added to the organic phase to enhance the properties of a solvent system are called modifiers. Modifiers can have a variety of functions, such as avoiding third phase formation, enhancing metal stripping, catalysing phase transfer reactions, or enhancing metal extraction. Examples of these types of modifiers are presented here as background for later discussions on mixing SX reagents to decrease the extent of cobalt poisoning of phenolic oximes, increase phase transfer kinetics for nickel, and to decrease the required extraction pH of Versatic 10.

2.4.1 Modifiers to hinder third phase formation

A common use of modifiers in SX is to improve phase separation and avoid third phase formation. Where needed, long chain esters or alcohols are added to the organic phase to increase the polarity or to solvate organic phase metal–reagent species and thereby decrease the chances of solid precipitation and subsequent third phase formation.

During development of a nickel and cobalt SX process for laterite leach liquors, Tsakiridis and Agatzini (2004) used 5% v/v of the phosphorus-based ester tri-butyl phosphate (TBP) as a phase modifier to aid in phase separation and to avoid formation of a third phase. Similar use of TBP as a phase modifier for organophosphorus-based acids (D2EHPA, mono(2-ethylhexyl)2-ethylhexyl phosphonate (HEH(EHP)) and Cyanex 272) in cobalt SX has also taken place (Cox, 2004; Barnard, 2010). Amine reagents often require high concentrations of alcohol-based modifiers such as *iso*-tridecanol (ITD) to solvate the metal–amine complex and so improve its solubility in the organic phase (Sudderth and Kordosky, 1986; Zhu and Cheng, 2011).

2.4.2 *Modifiers to enhance metal stripping*

Oxygen-based modifiers have been used extensively in the copper industry to alter the equilibrium distribution of copper with phenolic aldoximes. As phenolic aldoximes are such strong copper reagents, nonyl-phenol was originally used to decrease the acid concentration required for copper stripping (Tumilty *et al.*, 1977). Nonyl-phenol shifts the copper equilibrium more towards the aqueous phase, simultaneously decreasing the acidity required for stripping and increasing the pH required for extraction. That is, nonyl-phenol shifts the equilibrium of (EQ 1) to the left hand side.

$$2HL(org) + Cu^{2+}(aq) \rightleftharpoons CuL_2(org) + 2H^+(aq) \qquad \text{(EQ 1)}$$

where HL is a protonated chelating ligand and L is the deprotonated ligand.

More recently, other oxygen-based modifiers including TXIB (2,2,4-trimethyl-1,3-pentanediol diisobutyrate), ITD and low viscosity ketones have also been used to aid in stripping of copper (Kordosky and Virnig, 2003). All modifiers act to alter the extraction equilibrium of phenolic aldoximes due to a hydrogen bonded association between the modifier and the oxime reagent (Dalton *et al.*, 1986). This association disfavours copper extraction by shifting the equilibrium away from the copper–oxime association required for extraction and towards the oxime–modifier association (Figure 2-5).

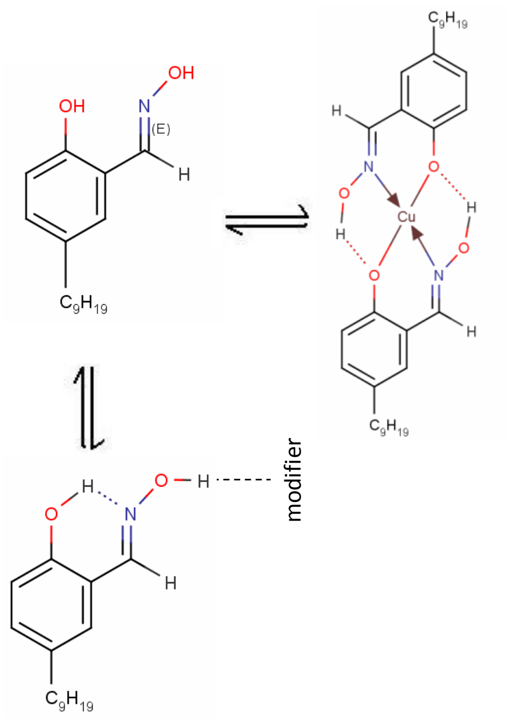

Figure 2-5: Mechanism for decreased copper affinity of LIX 860 in the presence of modifiers. Based on Bender *et al.* (2011) and Dalton and Seward (1986)

In early research, Hanson *et al.* (1976) reported that addition of 0.2 M nonyl-phenol to 0.1 M LIX 65 resulted in a 38% decrease in the rate of extraction of a solution containing 6 g/L copper at 28 °C. Dalton and Seward (1986) later investigated the effect of nonyl-phenol and ITD on the rate of copper extraction and stripping using a C_9 phenolic aldoxime (e.g., LIX 860N-I). The results are difficult to interpret as both extraction and stripping of copper are very fast with this reagent. At 25 °C both nonyl-phenol and ITD appeared to slightly increase the stripping rate (from 98% to 100% after 15 s) and slightly decrease the extraction rate (from 100% to 96% after 30 s). In contrast, at 0 °C the decrease in the extract rate was much more pronounced (97% down to 64% for nonyl-phenol or 86% for ITD after 30 s) and the strip rate changed from 90% for the oxime alone to 73% with nonyl-phenol and 91% with ITD after 15 s.

A decrease in the copper extraction rate maintained at both low (0 °C) and room (25 °C) temperatures can be rationalised by the following mechanism: an oxime–modifier complex in the bulk organic phase is favoured over oxime orientation at the interface. The copper stripping rate appears to depend on the temperature and the type of modifier being used. If extraction rates are decreased by modifiers favouring formation of an oxime–modifier complex, however, then it is reasonable that stripping rates would be increased via a similar mechanism. That is, the modifier may remove free oxime from the interface and so promote an interfacial reaction between hydrogen ions and the copper–oxime complex.

2.4.3 Modifiers for catalysing phase transfer

Modifiers can be used to catalyse the phase transfer reactions of a metal. Phase transfer catalysts physically participate in the phase transfer reaction without being involved in the organic phase metal complex formed at equilibrium. This often occurs via formation of unstable metal–modifier intermediates that can be rapidly transferred across the interface but have low thermodynamic stabilities or equilibrium constants. As the intermediates have low thermodynamic stabilities, only low concentrations of the catalyst are generally required.

Acceleration of the phase transfer for copper extraction with LIX 65 using catalytic concentrations of the aliphatic hydroxyoxime LIX 63 is a well-known example of phase transfer catalysis (Preston, 1980). D2EHPA similarly accelerates copper extraction with LIX 65 (Komasawa and Otake, 1983) and nickel extraction with LIX 84 (Narita *et al.*, 2006) by acting as a phase transfer catalyst. Acceleration of the phase transfer reactions for palladium with dialkyl sulfides by addition of amines is also known (Szymanowski *et al.*, 1990; Szymanowski and Cote, 1994). These three processes all take place due to formation of an unstable intermediate metal–ligand complex that forms rapidly but is replaced by the main reagent–ligand complex once the metal has entered the organic phase.

2.4.4 Modifiers to enhance metal extraction: synergistic solvent extraction

Mixtures of reagents can be used to increase the extraction of metals at a given pH. Although these additional reagents can be considered as modifiers that alter the distribution of a metal towards the organic phase, they are often referred to as synergists, or synergistic mixtures. Synergistic solvent extraction (SSX) is thus a phenomenon where the combination of two reagents increases the extraction of a metal at a given pH above that of either of the two reagents individually. Synergism is due to formation of a mixed ligand complex in the organic phase that is more thermodynamically stable than either of the single ligand metal complexes.

Three methods for determining a synergistic effect have been used in the literature. These include the synergistic coefficient (Elizalde *et al.*, 1996), comparisons of the individual and combined distribution coefficients (Flett and West, 1971; Sarkar *et al.*, 2014), or comparisons of the individual and combined pH_{50} values (Flett and Titmuss, 1969). Throughout the current work, synergism for a given metal was quantified by the change in pH_{50} of extraction (EQ 2) as used by previous authors (Preston and du Preez, 1995; du Preez and Preston, 2004; Cheng, 2006):

$$\Delta pH_{50} = \text{lowest } pH_{50} \text{ from single reagents} - pH_{50} \text{ of reagent mixture} \qquad \text{(EQ 2)}$$

Synergism is defined as occurring when (EQ 2) is positive and antagonism when (EQ 2) is negative.

Two major drawbacks to the use of Versatic 10 already discussed are the high pH required for nickel and cobalt extraction and the high aqueous solubility of Versatic 10 at this pH. For a high magnesium bearing liquor, like that generated by DNi, the incomplete rejection of magnesium at the high operating pH is also potentially problematic. As a result, the application of SSX to decrease the required nickel and cobalt extraction pH with Versatic 10 is of considerable interest. This has previously been investigated for a range of additive reagents. Examples include pyridine carboxylates (Preston and du Preez, 1994; Cheng *et al.*, 2010a), alkyl pyridines (Preston and du Preez, 2000), non-chelating oximes (Preston, 1983), and aliphatic hydroxyoximes (Cheng, 2006). In addition, synergism between phenolic oximes and the organophosphorus-based D2EHPA for nickel and cobalt extraction has also been reported (Andrade and Elizalde, 2005). These synergistic reagent mixtures may be applicable to separation of nickel and cobalt from magnesium and are discussed in more detail in the following sections of this chapter.

In summary, using modifiers or mixtures of reagents in the organic phase is particularly useful for tailoring a solvent system to specific requirements. Modifiers can be used to hinder third phase formation, alter the distribution of a metal between the aqueous and organic phase, alter the rates of extraction and stripping, and can change the organic phase metal complexes formed. The potential use of modifiers with phenolic oximes as well as with Versatic 10 should therefore be investigated to develop a solvent system able to separate nickel and cobalt from magnesium in a nitrate-based PLS.

2.5 Nickel and cobalt extraction using mixtures of phenolic oximes and organic acids

Phenolic oximes offer complete separation of nickel, cobalt and copper from magnesium, manganese and calcium (Section 2.3.2). Extraction of cobalt with phenolic oximes alone, however, results in cobalt poisoning of the reagent. It has been shown by various authors (Zhang *et al.*, 2001; Alguacil, 2002; Cerpa and Alguacil, 2004) that addition of D2EHPA to LIX 860 allows quantitative stripping of cobalt from phenolic aldoximes. Other impacts of D2EHPA on nickel and cobalt extraction with phenolic oximes include acceleration of nickel extraction (Narita *et al.*, 2006) and synergistic extraction of nickel and cobalt (Alguacil, 2002). Mixtures of phenolic oximes with D2EHPA and other organic acids are therefore of interest to develop a method for extraction of nickel and cobalt.

2.5.1 Synergism between phenolic oximes and organic acids

Ndlovu and Mahlangu (2008) reported a synergistic effect (ΔpH_{50}(Ni) of 1.8 units) for nickel extraction with a phenolic oxime (LIX 84) and a carboxylic acid (Versatic 10). This result is contrary to other research by Lakshmanan *et al.* (1975), which claimed that Versatic 911 did not affect the extraction of copper and iron using LIX 64. No other research looking into synergism of phenolic oximes with carboxylic acids has been found. It is therefore unknown whether carboxylic acids and phenolic oximes result in synergistic extraction of nickel or cobalt.

There is agreement in the literature regarding synergism between phenolic aldoximes and D2EHPA for nickel and cobalt extraction. Zhang *et al.* (2001) calculated a ΔpH_{50}(Ni) of 1.25 and a ΔpH_{50}(Co) of 0.95 when 20% v/v LIX 860 was mixed with 20% v/v D2EHPA in kerosene at an aqueous to organic ratio (A:O) of 1:1 on extracting 1.52 g/L metals as sulfates at 25 °C. These findings were then repeated by Alguacil (2002) using a dearomatised diluent (Exxon D100) and 1 g/L metals as sulfates resulting in a ΔpH_{50}(Ni) of 1.26 and a ΔpH_{50}(Co) of 0.82.

Mixing LIX 860 with D2HEPA is not desirable for separation of nickel and cobalt from magnesium as D2EHPA extracts calcium, manganese and some magnesium at the same pH value required for cobalt extraction with the synergistic mixture (Cheng, 2000; Qing *et al.*, 2003; Ritcey, 2006). There is no research investigating the effect of less acidic and more selective organic acids on extraction of nickel and cobalt using LIX 860.

Synergistic metal extraction using LIX 860 / D2EHPA occurs due to formation of a mixed–ligand metal complex in the organic phase. Most divalent d-block metals are known to adopt square planar coordination (Figure 2-6) with phenolic oximes such as LIX 860 (Keeney and Osseo-Asare, 1984b; Szymanowski, 1993) due to inter-ligand hydrogen bonding favouring this configuration (Szymanowski and Borowiak-Resterna, 1991). Tetragonal distortions of low spin (high ligand field strength) cobalt(II) complexes are favoured by the Jahn-Teller effect due to the degeneracy in the octahedral e_g orbitals. In the presence of strong donor ligands, the large increase in the octahedral ligand field stabilisation energy (Δ_o) may therefore favour an equilibrium closer to octahedral geometry as the energy of the two electrons in the d_{xy} orbital is reduced.

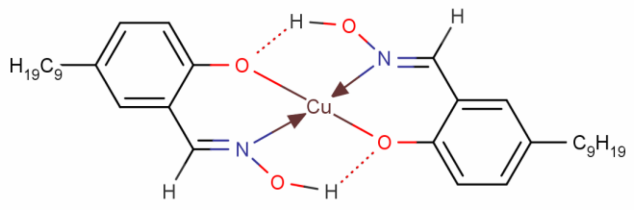

Figure 2-6: Hydrogen-bonded chelate structure of copper extracted by a C_9 phenolic aldoxime

Basolo and Matoush (1953) showed that addition of pyridine to various nickel complexes, including nickel–aldoxime, changes nickel from a square planar to an octahedral complex with a nickel:pyridine molar ratio of 1:2. For nickel extraction with the phenolic ketoxime LIX 84, it has also been proposed from X-ray absorption fine structure (XAFS) spectroscopy that nickel shifts from square planar to octahedral geometry on addition of D2EHPA (Narita *et al.*, 2006). Using this previous data as a guide, the synergistic metal complex extracted with phenolic oximes and D2EHPA M(II)-$(oxime)_2$-$(D2EHPA)_2$ is proposed here (Figure 2-7). Assignment of the hydrogen ions for charge balance is currently unknown. Cobalt is known to adopt tetrahedral configurations in a D2EHPA–only organic phase at increased temperature (Flett, 2005). Synergism for both nickel and cobalt with LIX 860 / D2EHPA, however, is expected to afford the same complex shown in Figure 2-7 due to the strong hydrogen-bonded chelate structure.

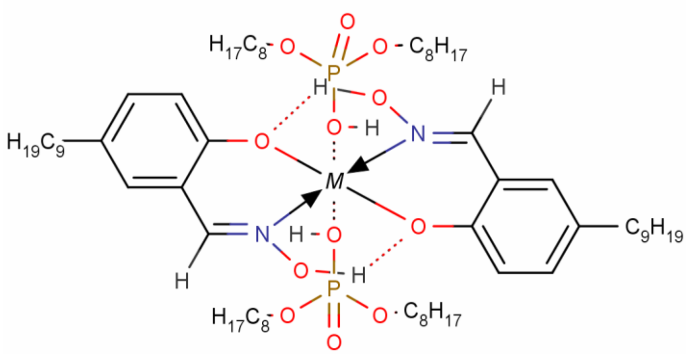

Figure 2-7: Proposed complex formed on synergistic extraction of a metal ion with LIX 860 / D2EHPA

Other research into mixed ligand complexes containing phenolic oximes and donor molecules did not suggest the same complex presented in Figure 2-7. For synergistic extraction using LIX 860, some authors have suggested that only one axial site will be occupied by the donor ligand. For nickel coordinated with LIX 860 (HL) and D2EHPA (HR) Andrade and Elizalde (2005) suggested two possible complexes on the basis of slope analysis, $(HL)NiL_2(HR)$ and $NiL_2(HR)_4$. As discussed, the chelating ligand occupies four binding sites on the nickel ion. Formation of $NiL_2(HR)_4$ requires breaking the stable chelate structure as well as the hydrogen bonds between the two oxime ligands to allow HL to behave as a monodentate ligand. The basis for Andrade and Elizalde (2005) proposing the formation of this species is therefore unclear. Of these two suggested complexes, only the formation of $(HL)NiL_2(HR)$ appears reasonable, but it is also unclear why the relatively weak donor ligand HL would replace HR in the mixed ligand complex.

Similar to the proposed $(HL)NiL_2(HR)$ species, Rafighi *et al.* (2010) more recently suggested that cobalt coordinated by a phenolic oxime (HL) and a weak donor ligand (S) in the presence of chloride forms $CoLSCl{\cdot}2H_2O$. Although, surprisingly, the formation of CoL_2SCl or CoL_2S_2 was not proposed, Rafighi *et al.*

(2010) stated that for oxime concentrations greater than 0.001 M two oxime ligands are present in the organic phase cobalt complex.

Although recent studies have not proposed a mixed ligand complex of the form (HR)NiL_2(HR) as in Figure 2-7, little justification has been given by these authors for their alternative proposals. The proposed complexes do not appear reasonable based on the known chelating nature of phenolic oximes. From the alternative research discussed previously, the synergistic extraction of metals using LIX 860 / D2EHPA is expected to occur via formation of the complex presented in Figure 2-7. Whether less acidic and more selective organic acids other than D2EHPA, such as Versatic 10 or Cyanex 272, can operate in a similar manner and provide synergistic extraction of nickel and cobalt with phenolic oximes is currently unknown and requires investigation.

2.5.2 *Acceleration of nickel extraction with phenolic oximes using organic acids*

Extraction of nickel from an acid sulfate matrix using phenolic oximes is slow. Andrade and Elizalde (2005) stated that four days of continuous shaking was required to reach equilibrium for extraction of nickel (0.0005 M) with LIX 860 (0.04 – 0.85 M) as a single reagent dissolved in toluene. Although much quicker than 4 days, Narita *et al.* (2006) reported that it took 80 min to reach equilibrium nickel (0.08 M) extraction with LIX 84 (0.5 M). On addition of sub-stoichiometric (0.05 M) D2EHPA to LIX 84, the time taken to reach equilibrium decreased to only 40 min (Narita *et al.*, 2006). In addition, this concentration of D2EHPA did not alter coordination of nickel at equilibrium in the organic phase. D2EHPA therefore acts as a phase transfer catalyst for nickel extraction using LIX 84. Whether organic acids other than D2EHPA can also act as phase transfer catalysts for nickel extraction with phenolic oximes is currently unknown.

2.5.3 *Possible cobalt poisoning mechanism of solvent extraction reagents*

It is widely accepted that cobalt poisoning of SX reagents, such as LIX 65, LIX 84 or Cyanex 301 occurs when cobalt(II) is oxidised to cobalt(III) in the organic phase (Guesnet *et al.*, 1980; Guesnet and Bauer, 1981; Nishihama *et al.*, 2000; Grigorieva and Fleitlikh, 2013). Oxidation of cobalt can occur under anaerobic conditions, but only in the presence of very strong electron donors such as methoxides (Pavlovic *et al.*, 1988). Oxidation of cobalt extracted using Kelex 100 (dodecenyl 8-quinolinol) / Versatic 10, for example, does not occur under an argon atmosphere (Guesnet *et al.*, 1980) suggesting that, in general, oxidation of cobalt proceeds via donation of an electron to dioxygen. As these cobalt(III) complexes are kinetically inert (Cotton and Wilkinson, 1980), stripping with mineral acids alone is not feasible. This results in reagent poisoning.

A range of chelating nitrogen-based square planar cobalt(II) compounds react with dioxygen to form dimers of the form Co(II)–O–O–Co(II) in equilibrium with Co(III)–O^-–O^-–Co(III) (Haim and Wilmarth, 1961; Bekâroğlu and Fallab, 1963; Fallab, 1967), where the cobalt ions are octahedral. The potential for a Co(III)–O^-–O^-–Co(III) dimer to exist was verified by Schaefer (1968) using x-ray crystallography. Ochiai (1973) later used electron spin resonance to argue that a slight distortion of square planar cobalt(II) complexes to tetragonal geometry is required to allow transfer of an electron to dioxygen. In this work it was suggested that axial binding of pyridine to square planar cobalt(II) bis(salicylaldehyde)ethylenediimino chelates increased the energy of the d_{z^2} orbital so that the unpaired d^7 electron sat in this axial orbital. Coordination and transfer of the axial d_{z^2} electron to dioxygen, forming a Co–O_2 monomer, then becomes possible. Ochiai (1973) further reported slow formation of the Co(III)–O–O–Co(III) dimer from this monomer by following oxygen absorption and release over time.

Disproportionation of cobalt(III) dioxygen dimers to individual octahedral monomers has been reported in some cases. Pignatello and Jensen (1979) stated that in the presence of an inorganic acid (HX) and acetic acid, an oxygen bridged dimer of pyridine (py), N,N'-ethylenebis(acetylacetoniminato) (HL) and cobalt(III) disproportionated to $2[Co(py)_2(L)_2]X$ and hydrogen peroxide. In a more recent study, Kufelnicki *et al.* (2010) studied autoxidation of cobalt(II) using the four-proton chelating ligands N,N'-bis(2-hydroxyiminopropionyl)-1,3-diaminopropane and N,N'-bis(2-hydroxyiminopropionyl)-1,3-diaminobutane (H_4L). Under an argon atmosphere, UV-Vis data from potentiometric titrations were combined with thermodynamics to suggest that a cobalt(II) square planar complex, potentially of the type $[Co(II)–(HL)]^-$, was formed. Kufelnicki *et al.* (2010) further demonstrated using x-ray crystallography that in an oxygen containing atmosphere and in the presence of an organic base such as imidazole (im) the octahedral cobalt(III) complex Co(III)–(HL)–$(im)_2{\cdot}CH_3OH$ could be generated, with the chelating ligand containing only one of four labile protons (HL) occupying the four equatorial binding sites. UV-Vis data from potentiometric titrations were used to suggest that the intermediate contained approximately 0.5 moles of oxygen per mole of cobalt, agreeing with the formation of $[(LH)Co–O–O–Co(LH)]^{2-}$. In both of these discussed cases the equatorial binding of the chelating ligand surrounding the initial square planer cobalt(II) was not disturbed by the oxidation reaction.

Guesnet and Bauer (1981) used kinetics data to suggest a potential mechanism for cobalt poisoning of LIX 65N (HL) consistent with the formation of a dioxygen intermediate. To satisfy the requirement of an octahedral cobalt(III) complex, the intermediate proposed by Guesnet and Bauer (1981) was $[(HL)Co(II)L_2]$–O–O–$[(HL)Co(II)L_2]$, presumably in equilibrium with $[(HL)Co(III)L_2]$–O^-–O^-–$[(HL)Co(III)L_2]$. Guesnet and Bauer (1981) further proposed disproportionation of the $[(HL)Co(II)L_2]$–O–O–$[(HL)Co(II)L_2]$ complex to $Co(III)L_3$ and H_2O_2 via analogy to Pignatello and Jensen (1979). For this octahedral $Co(III)L_3$ complex to form, the hydrogen bonded chelate structure of $Co(II)L_2$ (as for copper in Figure 2-6) would need to be broken. Evidence for chelating ligands maintaining their original equatorial binding sites was presented earlier and suggests that this might not occur. The actual Co(III) complex formed with commercial phenolic oximes such as LIX 65 is thus currently unknown.

The formation of cobalt(III) has often been indicated by a dark brown colour of the cobalt complex formed. This was reported by both Burkin and Preston (1975) for dioximes and Grigorieva and Fleitlikh (2013) for Cyanex 301. The colour of transition metal complexes is determined by both the metal valence and the strength and geometry of the surrounding ligands. Cobalt(II) is pink when in an octahedral field and blue in a tetrahedral field (Flett, 2005). The pink colour of octahedral cobalt(II) is relatively weak, $\varepsilon \approx 10$ 1/Mcm for cobalt nitrate (Vraneš *et al.*, 2010), as the d-d transition is Laporte forbidden. The blue colour of tetrahedral cobalt(II) is much more intense, $\varepsilon \approx 100$ 1/Mcm for cobalt chloride (Vraneš *et al.*, 2010), as the d-d transition is both spin allowed and Laporte allowed. Cobalt(III) in an octahedral field, in contrast, has an intense colour, with $\varepsilon > 10\ 000$ 1/Mcm for polyamines (Fallab, 1967) due to ligand to metal charge transfer. An intense, dark colour for cobalt is therefore indicative of cobalt(III).

As a result of the predictable colour intensities, UV-Vis is a convenient method to monitor cobalt(III) concentrations in an organic phase. Guesnet *et al.* (1980) demonstrated that an increase in the concentration of cobalt(III) in an organic phase containing Kelex 100 corresponded with an increase in UV-Vis absorbance between 450 and 600 nm. Fleitlikh *et al.* (2012) similarly reported a dramatic increase in the intensity of the UV-Vis spectrum for cobalt extracted using Cyanex 301 over time in the range 400 to 800 nm, corresponding with oxidation of cobalt(II) to cobalt(III).

2.5.4 Hindering cobalt poisoning using organic acids

Guesnet *et al.* (1980) noted that for mixtures of Kelex 100 with Versatic 10 and other small organic acids, the rate of cobalt poisoning of Kelex 100 decreased as the acidity and concentration of the additive organic acid increased. Decreased poisoning of Kelex 100 in the presence of organic acids was attributed by Guesnet *et al.* (1980) to the ability of the organic acid (HR) to form stable cobalt(II) organic salts with Kelex 100 (HL) of the form: $[Co_2L_2(HL)_2]^{2+}.2R^-$ or $(CoL(HL)_2)^+.R^-$. Guesnet *et al.* (1980) claimed that the formation of a mixed Co(II) complex of the form $CoL_2(HR)_2$ was unlikely for organic acids because they would react with Kelex 100 via an acid–base reaction to form H_2L^+ and R^-. UV-Vis spectra were used as evidence for this particular reaction by analogy to a similar known reaction of 8-quinolinol. It is not immediately clear, however, why the conjugate base of the organic acid would stabilise the cobalt(II) complex by acting as the anion of an organic salt, rather than complexing to the inner coordination sphere of the cobalt(II) ion.

The proposal of Guesnet *et al.* (1980) that organic acids hinder cobalt poisoning of Kelex 100 by acting as the anion of an organic salt differed from that of Hummelstedt (1977). Hummelstedt (1977) suggested instead that Versatic 911 inhibited the cobalt poisoning of Kelex 100 by occupying the axial coordination sites around the cobalt ion thereby hindering the coordination of dioxygen. The same mechanism has been proposed more recently by Grigorieva and Fleitlikh (2013) for hindering the cobalt poisoning of Cyanex 301 using electron donors such as trioctylphosphine oxide.

Quantitative stripping of cobalt, and therefore negligible cobalt poisoning, has been observed in all cases where cobalt was loaded into mixtures of phenolic aldoximes and D2EHPA (Zhang *et al.*, 2001; Alguacil, 2002; Cerpa and Alguacil, 2004). Cobalt was also quantitatively stripped from a mixture of phenolic aldoxime and D2EHPA after one month of "storage" (Cerpa and Alguacil, 2004), presumably under atmospheric conditions. On the basis of the proposed mixed ligand complex formed on synergistic extraction of cobalt by LIX 860 / D2EHPA (Figure 2-7), it is hypothesised here that D2EHPA blocks the axial sites required to form the octahedral dioxygen intermediate, and therefore stops cobalt poisoning. This is in agreement with the mechanism detailed above for hindering the cobalt poisoning of Kelex 100 by Hummelstedt (1977) and thiophosphinic acids by Grigorieva and Fleitlikh (2013). It is possible that organic acids other than D2EHPA, such as Versatic 10 or Cyanex 272, could also allow quantitative cobalt recovery from phenolic oximes. This has not been reported by any authors.

In summary, the addition of D2EHPA to phenolic oximes confers a number of benefits to the SX of nickel and cobalt. D2EHPA results in synergistic extraction of nickel and cobalt, increases the rate of nickel extraction and hinders cobalt poisoning of phenolic oximes. Whether organic acids other than D2EHPA can confer the same benefits is currently unknown and requires investigation. In future investigations into the effect of organic acids on cobalt poisoning of phenolic oximes, it would be possible to follow generation of cobalt(III) via UV-Vis spectroscopy due to the distinctive colour intensity of this ion.

2.6 Nickel and cobalt extraction using mixtures of aliphatic hydroxyoxime (LIX 63) with organic acids

2.6.1 Synergism between LIX 63 and organic acids

The active reagent in LIX 63 is the aliphatic hydroxyoxime 5,8-diethyl-7-hydroxy-6-dodecanone oxime (Figure 2-8). As with phenolic oximes, aliphatic hydroxyoximes can exist in both the active *anti* or E form and the inactive *syn* or Z form. The commercial LIX 63 reagent is provided containing both isomers in the approximate ratio *anti*:*syn* of 60:40, and isomerism readily occurs under commercially relevant SX conditions (Barnard and Turner, 2008). It was shown by Barnard and Tsuntsaeva (2012) that the *syn* isomer does not play a part in metal extraction.

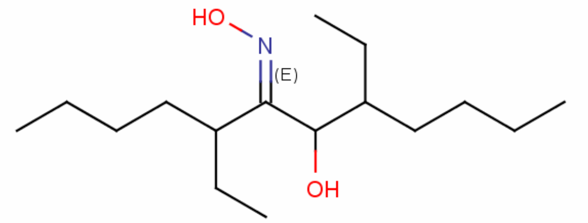

Figure 2-8: Chemical structure of the active hydroxyoxime in LIX 63

Synergism between aliphatic hydroxyoximes and organic acids was first noticed by Joe *et al.* (1966) for mixtures of LIX 63 and D2EHPA. Strong synergism between LIX 63 and D2EHPA has also been reported by other authors (Elizalde *et al.*, 1996; Inoue *et al.*, 1997). Inoue *et al.* (1997) stated that there is also considerable synergism between LIX 63 (20% v/v) and Cyanex 272 (7% v/v) where high ΔpH_{50} values were obtained for both nickel (2.39) and cobalt (1.44).

Synergism between hydroxyoximes and carboxylic acids was first reported by Flett and Titmuss (1969) for mixtures of LIX 63 and naphthenic acid ($\Delta pH_{50}Cu$ of 0.71 and $\Delta pH_{50}Co$ of 0.63). Flett and West (1971) subsequently investigated the differences in synergism between LIX 63 with naphthenic acid, Versatic 911 and 2-bromododecanoic acid. The strongest acid (2-bromodecanoic) produced the strongest synergism for copper (ΔpH_{50} of 2.04), cobalt (ΔpH_{50} of 3.22) and nickel (ΔpH_{50} of 2.68). Castresana *et al.* (1988) examined the effect of seven different carboxylic acids on nickel extraction using LIX 63. The authors obtained a straight line correlation between the synergistic coefficient for nickel and the pKa of the carboxylic acid, further refining the observations of Flett and West (1971) that stronger organic acids result in stronger synergism with LIX 63.

The various synergistic mixtures of LIX 63 and organic acids were not considered commercially viable due to slow extraction rates for nickel. Flett and West (1971) stated that 180 min was required to reach equilibrium nickel extraction using LIX 63 / naphthenic acid. In addition, as copper extraction was so strong with LIX 63 / bromodecanoic acid, stripping of copper was not possible. This was attributed to oxime protonation and subsequent extraction of a copper sulfate species above 150 g/L sulfuric acid (Flett and West, 1986). More recently, Cheng (2006) investigated mixtures of LIX 63 and Versatic 10 for the extraction of nickel and cobalt from sulfate-based laterite PLS. In contrast to the earlier research, nickel extraction was relatively fast with this system and reached equilibrium extraction within 10 min. Nickel stripping, however, was very slow and reached only 30% stripped after 5 min.

There is some uncertainty surrounding the structure of the organic phase LIX 63 / carboxylic acid complex formed from synergistic extraction of nickel. The first structure for a general mixed reagent nickel–hydroxyoxime–carboxylate was proposed by Castresana *et al.* (1988) from thermodynamic data. The complex had two oximes in equatorial positions *trans* to each other on the nickel ion. Crystallographic analysis of a solid state nickel complex containing short chain analogues of the reagent molecules presented by Barnard *et al.* (2010b) suggested, however, that the oxime groups were in the *cis* configuration (Figure 2-9).

Although the solid state evidence suggests a ratio of Ni:Oxime:Acid of 1:2:2, there is some uncertainty about this ratio in organic solution. It seems that synergistic complexes formed from LIX 63 with less sterically hindered organic acids, such as straight chained carboxylic acids, result in a stoichiometry of 1:2:2 (Flett *et al.*, 1974; Elizalde *et al.*, 1986). More sterically hindered organic acids such as Versatic 10, Versatic 911 and di-nonylnaphthalene sulfonic acid appear to result in a stoichiometry of 1:3:2 (Tammi, 1976; Osseo-Asare and Renninger, 1984; Zheng and Osseo-Asare, 1985; Barnard *et al.*, 2010a; Barnard and Turner, 2011a). As such, the synergistic nickel complex formed with LIX 63 / Versatic 10 may not resemble that of Figure 2-9.

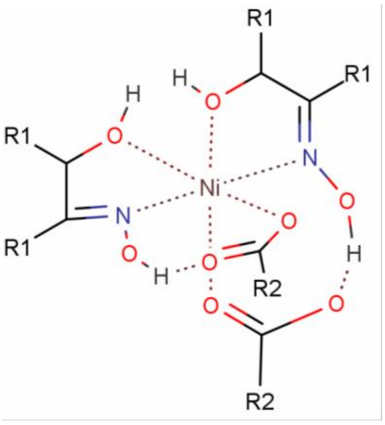

Figure 2-9: Solid-state crystal structure of nickel complex extracted by short chain analogues of LIX 63 and Versatic 10, adapted from Barnard *et al.* (2010b)

Extraction of cobalt with LIX 63 alone poisons the reagent in a similar manner to that of phenolic oximes discussed in Section 2.5.3 (Preston, 1975). In contrast, the synergistic SX of cobalt with LIX 63 / Versatic 10 does not result in cobalt poisoning of the reagent (Cheng, 2006). The organic phase cobalt complex is likely to be the same as that for nickel and may resemble the complex shown in Figure 2-9. A similar mechanism for avoiding cobalt poisoning to that given in Section 2.5.4 may therefore also apply here. That is, the formation of a stable octahedral mixed ligand cobalt complex hinders the binding of dioxygen to cobalt(II) and stops the pathway required for cobalt oxidation and subsequent reagent poisoning.

2.6.2 Acceleration of nickel stripping from LIX 63 / Versatic 10 using TBP

As noted in Section 2.6.1 the extraction of nickel using LIX 63 / Versatic 10 was relatively fast, but stripping of nickel was particularly slow. Cheng (2006) overcame this problem by the addition of a modifier (TBP) to increase the rate of nickel stripping. TBP dramatically increased nickel stripped from 20% to 95% after 3 min. The mixture of 0.5 M Versatic 10 / 0.45 M LIX 63 / 1 M TBP was selective for nickel and cobalt with high rejection of manganese, magnesium and calcium. Importantly, full extraction of nickel and cobalt occurred at a much lower pH than Versatic 10 alone (pH 5.5 compared with pH 7).

LIX 63 / Versatic 10 / TBP was further investigated at the pilot scale by Cheng *et al.* (2010b) for a synthetic sulfate-based nickel laterite leach. It was found that with four extraction and two scrubbing stages >99.9% nickel and cobalt extraction could be achieved into a loaded organic containing <5 mg/L of either manganese, magnesium or calcium. Nickel and cobalt stripping was greater than 95% after three stages using 50 g/L sulfuric acid containing 55 g/L nickel. Notably, cobalt stripping was quantitative, indicating that no cobalt poisoning occurred during the pilot plant trial. The very low magnesium co-extraction and relatively low operational pH meet two of the three goals required for a promising solvent system for application to nitrate-based nickel laterite PLS.

2.6.3 Effect of TBP addition to LIX 63 / Versatic 10

The addition of 0.5 to 1 M TBP to the synergistic system containing LIX 63 / Versatic 10 greatly increased the rate of nickel stripping (Cheng, 2006). The same addition of TBP, however, increased the pH_{50} for nickel extraction from 3.3

to 4.0 and the pH_{50} for cobalt extraction from 2.8 to 4.5. An increased extraction pH for nickel and cobalt puts a tighter limit on the upstream iron and aluminium removal from a PLS in order to avoid unwanted precipitation during SX. It also increases the potential for magnesium extraction with Versatic 10, which occurs at higher pH values.

It was claimed by Cheng (2006) that the extraction rate for nickel was slightly increased by the addition of TBP. According to Cheng (2015)[3] higher pH values were used for extract rate tests with LIX 63 / Versatic 10 with added TBP (pH 5.5 compared with pH 4), presumably due to the increase in extraction pH caused by TBP. The use of a higher extraction pH value may be the cause of the increase in extraction rate reported by Cheng (2006), as was previously observed for Versatic 10 / lauric acid by Flett *et al.* (1975). Subsequent data have shown that the initial rate of extraction measured using a Lewis cell was slightly reduced by the addition of high concentrations of TBP (above 0.5 M) when compared with extraction by LIX 63 / Versatic 10 at the same pH value (Zhang *et al.*, 2011).

Although a mechanism for the increased rate of nickel stripping in the presence of TBP has not been proposed in the literature, comparisons can be made with phenolic oximes mixed with oxygen-based modifiers for copper SX (Section 2.4.2). The addition of TBP to LIX 63 / Versatic 10 increases nickel stripping kinetics, results in a shift in the nickel extraction isotherm to higher pH values, and appears to slightly retard nickel extraction rates. In comparison, oxygen-based modifiers used for copper SX with phenolic oximes also generally increase the stripping rate, increase the pH of extraction, and decrease the extraction rate. On this basis, it is suspected that TBP accelerates nickel stripping with LIX 63 / Versatic 10 by forming TBP solvated hydroxyoxime molecules in the organic phase, similar to the effect of oxygen based modifiers on phenolic aldoximes shown in Figure 2-5. Lessons learned from application of modifiers to copper SX may therefore apply to the use of TBP in LIX 63 / Versatic 10 and hence are considered here.

High concentrations (≈1 M) of modifiers in copper SX circuits are known to increase crud formation, aqueous entrainment and reagent degradation

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[3] Cheng, C.Y., Original researcher for Cheng (2006), personal email, 2015

(Sudderth and Kordosky, 1986; Kordosky and Virnig, 2003; Bender *et al.*, 2011). The increase of crud and entrainment in the organic phase was followed by Dalton and Seward (1986) for a phenolic aldoxime with various modifiers. The composition of each organic phase was not disclosed in their research; it was simply noted that some modifiers caused a dramatic increase in entrainment and concurrent crud formation. Addition of high concentrations of TBP to the organic phase is therefore undesirable due to the potential for crud formation and excessive entrainment.

Kordosky and Virnig (2003) demonstrated that addition of modifiers to LIX 84 resulted in a significant increase in the rate of acid hydrolysis of the oxime in the presence of 35 g/L nitrate, from 0% loss to 20% loss in the presence of ITD after 35 days. This is expected to occur via extraction of inorganic acid into the organic phase. TBP is a known acid extraction reagent (Sudderth and Kordosky, 1986), and LIX 63 in the presence of Versatic 10 is known to be particularly susceptible to acid catalysed hydrolysis (Barnard and Urbani, 2007; Halford and Barnard, 2011). TBP may therefore also result in higher acid entrainment in the organic phase and increase the rate of acid hydrolysis over the lifetime of a commercial operation. To avoid these potential drawbacks of high TBP concentrations in LIX 63 / Versatic 10, as well as a known increase in the required extraction pH, it is necessary to identify a new nickel accelerator for LIX 63 / Versatic 10.

In summary, the synergistic mixture of LIX 63 / Versatic 10 is promising for the recovery of nickel and cobalt with good rejection of magnesium. The octahedral complex formed on synergistic extraction of cobalt provides the added benefit of hindering cobalt poisoning of the aliphatic hydroxyoxime. Unfortunately, the rate of nickel extraction and, in particular, nickel stripping is slow with LIX 63 / Versatic 10. The accelerator used in earlier work (TBP) requires high concentrations (0.5 – 1 M) that result in a large increase in the pH required for nickel and cobalt extraction (1.7 units) and may also increase the formation of crud, aqueous entrainment and reagent degradation. A different nickel accelerator that can be used at lower concentrations without increasing the required extraction pH should be investigated.

2.7 Nickel and cobalt extraction with mixtures of pyridine-based reagents with Versatic 10

2.7.1 Synergism between pyridine-based reagents and Versatic 10

Pyridine-based reagents can be used in SSX with carboxylic acids to achieve similar metal separations as obtained using LIX 63 / carboxylic acids. Pyridine-based reagents with Versatic 10 are appealing alternatives to LIX 63 / Versatic 10 as they do not suffer from slow rates of nickel stripping or extraction and are more stable to acid catalysed hydrolysis at moderate pH (Barnard *et al.*, 2004). The majority of research has focused on pyridine carboxylate esters (PC) although synergism between carboxylic acids and pyridine ethers (Preston and du Preez, 1995) and alkyl pyridines (Preston and du Preez, 2000) has also been reported. The organic phase complex formed on synergistic extraction of nickel with pyridine carboxylates and organic acids (HA) was proposed to be $Ni(PC)_2(A)_2(H_2O)_2$ on the basis of slope analysis (Preston and du Preez, 1994, 1995). At excess concentrations of organic acid, however, it is likely that water in the octahedral nickel complex might be substituted by HA.

The combination of decyl-4-pyridinecarboxylate (decyl-4PC, Figure 2-10) and Versatic 10 was tested by Cheng *et al.* (2010a) to extract nickel and cobalt from a synthetic sulfate-based nickel laterite leach solution. Full nickel and cobalt extraction occurred at slightly higher pH than LIX 63 / Versatic 10 / TBP (pH near 6.5 compared with 5.5). Good separation of nickel, cobalt and zinc from magnesium was achieved with this synergistic system, but the separation factors of nickel and cobalt over manganese were about five times higher with LIX 63 / Versatic 10 / TBP (Cheng *et al.*, 2010a). The pH_{50}(Mn-Ni) was 1.8 and pH_{50}(Mn-Co) was 1.2 for decyl-4PC / Versatic 10 compared with pH_{50}(Mn-Ni) of 2.4 and pH_{50}(Mn-Co) of 1.7 for LIX 63 / Versatic 10 / TBP.

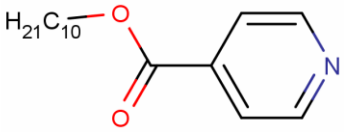


Figure 2-10: Chemical structure of decyl-4-pyridinecarboxylate

Work by Preston and du Preez (1995) investigated how the size of the alcohol derived group on the ester, as well as the location of the ester group on the pyridine ring, affected nickel and cobalt extraction. This work demonstrated that the position of the ester group on the pyridine ring had a strong effect on synergism, whilst the size of the alcohol group was much less important. Extraction at a given pH increased in the order 2-PC ($\Delta pH_{50}(Ni)$ of 1.41) << 4-PC ($\Delta pH_{50}(Ni)$ of 1.97) = 3-PC ($\Delta pH_{50}(Ni)$ of 1.95).

Pyridine derivatives with substituents in the 2-position are less effective synergists due to steric hindrance of the nitrogen lone pair. An ester group is a stronger electron withdrawing group than an alkyl group, hence pyridine carboxylates are also slightly weaker synergists than alkyl pyridines (Preston and du Preez, 2000) with $\Delta pH_{50}(Ni)$ falling slightly from 1.68 for benzyl-pyridine to 1.64 for benzyl-pyridine carboxylate. Similarly, an extra electron withdrawing ester group on ACORGA CLX50 (diisodecyl pyridine 3-5-dicarboxylate) makes it a weaker reagent than 3-PC with a single ester group (Preston and du Preez, 1994), with $\Delta pH_{50}(Ni)$ falling from 1.69 to 1.13.

Pyridine-based reagents with Versatic 10 suffer from poor phase separation characteristics at low pH (Cheng *et al.*, 2002; Masiiwa *et al.*, 2008). This is related to the uptake of mineral acid into the organic phase via the basic pyridine nitrogen. This is particularly problematic with alkyl-pyridines due to higher basicity of the nitrogen atom. One evaluation of 4-(5-nonyl)pyridine noted excessive entrainment in the organic phase after stripping, which required an additional wash stage for the stripped organic before re-loading (Masiiwa *et al.*, 2008). The final strip liquor pH when using 4-(5-nonyl)pyridine must therefore be kept above pH 2 to avoid excessive acid extraction (Mihaylov, 2003). This results in incomplete stripping of copper, iron, nickel and cobalt. Although the lower basicity of pyridine carboxylates results in lower synergism for nickel and cobalt, it improves metal stripping at a given pH. Lower basicity also decreases the potential for acid extraction into the organic phase, thereby improving phase separation under strip conditions. As a result, the majority of research into commercial applications of pyridine-based reagents has focused on the less basic pyridine carboxylate esters.

2.7.2 Potential for commercial applications of pyridine carboxylates with Versatic 10

Pyridine-based reagents with Versatic 10 are of interest for commercial application to nickel and cobalt extraction from a nitrate matrix as they offer faster rates of extraction and stripping than LIX 63 / Versatic 10 with comparable magnesium rejection. Pyridine carboxylates, in particular, have been the focus of process development as they exhibit better phase separation characteristics under strip conditions than the more basic alkyl pyridines.

There is no known commercial production of pyridine-based reagents for SX. ACORGA CLX 50 is no longer commercially available, although it was originally available through Cytec (now Solvay) as a copper chloride solvating reagent. Mintek in South Africa have, however, developed and successfully tested a proprietary synergist called Nicksyn for use with Versatic 10. Although the molecular structure of Nicksyn has not been identified, it is likely to be based on a pyridine carboxylate, given that Mintek has a long history of working with these reagents. The extraction pH_{50} values in Table 2-1 correspond well with those of other pyridine carboxylates and support this supposition.

Table 2-1: pH_{50} values for selected metals in a sulfate matrix extracted by 0.5 M Versatic 10 with a given pyridine carboxylate (0.35 M CLX 50, 0.5 M otherwise)

	CLX 50	decyl-4PC	octyl-3PC	Nicksyn
Cobalt	5.6	5.4	5.3	5.6
Nickel	5.1	4.8	4.6	4.4
Manganese	6.3	6.6	Not Reported	6.6
Reference	(Cheng *et al.*, 2015)	(Cheng *et al.*, 2010a)	(Preston and du Preez, 1995)	(du Preez and Kotze, 2009)

Nicksyn / Versatic 10 has been tested at pilot plant scale for the BioNIC™ project in Australia (du Preez and Kotze, 2009) as well as Çaldağ Nickel in Turkey (Larmour-Ship *et al.*, 2014). For the BioNIC project, a continuous counter current pilot plant was set up by du Preez and Kotze (2009) to separate 5 g/L nickel from 0.5–0.6 g/L calcium. Four extract stages at a final pH of 5.8 were required for quantitative nickel extraction using 0.26 M Nicksyn / 0.52 M Versatic 10. There was negligible calcium extraction and scrubbing of the organic phase was not required. Over 96% stripping of nickel was achieved using 60 g/L nickel in 50 g/L sulfuric acid. For Çaldağ Nickel a pilot plant run by Larmour-Ship *et al.* (2014) tested the extraction of 4 g/L nickel and 0.25 g/L cobalt from a real sulfate-based nickel laterite PLS using 0.5 M Nicksyn / 0.5 M Versatic 10. Before commencing the pilot trials, trace aluminium was precipitated from the as-received laterite PLS, indicating that the required extraction pH necessitates stringent upstream aluminium removal. Over 99.5%

of nickel and cobalt were extracted with 35% manganese co-extraction in four stages with a final pH of 6.2. Calcium and magnesium co-extractions under these conditions were negligible. Both these pilot trials demonstrate that Nicksyn / Versatic 10 can separate nickel and cobalt from magnesium and that pyridine carboxylates, in general, with Versatic 10 should be investigated for application to a nitrate matrix.

In summary, pyridine-based reagents, and pyridine carboxylates in particular, with Versatic 10 are promising for the extraction of nickel and cobalt with high rejection of magnesium. Although the separations of nickel and cobalt from manganese are slightly lower than for LIX 63 / Versatic 10, PC / Versatic 10 do not exhibit slow phase transfer rates. As a result of extensive piloting of the Nicksyn / Versatic 10 solvent system, the use of pyridine carboxylates for extraction of nickel and cobalt from sulfate-based nickel laterite PLS appears to be commercially viable.

2.8 Stability of organic chemicals used in solvent extraction

2.8.1 Stability of diluents in contact with nitric acid

Diluents are present in all the solvent systems discussed. Degradation of the hydrocarbons commonly making up the diluent is therefore one area for concern when operating under chemically aggressive conditions. Concentrated nitric acid is a strong oxidising agent and can oxidise both aldehydes and alcohols to carboxylic acids. It can also oxidise secondary alcohols to ketones. The oxidation of primary alcohols, common phase modifiers, will produce a carboxylic acid (Wade, 2013) as halting the reaction at the aldehyde requires careful chemical control. The oxidation of a primary alcohol to an acid may also result in the formation of an ester (Wade, 2013). Nitric acid is not a strong enough oxidising agent to auto-oxidise alkanes in the diluent (Deno, 1976). It can, however, react with alkanes to form nitro and nitroso compounds via *in-situ* HNO_2 formation from decomposition of HNO_3. Nitro compounds will react via acid hydrolysis to generate aldehydes, ketones or carboxylic acids with release of N_2O (Šunjić and Peroković, 2016). As a result, uncontrolled reaction of diluent with concentrated nitric acid may yield a range of reaction products.

Ishihara and Ohwada (1966) investigated the reaction products formed when kerosene was contacted with different concentrations of nitric acid at different temperatures. A yellowing of the diluent was noticed after only 6 h when contacting kerosene with 3 M nitric acid at 70 °C. Because the colour dissipated over an unspecified time frame, this yellowing was explained by the generation of HNO_2 and NO_x gases dissolving in the organic phase. In 10 – 14 M nitric acid at 110 °C, the kerosene turned brown after 2 h. At 14 M nitric acid, red solids precipitated out of solution after 1 week, indicating extensive degradation. Carboxylic acids, nitrate esters and nitro compounds were all identified in the degraded samples using infra-red (IR) spectroscopy. When unsaturated and aromatic compounds were removed from the diluent, no colour change was noticed after contacting the diluent with 6 M nitric acid at 70 °C for one week (Ishihara and Ohwada, 1966). This suggests that if a fully aliphatic diluent is used, then little degradation from nitric acid will be observed under commercial operating conditions.

An investigation into the effect of nitric acid and NO_x on aliphatic diluent compounds under reflux was carried out by Tallent *et al.* (1984). The loss of these diluent components was measured via gas chromatography with flame ionisation detection (GC-FID). The study found that degradation occurred readily when nitrogen dioxide was bubbled through samples contacted with either 4 M (1.6% loss in 6 h) or 8.2 M (21.3% loss in 6 h) nitric acid. Bubbling argon gas through the samples greatly reduced the degradation rate to 0.17% in 6 h for 4 M nitric acid and to 1.15% in 6 h for 8.2 M nitric acid, presumably by scrubbing of NO_x gases and nitrous acid from solution. This suggests that the majority of degradation of the diluent is occurring via reaction with nitrous acid and NO_x gases generated via reduction of nitric acid. Therefore, high NO_x concentrations in the organic phase can lead to extensive alkane degradation, whereas nitric acid in the absence of NO_x is less likely to cause concern.

In the Direct Nickel process there is a high concentration of nitrate anion (up to 9 M nitrate) due to high magnesium nitrate concentrations. Nitrate anions at high pH are poor oxidising agents and diluent degradation may therefore be limited under these conditions. This can be rationalised by substituting the reduction of nitrate (EQ 3) into the Nernst equation (EQ 4) and noting that the oxidation-reduction potential increases with the product of the nitrate activity and the proton activity *squared*.

$NO_3^- + 2\ H^+ + e^- \rightarrow H_2O + NO_2(g)$ $E^0 = 0.775$ V (vs. standard hydrogen electrode) (EQ 3)

$$E = 0.775 - 0.0257 \ln \frac{p_{NO2}}{a(H+)^2 \cdot a(NO3-)} \quad \text{(EQ 4)}$$

Although nitric acid is considered highly oxidising, the effects of diluent degradation can be managed in two ways. First, the activity of protons should be low enough that generation of NO_x is negligible. In the case of the DNi PLS the pH will be relatively high (pH 2.5) and so NO_x generation is not considered to be a concern. To avoid the generation of NO_x, stripping with an alternative to nitric acid is recommended. Secondly, only the use of fully aliphatic hydrocarbons should be considered to limit the potential degradation pathways. The potential diluent options for application to nitrate-based leach liquors should therefore be constrained to dearomatised options such as ShellSol™D70, Escaid™110 or equivalent diluents.

2.8.2 *Stability of phenolic oximes*

Phenolic oxime loss from a solvent system is known to occur via both acid catalysed hydrolysis to the corresponding carbonyl and *ortho*-nitration to a nitro-phenolic oxime. The rate of phenolic oxime hydrolysis has been studied in both nitric and sulfuric acids. In nitric acid systems, Bart *et al.* (1990) investigated the degradation of both phenolic aldoximes and ketoximes, quantifying oxime loss using residual copper loading. Bart *et al.* (1990) reported that 2-hydroyacetophenone and 2-hydroxybenzephenone oximes both lost all copper extraction ability after only 1 month and a solid sludge was found in the organic phase under the same conditions of 2 M nitric acid at 28 °C.

Bart *et al.* (1990) found that the phenolic aldoximes such as P50 (C_9 aldoxime) and LIX 860 (C_{12} aldoxime) were much more stable than the phenolic ketoximes with respect to 2 M nitric acid at 28 °C. After 1 month the residual copper transfer capacity for LIX 860 was 87% of the original, whereas that of PT 50 with 25% ITD was 92% of the original. Phenolic aldoximes therefore appear to be much more stable in general with respect to nitric acid attack than phenolic ketoximes.

In sulfuric acid systems, the degradation of phenolic ketoximes appears to be slower than in contact with nitric acid. Degradation of the benzophenone oxime LIX 65N in contact with 180 g/L sulfuric acid at 28 °C reported by Whewell *et al.* (1981) only resulted in 1% lost per month. Under the same sulfuric acid-based conditions the acetophenone oxime SME 529 degraded by 12% per month. This can be compared with complete loss of phenolic ketoximes in contact with a similar concentration of nitric acid as discussed above. Phenolic oxime loss in the study by Whewell *et al.* (1981) was quantified via maximum copper load tests and also back-calculated from the carbonyl concentration quantified using IR spectroscopy.

No data were found for the hydrolytic stability of phenolic aldoximes in contact with sulfuric acid without an added modifier. The identity of the modifier added to the organic phase, however, significantly alters the stability of the reagent. The half-life of P50 (C_9 aldoxime) at 30 °C in contact with acid concentrations required for copper stripping was 114 weeks with nonyl-phenol, 199 weeks with ITD and 238 weeks with an unidentified alcohol (Dalton and Seward, 1986). A similar trend was reported in later work by Virnig *et al.* (2003) where the amount of oxime hydrolysis product detected after 40 days continuous mixing in a copper electrolyte containing 32 g/L nitrate at pH 1.75 increased in the following order: ketoxime (0.1%) < aldoxime + ketoxime (0.15%) < ketoxime + ITD (0.8%) < aldoxime + ester modifier (0.95%) < aldoxime + ITD (1.8%). This increase in hydrolysis from different modifiers can be attributed to modifiers extracting varying quantities of acid into the organic phase via solvation.

The presence of organic acids such as D2EHPA and DNNSA (di-nonyl naphthalene sulfonic acid) also increases the rate of phenolic oxime hydrolysis (Oliver and Ettel, 1976). Additions of these acids to LIX 65 were tested in a semi continuous operation (12 h per day) at 50 °C stripping with 160 g/L sulfuric acid. After an unspecified timeframe a 2% v/v addition of D2EHPA decreased the copper loading capacity of LIX 65 to 79% of that with no additive whilst 2% v/v DNNSA decreased copper loading to only 11%. There are no data on the effect of D2EHPA or other organic acids on the hydrolysis of the commercially relevant reagents in LIX 860 or LIX 84. It is clear, however, that this should be investigated if a mixture of these reagents is found to be a viable solvent system for the extraction of nickel and cobalt with good magnesium rejection.

In addition to hydrolysis, loss of phenolic oxime functionality can occur via ortho-nitration. The nitration of organic molecules occurs via electrophilic addition of NO_2^+ to an area of high electron density, such as on aromatic compounds (Cotton and Wilkinson, 1980). The NO_2^+ ion is formed *in-situ* due to the reaction of un-dissociated nitric acid with a strong acid. This occurs most effectively with concentrated sulfuric acid, although it does occur to a lesser extent in concentrated nitric acid. The reactions involved in the formation of NO_2^+ are detailed by Nguyen and Hegarty (1984) and are given in (EQ 5) and (EQ 6):

$$HNO_3 + HA \rightleftharpoons H_2NO_3^+ + A^- \qquad \text{(EQ 5)}$$

$$H_2NO_3^+ \rightarrow NO_2^+ + H_2O \qquad \text{(EQ 6)}$$

where HA is an inorganic acid.

Nitration of a phenolic oxime with NO_2^+ is shown in Figure 2-11. Only one reaction product is formed due to the *ortho* / *para* directing phenol group on the aromatic ring. The resulting nitrated oxime produces a reagent with strong metal affinity due to the electronegativity of the nitro group, similar to that reported by Bart *et al.* (1990) with LIX 70 (an *ortho*-chloro phenolic ketoxime). Bart *et al.* (1990) further reported that, due to particularly strong copper extraction, copper stripping of the nitrated reagent was not possible via conventional acid stripping. Formation of this species therefore results in copper poisoning.

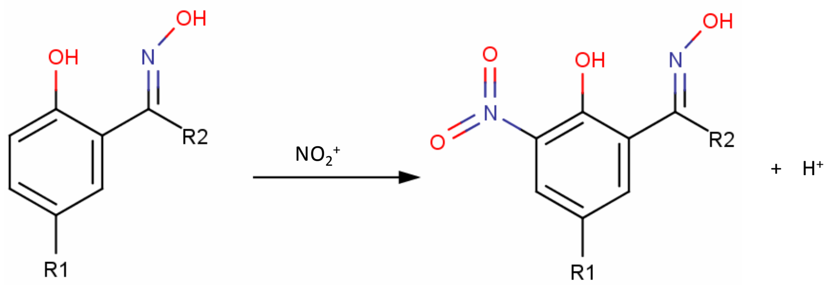


Figure 2-11: Reaction for nitration of phenolic oximes via NO^{2+}

Phenolic oxime nitration was first noted by Bart *et al.* (1990) in contact with a Moebius (silver refining) electrolyte for recovery of copper. The Moebius electrolyte contained 9.8 g/L copper, 0.15 M nitric acid and 1 g/L free NO_2.

Accelerated loss of the P50 aldoxime in this investigation correlated with an approximate doubling of the residual copper in the stripped organic phase after 42 days, suggesting copper poisoning via the formation of nitrated oximes. Bart *et al.* (1990) showed that ITD dramatically decreased the stability of the aldoximes P50 and LIX 860 in contact with the sample of Moebius electrolyte over 436 days; ultimate copper transfer capacity decreased from between 55% and 29% for unmodified reagents down to between 0 and 21% for reagents modified with ITD. Similar to the increase of phenolic aldoxime hydrolysis in the presence of modifiers, increased reagent loss in the presence of ITD was attributed by Bart *et al.* (1990) to solvation and extraction of NO_2 and acid into the organic phase.

