

**Western Australian School of Mines**

**Development of a Solvent Extraction Process for the Recovery of  
Nickel and Cobalt from Nitrate Solutions**

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**This thesis is presented for the Degree of  
Master of Philosophy (Mining and Metallurgical Engineering)  
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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 acknowledgement has been made.

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

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## ABSTRACT

The use of nitric acid in leaching nickel laterite ores has been receiving a significant attention over the past decade. This has resulted in the development of two nitric acid leaching technologies—nitric acid pressure leaching and atmospheric nitric acid leaching—that have recently achieved successful demonstration plant scale testing. They are attractive as they allow the regeneration and recycle of the excess acid and they yield comparable nickel and cobalt recoveries to that of the traditional high pressure sulphuric acid leaching (HPAL) but at much milder conditions. They are also applicable to the whole profile of nickel laterite ores, which is a distinct advantage over the HPAL technology that is suitable only to limonite ores.

No purifying technique yet has been developed specifically for the pregnant liquor solutions (PLS) of these nitric acid leaching technologies and both have adopted the mixed hydroxide precipitation (MHP) technique. It is, however, proving less than satisfactory as aluminium removal is incomplete, owing to the formation of colloidal aluminium hydroxide, leading to separation problems and contamination of the mixed hydroxide products. This contamination is deleterious as it significantly reduces the leachability of the nickel and cobalt in the subsequent ammonia-ammonium carbonate leaching, which has been the established route for the removal of manganese.

The present study was aimed to develop—up to a proof-of-concept level—a method of removing aluminium and separating nickel and cobalt from these PLS. Although little information on the solvent extraction of these metals from nitrate-based solutions is available, the literature review was helpful in conceiving a process of removing aluminium and separating nickel and cobalt directly from the PLS, and hence, a direct solvent extraction (DSX) process. This proposed process consists of two sequential solvent extraction circuits using only one extractant, bis(2,4,4 tri-methylpentyl) phosphinic acid (Cyanex<sup>®</sup> 272): the first is to remove aluminium and the second is to separate nickel and cobalt.

An experimental program to explore and evaluate the process was carried out using synthetic solutions that simulated the PLS of atmospheric nitric acid leaching of nickel laterite ores, post partial neutralisation. At optimum conditions, devised as a result of this investigation, it was found that:

- The first solvent extraction step allowed complete extraction of aluminium along with zinc in a single extraction stage using 20% Cyanex 272 in ShellSol 2046 at pH 2.1, temperature of 40 °C and phase ratio of unity. The co-extracted cobalt and manganese were completely scrubbed out in a single scrubbing stage with sulphuric acid at pH 1.38. Complete stripping of the aluminium and zinc was achieved in a single stripping stage with sulphuric acid at pH 0.8.
- The second solvent extraction step allowed complete separation of cobalt, along with manganese, from nickel, along with residual amounts of the soluble impurities magnesium and calcium, in four extraction stages, at a staggered pH profile of 4.0, 4.4, 4.5 and 4.0 in the first to fourth stages respectively, using 20% Cyanex 272 in ShellSol 2046 at 40 °C and a phase ratio of unity. A 6% cumulative co-extraction of nickel was observed but was completely scrubbed out with sulphuric acid at pH 2.0. Quantitative scrubbing of the cumulative co-extracted magnesium (16%) and calcium (3%) was difficult but not an issue in the downstream processing of cobalt as they are soluble. All metals in the loaded organic were able to be stripped out completely in a single stripping stage using sulphuric acid (0.5 mol/L).
- The use of sulphuric acid for scrubbing and stripping has the advantage of allowing their downstream processing, either by means of solvent extraction or selective precipitation, to be carried in sulphate media, which is better understood and has abundant relevant literature and plant experience data.

These results show that the aim of the study was achieved and the conceived process merit further investigation, including the use of actual PLS from the new nitric acid leaching technologies, toward the development of its application.