Virnig *et al.* (2003) showed that, for phenolic oximes, nitration was minimal below approximately 500 mV and above pH 1. At higher oxidation potentials and lower pH values, the loss in oxime functionality increased dramatically from near zero to above 18% lost per month. A similar result was also reported by Yáñez *et al.* (2009) for an indicative, aqueous soluble, model compound TAP (4-*tert*-butyl phenol). In the work by Yáñez *et al.* (2009) the amount of nitrated TAP generated at 40 °C over 619 h (approximately 1 month) was lower than detection below 550 mV for a wide range of nitrate concentrations (0.05 – 24 g/L), but increased to 100% at 650 mV and 0.21 g/L nitrate.

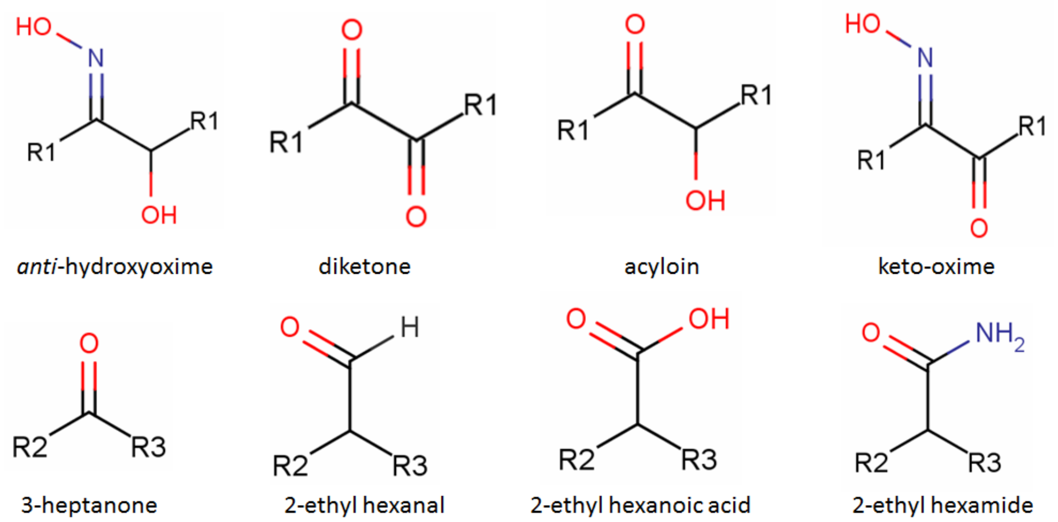
Ketoximes and modified ketoximes are more stable than modified aldoximes with respect to nitration (Virnig *et al.*, 2003). After 40 days in contact with 32 g/L nitrate at pH 1.75, LIX 622 (C_{12} aldoxime modified with ITD) contained 3% nitrated oxime. In comparison, LIX 84 and LIX 84 with the same level of ITD as LIX 622 contained no nitrated oxime after 40 days. Similar results were later obtained by Yáñez *et al.* (2009) under more aggressive conditions of 60 g/L nitrate at pH 1.35, where residual copper loading after stripping with 200 g/L sulfuric acid was used to determine the amount of nitrated oxime. After 50 h, a modified aldoxime contained 500 mg/L copper in the organic phase whereas the same concentration of residual copper in LIX 84 was only measured after 500 h. Yáñez *et al.* (2009) further reported that an aldoxime with an unidentified sacrificial agent in the organic phase resulted in no residual copper loading after 625 h, showing that it is possible to use modifiers to preferentially react with nitronium ions and temporarily avoid oxime nitration.

Clearly, the hydrolysis and nitration of phenolic oximes in contact with acidic or nitrate-bearing aqueous phases is a concern for potential application to nickel and cobalt recovery from a nitrate-based PLS. Phenolic ketoximes appear far less stable in nitric acid compared with phenolic aldoximes, although they were more stable to nitration and hydrolysis in later work based in sulfate matrices. Degradation of phenolic oximes also appeared to be accelerated by the presence of organic acids such as D2EHPA. If a mixture of a phenolic oximes and an organic acids is found to be a viable solvent system, it will be important to test the long term stability of this mixture in contact with a nitrate-based PLS and under the required strip conditions.

2.8.3 Stability of aliphatic hydroxyoxime (LIX 63)

The degradation of LIX 63 in the presence of Versatic 10 under different acid strengths, temperature and metal loadings has been thoroughly investigated in sulfate systems. Although the effect of chloride on degradation when compared to sulfate is reported to be minimal (Whewell *et al.*, 1981), the effect of nitrate on the stability of LIX 63 is unknown.

The known degradation products of LIX 63 are shown in Figure 2-12 and have been characterised through a number of studies (Barnard and Urbani, 2007; Barnard and Turner, 2011a; Barnard and Tsuntsaeva, 2013). It was noted in these studies that under sulfuric acid-based strip conditions the primary degradation products are acyloin, diketone and 2-ethyl-hexanoic acid. Under nickel laterite extract conditions the primary degradation products are diketone, keto-oxime, 2-ethyl-hexanoic acid, 2-ethyl-hexamide, 3-heptanone and 2-ethyl-hexanal. Acyloin only accumulates under strip conditions whereas keto-oxime, 2-ethyl-hexamide and 3-heptanone only accumulate under metal-loaded extract conditions. The majority of degradation products do not appear to affect metal selectivity or phase disengagement times (Barnard and Urbani, 2007; Barnard and Turner, 2011a). There was, however, some inconclusive evidence to suggest that 2-ethyl-hexanal, 2-ethyl-hexamide and 3-heptanone may have a small negative impact on metal selectivity (Barnard and Tsuntsaeva, 2013).



anti-hydroxyoxime diketone acyloin keto-oxime

3-heptanone 2-ethyl hexanal 2-ethyl hexanoic acid 2-ethyl hexamide

Figure 2-12: The identified LIX 63 degradation products. R1 = 1-ethylpentyl, R2 = butyl, R3 = ethyl

Accelerated degradation of LIX 63 in contact with organic acids was first speculated after LIX 65 was shown to degrade in the presence of DNNSA and D2EHPA (Oliver and Ettel, 1976). A solution of D2EHPA with LIX 63 resulted in a 23% drop in nickel distribution ratio and a 29% drop in cobalt distribution ratio after letting the unloaded organic stand for 6 months at ambient temperature (Inoue *et al.*, 1997). In contrast, phosphinic and phosphonic acids with LIX 63 did not cause enough degradation to alter the nickel or cobalt distribution ratios. An excess of LIX 63 was present initially and this experiment did not quantify any loss of oxime in the solutions or take into account *syn* to *anti* isomerism as a buffer for the active reagent. It is likely that in the work by Inoue *et al.* (1997) oxime degradation by phosphinic and phosphonic acids was taking place, but not to a high enough degree to affect distribution ratios over the timeframe studied.

Characterisation of LIX 63 degradation in the presence of D2EHPA and Versatic 10, as well as LIX 63 / Versatic 10 / TBP, was investigated under strip conditions (20 g/L H_2SO_4, 60 °C, A:O = 1:1) for six weeks by Barnard and Urbani (2007). Oxime loss in this more recent work was quantified directly using GC-FID. The results agreed with Inoue *et al.* (1997) in that the more acidic organic acid (D2EHPA) greatly increased degradation of LIX 63 (half-life less than one week) compared with Versatic 10 (half-life of 30 weeks). Unlike the phenomenon observed for phenolic oximes, where degradation increased in the presence of modifiers (Section 2.8.2), TBP added to increase the stripping rate of nickel did not appear to affect the rate of hydroxyoxime loss under the conditions tested.

The effect of temperature on the rate of LIX 63 degradation has been defined under both strip conditions and metal-loaded conditions. Whewell *et al.* (1981) noted that for LIX 63 in the absence of Versatic 10, a 2.2 times increase in degradation occurred after shaking with varying concentrations of sulfuric acid at 38 °C compared with that at 28 °C. This is consistent with more recent work for LIX 63 in the presence of Versatic 10, where the rate of oxime loss in LIX 63 / Versatic 10 / TBP in contact with 20 g/L sulfuric acid roughly doubled with every 10 °C increase in temperature (Barnard, 2008a). Under extract conditions, the rate of oxime loss in LIX 63 / Versatic 10 again roughly doubled with every 10 °C rise in temperature (Barnard and Turner, 2011a).

In addition to increasing temperature, increasing aqueous phase acidity also increases the rate of acid catalysed oxime hydrolysis. For LIX 63 without Versatic 10 (Whewell *et al.*, 1981), oxime loss over 3.5 weeks at 28 °C increased in the order 0 g/L sulfuric acid (0% loss), to 100 g/L (0.14% loss), to 250 g/L (0.46% loss). For LIX 63 / Versatic 10 (Halford and Barnard, 2011), oxime loss at 70 °C also increased, with oxime half-lives decreasing in the order 0 g/L sulfuric acid (9.0 weeks), to 20 g/L (7.5 weeks), to 50 g/L (4.8 weeks).

Redox active metals such as copper, iron, cobalt and manganese increase the rate of hydroxyoxime degradation in the order copper > manganese > cobalt > zinc > nickel (Turner and Barnard, 2012). These metals, and cobalt in particular, also increase the amount of keto-oxime formed as a percentage of total oxime lost. Nickel loading up to 4.6 g/L did not materially change the rate of oxime loss whereas copper loaded at 2 g/L decreased hydroxyoxime half-life from about 55 weeks to 13 weeks under otherwise comparable conditions. Manganese concentrations of 2.5 g/L in a cobalt–zinc-bearing aqueous phase decreased the half-life of LIX 63 in LIX 63 / Versatic 10 to 24 weeks, compared with 66 weeks with no manganese at the same pH. In the same comparison, manganese loading also resulted in increased cobalt poisoning of LIX 63, from 77% cobalt stripped to 7% stripped after 24 weeks (Barnard *et al.*, 2010a).

Under commercially relevant conditions hydroxyoxime half-lives in LIX 63 / Versatic 10 were 162 weeks under strip conditions (10 g/L sulfuric acid, 60 g/L nickel) at 35 °C (Barnard and Turner, 2011b) and 105 weeks under extract conditions required for nickel and cobalt extraction at 30 °C (Barnard and Turner, 2011a). These half-lives are similar to, although slightly less than, those obtained with the phenolic oximes widely used in the copper SX industry (Section 2.8.2), and so are considered acceptable. In addition, a commercial operation is currently using LIX 63 / Versatic 10 for cobalt and zinc extraction (Dreisinger *et al.*, 2010), further supporting the premise that the hydroxyoxime is sufficiently stable for commercial application.

With strict control of operating conditions, most importantly temperature, acid strip concentrations and manganese and copper loading, acceptable rates of hydroxyoxime loss can be maintained. Degradation products have little impact on the metal selectivity or phase disengagement properties of the organic phase and so reagent top-up can be easily managed by regular sampling and analysis. The LIX 63 / Versatic 10 system can therefore be used effectively for nickel and cobalt recovery from a sulfate system. Whether a nitrate-based PLS would also result in manageable rates of degradation is unknown and requires investigation.

2.8.4 Stability of pyridine carboxylates

Pyridine derivatives are likely to be chemically stable to nitration as the pyridine functional group is less prone to oxidation or nitration than other aromatics. The nitration of pyridine with a concentrated nitric acid–sulfuric acid mixture results in very low yields (Katritzky *et al.*, 2005). The only reported route for degradation of a pyridine carboxylate under operational SX conditions is via acid hydrolysis to an alcohol and a pyridine carboxylic acid (Figure 2-13). This has only been investigated under sulfate-based extract and strip conditions. The stability of pyridine carboxylates in contact with a nitrate-based PLS is currently unknown.

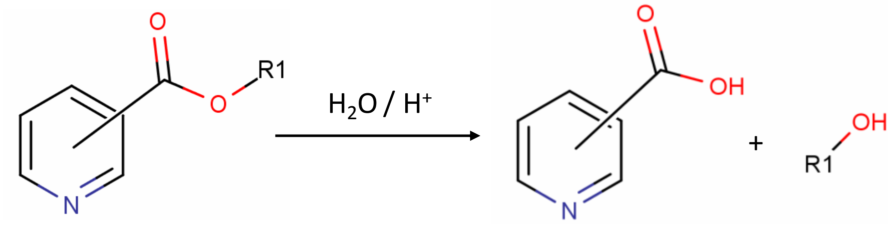


Figure 2-13: Reaction for acid catalysed hydrolysis of a pyridine carboxylate

There are several investigations suggesting that pyridine carboxylates are stable to hydrolysis by sulfuric acid at moderate pH. The nickel loading of Versatic 10 mixed with octyl-3-pyridine carboxylate did not change over 15 days after contacting with 98 g/L sulfuric acid at 30 °C (Preston and du Preez, 1994). Similarly there was no change in the CLX 50 concentration in CLX 50 / Versatic 10 noted by Cheng *et al.* (2002) using GC-FID or high performance liquid chromatography (HPLC) when contacted with 35 g/L sulfuric acid at 40 °C over 84 days. The stability of decyl-4PC in the presence of Versatic 10 has also been investigated under strip conditions using synthetic loaded strip liquor at pH 3 and 40 °C. Under these conditions, decyl-4PC only suffered a 1% loss per year by hydrolysis to decanol and isonicotinic acid (Barnard *et al.*, 2004). In this work, a single data point for hydrolysis at pH 1 after 32 days aligned with the rate expected from hydrolysis at pH 3. Additionally, only a small change in nickel pH_{50} was noticed for Nicksyn / Versatic 10 after mixing under strip conditions of 40 g/L sulfuric acid for 90 days (du Preez and Kotze, 2009). Although pyridine carboxylates appear stable at low acidity, the effect of higher acidity over long term operation and in the presence of nitrate anions is not known.

Pyridine carboxylate stability under extract conditions is not well documented. Decyl-4PC stability under extract conditions was only studied over 16 days by Barnard *et al.* (2004). Although no degradation was noted, this study was not long enough to be fully instructive. For Nicksyn / Versatic 10 no change in the nickel pH_{50} value was noticed under extract conditions of synthetic feed liquor at pH 6 after 90 days (du Preez and Kotze, 2009). Although promising, the analysis technique used was not sensitive enough to allow accurate determination of long term stability. More comprehensive studies of the stability of pyridine carboxylates under both nitrate and sulfate nickel laterite extract conditions are required.

In summary, the chemical stability of diluents, phenolic oximes, aliphatic hydroxyoximes and pyridine carboxylates from the standpoint of application to a nitrate-based DSX process have been discussed. It is recommended to use only fully aliphatic diluents and to not strip with nitric acid to maintain diluent stability. The nitration and hydrolysis of phenolic oximes was of particular concern, especially when mixed with an organic acid. Although LIX 63 stability can be managed by using low temperatures and low acid concentrations in the strip liquor, the effect of nitrate on reagent degradation has not previously been investigated and remains unknown. For pyridine carboxylates in general, chemical stability under extract conditions has not been thoroughly investigated, and the effect of nitrate anions on reagent stability also remains unknown. Clearly, stability studies using conditions expected for a nitrate-based DSX process will be important for development of a viable solvent system.

2.9 Conclusions

A review of the literature on the potential for developing an SX process for recovery of nickel and cobalt from a nitrate-based nickel laterite PLS has revealed that:

- There is limited information available on the development of solvent systems for nitrate matrices. One study was found for the separation of cobalt from nickel using D2EHPA, but no studies developing a process for the co-extraction of nickel and cobalt from nitrate exist. Some research has suggested, however, that there is a predictable difference between the extraction of metals from nitrate and sulfate matrices, where the extraction of a given metal occurs at a slightly lower pH from a nitrate matrix. A systematic investigation is required to determine if this effect persists for a range of base metals extracted by a range of SX reagents (Chapter 3).

- The three DSX processes applied to sulfate-based nickel laterite PLS in commercial operations (Bulong process, Goro process, QNi process) are not suitable for application to a nitrate-based PLS. The high magnesium content would saturate Cyanex 272 as used in the Bulong process, causing high neutralisation requirements and high reagent holdup. The susceptibility of Cyanex 301 used in the Goro process to oxidative degradation also precludes its use in contact with highly concentrated nitrate (> 8 M) under acidic (<pH 2.5) conditions. Cobalt poisoning of phenolic oximes, as used in the QNi process, excludes them for use as a single reagent for cobalt extraction from the nitrate-based PLS. The only commercially proven reagent promising for nickel and cobalt extraction with good magnesium rejection and chemical stability to high nitrate

concentrations is Versatic 10. This reagent unfortunately suffers from a high extraction pH and high solubility in the aqueous phase at this pH.

- Modifiers used in solvent systems are useful additives to improve phase separation, hinder third phase formation, enhance metal stripping by altering metal distribution between the aqueous and organic phases, catalyse phase transfer reactions, and to decrease the extraction pH of metals via SSX. Modifiers and mixed reagent solvent systems should therefore be considered for nickel and cobalt extraction from a nitrate matrix, particularly to decrease the required Versatic 10 extraction pH.

- D2EHPA mixed with phenolic oximes results in synergistic extraction of nickel and cobalt, and accelerates the extraction of nickel. Cobalt extracted by this mixture does not result in cobalt poisoning, possibly due to formation of an octahedral cobalt(II) mixed ligand complex. D2EHPA, however, is unselective for impurity metals, including magnesium, over nickel and cobalt. The effects of less acidic, more selective, organic acids, such as Cyanex 272 or Versatic 10, on metal extractions in a mixed metal aqueous phase are unknown and should be investigated (Chapter 4). Whether these organic acids can stop or slow cobalt poisoning of phenolic oximes is also unknown and requires further research (Chapter 5). Mixtures of phenolic oximes with organic acids are therefore the second promising solvent system for application to a nitrate-based nickel laterite PLS.

- LIX 63 / Versatic 10 is a promising reagent mixture for the rejection of magnesium at low pH. The stripping of nickel from this solvent system is, however, particularly slow. TBP can be used to accelerate nickel stripping, but causes an undesirable increase in the required extraction pH. The high TBP concentration required may also increase aqueous entrainment, crud formation and organic degradation. Nickel accelerators that operate at lower concentrations than TBP, and without increasing the required extraction pH, are therefore of interest (Chapter 6). LIX 63 / Versatic 10 with an appropriate modifier is a third promising solvent system for application to a nitrate-based nickel laterite PLS. The effects of the three reagents in the organic phase on extraction and striping would, however, be unknown and would therefore require further investigation (Chapter 7).

- Nickel and cobalt extraction with good magnesium rejection can be achieved using synergistic mixtures of pyridine-based reagents and Versatic 10. Pyridine carboxylates / Versatic 10 have been used at the pilot scale for extraction of nickel and cobalt from sulfate-based nickel laterite PLS. Although these mixtures operate at a higher pH than LIX 63 / Versatic 10, and with poorer separation from manganese, they remain of interest due to comparatively faster phase transfer rates and higher hydrolytic stability. A pyridine carboxylate with Versatic 10 is a fourth promising solvent system for application to a nitrate-based nickel laterite PLS. The various promising solvent systems identified for the solvent extraction of nickel and cobalt from a nitrate-based PLS would have to be compared to offer recommendations as to which are the most appropriate (Chapter 8).

- As unsaturated and aromatic compounds react readily with nitric acid, only aliphatic diluents should be considered for a solvent system applied to nitrate matrices. The nitration and hydrolysis of phenolic oximes in contact with nitric acid is also a concern and should be considered if a solvent system using phenolic oximes is found viable. The degradation of either LIX 63 or nonyl-4PC in contact with nitrate-based matrices is also unknown and requires further research (Chapter 9).

CHAPTER 3
Comparison of solvent extraction pH isotherms generated from sulfate and nitrate matrices

3.1 Introduction

A review of the literature suggested a number of promising solvent systems to recover nickel and cobalt from nitrate-based PLS. These were Versatic 10 as a single reagent, phenolic oximes with organic acids, LIX 63 with Versatic 10 and a suitable accelerator, and pyridine carboxylates with Versatic 10. The majority of work reviewed, however, was carried out in sulfate matrices and it is unknown whether it can be used as a reliable guide for a nitrate matrix.

Some limited studies on the difference between a nitrate and sulfate matrix on the extraction of metals in general all point towards a common trend. A consistent decrease in extraction pH of about 0.5 units on moving from a sulfate to a nitrate matrix was observed in these studies. It is hypothesised that this trend will continue for the extraction of metals in general using cation exchange reagents. If this is correct, then the literature review can be considered a useful guide for selecting solvent systems for application to nickel and cobalt recovery from a nitrate-based PLS.

The aim of this chapter was to test the above hypothesis and determine if the results from the literature survey of solvent extraction options for metal extraction from sulfate-based leach liquors can be used as a useful guide for nitrate-based leach liquors. This was done via systematic generation of pH extraction isotherms, using a range of different reagents and reagent mixtures from analogous nitrate and sulfate matrices that could be compared with available literature data from a sulfate matrix. As there are no literature data for mixtures of phenolic oximes with organic acids, a comparison could not be made and these solvent systems were not investigated here. Further investigations into the mechanisms behind any differences observed were then carried out via thermodynamic modelling of nitrate and sulfate matrices using hydroxide precipitation as an analogue to solvent extraction. UV-Vis analysis was then used as an analytical method to investigate the extraction of nickel using LIX 63.

3.2 Materials and Methods

The general materials and methods used in each results chapter of this thesis are mostly consistent. To avoid replication, the purity and supplier of chemicals will only be mentioned once at its first use. In most cases, this occurs in the present chapter. Where relevant, experimental and analytical methods will refer back to previous chapters with notes to any specific differences. Solvent extraction reagent chemical names are also presented in the glossary.

3.2.1 Aqueous and organic solutions

The following chemicals were used to make up nitrate aqueous phases in a sodium nitrate matrix at pH 1 containing the metals normally present in a nickel laterite leach liquor, after iron and aluminium removal, at 0.01 M: calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$, AR, Chem Supply, Australia), cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$, analytical reagent (AR), BDH Laboratory Supplies, UK), copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$, laboratory reagent (LR), Chem Supply, Australia), magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$, LR, Chem Supply, Australia), manganese nitrate ($Mn(NO_3)_2 \cdot 4H_2O$, AR, Chem Supply, Australia), nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$, AR, BDH Laboratory Supplies, UK), zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$, AR, Chem Supply, Australia).

The following chemicals were used to make up sulfate aqueous phases at pH 1, containing the same metals as the nitrate aqueous phase at 0.01 M: calcium sulfate ($CaSO_4$, technical reagent (TR), Sigma Aldrich, Australia), cobalt sulfate ($CoSO_4 \cdot 7H_2O$, LR, Rowe Scientific, Australia), copper sulfate ($CuSO_4 \cdot 5H_2O$, AR, Merck, Australia), magnesium sulfate ($MgSO_4 \cdot 7H_2O$, TR, Sigma Aldrich, Australia), manganese sulfate ($MnSO_4 \cdot H_2O$, AR, Rowe Scientific, Australia), nickel sulfate ($NiSO_4 \cdot 6H_2O$, AR, Ajax Fine Chemicals, Australia), zinc sulfate ($ZnSO_4 \cdot 7H_2O$, AR, BDH Laboratory Supplies, Australia).

Stock nitrate and sulfate solutions were generated with all base metals diluted to 0.01 M and acidified to pH 1 with either nitric acid (70%, AR, Asia Pacific Speciality Chemicals, Australia) or sulfuric acid (98%, AR, Merck, Australia). The aqueous matrix was made up with either 1 M sodium nitrate ($NaNO_3$, LR, Chem Supply, Australia) or 0.33 M sodium sulfate (Na_2SO_4, AR, Mallinckrodt, UK), unless otherwise stated, resulting in the same ionic strength (I) as calculated using (EQ 7):

$$I = 0.5 \times \sum c_i z_i^2 \qquad \text{(EQ 7)}$$

where c = ion concentration (M) and z = ion charge. Ionic strength was calculated assuming full ion dissociation and ignoring differences arising from metal extraction or acid and base addition as required for pH control. Sodium hydroxide solutions were prepared from sodium hydroxide pellets (AR, Chem Supply, Australia) for acid neutralisation.

The following SX reagents common to base metal extraction from sulfate matrices were used: di-2-ethylhexyl phosphoric acid (D2EHPA, 95%, Longlight Ltd., Cyprus), phosphonic acid (2-ethylhexyl)-mono(2-ethylhexyl)ester (HEH(EHP), 95%, Shanghai Rare Earth Chemicals Company, China), *bis*-2,4,4-trimethylpentyl phosphinic acid (Cyanex 272, 85%, Cytec, Australia), *iso*-decanoic acid (Versatic 10, 97%, Shell Chemicals, Singapore), 5,8-diethyl-7-hydroxy-6-dodecanone oxime (LIX 63, 55%, BASF, Australia) and nonyl-4-pyridine carboxylate (nonyl-4PC, 95%, China Central South University, China). Unless stated otherwise, all organic solutions were made up to 0.5 M with ShellSol D70 (TR, Shell Chemicals) in volumetric flasks. ShellSol D70 is a very low aromatic inert hydrocarbon solvent containing approximately 40 wt-% cycloalkanes (naphthenes) and 60 wt-% alkanes (paraffins).

Nonyl-4PC was used as the pyridine carboxylate in place of other pyridine carboxylates for this work as it was readily available and in sufficient volume from the laboratory supplies to complete the expected work. All solvent extraction reagents were used as received and the concentrations stated are based on those given by the manufacturer, except for LIX 63.

The concentration of LIX 63 is reported by the manufacturer to be 70%. In the literature, however, there is a debate over the hydroxyoxime concentration in the as-received product. In previous work, analysis of commercial LIX 63 using gas chromatography with flame ionisation detection (GC-FID) with pure *anti*-hydroxyoxime as a standard isolated by precipitation of the *anti*-isomer, revealed a concentration of 55% (Barnard and Urbani, 2007; Barnard *et al.*, 2010a). A concentration of 55% was also obtained in this work when repeating hydroxyoxime analysis using GC-FID as detailed in Appendix A.

3.2.2 Metal extraction procedure

Extraction pH isotherms were generated from the stock nitrate and sulfate solutions. Organic and aqueous solutions were contacted (A:O of 1:1) in a square stainless steel mixing box (9 × 9 × 14 cm) with an overhead stirrer (65 mm blade diameter, Figure 3-1) at laboratory temperature (23 °C). The speed of the stirrer was adjusted to give a visibly homogenous mixture (1300 rpm or a tip speed of 4.42 m/s). Throughout the work presented in this thesis solvent extraction tests took place in square or hexagonal containers instead of circular beakers. This was done to improve phase contact by promoting turbulence during mixing. Similar containers have been used by previous authors (Cheng, 2000; Barnard and Turner, 2008, 2011b; Zhang *et al.*, 2012).

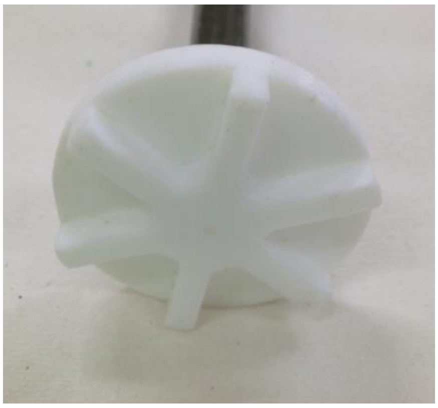


Figure 3-1: Impeller type used for contacting aqueous and organic phases

The pH of the aqueous–organic mixture or emulsion was continuously measured with an intermediate junction pH electrode (Ionode, IJ-44A) connected to a pH meter with a temperature probe and automatic temperature compensation (Hanna, HI 9025). This was in accordance with the method used by various other authors (Barnard and Urbani, 2007; Cheng *et al.*, 2010a; Zhang *et al.*, 2012). The pH probe was calibrated at pH 4 and pH 7 using buffer solutions (Chem Supply, Australia) before each test. The junction electrolyte potassium chloride gel (Ionode) was replaced intermittently when either the pH readings became unstable or, as a precaution, if the junction electrolyte began to visibly discolour.

The pH was increased from a low starting pH using sodium hydroxide (100 g/L for a nitrate matrix or 550 g/L for a sulfate matrix) added dropwise near to the desired pH. To increase low pH values in sulfate solutions, more concentrated sodium hydroxide was required to avoid excessive dilution (>10% v/v) of the aqueous phase. To generate the pH extraction isotherms, samples were taken every 0.5 pH units. The aqueous–organic mixture was allowed to equilibrate at each sample point until the pH was stable to two decimal points for at least one minute. Samples (10-15 mL) of the aqueous–organic mixture were taken with a glass syringe and filtered through Whatman 1PS phase separation paper into hexagonal glass jars.

For an investigation of nickel extraction with LIX 63, nickel (0.07 M) was extracted from a magnesium nitrate (2.5 M) matrix with commercial LIX 63 (0.31 M) in ShellSol D70 at pH 6 using a method similar to that described above, except that a smaller reaction volume was contacted in a hexagonal glass jar at a lower mixing speed with a smaller impeller (40 mm and 800 rpm or tip speed of 1.7 m/s). The methods differed as much lower volumes were used for this investigation where only one sample was required. The organic phase was sampled and the remainder contacted twice with magnesium sulfate (2.5 M) at A:O = 1:1 over 12 h in a hexagonal glass jar held at 23 °C in an incubator–shaker (Thermoline Scientific, TU-454, Australia) mixing at 250 rpm.

3.2.3 Analytical determinations

Aqueous phases were collected with a glass syringe and filtered through an Acrodisc® syringe filter (0.45 μm pore size) before metal determinations. All aqueous samples were analysed for metal content by atomic absorption spectroscopy (AAS) (Agilent Technologies, 200 Series 240FS AA, Australia).

A sample (5 mL) of the separated organic phase was stripped in a clean hexagonal glass jar with nitric acid (3 M) at A:O = 3:1 for 60 min at 60 °C in a heated orbital shaker (Thermoline Scientific, TU-454) at 250 rpm to generate an aqueous sample for analysis. For nonyl-4PC / Versatic 10, 50 g/L sulfuric acid was used instead of 3 M nitric acid to avoid phase separation problems that occurred when trying to use higher acid concentration. The glass jar was capped with a twist top lid, protected by a sheet of polytetrafluoroethylene (PTFE) coated glass fibre (Fiberflon Asia Pacific, Fiberflon 108.08) to prevent contamination from the lid. At the start of the project, the glass jars were put into a water bath at 60 °C and stirred with a magnetic stirrer. This procedure was later changed to allow stripping of more samples simultaneously using the orbital shaker. Stripped organic samples were separated into a clean hexagonal glass jar through phase separation paper.

The metal concentrations of the loaded strip liquor were used to calculate the organic phase metal concentrations assuming 100% stripping. Metal extraction was then calculated as the ratio of the raffinate metal content to the total metal content of raffinate plus loaded strip liquor. The combination of aqueous and organic metal concentrations with the feed solution also allowed calculation of mass balances for quality assurance. Mass balances were considered acceptable if they fell within a range of 80–120%.

Aqueous solutions with multiple metals at 0.01 M concentration were analysed using two different multi-element runs with two sets of standards. These were run under conditions recommended by the manufacturer at the lowest possible dilutions for the specific combinations of metals analysed. Analysis of calcium is complicated by interferences without use of nitrous oxide gas (Agilent Technologies, 2012). As nitrous oxide support was not available, acceptable conditions for analysis were found during this study to be 14.3 L/min of air, 1.5 L/min of acetylene, and 422.7 nm wavelength at a maximum standard concentration of 25 mg/L. In some cases, calcium repeatability was poor (>10% variation) and mass balances deviated outside the range of 80–120%. In these cases, calcium was re-analysed using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Varian 735-ES, Australia) by a Commonwealth Scientific Industrial Research Organisation (CSIRO, Australia) analytical laboratory.

As discussed in Section 2.5.3, UV-Vis spectra of metals depend on the number and strength of ligands around the central metal ion and so can provide an insight into the coordination chemistry of d-block transition metal ions. Organic phase analysis with UV-Vis (Varian, Cary 1-C, Australia) was therefore performed on some samples. Organic samples were analysed in a quartz vial (1 cm path length) scanned at a low scan rate with the background of ShellSol D70 diluent automatically subtracted. The baseline measurement for unloaded organic was manually subtracted from obtained spectra.

3.2.4 Thermodynamic modelling procedure

Thermodynamic speciation models for both sulfate and nitrate matrices, incorporating metal hydroxide precipitation as an analogue to solvent extraction, were generated to gain further insight into the differences between solvent extraction of base metals from nitrate and sulfate matrices. Hydroxide precipitation can be used as an analogue to solvent extraction in this case as it is a reflection of the competition for aqueous phase dissolution of a metal ion compared with removal of that ion by formation of a complex in a different phase, either solid or organic. Low ionic strength (0.1 m) was required for modelling, as higher ionic strengths require incorporation of ion interaction coefficients, which are not easily obtained.

The PHREEQC – pH, redox, equilibrium programme written in the C programming language – thermodynamic modelling package from the United States Geological Survey (USGS) was used to model the precipitation of metal hydroxides from single metal solutions of both sulfate and nitrate matrices. The mintek.v4 database that came with the downloaded package was used for this modelling exercise. PHREEQC was chosen as it is easily customised using a coded input format and can calculate saturation points of minerals in aqueous solution. The mintek.v4 database was chosen as it contains many metal nitrate and metal sulfate species of interest, and is easily modified to add new species not included by default.

The same metals used in the stock aqueous solutions, metals commonly found in a nickel laterite leach solution after neutralisation, were considered for the modelling exercise. Most aqueous metal sulfate and metal nitrate species were present in the database used. Additional equilibrium constants added to the database are given in Table 3-1. No aqueous magnesium nitrate species were present in the database and reliable sources for the formation constants of these species could not be found. A comparison between metal nitrate and metal sulfate speciation would not be possible without considering the formation of any nitrate species and as such the model results for magnesium were ignored.

Table 3-1: log K data added to the mintek.v4 thermodynamic database

Species Formed	logK value	Source
$Ni(NO_3)_2(aq)$	-0.60	(Duro *et al.*, 2006)
$Co(NO_3)_2(aq)$	0.66	(O'Day *et al.*, 1994)
$Ca(NO_3)_2(aq)$	0.65	(Högfeld, 1982)

The model equilibrated an initial solution with 0.001 molal of a single metal ion and either 0.1 molal of sodium nitrate or 0.033 molal sodium sulfate with atmospheric oxygen and carbon dioxide. The oxidation reduction potential (ORP) was calculated from the subsequent dissolved oxygen redox couple (O^0/O^{2-}). Any charge imbalance was satisfied with the anion used, either nitrate or sulfate. The pH was raised by addition of sodium hydroxide (NaOH) to the solution and the model was allowed to equilibrate with the least soluble form of the relevant metal hydroxide at 0.5 pH intervals from 1 to 14. Other solid phases were not allowed to precipitate. Model codes for nickel nitrate and nickel sulfate as examples for the other metals are shown in Appendix B. The remaining metal nitrate and metal sulfate models were adapted from this template by changing the metal and the precipitated hydroxide species as required. Aqueous metal concentrations and speciation were exported to comma separated value (csv) files for further analysis.

3.3 Results and Discussion

Extraction pH isotherms from a variety of matrices, both sulfate and nitrate, were generated for a range of metals commonly found in neutralised laterite leach solutions: calcium, cobalt, copper, magnesium, manganese, nickel and zinc. Comparisons of isotherms between the two matrices allowed experimental determination of the effect of the type and concentration of the anion on solvent extraction of these metals using acidic reagents. Thermodynamic models and UV-Vis analyses of the organic phases were then used to explain the differences uncovered.

3.3.1 Effect of anion (sulfate or nitrate) on cobalt extraction with Cyanex 272

Four exploratory extraction experiments were carried out for the extraction of cobalt with Cyanex 272 from both nitrate and sulfate matrices to determine if the experimental method for generating pH isotherms was sufficiently reproducible. An average pH isotherm for the four experiments from each matrix is shown in Figure 3-2 with associated error bars for the 95% confidence interval of cobalt extraction at each sample point.

The pH_{50} values for cobalt extraction were determined graphically from the individual pH isotherm plots. Results from the calculations of 95% confidence intervals around the mean for cobalt pH_{50} are shown in Table 3-2 for both nitrate and sulfate matrices. Because the two pH_{50} ranges do not overlap, the difference between the sulfate and nitrate isotherms was statistically significant ($p < 0.05$). These results further indicated that the experimental method (Section 3.2.2) was sensitive enough to measure pH_{50} differences between nitrate and sulfate matrices for cobalt extraction by Cyanex 272.

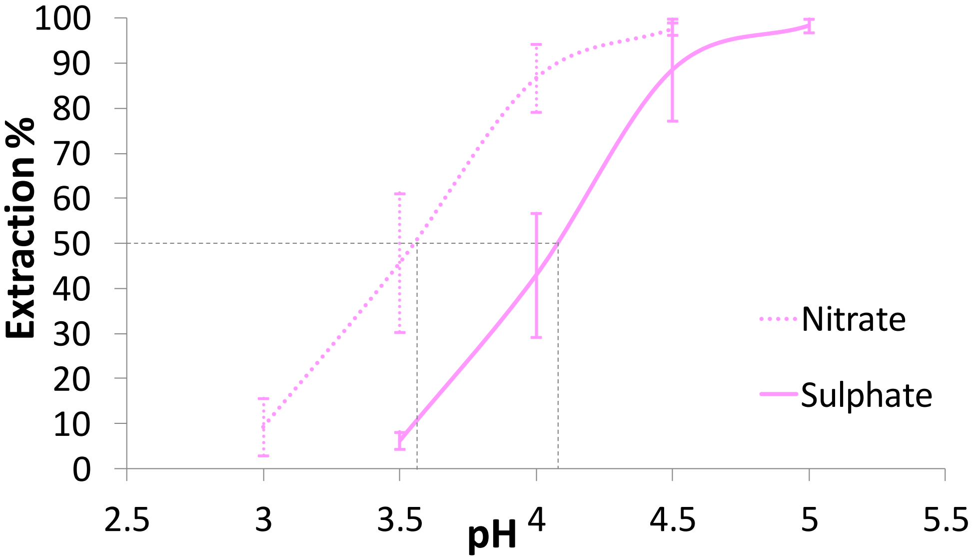


Figure 3-2: Extraction of cobalt with Cyanex 272 from sulfate and nitrate matrices showing error bars for the 95% confidence interval of Extraction % (Co(II) = 0.01 M, Cyanex 272 = 0.5 M, and sodium salt = 1 M)

Table 3-2: Calculations for cobalt extraction pH_{50} 95% confidence intervals from nitrate and sulfate matrices

	-95% CI	Mean	+95% CI	Standard Dev
Nitrate matrix	3.36	3.55	3.74	0.12
Sulfate matrix	3.92	4.08	4.24	0.10

A pH_{50} difference between nitrate and sulfate, $\Delta pH_{50(N\text{-}S)}$, of −0.53 was obtained for cobalt extraction using Cyanex 272. This shift in cobalt(II) extraction between the two matrices, as well as the magnitude of this shift, is consistent with results for different metals and reagents reported by previous authors. In matrices of different ionic strengths but with the same anion concentration, a

$\Delta pH_{50(N-S)}$ of about −0.5 units was observed for chromium extraction by Cyanex 272 (Lanagan and Ibana, 2003) and copper extraction by Cyanex 301 (El-Hefny and Daoud, 2007). With matrices of different anion concentrations but the same ionic strength, $\Delta pH_{50(N-S)}$ values of about −0.5 units were also calculated for all lanthanide metals extracted by Versatic 10 (du Preez and Preston, 1992). In all three referenced studies, this phenomenon was explained by the ability of sulfate anions to form stronger aqueous phase metal complexes than nitrate anions, thus hindering extraction. It is known that nitrate anions are weaker ligands than sulfate (USGS, 2006) so there is less of a drive to form aqueous phase nitrate complexes than sulfate complexes. Higher extraction of cobalt from a nitrate matrix compared with the sulfate matrix at a given pH using Cyanex 272 may therefore also be attributed to the formation of a non-extractable aqueous cobalt sulfate species such as $CoSO_4(aq)$.

Although the shift in extraction determined in the present section was only for cobalt extraction by Cyanex 272 from specific matrices of different ionic strength, data analysis demonstrated that the $\Delta pH_{50(N-S)}$ value was statistically significant. This metric, produced using the same experimental method, was therefore used to analyse the difference in extraction between nitrate and sulfate matrices in subsequent investigations.

3.3.2 Effect of the ionic strength of the sodium sulfate matrix on metal extraction with organophosphorus acids

The $\Delta pH_{50(N-S)}$ difference for cobalt extraction with Cyanex 272 was calculated at a constant anion concentration (1 M) of either nitrate or sulfate. This resulted in different ionic strengths between the nitrate (1 M) and sulfate (3 M) matrices as well as different sodium concentrations (1 M vs. 2 M). Depending on the aqueous metal speciation and the mechanism of metal extraction, increasing the ionic strength of the aqueous phase may increase metal extraction at a given pH via the phenomenon of salting-out (Rydberg *et al.*, 2004). An investigation into the effect of the ionic strength of the sodium sulfate matrix was therefore carried out to determine if this would affect the obtained $\Delta pH_{50(N-S)}$ values.

Multi-metal extraction pH isotherms for three organophosphorus based acids (D2EHPA, HEH(EHP) and Cyanex 272) were generated at two different sodium sulfate concentrations to produce either the same ionic strength as the nitrate matrix (0.33 M sodium sulfate) or the same sodium concentration as the nitrate matrix (0.5 M sodium sulfate). A comparison with the cobalt only Cyanex 272 isotherm from 1 M sodium sulfate in Section 3.3.1 could not be made due to the extractions of other metals in the mixed metal matrix. This competition alters the availability of the free reagent in the organic phase, impacting the individual metal extraction equilibria. Hence, a further comparison for extractions of mixed metals from a 1 M sodium sulfate matrix using Cyanex 272 was also carried out.

The effect of changing the sodium sulfate concentration on metal extractions with D2EHPA, HEH(EHP) and Cyanex 272 is shown in Table 3-3. The well-known increase in pH_{50}(Ni-Co), and the increase in metal extraction pH in general, on moving from D2EHPA, to HEH(EHP), to Cyanex 272 (Flett, 2005) was found in the current investigation. The relatively small change in ionic strength of the sulfate matrix had negligible effect, within experimental error, on the metal pH_{50} values obtained with these organophosphorus acids. The results in Section 3.3.1 were therefore due to differences in the matrix type (nitrate or sulfate) rather than the aqueous phase ionic strength (1 M or 3 M). To maintain consistency between results, and to be consistent with other authors (du Preez and Preston, 1992; Preston and du Preez, 2000), all subsequent investigations into the difference between sulfate and nitrate matrices were done at a single ionic strength of 1 M.

Table 3-3: Comparison of pH_{50} values of mixed metals extracted with organophosphorus acids from various sodium sulfate matrices

	D2EHPA		**HEH(EHP)**		**Cyanex 272**		
	0.33 M	**0.5 M**	**0.33 M**	**0.5 M**	**0.33 M**	**0.5 M**	**1 M**
Co	3.7	3.8	4.0	4.1	4.4	4.4	4.6
Cu	2.8	2.8	3.3	3.3	3.8	3.9	4.0
Ni	4.2	4.3	5.2	5.3	6.3	>6	>6
Zn	1.4	1.4	1.6	<2	2.2	2.2	2.3
Ca	1.8	1.7	3.1	3.2	5.2	5.2	5.3
Mg	3.3	3.3	4.4	4.5	5.3	5.3	5.3
Mn	2.3	2.3	3.2	3.2	4.1	4.1	4.2

Values out of the tested pH range are indicated by '<' or '>'.

3.3.3 Systematic investigation into metal extraction from sodium sulfate and sodium nitrate matrices at constant ionic strength

Metal extraction pH_{50} values determined from constructed pH isotherm plots are shown for a sulfate matrix in Table 3-4 and a nitrate matrix in Table 3-5. The extraction order of metals between sulfate (Table 3-4) and nitrate (Table 3-5) matrices in the present investigation was the same for D2EHPA, Cyanex 272, Versatic 10, LIX 63 / Versatic 10 and nonyl-4PC / Versatic 10. For HEH(EHP), the order of metal extraction was only altered slightly due to a slight preference for calcium extraction (pH_{50}(Cu-Ca) of 0.2 units) in the sulfate matrix compared with the nitrate matrix (pH_{50}(Cu-Ca) of −0.1). For LIX 63 only, nickel was extracted before cobalt in the nitrate system due to a particularly large $\Delta pH_{50(N\text{-}S)}$ difference not found for other metals or reagents.

Table 3-4: pH_{50} values for metal extraction with various acidic reagents from a sulfate matrix

	D2EHPA	HEH(EHP)	Cyanex 272	Versatic 10	LIX 63	LIX 63 / Versatic 10	nonyl-4PC / Versatic 10
Co	3.7	4.0	4.4	6.8	5.3	3.2	5.6
Cu	2.8	3.3	3.8	4.4	<3	<3	<3.5
Ni	4.2	5.2	6.3	6.6	5.4	4.3	5.0
Zn	1.4	1.6	2.2	6.1	6.3	3.9	5.4
Ca	1.8	3.1	5.2	7.1	>8	6.7	6.7
Mg	3.3	4.4	5.3	8.5	>8	8.1	8.2
Mn	2.3	3.2	4.1	7.0	8.1	5.4	6.5

Values outside the tested pH range are indicated by '<' or '>'

Table 3-5: pH_{50} values for metal extraction with various acidic reagents from a nitrate matrix

	D2EHPA	HEH(EHP)	Cyanex 272	Versatic 10	LIX 63	LIX 63 / Versatic 10	nonyl-4PC / Versatic 10
Co	3.1	3.5	3.9	6.3	5.0	2.7	5.2
Cu	2.2	2.7	3.4	<4	<3	<2	2.9
Ni	3.5	4.7	5.8	6.1	4.3	3.2	4.4
Zn	<1	<2	1.7	5.6	5.9	3.5	4.8
Ca	1.3	2.8	4.6	6.6	>8	6.4	6.2
Mg	2.7	3.9	4.9	7.9	>8	>7	7.9
Mn	1.7	2.6	3.6	6.4	7.8	4.9	6.1

Values outside the tested pH range are indicated by '<' or '>'

Differences in the experimental conditions of previously published work (temperature, metal concentration, reagent concentration, diluent and A:O ratio) make it difficult to directly compare the pH_{50} values generated from a sulfate matrix (Table 3-4) with those reported in the literature. Despite these differences, however, the order of metal extraction obtained here compares well with that obtained from the wider literature. The order of metal extraction for Cyanex 272 (Cytec, 2008), Versatic 10 (Cheng, 2006) and decyl-4PC (an analogue of nonyl-4PC) / Versatic 10 (Cheng *et al.*, 2010a) is exactly the same between Table 3-4 and the referenced studies.

In earlier work on metal extraction with D2EHPA (Cheng, 2000), magnesium extracted after nickel, probably because a much higher molarity of magnesium compared with the other tested metals was used (0.125 M compared to 0.043–0.075 M otherwise). For HEH(EHP), calcium was extracted after copper by Dreisinger and Cooper (1984), although as noted earlier, the small pH_{50} differences (less than 0.3 units) suggests this is within experimental error. For the LIX 63 and LIX 63/Versatic 10 isotherms, nickel is extracted preferentially in the literature. This can be attributed to higher nickel concentrations in the referenced work, where synthetic nickel laterite leach liquors were used. As the order of extraction was generally the same between Table 3-4 and Table 3-5, the order of extraction from a nitrate matrix also generally compares well with the literature studies on sulfate-based matrices.

The $\Delta pH_{50(N\text{-}S)}$ for each metal extracted with each reagent is given in Table 3-6. Under these comparable operating conditions, a clear and consistent $\Delta pH_{50(N\text{-}S)}$ difference was calculated, with lower pH_{50} values for extraction of base metals from a nitrate matrix (Table 3-6). This difference was greater for nickel extraction with either LIX 63 / Versatic 10 or LIX 63 as a single reagent (mean of −1.00 unit) when compared with any of the other $\Delta pH_{50(N\text{-}S)}$ values obtained in Table 3-6 (mean of −0.49 units). Statistical analysis of these two mean values was carried out using a two-sample *T*-test assuming equal variances. The assumption of equal variance is valid as the method was identical for both sets of variables. The *T*-test resulted in a *t* value of 5.0, greater than the critical *T* value of 2.0 for a 2-tailed *T*-test with 38 degrees of freedom. The two means are therefore statistically different ($p < 0.05$). There is a greater decrease in the

pH_{50}(Ni) on moving from a sulfate to a nitrate matrix using solvent systems containing LIX 63 compared with the other reagents and metals tested.

Table 3-6: $pH_{50(N-S)}$ for extraction of metals by various acidic reagents

	D2EHPA	HEH(EHP)	Cyanex 272	Versatic 10	LIX 63	LIX 63 / Versatic 10	nonyl-4PC / Versatic 10
Co	−0.6	−0.5	−0.5	−0.5	−0.3	−0.5	−0.4
Cu	−0.6	−0.6	−0.4	-	-	-	-
Ni	−0.7	−0.5	−0.5	−0.5	−1.1	−0.9	−0.6
Zn	-	-	−0.5	−0.5	−0.4	−0.4	−0.6
Ca	−0.5	−0.3	−0.6	−0.5	-	−0.3	−0.5
Mg	−0.6	−0.5	−0.4	−0.6	-	-	−0.3
Mn	−0.6	−0.6	−0.5	−0.6	−0.3	−0.5	−0.4

Results where at least one pH_{50} value was outside the pH range investigated are left blank

The lower pH_{50} from nitrate compared with sulfate matrices, and the magnitude of this difference, are consistent with the results from referenced studies for single cations extracted by specific reagents discussed in Section 3.3.1 (du Preez and Preston, 1992; Preston and du Preez, 2000; Lanagan and Ibana, 2003; El-Hefny and Daoud, 2007). Given that the ionic strength of the sulfate aqueous matrix had no effect on metal extraction pH (Table 3-3), the $\Delta pH_{50(N-S)}$ values in Table 3-6 can be attributed to the anion, rather than a different anion concentration. In general, a pH_{50} shift of approximately −0.5 units can therefore be expected for divalent base metals extracted with acidic reagents on changing from a moderate ionic strength sulfate matrix to a comparable nitrate matrix. An exception was nickel extraction with solvent systems containing LIX 63, where a $\Delta pH_{50(N-S)}$ of −1.0 units can be expected. Literature studies for solvent extraction from a sulfate-based matrix can be used as a guide to inform process development after taking into account lower extraction pH from a nitrate matrix.

3.3.4 Thermodynamic modelling of metal hydroxide precipitation from nitrate and sulfate matrices as an analogue to solvent extraction

In Section 3.3.1, it was proposed that the lower ligand strength of the nitrate compared with the sulfate anion decreased cobalt pH_{50} values when moving to the nitrate matrix. The same rationale can be applied to all the experimentally determined $\Delta pH_{50(N-S)}$ values presented in Section 3.3.3 and Table 3-6. A thermodynamic model was therefore constructed to assess the effect of metal speciation on metal hydroxide precipitation as an analogue to solvent extraction. The results of this modelling are presented both as metal speciation in Table 3-7 and as metal hydroxide solubility in Figure 3-3. No reliable log *K* values for magnesium nitrate species could be found in the literature and as such no magnesium nitrate species could be calculated using the modified database. Magnesium was therefore not included in this comparison. Calcium did not precipitate below 0.001 M in the model and so is not shown in Figure 3-3.

Table 3-7: Mole-percent speciation of the remaining dissolved metal as free (hydrated) metal ions after allowing for precipitation as the most soluble hydroxide at pH 7

	Ca^{2+}	Co^{2+}	Cu^{2+}	Mn^{2+}	Ni^{2+}	Zn^{2+}
Nitrate	75%	94%	60%	94%	80%	80%
Sulfate	32%	75%	28%	77%	34%	7%

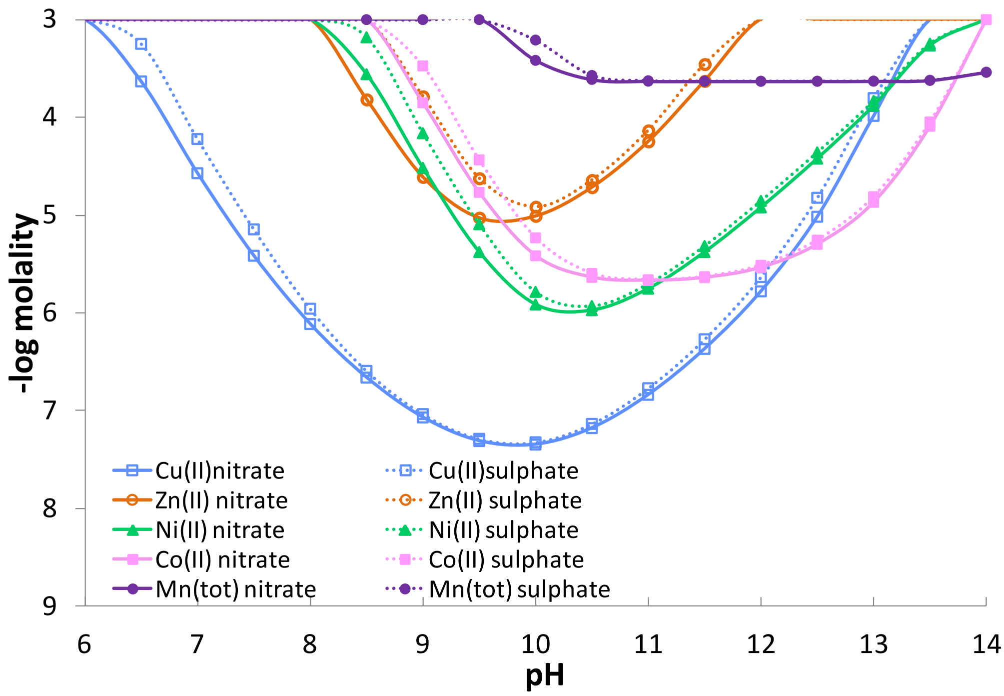


Figure 3-3: Predicted activity of metal ions at a given pH after precipitating as single metal hydroxides from either a low ionic strength sulfate (dotted line) or nitrate (solid line) matrix

Metal ions in a nitrate matrix were more likely to precipitate as hydroxides at lower pH (Figure 3-3). In addition, a greater percentage of metal ions were present as free cations (fully hydrated without a bonded anion) in the nitrate matrix compared with the sulfate matrix (Table 3-7). Higher proportions of metal present as sulfate species in the aqueous phase revealed stronger binding of sulfate anions to the metal than nitrate. Hence, metal equilibrium in the sulfate matrix will shift more towards the aqueous phase. For zinc, where there was the biggest difference of free cation concentration between sulfate (7%) and nitrate (80%), there was also the biggest difference in hydroxide solubility at a given pH. Extrapolation from the modelling results suggests that metal solvent extraction from a nitrate matrix will therefore occur at a lower pH_{50} than from a sulfate matrix due to the difference in aqueous speciation. Although this reasoning has been suggested for specific situations by previous authors, as discussed in Section 3.3.1 (du Preez and Preston, 1992; Lanagan and Ibana, 2003; El-Hefny and Daoud, 2007), a general trend linked with detailed speciation modelling has not previously been presented.

The results obtained here were considered with the following model limitations in mind: the ionic strength differs between the modelled and real solutions, the equilibrium constants for metal speciation in the mintek.v4 database may not represent all possible species formed, and hydroxide precipitation is not a perfect analogy for solvent extraction. Even so, because the model was only used to identify trends, it suggested a general tendency for removal of metal ions from an aqueous nitrate matrix at a lower pH than an aqueous sulfate matrix. It also indicated a preference for fully hydrated metal ions in a nitrate matrix. This helped to explain the trend of results from solvent extraction presented in Table 3-6 where extraction of metals from a nitrate matrix occurs at a lower pH than a sulfate matrix. The significant difference in nickel extraction with solvent systems containing LIX 63 between the two matrices, however, was not fully explained on the basis of these results.

3.3.5 UV-Vis study on nickel extracted by LIX 63 from a nitrate matrix

The thermodynamic model failed to explain the significant variation in $\Delta pH_{50(N\text{-}S)}$ for nickel extracted with LIX 63 compared with extraction of any other base metal using any other reagent. In order to investigate this discrepancy further, the organic phase nickel complex formed on extraction of nickel with LIX 63 was analysed using UV-Vis. As discussed in Section 2.6.1, synergistic extraction of nickel using mixtures of LIX 63 and organic acids such as Versatic 10 results from formation of octahedral mixed reagent complexes (Barnard *et al.*, 2010b). The UV-Vis spectrum for such a nickel complex, with a major peak at 600 nm, is shown in Figure 3-4. Nickel extracted by LIX 63 (hydroxyoxime) as a single reagent from a sulfate-based matrix at low acidity forms a square planar, orange, Ni(LIX 63)$_2$ complex (Keeney and Osseo-Asare, 1984a). This Ni(LIX 63)$_2$ complex has a UV-Vis spectrum with a major peak at 440 nm (Figure 3-4).

At high sulfuric acid concentrations, nickel extracted with LIX 63 (HL) can form an insoluble octahedral [Ni(HL)$_3$]SO$_4$ salt, which readily precipitates (Barnard *et al.*, 2014). 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.* (2014), indicating that this complex can also exist. It was further found by Barnard *et al.* (2014) that a stable nickel salt with a nickel:chloride ratio of 1:2 is extracted from 1.65 M acid chloride solutions into an organic phase. 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 3-4), suggesting that the nickel chloride complex is also octahedral. The possible structures to retain octahedral nickel geometry with protonated hydroxyoxime ligands and a nickel:chloride ratio of 1:2 are either [Ni(HL)$_3$]Cl$_2$ or Ni(HL)$_2$Cl$_2$.

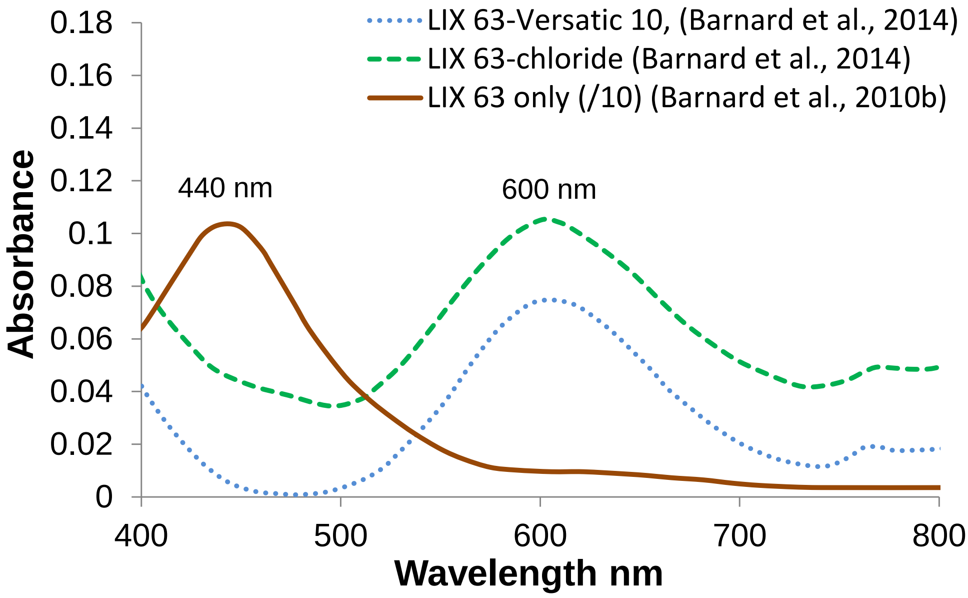


Figure 3-4: UV-Vis spectra for different nickel-LIX 63 complexes. Adapted from Barnard *et al.* (2014) and Barnard *et al.* (2010b). Baseline of unloaded organic was manually subtracted in cited papers

The UV-Vis spectrum of the nickel complex extracted from the concentrated nitrate matrix using LIX 63 had a major peak at 613 nm (Figure 3-5) 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 decreased the peak at 613 nm and produced a new peak at 430 nm, resembling that of the Ni(LIX 63)$_2$ square planar complex in Figure 3-4. Two different coordination environments (octahedral and square planar) therefore existed for nickel between the nitrate extract organic and the sulfate contacted organic.

The obtained UV-Vis spectra indicated that the sulfate matrix washed nitrate out of the organic phase, without the incorporation of sulfate anions into an organic phase nickel complex or salt. This was supported by a lack of precipitation of the [Ni(LIX 63)$_3$]SO_4 salt during this wash stage. The small residual peak around 600 nm after the sulfate wash in Figure 3-5 indicated that some residual nitrate remained in the organic phase after a new equilibrium had been established with the sulfate aqueous wash solution.

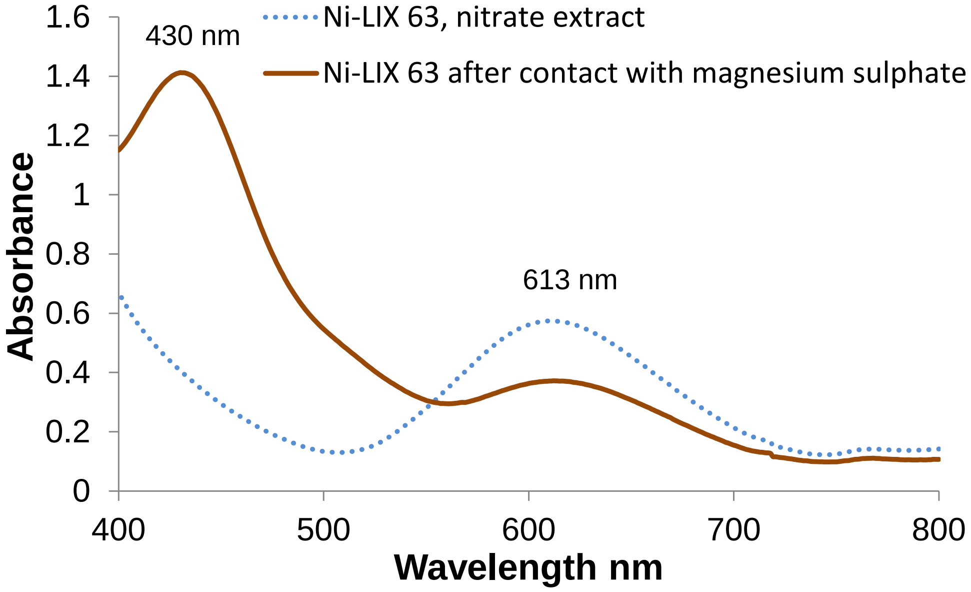


Figure 3-5: Change in UV-Vis spectrum of Ni-LIX 63 extracted from a nitrate matrix after washing with a concentrated sulfate solution ([Ni(II)] = 0.017 M, [LIX 63] = 0.31 M, magnesium salt concentrations = 2.5 M)

Nitrate anions in the aqueous phase can, therefore, potentially be co-extracted into organic systems containing LIX 63 at moderate pH to stabilise an octahedral nickel complex (either with or without Versatic 10) by forming an organic salt. This effect would be particularly promoted for nickel, which has a high octahedral ligand field stabilisation energy (Cotton and Wilkinson, 1980) and hence a preference for octahedral geometry. This phenomenon would then result in a larger $\Delta pH_{50(N-S)}$ difference (−1.0 units) for nickel in particular when compared with the common $\Delta pH_{50(N-S)}$ difference (−0.5 units) obtained in Section 3.3.3.

3.4 Conclusions

The aim of this chapter was to determine if the results from the literature survey of solvent extraction options for metal extraction from sulfate-based leach liquors can be a useful guide for nitrate-based leach liquors. Specifically, it was found that:

- As the 95% confidence intervals for the pH_{50}(Co) from a sulfate and nitrate matrix did not overlap, the pH isotherm method used was accurate enough to provide statistically significant results for an investigation into the difference in pH_{50} values between sulfate and nitrate matrices. Using this method, a pH_{50} difference ($\Delta pH_{50(N-S)}$) of −0.5 units was determined for cobalt extracted with Cyanex 272.

- A change in the ionic strength of the sodium sulfate matrix between 0.33 M and 1 M sodium sulfate did not affect metal extraction pH_{50} values. The identity of the anion, rather than the ionic strength, was therefore the reason behind any extraction pH differences noted between sulfate and nitrate matrices.

- Extraction of metals with acidic reagents, except for nickel extraction with LIX 63, resulted in a clear and consistent decrease in the pH_{50} of about 0.5 units on moving from a sulfate to a nitrate matrix ($\Delta pH_{50(N-S)}$ between −0.3 and −0.7 units). Despite this difference in metal extraction pH between nitrate and sulfate matrices, the order of metal extraction was mostly consistent between the 1 M sodium nitrate matrix and that reported in the literature for sulfate-based laterite leach liquors. It can therefore be concluded that the results of a literature review in a sulfate matrix can be used as a generally reliable guide for extraction of base metals with acidic reagents from a nitrate matrix.

- Thermodynamic modelling predicted both that metal hydroxide precipitation from a nitrate matrix should occur at a lower pH than a sulfate matrix, and that metals in a nitrate matrix were more likely to be present as fully hydrated cations. This suggested that metals are not removed as readily from a sulfate matrix via hydroxide precipitation due to the formation of stable aqueous metal-sulfate species. By analogy to solvent extraction, this confirmed the observations of the pH extraction isotherms and offered an explanation for the trend of metal extraction isotherms shifting to lower pH values in a nitrate matrix.

- The difference in the $\Delta pH_{50(N-S)}$ for nickel extracted with solvent systems containing LIX 63 was significantly higher than the values for extraction of metals in general using acidic reagents. This could not be fully explained by the thermodynamic model. UV-Vis analysis of organic phase nickel complexes suggested that nickel extracted with LIX 63 in the presence of high nitrate concentrations adopted octahedral geometry, which would be thermodynamically more stable than the alternative square planar geometry adopted when extracted from a sulfate system.

CHAPTER 4
Comparison of different solvent systems for nickel and cobalt separation from magnesium in a nitrate matrix

4.1 Introduction

The results of Chapter 3 demonstrated that studies of SX from a sulfate matrix can be used as a guide for extraction from a nitrate matrix after taking into account a shift in extraction to lower pH values. The following SX systems were identified in the literature review as promising options for the separation of nickel and cobalt from magnesium: (1) Versatic 10 as a single reagent, (2) phenolic oximes with organic acids, (3) LIX 63 with Versatic 10 and a nickel accelerator and (4) pyridine carboxylates with Versatic 10. In Section 3.3.3 extraction pH isotherms from a mixed metal nitrate matrix were generated for LIX 63 / Versatic 10, nonyl-4PC / Versatic 10 and Versatic 10 alone. These isotherms can be used alongside information from the literature for sulfate matrices to determine their applicability to a nitrate-based nickel laterite PLS. There is, however, no information available on the extraction of metals using mixtures of phenolic oximes and organic acids, although organic acids may be required in the organic phase both to increase the kinetics of nickel extraction and to mitigate cobalt poisoning of phenolic oximes.

The aim of this chapter was to select promising solvent systems for nickel and cobalt separation from magnesium at low pH by using the literature review as a guide and by determining the metal extraction characteristics of any novel reagent mixtures identified. Extraction pH isotherms were initially generated to address the gap in the literature regarding the extraction of metals using mixtures of phenolic oximes (LIX 860 and LIX 84) and organic acids (D2EHPA, HEH(EHP), Cyanex 272 and Versatic 10). Promising reagent mixtures for the separation of nickel and cobalt from magnesium at low pH identified from this research were then compared with the promising solvent systems identified from the pH isotherms in Section 3.3.3 (Versatic 10, LIX 63 / Versatic 10 and nonyl-4PC / Versatic 10).

4.2 Materials and Methods

4.2.1 *Aqueous and organic solutions*

The same stock nitrate matrix used in Chapter 3 containing metals of interest in a nickel laterite leach liquor (calcium, cobalt, copper, magnesium, manganese, nickel and zinc) was used for the investigation in this chapter. As the same stock solution was used to generate pH isotherms, a direct comparison of the extraction pH isotherms generated here could be made with those generated in Chapter 3.

A phenolic aldoxime, 5-nonylsalicyl aldoxime (LIX 860-NIC, 82.6%, BASF), and a phenolic ketoxime 2-hydroxy-5-nonyl-acetophenone oxime (LIX 84-I, 44%, BASF) were used in the current study. These phenolic oximes were mixed with the same organic acids used in Chapter 3 (D2EHPA, HEH(EHP), Cyanex 272 and Versatic 10). Unless stated otherwise, all organic solutions were made up to 0.5 M with ShellSol D70. All SX reagents were used as received and the concentrations stated are those given by the manufacturer, except for LIX 84. The concentration of LIX 84 was not provided by the manufacturer. The phenolic oxime concentration in as-supplied LIX 84 was previously reported by Narita *et al.* (2006) to be 44%. This was confirmed from a measurement made previously by CSIRO research staff of the LIX 84 sample provided using gas chromatography with flame ionisation detection (GC-FID).

4.2.2 *Determination of synergism and metal separation and comparing generated isotherms*

Extraction pH isotherms were generated using the same extraction method detailed in Section 3.2.2. The standard deviations for pH_{50} values in Section 3.3.1 were 0.10 units for nitrate and 0.12 units for sulfate. Values for pH_{50} readings should fall within ±2.58 standard deviations (0.26 to 0.31 units) of the true mean 99% of the time. Hence, 0.3 pH units, as the nearest decimal place, is a useful guide for the sensitivity of the extraction pH isotherm method used. A ΔpH_{50} difference was therefore only considered to indicate synergism or antagonism in this study if it was greater than 0.3 units. Metal separation was quantified from the pH isotherms using the pH_{50} difference between metal A and metal B, pH_{50}(A-B).

A limitation of this approach is that synergism was assessed via extraction from a mixed metal aqueous matrix and not from an aqueous phase containing a single metal. Metal extraction into the organic phase changes the availability of free reagents in the synergistic system. The free reagent concentrations therefore changed over the course of the pH isotherm depending on the degree of extraction for the individual metals. This may have affected the equilibrium distribution of metals at higher pH values. The goal of this study, however, was to determine the potential for separation of nickel and cobalt from impurities, particularly magnesium. Mixed metal pH isotherms are more useful for this particular aim.

The generated pH isotherms using this method were compared with those generated in Section 3.3.3 using the method in Section 3.2.2. The solvent systems with the most promise for separating nickel and cobalt from magnesium in a nitrate matrix were collated and the pH isotherms discussed from the viewpoint of improving metal separations and decreasing operational pH.

4.2.3 Analytical determinations

Aqueous phase metal concentrations were all analysed using the same method as detailed in Section 3.2.3. Organic samples were initially stripped using the method in Section 3.2.3 to generate an aqueous phase for analysis. The mass balances for cobalt were occasionally below 80% in this study, indicating cobalt poisoning. In these cases, cobalt extraction was calculated from the raffinate concentration and the feed concentration, and not the raffinate and loaded strip liquor concentrations.

4.3 Results and Discussion

A systematic approach to generating pH isotherms was used to investigate the effect of mixing a phenolic oxime with each different organic acid (D2EHPA, HEH(EHP), Cyanex 272 and Versatic 10 – Table 4-1) on the extraction of metals from a mixed-metal nitrate matrix. Synergistic or antagonistic metal extraction, as well as indicative metal separation, could then be calculated from the generated pH isotherms. The results obtained were compared with pH isotherms generated under the same conditions in Chapter 3 to identify the most promising solvent systems for the separation of nickel and cobalt from magnesium at low pH.

Table 4-1: pKa values for different organic acids used in the investigation

Organic Acid	pKa	Reference
D2EHPA (phosphoric)	3.01	(Zhang *et al.*, 1994)
HEH(EHP) (phosphonic)	4.21	(Zhang *et al.*, 1994)
Cyanex272 (phosphinic)	5.22	(Zhang *et al.*, 1994)
Versatic10 (carboxylic)	7.33	(Preston, 1994)

4.3.1 Effect of mixing organic acids with LIX 860 on metal extraction

When extracting metals with organic acids as single reagents, a decrease in organic acid strength (increasing pKa in Table 4-1) resulted in increased extraction pH_{50} values for all metals (Table 4-2). For mixtures of LIX 860 with organic acids, the decreasing acid strength also resulted in increasing metal pH_{50} values. This migration to higher pH_{50} values for mixtures of LIX 860 with weaker organic acids was less dramatic for nickel, cobalt and manganese than for calcium and magnesium.

Table 4-2: pH_{50} values for the extractions of metal nitrates with LIX 860 alone, organic acids alone (D2EHPA, HEH(EHP), Cyanex 272, Versatic 10), and their mixtures (in ShellSol D70, metal concentrations = 0.01 M, organic reagent concentrations = 0.5 M)

Reagents	Co	Cu	Ni	Zn	Ca	Mg	Mn
LIX 860	3.5	<2	3.2	5.1	>6.5	>6.5	>6.5
D2EHPA	3.1	2.2	3.5	(0.8)	1.3	2.7	1.7
HEH(EHP)	3.5	2.7	4.7	<2	2.8	3.9	2.6
Cyanex 272	3.8	3.6	5.8	1.7	4.6	4.8	3.5
Versatic 10	6.3	(3.8)	6.1	5.6	6.6	7.9	6.4
LIX 860 / D2EHPA	1.7	<1	1.4	1.1	1.7	2.4	1.5
LIX 860 / HEH(EHP)	2.7	<1	2.4	1.3	2.8	3.8	2.6
LIX 860 / Cyanex 272	3.5	<1	3.1	1.8	4.3	4.9	3.6
LIX 860 / Versatic 10	3.8	<2.5	3.7	4.8	>6	>6	5.9

Values outside the tested pH range are indicated by '<' or '>'. Extrapolated values are in brackets.

LIX 860 / Versatic10 resulted in the highest separation of nickel and cobalt from impurities; calcium and magnesium extractions were negligible over the tested pH range. LIX 860 / Cyanex 272 produced the next highest separations (pH_{50}(Mg-Ni) of 1.8 and pH_{50}(Mg-Co) of 1.4). LIX 860 / D2EHPA produced the poorest metal separations with pH_{50}(Mg-Ni) of 1.0 and pH_{50}(Mg-Co) of 0.7. These achievable metal separations indicated that significant co-extraction of magnesium may occur when using this mixed reagent system. More complete separations of nickel and cobalt from calcium and magnesium were therefore predicted for weaker acids mixed with LIX 860.

Synergism between LIX 860 and organic acids calculated from the pH$_{50}$ values in Table 4-2 decreased with decreasing organic acid strength (Table 4-3). Synergism occurred for extractions of nickel and cobalt using LIX 860 / D2EHPA (ΔpH$_{50}$(Ni) of 1.8 and ΔpH$_{50}$(Co) of 1.4) and LIX 860 / HEH(EHP) (ΔpH$_{50}$(Ni) of 0.8 and ΔpH$_{50}$(Co) of 0.8). In contrast, the mixture of LIX 860 / Cyanex 272 was not synergistic. Nickel, cobalt and copper were extracted at the pH$_{50}$ for LIX 860 alone while zinc, calcium, magnesium and manganese were extracted at the pH$_{50}$ for Cyanex 272 alone. LIX 860 / Versatic 10 was also not synergistic for cobalt, and appeared to be antagonistic for nickel (ΔpH$_{50}$(Ni) of −0.5). Although slight synergism was inferred for manganese extraction by LIX 860 / Versatic 10 (ΔpH$_{50}$(Mn) of 0.5), no synergism was found for manganese when extracted by combinations of LIX 860 with the stronger phosphorus-based acids.

Table 4-3: ΔpH50 values for extraction of base metals with mixtures of LIX 860 with organic acids

Reagents	Co	Cu	Ni	Zn	Ca	Mg	Mn
LIX 860 / D2EHPA	1.4	-	1.8	−0.3	−0.4	0.3	0.2
LIX 860 / HEH(EHP)	0.8	-	0.8	-	0.0	0.1	0.0
LIX 860 / Cyanex 272	0.0	-	0.1	−0.1	0.3	−0.1	−0.1
LIX 860 / Versatic 10	−0.3	-	−0.5	0.3	-	-	0.5

Values outside the tested pH range are left blank

Synergism between LIX 860 and D2EHPA for nickel and cobalt has also been reported from sulfate matrices. A ΔpH$_{50}$(Ni) of 1.5 and ΔpH$_{50}$(Co) of 0.9 was found by Zhang *et al.* (2001) when extracting nickel (0.026 M) into kerosene containing 20% v/v (~0.6 M) of LIX 860 (dodecyl analogue) / 20% v/v (~0.6 M) D2EHPA. Alguacil (2002) later repeated this work using the dearomatised diluent Exxon D100 and obtained similar ΔpH$_{50}$ values. A much smaller ΔpH$_{50}$ of 0.3 pH units was suggested for nickel extraction when a very low concentration of nickel (0.0005 M) was extracted into toluene containing 0.1 M of each reagent (Andrade and Elizalde, 2005). Although a ΔpH$_{50}$ of only 0.3 pH units would not be considered large enough to indicate synergism in this study, Andrade and Elizalde (2005) used a different experimental method and so it is possible they experienced lower variance in their results. The ΔpH$_{50}$ values noted from these previous studies are consistently smaller than those reported from the present study in Table 4-3. This is potentially due to the higher reagent concentration used in the current work. The ΔpH$_{50}$ values here were also increased by the nitrate matrix, as discussed for nickel extraction with LIX 63 in Section 3.3.5. Synergism between phenolic aldoximes and HEH(EHP) reported in the present work has not been previously reported.

4.3.2 Effect of mixing organic acids with LIX 84 on metal extraction

Extraction pH isotherms for the combination of LIX 84 (phenolic ketoxime) with organic acids were undertaken for comparison with LIX 860 (phenolic aldoxime) mixtures. The same trends as for LIX 860 mixed with organic acids were also obtained for mixtures of LIX 84 with organic acids. As LIX 84 has lower affinity for metals than LIX 860 (Watarai, 2001), LIX 84 alone and LIX 84 mixed with organic acids generally resulted in higher extraction pH$_{50}$ values for nickel and cobalt (Table 4-4) than those for LIX 860. One exception to this was nickel extracted by LIX 84 / Versatic 10, which occurred at a lower pH$_{50}$ value than LIX 860 / Versatic 10. The pH$_{50}$ for extraction of both nickel and cobalt, however, was still lower for LIX 860 / Versatic 10 (3.8) than for LIX 84 / Versatic 10 (4.2).

Table 4-4: pH$_{50}$ values for extraction of metal nitrates using LIX 84 alone, organic acids alone, and their mixtures in ShellSol D70 (metal concentrations = 0.01 M, organic reagent concentrations = 0.5 M)

Reagents	Co	Cu	Ni	Zn	Ca	Mg	Mn
LIX 84	4.0	<2	3.3	6	>6	>6	>6
D2EHPA	3.1	2.2	3.5	<1	1.3	2.7	1.7
HEH(EHP)	3.5	2.7	4.7	<2	2.8	3.9	2.6
Cyanex 272	3.8	3.6	5.8	1.7	4.6	4.8	3.5
Versatic 10	6.3	<4	6.1	5.6	6.6	7.9	6.4
LIX 84 / D2EHPA	2.4	<1	2.0	1.2	1.7	2.6	1.9
LIX 84 / HEH(EHP)	3.1	<1	2.8	1.4	2.9	3.7	2.7
LIX 84 / Cyanex 272	3.9	<1	3.5	1.8	4.3	4.9	3.7
LIX 84 / Versatic 10	4.2	<1	3.2	>5	>5	>5	>5

Values outside the tested pH range are indicated by '<' and '>'

Separations of nickel and cobalt from other metals in the stock solution improved with increasing organic acid pKa, in agreement with the results using LIX 860. The generally higher extraction pH values for nickel and cobalt when organic acids were mixed with LIX 84 compared with LIX 860, however, resulted in lower pH$_{50}$ differences between these target metals and either calcium or magnesium. This indicated that it would be more difficult to effect separations of nickel and cobalt from impurities using LIX 84 mixed with organic acids than for LIX 860 mixed with organic acids.

As with LIX 860, the greatest synergism (Table 4-5) was obtained with LIX 84 / D2EHPA (ΔpH_{50}(Ni) of 1.3 and ΔpH_{50}(Co) of 0.7) and HEH(EHP) (ΔpH_{50}(Ni) of 0.5, ΔpH_{50}(Co) of 0.4). There was no noticeable synergism with Versatic 10 or Cyanex 272. The slight antagonism indicated for nickel extraction with LIX 860 / Versatic 10 did not occur for LIX 84 / Versatic 10, explaining the lower extraction pH_{50} for nickel for LIX 84 / Versatic 10.

Table 4-5: ΔpH50 values for extraction of base metals with mixtures of LIX 84 with organic acids

Reagent Mixture	Co	Cu	Ni	Zn	Ca	Mg	Mn
LIX 84 / D2EHPA	1.6	-	1.3	-	−0.4	0.1	−0.2
LIX 84 / HEH(EHP)	0.9	-	0.5	-	−0.1	0.2	−0.1
LIX 84 / Cyanex 272	0.1	-	−0.2	−0.1	−0.3	−0.1	−0.2
LIX 84 / Versatic 10	−0.2	-	0.1	-	-	-	-

Values outside the tested pH range are left blank

Earlier research by Ndlovu and Mahlangu (2008) conducted in a sulfate matrix reported synergism between LIX 84 and Versatic 10 where a ΔpH_{50}(Ni) of 1.5 units can be calculated from the reported data. This contrasted with the result of the current investigation in a nitrate matrix that LIX 84 / Versatic 10 was not synergistic for nickel extraction. In the present work, the trend of decreasing synergism with decreasing acid strength was clear. Given that Versatic 10 was the weakest acid investigated, this trend is consistent with a conclusion that LIX 84 / Versatic 10 is not synergistic for nickel extraction from a nitrate matrix. Generation of nickel-only pH isotherms with LIX 84 and LIX 84 / Versatic 10 from both sulfate and nitrate matrices would be required to provide certainty on this matter but further test work was not warranted, given that the primary aim of this study was to investigate the rejection of magnesium from a nitrate-based PLS.

LIX 84 is less attractive than LIX 860 from the perspective of nickel and cobalt recovery due to: (1) smaller pH_{50} differences, and therefore poorer separation, for nickel and cobalt from magnesium when mixed with organic acids, and (2) the higher pH required for nickel and cobalt extraction that would result in more stringent upstream iron and aluminium removal as well as higher neutralisation requirements. Therefore, based on the work in Section 4.3.1, LIX 860 mixed with either of the two weakest organic acids (Versatic 10 or Cyanex 272) are considered promising for the separation of nickel and cobalt from magnesium. Although these mixtures were not synergistic, the organic acids may still be required in the organic phase to increase nickel phase transfer kinetics and to reduce cobalt poisoning.

4.3.3 Effect of reducing the Cyanex 272 concentration mixed with LIX 860

Cyanex 272, although potentially required in a mixture with LIX 860 to reduce cobalt poisoning and to accelerate the phase transfer of nickel, resulted in significant calcium and manganese loading. Extractions of nickel and cobalt occurred at the pH_{50} obtained with LIX 860 alone. The extractions of magnesium, calcium, zinc and manganese occurred at the pH_{50} obtained with Cyanex 272 alone. Although the formation of mixed ligand complexes cannot be ruled out, these data suggested that impurity metals were extracted by Cyanex 272 alone and nickel and cobalt were extracted by LIX 860 alone. The concentration of Cyanex 272 could thus potentially be optimised to lower the extraction of impurity metals whilst still enabling complete nickel and cobalt extraction. To explore this hypothesis, a pH isotherm was generated using comparable conditions to those generated in Section 4.3.1, except the Cyanex 272 concentration was lowered by a factor of 10 to 0.05 M.

The pH isotherm using LIX 860 / 0.05 M Cyanex 272 showed full extraction of nickel, cobalt, copper and zinc with only minimal manganese, calcium and magnesium extractions (Figure 4-1, a). Suppression of manganese and magnesium extractions compared with LIX 860 / 0.5 M Cyanex 272 (Figure 4-1, b) can be ascribed to insufficient Cyanex 272 in the organic phase, which must have been sequestered into complexes with one or more of the metals copper, zinc, nickel or cobalt. In agreement with the results in Table 4-2, LIX 860 / 0.05 M Cyanex 272 was not synergistic for any metals. No previous studies have considered mixing low concentrations of Cyanex 272 with LIX 860, but the effect was as predicted from limiting the organic acid concentration.

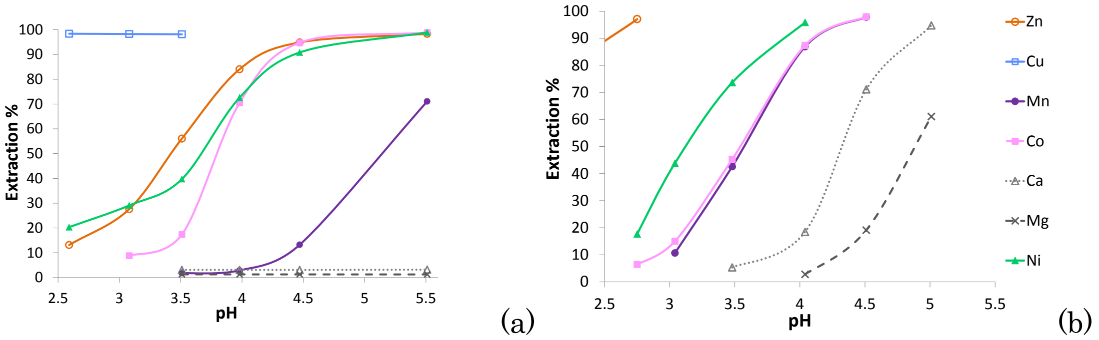


Figure 4-1: Extraction pH isotherm for 0.5 M LIX 860 / 0.05 M Cyanex 272 (a) and 0.5 M LIX 860 / 0.5 M Cyanex 272 (b) in ShellSol D70 from mixed metal nitrate solution at 23 °C (metal concentrations = 0.01 M)

Decreasing the Cyanex 272 concentration mixed with LIX 860 resulted in better rejection of impurity metals by limiting the co-extraction from the organic acid reagent. Full extractions of nickel and cobalt were still achieved and this mixed reagent system was therefore promising for application to nickel and cobalt separation from magnesium in a nitrate-based PLS.

4.3.4 Comparison of the promising solvent systems for nickel and cobalt separation from magnesium in a nitrate matrix

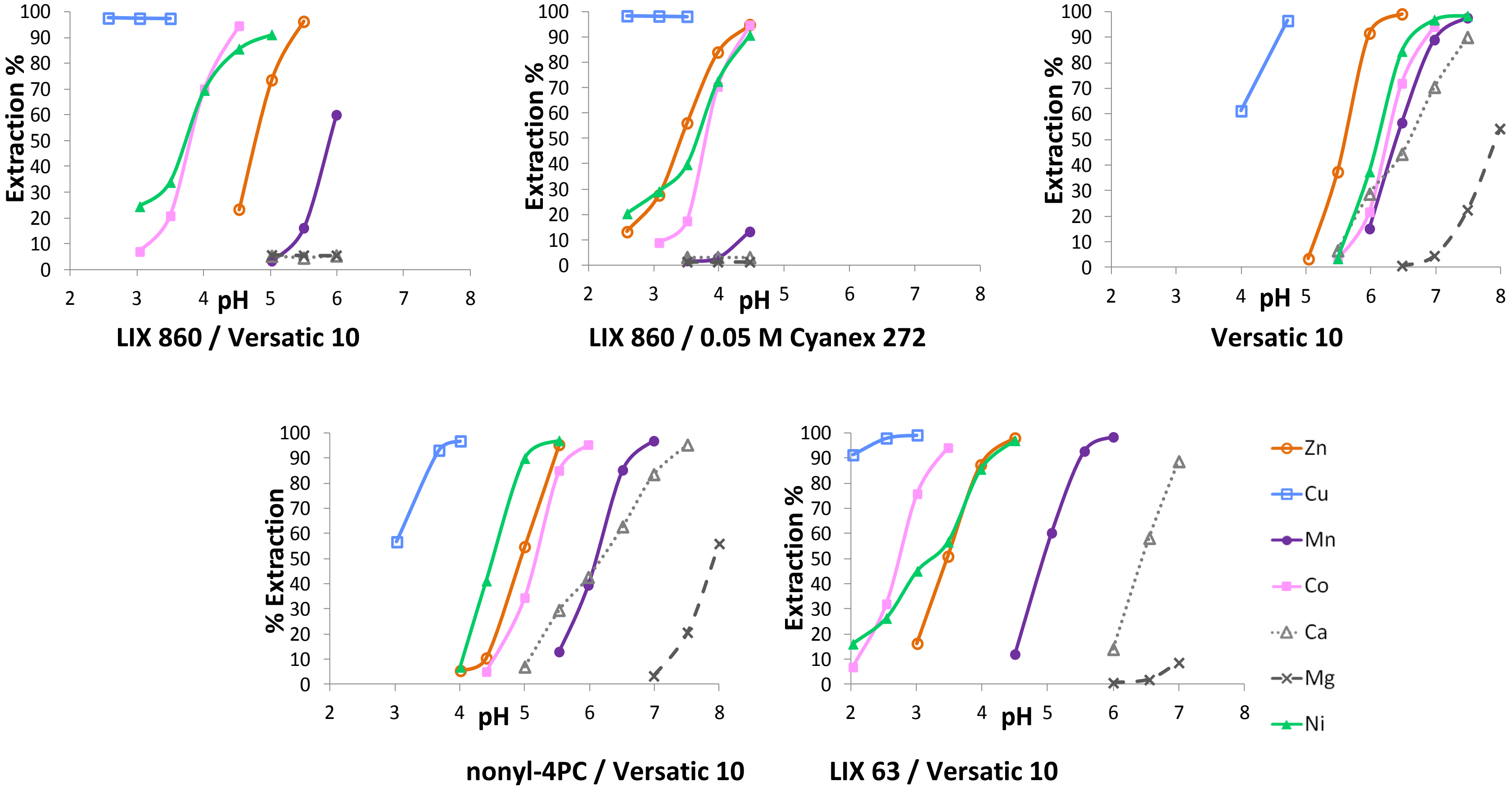
Based on the work completed in Section 4.3.1 and Section 3.3.3, the following solvent systems were identified for separation of nickel and cobalt from magnesium in a nitrate matrix: (1) Versatic 10 as a single reagent, (2) LIX 860 / Versatic 10, (3) LIX 860 / low Cyanex 272, (4) LIX 63 / Versatic 10 and (5) nonyl-4PC / Versatic 10. Extraction pH isotherms from the same mixed metal nitrate matrix with all base metals at 0.01 M were generated using these solvent systems. A direct comparison of the pH isotherms for these five solvent systems (Figure 4-2) can therefore be made to inform the next stage of process development. From the goals identified in Section 1.2, both the rejection of magnesium and operation at low pH can be assessed from these isotherms. Although not yet tested in this chapter, a low concentration of TBP (0.18 M) may be required with Versatic 10 alone in future work to improve phase separation by hindering third phase formation (Tsakiridis and Agatzini, 2004). This would be expected when extracting nickel and cobalt from nickel laterite PLS, as the PLS will contain higher metal concentrations than used to generate Figure 4-2.

The pH required for greater than 90% extraction of both nickel and cobalt decreased in the following order: Versatic 10 (pH 7), nonyl-4PC / Versatic 10 (pH

6), LIX 860 / Versatic 10 (pH 5), LIX 63 / Versatic 10 (pH 4.5), LIX 860 / 0.05 M Cyanex 272 (pH 4.5). The amount of magnesium extracted at these pH values was negligible in most cases, except for Versatic 10 where 11 mg/L, or 4.5% of the available magnesium, was extracted. Extraction of another common nickel laterite PLS impurity, manganese, at these pH values decreased in the following order: Versatic 10 (89%), nonyl-4PC / Versatic 10 (40%), LIX 860 / Cyanex 272 (13%), LIX 63 / Versatic 10 (12%), LIX 860 / Versatic 10 (3%). The most promising systems from the perspective of both low operating pH and good selectivity of nickel and cobalt over magnesium and other impurities were therefore the mixed reagent systems, and particularly those containing oximes (phenolic or aliphatic) with organic acids.

Where literature data for real or synthetic sulfate-based nickel laterite PLS were available, the order of metal extraction was the same as that from Figure 4-2. From the literature, extraction with Versatic 10 occurred in the order Cu, Zn, Ni, Co, Mn, Ca, Mg (Cheng, 2006), with Versatic 10 / decyl-4PC (analogous to nonyl-4PC) in the order Ni, Zn, Co, Mn, Ca, Mg (Cheng *et al.*, 2010a), and with LIX 63 / Versatic 10 in the order Cu, Co, Ni, Zn, Mn, Ca, Mg (Cheng, 2006). This consistency with a real-world application to the nickel laterite industry is promising for application of these three solvent systems to a real nitrate-based PLS.

There are no literature data available for the effect of mixing LIX 860 with either Versatic 10 or Cyanex 272 for the recovery of nickel and cobalt. As such, these are the only two solvent systems in Figure 4-2 where the application of the solvent system to nickel and cobalt recovery cannot be informed by previous research. To understand their behaviour and optimise their performance, they therefore require the most development for application to a nickel–cobalt extraction process from a nitrate-based PLS. Phenolic oximes are susceptible to cobalt poisoning, which results in poor net cobalt transfer and rapid reagent sequestration. Cobalt poisoning is therefore the biggest hurdle to application of these reagent mixtures and requires investigation.



LIX 860 / Versatic 10

LIX 860 / 0.05 M Cyanex 272

Versatic 10

nonyl-4PC / Versatic 10

LIX 63 / Versatic 10

Figure 4-2: Extraction pH isotherms for mixed metals from stock nitrate solution using various reagents dissolved in ShellSol D70 (cation concentrations = 0.01 M, organic reagent concentrations = 0.5 M unless stated otherwise)

4.4 Conclusions

The aim of this chapter was to select promising solvent systems for nickel and cobalt separation from magnesium at low pH by using the literature review as a guide and by determining the metal extraction characteristics of any novel reagent mixtures identified. The results of the investigation to meet this objective revealed that:

- The separations of nickel and cobalt from impurity metals obtained on mixing LIX 860 with organic acids increased with decreasing organic acid strength (from pH_{50}(Mg-Co) of 0.7 for LIX 860 / D2EHPA to pH_{50}(Mg-Co) of 1.4 for LIX 860 / Cyanex 272). Synergism for nickel and cobalt conversely decreased with decreasing acid strength. No synergism was obtained for mixtures of LIX 860 with Versatic 10 or Cyanex 272 whereas a ΔpH_{50}(Ni) of 1.8 was obtained for LIX 860 / D2EHPA.

- The same trends as described for mixtures of LIX 860 with organic acids were also obtained for mixtures of LIX 84 with organic acids. These trends, however, occurred at higher pH values due to weaker metal extractions with LIX 84 (pH_{50}(Co) of 4.0) compared with LIX 860 (pH_{50}(Co) of 3.5). Mixtures of LIX 860 with organic acids were therefore preferable to separate nickel and cobalt from magnesium at low pH.

- LIX 860 mixed with low concentrations of Cyanex 272 resulted in full extractions of copper, zinc, nickel and cobalt whilst suppressing manganese, magnesium and calcium loading. Limiting the concentration of Cyanex 272 likely resulted in insufficient ligands to allow loading of manganese, magnesium and calcium as it became sequestered into complexes with one or more of copper, zinc, nickel and cobalt.

- All of the promising solvent systems were capable of extracting nickel and cobalt whilst rejecting magnesium in a nitrate matrix, although mixed reagent systems operated at a lower pH and with higher rejection of manganese. In addition, the order of metal extraction when compared with available literature data from nickel laterite leach liquors was exactly the same from the stock nitrate matrix. This offers confidence in the identified solvent systems for application to a nitrate-based PLS.

CHAPTER 5

Minimising cobalt poisoning of LIX 860 using organic acids

5.1 Introduction

It was shown in Section 4.3.1 that the phenolic aldoxime present in LIX 860 offers selective extraction of nickel and cobalt over impurity metals in a nickel laterite PLS, especially magnesium (pH_{50} differences > 3). Unfortunately, the extraction of cobalt with LIX 860 results in extensive poisoning of the reagent. Cobalt poisoning, discussed at length in Section 2.5.3, results in much of the extracted cobalt remaining in the organic phase as cobalt(III), so that full cobalt recovery and reagent regeneration are not achieved. Previous authors have demonstrated that D2EHPA is able to mitigate cobalt poisoning of LIX 860. After a review of the literature, it was proposed in Section 2.5.4 that this occurs because D2EHPA blocks the axial sites required for di-oxygen binding in the cobalt poisoning mechanism. The effect of other organic acids is unknown.

It was shown in Section 4.3.1 that extraction of nickel and cobalt with LIX 860 / D2EHPA results in poor rejection of magnesium (pH_{50}(Mg-Co) = 0.7). More selective extractions of nickel and cobalt were achieved using weaker organic acids such as low Cyanex 272 concentrations (pH_{50}(Mg-Co) > 1.8) and Versatic 10 (pH_{50}(Mg-Ni) > 2.2). It is therefore of significant interest to determine if these weaker organic acids are able to mitigate cobalt poisoning of LIX 860 in a similar manner to D2EHPA.

The aim of this chapter was to assess the potential to slow or stop cobalt poisoning of any solvent system identified by the literature to be susceptible to this phenomenon. This was achieved by investigating the effect of different variables on the amount of cobalt stripped from mixtures of LIX 860 with the organic acids HEH(EHP), Cyanex 272 and Versatic 10, using D2EHPA as the benchmark. Besides the organic acid used, additional variables assessed were oxygen availability from bubbling air through the organic phase and the organic acid concentration. A sequential load–strip study was carried out on LIX 860 / D2EHPA to further investigate this system as it was the only reagent mixture to exhibit near-quantitative cobalt stripping.

5.2 Materials and Methods

5.2.1 *Aqueous and organic solutions*

The following chemicals were used in the preparation of aqueous solutions: sodium nitrate, cobalt nitrate, sodium hydroxide pellets, sulfuric acid and nitric acid as per Section 3.2.1. The following solvent extraction reagents were used: LIX 860, D2EHPA, HEH(EHP), Cyanex 272 and Versatic 10. The organic acids chosen are the four common organic acids used commercially. All reagents were used as supplied and purities are as stated by the manufacturer. All organic solutions were made up with ShellSol D70.

5.2.2 *Extraction and stripping procedure for investigating cobalt poisoning over time*

Initial investigations were conducted to determine the effect of different variables (organic acid type, oxygen availability and organic acid concentration) on cobalt poisoning of LIX 860 over time. To generate each separate loaded organic phase, 50 mL of aqueous cobalt nitrate (0.01 M in 1 M sodium nitrate) and 50 mL of LIX 860 (0.05 M) / organic acid (0 to 0.1 M) in ShellSol D70 were mixed in a hexagonal glass jar for 20 min at a pH depending on the reagent mixture used. The two phases were mixed with a magnetic stirrer bar at 1000 rpm at the given pH using the same pH control method as for metal extraction pH isotherms in Section 3.2.2.

The loading pH values used for cobalt were different for each organic phase due to the differences in extraction pH when mixing LIX 860 with various organic acids (Table 5-1) at different concentrations. After loading was complete, the organic phase was filtered through Whatman 1PS phase separation paper. All filtered organic phases loaded with cobalt were then stored in a glass jar with a loose fitting lid at the back of a fume cupboard.

Samples of each loaded organic (5 mL) were taken over 192 h. The first sample was taken one hour from the start of cobalt loading to allow enough time for extraction, phase separation and filtration of each separate loaded organic. Each sample was stripped using sulfuric acid (350 g/L) at A:O of 3:1 and 50 °C for 40 min in an orbital shaker at 250 rpm. The phases were then separated through 1PS paper. Harsh strip conditions were used to ensure only cobalt(III) remained in the stripped organic phase. More mild conditions (12 g/L sulfuric acid at A:O = 1:1, 20 °C for 30 min) were shown previously by Cerpa and Alguacil (2004) to fully strip cobalt(II) from a comparable reagent mixture of ACORGA M5640 / D2EHPA.

Table 5-1: Extraction pH_{50} values for cobalt with 0.5 M LIX 860, 0.5 M of different organic acids, and their 1:1 mixtures (Section 4.3.1)

Solvent System	pH_{50}(Co)
LIX 860	3.5
D2EHPA	3.1
HEH(EHP)	3.5
Cyanex 272	3.8
Versatic 10	6.3
LIX 860 / D2EHPA	1.7
LIX 860 / HEH(EHP)	2.7
LIX 860 / Cyanex 272	3.5
LIX 860 / Versatic 10	3.8

For investigating the effect of oxygen availability in the organic phase on the rate of cobalt poisoning, laboratory air (3 L/min) was bubbled into two cobalt-loaded organic phases held in Drechsel bottles to give a steady stream of bubbles. The air was first passed through a Drechsel bottle containing diluent (ShellSol D70) to saturate the air stream with diluent and so minimise evaporation of the organic phase. The volume of each loaded organic was checked after each sample was taken to account for any solvent evaporation that did occur, and then later topped up to the same volume with ShellSol D70 immediately prior to taking the next sample.

5.2.3 Sequential load–strip procedure

A sequential load–strip cycle was carried out by loading LIX 860 (0.5 M) / D2EHPA (0.5 M) with cobalt (0.01 M in 1 M sodium nitrate) in a stainless steel mixer box (9 × 9 × 14 cm). The two phases were contacted using a magnetic stirrer bar at 1000 rpm. The organic was loaded at A:O = 1:1, laboratory temperature (23 °C) and pH 4.5 for 10 min. Higher reagent concentrations were used here to mimic a similar ratio of reagent to cobalt as would be expected in a commercial operation where nickel concentrations are 10 times that of cobalt. A high load pH was chosen to mimic potential excursions to high pH that could occur in an operating plant as well as to maximise cobalt extraction. Shorter contact times were used in this study as previous extract tests showed via pH measurements that equilibrium was reached after only a few minutes.

Immediately after phase separation in a separating funnel, the entire organic volume was stripped (350 g/L sulfuric acid for 40 min) in another stainless steel mixer box in a water bath at 50 °C agitated with an overhead stirrer (65 mm blade diameter) at 1300 rpm (tip speed of 4.42 m/s). A lower strip A:O of 1:1 was used in the strip stage due to the higher reaction volume to minimise the size of the required mixing vessel. This was considered acceptable given that Cerpa and Alguacil (2004) achieved full stripping from a comparable system at A:O of 1:1. The phases were then separated in another separating funnel. This extraction and stripping process was repeated a total of 10 times. The volume of organic was measured after each aqueous contact to ensure an A:O of 1:1 was used at all times.

Had the mixing or separating vessels been washed after each contact or if phase separation paper had been used, there would have been very high loss of the organic after 10 stages. Because each of the mixing and separation vessels was dedicated to a specific part of the extract–stripping process and no contamination could occur, the vessels for both extraction and stripping were not washed between each stage of the cycle. Samples of the raffinate, loaded strip liquor and stripped organic were taken after each extract or strip stage. Samples of stripped organic were washed with sulfuric acid (100 g/L A:O of 3:1) for 20 s and dried over anhydrous sodium sulfate (AR, Chem Supply).

5.2.4 Analytical determinations

Aqueous cobalt levels were assayed using atomic absorption spectroscopy (AAS) as per Section 3.2.3. Cobalt poisoning was assessed via the level or residual organic phase cobalt after an aggressive strip. The loaded organic cobalt concentration was calculated from the difference between the feed and the raffinate. For all tests except the load–strip investigation, residual cobalt poisoning of the organic phase was then calculated as the difference in cobalt content between the loaded organic and the aqueous strip liquor.

Cobalt was only measured directly from the organic phase for the sequential load–strip tests as it was decided that the cumulative error for calculating small residual cobalt concentrations by difference from the aqueous phases over 10 cycles would become too great to provide meaningful analysis. Organic phase cobalt in the load–strip investigation was analysed directly with AAS using standards made up by contacting a 50 mg/L cobalt nitrate aqueous standard at A:O of 1:1 with 0.5 M LIX 860 / 0.5 M D2EHPA in ShellSol D70 at pH 6. The raffinate from this extraction was analysed using AAS to ensure cobalt was below detection limits. The 50 mg/L cobalt organic standard was diluted with 0.5 M LIX 860 / 0.5 M D2EHPA in ShellSol D70 to give standards of 5, 10, 15, 20 and 25 mg/L. Flame conditions for organic phase cobalt analysis were 13.7 L/min air and 1.7 L/min acetylene.

Samples of stripped organic from the sequential load–strip investigation were also analysed using UV-Visible spectroscopy (UV-Vis) using the same method as Section 3.2.3. This was used as another indicator of organic phase cobalt(III) concentration, made possible due to the distinctive intense dark brown colour of cobalt(III) as discussed in Section 2.5.3.

5.3 Results and Discussion

The organic acids used in the present investigations and their pKa values are shown in Table 5-2. Initially, all organic reagents were used at 2.5 times stoichiometric excess, assuming two phenolic oxime and two acid ligands binding per cobalt atom (Figure 5-1) as discussed in Section 2.5.1. Of the organic acids tested, D2EHPA was the only acid to afford near quantitative cobalt stripping under any of the tested conditions. To provide insight into the mechanism of poisoning, an investigation into the effect of sequential extract–strip cycles on the cobalt poisoning of LIX 860 / D2EHPA was therefore carried out.

Table 5-2: pKa values of the organic acids mixed with LIX 860 for investigation of cobalt poisoning

Organic Acid	pKa	Reference
D2EHPA (phosphoric)	3.01	(Zhang *et al.*, 1994)
HEH(EHP) (phosphonic)	4.21	(Zhang *et al.*, 1994)
Cyanex 272 (phosphinic)	5.22	(Zhang *et al.*, 1994)
Versatic 10 (carboxylic)	7.33	(Preston, 1994)

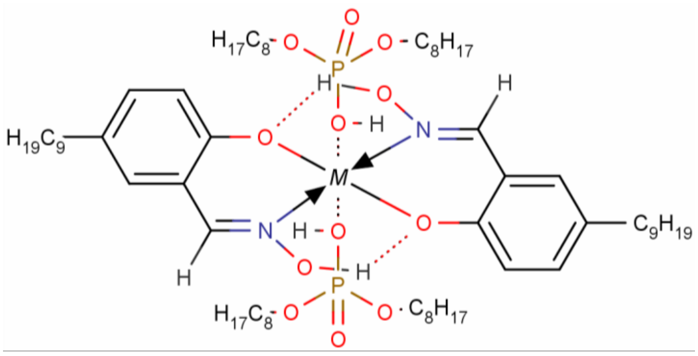


Figure 5-1: Proposed synergistic structure for the extraction of nickel and cobalt using mixtures of LIX 860 and organic acids (e.g. D2EHPA)

5.3.1 Effect of organic acid type on extent of cobalt stripping from LIX 860

The results for stripping of cobalt from LIX 860 mixed with various organic acids are shown in Figure 5-2. Different loading pH values were initially assessed for three organic acids (D2EHPA, Cyanex 272 and Versatic 10) to determine if this was an important variable for cobalt poisoning. It was found that the loading pH for a mixed reagent solvent system had only a minimal effect on cobalt stripping over time. In all cases, cobalt stripping from solvent systems loaded at different pH units was within ±10% and the cobalt stripped values did not overlap between the different organic acids tested. Hence, only one loading pH value, that giving near 100% cobalt extraction, was used to analyse the effect of each acid type on cobalt stripping in Figure 5-2.

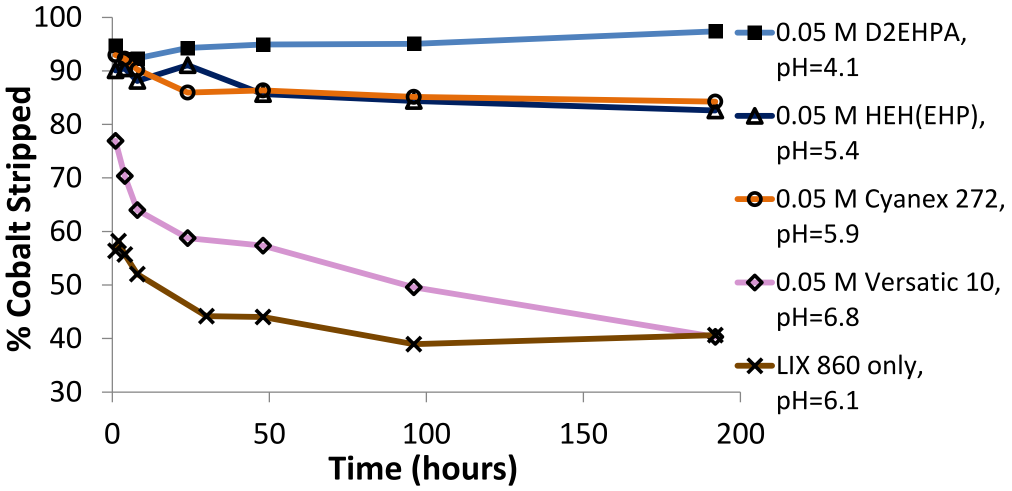


Figure 5-2: Extent of cobalt stripping from solvent systems containing LIX 860 and organic acids in ShellSol D70. Loading pH given in legend. (Organic phase cobalt = 0.01 M, Organic reagents = 0.05 M)

There was a correlation between stronger organic acids (lower pKa in Table 5-2) mixed with LIX 860 resulting in higher stripping of cobalt than weaker organic acids. The stronger phosphorus-based organic acids (D2EHPA, HEH(EHP) and Cyanex 272) resulted in relatively high cobalt stripping (>83% stripped) in all cases and did not decrease dramatically over time, indicating limited cobalt poisoning. Of these systems, the highest cobalt stripping was obtained with LIX 860 / D2EHPA (92–100%). In contrast, there was a steady decrease in the amount of cobalt stripped from LIX 860 / Versatic 10 (75% to 40% stripped) and LIX 860 alone (56% to 41% stripped) after 192 h. This is indicative of ongoing cobalt poisoning of LIX 860, which was only slightly retarded by the presence of Versatic 10.

UV-Vis analysis was used to determine the oxidation state of cobalt in the LIX 860 / D2EHPA organic phase. Figure 5-3 shows spectra for 150 mg/L cobalt(III) remaining in LIX 860 after an intensive strip, diluted 1000 times with ShellSol D70, and total cobalt (250 mg/L) loaded into LIX 860 / D2EHPA. Spectra are only plotted between 700 and 450 nm as absorbance was minimal above 700 nm and the reagents in the unloaded organic phase began to strongly absorb below 450 nm. The relative molar attenuation coefficients at 450 nm were 48 000 1/Mcm for cobalt in LIX 860 and 32 1/Mcm for cobalt in LIX 860 / D2EHPA. As discussed in Section 2.5.3, a very intense brown colour for cobalt (ε of 10^3) is indicative of cobalt(III). The much lower intensity in LIX 860 / D2EHPA (ε in region of 10^1) is thus indicative of octahedral cobalt(II), and hence very low levels of cobalt(III) in the organic phase. Very low levels of cobalt(III) explain the high stripping of cobalt from LIX 860 / D2EHPA and the lack of cobalt poisoning. This is also consistent with the proposal of octahedral nickel coordination in LIX 84 / D2EHPA by Narita *et al.* (2006), and supports extrapolation of Figure 5-1 to cobalt coordination with LIX 860 / D2EHPA.

As the intense dark brown colour of the organic phase is indicative of cobalt(III), and therefore cobalt poisoning, it is instructive to discuss the colours of the other LIX 860 / organic acid mixtures here. Cobalt in LIX 860 / Cyanex 272 and LIX 860 / HEH(EHP) was opaque and initially blue black, but turned dark brown over the first 24 h. It is known that cobalt(II) extracted with Cyanex 272 or HEH(EHP) alone results in a blue organic phase as a result of tetrahedral coordination of the cobalt ion (Flett, 2005). The initial blue-black colour suggests some tetrahedral cobalt coordinated by the organic acid alone. The intense dark brown of cobalt(III) later obscured the weaker blue colour, suggesting ongoing cobalt oxidation. A dark brown colour of the organic phases for LIX 860 / Versatic 10 was observed immediately after loading, indicating more rapid oxidation of cobalt(II) to cobalt(III), explaining the extensive poisoning in this reagent mixture.

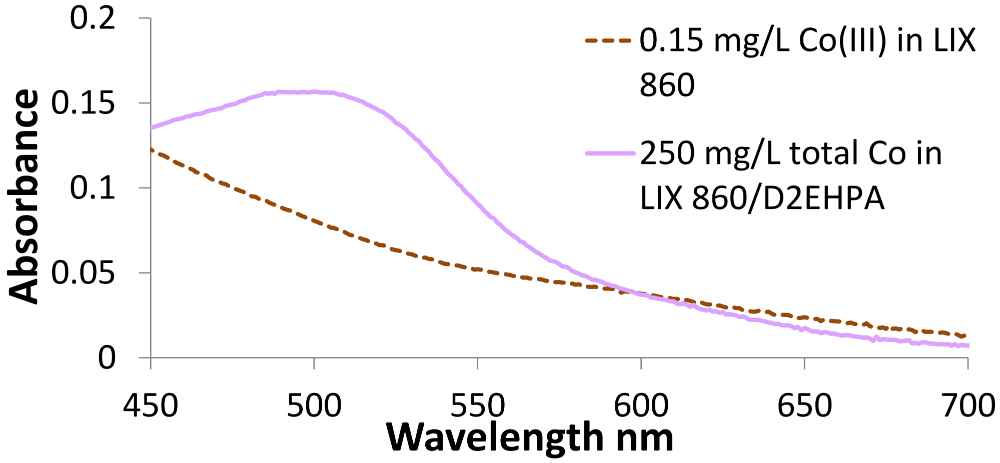


Figure 5-3: Visible light absorption from cobalt(III) in LIX 860 and total cobalt in LIX 860 / D2EHPA

Although mixing Versatic 10 or Cyanex 272 with LIX 860 allowed extraction of nickel and cobalt with rejection of magnesium (Section 4.3.1), neither was as successful as D2EHPA at hindering cobalt poisoning of LIX 860. HEH(EHP) resulted in poor rejection of magnesium and also did not improve cobalt stripping, hence this solvent system was not investigated further. Cobalt poisoning of LIX 860 / Versatic 10 was particularly extensive and so investigation of this reagent mixture was similarly not pursued.

5.3.2 Effect of oxygen availability on cobalt stripping from LIX 860 with organic acids

Cobalt poisoning of LIX 860 in the presence of D2EHPA or Cyanex 272 reached a plateau within 24 h. As oxygen is the only external reagent required for cobalt to oxidise (Section 2.5.3), it was suspected that the reaction could be oxygen limited. To investigate this hypothesis, air was bubbled through the cobalt loaded organic phases as per the method in Section 5.2.2, to both agitate and provide additional oxygen into the organic solution. Stripping of cobalt from the loaded organic was measured over 48 h (Figure 5-4) to determine the effect of oxygen availability on the initial rate of cobalt poisoning. Cobalt loading was done at a higher pH value for LIX 860 / D2EHPA in this investigation to maximise cobalt extraction (from 97 to 100% extracted).

For LIX 860 / D2EHPA, cobalt stripping both with and without air bubbling did not change over 48 h and remained near-quantitative (92–95% stripped). For LIX 860 / Cyanex 272 both with and without air bubbling, cobalt stripping decreased over the first 24 h from a maximum of 93–95% to reach a minimum of 86–88% stripped. Oxygen is therefore not a limiting reagent for cobalt poisoning of the mixed reagent systems for the first 48 h after loading, where cobalt stripping levels out.

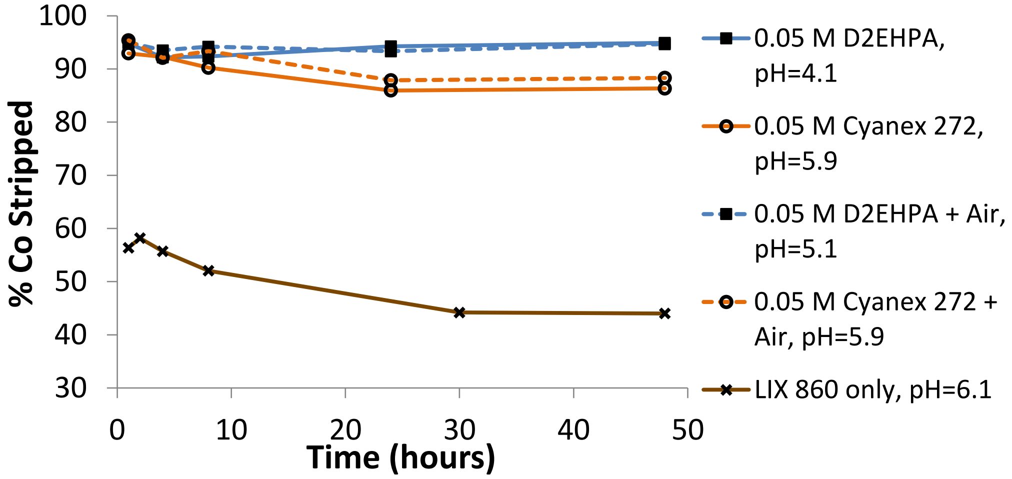


Figure 5-4: Extent of cobalt stripping from LIX 860 with different organic acids in ShellSol D70 with and without air bubbling (Organic phase cobalt = 0.01 M, [LIX 860] = 0.05 M)

5.3.3 *Effect of organic acid concentration on cobalt stripping from LIX 860 with organic acids*

As D2EHPA at a stoichiometric excess of 2.5 (0.05 M) resulted in near-quantitative cobalt stripping, the effects of lower D2EHPA concentrations on cobalt stripping were considered. To further explore the potential of using Cyanex 272 to mitigate cobalt poisoning of LIX 860, the effect of low and high Cyanex 272 concentrations on cobalt stripping were also considered. The effect of altering the concentrations of D2EHPA on cobalt stripping over time is shown in Figure 5-5 and that of Cyanex 272 in Figure 5-6.

Increasing either D2EHPA or Cyanex 272 concentrations above 0.02 M had little effect on the quantity of cobalt stripped from either sample. This suggested that the amount of cobalt poisoned is related to the organic acid used, rather than its concentration. For LIX 860 with 0.015 M D2EHPA, the stripping efficiency levelled out at 75% stripped and with 0.010 M D2EHPA at 50% stripped after 192 h (Figure 5-5). For LIX 860 mixed with 0.012 M Cyanex 272, cobalt stripping levelled out at 60% after 192 h (Figure 5-6).