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## LIST OF SYMBOLS

|                  |   |
|------------------|---|
| % v/v            | Relative volume of a component in a mixture of two or more liquids<br>e.g. 20 % v/v = 20 mL of component in 100 mL total volume |
| (aq)             | Aqueous phase   |
| (org)            | Organic phase   |
| M                | Metal   |
| $D$              | Distribution coefficient, $\frac{[M]_{(org)}}{[M]_{(aq)}}$  |
| $\beta_{Al-Co}$  | Separation factor of aluminium and cobalt, $\frac{D_{Al}}{D_{Co}}$  |
| HA               | Acidic form of organic extractant   |
| $K$              | Equilibrium constant for extraction reaction  |
| $\Delta pH_{50}$ | Difference of pH at which 50% of the metal extracted  |

## LIST OF ABBREVIATIONS

|          |  |
|----------|--|
| Al-Zn SX | Aluminium and zinc solvent extraction circuit        |
| BTMPPA   | Bis(2,4,4 tri-methylpentyl) phosphinic acid          |
| C272-R   | Cyanex 272 recovery circuit                          |
| CCD      | Counter-current decantation                          |
| Co SX    | Cobalt solvent extraction circuit                    |
| D2EHPA   | Di(2-ethylhexyl) phosphoric acid                     |
| DSX      | Direct solvent extraction                            |
| DW       | Diluent wash   |
| EHPNA    | 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester |
| EW       | Electrowinning                                       |
| HPAL     | High pressure sulphuric acid leaching                |
| IX       | Ion exchange   |
| J-Cell   | Jameson cell, a flotation cell                       |
| MHP      | Mixed hydroxide precipitation                        |
| NAPL     | Nitric acid pressure leaching                        |
| Ni SX    | Nickel solvent extraction circuit                    |
| O/A      | Volume ratio of organic to aqueous phases            |
| PLS      | Pregnant leach solution                              |
| rpm      | Revolutions per minute                               |
| SX       | Solvent extraction                                   |
| SSX      | Synergistic solvent extraction                       |
| TBP      | Tri-n-butyl phosphate                                |
| Zn SX    | Zinc solvent extraction                              |

# Chapter 1

## INTRODUCTION

### 1.1 Background of the Study

Nickel is an important metal in modern lives as can be appreciated from its prominent role in numerous industrial and domestic applications. The major uses of nickel are in stainless steels, alloy steels and nickel-based alloys. Together, they consume about 80% of the current global nickel production (Eramet 2014, Pariser 2011). Nickel offers good corrosion resistant and strength at low and high temperature and hence, these nickel-containing alloys have been especially important in modern infrastructure, transport, power generation, food processing, medical appliances and household equipment among many others. Other uses of nickel include electroplating, catalysts and rechargeable batteries (Eramet 2014, Pariser 2011). These uses have been increasing over the years particularly during economic booms and thus explains the increasing production of nickel at an average growth rate of 5% per annum over the period of 1950 to 2012 (Goonan and Kuck 2014). Given the historical growth of the economy notwithstanding the cyclical fluctuations, it is reasonable to expect this trend to continue.

There are two types of nickel ores: sulphides and laterites (oxides). Traditionally, the bulk of global nickel production has been derived from sulphide deposits. This is mainly because sulphide ores are amenable to the conventional concentration method, such as flotation, prior to extraction whereas laterite ores cannot be extensively beneficiated and hence, the whole bulk of the ore must be processed. In addition, the production of nickel metal from laterite ores can only be achieved via a hydrometallurgical route, which is particularly expensive with the current processing technologies. This has resulted in the depletion of sulphide ores and hence, the majority of the currently known nickel resources are contained in laterite deposits.