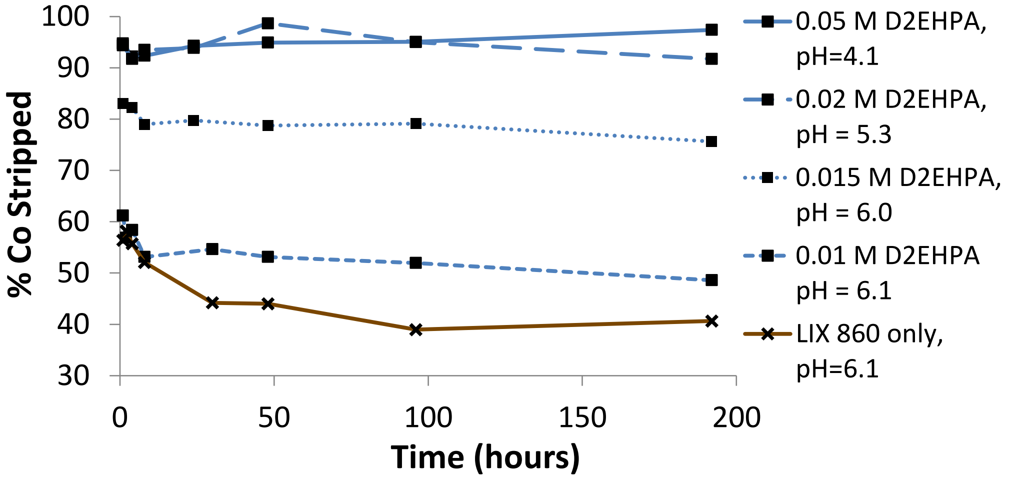


Figure 5-5: Extent of cobalt stripping from LIX 860 with different concentrations of D2EHPA in ShellSol D70 (Organic phase cobalt = 0.01 M, [LIX 860] = 0.05 M)

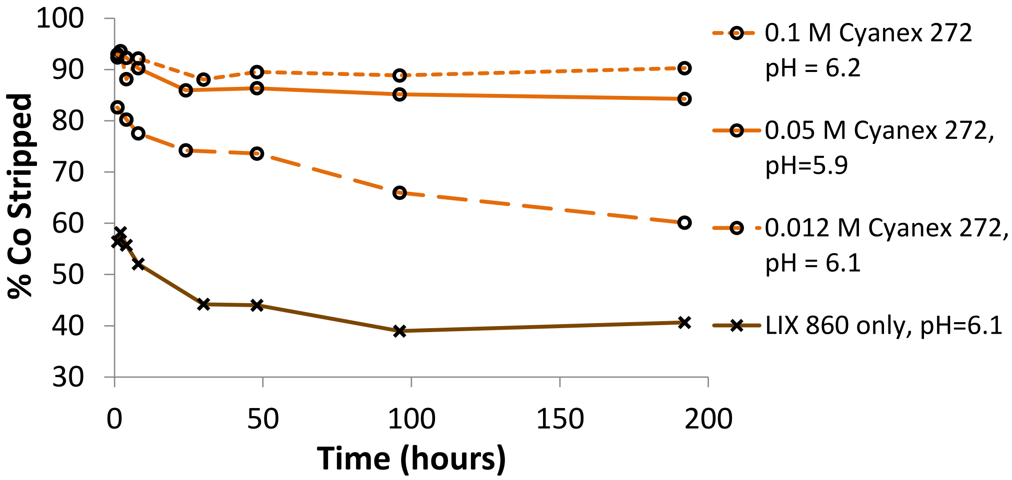


Figure 5-6: Extent of cobalt stripping from LIX 860 with different concentrations of Cyanex 272 in ShellSol D70 (Organic phase cobalt = 0.01 M, [LIX 860] = 0.05 M)

As was extensively discussed in Section 2.5.1, the proposed mixed ligand cobalt complex extracted by LIX 860 with an organic acid has the structure presented in Figure 5-1: $Co(LIX\ 860)_2(Acid)_2$. As 0.01 M cobalt was extracted into the organic phase in the presented investigations, when less than 0.02 M organic acid was present not all cobalt could adopt the expected mixed ligand complex. The remaining cobalt in the organic phase still had free axial sites to accept dioxygen and therefore could poison the organic. Cobalt stripped from the organic in Figure 5-5 for D2EHPA at 75% (0.015 M) or 50% stoichiometry (0.01 M) as well as Figure 5-6 for Cyanex 272 at 60% stoichiometry (0.012 M) was consistent with this ratio of cobalt:organic acid of 1:2. The amount of cobalt forming these stable cobalt(II) complexes thus confirmed a cobalt:organic acid ratio of 1:2 in the organic phase cobalt complex.

Cobalt(II) extracted with LIX 860 / 0.1 M Cyanex 272 was initially a distinctive dark blue colour suggesting more tetrahedral cobalt(II) coordination than in the blue-black organic of LIX 860 / 0.05 M Cyanex 272 (Section 5.3.1). The organic then turned dark brown over the first 24 h, indicating formation of cobalt(III). Tetrahedral cobalt(II) coordinated exclusively by Cyanex 272 would be unable to accept dioxygen. Oxidation and subsequent poisoning, therefore, would not occur. Despite this, doubling the concentration of Cyanex 272 in the LIX 860 / Cyanex 272 organic phase to a five times stoichiometric excess (0.1 M) only marginally increased cobalt stripped after 192 h to 90%, compared with 84% stripped from LIX 860 / 0.05 M Cyanex 272 (Figure 5-6). This suggests that some initial ongoing cobalt poisoning of LIX 860 cannot be avoided using Cyanex 272.

In summary, sub-stoichiometric concentrations of Cyanex 272 mixed with LIX 860 for a potential solvent system for extraction of nickel and cobalt, as presented in Section 4.3.3, would not be feasible. Ongoing cobalt poisoning with this reagent mixture was observed which would be problematic from an operational perspective. Cobalt would likely build up in a commercial operation, requiring a reductive strip bleed operation such as that practiced at Queensland Nickel (Fittock, 1992).

5.3.4 Effect of sequential load–strip cycles on cobalt poisoning of LIX 860 / D2EHPA

From the results presented so far, it was unknown whether there was a small level of cobalt poisoning occurring in LIX 860 with greater than stoichiometric D2EHPA or if, within experimental error, there was no cobalt poisoning. Even though LIX 860 / D2EHPA is not appropriate for extraction of nickel and cobalt with high magnesium rejection, it has been proposed in the literature as a successful synergistic system for extraction of nickel and cobalt. It was therefore of interest to determine if cobalt slowly poisoned this organic over several load–strip cycles relevant to a commercial process, or if cobalt could be quantitatively stripped after each extract stage. This would grant mechanistic information that may be useful for further mitigating cobalt poisoning of more selective reagent mixtures such as LIX 860 / Cyanex 272. Extract and stripping cycles for cobalt that more closely emulated a commercial SX process were therefore carried out on the LIX 860 / D2EHPA system.

The results, summarised in Figure 5-7 and Figure 5-8, show that cobalt slowly accumulated in the organic phase with each load–strip cycle. The AAS results revealed approximately 0.044 mM additional cobalt poisoned the organic with each load–strip cycle after the first. The residual loaded cobalt concentration also correlated well with the observed change in colour ($\varepsilon \sim 10^3$) of the organic phase (Figure 5-8 inset). As the two analytical techniques used were consistent, the slow increase in cobalt concentrations in the organic phase can be attributed to residual cobalt(III) loaded into the organic phase.

If the accrual of 0.01 mM of cobalt per cycle remained constant, and three phenolic oxime molecules are present in each cobalt(III) complex, as has been speculated by previous authors (Burkin and Preston, 1975; Guesnet and Bauer, 1981; Mackenzie *et al.*, 2005), 16 700 cycles would result in complete poisoning of 0.5 M LIX 860. Assuming an average residence time of 30 min per cycle, this results in complete reagent poisoning in 347 days. This rate of poisoning could potentially be acceptable in a commercial operation employing a reductive strip. This would, however, increase process complexity and accelerate reagent degradation (Mackenzie *et al.*, 2006). When considered next to the poor metal separations achievable using the mixture of LIX 860 / D2EHPA, ongoing cobalt poisoning makes this solvent system undesirable for nickel and cobalt extraction from a nitrate PLS. In addition, it is clear that the more selective LIX 860 / Cyanex 272 solvent system would likely suffer from the same slow accrual of cobalt over successive load–strip cycles under commercially relevant time frames.

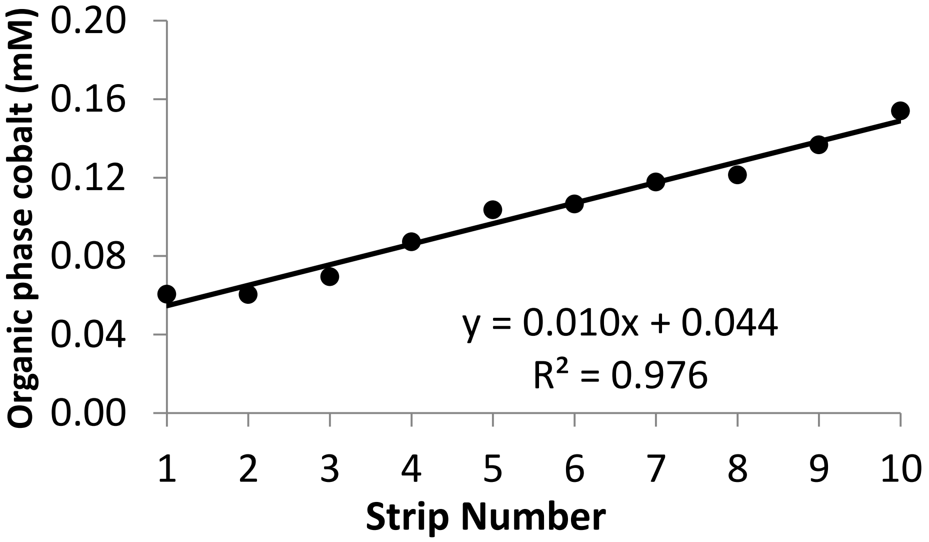


Figure 5-7: Residual organic phase cobalt concentration measured using AAS after each load–strip cycle showing a linear trend line and R^2 value (aqueous cobalt = 0.01 M, organic phase reagents = 0.5 M)

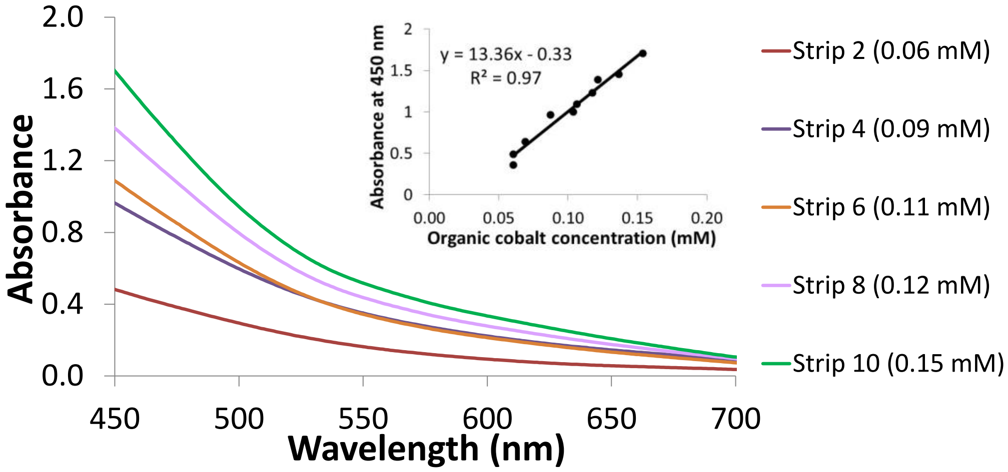


Figure 5-8: Visible spectra of LIX 860 / D2EHPA after every second strip (baseline of fresh organic manually subtracted), organic phase cobalt concentration determined using AAS in brackets. Inset: A plot of absorbance at 450 nm versus residual organic cobalt concentration for each successive stripped organic sample (aqueous cobalt = 0.01 M, organic phase reagents = 0.5 M)

Cobalt poisoning of LIX 860 in the presence of D2EHPA has not been reported by previous studies investigating cobalt stripping from this reagent mixture. This can be attributed to the low cobalt concentration remaining in the organic phase after just one load–strip cycle falling within experimental error. In both the current and earlier work, this was determined by the difference between the loaded organic and the aqueous loaded strip liquor. As shown here, any future studies should also include direct analysis of cobalt in the organic phase to ascertain ongoing poisoning in these solvent systems.

5.3.5 Discussion on the potential mechanism for cobalt poisoning of LIX 860 with organic acids

In LIX 860 systems with weak donor ligands, such as Versatic 10, a weak octahedral complex would be formed with labile axial ligands. Equilibrium in the tetragonal distortion of this complex would fall further towards the square planar complex to allow ongoing oxidation, and therefore poisoning of LIX 860. Octahedral cobalt complexes that form faster and have larger stability constants, such as Co(II)(LIX 860)$_2$(D2EHPA)$_2$, would therefore result in less cobalt poisoning. Further, cobalt oxidation is likely to occur in the bulk organic phase as ongoing poisoning was observed in aqueous-free systems throughout this work via both measurements of cobalt stripping and observations of the organic colour. Given this information, a potential pathway for mitigating cobalt poisoning in LIX 860 / D2EHPA is shown in Figure 5-9.

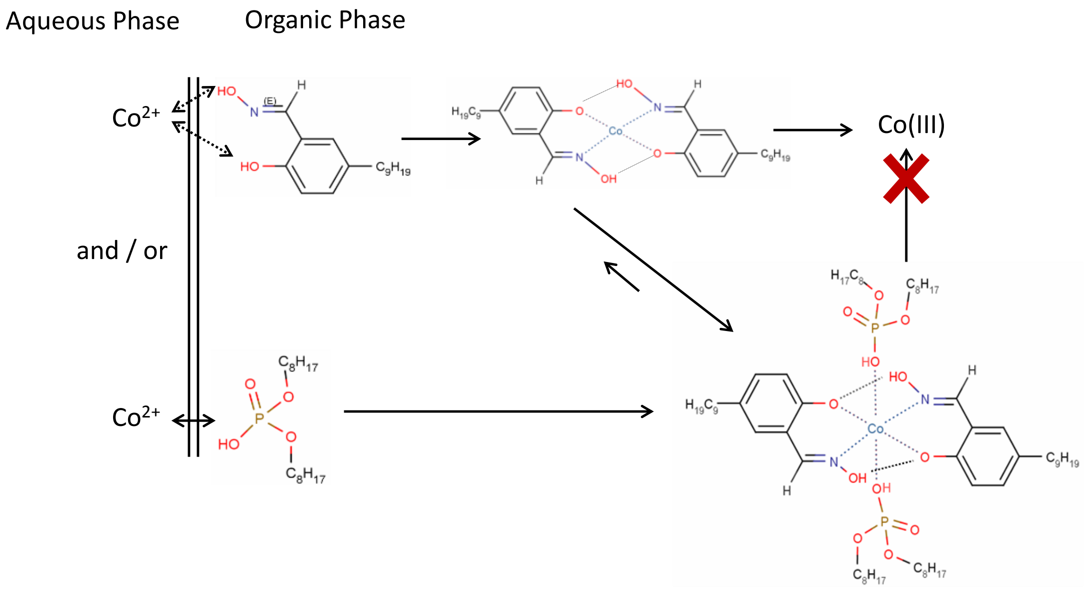


Figure 5-9: Potential extraction mechanisms for cobalt with LIX 860 / D2EHPA and the resulting effect on potential for cobalt oxidation and subsequent poisoning. Assignment of deprotonated OH groups and associated hydrogen bonds in the octahedral cobalt complex is not currently known

For LIX 860 / D2EHPA, cobalt can be initially complexed at the interface by either LIX 860 or D2EHPA (Figure 5-9). Only cobalt initially complexed by LIX 860 would result in cobalt poisoning. As this chelation reaction is slower that the phase transfer reaction involving D2EHPA, only a small proportion of cobalt is oxidised after each load-strip cycle. Conversely, removal of D2EHPA during stripping may potentially provide an opportunity for cobalt poisoning. Verification of this mechanism for cobalt inhibition is of interest but outside the scope of this thesis, which is focused on finding a viable method for the extraction of nickel and cobalt from a nitrate-based PLS.

5.4 Conclusions

This investigation determined the extent of cobalt poisoning of LIX 860 in contact with various organic acids. The aim of this chapter was to assess the potential to slow or stop cobalt poisoning of any solvent systems identified by the literature to be susceptible to this phenomenon. Although only D2EHPA resulted in near-quantitative cobalt stripping, and thus limited cobalt poisoning, it was deemed unsuitable for application to a nitrate-based PLS in in Section 4.3.1 due to poor magnesium rejection. Specifically, this investigation revealed that:

- D2EHPA, HEH(EHP) and Cyanex 272 were all effective in slowing the cobalt poisoning of LIX 860 with cobalt stripping consistently greater than 83%. D2EHPA was the only acid tested to enable near-quantitative cobalt stripping from a LIX 860 organic phase over time. Extensive ongoing cobalt poisoning of LIX 860 / Versatic 10 occurred, increasing over 192 h to only 41% cobalt stripped, the same as with LIX 860 alone. Commercial use of LIX 860 / Versatic 10 for cobalt extraction would, therefore, not be feasible.

- Altering the availability of oxygen to the organic phase did not materially change the amount of cobalt stripped from mixtures of LIX 860 with organic acids. The availability of oxygen to the organic phase after loading was therefore not a limit to the level of cobalt poisoning occurring in these solvent systems after loading.

- Altering the organic acid concentration above stoichiometric requirements did not materially increase the quantity of cobalt stripped from LIX 860 / D2EHPA or LIX 860 / Cyanex 272. Decreasing the concentration of organic acid to below the stoichiometric requirements decreased the amount of cobalt stripped that was consistent with the formation of Co(LIX 860)$_2$(Acid)$_2$. These results also demonstrated that the suggested mixture of LIX 860 with sub-stoichiometric Cyanex 272 for extraction of nickel and cobalt from a nitrate-based PLS would be commercially complicated to operate due to ongoing cobalt poisoning. LIX 860 / Cyanex 272 was therefore not pursued further.

- Cobalt gradually accumulated in the LIX 860 / D2EHPA organic phase over several load–strip cycles at a rate of approximately 0.01 mM per cycle. This rate of cobalt poisoning would require a reductive strip bleed stream to mitigate the decrease in net cobalt transfer and to regenerate the organic reagent. This would add process complexity and increase reagent degradation, thereby increasing costs. Slight cobalt poisoning of LIX 860 / D2EHPA has not been previously reported in the literature.

- Cobalt poisoning of LIX 860 with organic acids is expected to occur in the bulk organic phase before formation of a stable octahedral mixed-ligand complex has occurred. Mixed ligand complexes that form quickly with large stability constants (for example, LIX 860 / D2EHPA) would therefore be less prone to poisoning, which could only occur during loading and potentially stripping.

CHAPTER 6

Modifiers to improve the rates of extraction and stripping of nickel with LIX 63 / Versatic 10

6.1 Introduction

Mixtures of the phenolic oxime LIX 860 with organic acids were previously assessed for their viability to extract nickel and cobalt from nitrate-based liquors. Poor rejection of magnesium with LIX 860 with D2EHPA (pH_{50}(Mg-Co) = 0.7) and HEH(EHP) (pH_{50}(Mg-Co) = 1.1) precluded the use of these particular reagent mixtures (Section 4.3.1). In addition, ongoing cobalt poisoning of LIX 860 mixed with Versatic 10 or Cyanex 272 made these remaining solvent systems undesirable for cobalt extraction.

A discussion of previous research (Section 2.6) revealed that the LIX 63 / Versatic 10 synergistic system allows high separation of nickel and cobalt from magnesium whilst being resistant to cobalt poisoning. LIX 63 / Versatic 10 suffers from slow nickel extraction rates and, more importantly, very slow nickel stripping rates. Previously this has been addressed by the addition of high concentrations (0.5–1 M) of TBP to the organic phase. These high TBP additions, however, introduce other complications, such as greatly increasing the pH required for nickel and cobalt extraction.

The aim of this chapter was to investigate methods to accelerate the phase transfer of nickel for any potentially promising solvent systems identified that suffer from slow nickel extraction or stripping rates. The work in this chapter therefore sought alternative modifiers for LIX 63 / Versatic 10 to (1) increase the rate of nickel stripping, (2) at lower concentration than required with TBP and (3) without increasing the required extraction pH. The effect of promising modifiers on extraction rates was considered to determine if faster extraction could also be achieved. The mechanism for action of the modifier best meeting these goals was then investigated to better understand the selected solvent system.

6.2 Modifier types for accelerating phase transfer of nickel with LIX 63 / Versatic 10

In solvent extraction, modifiers used to accelerate the phase transfer rates of metals are called accelerators. In this chapter, potential accelerators will be referred to as modifiers until experimental results can demonstrate that they behave as accelerators. Addition of TBP as an accelerator to LIX 63 / Versatic 10 to increase the rate for stripping of nickel has been demonstrated by Cheng (2006). In that work, addition of 0.5 M TBP to LIX 63 / Versatic 10 resulted in an increase in the amount of nickel stripped after 5 min of mixing from 30% to 100%. The same addition of TBP increased the $pH_{50}(Ni)$ from 3.3 to 4.0 and the $pH_{50}(Co)$ from 2.8 to 4.5.

The high TBP concentration required in the LIX 63 / Versatic 10 system is potentially problematic over long-term operation in a commercial plant. High modifier concentrations in general are known to increase organic phase viscosity, crud formation, aqueous entrainment and reagent degradation in copper solvent extraction plants (Kordosky and Virnig, 2003; Bender *et al.*, 2011). The increase in extraction pH from using TBP is also problematic because a higher required pH for nickel and cobalt extraction increases the potential for extraction of magnesium and manganese with Versatic 10, as well as the solubility of Versatic 10 in the aqueous phase. Use of a higher extraction pH also puts a tighter limit on the upstream iron and aluminium removal from the PLS to avoid unwanted precipitation during SX. The use of TBP to accelerate nickel stripping is therefore undesirable.

It was proposed in Section 2.6.3 that the phosphorus-based modifier TBP operated as a stripping modifier via a similar mechanism to oxygen-based modifiers used extensively in copper solvent extraction. TBP may therefore interact with the hydroxyoxime reagent to remove hydroxyoxime from the aqueous–organic interface and hinder formation of a nickel–hydroxyoxime complex. This would increase the stripping rate for nickel and also increase the required extraction pH. Other oxygen and phosphorus-based modifiers may therefore confer the same effect as TBP, although potentially at a lower concentration and with a smaller increase in the required nickel extraction pH.

As discussed in Section 2.7.1, pyridine-based reagents with Versatic 10 extract nickel at higher pH values than required for nickel extraction with LIX 63 / Versatic 10 but with faster rates of nickel stripping. It was thus hypothesised in the current work that pyridine-based reagents may be able to act as phase transfer catalysts in the LIX 63 / Versatic 10 system. This is by analogy to adding catalytic concentrations of LIX 63 to LIX 65 to accelerate the phase transfer of copper (Preston, 1980) where LIX 63 accelerates extraction of copper below the pH where LIX 63 is able to extract copper in its own right. Oxygen, phosphorus and pyridine-based modifiers were therefore all investigated as potential nickel accelerators for LIX 63 / Versatic 10.

6.3 Materials and Methods

6.3.1 Aqueous and organic solutions

The following chemicals were used in the preparation of aqueous solutions: magnesium nitrate, nickel nitrate, nitric acid, sodium hydroxide pellets and sulfuric acid. Aqueous phases were made up with 50 g/L magnesium as nitrate to give a high ionic strength magnesium nitrate matrix, as expected from a nitrate-based leach liquor. As the DNi pilot plant had not begun operations when this work was planned, 50 g/L magnesium as nitrate was used as an estimate for the aqueous phase matrix.

LIX 63 and Versatic 10 were used as solvent extraction reagents for all organic phases. The following organic phase modifiers were also used: tributylphosphate (TBP, 97%, Sigma Aldrich), trioctylphosphine oxide (Cyanex 921, 93%, Cytec), 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (TXIB, 98%, BASF), *iso*-tridecanol (ITD, 99%, BASF), nonyl-phenol (98%, Aldrich Chemicals Company), diisobutyl ketone (DIBK, 96%, Dow Chemicals), 4-benzylpyridine (4-BP, 97%, Thermo Fisher Scientific), di-isodecyl pyridine 3-5-dicarboxylate (Acorga CLX 50, 89%, Cytec) and nonyl-4PC.

All organic solutions were made up with ShellSol D70 or ShellSol A150. ShellSol A150 is an aromatic hydrocarbon mixture containing mostly C_9 hydrocarbons, of which more than 99% are aromatic. As 4-BP was only soluble in aromatic diluents, ShellSol A150 was required for the initial investigation to give a common diluent in which all the tested modifiers were soluble. The diluent was later changed to ShellSol D70.

In the following study a constant volume percent, rather than a constant molar concentration, was used for oxygen and phosphorus-based modifiers (TBP, Cyanex 921, TXIB, DIBK, ITD and *p*-nonyl-phenol). As mentioned in Section 6.2, it is expected that oxygen and phosphorus-based modifiers will work in the same manner as TBP. High concentrations (0.5 to 1 M) of these modifiers were therefore likely to be required to sufficiently accelerate nickel stripping. As there is a large differences in molecular volume and molecular weight between these modifiers, high constant molarities would result in very different volume concentrations. This, in turn, can alter the surface area of the aqueous–organic interface occupied by the modifier, affecting variables such as the droplet size and phase separation times. This could create unwanted additional deviations in the nickel extraction and stripping rates. Consequently, a constant volume percent (15% v/v) was used to compare these modifier types. This equated to the following molar concentrations for each modifier (in M): TPB 0.53, Cyanex 921 0.32, TXIB 0.48, DIBK 0.84, ITD 0.61 and nonyl-phenol 0.64.

Pyridine-based reagents (nonyl-4PC, CLX 50 and 4-BP) may act as phase transfer catalysts (Section 6.2). Hence, these were initially used at a low (sub-stoichiometric) concentration of 0.1 M, and not 15% v/v. The drawback of using different volume percentages was not relevant at this low concentration and so a constant molarity was used instead. Comparison of CLX 50 at a higher concentration (0.35 M) was later undertaken as it did not exhibit any accelerating effect at 0.1 M. Nonyl-4PC was also later tested at 0.35 M to determine if higher concentrations would further accelerate stripping of nickel.

6.3.2 Nickel extraction procedure

All extraction tests were carried out as per Section 3.2.2 with an aqueous feed made up with 50 g/L magnesium and 4 g/L nickel as nitrates to mimic a potential feed from a nitric acid leach of a nickel laterite ore. The organic and aqueous tests solutions were combined (A:O of 1:1) in a smaller stainless steel mixing box (7 × 7 × 15 cm) than used in Section 3.2.2 with a smaller overhead stirrer (40 mm blade diameter) at 35 °C in a water bath. Smaller equipment was required because lower solution volumes were used to limit waste production. The speed of the stirrer was adjusted to give a visibly homogenous mixture (1780 rpm, tip speed of 3.7 m/s).

6.3.3 Determination of stripping and extraction rates

Nickel stripping rates were determined using organic solutions previously loaded with nickel from the pH isotherm tests in Section 6.3.2 and generally left loaded overnight, but for no more than three days, in a sealed glass jar. This was considered acceptable as a preliminary experiment revealed that there was no effect on the rate of nickel stripping after aging LIX 63 / Versatic 10 without a modifier for three days. The relevant organic solution (50 mL) was stirred with an overhead stirrer in a square (250 mL) glass jar at 800 rpm (tip speed of 1.7 m/s) in a water bath at 35 °C with the impeller (40 mm diameter) just off the bottom of the jar to ensure the same stirring characteristics between each rate test. The strip solution of sulfuric acid was added (A:O of 1:1) to the glass jar after both phases had reached the desired temperature. For organic phases using ShellSol A150 as a diluent, 100 g/L sulfuric acid was used as the strip feed solution. For organic phases using ShellSol D70, difficulties in separating the two phases occurred when contacting the fresh organic containing nonyl-4PC with 100 g/L sulfuric acid, so 50 g/L sulfuric acid was used instead. Timing was started immediately after combining the aqueous and organic phases. Samples (8 mL) of the resulting aqueous–organic mixture were taken at 0.5, 1, 1.5, 2, 3 and 5 min with a glass syringe and immediately filtered through 1PS paper.

Nickel extraction rates were determined for fresh organic solutions contacted with an aqueous phase containing nickel (4 g/L) and magnesium (50 g/L) as nitrate salts using the same setup as the stripping rate investigation. The pH was continuously measured, as for extraction tests as described in Section 3.2.2. The organic was initially pre-equilibrated with sodium hydroxide (1 mL of 100 g/L solution). After both phases had reached the desired temperature, the aqueous feed was added to the agitated pre-neutralised organic and timing was started immediately. During the entire extraction rate test, the pH was maintained at ±0.5 pH units from a target pH using sodium hydroxide (100 g/L). Samples (8 mL) of the resulting aqueous-organic mixture were taken with a glass syringe after 0.5, 1, 1.5, 2, 3 and 5 min and immediately filtered through 1PS paper.

6.3.4 Analytical determinations

Aqueous and organic phases were analysed as in Section 3.2.3, except sulfuric acid was used for stripping in place of 3 M nitric acid. For organic solutions made up with ShellSol A150, 100 g/L sulfuric acid was used. For organic solutions containing nonyl-4PC in ShellSol D70, weaker sulfuric acid (50 g/L) was used to avoid the phase separation problems noted at higher acid concentrations. UV-Visible (UV-Vis) analysis was used to investigate the metal bonding in a nickel-LIX 63-Versatic 10-modifier solvent system as per the method in Section 3.2.3.

6.4 Results and Discussion

Stripping kinetics and extraction pH isotherms for nickel were determined using LIX 63 / Versatic 10 mixed with a range of modifiers with the potential to accelerate stripping of nickel and meet the primary aim of this chapter. Extraction kinetics were subsequently measured using those modifiers offering fast stripping of nickel with the lowest required extraction pH. Using the data from these investigations, the modifier offering the fastest stripping and extraction of nickel with the lowest $pH_{50}(Ni)$ was selected as the preferred modifier for use with LIX 63 / Versatic 10 and the mechanism of action was further investigated.

6.4.1 Effect of various modifiers on nickel stripping rates

The effect of various oxygen (Figure 6-1), phosphorus (Figure 6-2) and pyridine-based (Figure 6-3) modifiers on the rate of nickel stripping from LIX 63 / Versatic 10 was determined. Nickel stripped slowly from unmodified LIX 63 / Versatic 10 in the current work (only 64% stripped after 5 min), as expected from previous studies in sulfate systems (Cheng, 2006). Oxygen-based modifiers TXIB, DIBK and nonyl-phenol only slightly accelerated nickel stripping above that of unmodified LIX 63 / Versatic 10. Nickel stripping from the loaded organic containing ITD (0.61 M) was an exception, and increased to 90% stripped after 5 min, compared with only 70% for the next fastest modifier (0.84 M DIBK).

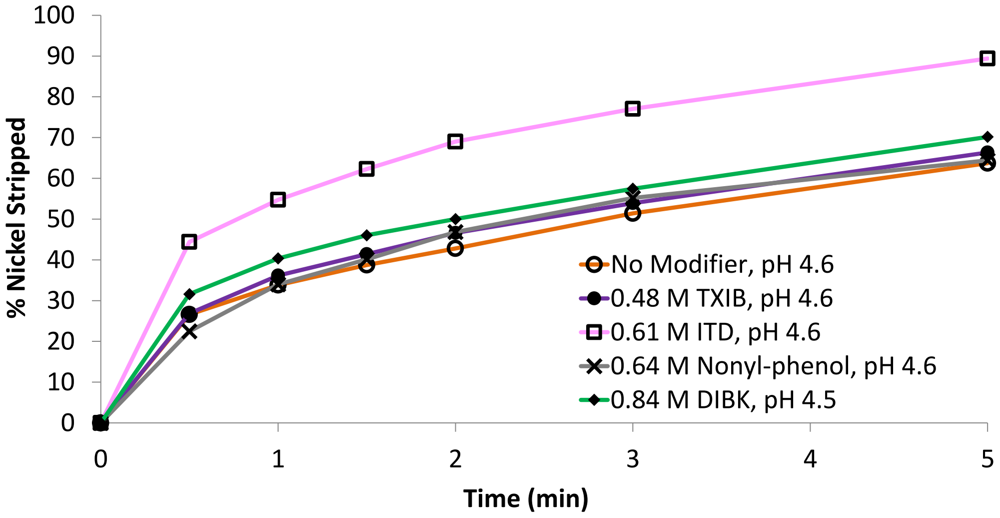


Figure 6-1: Effect of oxygen-based modifiers on nickel stripping rate from LIX 63 / Versatic 10 in ShellSol A150 by sulfuric acid (100 g/L). Loading pH given in legend. (Organic nickel = 3.7 – 3.9 g/L)

A substantial increase in the rate of nickel stripping on addition of TBP (0.53 M) to the organic phase (Figure 6-2), as previously observed by Cheng (2006) on loading from a sulfate matrix, persisted when loaded from a nitrate matrix. In the current work, accelerated nickel stripping similar to the effect of TBP was also observed with addition of Cyanex 921 (0.32 M) to the organic phase, a previously unreported outcome.

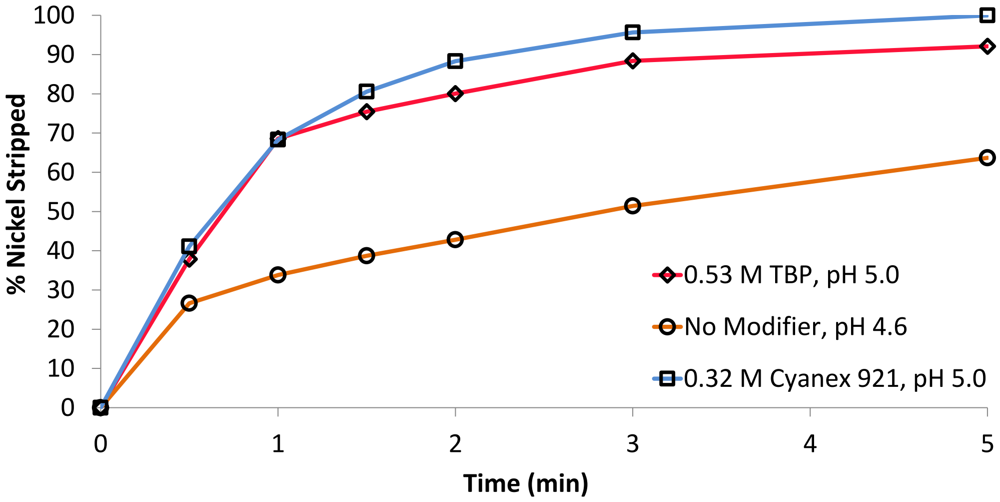


Figure 6-2: Effect of phosphorus-based modifiers on nickel stripping rate from LIX 63 / Versatic 10 in ShellSol A150 by sulfuric acid (100 g/L). Loading pH given in legend. (Organic nickel = 3.4 – 3.9 g/L)

The pyridine-based modifiers nonyl-4PC and 4-BP at a low concentration (0.1 M) both slightly increased the rate of nickel stripping from LIX 63 / Versatic 10

(Figure 6-3). CLX 50 at 0.1 M only had a minimal effect on nickel stripping and a greater concentration of CLX 50 (0.35 M) resulted in only a moderate increase in nickel stripping rate, very similar to that of 0.1 M 4-BP (69% nickel stripped after 5 min). In comparison, 80% of nickel was stripped in the presence of only 0.1 M nonyl-4PC after 5 min. Increasing the concentration of nonyl-4PC to 0.35 M further improved stripping rates over 0.1 M nonyl-4PC, resulting in full stripping of nickel within 2 min. Importantly, this resulted in faster nickel stripping than in the presence of 0.53 M TBP as used previously, where full stripping only occurred after 3 min.

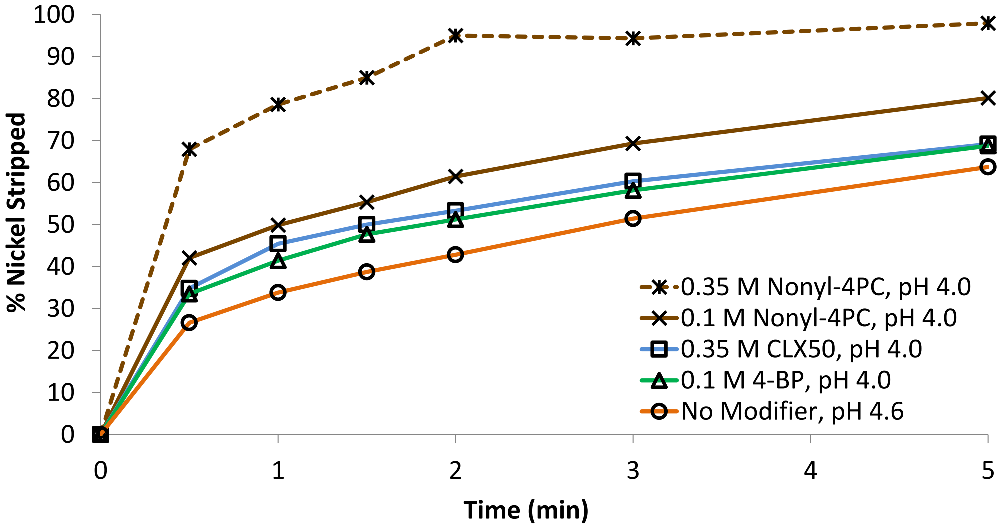


Figure 6-3: Effect of pyridine-based modifiers on nickel stripping rate from LIX 63 / Versatic 10 in ShellSol A150 by sulfuric acid (100 g/L). Loading pH given in legend. (Organic nickel = 3.6 – 4.0 g/L)

6.4.2 Effect of various modifiers on nickel extraction pH

Extraction pH isotherms were constructed to determine the effect of various modifiers on the pH of nickel extraction using LIX 63 / Versatic 10. The oxygen-based modifiers tested (TXIB, ITD, DIBK and nonyl-phenol) all shifted the extraction pH of nickel to slightly higher pH values. The pH_{50} shift for oxygen-based modifiers (Table 6-1) was generally under 0.3 units, with the exception of ITD (0.5 units).

Table 6-1: pH_{50} values for nickel extraction using LIX 63 / Versatic 10 with an added modifier and the calculated $\Delta pH_{50}(Ni)$ between the modified and unmodified organic phases

Modifier	$pH_{50}(Ni)$	$\Delta pH_{50}(Ni)$
No Modifier	2.2	0.0
0.48 M TXIB	2.5	0.3
0.61 M ITD	2.7	0.5
0.84 M DIBK	2.4	0.2
0.64 M nonyl-phenol	2.4	0.2
0.53 M TBP	3.3	1.1
0.32 M Cyanex 921	3.0	0.8
0.1 M 4-BP	2.2	0.0
0.1 M nonyl-4PC	2.2	0.0
0.35 M nonyl-4PC	2.3	0.1
0.35 M CLX 50	2.2	0.0

Both phosphorus-based modifiers (TBP and Cyanex 921) greatly increased the extraction pH_{50} for nickel. In the current work, adding Cyanex 921 to LIX 63 / Versatic 10 increased the extraction pH_{50} for nickel by 0.8 units (Table 6-1), just under the pH_{50} increase from addition of TBP (1.1 units). The increase in pH_{50} in the presence of TBP is consistent with the 0.5 to 1 pH unit shift known to occur in sulfate matrices (Cheng, 2006).

Cyanex 921 resulted in faster nickel stripping than TBP but still greatly increased the pH_{50} for nickel extraction. A large increase in the pH_{50} for nickel extraction somewhat negates the benefit of using the LIX 63 / Versatic 10 synergistic solvent system, as discussed in Section 6.2. In addition, a white waxy precipitate formed in the organic phase at pH 4 or above in the presence of Cyanex 921. This also occurred when using the aliphatic diluent ShellSol D70. The precipitate was insoluble in fresh diluent, deionised water or toluene, but was soluble in a nitric acid / diluent mixture. The acceleration of nickel stripping persisted after the precipitate was removed. Reloading the stripped organic then afforded further precipitate. It was suggested by Szolga (2015)[4] that the precipitate could be the sodium or magnesium salt of an impurity of Cyanex 921 (tri-octyl phosphinic acid), which is consistent with the observations already discussed. As Cyanex 921 was deemed unsuitable as a modifier due to a large pH_{50} increase for nickel, this phenomenon was not investigated further.

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[4] Szolga B., Applications Engineer for Cytec, personal email, 2015

Below pH 3.5 pyridine-based modifiers (4-BP, nonyl-4PC and CLX 50) had little effect on the extraction of nickel using LIX 63 / Versatic 10 at a given pH (Table 6-1). Above pH 3.5 the amount of nickel extracted in the modified solvent systems increased slightly above that of unmodified LIX 63 / Versatic 10 (Figure 6-4). When mixed with Versatic 10, pyridine-based reagents are known to extract nickel and cobalt synergistically from both nitrate and sulfate matrices. This was documented for alkyl-pyridines in nitrate by Preston and du Preez (2000) and for pyridine carboxylates in nitrate from current work (Section 4.3.4). It has been well documented from sulfate matrices for both pyridine carboxylates and alkyl-pyridines (Preston and du Preez, 1995, 2000; Cheng *et al.*, 2010a). In Section 4.3.4 the nickel pH_{50} for nonyl-4PC / Versatic 10 in a nitrate matrix was 4.4, 1.2 units higher than for LIX 63 / Versatic 10. A slight increase noted for nickel extraction above pH 3.0 in Figure 6-4 was therefore concluded to be attributable to the formation of nickel-pyridine-Versatic 10 complexes.

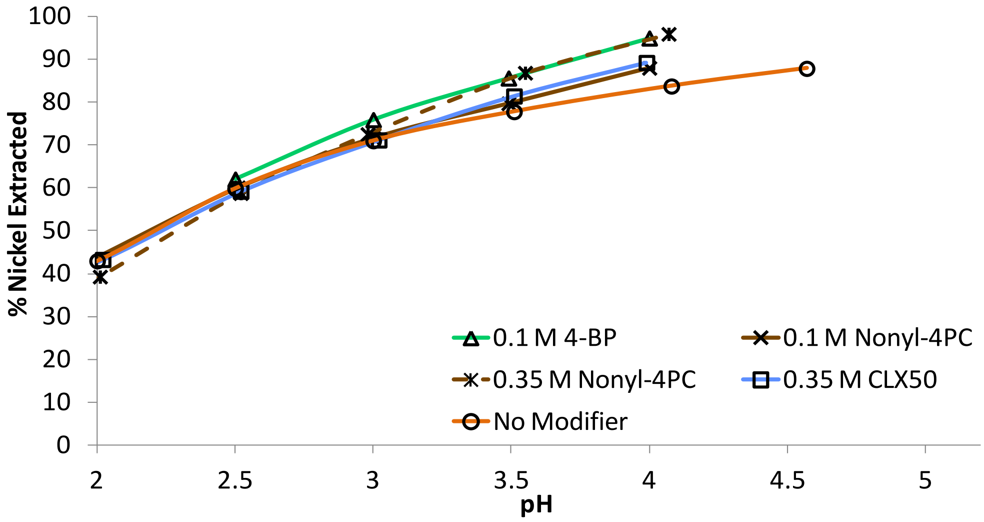

Figure 6-4: Effect of pyridine-based modifiers on nickel extraction pH with LIX 63 / Versatic 10 from magnesium nitrate (nickel = 4 g/L, magnesium = 50 g/L)

6.4.3 Effect of selected modifiers on nickel extraction rates

Nickel extraction rates for LIX 63 / Versatic 10 were determined in the presence of pyridine-based modifiers as these were the only modifiers that did not result in an increase in the nickel extraction pH. The individual effects on nickel extraction rates of ITD, as the most effective oxygen-based modifier, and TBP to benchmark against the work of previous authors, were also included. Extraction rates were measured at the pH_{90} for nickel extraction (approximately 3.7 g/L nickel), based on the pH isotherms constructed for Section 6.4.2. Higher loading pH values are known to accelerate nickel extraction with LIX 63 / Versatic 10 (Flett *et al.*, 1974). The pH_{90}(Ni) was thus used as a benchmark that compared rates at similar pH values but using the same total mass of loaded nickel. Results are reported as a percentage of equilibrium nickel loading.

Nickel extraction rates in the presence of 0.61 M ITD at pH 5.0 were very similar to those of unmodified LIX 63 / Versatic 10 at the same pH (Figure 6-5). Extraction rates for nickel using 0.53 M TBP as a modifier at pH 5.5 were slightly slower than that of unmodified LIX 63 / Versatic 10 at pH 5.0 (Figure 6-5). It is clear in the current work that TBP does not accelerate nickel extraction under the nitrate-based conditions tested. This observation for TBP differed from that of Cheng (2006) for nickel extraction from a sulfate matrix. Cheng (2006) claimed that TBP increased the rate of extraction from a sulfate matrix, from 80% to 95% after 5 min. The pH values used by Cheng (2006) were 4.0 for LIX 63 / Versatic 10 and 5.5 for LIX 63 / Versatic 10 / TBP to overcome the higher extraction pH (Cheng, 2015)[5]. The much higher pH value used for the TBP modified organic likely accelerated nickel extraction over that of LIX 63 / Versatic 10 at a lower extraction pH, as has also been noted for nickel extraction with LIX 63 / lauric acid by Flett *et al.* (1975).

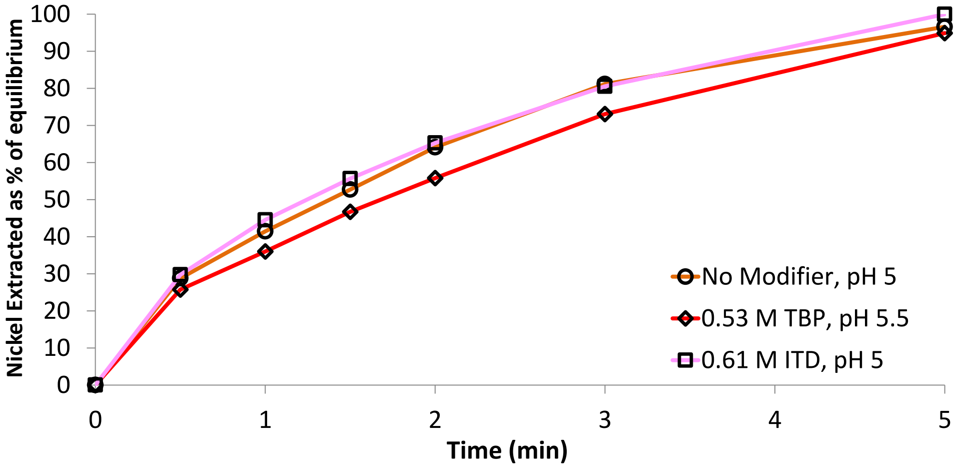

Figure 6-5: Effect of TBP and ITD on nickel extraction rate with LIX 63 / Versatic 10 in ShellSol A150 from magnesium nitrate (nickel = 4 g/L, magnesium = 50 g/L)

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[5] Cheng C.Y., original researcher for Cheng (2006), personal email, 2015

Compared with unmodified LIX 63 / Versatic 10 at pH 5, addition of either 0.1 M nonyl-4PC or 0.35 M CLX 50 had little effect on the rate of nickel extraction at pH 4 (Figure 6-6). Increasing the concentration of nonyl-4PC to 0.35 M slightly accelerated nickel extraction at pH 4, increasing extraction from 64% to 75% after 2 min. A 0.1 M 4-BP concentration further increased the extraction of nickel to 88% in 2 min. Of the modifiers tested only nonyl-4PC (0.35 M) and 4-BP (0.1 M) resulted in accelerated extraction kinetics for nickel with LIX 63 / Versatic 10.

Faster nickel extraction with 4-BP may be attributable to the higher basicity of this alkyl-pyridine compared with that of a pyridine carboxylate. The higher basicity of alkyl pyridines compared with pyridine carboxylates is due to the electron withdrawing effect of the carboxylate group decreasing the electron density on the pyridine nitrogen (Preston and du Preez, 1995). Faster nickel extraction may also be related to the higher aqueous solubility of 4-BP, which gives the reagent higher interfacial activity.

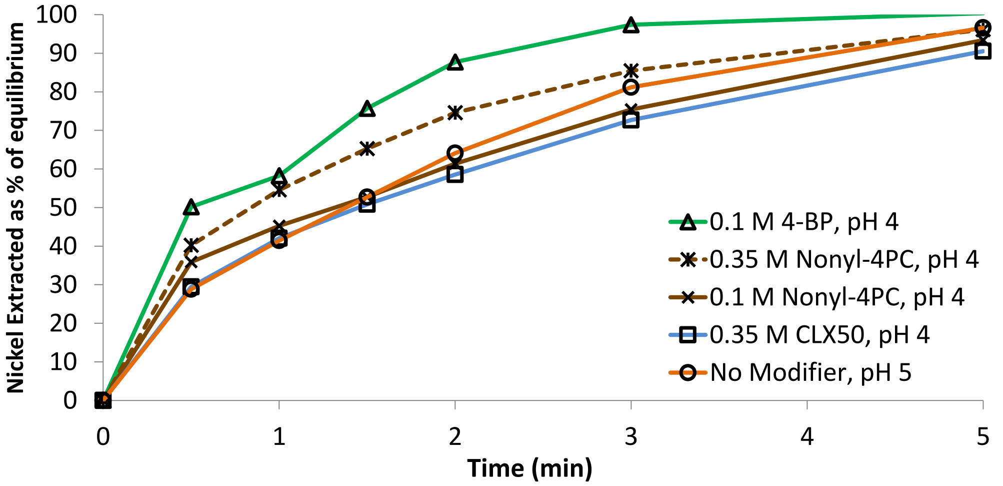


Figure 6-6: Effect of pyridine-based modifiers on nickel extraction rate with LIX 63 / Versatic 10 in ShellSol A150 from magnesium nitrate (nickel = 4 g/L, magnesium = 50 g/L)

6.4.4 Selection of the most appropriate accelerator for further work

Both phosphorus-based modifiers (TBP and Cyanex 921) greatly increased the rate of nickel stripping, doubling the amount stripped after 2 min (Figure 6-1). These two accelerators also greatly increased the pH_{50} for nickel extraction by at least 0.8 units (Table 6-1). The oxygen-based modifier offering the greatest nickel acceleration (ITD) marginally increased the rate of nickel stripped after 2 min to 69% from 43% (Figure 6-2) and also marginally increased the $pH_{50}(Ni)$ by 0.5 units (Table 6-1). These data support a correlation between faster nickel stripping and a larger increase in the equilibrium pH for nickel extraction. In copper SX, oxygen-based modifiers used with phenolic aldoximes to enhance copper stripping also increase the equilibrium pH and increase the stripping rate, discussed at length in Section 2.4.2. It is therefore likely that oxygen and phosphorus-based modifiers accelerate nickel stripping from LIX 63 / Versatic 10 via the same mechanism. That is, they associate with the active reagent in the organic phase and hinder formation of a metal–reagent complex. A definitive mechanism for the acceleration effect of oxygen and phosphorus-based modifiers is of interest, but was not pursued in the present work as they were not deemed superior to TBP for application to LIX 63 / Versatic 10.

Nonyl-4PC and 4-BP both increased stripping rates of nickel but did not increase the pH required for nickel extraction. Faster extraction rates were also found when using 4-BP as an accelerator, but it suffered from limited solubility in non-polar diluents. Aliphatic diluents are industrially preferred over highly aromatic diluents due to health and safety reasons (Bien, 2014). Aromatic diluents were also considered inappropriate for application to a DNi PLS (Section 2.8.1) because of the potential for degradation of the diluent. Nonyl-PC best satisfied the three selection criteria laid out in Section 6.1; it offered accelerated nickel stripping at relatively low concentration compared with TBP without increasing the required pH for extraction. Nonyl-4PC was therefore selected as the most promising nickel accelerator for LIX 63 / Versatic 10 in a de-aromatised diluent (ShellSol D70).

6.4.5 Effect of nonyl-4PC on nickel extraction with LIX 63 / Versatic 10

As the mixture of nonyl-4PC / Versatic 10 is known to be synergistic for nickel, the behaviour of nonyl-4PC in the presence of LIX 63 / Versatic 10 and the mechanism for increased phase transfer rates was of particular interest. In Section 6.4.1, it was found that progressive addition of nonyl-4PC (0, 0.1, 0.35 M) to LIX 63 / Versatic 10 resulted in progressively faster nickel stripping and extraction with no change to the obtained pH isotherm below pH 3.5 (Figure 6-4). Based on these results it was hypothesised that nonyl-4PC may be acting as a phase transfer catalyst, helping to move nickel across the interface without being involved in any thermodynamically stable nickel complex, or reagent–

modifier hydrogen-bonded arrangement, in the organic phase. The following sections describe the work investigating this hypothesis.

Nickel extraction pH isotherms were generated using LIX 63, Versatic 10, nonyl-4PC, and their mixtures, dissolved in ShellSol D70 (Figure 6-7). Nonyl-4PC as a single reagent did not extract nickel in the tested pH range. Comparing the pH_{50} of nickel extracted by Versatic 10 alone (pH_{50} 5.4) and LIX 63 alone (pH_{50} 4.6) with the combined reagents (pH_{50} 1.9) revealed the well-documented synergistic shift of this mixture. Addition of nonyl-4PC to Versatic 10 similarly resulted in the expected synergistic shift in nickel extraction (pH_{50} 3.8) as has been observed from both sulfate and lower ionic strength nitrate matrices (Section 3.3.3). In contrast to these synergistic effects, the addition of nonyl-4PC to the LIX 63 / Versatic 10 synergistic system had little effect on the extraction pH isotherm for nickel below pH 3.5 (Figure 6-7).

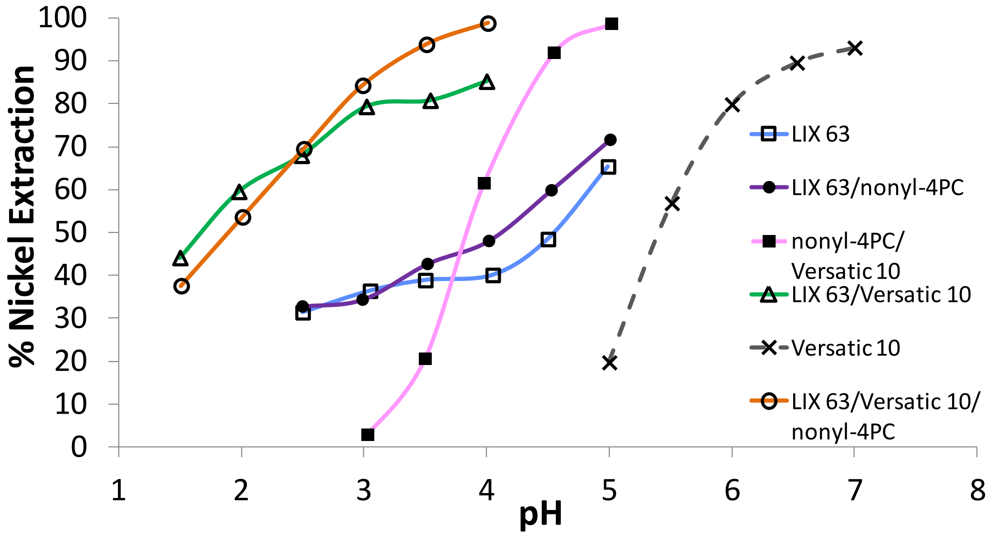


Figure 6-7: Nickel extraction pH isotherms for LIX 63, Versatic 10, nonyl-4PC, and their mixtures, from magnesium nitrate (nickel = 4 g/L, magnesium = 50 g/L)

As was determined from Figure 6-4, nickel extraction with LIX 63 / Versatic 10 / nonyl-4PC actually increased above that of the unmodified organic phase at pH values of 3.5 and above. This suggested the formation of nickel complexes containing nonyl-4PC. Similar differences in the extraction pH isotherms for LIX 63 and LIX 63 / nonyl-4PC could also potentially be explained by formation of mixed ligand complexes containing both nonyl-4PC and LIX 63, thereby shifting nickel equilibrium towards the organic phase. Additional UV-Vis data (Appendix C) collected when generating the pH isotherms supported this possibility by revealing different organic phase UV-Vis spectra, and therefore different nickel coordination environments, between the two solvent systems. As nickel extraction with LIX 63 alone or LIX 63 / nonyl-4PC occurred at a much higher pH than LIX 63 / Versatic 10, these reagent combinations were not of interest for further study.

Although nonyl-4PC / Versatic 10 did not extract nickel at pH 3 (Figure 6-7), nickel extraction by LIX 63 / Versatic 10 was greatly accelerated by the presence of nonyl-4PC regardless of the pH (Figure 6-8). At pH 3, where nonyl-4PC / Versatic 10 did not extract nickel in its own right, the rate of nickel extraction by LIX 63 / Versatic 10 / nonyl-4PC was the same as at pH 5, where nonyl-4PC / Versatic 10 extracted the majority of nickel present. Formation of thermodynamically stable nonyl-4PC / Versatic 10 complexes with nickel are not, therefore, the sole reason for accelerated nickel extraction.

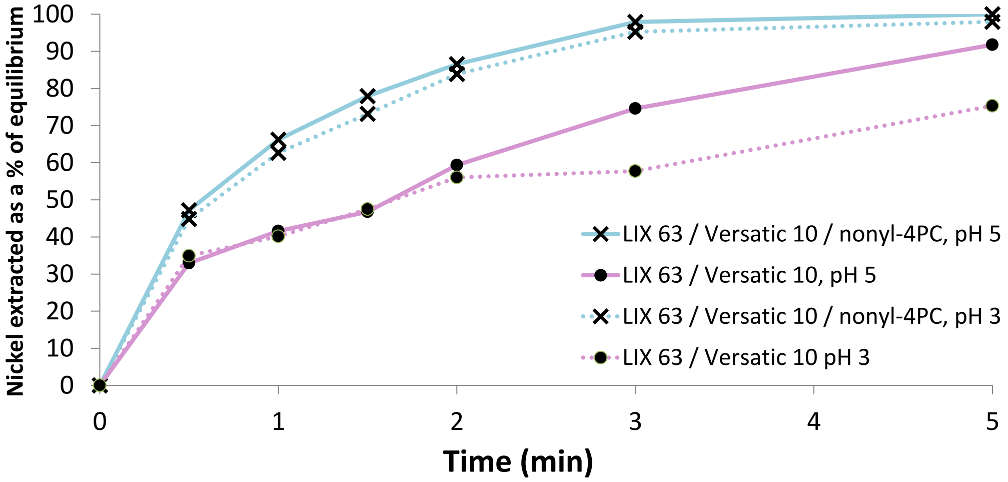


Figure 6-8: Effect of nonyl-4PC on the extraction of nickel by LIX 63 / Versatic 10 in ShellSol D70 above and below the pH where nonyl-4PC / Versatic 10 extracted nickel (nickel = 4 g/L, magnesium = 50 g/L)

6.4.6 Effect of nonyl-4PC on nickel stripping from LIX 63 / Versatic 10

In the current investigation, only 48% of nickel was stripped from LIX 63 alone after 5 min (Figure 6-9). Stripping from Versatic 10 itself was fast and reached equilibrium (100%) after only 0.5 min. Addition of Versatic 10 to LIX 63, however, only marginally increased the rate of nickel stripping from LIX 63 to 62% after 5 min. Although slow stripping of nickel from LIX 63 / Versatic 10 has been well documented in the literature, the mechanism for nickel stripping from

LIX 63 and LIX 63 / Versatic 10 is still uncertain. This was not investigated in the current thesis as this work was concerned with the application of modifiers to accelerate the stripping of nickel from LIX 63 / Versatic 10.

Nickel stripping from both LIX 63 and LIX 63 / Versatic 10 was dramatically accelerated by the presence of nonyl-4PC (Figure 6-9). This increase in nickel stripping rate occurred despite negligible changes in the position of the extraction pH isotherms for either LIX 63 or LIX 63 / Versatic 10 (Figure 6-7). This additional evidence supports the premise that nickel stripping is accelerated by nonyl-4PC alone, and not an association between nonyl-4PC and Versatic 10.

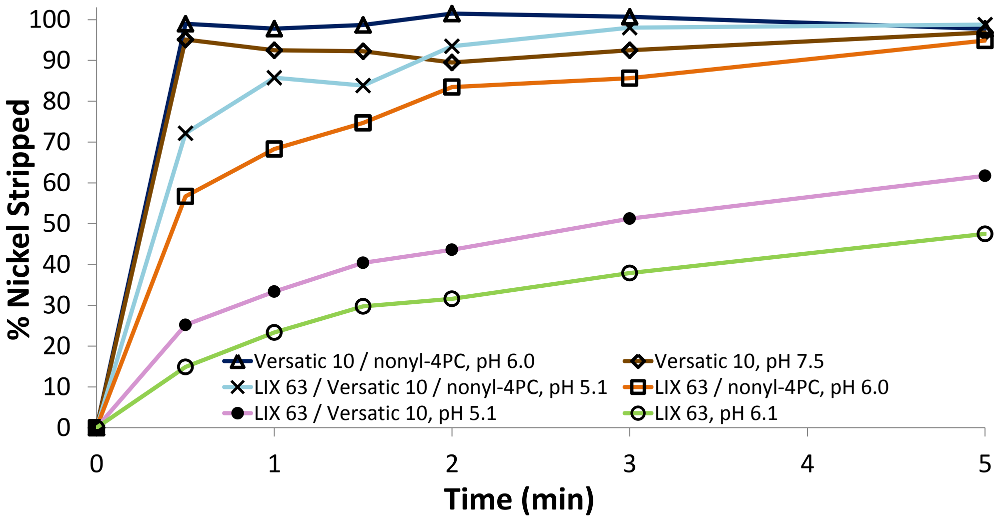


Figure 6-9: Nickel stripping from LIX 63, Versatic 10 and LIX 63 / Versatic 10, with and without nonyl-4PC, dissolved in ShellSol D70 by sulfuric acid (50 g/L). Loading pH given in legend. (Organic nickel = 3.7 – 4.0 g/L)

6.4.7 Effect of nonyl-4PC on nickel coordination with LIX 63 / Versatic 10

UV-Vis analysis was used in the following section to determine if nonyl-4PC was affecting the coordination environment of nickel in LIX 63 / Versatic 10. Formation of different mixed ligand complexes of a metal ion can sometimes be determined from changes in the UV-Vis spectra of the loaded organic phase. These changes arise from alterations in the electron transition energies due to different coordinating ligands and central metal ion geometry.

As LIX 63 / Versatic 10 and nonyl-4PC / Versatic 10 are synergistic for nickel, nickel extraction with these mixtures will result in mixed ligand nickel complexes in the organic phase. Such a finding is well-documented for nickel extraction with LIX 63 / Versatic 10, where the organic phase nickel complex is predicted to be octahedral as either Ni(Oxime)$_2$(Versatic 10)$_2$ or [Ni(Oxime)$_3$](Versatic 10)$_2$ (Castresana *et al.*, 1988; Barnard *et al.*, 2010b; Barnard, 2011). Formation of octahedral mixed ligand complexes for nickel is also well documented for Versatic 10 / pyridine carboxylates (PC) where the organic phase nickel complex is predicted by Preston and du Preez (1994, 1995) to be Ni(PC)$_2$(Versatic 10)$_2$(H$_2$O)$_2$.

Addition of nonyl-4PC to Versatic 10 resulted in a shift in the absorbance maximum for nickel from 675 nm down to 625 nm (Figure 6-10). Addition of LIX 63 to Versatic 10 resulted in a different shift from nonyl-4PC, down to 600 nm at low concentration (Figure 6-10) or similarly 605 nm at a higher concentration (Figure 6-11). A comparable UV-Vis spectrum containing a major peak at 601 nm was also reported for nickel extracted from a sulfate matrix with LIX 63 / Versatic 10 by Barnard *et al.* (2010b). As already discussed above, nickel is expected to be octahedral in both nonyl-4PC / Versatic 10 and LIX 63 / Versatic 10. LIX 63 binds via an oxime nitrogen and alcohol oxygen, Versatic 10 via a carboxylate group, and nonyl-4PC via a pyridine nitrogen. Different shifts are therefore obtained for the nickel peaks between nonyl-4PC / Versatic 10 and LIX 63 / Versatic 10.

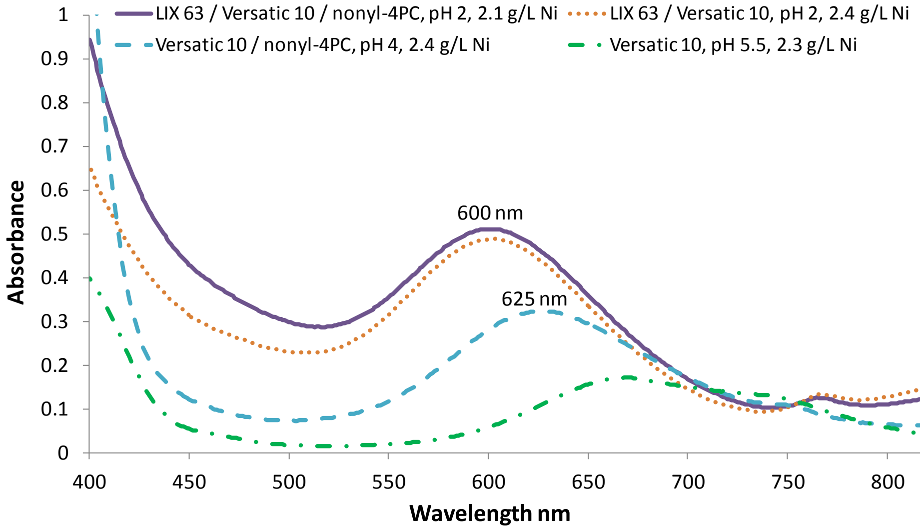


Figure 6-10: UV-Vis spectra for low concentrations of nickel extracted with different mixtures of LIX 63, Versatic 10 and nonyl-4PC

Addition of nonyl-4PC to LIX 63 / Versatic 10 had no effect on the absorbance maxima in the UV-Vis spectrum. This persisted both at low loading pH where nonyl-4PC / Versatic 10 did not extract nickel (Figure 6-10) and at higher loading pH where nonyl-4PC / Versatic 10 was able to extract nickel (Figure 6-11). Nonyl-4PC was therefore not able to displace either of the other two ligands to enter the nickel coordination sphere in sufficient amounts to change the UV-Vis spectrum, regardless of the extraction pH.

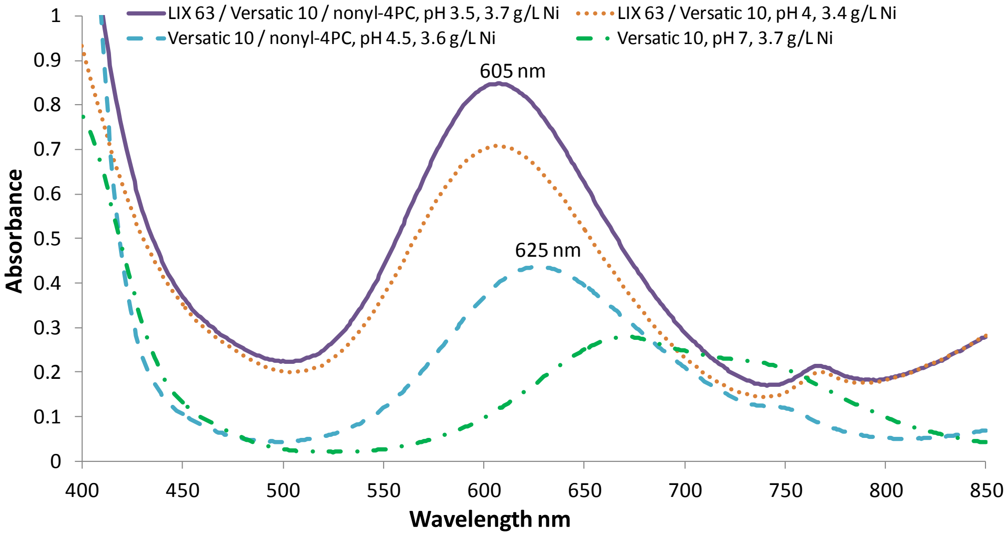


Figure 6-11: UV-Vis spectra for high concentrations of nickel extracted with different mixtures of LIX 63, Versatic 10 and nonyl-4PC

The results presented in the preceding sections show that there are different coordination environments for nickel in the LIX 63 / Versatic 10 organic phase and the nonyl-4PC / Versatic 10 organic phase. Additionally, there is no evidence to suggest that addition of nonyl-4PC to LIX 63 / Versatic 10 resulted in a change in the coordination environment for nickel. Whilst this outcome is not definitive by itself, when combined with the lack of change in nickel extraction pH isotherms on addition of nonyl-4PC to LIX 63 / Versatic 10, it demonstrates that nonyl-4PC is not involved in the equilibrium nickel complex extracted by LIX 63 / Versatic 10 / nonyl-4PC. This is further supported by both (a) the increase in nickel extraction rates on addition of nonyl-4PC to LIX 63 / Versatic 10 above and below the pH of nickel extraction by nonyl-4PC / Versatic 10 and (b) the increase in nickel stripping rates on addition of nonyl-4PC to either LIX 63 / Versatic 10 or LIX 63 alone. Nonyl-4PC therefore acts as a phase transfer catalyst in the three-reagent system, helping to move nickel across the aqueous–organic interface without taking part in the organic phase nickel complex formed at equilibrium.

It is known that at low pH pyridine-based reagents are able to extract protons into the organic phase by acting as an organic base (du Preez *et al.*, 2007). It is proposed here that nonyl-4PC aids nickel stripping by extracting protons at low pH. This would result in a rapid intra-phase reaction between the organic phase-based protons and nickel complex, overcoming the need for proton transfer between the nickel complex and aqueous phase protons at the interface (Figure 6-12). This proposed mechanism is consistent with the observation that more basic and more aqueous soluble pyridine-based modifiers (nonyl-4PC and 4-BP) resulted in improved phase transfer rates for nickel over the less basic and more organic soluble CLX 50. It is also consistent with a progressively faster rate of nickel stripping with increasing nonyl-4PC concentrations.

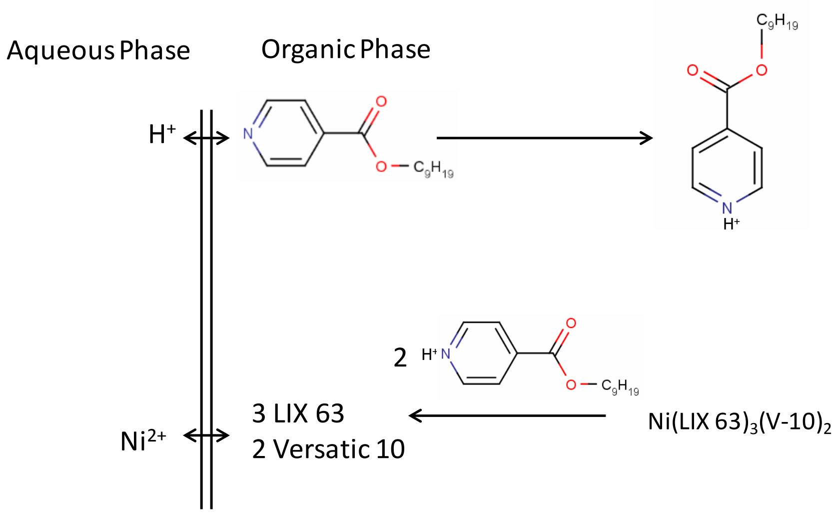


Figure 6-12: Schematic for the proposed stripping mechanism of nickel from LIX 63 / Versatic 10 (V-10) in the presence of nonyl-4PC

The mechanism for the enhanced rate of nickel extraction is less clear. As nonyl-4PC is an organic base it could potentially facilitate deprotonation of either the hydroxyoxime or carboxylic acid, thereby making them more interfacially active (Figure 6-13). Alternatively, it may allow formation of a thermodynamically unstable nonyl-4PC-based nickel complex, which can convert to a stable nickel–LIX 63–Versatic 10 complex once in the organic phase (Figure 6-14). Although this mechanism warrants further research it was outside the scope of the current project, which was to find a modifier that could accelerate phase transfer of nickel without increasing the required extraction pH. This objective has been met.

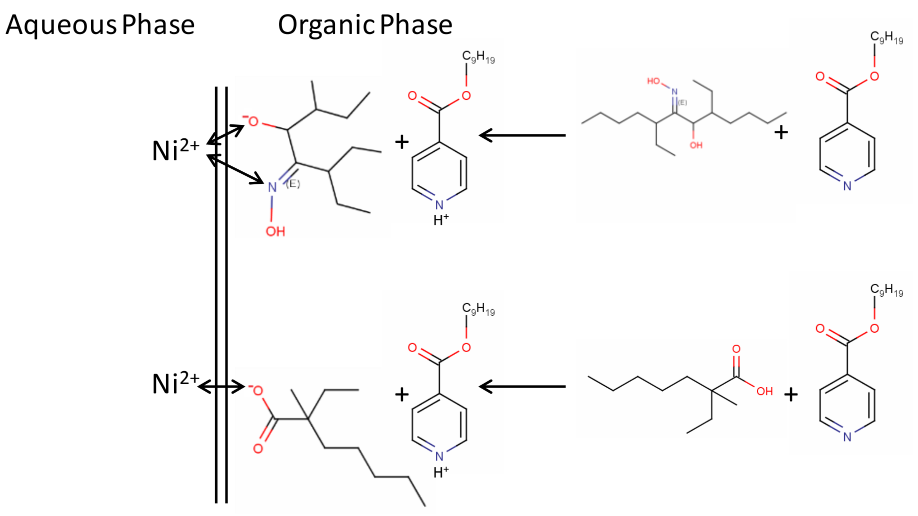


Figure 6-13: Schematic for a potential nickel extraction mechanism for LIX 63 / Versatic 10 in the presence of nonyl-4PC

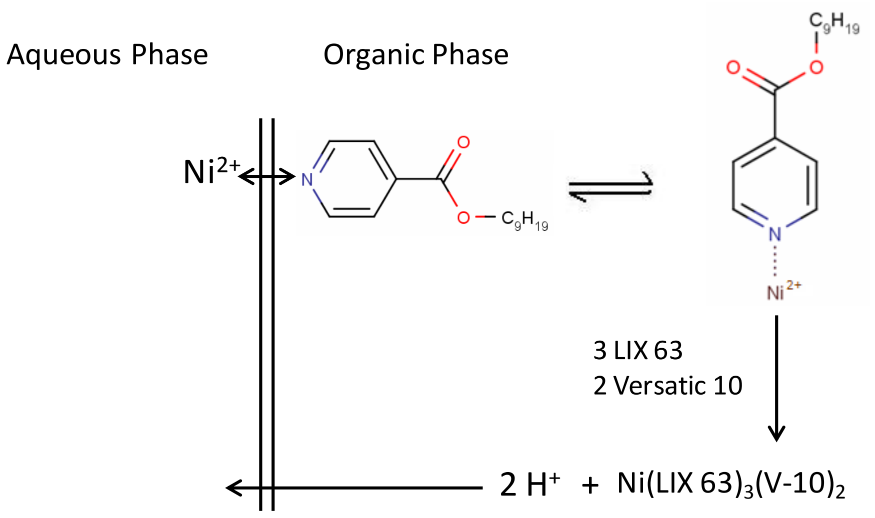


Figure 6-14: Schematic for a potential nickel extraction mechanism for LIX 63 / Versatic 10 (V-10) in the presence of nonyl-4PC

6.5 Conclusions

The current chapter investigated the effect of modifiers on nickel stripping from LIX 63 / Versatic 10. The aim of the chapter was to investigate methods to accelerate the phase transfer of nickel for any potentially promising solvent systems identified that suffer from slow nickel extraction or stripping rates. In this regard, a modifier was required that could accelerate nickel stripping from LIX 63 / Versatic 10 at lower concentrations than for the currently proposed modifier TBP, without dramatically increasing the required pH for extraction of nickel. The results of this investigation revealed that:

- Phosphorus-based modifiers (TBP and Cyanex 921) greatly increased the rate of nickel stripping (80% stripped with TBP after 2 min) above that of oxygen-based modifiers (ITD, TXIB, DIBK and nonyl-phenol) under similar conditions (69% stripped with ITD after 2 min). In comparison, lower concentrations (0.35 M compared to >0.5 M) of the pyridine-based modifier nonyl-4PC accelerated the rate of nickel stripping over that of either oxygen or phosphorus-based modifiers (95% stripped in 2 min).

- Oxygen or phosphorus-based modifiers that resulted in faster stripping of nickel (TBP, Cyanex 921 and ITD) also resulted in a higher pH of extraction (ΔpH_{50} of 1.1 for TBP compared with 0.5 for ITD). Pyridine-based modifiers had no effect on the extraction pH for nickel with LIX 63 / Versatic 10 below the point where nickel was extracted by nonyl-4PC / Versatic 10. Above this pH point, the extraction of nickel began to increase above that of LIX 63 / Versatic 10 as the nickel equilibrium was shifted slightly towards the organic phase, likely via formation of nickel–pyridine–Versatic 10 complexes.

- Nickel extraction from a nitrate matrix with LIX 63 / Versatic 10 was slightly retarded by the addition of TBP (64% to 56% stripped after 2 min), contrary to the claims of previous authors studying sulfate-based matrices. In contrast, pyridine-based modifiers accelerated the rate of nickel extraction, increasing to 75% after 2 min on addition of 0.35 M nonyl-4PC and 88% on addition of 0.1 M 4-BP.

- It was hypothesised that oxygen and phosphorus-based modifiers accelerated the stripping of nickel via the same mechanism as oxygen-based modifiers enhance copper stripping from phenolic oximes, based on their similar equilibria and kinetic behaviours. That is, they form oxime–modifier complexes in the organic phase that hinder metal extraction by shifting the extraction to higher pH values. This was proposed on the basis of increasing extraction pH, accelerating stripping, and retarding extraction rates.

- Addition of nonyl-4PC to LIX 63 / Versatic 10 increased both the nickel stripping and extraction rates without affecting the extraction pH or the UV-Vis spectrum of the extracted nickel complex. This behaviour is consistent with nonyl-4PC behaving as a phase transfer catalyst. The mechanism for stripping of nickel appeared to be facilitated by the ability of nonyl-4PC to extract protons into the organic phase and thereby overcome the requirement of inter-phase or near inter-phase transfer between the organic phase nickel complex and aqueous phase protons.

- The modifier nonyl-4PC satisfied the criteria of generating faster stripping of nickel than that of TBP at a comparably lower concentration (0.35 M for nonyl-4PC compared with 0.53 M for TBP) without increasing the required extraction pH for nickel. Nonyl-4PC was therefore the most suitable modifier for nickel recovery using LIX 63 / Versatic 10.

CHAPTER 7
Modelling the effect of reagent concentrations in LIX 63 / Versatic 10 / nonyl-4PC on nickel extraction, nickel stripping and cobalt extraction

7.1 Introduction

Earlier in this thesis, LIX 63 / Versatic 10 with nonyl-4PC as an accelerator for nickel stripping was developed as a promising solvent system for the separation of nickel and cobalt from magnesium. This is a novel combination of three reagents and the effect of variations in the different reagent concentrations on the performance of the solvent system was unknown.

The aim of the current chapter was to determine optimal reagent concentrations for any novel solvent systems suited to separation of nickel and cobalt from magnesium. Nickel extraction and nickel stripping are key parameters for the economic success of a solvent system applied to a nickel laterite PLS. Statistical experimental design was therefore used to generate predictive models for the extraction and stripping of nickel, as well as the extraction of cobalt as a valuable co-product, to investigate the effect of the three reagent concentrations on these three factors. The predictive models were then used to generate optimum reagent concentrations for maximising nickel extraction and stripping whilst minimising reagent concentrations. Lower reagent concentrations reduce costs by lowering reagent hold-up and by reducing organic viscosity thereby improving settling performance.

7.2 Materials and Methods

7.2.1 Aqueous and organic solutions

The following chemicals were used to make up the aqueous phases: magnesium nitrate, nickel nitrate, cobalt nitrate, nitric acid and sulfuric acid. The aqueous feed for metal extraction tests consisted of nickel (4 g/L), cobalt (0.15 g/L) and magnesium (60 g/L) as nitrates to mimic the matrix and nickel and cobalt concentrations expected from a nitrate-based nickel laterite PLS. The magnesium concentration of 60 g/L was higher than that used in Section 6.3.1 as Direct Nickel staff advised that actual leach liquors would likely contain concentrations of magnesium higher than 50 g/L. The aqueous strip solution was sulfuric acid (50 g/L) in deionised water. The following solvent extraction reagents diluted with ShellSol D70 were used in this investigation: LIX 63, Versatic 10 and nonyl-4PC.

7.2.2 Metal extraction and stripping procedures

Organic phases for each extraction and stripping test were made up of varying concentrations of LIX 63, Versatic 10 and nonyl-4PC in ShellSol D70 and contacted using a comparable method to the stripping and extraction rates detailed in Section 6.3.3, except at 40 °C. A slightly higher temperature for this investigation was useful as it was easier to control a water bath in the laboratory at a constant 40 °C. For the extraction tests, the aqueous–organic mixtures were kept at pH 2. After 2 min a sample was taken and immediately filtered through Whatman 1 PS phase separation paper. After sampling, the mixture was brought to pH 4 for 10 min to ensure it was fully loaded for use in the stripping test. For the stripping test, the aqueous strip solution was added to the agitated residual loaded organic from the extraction test after they had both reached 40 °C. A sample of the aqueous–organic mixture was taken after 2 min and immediately filtered through 1PS paper.

7.2.3 Analytical determinations

Aqueous phases for analysis were prepared as in Section 6.3.4. Aqueous metal concentrations were determined as per Section 3.2.3.

7.2.4 Development of the statistical experimental design

A statistical experimental design, often abbreviated as DOE (design of experiment), is an efficient experimental matrix to generate the maximum information from the smallest number of experiments (Anderson and Whitcomb, 2000). The conventional method for optimising reagent concentrations in two reagent solvent systems involves changing one reagent concentration whilst holding the other constant (Preston and du Preez, 1995; Cheng, 2006; du Preez *et al.*, 2007). This method of testing only one reagent concentration at a time often fails to determine potential interactions between the two reagents because only one concentration is changed between experiments, and often insufficient experiments are carried out.

DOE allows prediction of interaction effects between the reagents in the organic phase through fewer experiments than a conventional matrix changing one reagent at a time. It also allows the generation of predictive models via statistical regression techniques and the method of least squares. There are many examples where DOE has been successfully applied to solvent extraction and ion exchange, including investigations of nickel loading of Cyanex 272 (Olivier *et al.*, 2012), optimising a process for nickel and cobalt recovery using Versatic 10 and Cyanex 272 (Tsakiridis and Agatzini, 2004), and the recovery of heavy metals using ion exchange (Lee *et al.*, 2006).

For the DOE generated in this work, the responses measured were nickel extracted at pH 2.0 after 2 min, cobalt extracted at pH 2.0 after 2 min and nickel stripped with 50 g/L sulfuric acid after 2 min. A loading pH of 2.0 was chosen to produce a large enough variation in nickel extraction to adequately model the effect of the three reagents. If a high loading pH was chosen (e.g., pH 4.0), then nickel extraction would be clustered just below 100%. Conversely, at a very low loading pH (e.g., pH < 1), nickel extraction would be clustered just above 0%. A reaction time of 2 min was chosen to allow an assessment of the effect of different reagent concentrations in a time-limited scenario of relevance to a commercial operation. For 0.31 M LIX 63 / 0.35 M Versatic 10 / 0.35 M nonyl-4PC, nickel extraction and stripping only reached equilibrium after two or more minutes in Section 6.4.1 and Section 6.4.3.

The solvent extraction of nickel and cobalt should result in 'S' shaped extraction or stripping curves over a very wide range of reagent concentrations. Too many experiments would be required to accurately model this full system. It is often possible, however, to predict the response of a chemical system with simpler linear or quadratic models when using a smaller defined range of process factors (Anderson and Whitcomb, 2005). Initial experiments therefore produced linear (straight line) models. The DOE was constructed so that augmenting the models to quadratic (parabolic) models was possible if the results obtained fell over a curved portion of the S curve.

A full factorial 2^3 (two-level, three-factor) DOE with four centre point replicates, requiring 12 experiments, was chosen as it provides the highest possible data resolution to generate linear models for three factors. This means that coefficients could be calculated for every factor in the generated models; hence interaction effects between the three different reagent concentrations could be accurately predicted. In the DOE generated, the factors were the three reagent concentrations and their levels were the varying concentrations. The three experimental factors and their chosen low (−1) and high (+1) levels used in the 2^3 design are shown in Table 7-1. The statistical software Design Expert 8.0.5 (Stat-Ease, U.S.A.) was used to perform analysis of variance (ANOVA) calculations and to generate predictive models using the method of least squares.

Table 7-1: Experimental factors and their levels used for the 2^3 full factorial experimental design

Factor	Name	Low Level (−1) M	High Level (+1) M
A	[LIX 63]	0.22	0.44
B	[Versatic 10] ([V10])	0.15	0.50
C	[nonyl-4PC] ([4PC])	0.15	0.50

The levels of each factor were chosen based on their stoichiometric requirements. The low level (−1) for Versatic 10 was chosen to be close to stoichiometry for full extraction of nickel and cobalt assuming two Versatic 10 molecules extracted per synergistic complex, as described by other authors (Flett *et al.*, 1974; Tammi, 1976; Castresana *et al.*, 1988). The LIX 63 low level was chosen to be about 65% of the stoichiometric requirement assuming three LIX 63 molecules are extracted per synergistic complex (Tammi, 1976; Barnard *et al.*, 2010a; Barnard and Turner, 2011b) and assuming a ratio of active *anti* to inactive *syn* oxime isomers of 60:40 in commercial LIX 63 (Barnard and Turner, 2008). A LIX 63 concentration of 0.35 M is required to extract 4 g/L nickel using these same assumptions. A sub-stoichiometric low level for LIX 63 allowed an assessment of limiting the concentration of this more costly reagent. High levels of LIX 63 and Versatic 10 (+1) were all chosen to be in excess of stoichiometric requirements and to give the same mid-point (factor level 0) for the reagents (0.33 M).

A possible acid–base reaction exists between nonyl-4PC and Versatic 10 at a 1:1 molar ratio to form an organic salt. This reaction may alter the efficacy of nonyl-4PC as a nickel accelerator by sequestering it into an organic salt. The same high and low levels as Versatic 10 were therefore chosen for nonyl-4PC so that nonyl-4PC speciation was not always dominated by association with the organic acid.

7.2.5 Optimisation of reagent concentrations

The reagent concentration models generated from the DOE were used as inputs to an optimisation calculation that minimised reagent concentrations whilst maximising nickel extraction and nickel stripping. The calculation converted all defined criteria into individual desirabilities (d_i) to generate an overall desirability (D) as the geometric mean of d_i. Each d_i (between 0 and 1) was calculated by plotting a straight line between the minimum and maximum values used for a factor (reagent concentration) or obtained for a response (e.g., nickel extraction). If the goal was to minimise a given parameter, the low value (e.g., 0.15 M) was set to 1 and the high value (e.g., 0.5 M) to 0. If the goal was to maximise, the high value was set to 1 and the low value to 0. Importance factors (r_i) between 1 and 5 were applied to each individual d_i and the overall D was calculated (EQ 8). The highest value of D was then obtained by iterating this calculation using a variable-sized simplex optimisation.

$$D = \left(\prod_{i=1}^{n} {d_i}^{r_i}\right)^{\frac{1}{\Sigma r_i}} \tag{EQ 8}$$

7.3 Results and discussion

Linear and subsequently augmented quadratic models were initially produced to predict the experimental results. These models were used to provide insight into nickel extraction, nickel stripping and cobalt extraction. They were then used to produce optimised reagent concentrations for the extraction and stripping of nickel whilst minimising their concentrations in the organic phase.

7.3.1 Generation of linear models

The results for each experiment from the 2^3 full factorial design to generate linear models are shown in Table 7-2. The ratio of maximum to minimum response for cobalt extraction was less than 10 (9.06), suggesting that a logarithmic (log) transformation of the data was required. A Box-Cox plot of the natural log of the residual sum-of-squares (ln(residualSS) or the sum of the squared deviations between the model prediction and the measured result) versus lambda (the power to which the results are raised) was used to determine the suitability of this data transformation (Figure 7-1). A minimum ln(residualSS) at 0 lambda indicated that a log transformation of the data may be required. The model for cobalt extraction was therefore generated for $\log_{10}$(%Co Extracted). No data transformation was required for the other linear models of %Ni Extracted and %Ni Stripped.

Table 7-2: Untransformed results of the randomised 2^3 full factorial design against reagent concentrations as coded factor levels (for factor levels given in Table 7-1)

Run	A [LIX63]	B [V10]	C [4PC]	% Ni Ex	% Ni St	% Co Ex
1	1	1	1	81.9	86.3	18.3
2	−1	1	−1	46.9	88.4	6.3
3	−1	−1	−1	41.9	78.5	3.1
4	1	1	−1	58.4	61.2	28.3
5	−1	−1	1	50.4	98.7	3.1
6	1	−1	−1	54.9	51.0	11.8
7	0	0	0	64.6	87.0	8.7
8	0	0	0	63.2	88.8	7.4
9	0	0	0	63.2	86.6	9.3
10	0	0	0	64.2	86.2	8.0
11	−1	1	1	58.3	96.1	3.7
12	1	−1	1	73.6	88.3	10.2

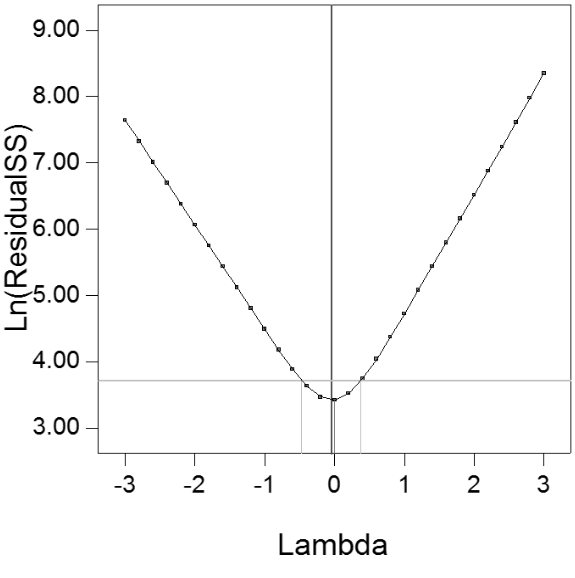


Figure 7-1: Box-Cox plot used as justification for selecting a log transform for cobalt extraction data

The ANOVA calculations for the linear models generated from the results in Table 7-2 were used to assess the viability of the models. An *F*-test on the difference between the weighted average of the replicated centre points and the weighted average of the factorial points produced significant curvature ($p < 0.05$) for all linear models. In addition, lack of fit F-tests for the linear regression models comparing the weighted sum of squared deviations between the mean response and the corresponding fitted value at each factor level were significant ($p < 0.05$) for all three models. These results indicated that none of the linear models accurately predicted the experimental results.

7.3.2 Generation of quadratic models

As statistical tests strongly indicated that linear models did not accurately predict the measured results, the experimental design was augmented to a central composite design (CCD) to account for curvature in the responses. This allowed quadratic models to be generated for each response. The experimental design was augmented to create a 'practical' CCD using an alpha of 1.316 (the fourth root of the number of factors), incorporating two extra replicate centre points. A practical CCD is the recommended default augmentation in the Design Expert software as it can simultaneously handle the requirements of rotatability and orthogonality for a CCD. Using the replicate centre points as a benchmark, these extra experiments were assigned to a separate statistical block. This allowed for unknown factors acting on the responses over the two experimental groups to be accurately handled by the statistical calculations. There were eight extra runs in the augmented experimental design, giving an overall total of 20 experiments. The randomised experimental design matrix for the extra runs, with the experimental results for each run, is shown in Table 7-3.

Table 7-3: Untransformed results of augmented experimental design against reagent concentrations in coded factor levels (factor levels given in Table 7-1)

Run	A [LIX63]	B [V10]	C [4PC]	%Ni Ex	%Ni St	%Co Ex
13	0	0	0	61.3	86.0	7.9
14	0	1.316	0	66.7	94.3	10.9
15	1.316	0	0	75.0	66.0	17.3
16	0	0	−1.316	50.0	63.4	20.2
17	−1.316	0	0	45.8	95.9	5.3
18	0	0	1.316	73.0	92.1	11.5
19	0	0	0	66.7	87.4	9.7
20	0	−1.316	0	56.4	92.3	5.0

Quadratic models, with reagent concentrations (in M) as inputs, were generated from the results in Table 7-2 and Table 7-3 for each of the following responses: %Ni extracted (EQ 9), %Ni stripped (EQ 10) and log(%Co extracted) (EQ 11).

Model fitting F-tests for all three models were significant ($p < 0.05$) and the lack of fit tests were insignificant ($p > 0.05$). The correlations between the actual experimental results and the predicted results from the quadratic models are shown in Figure 7-2. The strong 1:1 correlation for all three models, combined with the results from significance testing, is a good indication that they can be used to accurately analyse the effect of the three reagent concentrations on nickel extraction, nickel stripping and cobalt extraction within the concentration ranges given in Table 7-1. The following results sections in this chapter will therefore use these generated models to provide insight into the solvent extraction process and to perform optimisation calculations.

$$\%\text{Ni Ex} = 0.5 + 174[\text{LIX63}] + 19[\text{V10}] + 37[\text{4PC}] + 144[\text{LIX63}][\text{4PC}] - 204[\text{LIX63}]^2 - 60[\text{4PC}]^2 \qquad \text{(EQ 9)}$$

$$\%\text{Ni St} = 66 + 41[\text{LIX63}] - 31[\text{V10}] + 140[\text{4PC}] + 223[\text{LIX63}][\text{4PC}] - 101[\text{V10}][\text{4PC}] - 309[\text{LIX63}]^2 + 112[\text{V10}]^2 - 181[\text{4PC}]^2 \qquad \text{(EQ 10)}$$

$$\log(\%\text{Co Ex}) = 0.06 + 2.5[\text{LIX63}] + 2.6[\text{V10}] - 2.4[\text{4PC}] - 2.8[\text{V10}]^2 + 3.1[\text{4PC}]^2 \qquad \text{(EQ 11)}$$

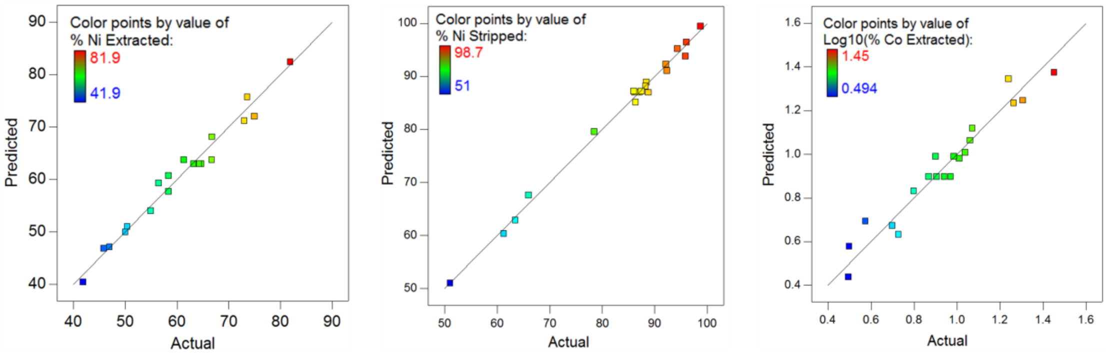
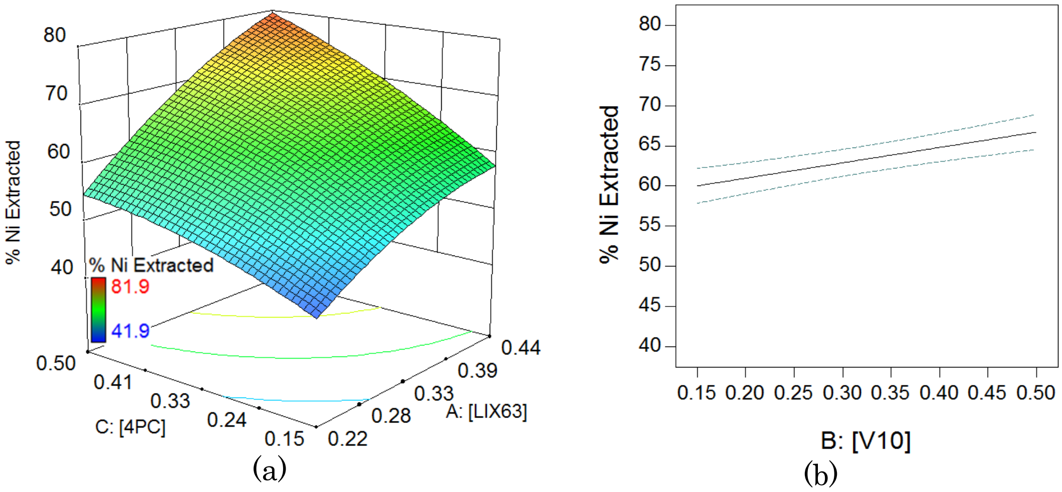


Figure 7-2: Experimental results plotted against the predictions from the three response models for %Ni Extracted (left), %Ni Stripped (middle), and log(%Co Extracted) (right)

7.3.3 Effect of the concentration of each reagent on nickel extraction

The interaction between LIX 63 and nonyl-4PC had the greatest effect on nickel extraction (EQ 9). As a result of this interaction, high LIX 63 concentrations (0.44 M) resulted in a more dramatic increase in nickel extraction with increasing nonyl-4PC concentration, from 58% to 82% (Figure 7-3, a). Similarly, at high concentrations of nonyl-4PC (0.5 M) there was a more dramatic increase in nickel extraction with increasing LIX 63 concentration from 55% to 82%. In contrast, increasing Versatic 10 concentrations with 0.33 M LIX 63 and 0.33 M nonyl-4PC had minimal effect on nickel extraction, improving from 60% at 0.15 M to only 65% at 0.5 M (Figure 7-3, b).



(a)

(b)

Figure 7-3: Graphical representation of model prediction for the effect of LIX 63 and nonyl-4PC (a) or Versatic 10 (b) in M on nickel extraction with LIX 63 / Versatic 10 / nonyl-4PC. Factors not plotted are set at level 0 – the mid-point (Mg = 60 g/L, Ni = 4 g/L)

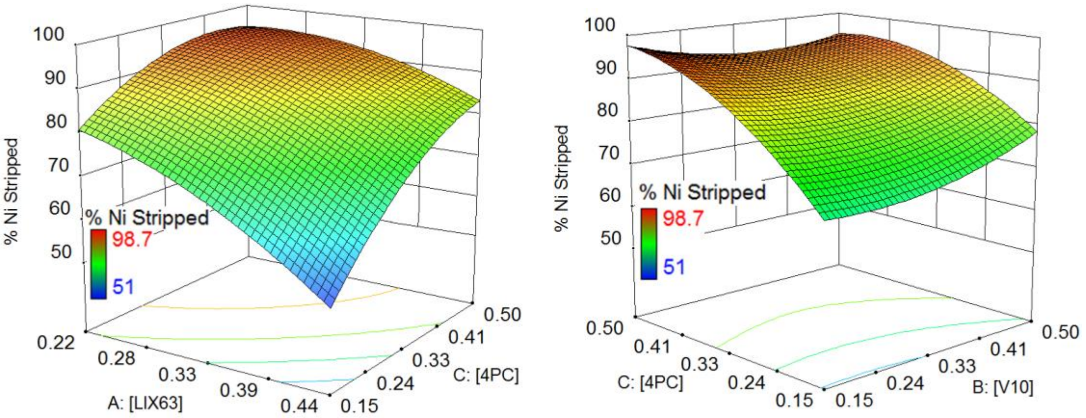
Results from Section 6.4.3 are of use for interpreting the results of Figure 7-3. Specifically, at high nonyl-4PC concentrations it is expected that the nickel extraction reaction is near equilibrium, justified by the increase in nickel extraction from 56% to 84% at the pH_{90}(Ni) after 2 min when adding 0.35 M nonyl-4PC to 0.31 M LIX 63 / 0.35 M Versatic 10 (Figure 6-6). Conversely, at low nonyl-4PC nickel extraction is expected to be far from equilibrium, justified by an increase to only 61% nickel extracted after 2 min when adding 0.1 M nonyl-4PC to 0.31 M LIX 63 / 0.35 M Versatic 10 (Figure 6-6).

High extraction of nickel was only achieved when high concentrations of both nonyl-4PC and LIX 63 were used. Lower LIX 63 levels in Figure 7-3 were stoichiometrically limiting and an additional test revealed that 0.35 M nonyl-4PC / 0.35 M Versatic 10 was unable to extract nickel under the DOE conditions. Thus, nonyl-4PC only acted to increase the rate of nickel extraction, not its equilibrium position, and only up to a point where LIX 63 became near saturated. Nickel extraction at low nonyl-4PC concentrations in Figure 7-3 was therefore rate-limited. The potential for increased equilibrium nickel extraction gained by increasing the LIX 63 concentration was therefore not realised after 2 min, and increasing LIX 63 concentrations only slightly increased nickel extraction. Conversely, at low LIX 63 and high nonyl-4PC the resulting sub-stoichiometric LIX 63 concentrations limited the potential for high nickel extraction.

There was no interaction between LIX 63 and Versatic 10 for nickel extraction above the stoichiometric requirements of Versatic 10. Increasing the Versatic 10 concentration over the range of the design space gave only a very slight increase in nickel extraction. This shows that the concentration of Versatic 10 above stoichiometric requirements had minimal effect on nickel extraction, despite being a requirement for nickel coordination. If Versatic 10 concentration was reduced below the stoichiometric requirement for nickel extraction, then nickel extraction would be expected to fall proportionally. This is because progressively less of the nickel synergist complex containing both LIX 63 and Versatic 10 would be able to form.

7.3.4 Effect of the concentration of each reagent on nickel stripping

Nickel stripping was most affected by an interaction between LIX 63 and nonyl-4PC (EQ 10). High nickel stripping after 2 min was achieved at either high nonyl-4PC concentrations or low LIX 63 concentrations (Figure 7-4, a). Decreasing nonyl-4PC greatly decreased nickel stripping from 83% to 53% at 0.44 M LIX 63, whereas at 0.22 M LIX 63 high nickel stripping was achieved for any nonyl-4PC concentration. In comparison, increasing LIX 63 only slightly decreased nickel stripping at 0.5 M nonyl-4PC from 95% at 0.22 M LIX 63 to 83% at 0.44 M, whereas at 0.15 M nonyl-4PC, nickel stripping decreased dramatically with increasing LIX 63 from 80% to 55%.



(a) (b)

Figure 7-4: Graphical representation of model prediction for the effect of LIX 63 and nonyl-4PC (a) or nonyl-4PC and Versatic 10 (b) in M on nickel stripping from LIX 63 / Versatic 10 / nonyl-4PC. Factors not shown have been set at level 0 – the mid-point (H_2SO_4 = 50 g/L)

In a comparative test under the DOE conditions, quantitative nickel stripping was achieved within 180 min from 0.44 M LIX 63 / 0.33 M Versatic 10. In Section 6.4.1 only 61% of nickel was stripped after 2 min from 0.31 M LIX 63 / 0.35 M Versatic 10 / 0.1 M nonyl-4PC compared with 95% stripped using 0.35 M nonyl-4PC. Equilibrium nickel stripping is therefore expected to be near quantitative under the conditions in Figure 7-4 (a), and any deviations from 100% nickel stripping after 2 min were concluded to result from variations in the stripping rate. Hence, nickel stripping was slow at low nonyl-4PC concentrations in Figure 7-4 (a), whereas at 0.5 M nonyl-4PC nickel stripping was much faster.

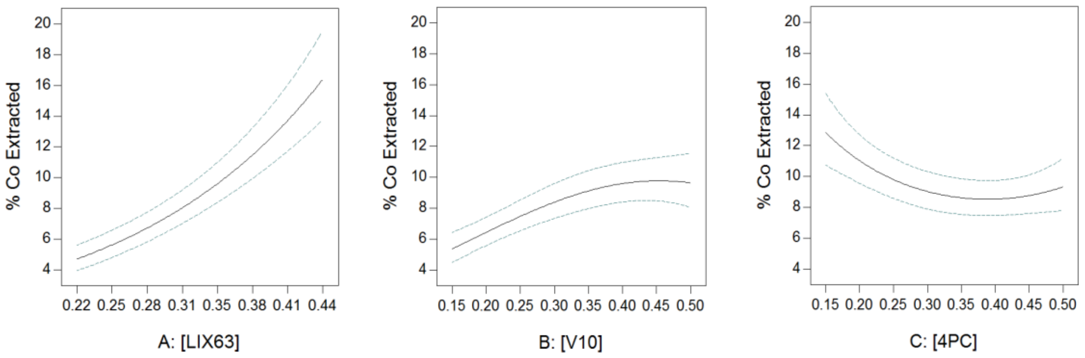
Increasing LIX 63 concentrations decreased nickel stripping more dramatically at low nonyl-4PC concentrations. As equilibrium stripping was still expected to be near quantitative under these conditions, higher LIX 63 concentrations must then have decreased the rate of nickel stripping and masked the moderate acceleration effect of low nonyl-4PC concentrations. Flett *et al.* (1975) reported a similar phenomenon measured in an extraction kinetics study using an AKUFVE, an apparatus for continuous measurement of partition factors in solvent extraction, where the backwards, or strip, reaction for nickel during extraction at pH 3.4 decreased with increasing LIX 63 concentrations. The study by Flett *et al.* (1975) was focused on metal extraction and no explanation for the retardation of the strip reaction was given.

The results of the model indicated that nickel stripping was slightly affected by an interaction between Versatic 10 and nonyl-4PC concentrations (EQ 10). This effect was predicted as a subtle saddle shape in Figure 7-4, (b) that reflects a slight increase in nickel stripping with increasing Versatic 10 at low nonyl-4PC concentrations, and a very slight decrease in nickel stripping with increasing Versatic 10 at high nonyl-4PC concentrations. The slight decrease in nickel stripping with increasing Versatic 10 at high nonyl-4PC concentrations can be rationalised by taking into account the potential acid–base reaction between nonyl-4PC and Versatic 10. This would decrease the availability of nonyl-4PC to extract protons into the organic phase. In general, Figure 7-4 (b) demonstrates that Versatic 10 played only a minimal role in the stripping of nickel when present in excess. Further work on this phenomenon, although interesting, was not necessary for the scope of this project.

7.3.5 Effect of the concentration of each reagent on cobalt extraction

The effects of the three reagent concentrations on cobalt stripping are shown in Figure 7-5. Only individual factors were predicted to affect cobalt extraction and hence only one-dimensional graphs of the results are plotted. Interactions between LIX 63 and Versatic 10, where Versatic 10 was above stoichiometric requirements, again did not affect cobalt extraction. This is in agreement with the result for nickel extraction.

LIX 63 concentrations had the largest effect on cobalt extraction (Figure 7-5, a). Increasing LIX 63 concentration from 0.22 to 0.44 M resulted in a fourfold increase in cobalt extraction to 16%. LIX 63 concentration had the greatest effect on cobalt extraction because it was stoichiometrically limiting at low levels. In Figure 7-3 (a), nickel extraction at low LIX 63 concentrations was between 40% and 60% after 2 min and therefore consumed approximately 77% of the reagent, based on the assumptions of a 3:1 LIX 63:cobalt ratio and only a 60:40 ratio of *anti:syn* isomers, as in Section 7.2.4. With increasing LIX 63 concentrations, the amount of reagent available increased and the cobalt extraction equilibrium therefore shifted towards the organic phase.



(a) (b) (c)

Figure 7-5: Graphical representation of model predictions for effect of LIX 63 (a), Versatic 10 (b) and nonyl-4PC (c) in M on cobalt extraction with LIX 63 / Versatic 10 / nonyl-4PC. Dotted lines are 95% confidence intervals. Factors not shown have been set at level 0 – the mid-point. (Mg = 60 g/L, Co = 0.15 g/L)

Versatic 10 and nonyl-4PC had small but opposite effects on cobalt extraction. Increasing Versatic 10 in Figure 7-3 (b) slightly increased cobalt extraction from 5% to a maximum of about 10% with the other two factors at level 0. This maximum levelling off for cobalt extraction at high Versatic 10 concentration probably reflects the limit for cobalt extraction at pH 2 for the near-stoichiometric LIX 63 concentration (0.33 M).

Increasing nonyl-4PC slightly decreased cobalt extraction from 13% to a minimum of about 9% (Figure 7-3, c). Cobalt extraction with increasing nonyl-4PC concentration was predicted to initially decrease slightly, before slightly increasing again at higher nonyl-4PC concentrations. As quadratic models cannot predict a plateau, this result was instead ascribed to attempting to fit a quadratic model to data that have actually reached a minimum.

The inhibition of cobalt extraction as a result of increasing nonyl-4PC concentrations occurred even though nonyl-4PC is a known synergist for cobalt extraction with Versatic 10. This is because of the low operational pH where nonyl-4PC / Versatic 10 did not extract cobalt. As cobalt extraction by LIX 63 / Versatic 10 is fast, and can reach equilibrium within 0.5 min in sulfate-based laterite leach solutions (Cheng, 2006), it will be extracted before nickel. As nickel is extracted, cobalt may then be displaced from the LIX 63 limited organic phase to reach a lower equilibrium concentration. A minimum cobalt extraction with increasing nonyl-4PC is therefore attributed to cobalt being crowded out of the organic phase after 2 min as a result of faster nickel extraction in the presence of more nonyl-4PC.

7.3.6 Optimisation of the three reagent concentrations

An optimisation calculation was carried out to determine the optimum concentration of each reagent in the developed solvent system. This took into account a balance between nickel stripping and nickel extraction, as the drivers to economic success of a solvent system applied to a nickel laterite PLS, as well as a requirement to avoid excessive organic phase reagent concentrations. Cobalt extraction was not considered important when balancing the effects of reagent concentrations between nickel extraction and nickel stripping. Hence, as cobalt is generally only present at one tenth of the nickel concentration in a laterite PLS, the extraction of cobalt was not considered in this optimisation. This calculation was iterated to generate optimum reagent concentrations using the three model equations and the goals given in Table 7-4.

Minimising the reagent concentrations is important to avoid excess costs associated with higher reagent hold-up and the potential for excessive organic phase viscosity. Minimising the exotic reagents LIX 63 and nonyl-4PC was considered more important than minimising Versatic 10, which is cheap, readily available and has low viscosity. Maximising nickel extraction and stripping were selected to be of most importance as these determine net nickel transfer, which will be the main driver for revenue in a nickel laterite operation.

Table 7-4: Importance factors* set for determining organic phase reagent concentrations using an optimisation calculation

Factor or Response	Goal	Importance Factor
[LIX 63]	minimise	2
[Versatic 10]	minimise	1
[nonyl-4PC]	minimise	2
% Ni Extracted	maximise	4
% Ni Stripped	maximise	4

* Higher numbers have larger weighting in the optimisation calculation.

The optimisation calculation produced an organic phase composition of 0.31 M LIX 63 / 0.15 M Versatic 10 / 0.36 M nonyl-4PC with a desirability of 0.60. The optimised reagent concentrations resulted in predicted nickel extraction of 60%

at pH 2 after 2 min, predicted cobalt extraction of 4.7% at pH 2 after 2 min and predicted nickel stripping of 93% by 50 g/L sulfuric acid after 2 min.

Modelling indicated an optimum Versatic 10 concentration of 0.15 M. Optimisation minimised Versatic 10 concentration to the lowest value in the design space (just above stoichiometric) because it had very little effect on the tested responses of nickel extraction and nickel stripping. In reality, an excess of Versatic 10 (above stoichiometry) in the organic phase allows for some unintended loss of the reagent by dissolution in the aqueous phase. For future experimental work Versatic 10 was therefore increased to 0.25 M.

The responses for the adjusted organic phase (0.31 M LIX 63 / 0.25 M Versatic 10 / 0.36 M nonyl-4PC) under the DOE conditions were predicted from the model equations as follows: nickel extraction of 61%, cobalt extraction of 6.4% and nickel stripping of 91%. Interestingly, these predicted nickel and cobalt extractions resulted in a theoretical (kinetic) separation factor of $SF_{(Ni/Co)} = 23$. These results indicated that separation of nickel and cobalt might be possible using this solvent system. Nickel–cobalt separation was not a goal of the current thesis and so this was not investigated further. It could form the basis of future work.

7.4 Conclusion

The aim of this chapter was to determine optimal reagent concentrations for any novel solvent systems suited to separation of nickel and cobalt from magnesium. This was achieved for the novel solvent system LIX 63 / Versatic 10 / nonyl-4PC by completing a statistical experimental design to generate quadratic models predicting nickel stripping with 50 g/L sulfuric acid after 2 min, nickel extraction at pH 2 after 2 min and cobalt extraction at pH 2 after 2 min. Specifically the work in this chapter revealed that:

- The effect of the three reagent concentrations on the three tested responses of nickel extraction, nickel stripping and cobalt extraction could not be accurately predicted using a linear model. Quadratic models, however, did accurately predict these responses and F-tests showed that the models were significant and could be used to further investigate the solvent extraction process.

- At stoichiometric requirements there was enough Versatic 10 to complex with all the nickel and cobalt extracted, and an excess did not result in substantially higher extraction, only increasing it from 60% at 0.15 M to 65% at 0.5 M. In contrast, nickel extraction was only maximised at both high LIX 63 concentrations and high nonyl-4PC concentrations, increasing from 42% at low LIX 63 and nonyl-4PC levels to 82% at their high levels. As nonyl-4PC / Versatic 10 did not extract nickel at pH 2, LIX 63 was the driving force for high equilibrium extraction of nickel, where high nonyl-4PC concentrations increased the rate of extraction.

- Interaction effects between LIX 63 and nonyl-4PC were particularly important for nickel stripping. At high LIX 63 and low nonyl-4PC concentrations only 53% nickel was stripped after 2 min compared with 95% at low LIX 63 and high nonyl-4PC. Equilibrium stripping without nonyl-4PC was found to be near quantitative for 0.44 M LIX 63 (level +1) with 0.33 M Versatic 10 (level 0). An increasing LIX 63 concentration therefore retarded the stripping of nickel by counteracting the moderate acceleration effect of low concentrations of nonyl-4PC. High nonyl-4PC concentrations, however, overcame this effect to allow high stripping of nickel after 2 min.

- LIX 63 concentrations were particularly important in determining cobalt extraction. As there is limited LIX 63 availability at the low LIX 63 level, cobalt extraction increased dramatically from 4.7% at 0.22 M LIX 63 to 16.4% at 0.44 M LIX 63. At higher LIX 63 concentrations more reagent was available for cobalt coordination, and cobalt extraction was therefore thermodynamically favoured.

- The optimum organic phase reagent concentrations in LIX 63 / Versatic 10 / nonyl-4PC as calculated via an iterative optimisation calculation prioritising nickel extraction and nickel stripping whilst constraining the maximum reagent concentration in the organic phase were 0.31 M LIX 63 / 0.15 M Versatic 10 / 0.36 M nonyl-4PC. Reagent concentrations for future work of 0.31 M LIX 63 / 0.25 M Versatic 10 / 0.36 M nonyl-4PC were chosen to allow for some unintended dissolution of Versatic 10 into the aqueous phase during extraction.

CHAPTER 8
Comparison of three promising solvent systems for practical application to a nitrate-based laterite PLS

8.1 Introduction

In Section 4.3.4 LIX 860 / Versatic 10, LIX 860 / low concentrations of Cyanex 272, Versatic 10 alone, nonyl-4PC / Versatic 10, and LIX 63 / Versatic 10 were identified as promising solvent systems for separation of nickel and cobalt from magnesium in a nitrate matrix. As ongoing cobalt poisoning could not be avoided in solvent systems containing LIX 860, these were not considered viable (Chapter 5). In Chapter 6 nonyl-4PC was identified as the most appropriate nickel accelerator for LIX 63 / Versatic 10 that did not increase the required operational pH. From the work in this thesis, three promising solvent systems have therefore been identified, (1) Versatic 10 (with TBP as recommended by previous research), (2) nonyl-4PC / Versatic 10 and (3) LIX 63 / Versatic 10 / nonyl-4PC. Versatic 10 / TBP, nonyl-4PC / Versatic 10, and LIX 63 / Versatic 10 / TBP have previously been optimised at the pilot scale by other authors using sulfate-based nickel laterite leach solutions with similar levels of nickel and cobalt. Optimisation testwork detailed in Chapter 7 further determined the reagent concentrations for application of LIX 63 / Versatic 10 / nonyl-4PC to a typical nitrate-based nickel laterite PLS.

The aim of this chapter was to compare any promising solvent systems identified for application to separation of nickel and cobalt from magnesium in a nitrate-based PLS from the standpoint of a potential industrial application. The comparison presented in this chapter thus used industrially relevant operating parameters (reagent concentrations, temperature and strip acidity) informed from previously published optimisation work for each solvent system. The comparison in this chapter specifically targeted the following criteria: high rejection of magnesium, low operating pH, separation of nickel and cobalt from manganese and calcium, ease of metal stripping, rates of metal extraction and metal stripping, and phase disengagement times.

8.2 Conceptual processing route for recovery of nickel and cobalt from a nitrate-based nickel laterite PLS

All three of the selected solvent systems will co-extract nickel and cobalt from the aqueous feed, leaving magnesium in the raffinate. The same conceptual DSX processing route shown in Figure 8-1 is therefore applicable in all cases. In the proposed processing route, nickel and cobalt extracted by the solvent system are stripped into sulfuric acid and conventional nickel–cobalt separation and refining can then take place using Cyanex 272, as suggested by numerous authors for sulfate-based leach liquors (Tsakiridis and Agatzini, 2004; Cheng *et al.*, 2010b; Larmour-Ship *et al.*, 2014). On the basis of this processing route, the comparison in this chapter considered the loading of the identified solvent systems from a nitrate matrix and subsequent stripping into sulfuric acid.