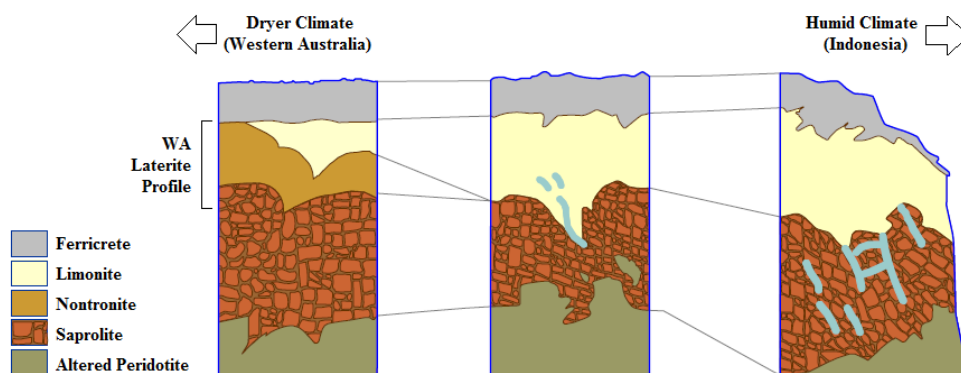
Given the continuing need to sustain the historical nickel production, even with due consideration to the cyclical fluctuation of demand mirroring the global economic cycle, exploitation of laterite ores has been increasing. In 2009, for example, the proportion of the nickel production from laterite ores overtook sulphide output (Mudd 2010). This trend is likely to continue given the increasing dominance of nickel laterite

resources in the newly commissioned and committed expansion projects over the period of 2012 to 2017 (Kuck 2015) although fluctuations may continue to occur because nickel laterite projects are much more susceptible to fluctuations in nickel price as their production costs remain much higher than those of sulphide projects.

## 1.2 Overview of Nickel Laterite Ores

The nature of nickel laterite ores has a significant implication on their processing. So it is helpful to briefly describe their occurrence and characteristics.

Economic laterite deposits are widely found in tropical to sub-tropical regions such as Australia, New Caledonia, Cuba, Indonesia and the Philippines. They have developed near the surface by weathering of olivine-rich igneous rocks (Alcock 1988, Golightly 1979). The development of the weathering profiles involves dissolution of the nickel-bearing parent rocks, movement of elements in the solution and precipitation of some elements in another location. This process is obviously influenced by climatic conditions particularly the frequency and amount of rain or otherwise. As such, there is a different profile between those formed in dryer climate, e.g. Western Australia, and those in humid climate, e.g. Indonesia. A simplified illustration of this profile variation is shown in Figure 1.



**Figure 1. Nickel laterite profiles and distribution of ore type (Dalvi et al. 2004).**

Generally, the weathering leads to three distinct ore types: limonite at the top, nontronite just below and saprolite at the bottom. Nickel and magnesium are commonly enriched in the saprolite zone and relatively depleted in the limonite zone due to the relative ease of their dissolution, downward percolation and precipitation in the saprolite zone. The removal of soluble elements in limonite zone thus increases the

concentration of relatively insoluble elements such as iron, aluminium and chromium in this zone. The formation of nontronite ores is limited to areas with long-dry season where water circulation was either retarded or episodic (Alcock 1988, Golightly 1979). This allows the build-up of magnesium and silica in soil water resulting in the formation of nontronite instead of serpentine-rich saprolites. Nickel enrichment can be considerable in this zone, but is commonly less than that in the serpentinous saprolites (Golightly 1979). Table 1 shows the typical compositional profile of a lateritic ore. Particular laterite ore bodies in either dryer or humid climates, however, can be significantly different even at pit to pit level (Griffin et al. 2002).

**Table 1. Typical chemical composition of nickel laterite ores (Wedderburn 2009).**

|                   | <b>%Ni</b> | <b>%Co</b> | <b>%Fe</b> | <b>%MgO</b> |
|-------------------|------------|------------|------------|-------------|
| <b>Limonite</b>   | 0.8-1.5    | 0.1-0.2    | 40-50      | 0.5-5       |
| <b>Nontronite</b> | 1.5-2      | 0.02-0.1   | 25-40      | 5-15        |
| <b>Saprolite</b>  | 1.8-3      | 0.02-0.1   | 10-25      | 15-35       |

Being the major impurities, the iron and magnesium contents are main considerations in the choice of processing options of nickel laterite ores.

### **1.3 Processing of Nickel Laterite Ores**

Smelting has been the traditional route to extract nickel from laterite ores. This route is straightforward, well-proven and able to provide high nickel recovery. This route is only suitable for treating high-grade saprolite ores, which have high nickel (>1.8%) and low iron (<25%) contents, as they require much lesser energy to be smelted than limonite ores. This route, however, produces only either ferronickel or nickel pig iron and hence, suitable only for producers of stainless steel and related ferro-alloys. Smelting, therefore, would not provide the value that high purity nickel products command. Also, this route does not allow the recovery of cobalt, which is a common valuable by-product of nickel laterite ores, although it does form part of the ferronickel or nickel pig iron products.