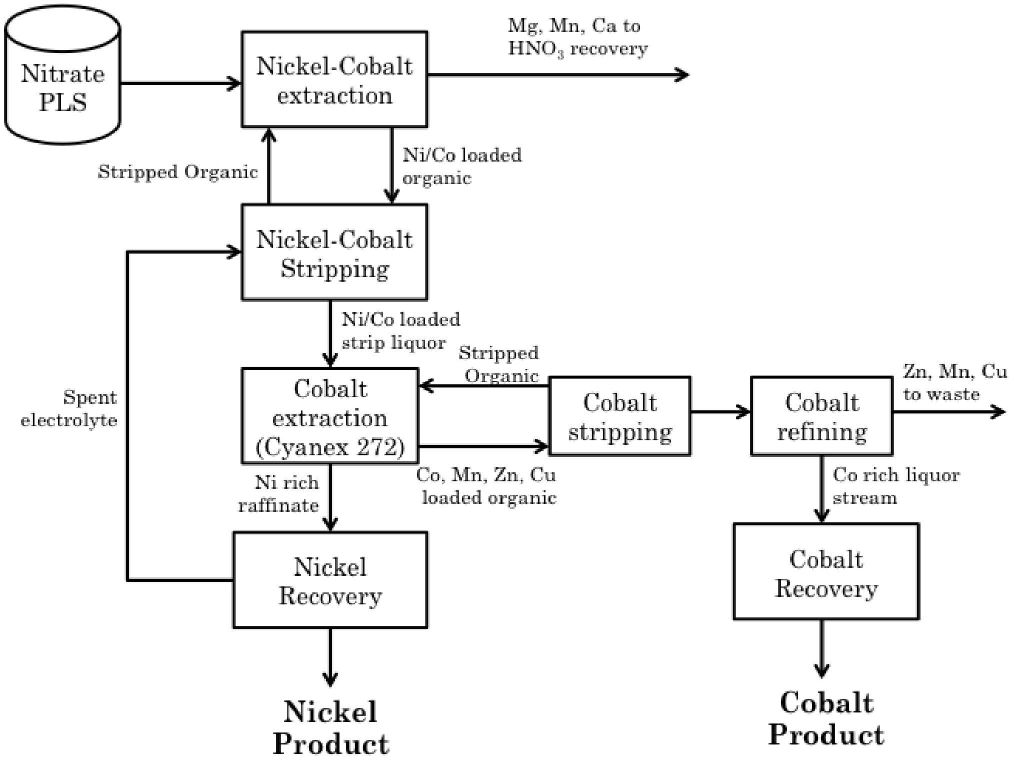


Figure 8-1: Proposed conceptual processing route for DSX of nickel and cobalt from a nitrate PLS

Any copper, zinc or manganese reporting to the initial loaded strip liquor would be extracted in the second SX stage with Cyanex 272 at the pH required for cobalt extraction (Cytec, 2008). Copper, zinc and manganese would have to be removed during cobalt refining, as is currently practiced at Murrin-Murrin (Motteram *et al.*, 1996) and historically at Bulong Nickel (Griffin, 2000), both in

Western Australia. The cobalt refining process involves precipitating cobalt as a sulfide to reject manganese, releaching the sulfide, removal of zinc using solvent extraction and removal of copper using ion exchange.

8.3 Materials and Methods

8.3.1 Aqueous and organic solutions

The following chemicals were used to make up the wash solution and synthetic strip aqueous phases: sodium hydroxide, sodium sulfate, nickel sulfate and sulfuric acid. A nitrate PLS feed was produced by blending different samples collected from the mixed hydroxide precipitation (MHP) feed tank (Section 1.1.2, Figure 1-2) during various campaigns of the DNi pilot plant operation. Some solutions had already been allowed to cool to room temperature and separated from any precipitates formed by collecting the supernatant. Other solutions had been diluted with deionised water by plant operators to avoid precipitation of solids (mainly magnesium nitrate) on cooling.

The collected solutions were blended together to generate a bulk aqueous sample that contained a significant concentration of aluminium (>50 mg/L). This remaining aluminium was removed by raising the aqueous pH to 5.75 at 40 °C with sodium hydroxide (100 g/L). The solution was filtered to generate a DNi PLS for comparing the three solvent systems. Metal concentrations in this DNi PLS were (in mg/L): Al 5, Ca 1 512, Co 109, Cr <0.2, Fe <0.2, Mg 76 837, Mn 568, Ni 2 838, Zn <0.2, Cu <0.2. The concentrations of copper and zinc fell below detection limits due to the high neutralisation pH used for aluminium removal. As such, their deportment could not be followed in this comparison. This is not a concern in this comparison as any trace copper or zinc reporting to the loaded organic would be removed by the cobalt refining process (Figure 8-1).

The following solvent extraction reagents diluted in ShellSol D70 were used in this investigation: Versatic 10, TBP, nonyl-4PC and LIX 63. All fresh organic phases were initially washed with sodium sulfate (50 g/L) in sulfuric acid (10 g/L) and filtered through Whatman 1PS phase separation paper before use to remove any aqueous soluble impurities.

8.3.2 Extraction and stripping pH isotherm procedure

Extraction pH isotherms for fresh organic contacted with DNi PLS were generated as per the method in Section 3.2.2, except using a smaller overhead mixer (40 mm diameter impeller) at 800 rpm (tip speed of 1.68 m/s) in a stainless steel mixing box (7 × 7 × 15 cm) due to lower (varying) reaction volumes. Stripping pH isotherms were generated using the residual organic phase from the extraction pH isotherm tests contacted with nickel (60 g/L) as sulfate. Stripping pH isotherms were constructed under the same conditions as extraction pH isotherms except that sulfuric acid (250 g/L) was used for pH adjustment.

8.3.3 Distribution isotherms and phase disengagement time procedures

Extraction distribution isotherms were generated with DNi PLS contacted with previously unloaded organic at varying A:O ratios at a predetermined pH. The two phases were added at the varying A:O ratios (1:8, 1:4, 1:2, 1:1, 2:1, 4:1, 8:1) to a 250 mL hexagonal glass jar and allowed to come to the required temperature in a water bath. After reaching the required temperature the phases were contacted for 15 min, after which the mixtures were transferred to a separating funnel. McCabe-Thiele diagrams under extract conditions were constructed from the generated distribution isotherms using an operating line at A:O of 1:1, an initial aqueous phase nickel concentration of 3000 mg/L and initial cobalt concentration of 100 mg/L. These concentrations were chosen to be close to the actual feed concentrations.

For stripping distribution isotherms the aqueous strip feed was contacted with an organic phase previously loaded at A:O of 1:1 at the same pH as the extraction distribution isotherms. Stripping distribution isotherms were generated using the same method as extraction distribution isotherms except that the two phases were contacted for 20 min, as stripping was noted to be slightly slower than loading during the course of this investigation. McCabe-Thiele diagrams under strip conditions were generated using an initial organic phase nickel concentration of 3000 mg/L and an initial cobalt concentration of 100 mg/L taken from the extraction distribution isotherms using an A:O of 1:1. The number of required stages was calculated using an operating line A:O of 1:9. This value was chosen to give an increase in nickel concentration similar to the increase between a lean and pregnant nickel electrowinning (EW) liquor to simulate potential requirements in a hypothetical nickel SX-EW operation, 68–96 g/L as reported by Brown and Mason (1977).

The stripping distribution isotherm data obtained for LIX 63 / Versatic 10 / nonyl-4PC did not produce an aqueous phase with sufficiently high nickel and cobalt concentrations to generate a McCabe-Thiele diagram using the operating line at A:O of 1:9. Data points for an initial organic phase nickel concentration of 3000 mg/L and organic phase cobalt of 100 mg/L were therefore extrapolated from the available data using a straight line. This provided sufficient accuracy to allow a comparison with the other two solvent systems under the same experimental conditions.

Phase disengagement times were recorded from distribution isotherm samples contacted at phase ratios A:O of 1:2, 1:1 and 2:1 by transferring the aqueous-organic mixtures as quickly as possible (between 10 and 12 s) to a separating funnel after turning off the overhead mixer. Phase disengagement from the start of pouring into the funnel was recorded using a digital camera. Aqueous continuous or organic continuous mixing was determined from videos of the phase disengagement. Images from each video are shown in Appendix D.

8.3.4 Extraction and stripping rate procedure

Extraction and stripping rates were measured under similar conditions and setup as the distribution isotherms, except carried out in a stainless steel mixing box. Organic and aqueous phases were pre-heated in separate containers to the desired temperature prior to quickly adding the aqueous phase to the stirred organic phase. Samples (5 mL) of the aqueous-organic mixture were taken at 0.5, 1, 1.5, 2, 3, 5 and 10 min using a glass syringe.

To obtain extraction rates, DNi PLS was contacted with fresh organic phases pre-equilibrated with the required volume of sodium hydroxide to give a pH near a predetermined extraction pH (Section 8.3.6). The impeller was kept in a constant position (2.5 cm off the bottom of the mixing box) to ensure consistent mixing for all extraction rate tests. To determine stripping rates, the residual organic phase from the extraction rate test was contacted with nickel (60 g/L) as sulfate in sulfuric acid (concentration depending on organic system used). The impeller was kept 0.5 cm off the bottom of the mixing box due to the lower total reaction volume (100 mL compared with 200 mL).

8.3.5 *Analytical determinations*

Aqueous and organic phases were handled as in Section 3.2.3 except Versatic 10 / TBP organic phases were stripped using nitric acid (1 M) and organic phases containing nonyl-4PC were stripped using sulfuric acid (50 g/L). This was done to avoid phase separation issues noted when using 1 M nitric acid with organic phases containing nonyl-4PC.

All metal concentrations of aqueous phases were determined by the CSIRO analytical laboratory using inductively coupled plasma atomic emission spectroscopy (ICP-AES). One solid residue was analysed by the CSIRO analytical laboratory using a scanning electron microscope (SEM, Jeol, JSM-7001F) with energy dispersive X-ray spectroscopy (EDX).

8.3.6 *Selected parameters for the industrially relevant comparison*

In this section justifications are given for the parameters selected to compare each solvent system (Table 8-1). Where possible, parameters were selected from published studies of pilot scale operations using sulfate-based nickel laterite feed liquors. The nickel, cobalt and manganese concentrations of these leach solutions were similar to those in the DNi PLS. Magnesium concentrations, however, were considerably lower than in the DNi PLS.

Table 8-1: Parameters varied for comparing the three selected solvent systems from an industrially relevant standpoint

	Versatic 10 / TBP	**nonyl-4PC / Versatic 10**	**LIX 63 / Versatic 10 / nonyl-4PC**
Reagent concentrations M	0.8 / 0.18	0.25 / 0.5	0.31 / 0.25 / 0.36
Operating temperature °C	40	30	30
Strip feed sulfuric acid g/L	200	50	50
Optimisation study reference	Tsakiridis and Agatzini (2004)	du Preez and Kotze (2009)	(Cheng *et al.*, 2010b) / Current study

Compared with the sulfate-based solutions from the referenced pilot studies, it was expected from the work in Chapter 3 that the operating pH of the solvent systems would be lower from the nitrate-based DNi PLS, but that metal selectivity would be unaffected. From the results of the pH isotherms reported later (Section 8.4.1) cobalt was consistently extracted at a higher pH than nickel using the three tested solvent systems, but at a lower pH than manganese or magnesium. The pH for 90% cobalt extraction, $pH_{90}(Co)$, was thus used as a useful comparative pH where the majority of target metals were extracted whilst rejecting impurities. The $pH_{90}(Co)$ was also used as a comparative pH to generate distribution isotherms and extraction rates. The results of the pH isotherms in Section 8.4.1 consistently revealed a maximum separation factor of cobalt over manganese, $SF_{(Co/Mn)}$, near the $pH_{90}(Co)$, supporting the choice of this comparative extraction pH value.

The organic phase for Versatic 10 / TBP was made up to mimic that of the referenced optimisation study (Tsakiridis and Agatzini, 2004). TBP was added to the Versatic 10 solvent system by Tsakiridis and Agatzini (2004) to aid in phase disengagement times and to hinder crud formation; this was replicated in the current work. TBP was not added to the other two solvent systems for the present comparison since its addition is known to increase the required pH for nickel extraction with LIX 63 / Versatic 10 (Section 6.4.2) and acceptable phase disengagement occurred in both cases without this addition. Comparative work using Versatic 10 / TBP was done at 40 °C and with a strip feed of 200 g/L, as per Tsakiridis and Agatzini (2004). The organic reagents are chemically stable and these more aggressive conditions compared with those of the other two solvent systems can be used to accelerate phase transfer rates and phase disengagement.

Nonyl-4PC / Versatic 10 concentrations were selected from a pilot plant investigation detailed by du Preez and Kotze (2009) using Nicksyn / Versatic 10. The referenced study recommended maintaining a carboxylic acid to synergist ratio of 2:1. For a sulfate-based nickel laterite leach with similar nickel and cobalt concentrations as the DNi PLS, the reagent concentrations selected by du Preez and Kotze (2009) were 0.25 M Nicksyn / 0.5 M Versatic 10. As no previous investigations were available specifically for LIX 63 / Versatic 10 / nonyl-4PC, the reagent concentrations were taken from the optimisation carried out in Section 7.3.6 of the present work.

For both of the solvent systems containing nonyl-4PC the aqueous strip feed contained only 50 g/L sulfuric acid, as per du Preez and Kotze (2009). It is advisable to keep the acid concentration in the strip feed solution low for solvent systems containing LIX 63 or nonyl-4PC due to the potential for acid hydrolysis of these reagents. Halford and Barnard (2011) showed, for example, that the rate of LIX 63 degradation at 70 °C doubles when increasing the aqueous phase acidity from 0 to 50 g/L sulfuric acid. In addition, pyridine derivatives in general are known to extract acid into the organic phase from low pH strip solutions, which can cause poor phase separation (Cheng *et al.*, 2002; Mihaylov, 2003; Masiiwa *et al.*, 2008). Stripping in semi-continuous stripping circuits has therefore been carried out at either pH 2.5 for CLX 50 / Versatic 10 (Cheng *et al.*, 2015) or pH 2 for Nicksyn / Versatic 10 (Larmour-Ship *et al.*, 2014).

The rates of degradation of LIX 63 and nonyl-4PC both increase with increasing temperatures. An increase in temperature of approximately 10 °C is known to double the rate of LIX 63 degradation in LIX 63 / Versatic 10 under both extract and strip conditions (Barnard, 2008a). Slight degradation (1% per annum) of decyl-4PC (an analogue of nonyl-4PC) in decyl-4PC / Versatic 10 was noticed at 40 °C and pH 3 by Barnard *et al.* (2004) but increased six-fold when the temperature was raised to 60 °C. Pilot scale testing of Nicksyn / Versatic 10 has previously been carried out at either ambient temperature (du Preez and Kotze, 2009) or 35 °C (Larmour-Ship *et al.*, 2014). Using this information as a guide, LIX 63 / Versatic 10 / nonyl-4PC and nonyl-4PC / Versatic 10 were both tested at 30 °C in the current work.

8.4 Results and discussion

The work reported in the current chapter compared the three different solvent systems on an equal footing from the standpoint of industrial application, using a real PLS generated by the DNi pilot plant. This allowed identification of the most promising solvent system or systems for application to a potential commercial process. The limitation of this approach is that the results can only be used as a comparative assessment and not as parameters for plant optimisation or plant design.

The following section presents and compares the results for pH isotherms, McCabe-Thiele diagrams and rate investigations for a nitrate-based extract and sulfate-based strip at conditions chosen to allow a comparison of each system under industrially relevant conditions. A comparison of the phase disengagement times is then presented as a final consideration for selecting the most promising solvent system or systems.

8.4.1 Metal extraction from the DNi PLS using the three solvent systems

Impurity extraction by Versatic 10 / TBP was particularly high (Figure 8-2, a). Magnesium extraction was substantial, with 2086 mg/L extracted at pH 5.5. This means at least 21% of the reagent was occupied by magnesium, assuming a low molar ratio of 2:1 for Versatic 10 and magnesium based on high water association in magnesium carboxylate complexes as observed by previous investigators (Mikhailichenko *et al.*, 1972; Preston, 1985). The separation of cobalt from manganese was also particularly poor ($SF_{(Co/Mn)}$ of 2.74). Calcium extraction using Versatic 10 / TBP was, however, suppressed over nickel extraction in the current work (pH_{50}(Ca-Ni) greater than 1.5 units), which is in agreement with the findings of Tsakiridis and Agatzini (2004) from sulfate-based media. Reduced calcium extraction is beneficial as stripping of high calcium concentrations into sulfuric acid can lead to gypsum precipitation and scale formation, as noted by Griffin (2000).

At the pH_{90}(Co) of 5.5 and an A:O of 1:1, two stages of extraction were required to extract both nickel and cobalt using Versatic 10 / TBP (Figure 8-2, c and Figure 8-2, d). The rate of extraction for all metals using Versatic 10 / TBP was fast at pH 5.5 (Figure 8-2, b), reaching equilibrium within 2 min under the investigated conditions. This is beneficial for a commercial operation as minimal contact time is required in the mixers for metal extraction.

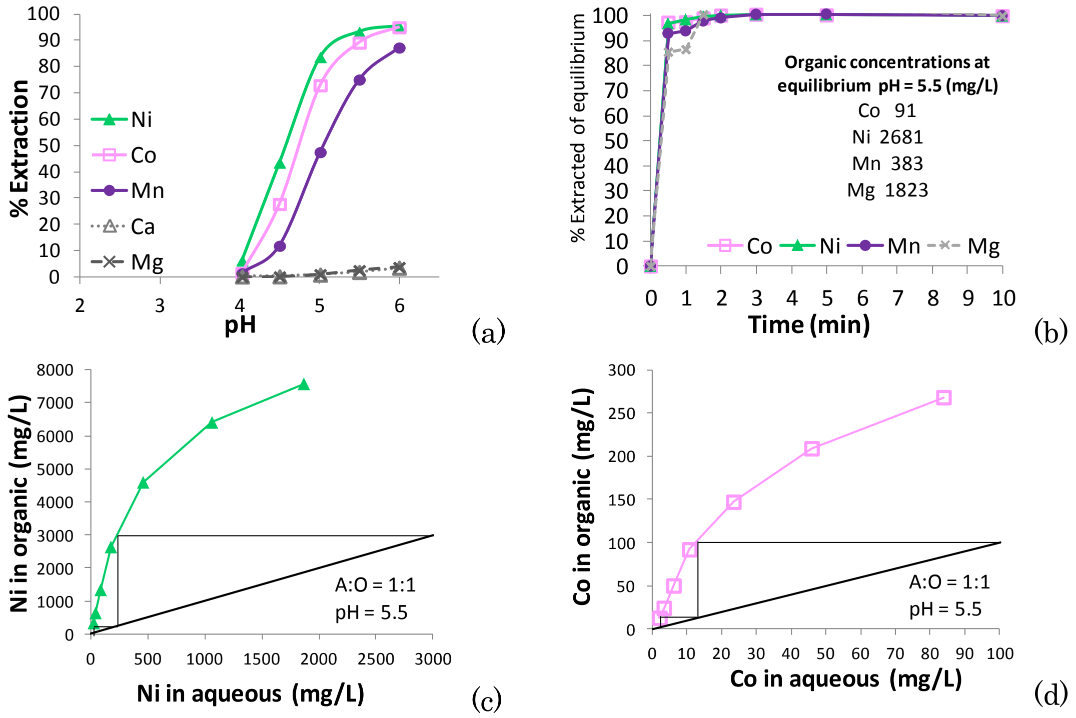


Figure 8-2: Metal extraction behaviour with Versatic 10 / TBP: (a) pH extraction isotherm, (b) metal extraction rates, (c) nickel distribution isotherm, (d) cobalt distribution isotherm (pH_{90}(Co) = 5.5)

The pH_{90}(Co) calculated for nonyl-4PC / Versatic 10 was 4.75 and high rejection of calcium and magnesium was achieved (Figure 8-3, a). The separation factor for cobalt over manganese $SF_{(Co/Mn)}$ was 53, and only 133 mg/L of magnesium was extracted at the pH_{90}(Co), as averaged from results at pH 4.5 and 5. Only one stage of extraction was required for full nickel extraction using nonyl-4PC / Versatic 10 at pH 4.75 (Figure 8-3, c), although two stages were required for full cobalt extraction (Figure 8-3, d).

The rate of nickel and cobalt extraction using nonyl-4PC / Versatic 10 was fast, reaching equilibrium in 2 min (Figure 8-3, b). Manganese extraction with nonyl-4PC / Versatic 10 was slow. After 0.5 min, manganese extraction was further hindered due to competition with nickel extraction. After 1 min, nickel extraction was near complete and so manganese was extracted at a constant rate thereafter to reach equilibrium within 10 min. Magnesium extraction with nonyl-4PC / Versatic 10 over time was similar to manganese, except with faster extraction kinetics. In the first 0.5 min magnesium was loaded to a high concentration (above equilibrium) in the organic phase before being crowded off by nickel to below equilibrium concentration after 1.5 min. Shorter contact times in the extract circuit around 2 min should favour rejection of magnesium and manganese.

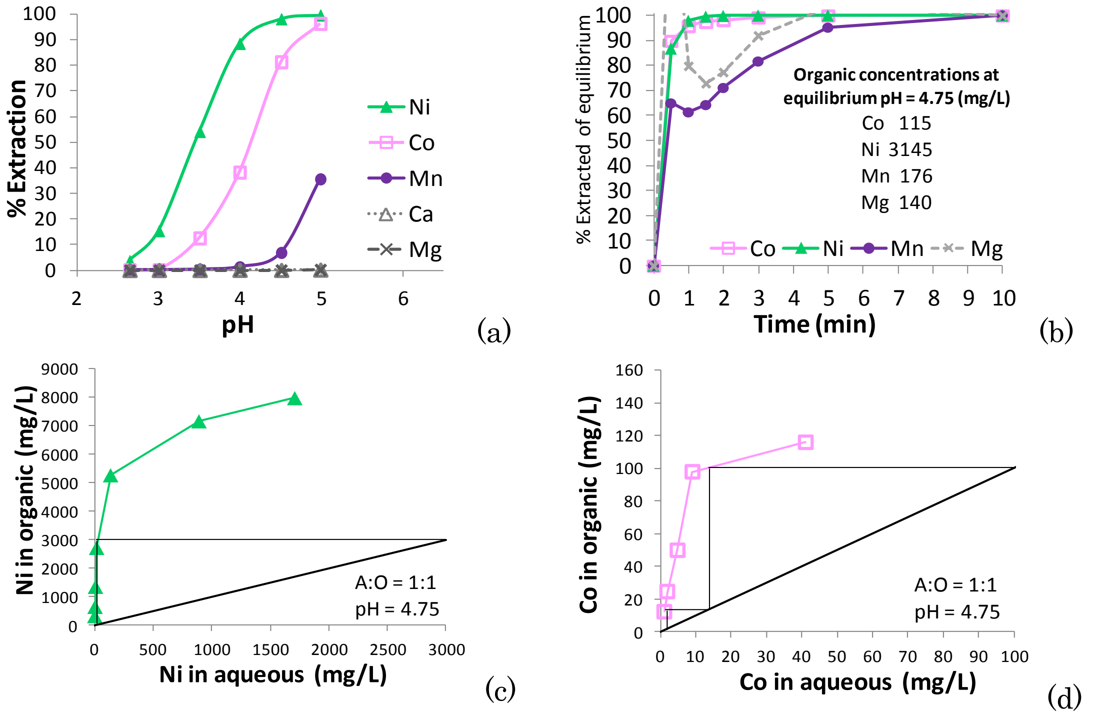


Figure 8-3: Metal extraction behaviour with nonyl-4PC / Versatic 10: (a) pH extraction isotherm, (b) metal extraction rates, (c) nickel distribution isotherm, (d) cobalt distribution isotherm (pH$_{90}$(Co) = 4.75)

Very high separation of nickel and cobalt from manganese, magnesium and calcium was achieved using LIX 63 / Versatic 10 / nonyl-4PC (Figure 8-4, a). At the pH$_{90}$(Co) of 3.5 cobalt–manganese separation was substantial (SF$_{(Co/Mn)}$ of 2408) and the corresponding magnesium extraction was negligible (12 mg/L). Only one stage was required for full extraction of nickel (Figure 8-4, c). One extraction stage resulted in a cobalt raffinate concentration of 3 mg/L (97% extraction), although two extraction stages were required to generate a raffinate with <0.2 mg/L cobalt, equating to >99% cobalt extraction (Figure 8-4, d).

Nickel and cobalt extractions using LIX 63 / Versatic 10 / nonyl-4PC were fast, reaching equilibrium within 2 min (Figure 8-4, b). Extraction of manganese with LIX 63 / Versatic 10 / nonyl-4PC was also fast, but resulted in a similar extraction curve to magnesium with nonyl-4PC / Versatic 10 due to its eventual crowding out of the organic due to nickel extraction. Longer contact times in the extract circuit using LIX 63 / Versatic 10 / nonyl-4PC would favour the rejection of manganese and magnesium.

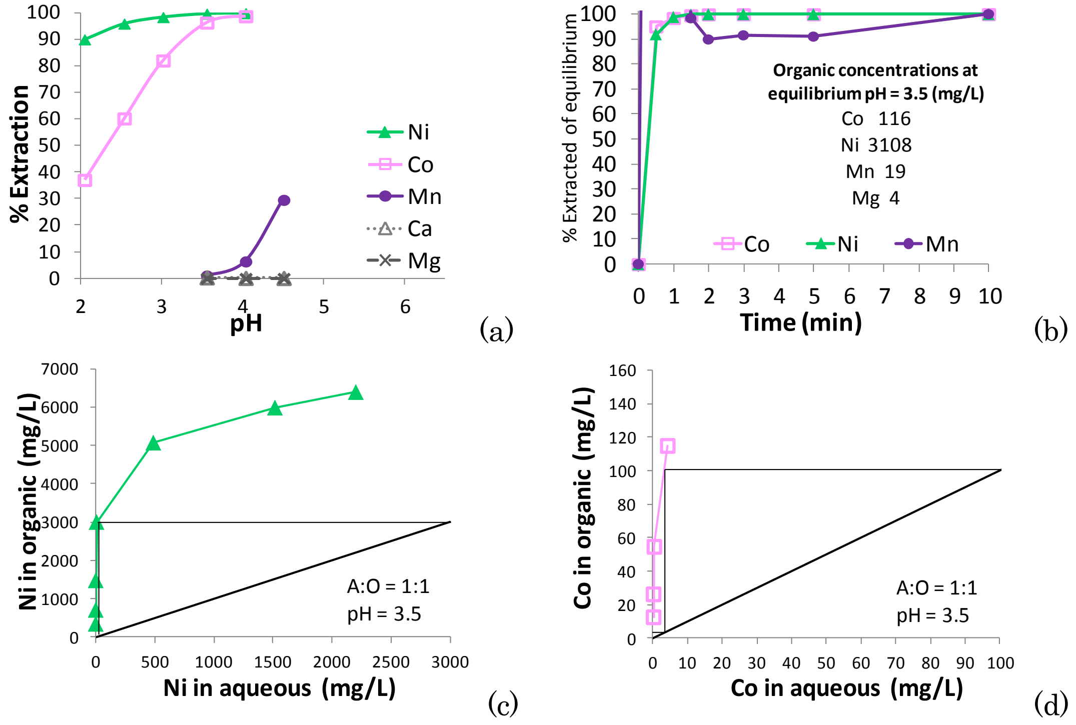


Figure 8-4: Metal extraction behaviour with LIX 63 / nonyl-4PC / Versatic 10: (a) pH extraction isotherm, (b) metal extraction rates, (c) nickel distribution isotherm, (d) cobalt distribution isotherm (pH_{90}(Co) = 3.5)

8.4.2 Metal stripping from the three solvent systems using sulfuric acid

Stripping of all metals from Versatic 10 / TBP occurred at pH 2 and below (Figure 8-5, a). Only one stage at A:O of 1:9 was required to fully strip both nickel and cobalt using 200 g/L sulfuric acid. The rates of stripping for all metals were fast and full stripping was achieved within 0.5 min (Figure 8-5, b).

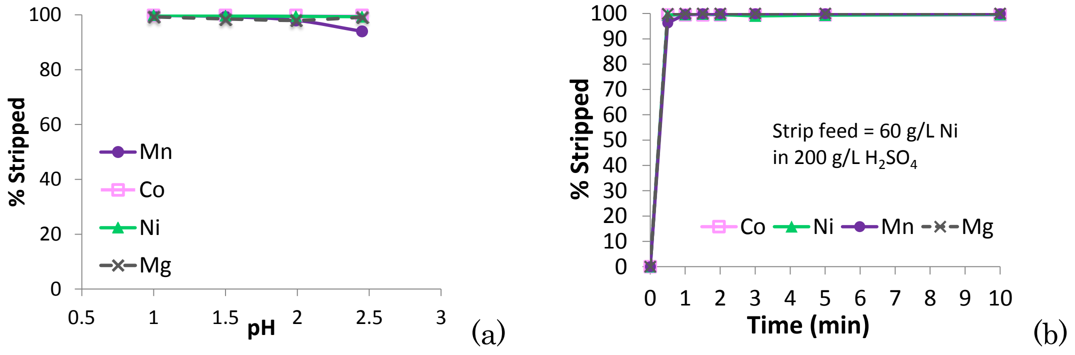


Figure 8-5: Results for metal stripping behaviour with Versatic 10 / TBP: (a) pH stripping isotherm, (b) metal stripping rates

Metal stripping from nonyl-4PC / Versatic 10 was complete below pH 1 for all metals (Figure 8-6, a) and only one stage was required to fully strip nickel and cobalt at A:O of 1:9 using 50 g/L sulfuric acid. Although cobalt stripped much more slowly than nickel (Figure 8-6, b), both nickel and cobalt stripping reached equilibrium within 10 min. Magnesium stripping was not included in the analysis as only minimal magnesium extraction occurred at the operational pH used.

Stripping of manganese from nonyl-4PC / Versatic 10 peaked at 95% until acidification to pH 1, where complete stripping was achieved (Figure 8-6, a), suggesting that that stripping of manganese requires a higher acid concentration than stripping of nickel and cobalt from this solvent system. This was despite negligible manganese extraction below pH 4 in Figure 8-3 (a). Manganese stripping from nonyl-4PC / Versatic 10 was particularly slow (Figure 8-6, b) and reached only 68% after 10 min. Manganese stripping in Figure 8-6 (a) may therefore be a result of very slow manganese stripping or the formation of different manganese species in the organic phase.

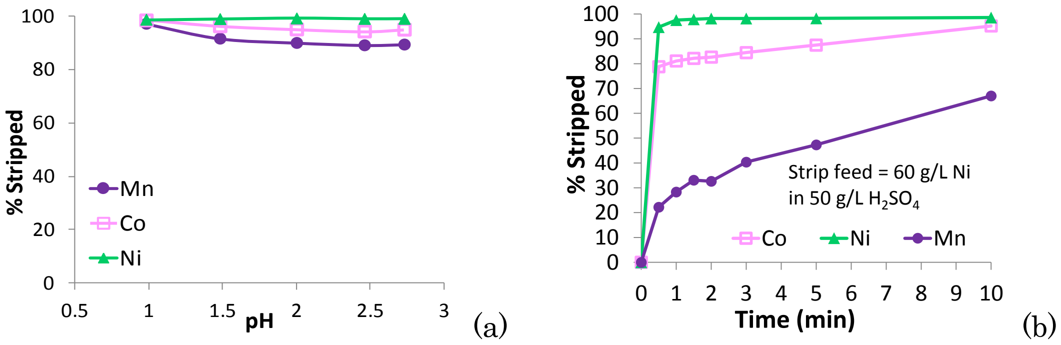


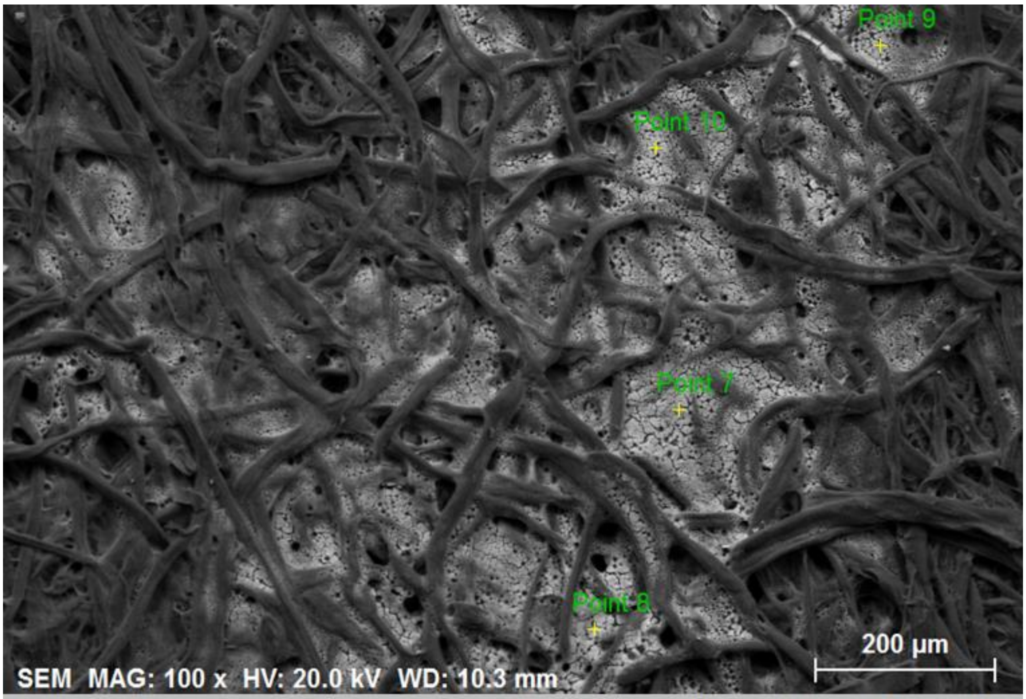
Figure 8-6: Results for metal stripping behaviour with nonyl-4PC / Versatic 10: (a) pH stripping isotherm, (b) metal stripping rates

Erratic stripping of manganese (68-93%) was observed previously from Nicksyn / Versatic 10 by Larmour-Ship *et al.* (2014) in pilot plant trials stripping at pH 2.0. Cheng *et al.* (2010a) also noticed very slow rates of manganese stripping from decyl-4PC / Versatic 10 (2.5% after 10 min). Higher temperatures would accelerate the rate of manganese stripping and might therefore be required in future work, depending on commercial requirements.

Full manganese stripping in the current work was achieved from a sample left loaded over three weeks after 40 min using 50 g/L sulfuric acid at 40 °C and A:O of 3:1. During stripping, a black precipitate containing manganese and oxygen in a molar ratio near 1:2 was found using EDX analysis (Figure 8-7). Trace sulfur and silicon were also present in this analysis. Sulfur was likely present as residual sulfuric acid. Silicon was likely a contaminant from the filter paper used to collect the precipitate. These results therefore strongly suggested that the precipitate was Mn(IV)O_2. Compounds of Mn(III) with organic acid ligands (e.g. Mn(III) acetate) are stable and well known. It is also well known that Mn(III) compounds undergo disproportionation via hydrolysis (EQ 12) to Mn(IV) and Mn(III) (Cotton and Wilkinson, 1980).

$$2\text{Mn(III)} + 2H_2O \rightarrow \text{Mn(II)} + MnO_2\downarrow + 2H^+ \qquad \text{(EQ 12)}$$

Hence, slow stripping of manganese from nonyl-4PC / Versatic 10 was attributed to the oxidation of Mn(II) to Mn(III) in the organic phase. This idea was previously suggested by Cheng *et al.* (2010a) for decyl-4PC / Versatic 10, although no evidence was included to support the claim.



Spectrum	O	Na	Al	Si	S	Cl	Mn	Co	Ni	Cu
Point 7	1.84	0.01	0.00	0.18	0.11	0.00	1.08	0.01	0.03	0.00
Point 8	2.09	0.01	0.00	0.19	0.09	0.00	1.02	0.00	0.02	0.00
Point 9	1.74	0.01	0.00	0.26	0.11	0.00	1.08	0.00	0.02	0.00
Point 10	1.80	0.01	0.00	0.18	0.10	0.01	1.10	0.01	0.03	0.00

Figure 8-7: SEM image with EDX results (as molar ratio) for collected black precipitate on a matrix of filter paper

Although difficult to control in a continuous operation, shorter residence times in a nonyl-4PC / Versatic 10 strip circuit would enhance the separation of nickel and cobalt from manganese due to only partial manganese stripping. A bleed stream would then be required to strip manganese and limit the recirculating manganese load. Optimisation of this potential process for future application would require further investigation.

Full cobalt stripping from LIX 63 / Versatic 10 / nonyl-4PC occurred at pH 2 or below (Figure 8-8, a). Full stripping of nickel, however, was not achieved even at pH 0.5. To avoid excessive acid extraction into the organic phase, as discussed in Section 8.3.6, it is recommended not to decrease the final strip pH below pH 1. At pH 1 only 85% nickel stripping occurred from LIX 63 / Versatic 10 / nonyl-4PC. Stripping of nickel from LIX 63 / Versatic 10 / nonyl-4PC with 60 g/L nickel sulfate could therefore be complicated in a commercial setting. As with nonyl-4PC / Versatic 10, magnesium stripping was not included in this analysis due to only minimal magnesium extraction.

Difficult stripping of nickel was further demonstrated in the current work where cobalt was fully stripped in one stage (Figure 8-8, d), but three stages were required to lower the concentration of nickel in the stripped organic to 225 mg/L (9% of the feed) at A:O of 1:9 (Figure 8-8, c). Nickel in the stripped organic could not be reduced below 140 mg/L using 60 g/L nickel in 50 g/L sulfuric acid, even at A:O of 8:1. A recirculating load of nickel would therefore become established in a commercial setting under the tested conditions, thereby decreasing net nickel transfer to the loaded strip liquor. This would not be a concern for the other two solvent systems tested. Decreasing the nickel concentration in the aqueous strip feed may help to improve nickel stripping, although the strip feed would likely be determined by the downstream nickel recovery process.

Stripping of cobalt from LIX 63 / Versatic 10 / nonyl-4PC was rapid (Figure 8-8, b), whereas nickel stripping was much slower and only reached equilibrium after 10 min. Slow stripping of nickel from LIX 63 / Versatic 10 in general is well known and has been discussed at length throughout the current thesis in Section 2.6 and Section 6.4.1. Although Section 6.4.4 revealed that nonyl-4PC was a useful nickel accelerator for LIX 63 / Versatic 10, stripping of nickel in Figure 8-8 (b) was still relatively slow compared with that of the other metals in the DNi PLS.

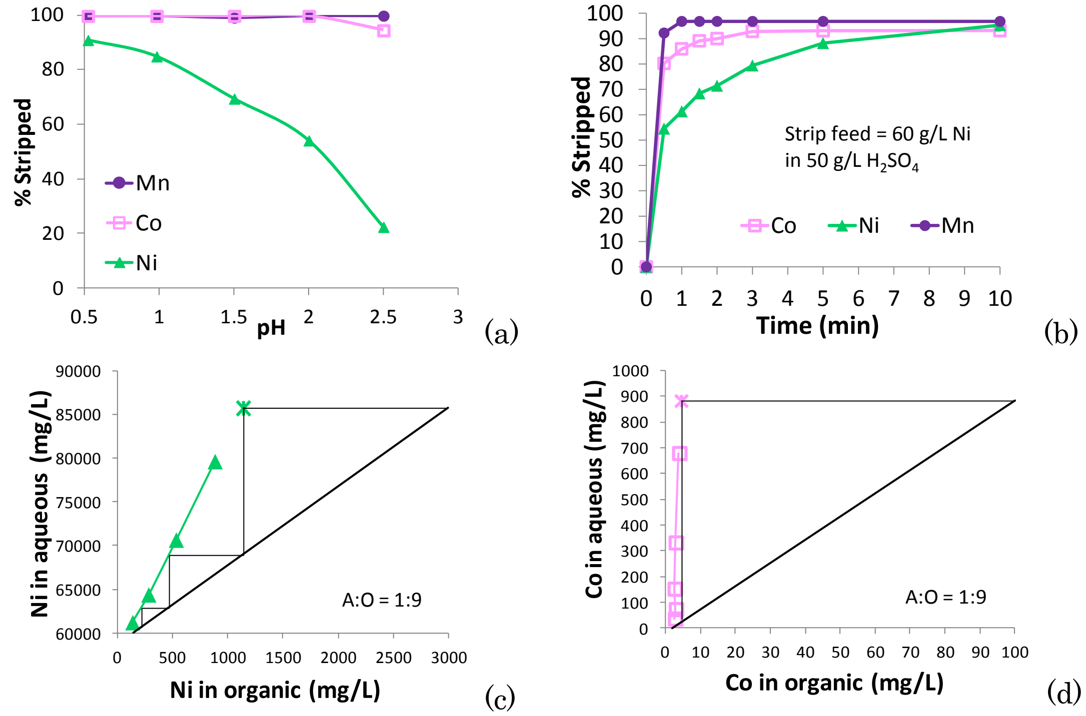


Figure 8-8: Results for metal stripping behaviour with LIX 63 / nonyl-4PC / Versatic 10: (a) pH stripping isotherm, (b) metal stripping rates, (c) nickel distribution isotherm, (d) cobalt distribution isotherm (extrapolated points shown as an asterisk)

8.4.3 Comparison of metal extraction and metal stripping for the three selected solvent systems

A comparison of the three tested solvent systems for application to nickel-cobalt extraction from a high magnesium nitrate bearing PLS based on the results from Section 8.4.1 and Section 8.4.2 is shown in Table 8-2. The majority of these data have been presented in the preceding sections, but a summary here is useful to inform a discussion comparing the three different solvent systems.

The pH$_{90}$(Co) for each solvent system decreased in the following order: Versatic 10 / TBP (5.5) > nonyl-4PC / Versatic 10 (4.75) > LIX 63 / Versatic 10 / nonyl-4PC (3.5). This decreasing pH was as expected given the known synergistic behaviour of pyridine carboxylates and LIX 63 when combined with Versatic 10, discussed extensively throughout the current thesis. For example, in Section 4.3.4, the pH$_{50}$(Ni) extraction from a 1 M nitrate matrix also decreased in the order Versatic 10 (6.1) > nonyl-4PC / Versatic 10 (4.4) > LIX 63 / Versatic 10 / nonyl-4PC (3.2).

Table 8-2: Comparison of the three investigated solvents for application to a high magnesium nitrate bearing nickel laterite PLS

		Versatic 10 / TBP	nonyl-4PC / Versatic 10	LIX 63 / Versatic 10 / nonyl-4PC
Extraction pH for 90% cobalt loading	**$pH_{90}(Co)$**	5.50	4.75	3.50
Metal concentration at equilibrium at $pH_{90}(Co)$ (mg/L)	**Co**	91	115	116
	Ni	2 681	3 145	3108
	Mn	383	176	19
	Mg	1 823	140	4
Metal separation at $pH_{90}(Co)$	**$SF_{(Co/Mn)}$**	2.7	53	2 408
	$SF_{(Co/Mg)}$	311	7 867	170 999
Neutralisation requirement	**mol/L**	0.37	0.15	0.14
Extraction stages required (A:O = 1:1)	**Ni**	2	1	1
	Co	2	2	2
% Extracted of equilibrium loading after 2 mins	**Co**	100	98	100
	Ni	100	100	100
	Mn	100	71	90
	Mg	100	77	291
pH for >95% metal stripping	**All Metals**	2	1	<0.5
Stripping Stages Required (A:O = 1:9)	**Ni**	1	1	3
	Co	1	1	1
% Stripped at 2 mins	**Ni**	100	99	71
	Co	100	83	90
	Mn	100	33	97
	Mg	100	99	100

The separation of impurity metals from nickel and cobalt improved with a decrease in the $pH_{90}(Co)$. Considerable magnesium extraction occurred with Versatic 10 / TBP, which occupied at least 21% of the organic reagent. Good magnesium rejection was achieved using nonyl-4PC / Versatic 10 although a significant level of manganese was co-extracted at pH 4.75 (176 mg/L). A lower operational pH may improve the separation of nickel and cobalt from manganese in a continuous operation when combined with more extraction stages. The highest $SF_{(Co/Mn)}$ for nonyl-4PC / Versatic 10 after a single contact at A:O of 1:1, however, was achieved near pH 4.5 in the current investigation.

Downstream removal of manganese in the cobalt recovery circuit would have to be considered when using nonyl-4PC / Versatic 10. In contrast, excellent separation of nickel and cobalt from both magnesium and manganese was achieved using LIX 63 / Versatic 10 / nonyl-4PC.

As a result of the higher extraction pH and impurity extraction with Versatic 10 / TBP, base addition for neutralisation requirements was more than twice as high (0.37 mol/L) than for nonyl-4PC / Versatic 10 (0.15 mol/L) or LIX 63 / Versatic 10 / nonyl-4PC (0.14 mol/L). From an economic perspective, doubling the consumption of neutralisation reagents and associated cost would be undesirable for nickel and cobalt extraction using Versatic 10 / TBP.

In general, metal extraction for all three systems was rapid. Manganese extraction exhibited peculiar rates with nonyl-4PC / Versatic 10 and LIX 63 / Versatic 10 / nonyl-4PC in that it was scrubbed off the loaded organic by nickel over time. As manganese extraction was slow with nonyl-4PC / Versatic 10, shorter residence times in the extract circuit would reduce manganese removal using this solvent system. In contrast, as manganese extraction with LIX 63 / Versatic 10 / nonyl-4PC was fast, longer residence times would favour manganese removal with this solvent system.

With the exception of nickel stripping from LIX 63 / Versatic 10 / nonyl-4PC, the stripping of metals from the three tested solvent systems was near quantitative at pH 1. Nickel stripping from LIX 63 / Versatic 10 / nonyl-4PC was still not complete at pH 0.5. For solvent systems containing nonyl-4PC, however, it is recommended not to reduce the aqueous pH below 1. Three stages were predicted to generate a stripped organic containing 227 mg/L nickel using a strip feed containing 60 g/L nickel in 50 g/L sulfuric acid. A complicated stripping process with an established recirculating nickel load would likely be required to strip nickel from LIX 63 / Versatic 10 / nonyl-4PC.

Stripping of all metals from Versatic 10 / TBP was particularly rapid, whereas the stripping of metals from either nonyl-4PC / Versatic 10 or LIX 63 / Versatic 10 / nonyl-4PC was less simple. Nickel stripped rapidly from nonyl-4PC / Versatic 10 but cobalt stripping was relatively slow, reaching only 83% after 2 min. Only 60% of manganese was stripped from nonyl-4PC / Versatic 10 after 10 min under the same conditions. For LIX 63 / Versatic 10 / nonyl-4PC, cobalt and manganese stripped rapidly, but nickel stripped slowly and reached only 71% after 2 min. Higher operating temperatures could be used to increase stripping rates, if required.

In summary, Versatic 10 / TBP resulted in high co-extraction of magnesium and a high operational pH requirement, making the use of this solvent system unattractive. LIX 63 / Versatic 10 / nonyl-4PC offered very good rejection of magnesium and manganese, with acceptable rates of metal extraction and stripping. Stripping of nickel from LIX 63 / Versatic 10 / nonyl-4PC was, however, particularly difficult with the tested strip feed solution. Lower nickel concentrations in the strip feed solution could be used to overcome this issue, although the concentration of nickel present in the strip feed would depend on the preferred downstream nickel recovery process. Nonyl-4PC / Versatic 10 offered a good compromise between the rejection of magnesium and manganese and ease of metal stripping. Nonyl-4PC / Versatic 10 is therefore the preferred option for application to nickel and cobalt extraction from a nitrate-based PLS. LIX 63 / Versatic 10 / nonyl-4PC remains a promising secondary option that offers improved manganese and magnesium rejection with a lower operational pH.

8.4.4 Comparison of phase disengagement times for the three solvent systems under both extract and strip conditions

Acceptable phase disengagement times (PDT) are important in a commercial SX operation where larger, more expensive settlers are required to accommodate slower separation. PDT and phase continuity of the selected samples from the extraction and stripping distribution isotherms (A:O of 2:1, 1:1 and 1:2) were therefore monitored via video recordings of the phase disengagement process. These videos revealed that the phase continuity for samples containing nonyl-4PC under extract conditions favoured organic continuous (O/C) mixing at A:O of 1:1. Under strip conditions at A:O of 1:1 solvents containing nonyl-4PC favoured aqueous continuous (A/C) mixing. Despite this favoured continuity, organic phases containing nonyl-4PC could also be forced to operate under organic continuous mixing under strip conditions by decreasing the A:O ratio to 1:2. Under extract conditions at higher A:O ratios (2:1), solvents containing nonyl-4PC did not switch to aqueous continuous operation. If required in a commercial operation, higher internal A:O ratios would therefore likely be required to promote aqueous continuous operation within the mixer.

Table 8-3: Phase disengagement times (s) under extract and strip conditions and different phase continuities

	Extract Conditions		Strip Conditions	
	A/C	**O/C**	**A/C**	**O/C**
Versatic 10 / TBP	14	14	35	12
nonyl-4PC / Versatic 10	N/A	36	73	52
LIX 63 / Versatic 10 / nonyl-4PC	N/A	69	85	81

N/A – This mixing continuity under these conditions was not observed

In all cases, PDT was less than 2 min for all the tested solvent systems for both extract and strip conditions (Table 8-3). PDT increased under all conditions in the order Versatic 10 / TBP < nonyl-4PC / Versatic 10 < LIX 63 / Versatic 10 / nonyl-4PC. This suggests that the addition of LIX 63 or nonyl-4PC to the organic phase slows phase separation under all operating conditions. Despite these differences, PDT of less than 2 min for all tested scenarios suggested that phase disengagement should not be problematic in a commercial operation.

8.5 Conclusion

The aim of this chapter was to compare promising solvent systems identified for application to separation of nickel and cobalt from magnesium in a nitrate-based PLS from the standpoint of a potential industrial application. The current chapter compared the following solvent systems: Versatic 10 / TBP, nonyl-4PC / Versatic 10, and LIX 63 / Versatic 10 / nonyl-4PC. Specifically, the results of this comparison revealed that:

- Versatic 10 / TBP was the only solvent system to result in unacceptable magnesium extraction from the magnesium nitrate PLS (occupying at least 21% of the reagent). It also operated at the highest pH value (5.5). A high operational pH is undesirable, as it would increase neutralisation requirements and generate more stringent requirements for iron and aluminium removal prior to SX to avoid precipitation. Rejection of magnesium was almost complete for both nonyl-4PC / Versatic 10 and LIX 63 / Versatic 10 / nonyl-4PC, making these two solvent systems more promising for nickel and cobalt separation from magnesium and subsequent application to a magnesium nitrate PLS.

- Stripping of all metals from Versatic 10 / TBP occurred rapidly (0.5 min) and could be achieved at moderately high pH (pH 2). In comparison, manganese stripped very slowly (60% stripped after 10 min) from nonyl-4PC / Versatic 10. Slow manganese stripping from nonyl-4PC / Versatic 10 was attributed to the formation of Mn(III) in the organic phase. In addition, nickel stripping from LIX 63 / Versatic 10 / nonyl-4PC did not occur at the recommended pH range of 1 or above, given only 90% stripped at pH 0.5. A recirculating nickel load may therefore be required in the organic phase, decreasing net nickel transfer to the loaded strip liquor.

- Nonyl-4PC / Versatic 10 was the most prospective system for application to a high magnesium nitrate bearing PLS. It offered a compromise between good separation of nickel and cobalt from magnesium ($SF_{(Co/Mg)}$ of 7867) and manganese ($SF_{(Co/Mn)}$ of 53) at a moderate pH of 4.75 and a complete nickel and cobalt stripping with the tested strip feed solution in one stage at A:O of 1:9. LIX 63 / Versatic 10 / nonyl-4PC also remained of interest due to very high rejection of impurities ($SF_{(Co/Mg)}$ of 170999 and $SF_{(Co/Mn)}$ of 2408) and a low operational pH (3.5).

- The addition of nonyl-4PC and LIX 63 to the organic phase increased the phase disengagement times under all operating conditions, from a minimum of 12 s to a maximum of 85 s. This indicated that phase separation was unlikely to be a problem for commercial application of these solvent systems.

CHAPTER 9

Chemical stability of LIX 63 and nonyl-4PC under expected operating conditions relevant to a nitrate-based laterite PLS

9.1 Introduction

LIX 63 is the commercial name for a reagent containing an active *anti*-hydroxyoxime, an inactive *syn*-hydroxyoxime, several impurities, including the primary degradation products diketone, acyloin and keto-oxime, and a diluent. Throughout this chapter the sum of the active *anti*-hydroxyoxime and inactive *syn*-hydroxyoxime will be referred to collectively as 'hydroxyoxime'. The active reagent in nonyl-4PC is nonyl-4-pyridine carboxylate and will be referred to as 'nonyl-4PC'. The only known degradation pathway for nonyl-4PC under commercially relevant SX conditions is hydrolysis to nonanol and iso-nicotinic acid.

The solvent systems LIX 63 / Versatic 10 / nonyl-4PC and nonyl-4PC / Versatic 10 were both promising for the separation of nickel and cobalt from magnesium (Section 8.4.3). Although pyridine carboxylates are generally stable to acid catalysed hydrolysis at pH values of pH 1 or above, the stability of pyridine carboxylates / Versatic 10 under extract conditions in either nitrate or sulfate matrices has not been well documented. In contrast, the rate of reagent degradation in the LIX 63 / Versatic 10 system has been well documented under both extract and strip conditions relevant to a sulfate-based nickel laterite DSX process. The stability of either LIX 63 / Versatic 10 / nonyl-4PC or nonyl-4PC / Versatic 10 in the presence of nitrate anions, however, was unknown.

The aim of this chapter was to investigate the chemical stability of the reagents in promising solvent systems with respect to operating conditions relevant to nickel and cobalt recovery from a nitrate-based PLS. These operating conditions involve a concentrated magnesium nitrate PLS at the pH required for extraction of both nickel and cobalt followed by a sulfuric acid strip. The first half of this chapter covers the stability of hydroxyoxime under these conditions. The effect of Versatic 10 concentration and the presence of nonyl-4PC on cobalt poisoning of LIX 63 / Versatic 10 was also investigated due to cobalt poisoning noted during the long-term studies. The second half of this chapter discusses the stability of nonyl-4PC in both nonyl-4PC / Versatic 10 and LIX 63 / Versatic 10 / nonyl-4PC.

9.2 Materials and Methods

9.2.1 Aqueous and organic solutions

Aqueous phases were made up using the following chemicals: sodium nitrate, cobalt nitrate, nickel sulfate, nitric acid, sulfuric acid and sodium sulfate. Several different samples of DNi PLS were used to carry out reagent stability investigations under extract conditions. Samples were collected from the mixed hydroxide precipitate (MHP) feed tank (Section 1.1.2, Figure 1-2) during operation. The solutions were allowed to cool to room temperature before filtering and storing for use.

The initial sample of pregnant leach solution (DNi High Al) had an aluminium concentration of 486 mg/L. As a result, aluminium began to precipitate above pH 2, forming a gel. The pilot plant trial did not aim to fully remove aluminium when this sample was taken. In a commercial operation when DNi have optimised the aluminium removal stage, it would be reasonable to expect low aluminium concentrations amenable to solvent extraction above pH 2. Therefore, one litre of this sample was raised to pH 3.15 at 40 °C using sodium hydroxide (100 g/L) and left for 30 min to allow precipitation of the majority of aluminium. The resulting suspension was filtered and the filtrate stored for tests under nitrate extract conditions (DNi Moderate Al). A different DNi PLS sample as employed in Section 8.3.1 was also used here due to the very low aluminium concentration (DNi Low Al), required for tests with an extraction pH greater than 4. Lastly, a sulfate-based nickel laterite PLS (Sulfate) was obtained from a bulk synthetic sample of nickel laterite PLS held by CSIRO (Perth, Australia) as used by previous authors (Cheng *et al.*, 2010a; Cheng *et al.*, 2010b). Metal concentrations of the aqueous feeds used are shown in Table 9-1.

LIX 63, Versatic 10 and nonyl-4PC diluted in ShellSol D70 were used to make up the organic phases. All organic solutions contained hexadecane (20 g/L, AR, Sigma Aldrich) as an internal standard for gas chromatography. The target reagent concentrations were 0.31 M LIX 63 / 0.25 M Versatic 10 / 0.36 M nonyl-4PC and 0.25 M nonyl-4PC / 0.5 M Versatic 10. All organic phases were washed before use with 5 g/L sulfuric acid then 50 g/L sodium sulfate and finally with deionised (DI) water, to remove aqueous soluble impurities, and then dried over anhydrous sodium sulfate.

Table 9-1: Metal concentrations (mg/L) for the aqueous PLS samples used in the stability studies

	DNi High Al	DNi Moderate Al	DNi Low Al	Sulfate
Aluminium	438	58	5	9.1
Calcium	1 875	1 905	1 512	413
Cobalt	179	177	109	244
Chromium	5.6	5.5	<0.2	8.7
Iron	2.9	0.3	<0.2	2.7
Magnesium	86 066	86 286	76 837	37 886
Manganese	604	599	568	1 857
Nickel	4 675	4 518	2 838	5 695
Zinc	46	39	<0.2	144
Copper	8.8	1.6	<0.2	16

9.2.2 Long term stability test procedure

All stability studies were carried out by shaking the organic and aqueous phases in 250 mL hexagonal glass jars in an orbital shaker–incubator at 200 rpm. Stability studies on LIX 63 / Versatic 10 / nonyl-4PC were all conducted at 40 °C. As only minimal degradation was expected for nonyl-4PC / Versatic 10, based on the literature survey in Section 2.8.4, stability studies on nonyl-4PC / Versatic 10 were carried out at 50 °C, to accelerate any degradation. All jars were initially cleaned with soap and water, followed by a DI water wash, an ethanol wash, a further DI water wash and a final ethanol wash. The jars were dried in an oven at 100 °C before use and the top of each jar was covered with Fiberflon 108.08 with the lid secured over the top of the fabric. All stability studies were carried out with an A:O of 1:1 when an aqueous phase was present. The experimental matrix describing each test condition is shown in Table 9-2.

Table 9-2: Experimental matrix for stability studies

Experiment Code*	Start pH	Extract Aqueous Feed†	Aqueous Phase	Organic Phase
No Aqueous	N/A	N/A	N/A	Fresh LIX 63/V10/4PC
Ex4.0-N	4.87	DNi Moderate Al (A:O = 1:1)	pH 4 NO_3^- raffinate	Load pH 4 LIX 63/V10/4PC
Ex6.0-S_0	5.79	Sulfate (A:O = 1:1)	pH 6 SO_4^{2-} raffinate	Load pH 6 LIX 63/V10/4PC
St1.0-S_0	0.87	N/A	60 g/L Ni as SO_4^{2-}, H_2SO_4	Fresh LIX 63/V10/4PC
St0.5-S_0	0.50	N/A	30 g/L Ni 0 g/L NO_3^-, H_2SO_4	Fresh LIX 63/V10/4PC
St0.5-S_5	0.50	N/A	30 g/L Ni 5 g/L NO_3^-, H_2SO_4	Fresh LIX 63/V10/4PC
St0.5-S_10	0.50	N/A	30 g/L Ni 10 g/L NO_3^-, H_2SO_4	Fresh LIX 63/V10/4PC
St0.5-N	0.50	N/A	30 g/L Ni as NO_3^-, HNO_3	Fresh LIX 63/V10/4PC
Ex4.75-N-4PC/V10	4.77	DNi Low Al (A:O = 1:1)	pH 4.75 NO_3^- raffinate	Load pH 4.75 4PC/V10
St0.5-S_0-4PC/V10	0.46	N/A	60 g/L Ni as SO_4^{2-}, H_2SO_4	Fresh 4PC/V10
St1.0-S_0-4PC/V10	0.83	N/A	60 g/L Ni as SO_4^{2-}, H_2SO_4	Fresh 4PC/V10

* Ex4.0 = Extract at pH 4.0, St1.0 = Strip at pH 1.0, N = nitrate matrix, S_0 = sulfate matrix with 0 g/L nitrate, 4PC/V10 = nonyl-4PC / Versatic 10 organic phase (otherwise LIX 63 / Versatic 10 / nonyl-4PC)

† N/A = not applicable (organic phase not loaded before test commenced / aqueous phase not present)

Samples (5 mL) of the organic phases were taken at regular intervals and the same volume of aqueous phase was also removed with each organic sample. Organic samples from extract tests were stripped with sulfuric acid (50 g/L at A:O of 3:1 and 50 °C for 60 min). The two phases were separated using Whatman 1PS phase separation paper. Stripped organic from samples under extract conditions and samples of organic phases from tests under strip conditions were shaken with sodium sulfate (50 g/L at A:O of 3:1 for 20 s) and then dried over anhydrous sodium sulfate before storing at 3 °C.

Degradation of hydroxyoxime under sulfate-based extract and strip conditions is a first-order reaction (Barnard, 2008a). Half-lives ($t_{½}$) for reagent loss under different experimental conditions can thus be calculated from the slopes of first-order reaction plots, equal to the rate constants (k), using the correlation (EQ 13):

$$t_{½} = \ln(2)/k \qquad \text{(EQ 13)}$$

In the current work, first-order reaction plots of $-\ln([\text{Reagent}]_t/[\text{Reagent}]_0)$ versus time (days) were used confirm first-order reaction kinetics for degradation of both hydroxyoxime and nonyl-4PC. Where first order reaction kinetics were confirmed, half-lives for the reagents were calculated using (EQ 13).

Where measured, oxidation–reduction potentials were obtained using an intermediate junction Ag/AgCl electrode (Ionode, IJ-64) connected to a pH/mV meter (Hanna, HI 9025). The junction electrolyte was saturated potassium chloride gel (Ionode).

9.2.3 Cobalt poisoning study procedures

Cobalt poisoning of LIX 63 / Versatic 10 with and without nonyl-4PC at varying Versatic 10 concentrations was investigated using the same batch of organic as the stability studies. The method and aqueous feed for measuring the rate of cobalt poisoning described in Section 5.2.2 were used in this study. One exception was that organic phase cobalt concentrations were measured directly from the stripped organic using AAS, as a more accurate analysis method, rather than by difference from the aqueous loaded strip liquor. The method and aqueous feed used for investigating cobalt poisoning over successive load-strip cycles was the same as that Section 5.2.3. Samples were stripped with sulfuric acid (50 g/L) at 40 °C and washed with sulfuric acid (50 g/L), instead of 350 g/L at 50 °C as per Section 5.2.4, due to ease of cobalt(II) stripping noted in Section 8.4.2.

9.2.4 Analytical determinations

All organic phases were analysed using gas chromatography with flame ionisation detection (GC-FID, Varian, CP-3800 gas chromatograph). For analysis of LIX 63, diketone and keto-oxime, samples (0.1 mL) were first derivatised using 0.3 mL N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA, Sigma Aldrich) diluted with 1 mL 50:50 toluene (AR, Sigma Aldrich):N,N-dimethylformamide (DMF, AR, Rowe Scientific) at 80 °C for 20 min. Sub-samples (0.7 µL) were injected into an AT1-MS gas chromatography column (Grace, 30 m column, 0.32 mm inside diameter, 0.25 µm film thickness) with the injection port held at 220 °C with a split ratio of 80. The initial oven temperature (100 °C) was increased by 10 °C/min to 240 °C and held for 0.5 min. The detector port was held at 270 °C and FID sensitivity was set to 12.

For analysis of nonyl-4PC, nonanol, acyloin and Versatic 10, samples (0.1 mL) were diluted in 50:50 toluene:DMF (1 mL) and sub-samples (0.7 µL) were injected into an EC-1000 gas chromatography column (Grace 30 m column, 0.32 mm inside diameter, 0.25 µm film thickness) with an injection port held at 250 °C with a split ratio of 50. The initial oven temperature (85 °C) was increased by 10 °C/min to 170 °C, then by 2 °C/min to 178 °C, then by 15 °C/min to 220 °C and held for 2 min, and then to 250 °C at 15 °C/min and held for 3 min. The detector port was held at 270 °C and FID sensitivity was set to 11.

LIX 63 and nonyl-4PC results were standardised against the day 0 samples of each sample set. Hydroxyoxime in the day 0 sample was quantified against an assumed pure sample of *anti*-hydroxyoxime produced using the method in Appendix A. Pure nonyl-4PC could not be purchased or isolated within the constraints of this project, and so the nonyl-4PC purity quoted by the manufacturer was assumed to be accurate. This proved to be sufficient as reagent balances of 92–109% were obtained from the results for nonyl-4PC degradation (Sections 9.3.5 and 9.3.4).

Degradation products were standardised against the sample with the highest level of those degradation products. Assumed pure samples isolated by CSIRO were used to quantify keto-oxime (Barnard, 2008b) and diketone (Barnard and Urbani, 2007). Acyloin was quantified against a sample provided by Cognis (92.9%). The nonanol isomer from degradation of nonyl-4PC was confirmed to be 3,5,5-trimetyl-1-hexanol by comparison with a purchased sample (85%, Sigma Aldrich). Elution times were identical for both underivatised and BSTFA derivatised samples of the two compared compounds using GC-FID on an AT-1MS column as well as for underivatised samples on an EC-1000 column. As a pure sample of 3,5,5-trimetyl-1-hexanol could not be purchased or isolated within the constraints of the project, nonanol was quantified against a different pure nonanol isomer with a similar elution time under the GC conditions used (1-nonanol, 99%, Sigma Aldrich). This was justified as the FID response was expected to be comparable for these two geometric isomers as they both contain nine carbons and only a primary alcohol functional group.

Aqueous phases for analysis were generated and collected using the method in Section 3.2.3. Aqueous metal concentrations were determined by the CSIRO analytical laboratory using inductively coupled plasma atomic emission spectroscopy. Cobalt concentrations measured directly from an organic phase were analysed using the method in Section 5.2.4.

9.3 Results and Discussion

Reagent stabilities in the LIX 63 / Versatic 10 / nonyl-4PC and nonyl-4PC / Versatic 10 solvent systems under nitrate-based extract and sulfuric acid-based strip conditions were assessed to gain an understanding of the potential life of the reagents under these industrially relevant conditions. Extensive cobalt poisoning of LIX 63 was observed when LIX 63 / Versatic 10 / nonyl-4PC was loaded from either sulfate-based or nitrate-based solutions. As LIX 63 / Versatic 10 was shown to be resistant to cobalt poisoning in work by previous authors (Cheng, 2006; Barnard *et al.*, 2010a), investigations into the effect of the Versatic 10 concentration and the presence of nonyl-4PC on cobalt poisoning of LIX 63 were also carried out.

9.3.1 *Stability of hydroxyoxime in LIX 63 / Versatic 10 / nonyl-4PC under extract conditions*

LIX 63 / Versatic 10 stability in general is well understood under sulfate-based extract conditions. The effects of nonyl-4PC or high nitrate concentrations on hydroxyoxime stability are, however, unknown. The extraction pH for the nitrate-based feed was chosen as the pH_{90}(Co), pH 4, taken from a preliminary pH isotherm (Appendix E) constructed using the 'DNi Moderate Al' feed (Table 9-1). At this pH, most of the nickel and cobalt were extracted with minimal extraction of magnesium, calcium or manganese. The pH for the sulfate-based aqueous feed, pH 6, was chosen to give a similar loaded organic concentration of cobalt as the nitrate loaded organic. The concentrations of metals in the loaded organic phases are shown in Table 9-3.

Table 9-3: Organic phase metal concentrations in mg/L for the loaded organic samples

	Ex4.0-N	**Ex6.0-S_0**
Chromium	4	3
Cobalt	155	178
Copper	9	18
Magnesium	12	5
Manganese	5	8
Nickel	4841	5720
Zinc	33	128

Ex4.0-N – extract, pH 4.0, nitrate; Ex6.0-S_0 – extract, pH 6.0, sulfate

Hydroxyoxime concentrations over 112 days and subsequent half-lives are given in Table 9-4. The rate of hydroxyoxime loss from each system is shown as a first order reaction plot in Figure 9-1, confirming first-order reaction kinetics. LIX 63 / Versatic 10 / nonyl-4PC without an aqueous phase was included as a comparison with LIX 63 / Versatic 10 degradation without nonyl-4PC, as reported by Barnard (2008a). Hydroxyoxime losses in either sulfate or nitrate matrices were comparable, within experimental error ($t_{½}$ of 35 weeks for nitrate and 34 weeks for sulfate). The presence of concentrated nitrate anions under metal-loaded extract conditions did not, therefore, alter hydroxyoxime stability in LIX 63 / Versatic 10 / nonyl-4PC.

Table 9-4: Hydroxyoxime concentrations as a percentage of day 0 values in LIX 63 / Versatic 10 / nonyl-4PC under both nitrate and sulfate-based extract conditions and an aqueous free comparison (40 °C)

Experiment code	Start pH	Final pH	Day						t½
			7	28	49	70	91	112	weeks
Ex4.0-N	4.87	3.89	100	94	85	80	79	72	35
Ex6.0-S_0	5.79	5.69	96	92	87	82	77	72	34
No Aqueous	N/A	N/A	98	96	95	91	89	88	83

Ex4.0-N – extract, pH 4.0, nitrate; Ex6.0-S_0 – extract, pH 6.0, sulfate

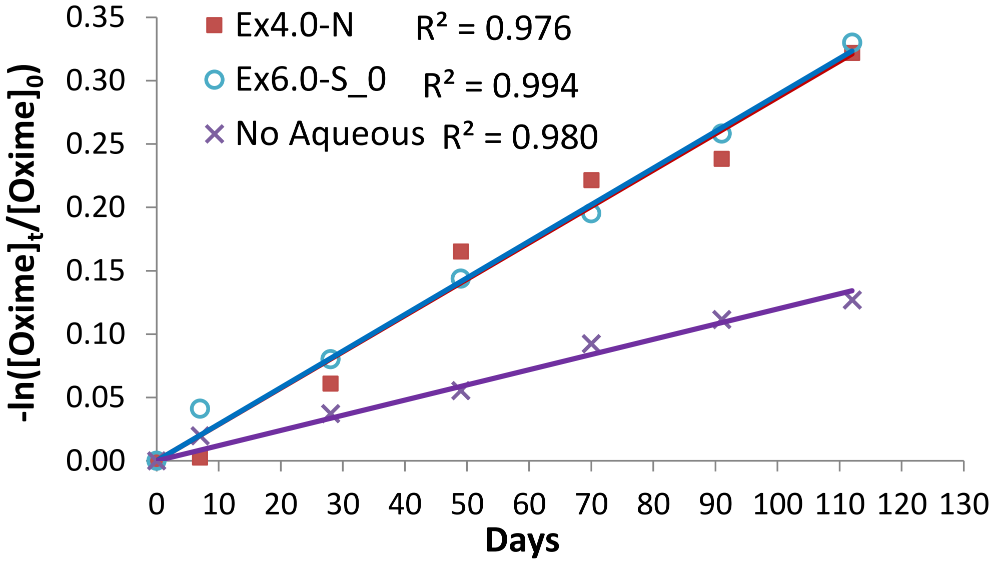


Figure 9-1: First-order reaction plots for hydroxyoxime loss from LIX 63 / Versatic 10 / nonyl-4PC under extract conditions with a no aqueous comparison (40 °C). Trend lines for Ex4.0-N and Ex6.0-S_0 overlap

As discussed in Section 2.8.3, Barnard *et al.* (2010a) demonstrated that the rate of hydroxyoxime loss under extract conditions is related cobalt, copper and manganese concentrations in the loaded organic. When similar concentrations of these metals are present in the organic phase, any major differences in hydroxyoxime stability will be a result of the temperature. It is possible to draw a reasonable comparison between half-lives at similar temperatures by applying the correlation of a doubling in the rate of hydroxyoxime loss for every 10 °C rise in temperature (Barnard and Turner, 2011a). Comparisons from earlier work using this correlation are shown in Table 9-5.

The rate of hydroxyoxime loss from LIX 63 / Versatic 10 / nonyl-4PC in an aqueous free system ($t_{½}$ of 83 weeks) was comparable with that of LIX 63 / Versatic 10 from previous work ($t_{½}$ of 76 weeks). This indicated that nonyl-4PC did not decrease the rate of hydroxyoxime degradation under aqueous free conditions. Further, the comparison between sulfate and nitrate-based extract conditions at various pH values in Table 9-5 demonstrated that neither nonyl-4PC nor the high nitrate concentrations in the DNi PLS had a noticeable effect on hydroxyoxime stability for extraction of nickel and cobalt at pH 4.

Table 9-5: Comparison of hydroxyoxime half-lives in LIX 63 / Versatic 10 under comparable experimental extract conditions extrapolated to 40 °C

Aqueous matrix	Organic Metal mg/L Co	Cu	Mn	Tested Temp °C	t½ weeks	t½ at 40 °C weeks	Reference
No aqueous	N/A	N/A	N/A	40	76	76	(Barnard, 2008a)
No aqueous†	N/A	N/A	N/A	40	83	83	This work
Sulfate pH 4.5	570	3	190	30	67	34	(Barnard *et al.*, 2010a)
Sulfate* pH 5.5	270	190	140	37	47	36	(Barnard and Turner, 2011a)
Sulfate† pH 6.0	178	18	8	40	34	34	This work
Nitrate† pH 4.0	155	9	5	40	35	35	This work

N/A = not applicable, † Organic phase contains nonyl-4PC, * Organic phase contains TBP

The final day (112 day) analyses of hydroxyoxime and associated primary degradation products from LIX 63 / Versatic 10 / nonyl-4PC are shown in Table 9-6. The reagent sums, also known as mass balances, for quantified degradation products were all above 80%. These were slightly lower than the 87–93% obtained by Barnard *et al.* (2010a) under various extract conditions at 30 °C, but within the range obtained by Turner and Barnard (2012) under nickel laterite extract conditions at 45 °C (68–83%).

The actual hydroxyoxime concentration in the day 0 sample was only 0.25 M (81% of the target). This was potentially due to a lower hydroxyoxime concentration in the laboratory compared with that of the bulk storage container, or to some degradation of LIX 63 occurring in the laboratory stored batch sample over time. Despite the low (sub-stoichiometric) concentration, full nickel and cobalt extraction was still obtained. This was attributed to some co-extraction by nonyl-4PC / Versatic 10 occurring at the operating pH.

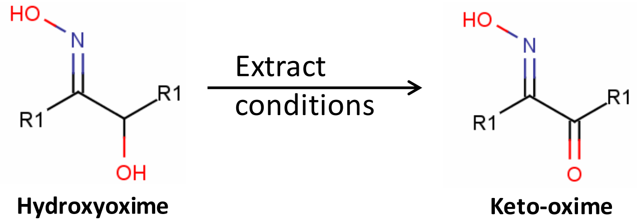
In Cheng (2006), cobalt extraction from a sulfate-based nickel laterite PLS using 0.35 M LIX 63 / 0.5 M Versatic 10 in ShellSol 2046 was complete at pH 4.5. In the current work, a pH of 6.0 was required for extraction of most of the cobalt. The low hydroxyoxime concentration noted (0.25 M) for the fresh organic, combined with a high nickel concentration for the sulfate-based PLS (5.7 g/L), is likely to be the cause of this relatively high extraction pH. Assuming only 60% of the total hydroxyoxime was present as the active *anti*-hydroxyoxime, 0.25 M hydroxyoxime equates to only 0.15 M active reagent. This is nearly sufficient for extraction of 5.7 g/L (0.1 M) nickel at a nickel:oxime ratio of 1:2, but not at 1:3 where 0.3 M active reagent is required. It is therefore expected that the higher extraction pH results from extraction of some nickel and cobalt via nonyl-4PC / Versatic 10 complexes. For Cheng *et al.* (2010a) this occurred at pH 6.0 in a sulfate matrix using 1.0 M decyl-4PC / 0.5 M Versatic 10.

Table 9-6: Fresh and final day concentrations of hydroxyoxime and primary degradation products and reagent sum accountabilities under extract conditions (40 °C)

Experiment code	Hydroxyoxime mM	Diketone mM	Keto-oxime mM	Acyloin mM	Reagent sum mM	Reagent sum %
Fresh Organic	246	17	9	6	278	100
Ex4.0-N	178	18	34	4	234	84
Ex6.0-S_0	177	19	29	4	229	82
No Aqueous	217	14	13	7	251	90

Ex4.0-N – extract, pH 4.0, nitrate; Ex6.0-S_0 – extract, pH 6.0, sulfate

Diketone concentrations in the organic phase fluctuated within 20% of their initial concentration (17 mM), indicating that diketone formation was not favoured under extract conditions. Although acyloin concentrations decreased slightly under extract conditions (Table 9-6), the net change in concentration was negligible. Only keto-oxime was generated throughout the stability studies under extract conditions. Under extract and aqueous free conditions at 40 °C the degradation of hydroxyoxime therefore proceeds via (EQ 14), as has been discussed by previous authors (Barnard and Turner, 2008, 2011a). The presence of high nitrate concentrations (~500 g/L) under extract conditions did not have a noticeable effect on the relative formation of degradation products, and so did not appear to change the mechanism of hydroxyoxime degradation.



(EQ 14)

9.3.2 Stability of hydroxyoxime in LIX 63 / Versatic 10 / nonyl-4PC under strip conditions

There is potential for some nitrate entrainment in the organic phase to be transferred to the acid strip circuit if no intermediate wash stage is implemented. As such, it was of interest to determine the effect of low nitrate concentrations on hydroxyoxime stability in a primarily sulfuric acid-based strip. This was achieved by substituting a portion of the nickel sulfate with nickel nitrate in the otherwise sulfate-based aqueous phase (St0.5-S_0, St0.5-S_5 and St0.5-S_10). A comparison nitrate only system containing only nickel nitrate acidified with nitric acid (St0.5-N) was also included to further assess the effect of nitric acid on hydroxyoxime stability.

The effect of nitrate concentrations on the rate of hydroxyoxime loss under strip conditions is summarised in Table 9-7. First-order reaction plots, displayed in Figure 9-2, confirmed first-order reaction kinetics. Degradation of hydroxyoxime at pH 1.0, the expected strip conditions from the proposed DSX process, is included as a comparison with expected operating conditions. There was a clear difference in the rate of degradation between a sulfuric acid strip at pH 1 (t½ of 110 weeks) compared with a sulfuric acid strip at pH 0.5 (t½ of 38 weeks). The rate of hydroxyoxime degradation in nitric acid at pH 0.5 was slightly faster (t½ of 27 weeks) than this sulfuric acid strip at the same pH. The rate of hydroxyoxime loss from the three sulfate strips with increasing nitrate concentrations revealed no clear trend, leading to the conclusion that a low nitrate concentration in a sulfuric acid strip would have only a minimal effect on hydroxyoxime loss.

Table 9-7: Hydroxyoxime concentrations as a percentage of the day 0 concentration and hydroxyoxime half-lives under acidic strip conditions with varying nitrate concentrations (40 °C)

Experimental code	Start pH	Final pH	Day						$t_{½}$ weeks
			21	**42**	**63**	**84**	**105**	**126**	
St0.5-S_0	0.50	0.53	92	88	83	80	77	73	38
St0.5-S_5	0.50	0.57	97	92	90	84	83	79	53
St0.5-S_10	0.50	0.63	96	91	86	82	79	76	44
			7	**28**	**49**	**70**	**91**	**112**	
St1.0-S_0	0.87	0.98	98	96	95	93	91	89	110
St0.5-N	0.50	0.63	93	87	80	74	67	61	27

St1.0 = Strip at pH 1.0, N = nitrate matrix, S_0 = sulfate matrix at 0 g/L nitrate

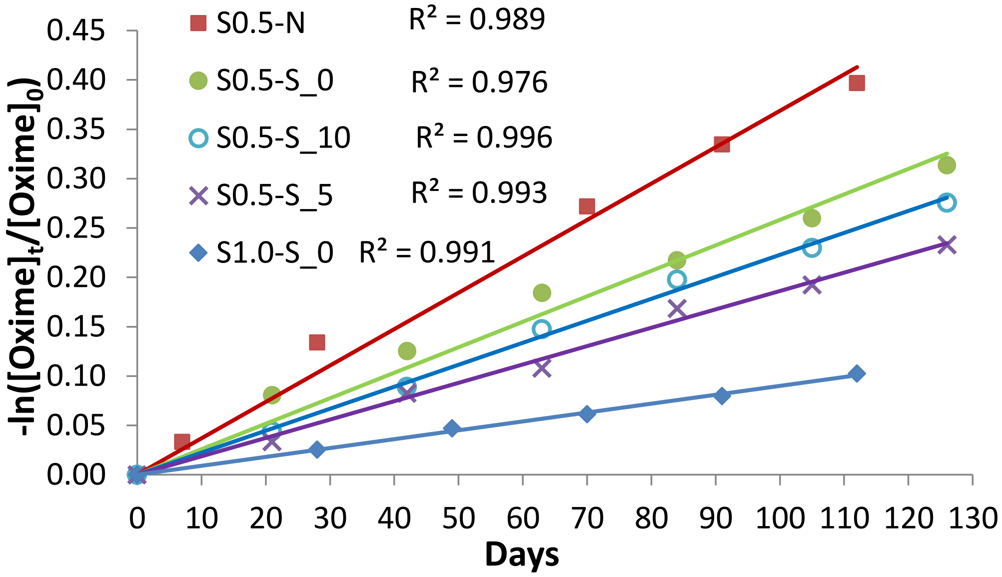


Figure 9-2: First-order reaction plot for hydroxyoxime degradation from LIX 63 / Versatic 10 / nonyl-4PC under acidic strip conditions with varying pH and nitrate concentrations (40 °C)

A comparison with earlier work allowed a determination of the effect of nonyl-4PC on hydroxyoxime stability in LIX 63 / Versatic 10 / nonyl-4PC under strip conditions. A hydroxyoxime half-life of 90 weeks was obtained by Barnard (2008a) for LIX 63 / Versatic 10 in contact with 10 g/L sulfuric acid in deionised water (approximately pH 1) at 40 °C. This compares well with the half-life of 110 weeks obtained in the current work for LIX 63 / Versatic 10 / nonyl-4PC in contact with 60 g/L nickel sulfate at pH 1 (Table 9-7). This comparison suggested that nonyl-4PC did not affect the rate of hydroxyoxime loss under sulfate-based strip conditions at pH 1.

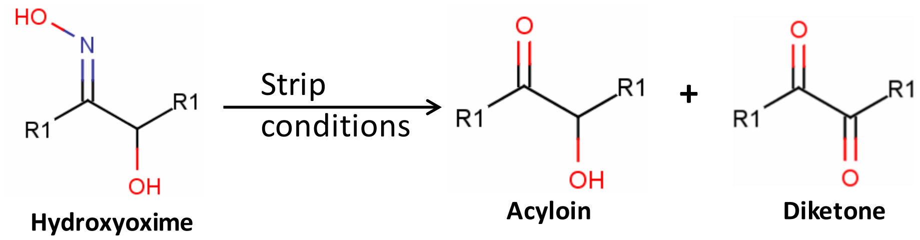
The hydroxyoxime concentrations and primary degradation products for the final day (112 or 126 day) samples under strip conditions are shown in Table 9-8. The reagent sum accountabilities from analysis of hydroxyoxime and primary degradation products were all between 86–94%. These fell below the 95% accountability obtained by Barnard and Turner (2011a) at 60 °C, but are still above 80% and so suggest reliable analysis results and that the quantified degradation products before carbon–carbon cleavage account for the majority of hydroxyoxime degradation.

Table 9-8: Final day concentrations of hydroxyoxime and primary degradation products and associated reagent sum accountabilities for LIX 63 / Versatic 10 / nonyl-4PC under various strip conditions (40 °C)

Experiment code	Hydroxyoxime mM	Diketone mM	Keto-oxime mM	Acyloin mM	Reagent sum mM	Reagent sum %
Fresh Organic	246	17	9	6	278	100
St0.5-S_0	180	20	9	44	253	91
St0.5-S_5	195	19	9	28	251	90
St0.5-S_10	187	17	10	25	239	86
St0.5_N	165	23	10	37	235	85
St1.0-S_0	222	13	11	14	260	94

St1.0 = Strip at pH 1.0, N = nitrate matrix, S_0 = sulfate matrix at 0 g/L nitrate

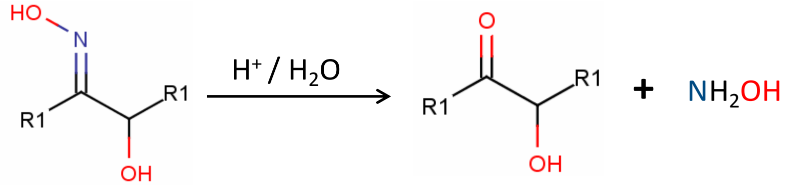
Under all the tested strip conditions, only diketone and acyloin concentrations increased over time. Keto-oxime concentrations did not change outside expected experimental error. Under strip conditions at 40 °C hydroxyoxime degraded to form acyloin and diketone (EQ 15), which is consistent with the previous findings of Barnard (2008a) and Barnard and Turner (2011a).



(EQ 15)

The net amount of diketone formed as a percentage of oxime loss was higher in the nitrate strip (7%) than the three sulfate strips (an average of 1.3%). In comparison, the amount of acyloin formed as a percentage of oxime loss in nitric acid (38%) was less than the sulfuric acid strips (an average of 45%). The difference in oxidation–reduction potential measured between the sulfate and nitrate aqueous strip solutions (496 vs. 615 mV) suggested that the presence of nitrate at low pH increased the oxidative power of the aqueous phase, thereby increasing the rate of diketone formation. As the aim of this study was to develop a solvent extraction process employing a sulfuric acid strip, this was not investigated further.

In all cases under strip conditions, the pH increased over the course of the study (Table 9-7). For the aqueous pH to increase, acid must be consumed. This could have occurred either via nitrate reduction or acid consumption from a hydroxyoxime degradation product. As only acyloin and diketone were formed in the nitrate only strip, it was suspected that degradation occurred via generation of hydroxylamine (NH_2OH) according to the hydrolysis of the oxime functional group (EQ 16):



(EQ 16)

Any hydroxylamine produced would react with the acidic aqueous phase (HA) to produce a hydroxylammonium salt (Rappoport and Liebman, 2008), consuming acid and preventing the reverse reaction back to the oxime (EQ 17).

$$NH_2OH + HA \rightarrow NH_3OH^+A^- \qquad \text{(EQ 17)}$$

As nitrate was added to the sulfate strip solutions as nickel nitrate, less sulfate was present in samples with higher nitrate concentrations to maintain the total nickel concentration at 30 g/L. Sulfate anions are able to buffer pH via the sulfate–bisulfate equilibrium (EQ 18). As a result of this buffering effect, more total acidity was required to bring the high sulfate samples down to pH 0.5. When acid was consumed during the degradation study there was therefore a greater increase in pH for the higher nitrate studies. Hence lower sulfate samples had a lower buffering capacity.

$$SO_4^{2-} + H^+ \rightleftharpoons HSO_4^- \qquad \text{(EQ 18)}$$

A pH change of 0.5 to 0.63 in the nitrate only strip can be approximated to consumption of 82 mM of acid due to a lack of buffering in this solution. This can be compared with the 81 mM of oxime lost over the course of the study (Table 9-8), supporting the premise that a hydroxyoxime degradation product, potentially hydroxylamine, consumed acid. In light of this discussion, the slight variation in degradation rates with increasing nitrate concentrations in a sulfuric acid strip at pH 0.5 (Table 9-7) might potentially be due to an interplay between accelerated oxidation in the presence of nitrate and decreased hydrolysis with a larger increase in aqueous phase pH over the course of the stability study. In a commercial process the aqueous phase would be continuously replaced and ongoing neutralisation of the aqueous phase would not occur.

9.3.3 Effect of Versatic 10 concentration and the presence of nonyl-4PC on cobalt poisoning of LIX 63

It was observed during the degradation study that cobalt stripping was very low under either nitrate or sulfate-based extract conditions, with only 30% stripped after week 4. This is inconsistent with previous work by Cheng (2006) where the presence of Versatic 10 was found to mitigate cobalt poisoning of LIX 63 in contact with sulfate-based aqueous phases. High organic phase manganese concentrations (>1000 mg/L) increase cobalt poisoning of LIX 63 in LIX 63 / Versatic 10 (Barnard *et al.*, 2010a), but low manganese loading (5 mg/L) in the current work still resulted in cobalt poisoning. As cobalt poisoning occurred in both the sulfate and nitrate systems to comparable degrees in the current work, the composition of the organic phase was suspected to have accelerated cobalt poisoning of LIX 63. An investigation into the effect of both Versatic 10 concentration and the presence of nonyl-4PC was therefore carried out to assess their importance on the cobalt poisoning of LIX 63.

It was found that the concentration of Versatic 10 had no effect on cobalt stripping or on the rate of cobalt poisoning (Figure 9-3). This is likely due to the Versatic 10 concentration being above the theoretical stoichiometry of cobalt:Versatic 10 of 1:2 (Flett *et al.*, 1974; Tammi, 1976; Castresana *et al.*, 1988), and hence there was no limitation to forming a synergistic octahedral cobalt complex that is expected to be resistant to cobalt poisoning, as discussed in Section 2.6.3.

The presence of nonyl-4PC greatly increased the rate of cobalt poisoning. After leaving the organic phase loaded with cobalt for only one hour there was a similar level of residual cobalt in stripped LIX 63 / 0.25 M Versatic 10 (0.04 mM) compared with LIX 63 / 0.25 M Versatic 10 / nonyl-4PC (0.06 mM). In contrast, after 192 h there was 10 times as much residual cobalt poisoning in LIX 63 / Versatic 10 / nonyl-4PC (1.05 mM, 90% stripped) as LIX 63 / Versatic 10 (0.10 mM, 99% stripped).

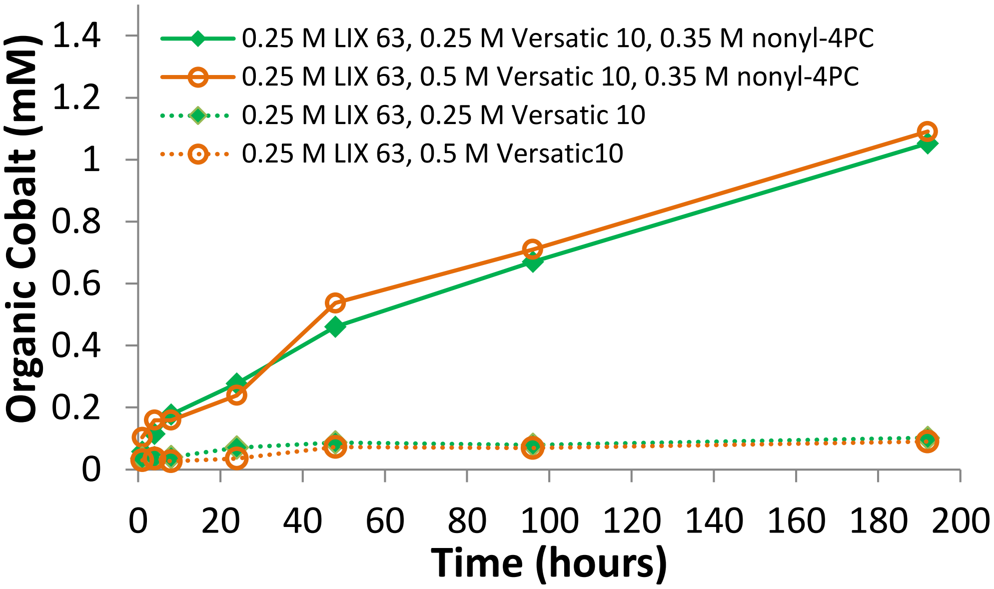


Figure 9-3: Residual organic phase cobalt concentration in stripped LIX 63 / Versatic 10 over time with and without nonyl-4PC after being loaded with cobalt at 23 °C (loading pH = 5.5, initial loaded organic phase cobalt = 0.01 M)

Very low levels of cobalt poisoning occurred when stripping LIX 63 / Versatic 10 with and without nonyl-4PC after being left loaded for only one hour. It was possible that acceptable stripping of cobalt would be achieved for LIX 63 / Versatic 10 / nonyl-4PC left loaded using time frames comparable to those of an industrial process. As such, sequential load–strips of both LIX 63 / Versatic 10 and LIX 63 / Versatic 10 / nonyl-4PC were carried out to determine the extent of cobalt poisoning that could be expected under these conditions.

The results, summarised in Figure 9-4, revealed that organic phase cobalt accumulated with each load–strip cycle in both the organic phases tested. The rate of cobalt accumulation was much faster in the presence of nonyl-4PC. The trend lines shown in Figure 9-4 suggested that, with every load–strip cycle, 0.008 mM of cobalt poisoned LIX 63 / Versatic 10 / nonyl-4PC (0.08% of loaded cobalt) compared with only 0.002 mM cobalt for LIX 63 / Versatic 10 (0.02% of loaded cobalt). Accumulation of cobalt on LIX 63 / Versatic 10 without nonyl-4PC as an accelerator over sequential load–strip cycles has not previously been observed by any authors and may be problematic for future operations using LIX 63 / Versatic 10 for cobalt recovery. This merits further investigation, although it is outside the scope of the current work as LIX 63 / Versatic 10 cannot be used to extract nickel without an accelerator.

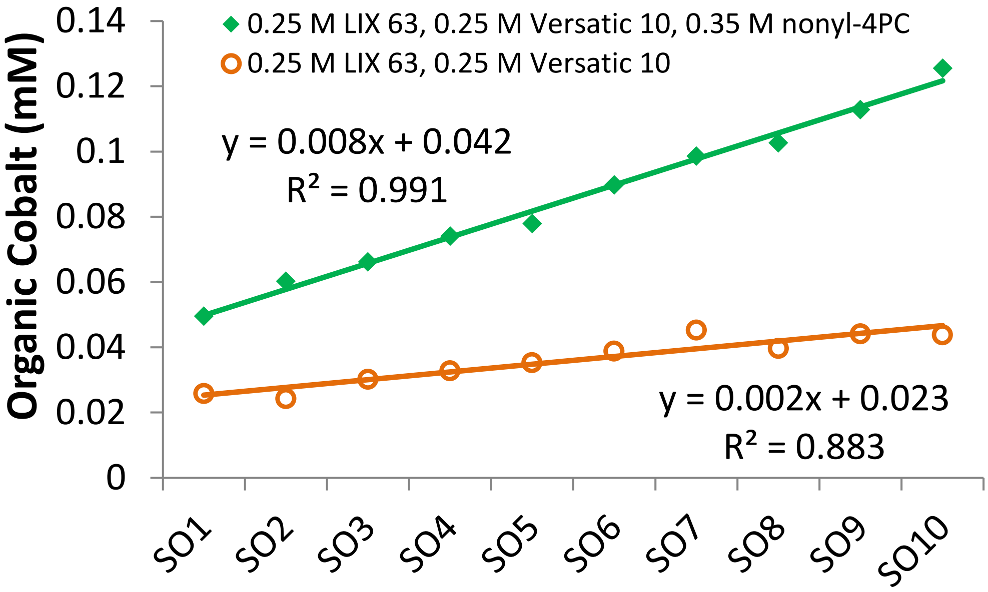


Figure 9-4: Residual organic phase cobalt concentration after sequential load–strip cycles for LIX 63 / Versatic 10 with and without nonyl-4PC (Loading pH = 5.5, aqueous feed = 1 M sodium nitrate, 0.01 M cobalt nitrate. Aqueous strip = 50 g/L sulfuric acid at 40 °C)

Under the assumption that the cycle time for the organic phase in an SX circuit is 30 min, and that three hydroxyoxime molecules are sequestered in each cobalt(III) complex, as suggested by Preston (1975), there would be a loss of 1.15 mM (0.37%) of available LIX 63 from LIX 63 / Versatic 10 / nonyl-4PC each day. This equates to complete loss of hydroxyoxime in 217 days (31 weeks). This rate of hydroxyoxime loss is high when compared with the half-lives obtained in this chapter (>28 weeks). Any process proposing the use of this reagent combination for cobalt extraction would have to consider a reductive strip bleed stream of the stripped organic. This would help to control the recirculating cobalt load and to regenerate the active reagent. A reductive strip bleed stream would, however, increase both the capital and operating costs of a potential operation. This is due to the extra unit process required and the potential for increased reagent degradation, given results from earlier work where some keto-oxime was formed during the reductive stripping of cobalt from LIX 63 / Versatic 10 (Barnard *et al.*, 2010a).

As discussed in Section 2.5.3, an initial tetragonal distortion of a square planar cobalt(II) complex is required via the binding of an organic base to allow oxygen binding. In previous work this was achieved using organic bases such as pyridine (Pignatello and Jensen, 1979) or imidazole (Kufelnicki *et al.*, 2010). Nonyl-4PC (PC) potentially acts in a similar manner to these organic bases and so allows some formation of a PC–Co(II)–O_2 complex, despite the predominant formation of the synergistic Co(II)–hydroxyoxime–Versatic 10 complex in the organic phase.

Alternatively, nonyl-4PC potentially accelerates cobalt poisoning by assisting in deprotonation of the hydroxyoxime to form the triply deprotonated Co(III)L_3 complex suggested by previous authors (Burkin and Preston, 1975; Preston, 1975). This hypothesis is consistent with observations of Barnard *et al.* (2010a) where a higher equilibrium extraction pH, which would favour oxime deprotonation, favours cobalt poisoning of LIX 63 / Versatic 10. This hypothesis also agrees with speculation made in the current thesis (Section 6.4.7) that nickel extraction with LIX 63 / Versatic 10 may have been accelerated with nonyl-4PC by deprotonation of the hydroxyoxime.

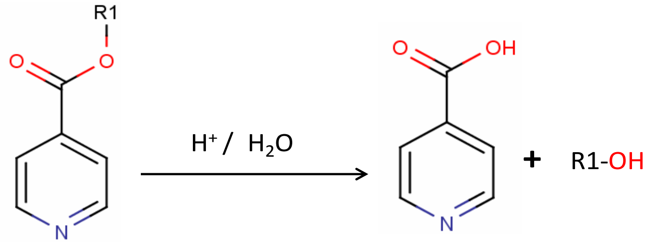
Although interesting, elucidating a conclusive mechanism for cobalt poisoning of LIX 63 in the presence of Versatic 10 and nonyl-4PC is outside the scope of this work and was not investigated further. It is sufficient to note that cobalt poisoning of LIX 63 / Versatic 10 was greatly accelerated by the addition of nonyl-4PC.

9.3.4 Stability of nonyl-4PC under extract conditions

Within experimental error, there was no decrease in nonyl-4PC concentration over 78 days (11 weeks) at 50 °C when nonyl-4PC / Versatic 10 was loaded with 'DNi low Al' (Table 9-1) aqueous at pH 4.75 (Ex4.75-N-4PC/V10). There was similarly no change in the concentration of the nonanol hydrolysis product (2,4,4-trimethyl hexanol) and no new products were detected in the GC-FID spectra over the same timeframe. A lack of degradation under nitrate extract conditions at 50 °C is promising for application of nonyl-4PC / Versatic 10 to a nitrate-based PLS.

Nonyl-4PC analysis from LIX 63 / Versatic 10 / nonyl-4PC under extract conditions resulted in large intra-sample errors, potentially due to a poor FID response for the high nonyl-4PC concentration (0.36 M) that was near constant over the course of the stability study. As there was a small but steady increase in the measured nonanol concentration, nonyl-4PC degradation could instead be followed via quantification of the nonanol degradation product for these conditions. This is shown in Table 9-9. As discussed in Section 2.8.4, hydrolysis (EQ 19) is the only expected degradation mechanism and mass balances (>90%) for both nitrate and sulfate-based extract conditions in Table 9-10 supported this. Back calculating nonyl-4PC loss from the nonanol concentration according to the 1:1 molar ratio expected from the hydrolysis reaction and assuming an initial nonyl-4PC concentration of 360 mM was therefore reasonable.

No degradation of nonyl-4PC occurred from LIX 63 / Versatic 10 / nonyl-4PC without an aqueous phase (Table 9-9). This is consistent with nonyl-4PC degradation proceeding via hydrolysis (EQ 19), which can only occur in the presence of water. Some limited loss of nonyl-4PC was, however, observed for both sulfate extract conditions at pH 6.0 (Ex6.0-S_0) and nitrate extract conditions at pH 4.0 (Ex4.0-N).



(EQ 19)

Table 9-9: Nonyl-4PC concentrations, back calculated from nonanol, as a percentage of the day 0 concentration in LIX 63 / Versatic 10 / nonyl-4PC under extract conditions, and with no aqueous phase

Experiment code	Start pH	Final pH	Day 7	Day 28	Day 70	Day 112
Ex4.0-N	4.87	3.89	100	99	97	96
Ex6.0-S_0	5.79	5.69	99	98	95	94
No Aqueous	N/A	N/A	99	99	100	100

Ex4.0-N – extract, pH 4.0, nitrate; Ex6.0-S_0 – extract, pH 6.0, sulfate

Table 9-10: Final day nonyl-4PC and nonanol concentrations for LIX 63 / Versatic 10 / nonyl-4PC and associated reagent balances under extract conditions

Experiment code	Nonyl-4PC	Nonanol	Reagent sum	
	mM	mM	mM	%
Fresh Organic	360	48	408	100
Ex4.0-N	328	61	389	95
Ex6.0-S_0	313	67	380	93

Ex4.0-N – extract, pH 4.0, nitrate; Ex6.0-S_0 – extract, pH 6.0, sulfate

A first-order reaction plot for nonyl-4PC loss using the recalculated data in Table 9-9 is shown in Figure 9-5. The R^2 correlation coefficient for the first-order reaction plot for back-calculated nonyl-4PC concentrations from LIX 63 / Versatic 10 / nonyl-4PC under nitrate-based extract conditions (Ex4.0-N) was high (0.977) supporting hydrolysis as a degradation mechanism. The R^2 value of 0.929 for nonyl-4PC loss under sulfate-based extract conditions (Ex6.0-S_0) was, however, relatively low compared with other values obtained throughout this investigation (0.976 to 0.996). The straight line model as a predictor of the $-\ln([4PC]_t/[4PC]_0)$ variable was therefore subjected to an *F*-test using the statistical analysis regression package of Microsoft Excel. Using this test, the straight line generated in Figure 9-6 was statistically significant ($p > 0.95$). Slight hydrolysis of nonyl-4PC under extract conditions for LIX 63 / Versatic 10 / nonyl-4PC was therefore a first-order reaction.

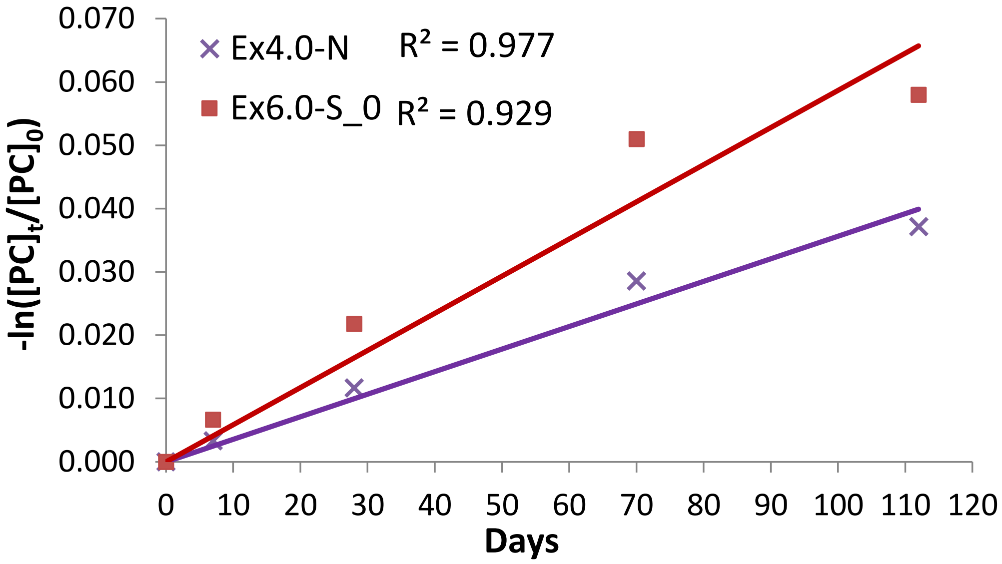


Figure 9-5: First-order reaction plot for nonyl-4PC concentrations in LIX 63 / Versatic 10 / nonyl-4PC under extract conditions back calculated from measured nonanol concentrations (40 °C)

As the first-order reaction plots produced reliable straight lines, half-lives for nonyl-4PC under nitrate-based and sulfate-based extract conditions in LIX 63 / Versatic 10 / nonyl-4PC were calculated. The calculated half-lives (278 weeks for Ex4.0-N and 169 weeks for Ex6.0-S_0) were well above 156 weeks (three years), suggesting that degradation of nonyl-4PC under extract conditions in LIX 63 / Versatic 10 / nonyl-4PC would be limited. The half-lives further demonstrated that the nitrate-based PLS did not increase the rate of nonyl-4PC loss in LIX 63 / Versatic 10 / nonyl-4PC compared with the sulfate-based PLS tested.

Degradation of nonyl-4PC in LIX 63 / Versatic 10 / nonyl-4PC under extract conditions was unexpected given that the pH was relatively high, that little nonyl-4PC hydrolysis occurred in LIX 63 / Versatic 10 / nonyl-4PC at pH 1 under strip conditions (discussed later in Section 9.3.5), and that no hydrolysis was measured at pH 4.75 in nonyl-4PC / Versatic 10. An additional test revealed that the degradation products formed from LIX 63 / Versatic 10 under extract conditions without nonyl-4PC did not overlap with the 2,4,4-trimethyl hexanol peak under the GC conditions used. Hence, an additional degradation product from LIX 63 was not responsible for a growing peak at the same retention time as nonanol. It therefore appeared that both the presence of LIX 63 and metal-loaded extract conditions were required to promote slow hydrolysis of nonyl-4PC at pH values greater than 1. One of the hydroxyoxime degradation products generated only under extract conditions potentially promoted this increase in hydrolysis. This nonyl-4PC degradation, however, is minimal and unlikely to cause concern in a commercial operation. Hence, this discrepancy was not investigated further.

9.3.5 Stability of nonyl-4PC under strip conditions

Results for the loss of nonyl-4PC in nonyl-4PC / Versatic 10 under strip conditions are shown in Table 9-11. A first-order reaction plot for St0.5-S_0-4PC/V10 is shown in Figure 9-6 to test for first-order reaction kinetics.

Although the R^2 value of 0.923 for nonyl-4PC loss in Figure 9-6 was relatively low, the straight line was statistically significant ($p > 0.95$) when tested using an F-test as in Section 9.3.4, suggesting first-order reaction kinetics. A corresponding half-life of only 14 weeks was therefore obtained from this slope. A first-order reaction plot for the St0.5-S_0-4PC/V10 sample was also generated from nonyl-4PC concentrations back calculated from the nonanol concentration, as carried out in Section 9.3.4. The resulting plot resulted in a correlation coefficient of 0.998 (Figure 9-6). A nonyl-4PC half-life of 12 weeks was calculated using these back calculated nonyl-4PC concentrations. This was very similar to the half-life generated from directly measured nonyl-4PC concentrations (14 weeks), further supporting a conclusion that the hydrolysis of nonyl-4PC to nonanol in nonyl-4PC / Versatic 10 at pH 0.5 was first order.

Table 9-11: Nonyl-4PC concentrations as a percentage of day 0 concentration in nonyl-4PC / Versatic 10 (-V10/4PC) under strip conditions (50 °C)

Experiment Code	Start pH	Final pH	Day			
			14	21	63	78
St0.5-S_0-4PC/V10	0.45	0.33	88	80	63	61
St1.0-S_0-4PC/V10	0.84	0.83				95

Data for samples were left blank where samples were not collected or not analysed
St1.0 = Strip at pH 1.0

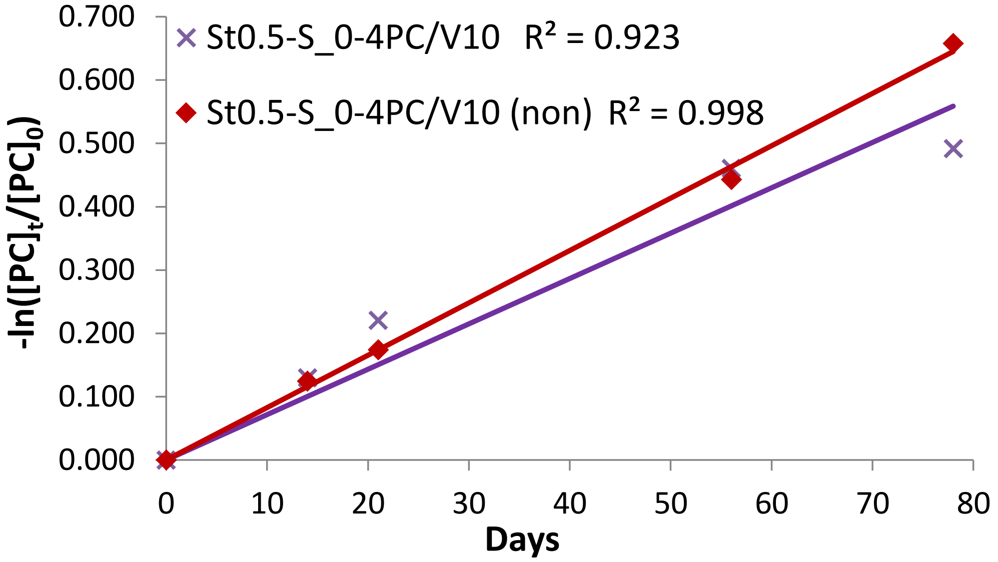


Figure 9-6: First-order reaction plot for nonyl-4PC loss in nonyl-4PC / Versatic 10 under sulfuric acid strip conditions using direct analysis of nonyl-4PC, or concentrations back calculated from nonanol (non) (pH = 0.5, 50 °C)

Nonyl-4PC degradation was limited in contact with a strip solution at pH 0.83 and 50 °C (Table 9-11, St1.0-S_0-4PC/V10). Over the course of 78 days a 5% decrease in the nonyl-4PC concentration was measured. Assuming the reaction was first order, based on first-order reaction kinetics for hydrolysis at pH 0.5, this corresponded to a half-life of 142 weeks. At lower temperatures and even higher strip pH values it is expected that this rate would continue to decrease.

For example, at pH 3 and 40 °C there was only minimal degradation (1% per annum) of decyl-4PC from decyl-4PC / Versatic 10 measured over 84 days (Barnard *et al.*, 2004). Similarly, no loss of CLX 50 was measured from contact with a synthetic strip liquor (35 g/L sulfuric acid, pH ≈ 0.5) over 12 weeks at 40 °C (Cheng *et al.*, 2002).

Acid extraction into the organic phase for nonyl-4PC is expected to increase with decreasing pH, as discussed by other authors (Mihaylov, 2003; Masiiwa *et al.*, 2008). The higher organic phase acid concentrations likely catalysed the nonyl-4PC hydrolysis reaction at lower pH values. The stability of CLX 50 in 35 g/L sulfuric acid reported by Cheng *et al.* (2002), however, suggests that CLX 50 at a pH value less than 1 is more stable than nonyl-4PC. CLX 50 is less basic than nonyl-4PC as it contains two carboxylate electron withdrawing groups on the pyridine ring. CLX 50 will therefore extract less acid than nonyl-4PC at a given pH, hence the higher stability of CLX 50 to acid catalysed hydrolysis.

The final day (day 78) concentrations of nonyl-4PC and nonanol for nonyl-4PC / Versatic 10 under strip conditions are shown in Table 9-12. The reagent sums (98% and 110%) supported hydrolysis as the primary or only degradation mechanism. This agrees with earlier work by Barnard *et al.* (2004) where the same mechanism was proposed for loss of decyl-4PC in contact with an aqueous phase at pH 1 to 3.

Table 9-12: Final day nonyl-4PC and nonanol concentrations for nonyl-4PC / Versatic 10 and associated reagent balances under strip conditions

Experiment code	Nonyl-4PC	Nonanol	Reagent sum	
	mM	mM	mM	%
Fresh Organic	250	27	277	100
St0.5-S_0-4PC/V10	153	147	300	109
St1.0-S_0-4PC/V10	237	35	272	98

St1.0 = Strip at pH 1.0, 4PC/V10 = nonyl-4PC / Versatic 10

In the current work, the stability of nonyl-4PC under strip conditions in LIX 63 / Versatic 10 / nonyl-4PC was also studied (Table 9-13). There was no loss of nonyl-4PC detected or increase in nonanol under strip conditions at pH 1. Significant hydrolysis of nonyl-4PC to nonanol was, however, observed at pH 0.5, in agreement with the work done in the absence of LIX 63. First-order reaction plots (Figure 9-7) demonstrated that nonyl-4PC hydrolysis in LIX 63 /

Versatic 10 / nonyl-4PC was a first-order reaction under strip conditions ($R^2 > 0.93$). As noted for hydroxyoxime loss, it is clear that to avoid accelerated nonyl-4PC degradation an aqueous phase pH of 1 or above must be maintained in the strip circuit.

Table 9-13: Nonyl-4PC concentrations as a percentage of day 0 concentration in LIX 63 / Versatic 10 / nonyl-4PC under various strip conditions (40 °C)

Experiment code	Start pH	Final pH	Day				t½
			21	**42**	**84**	**126**	**weeks**
St0.5-S_0	0.50	0.53	89	82	70	59	23
St0.5-S_5	0.50	0.57	92	85	74	64	27
St0.5-S_10	0.50	0.63	89	79	66	56	21
			7	**28**	**70**	**112**	
St0.5-N	0.50	0.63	97	91	86	81	50
St1.0-S_0	0.87	0.97	102	100	100	98	N/A

N/A – not applicable, no degradation measured

St1.0 = Strip at pH 1.0, N = nitrate matrix, S_0 = sulfate matrix at 0 g/L nitrate

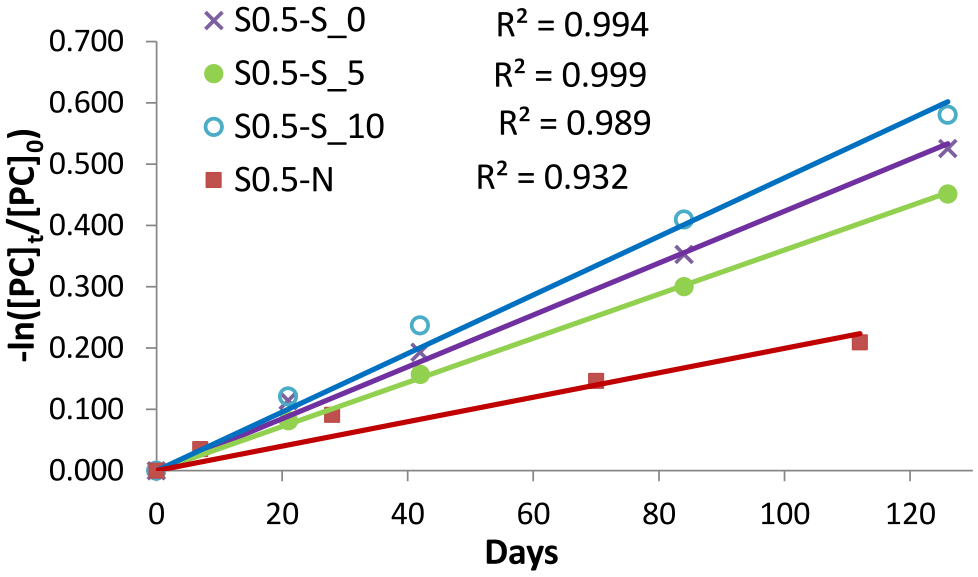


Figure 9-7: First-order reaction plots for nonyl-4PC loss from LIX 63 / Versatic 10 / nonyl-4PC under strip conditions with varying nitrate (pH = 0.5, 40 °C)

Nonyl-4PC in contact with a sulfate only strip liquor at pH 0.5 had a half-life of 23 weeks (Table 9-13). The presence of low nitrate concentrations in a sulfuric acid strip had no clear trending effect on nonyl-4PC loss. Increasing the nitrate concentration from 10 g/L to a nitrate-only strip solution at pH 0.5 reduced the rate of nonyl-4PC degradation. As the only degradation product detected was the hydrolysis product nonanol, the more oxidising nitrate-based aqueous phase had no effect on the mechanism of nonyl-4PC degradation. The absence of a bisulfate equilibrium in the nitrate only strip may therefore have reduced nonyl-4PC degradation by increasing the rate of pH increase over course of the study. As a sulfuric acid strip is the preferred option for the proposed solvent extraction process there was no need to investigate this phenomenon further.

The final (126 or 112) day nonyl-4PC and nonanol concentrations measured for LIX 63 / Versatic 10 / nonyl-4PC are shown in Table 9-14. The reagent sums were all above 90%, again supporting hydrolysis as the primary or only mechanism for nonyl-4PC loss.

Table 9-14: Final day nonyl-4PC and nonanol concentrations for LIX 63 / Versatic 10 / nonyl-4PC and associated reagent balances under strip conditions

Experiment code	Nonyl-4PC mM	Nonanol mM	Reagent sum mM	%
Fresh Organic	360	46	406	100
St0.5-S_0	213	181	394	97
St0.5-S_5	229	161	390	96
St0.5-S_10	201	175	377	93
St0.5-N	292	82	374	92
St1.0-S_0	352	43	395	97

St1.0 = Strip at pH 1.0, N = nitrate matrix, S_0 = sulfate matrix at 0 g/L nitrate

9.4 Conclusions

The aim of this chapter was to investigate the chemical stability of the reagents in promising solvent systems (LIX 63 / Versatic 10 / nonyl-4PC and nonyl-4PC / Versatic 10) with respect to expected operating conditions relevant to nickel and cobalt recovery from a nitrate-based PLS – a high magnesium nitrate bearing aqueous feed and a sulfuric acid strip solution. This investigation revealed that:

- Hydroxyoxime half-lives (34-35 weeks) in LIX 63 / Versatic 10 and distribution of degradation products were unaffected by a nitrate matrix compared with a traditional sulfate matrix or the presence of nonyl-4PC under extract conditions. As LIX 63 / Versatic 10 is already used in commercial operations, LIX 63 / Versatic 10 / nonyl-4PC can also be applied to a nitrate-based PLS.

- The presence of low nitrate concentrations at pH 0.5 had no trending effect on hydroxyoxime half-lives (38 weeks at 0 g/L nitrate, 53 weeks at 5 g/L and 44 weeks at 10 g/L). The presence of nitrate entrainment into the strip circuit would thus have a minimal effect on hydroxyoxime degradation in LIX 63 / Versatic 10 / nonyl-4PC. On moving to a nitric acid strip at the same pH, however, hydroxyoxime degradation was increased (half-life of 27 weeks). This increase in degradation corresponded with an increase in the diketone oxidation product and a decrease in the relative amount of the acyloin hydrolysis product, potentially due to the oxidising nature of nitric acid.

- Nonyl-4PC accelerated the rate of cobalt poisoning of LIX 63 so that after each load–strip cycle under the conditions used 0.08 mM cobalt poisoned LIX 63 / Versatic 10 / nonyl-4PC compared with only 0.02 mM for LIX 63 / Versatic 10. Any process using LIX 63 / Versatic 10 / nonyl-4PC would have to consider the implementation of a reductive strip bleed stream to limit the recirculating cobalt load and to regenerate hydroxyoxime.

- No nonyl-4PC loss in nonyl-4PC / Versatic 10 was noted under extract conditions (~500 g/L nitrate) at 50 °C after 11 weeks. Only minimal degradation of nonyl-4PC was noted at 40 °C in LIX 63 / Versatic 10 / nonyl-4PC (half-lives over 3 years). Nonyl-4PC is thus sufficiently stable under extract conditions for commercial application to a nitrate PLS.