The production of high purity nickel products including cathode can only be achieved via hydrometallurgical routes. This route has the added advantage of recovering cobalt



as a high purity by-product allowing maximum return. Hence, newer projects have turned to hydrometallurgical routes. This is evident in the fact that nickel production from the newly commissioned and committed hydrometallurgical plants over the period of 2012 to 2017 is almost twice the size of those from pyrometallurgical plants (Kuck 2015).

There are two hydrometallurgical routes that are currently in commercial operation namely Caron process and high-pressure sulphuric acid leaching (HPAL). The former involves selective reduction of nickel, along with cobalt and some iron, to their metallic form at 700 to 850 °C, and leaching of the roasted product with ammonia-ammonium carbonate solution. The latter involves the use of pressurised acid leaching at around 250 °C to dissolve most of the nickel and cobalt from the ores at relatively fast reaction times while being selective over iron. Despite being a well proven technology, the former is no longer considered efficient due to high energy costs for roasting and low recoveries of the nickel and cobalt (Dalvi et al. 2004) and thus, the latter has been the choice over the last 20 years.

First commercialised more than 60 years ago in Cuba, HPAL has since been the subject of extensive and continuing research efforts to enhance its efficiency and economics. In spite of this and the long years of plant experience, the HPAL process remains marginal in terms of process economics. In addition, it is only viable in treating ores that contain low amount of acid consuming compounds such as those of magnesium, as acid is the highest cost component of the process (Griffin et al. 2002). It also suffers from waste disposal issues especially in regards to the neutralisation of the excess acid and magnesium-rich effluent liquor (Canterford 2009, Kyle 2010). As such, HPAL is only favourable for treating limonite ores leading to minimal utilisation of the saprolite component in orebodies. This process also demands sophisticated materials of construction such as, for example, titanium-clad autoclaves, due to its extreme operating conditions of high acidity, temperature and pressure. This entails high capital and maintenance costs. Given these issues, there is an increasing interest in the development of new hydrometallurgical methods to make the processing of nickel laterite ores much more economically attractive (Duyvesteyn et al. 1979, Griffin et al. 2002, Harris and Magee 2003, Kyle 2010, Liu et al. 2004, McDonald and Whittington 2008).

## **1.4 Nitric Acid Processes for Nickel Laterite Ores**

The use of nitric acid as lixiviant has been receiving a significant attention in the past decade. It is attractive owing to its chemistry that allows the regeneration and recycle of the excess acid and its ability to give a comparable nickel and cobalt recoveries to that of HPAL but at much milder conditions and it is applicable to the whole profile of nickel laterite ores (Agacayak and Zedef 2014, Ma et al. 2015, McCarthy and Brock 2011, McCarthy and Brock 2014). This has resulted in the development of two nitric acid-based processes, namely nitric acid pressure leaching (NAPL) and atmospheric nitric acid leaching (DNi process), which have already been successfully proven in a demonstration-plant scale. Although both yielded satisfactory results in treating the whole laterite profiles (Ma et al. 2015, McCarthy and Brock 2014), the so-called DNi process has an advantage over NAPL as it is carried out under atmospheric conditions only and it allows the regeneration and recycle of the excess magnesia. The DNi process, therefore, avoids the need for expensive titanium-clad autoclaves, simpler to operate and has less waste disposal issues compared to NAPL. In addition, NAPL loses the advantage of the use of pressurised conditions if the feed ores contain significant amount of magnesium-rich saprolites.

Similar to that of HPAL, nitric acid leaching dissolves not only nickel and cobalt, but also significant amount of impurities that must be removed to meet the required specifications for the nickel and cobalt products. These impurities include iron, chromium, aluminium, copper, zinc, manganese, magnesium, calcium and minor impurities depending on the minor components of the ore. The DNi process incorporates different circuits for the iron and aluminium removal steps, wherein most chromium is also removed, and uses chemical precipitation for the recovery of nickel and cobalt as mixed hydroxide product (Appendix A). This process uses and recycles magnesia as neutralisation agent and thus, the nitric acid leach solution contains particularly high magnesium content.