- Under strip conditions at pH 0.83 and 50 °C the nonyl-4PC half-life was 142 weeks in nonyl-4PC / Versatic 10. At pH 0.87, increasing to 0.93 over the 112 day investigation, no nonyl-4PC loss was noted in LIX 63 / Versatic 10 / nonyl-4PC at 40 °C. Nonyl-4PC is therefore expected to be stable under strip conditions at pH values greater than pH 1. At pH 0.5, rapid hydrolysis of nonyl-4PC to nonanol occurred in all cases (half-lives less than 50 weeks). This was attributed to higher extraction of acid into the organic phase at low pH, accelerating acid catalysed hydrolysis of the carboxylate ester. Operation of a strip circuit below pH 1 for reagent systems containing nonyl-4PC is not recommended.

- Concentrated nitrate under extract conditions, or dilute nitrate under sulfuric acid strip conditions (> pH 1), had minimal effect on the rate of degradation for either hydroxyoxime or nonyl-4PC. Compared with a traditional sulfate-based PLS, reagent degradation in relation to LIX 63 / Versatic 10 / nonyl-4PC or nonyl-4PC / Versatic 10 is not a concern for a potential DSX operation designed for a nitrate-based nickel laterite PLS.

CHAPTER 10
Conclusions of the thesis and recommendations for further study

10.1 Conclusions of the present thesis

The hypothesis of the current thesis was that a solvent system can be developed to recover nickel and cobalt from a concentrated magnesium nitrate PLS that successfully rejects magnesium and is chemically stable under expected operating conditions. In Chapter 1 nitric acid-based leaching processes were discussed as an attractive alternative to PAL for dissolution of nickel laterite ores. There is, however, no industry standard route for treatment of nickel laterite PLS to generate marketable nickel and cobalt products.

The product recovery route currently proposed for nitric acid PLS (mixed hydroxide precipitation) is inefficient as it requires numerous unit operations to generate an impure mixed product. Development of a direct solvent extraction (DSX) option for recovering nickel and cobalt directly from a concentrated magnesium nitrate PLS will allow the generation of separate, higher value products without the extra requirements of precipitation, solid–liquid separation and re-leaching. There is, however, little information available on SX from nitrate matrices. Research into this area was essential to the development of a DSX process for separation of nickel and cobalt from magnesium at moderate pH with reagents resistant to oxidative degradation from a concentrated nitrate matrix.

The literature review revealed the following promising solvent systems for application to a concentrated magnesium nitrate-based PLS: Versatic 10 as a single reagent, mixtures of phenolic oximes with an organic acid, a mixture of LIX 63 and Versatic 10 with a nickel accelerator, and a mixture of a pyridine carboxylate with Versatic 10. Specifically, the following aims of the thesis were developed from the conclusions of Chapter 2 to fill the identified gaps in the literature and so aid in developing a viable DSX process for a high magnesium nitrate-bearing nickel laterite PLS:

1. determine the extraction behaviour of metals of interest from a nitrate matrix compared with a traditional sulfate matrix;

2. identify promising solvent systems for application to nickel and cobalt recovery from nitrate-based leach liquors;
3. assess the potential to slow or stop cobalt poisoning of solvent systems identified by the literature to be susceptible to this phenomenon;
4. investigate methods to accelerate nickel phase transfer for any solvent systems that suffer from slow nickel phase transfer rates;
5. determine the effect of reagent concentrations in any novel solvent systems suited to separation of nickel and cobalt from magnesium;
6. compare the promising solvent systems from the standpoint of commercial application; and
7. investigate the chemical stability of the reagents in any promising solvent systems with respect to expected operating conditions.

In pursuing aim (1) in Chapter 3, it was found that the separation of nickel and cobalt from impurities was maintained between sulfate and nitrate matrices. The pH_{50} values for the extraction of various base metals (Ca, Co, Cu, Mg, Mn, Ni and Zn) from nitrate media with various reagents (D2EHPA, HEH(EHP), Cyanex 272, Versatic 10, LIX 63, LIX 63 / Versatic 10, and nonyl-4PC / Versatic 10) were consistently 0.5 units lower than those from sulfate media ($pH_{50(N\text{-}S)}$ of −0.3 to −0.7). This was attributed to the weaker complexing nature of the nitrate ion compared with that of the sulfate anion. An exception to this was the larger $pH_{50(N\text{-}S)}$ shift for the extraction of nickel using solvent systems containing LIX 63 ($pH_{50(N\text{-}S)}$ of −1.0), likely owing to the formation of a stable octahedral nickel–hydroxyoxime–nitrate complex. The solvent extraction data for sulfate systems would therefore be helpful in process development for nitrate systems.

Addressing aim (2) in Chapter 4 revealed that the following solvent systems were the most promising for extraction of nickel and cobalt from a nitrate matrix: LIX 860 / Versatic 10, LIX 860 / sub-stoichiometric Cyanex 272, LIX 63 / Versatic 10, nonyl-4PC / Versatic 10, and Versatic 10 with TBP as a phase modifier. Mixtures of LIX 860 with the relatively weak organic acids Versatic 10 or Cyanex 272 were promising due to high separations of nickel and cobalt from magnesium and manganese. Limiting the Cyanex 272 concentration in LIX 860 / Cyanex 272 to sub-stoichiometric requirements could hinder extraction of impurities whilst still allowing full extraction of nickel and cobalt. All solvent systems were all able to extract nickel and cobalt whilst rejecting magnesium.

Research into aim (3) in Chapter 5 revealed that the LIX 860 / Versatic 10 and LIX 860 / sub-stoichiometric Cyanex 272 were unsuitable for application to nickel and cobalt extraction from a nitrate matrix due to high levels of cobalt poisoning (<90% stripped after 1 hour). The use of a stronger organic acid (D2EHPA), although unsuitable for magnesium rejection, was found to greatly reduce cobalt poisoning. Decreases in cobalt stripping with decreasing organic acid concentrations were consistent with the formation of a $Co(LIX\ 860)_2(Acid)_2$ complex in the organic phase, which blocked the axial cobalt sites required for dioxygen binding and subsequent oxidation of cobalt(II) to cobalt(III).

In pursuing aim (4) in Chapter 6 it was found that nonyl-4-pyridine carboxylate (nonyl-4PC) was the most appropriate modifier for acceleration of nickel stripping. Nonyl-4PC accelerated both nickel stripping and nickel extraction, at a lower concentration than required with TBP, without increasing the required nickel extraction pH. It was proposed that nonyl-4PC acted as a phase transfer catalyst, potentially by increasing the hydrogen ion content of the organic phase, and possibly the interfacial activity of the reagents. This was based on a lack in change in either the pH isotherm or the UV-Visible spectra when extracting nickel with either LIX 63 / Versatic 10 or LIX 63 / Versatic 10 / nonyl-4PC.

Addressing aim (5) in Chapter 6 revealed that interactions between LIX 63 and nonyl-4PC had the greatest effect on both nickel extracted (44% extracted at 0.22 M LIX 63 and 0.15 M nonyl-4PC to 79% at 0.44 M LIX 63 and 0.5 M nonyl-4PC) and nickel stripped (53% nickel stripped at 0.44 M LIX 63 and 0.15 M nonyl-4PC to 95% at 0.22 M LIX 63 and 0.5 M nonyl-4PC). This was attributed to a balance between the reaction equilibria and phase transfer rates where increasing LIX 63 increased the equilibrium of nickel extraction but decreased the rate of stripping, and where increasing nonyl-4PC accelerated the rates of both nickel extraction and nickel stripping. Reagent concentrations for future work of 0.31 M LIX 63 / 0.25 M Versatic 10 / 0.36 M nonyl-4PC were selected using an optimisation calculation as a guide.

Research into aim (6) in Chapter 8 found that nonyl-4PC / Versatic 10 was the most promising solvent system for nickel and cobalt recovery from a nitrate-based PLS as it produced a good compromise between rejection of magnesium, calcium and manganese at moderate pH (4.75), and ease of nickel stripping. LIX 63 / Versatic 10 / nonyl-4PC may be a viable alternative to nonyl-4PC / Versatic 10 as it produced the highest rejection of impurities at a low pH (3.5), although stripping of nickel from this solvent system was not completely achieved even at pH 1, the lowest recommended pH for solvent systems containing nonyl-4PC. Versatic 10 / TBP was considered unacceptable for application to a concentrated magnesium nitrate-based PLS due to high magnesium extraction (occupying at least 21% of the reagent) and a high required extraction pH (5.5).

In pursuing aim (7) in Chapter 9 it was found that the stability of hydroxyoxime and nonyl-4PC in both LIX 63 / Versatic 10 / nonyl-4PC and nonyl-4PC / Versatic 10 was unaffected by the presence of concentrated magnesium under extract conditions, or low nitrate concentrations (0 – 10 g/L) in a sulfuric acid strip (50 g/L sulfuric acid). Although nonyl-4PC did not affect the stability of hydroxyoxime, its use in LIX 63 / Versatic 10 / nonyl-4PC may necessitate a reductive strip bleed stream for cobalt stripping, as the presence of nonyl-4PC accelerated four-fold the accumulation of cobalt after successive load–strip cycles.

Finally, in terms of the hypothesis of this thesis that '*a solvent system can be developed to recover nickel and cobalt from a concentrated magnesium nitrate PLS that successfully rejects magnesium and is chemically stable under expected operating conditions*', two solvent systems were developed. LIX 63 / Versatic 10 / nonyl-4PC offers far superior rejection of magnesium and manganese at a lower extraction pH than nonyl-4PC / Versatic 10. The following disadvantages of LIX 63 / Versatic 10 / nonyl-4PC, however, need to be highlighted: (1) inferior stripping of nickel compared with nonyl-4PC / Versatic 10, (2) increased cobalt poisoning due to the presence of nonyl-4PC and (3) high rates of hydroxyoxime degradation compared with nonyl-4PC under metal loaded extract conditions. As a result of these disadvantages of LIX 63 / Versatic 10 / nonyl-4PC, the solvent system nonyl-4PC / Versatic 10 dissolved in an aliphatic diluent is recommended as the most promising solvent system for application to recovery of nickel and cobalt from a nitrate-based nickel laterite PLS.

10.2 Recommendations for further study

As with any study of this nature, some results of the present study revealed that further work may lead to advancements of the knowledge of the topic area. These were, however, outside the scope of the present study. In light of this, the following recommendations are made for further investigation:

- The separation of nickel from cobalt using LIX 63 / Versatic 10 / nonyl-4PC at low pH might be viable (predicted $SF_{(Ni/Co)}$ of 23 at pH 2) and is of interest for further work. The pursuit of this would have involved full investigation of a separate nitrate-based DSX process, and thus, was too large to complete within the constraints of the present work. It was preferable to extract nickel and cobalt in one step and then strip to sulfuric acid where proven nickel–cobalt separation techniques could then be used.

- The oxidation of manganese in nonyl-4PC / Versatic 10 and the potential for this to affect the rate of manganese stripping should be investigated in future work. Although the present work demonstrated that manganese could be fully removed via acid stripping, the effect of aging time on the rate of stripping should be investigated further to determine the potential for improving rejection of manganese via a kinetic stripping process.

- Ongoing cobalt poisoning of LIX 63 / Versatic 10 without any modifier in the organic phase over sequential load–strip cycles, although slight, was inconsistent with previously published results from other studies of this system. This phenomenon should be investigated further as it may be problematic for SX processes planning to extract cobalt using this solvent system, such as the cobalt extraction process being commissioned at El Boleo by Baja Mining.

- The effect of pyridine derivatives other than nonyl-4PC on solvent extraction of nickel and cobalt from a nitrate matrix should be investigated. Although it has been shown that nonyl-4PC is a viable pyridine carboxylate for separation of nickel and cobalt from magnesium, further research would determine if the use of a commercially available pyridine derivative, such as Nicksyn, could be used in place of nonyl-4PC to simplify future process commercialisation.

- Although outside the scope of the current investigation, further fundamental studies into the bonding arrangements and energies of the synergistic metal complexes formed via mixtures of phenolic oximes with phosphoric acids, nonyl-4PC / Versatic 10 and LIX 63 / Versatic 10 / nonyl-4PC should be considered. Greater understanding in this area would help to futher explain some of the phenomena discussed in this thesis, such as synergism, cobalt poisoning, slow stripping rates and accelerated phase transfer kinetics. Advances in this area may also reveal methods to improve on existing synergistic solvent extraction systems.

CHAPTER 11

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APPENDIX A: Procedure for quantification of hydroxyoxime in commercial LIX 63

The concentration of hydroxyoxime in the bulk sample was measured against an assumed pure standard of *anti*-hydroxyoxime prepared in the laboratory. This sample was prepared using the following method. An organic solution of LIX 63 in ShellSol D70 was contacted with 60 g/L nickel sulphate in 100 g/L sulphuric acid over 12 hours. The light blue precipitate of nickel-*tris*-oxime was collected and washed with ethanol and dried in an oven at 80 °C. The collected solid was subsequently stripped using hexane and 63 g/L nitric acid to yield nickel nitrate dissolved in the aqueous phase and pure *anti*-oxime in the organic phase. Hexane was evaporated in a fume cupboard. The white waxy solid collected was fully dried in a vacuum desiccator for 48 hours. A gas chromatograph for the collected solid did not reveal any impurities hence the white solid collected was assumed to be pure *anti*-hydroxyoxime.

Hydroxyoxime concentration in LIX 63 was analysed using gas chromatography with flame ionisation detection (GC-FID, Varian, CP-3800 gas chromatograph). Samples (0.1 mL) were first derivatised using 0.3 mL N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA, Sigma Aldrich) diluted with 1 mL 50:50 toluene (AR, Sigma Aldrich) : N,N-dimethylformamide (DMF, AR, Rowe Scientific) at 80 °C for 20 minutes. Sub-samples (0.7 µL) were injected into an AT1-MS gas chromatography column (Grace, 30 m column, 0.32 mm inside diameter, 0.25 µm film thickness) with the injection port held at 220 °C at a split ratio of 80. The initial oven temperature (100 °C) was increased by 10 °C/min to 240 °C and held for 0.5 min. The detector port was held at 270 °C and FID sensitivity was set to 12.

APPENDIX B: Example code for thermodynamic models comparing the precipitation of metal hydroxides from sulphate and nitrate aqueous matrices

The thermodynamic model code for precipitation of nickel hydroxide from sodium nitrate is as follows:

```
knobs
-iterations 50000

TITLE define sol

Phases
Fix_pH
H+ = H+
   log_k 0

Solution 1
pH 1
pe 4
redox O(0)/O(-2)
temp 25
units mmol/L
Ni 1
N(5) 100 as NO3- charge
Na 100
O(0) 0.01 O2(g) -0.7
C(4) 0.01 CO2(g) -2
END

Selected_output
-file niohno3.csv
-totals Ni
-m NiNO3+ Ni(NO3)2 Ni+2
-water true
-ionic_strength
END

Use Solution 1
Equilibrium_phases 1
Fix_pH -1.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -2 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -2.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -3 NaOH
Ni(OH)2 0 0
```

```
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -3.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -4 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -4.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -5.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -6 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -6.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -7 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -7.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -8 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -8.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -9 NaOH
Ni(OH)2 0 0
END
```

```
Use Solution 1
Equilibrium_phases 1
Fix_pH -9.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -10 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -10.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -11 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -11.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -12 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -12.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -13 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -13.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -14 NaOH
Ni(OH)2 0 0
END
```

The thermodynamic model code for precipitation of nickel hydroxide from sodium sulphate is as follows:

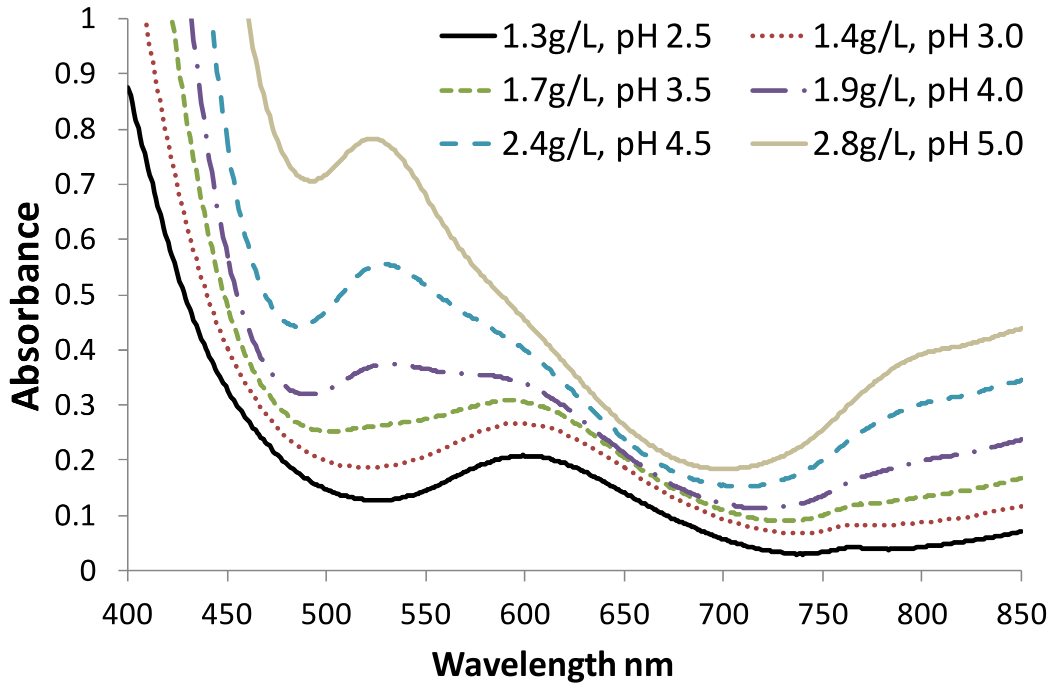
```
knobs
-iterations 50000

TITLE define sol

Phases
```

```
Fix_pH
H+ = H+
   log_k 0

Solution 1
pH 1
pe 4
redox O(0)/O(-2)
temp 25
units mmol/L
Ni 1
S(6) 33 as SO4-2 charge
Na 66
O(0) 0.01 O2(g) -0.7
C(4) 0.01 CO2(g) -2
END

Selected_output
-file niohso4.csv
-totals Ni
-m Ni(SO4)2-2 NiSO4 Ni+2
-water true
-ionic_strength
END

Use Solution 1
Equilibrium_phases 1
Fix_pH -1.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -2 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -2.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -3 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -3.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -4 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -4.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
```

```
Equilibrium_phases 1
Fix_pH -5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -5.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -6 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -6.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -7 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -7.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -8 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -8.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -9 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -9.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -10 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -10.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
```

```
Fix_pH -11 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -11.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -12 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -12.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -13 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -13.5 NaOH
Ni(OH)2 0 0
END
Use Solution 1
Equilibrium_phases 1
Fix_pH -14 NaOH
Ni(OH)2 0 0
END
```

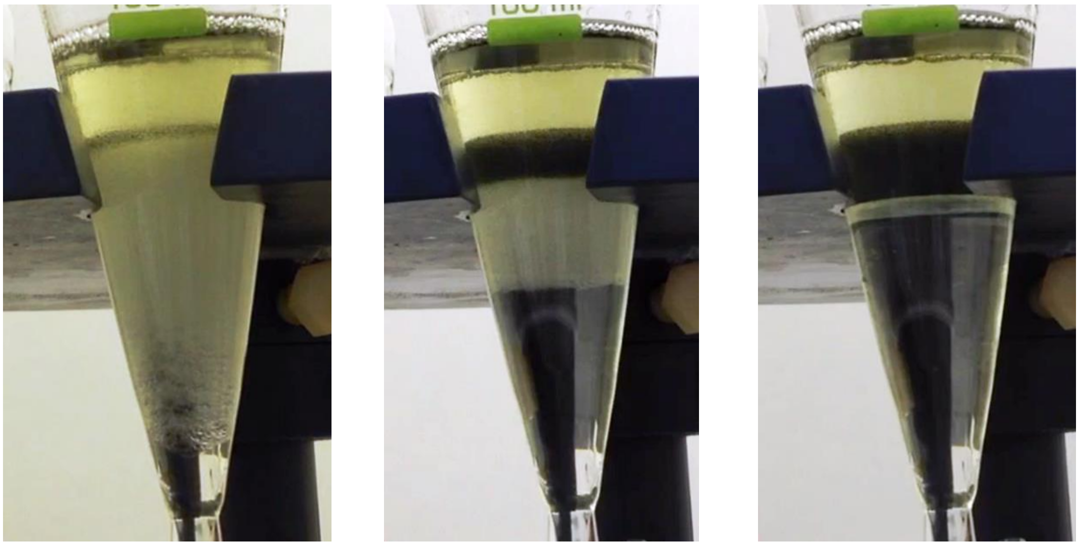
APPENDIX C: UV-vis spectra for nickel extracted using LIX 63 / nonyl-4PC from a nitrate matrix



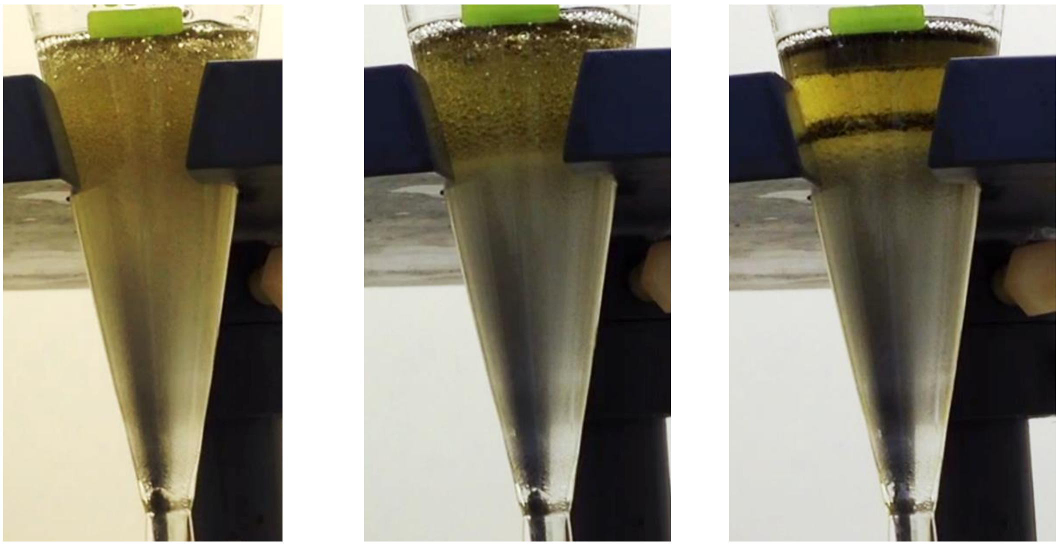
UV-vis spectra for varying organic phase nickel concentrations at varying pH values after extraction into 0.31 M LIX 63 / 0.35 M nonyl-4PC.

APPENDIX D: Images from the disengagement of selected organic phases under extract and strip conditions

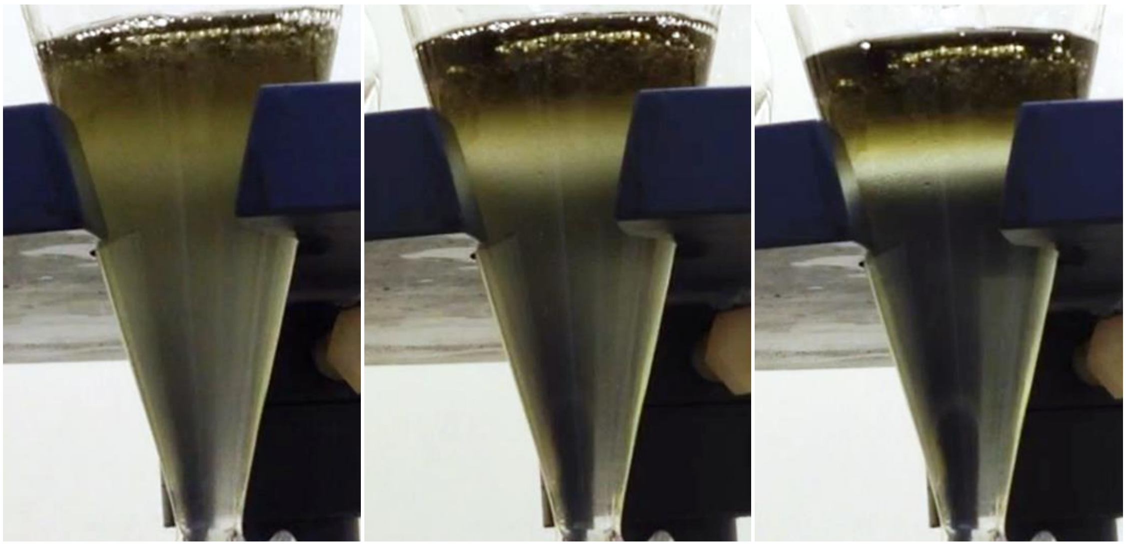
All of the following images were taken as screenshots from videos of the phase disengagement at the start, middle, and end of disengagement. Every image has been cropped around the separating funnel. The images were edited using Microsoft Office Picture Manager using the 'Auto Correct' function to enhance their clarity.



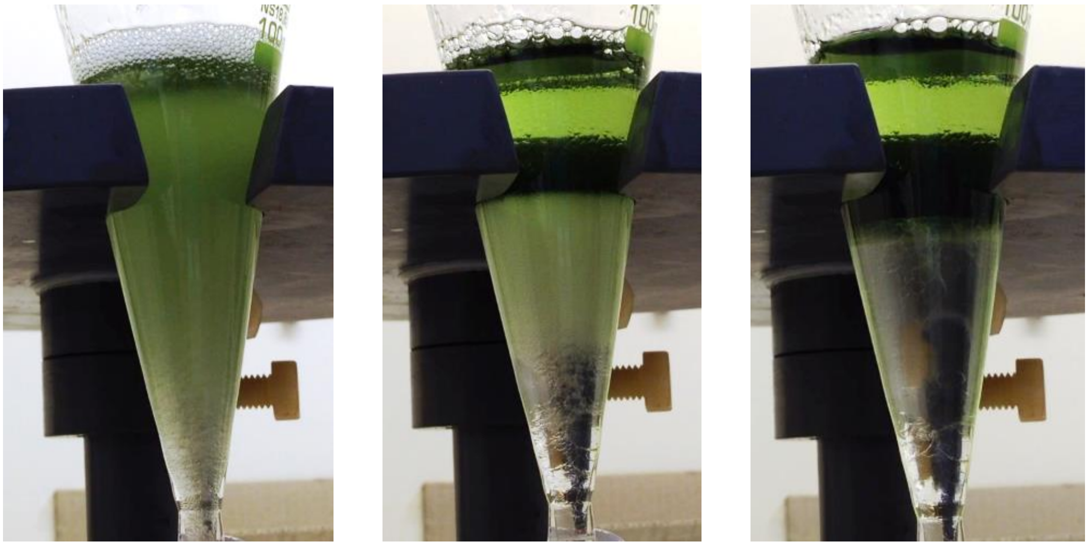
Phase disengagement of Versatic 10 / TBP under extract at A:O 1:2



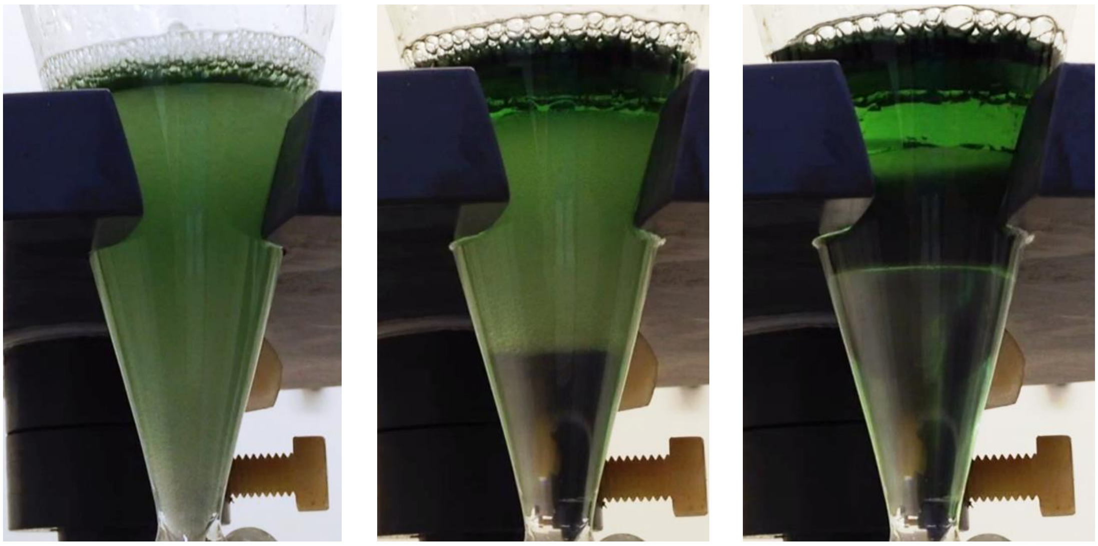
Phase disengagement of Versatic 10 / TBP under extract at A:O 1:1



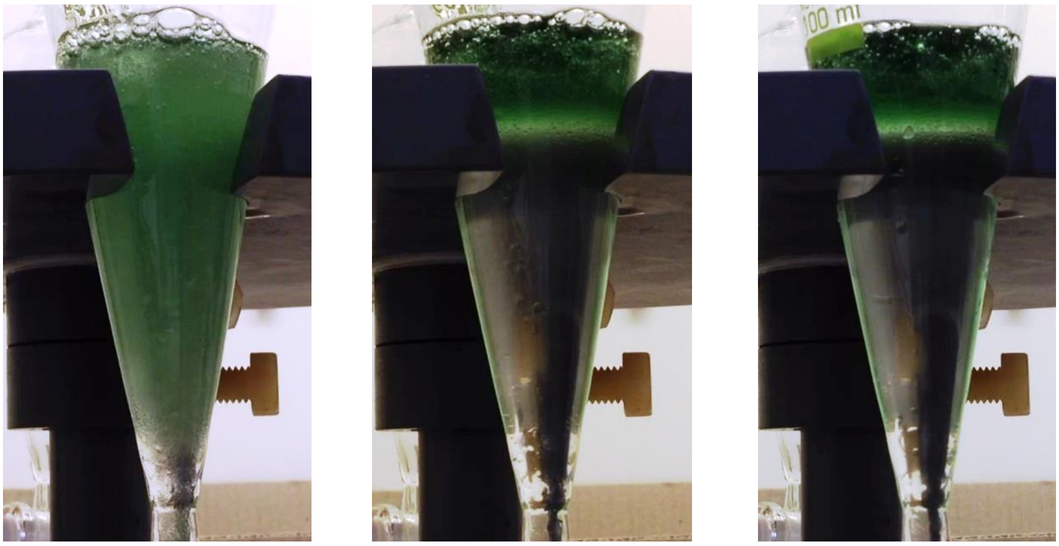
Phase disengagement of Versatic 10 / TBP under extract at A:O 2:1



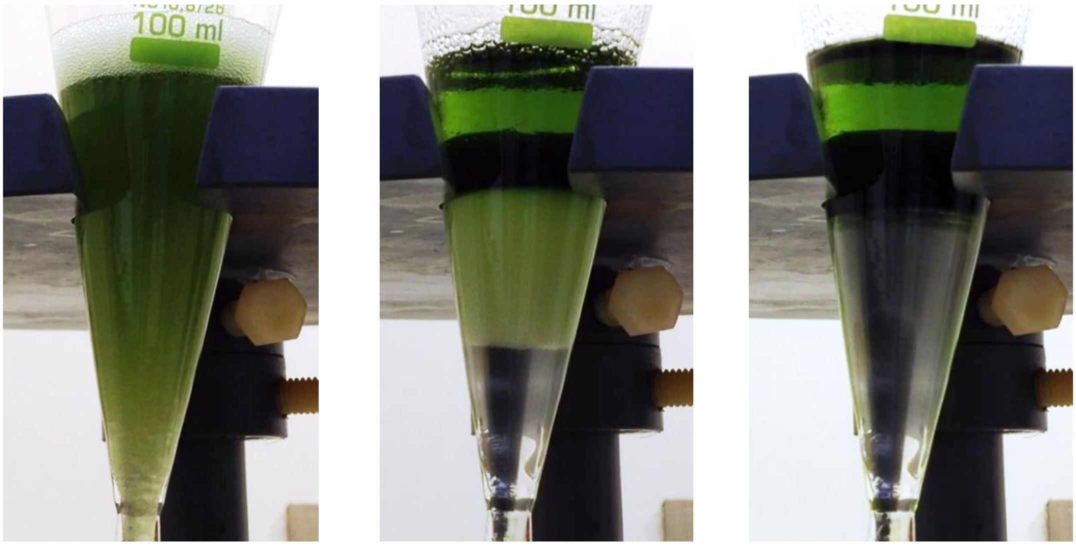
Phase disengagement of nonyl-4PC / Versatic 10 under extract at A:O 1:2



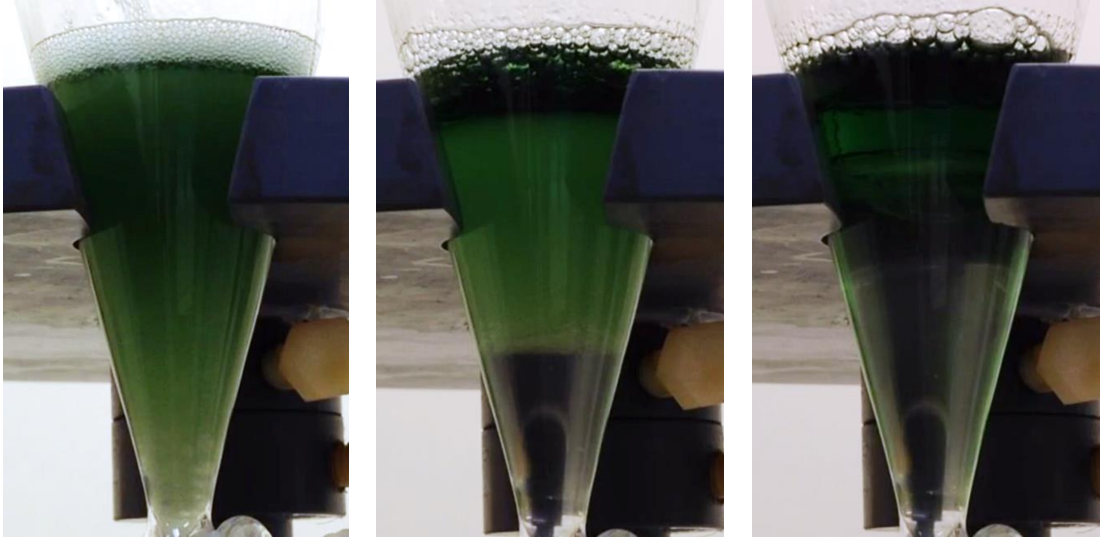
Phase disengagement of nonyl-4PC / Versatic 10 under extract at A:O 1:1



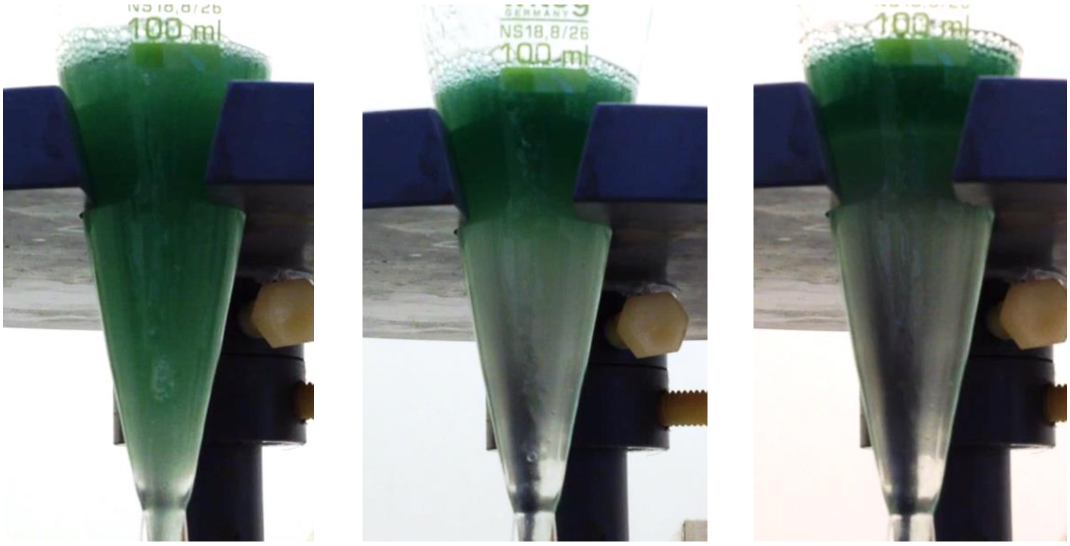
Phase disengagement of nonyl-4PC / Versatic 10 under extract at A:O 2:1



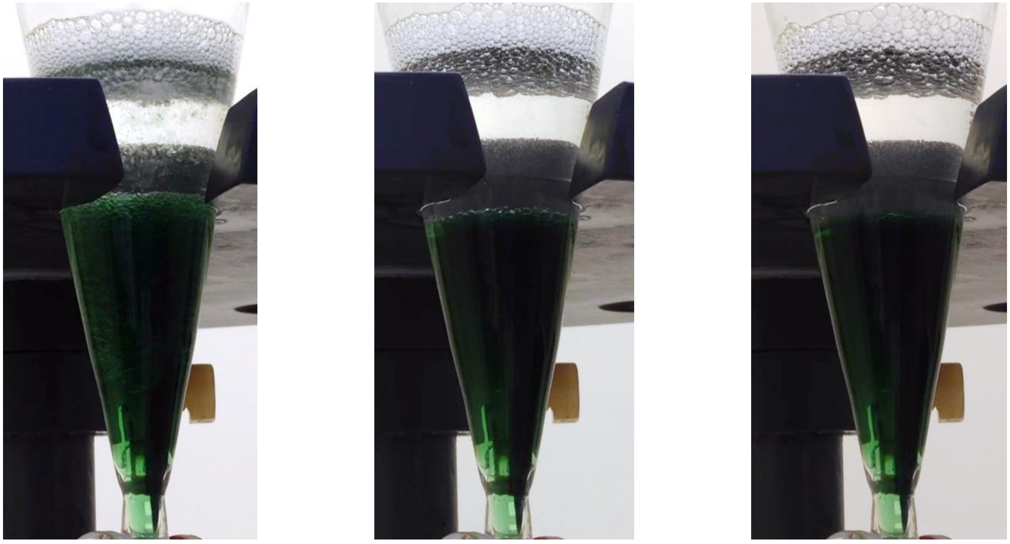
Phase disengagement of LIX 63 / Versatic 10 / nonyl-4PC under extract at A:O 1:2



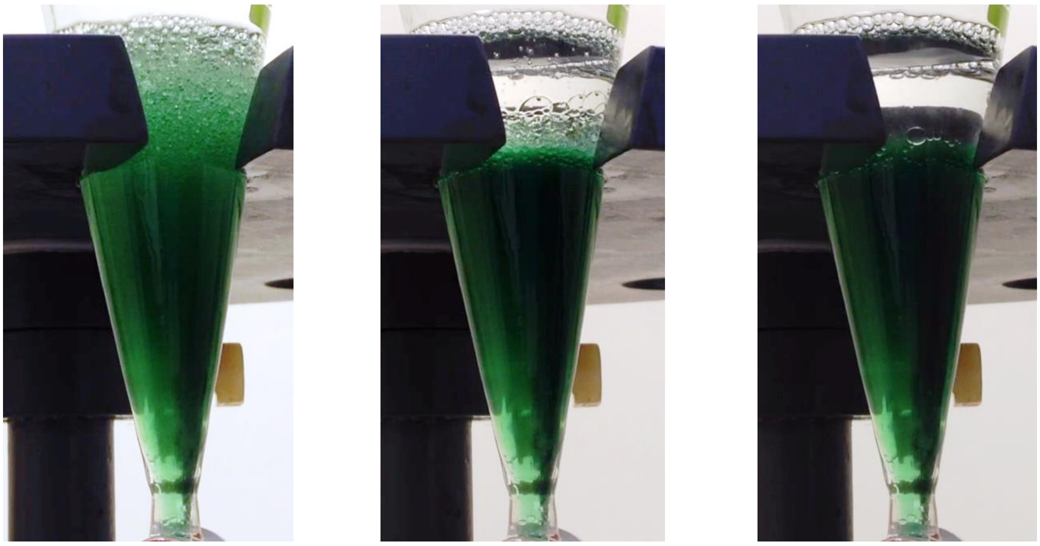
Phase disengagement of LIX 63 / Versatic 10 / nonyl-4PC under extract at A:O 1:1



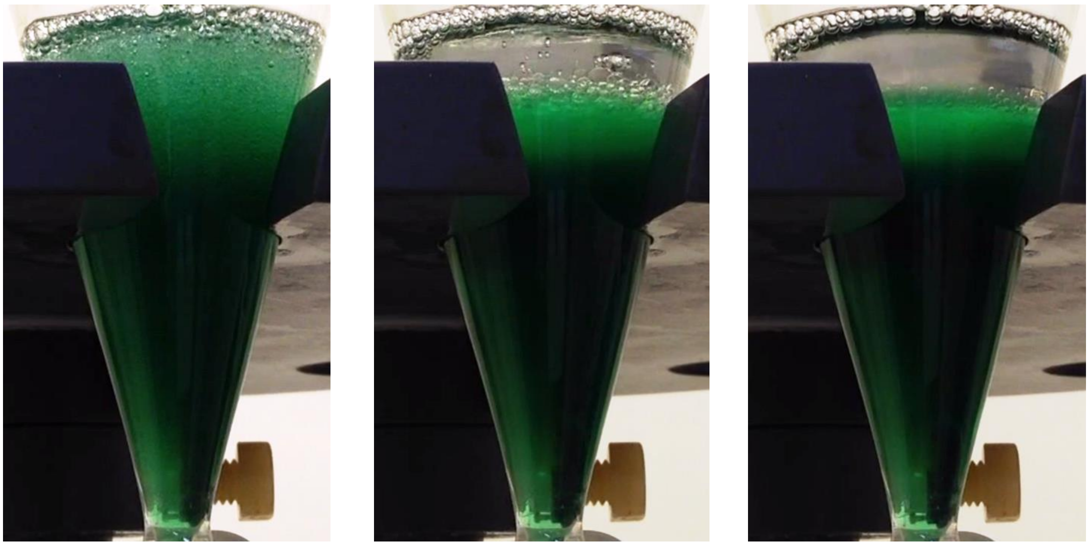
Phase disengagement of LIX 63 / Versatic 10 / nonyl-4PC under extract at A:O 2:1



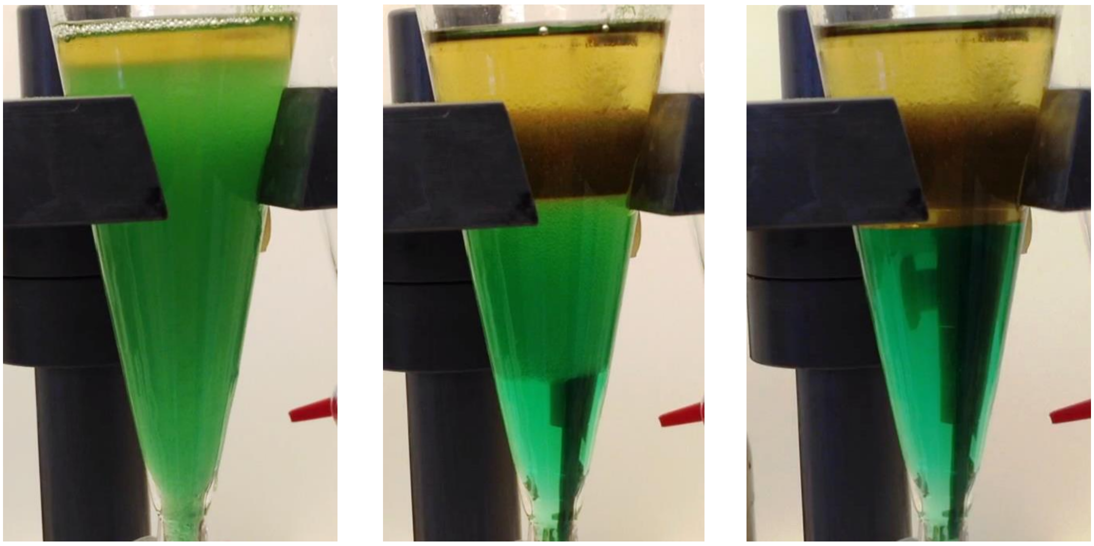
Phase disengagement of Versatic 10 / TBP under strip at A:O 1:2



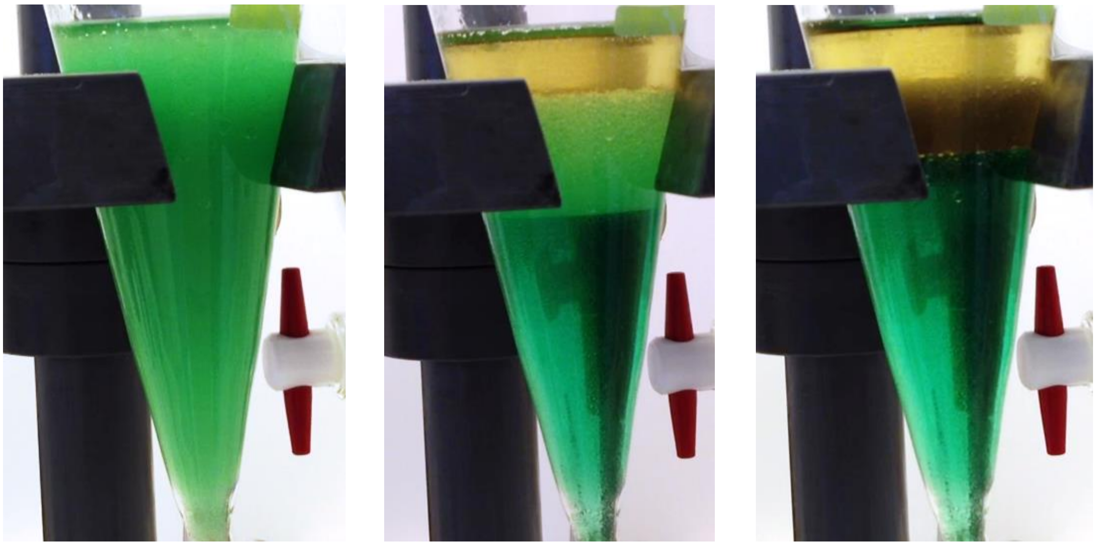
Phase disengagement of Versatic 10 / TBP under strip at A:O 1:1



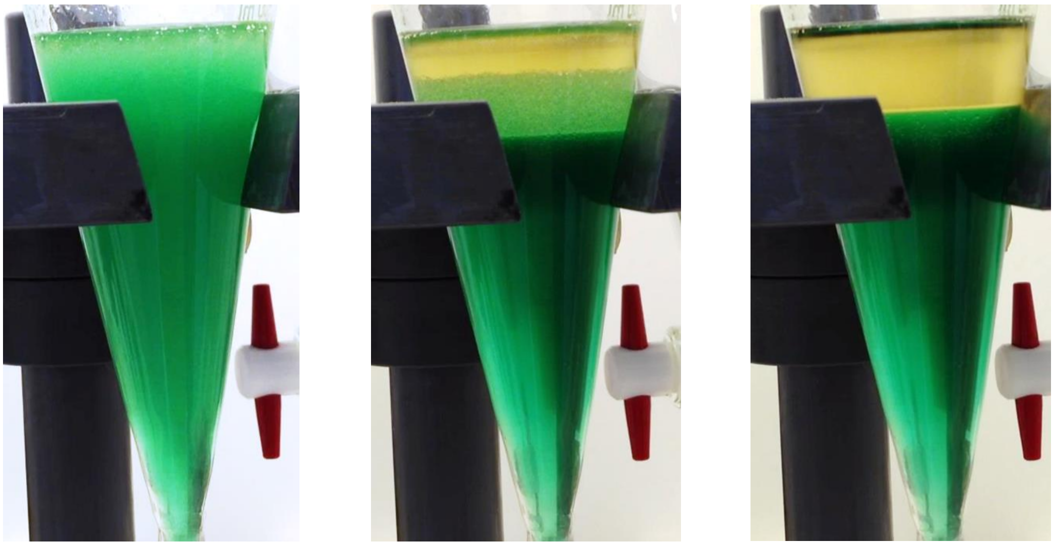
Phase disengagement of Versatic 10 / TBP under strip at A:O 2:1



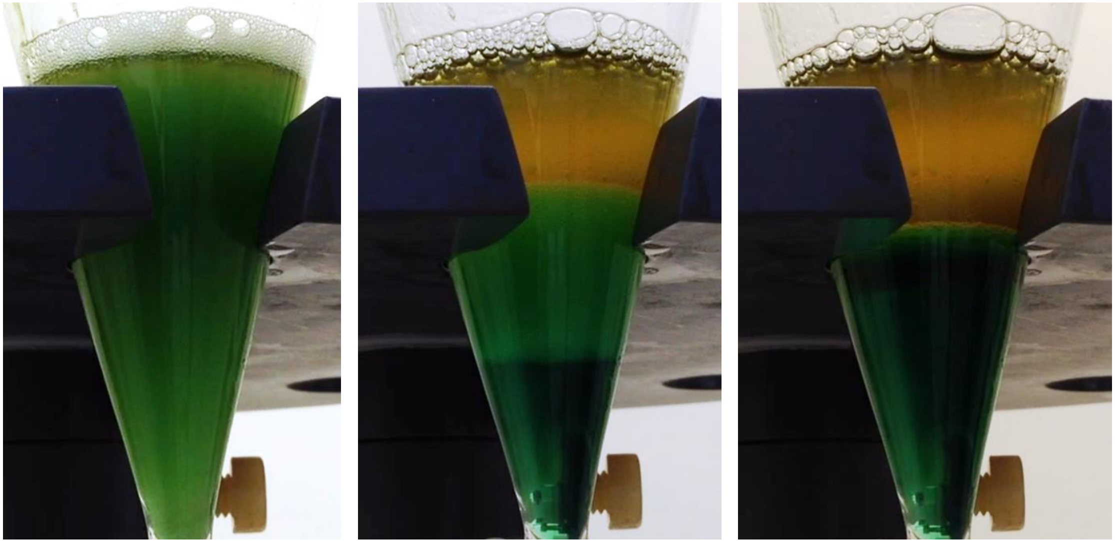
Phase disengagement of nonyl-4PC / Versatic 10 under strip at A:O 1:2



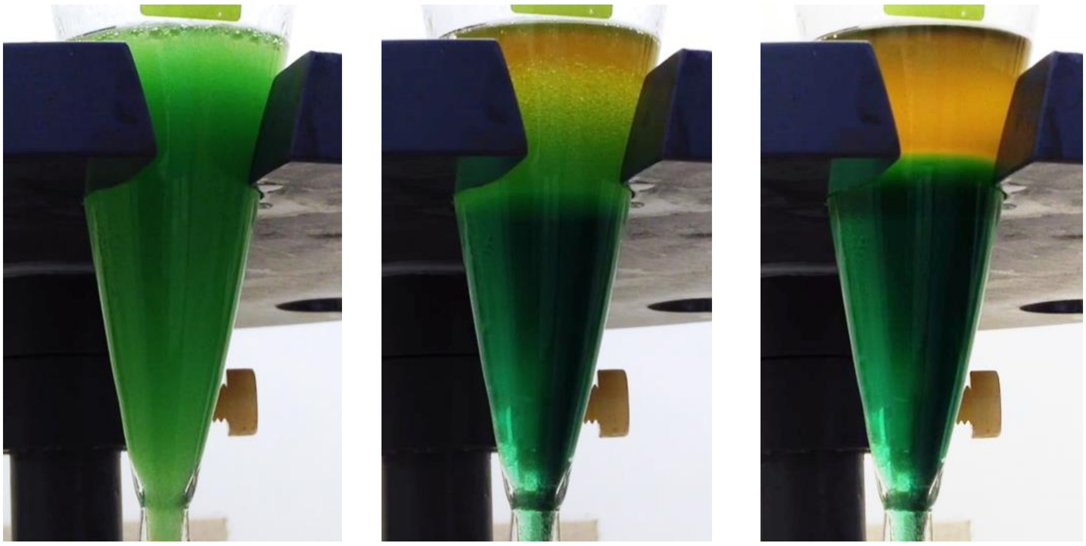
Phase disengagement of nonyl-4PC / Versatic 10 under strip at A:O 1:1



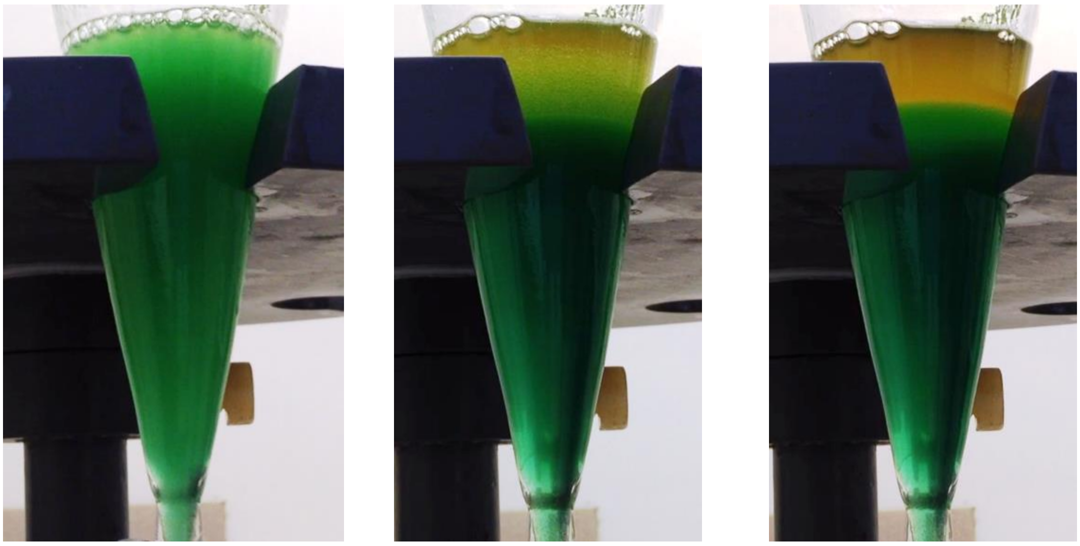
Phase disengagement of nonyl-4PC / Versatic 10 under strip at A:O 2:1



Phase disengagement of LIX 63 / Versatic 10 / nonyl-4PC under strip at A:O 1:2

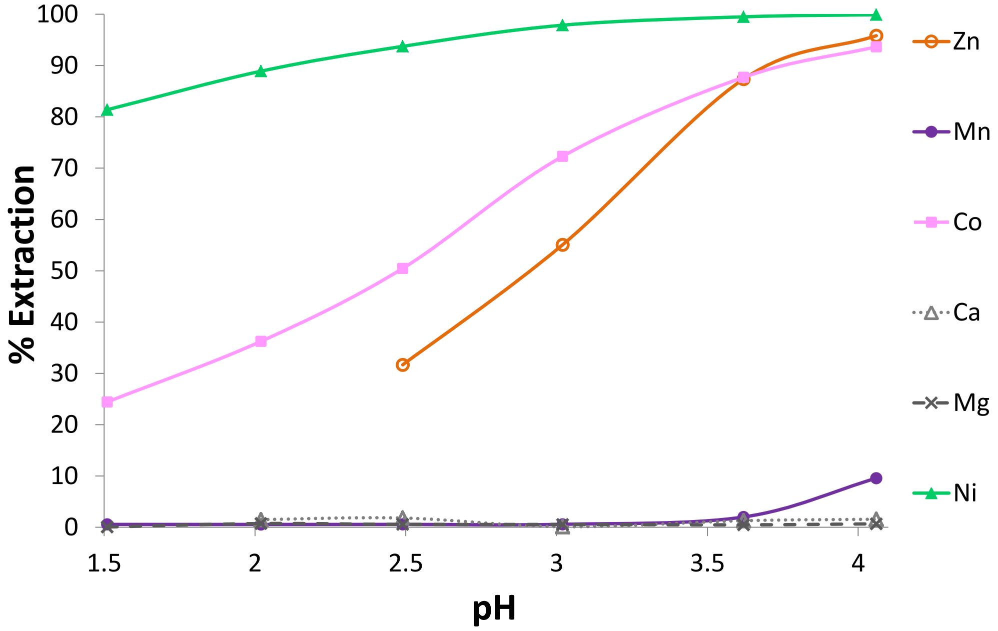


Phase disengagement of LIX 63 / Versatic 10 / nonyl-4PC under strip at A:O 1:1

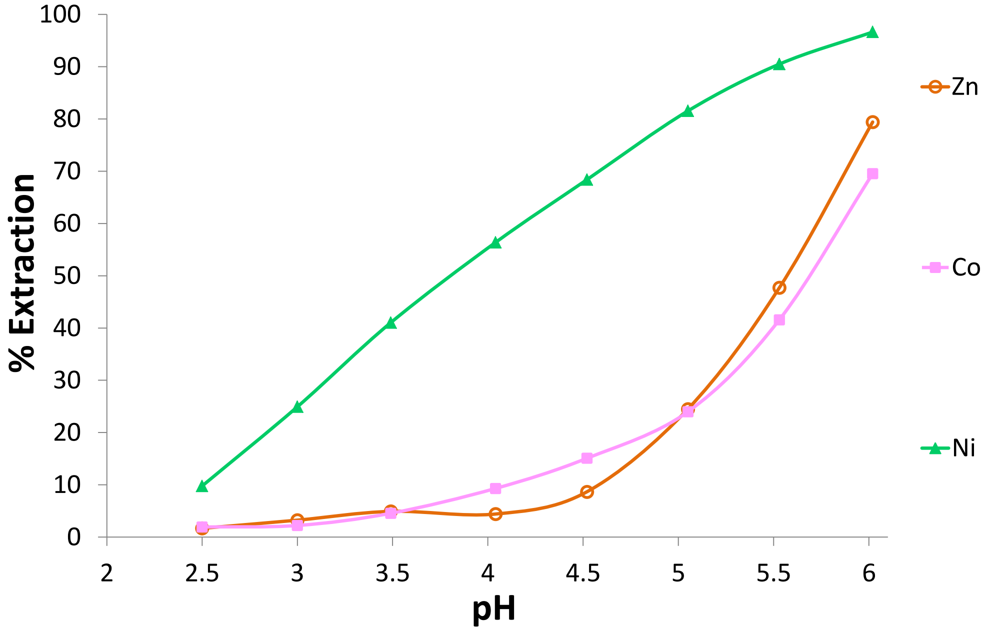


Phase disengagement of LIX 63 / Versatic 10 / nonyl-4PC under strip at A:O 2:1

APPENDIX E: Preliminary pH extraction isotherms for extraction of metals from 'DNi Moderate Al' and 'Sulphate' aqueous feeds



Preliminary pH isotherm for 0.31 M LIX 63 / 0.25 M Versatic 10 / 0.36 M nonyl-4PC from the nitrate-based 'DNi Moderate Al' PLS at A:O = 1:1 and 45 °C



Preliminary pH isotherm for 0.31 M LIX 63 / 0.25 M Versatic 10 / 0.36 M nonyl-4PC from the sulphate-based 'Sulphate' PLS at A:O = 1:1 and 45 °C