## **1.5 Problem Statement**

A major weakness of the use of nitric acid in leaching nickel laterite ores is the removal of the dissolved aluminium. Unlike sulphuric acid leaching, wherein the bulk of aluminium is precipitated during the leaching process while residual in the discharged

liquor is easily removed during the partial neutralisation step, it is now known that is particularly difficult to remove due to the formation of colloidal aluminium hydroxide,  $\text{Al}(\text{OH})_3$ , at pH 4.0 that ultimately results in separation problem (Ma et al. 2013). Hence, a new method of aluminium removal from the leach solution must be developed to prevent the contamination of the nickel and cobalt products.

To address this issue, the NAPL process adds fibrous calcium sulphate ( $\text{CaSO}_4$ ) to improve the property of the generated slurry at pH 4.0. The DN<sub>i</sub> process, on the other hand, operates the aluminium removal step at pH range of 2.0 to 3.0 to minimise the colloid formation. Neither is satisfactory as the aluminium content in the mixed hydroxide precipitation (MHP) products from either NAPL and DN<sub>i</sub> process remains high at about 2% and 4%, respectively (Ma et al. 2015, McCarthy and Brock 2014). These values are far higher than the aluminium content in the MHP products generated by HPAL such as those in Ravensthorpe pilot plant and Cawse commercial plants which were below 0.05% (White 2009, White et al. 2006).

This is a significant complicating factor because the nickel and cobalt in the MHP products, or any other intermediate precipitation products such as mixed sulphides or carbonates, have to be separated eventually to obtain the maximum values for each metal via re-leaching and solvent extraction (SX) steps. The presence of aluminium in the MHP products significantly reduces the nickel and cobalt leachability if ammonia-ammonium-carbonate solution is used in the refining process (Mason and Hawker 1998, White et al. 2006), which has been the established route for MHP to allow the removal of manganese. As such, refineries typically require the MHP products to contain less than 0.2% aluminium (DN<sub>i</sub> 2014).

Given the theoretical and practical merits of solvent extraction as a purifying technique, this method may provide a better option for removing aluminium from the nitric acid leach solutions, and also for separating nickel and cobalt without any intermediate precipitation step. This approach of separating nickel and cobalt directly from the pregnant leach solution (PLS), which is known as direct solvent extraction (DSX), offers significant economic advantage as it circumvents the need for intermediate precipitation, solid-liquid separation and re-leaching steps of the nickel and cobalt. As the use of nitric acid leaching is new, no such method exists yet and the present study will attempt to address this.

## **1.6 Aim and Scope of the Study**

This study was aimed to develop a solvent extraction method of purifying the nickel and cobalt from nitrate solution that has comparable composition to the discharge liquor following the partial neutralisation step, which removes the iron, chromium and, in the case of nitric acid leaching process, some of the aluminium only. In the DN<sub>i</sub> process, this partial neutralisation step is referred as aluminium removal step. Specifically, it was aimed to:

1. review studies that relevant to the use of solvent extraction for the separation of aluminium, nickel and cobalt from nitrate matrices;
2. conceive and explore a solvent extraction method for separating aluminium, nickel and cobalt from nitrate solution that simulates the PLS of the atmospheric nitric acid leaching of nickel laterite ores (DN<sub>i</sub> process) using commercially available extractants on the basis of their selectivity, loading, phase disengagement, chemical stability and kinetics of both extraction and stripping steps;
3. identify the key variables of the extraction, scrubbing and stripping steps and optimise them in terms of the goals of the process;
4. evaluate the performance of the conceived solvent extraction process in series of batch and semi-batch test conditions.

As a research project for two-year master degree program, the experimental work was limited to bench scale studies using synthetic nitrate-based tests solutions that simulated the PLS of the DN<sub>i</sub> process post partial neutralisation step. The development work was aimed to be up to proof-of-concept level.

## **1.7 Significance of the Study**

To satisfy the demand for nickel in the face of decreasing production from sulphide ores, the processing of low-grade and complex nickel laterite ores is increasingly important. The current commercial hydrometallurgical methods for processing these ores, however, remain economically marginal, and hence the continuing interest in developing new technologies. The development of a breaking nitric acid leaching technology to treat such ores is a significant advancement in this field but, as often occur with any new technology, it has its own difficulties that emerged only during the

piloting stage. Unless addressed satisfactorily, these can hinder the commercialisation of the technology.

The present study attempted to address the removal of aluminium, which is a major difficulty in purifying nitrate-based leach solution. The approach taken was to use solvent extraction to remove the aluminium and then separate nickel and cobalt without any intermediate precipitation step. This offers a significant economic advantage by circumventing the need for intermediate precipitation, solid-liquid separation and re-leaching steps of the nickel and cobalt that are currently practised in sulphuric acid techniques. This approach is novel as it has not been previously attempted.

Clearly, the results of this study would contribute towards further development of nitric acid leaching of nickel laterite ores and fill a gap in the knowledge of this field. This study, therefore, will benefit the nickel laterite industry, which is global, but particularly in countries that host abundant nickel laterite reserves such as Australia, New Caledonia, Cuba, Indonesia and the Philippines.

## Chapter 2

# REVIEW OF STUDIES ON SOLVENT EXTRACTION OF NICKEL AND COBALT FROM NITRATE SOLUTIONS

### 2.1 Introduction

This chapter presents the review of studies relevant to the use of solvent extraction for purifying nickel and cobalt in general, and from nitrate matrices in particular. The aim of the review was to explore for a suitable solvent extraction process, particularly DSX, for separating nickel, cobalt and aluminium and other impurities from nitrate solutions. To achieve this, the main considerations were the extraction behaviour of nickel, cobalt and impurities in acidic PLS of nickel laterite ores including nitric acid, properties of extractants including metal extraction selectivity, kinetics of both extraction and stripping steps, chemical stability and commercial availability among others.

### 2.2 Extraction of Nickel and Cobalt form Nitrate Solutions

Little information is available on the solvent extraction of nickel and cobalt as well as the rest of the base metals from nitrate matrices, which is understandable since such application has not gained much attention until recent times. Studies that include a comparison of metal extraction from sulphate, chloride and nitrate matrices show that the order of metal extraction for a given extractant is the same. In a fundamental study on the solvent extraction of nickel and cobalt with organophosphorus acids, for example, Preston (1982) compared the extraction behaviour of the two metals from three matrices namely sulphate, chloride and nitrate. He found that selectivity for the nickel and cobalt separation using an alkyl phosphonic acid, RD577, was essentially the same in all three media. He attributed this to the similarity of their complexation constants within each of the three media. In a study on the solvent extraction and stripping of chromium with an alkyl phosphonic acid, Cyanex 272, from solutions that simulate pregnant leach solution from HPAL of nickel laterite ores, Lanagan and Ibana (2003) compared the effect of sulphate, chloride and nitrate anions on the extraction behaviour of chromium. They found that the extraction of chromium from nitrate matrices follows the same order, as with all first row transition metals, but shifted to

the lower pH values compared to those from sulphate and chloride. They attributed this to the formation of weaker complexes between the metal and the nitrate ion, which is consistent with that predicted from the spectrochemical series. More recently, Hutton-Ashkenny et al. (2014) have shown that the metal extraction from a nitrate solution with various extraction systems including those containing alkyl phosphorus acids, carboxylic acids and hydroxyoximes follows the same order and exhibits similar selectivity to those from a comparable sulphate solution except that the extraction from the nitrate solution occurs at slightly lower pH values. They also attributed this to the weaker complexing properties of the nitrate ligand than sulphate. This shift to the lower pH values has a practical advantage as it meant that solvent extraction from nitrate solutions requires less neutralisation agent. The comparable extraction selectivity in all three media means that the information on the solvent extraction of base metals from sulphate media, which is abundant, can be extrapolated and used as guide in predicting extraction behaviour of these metals from nitrate ones and even chlorides.

In selecting an extractant for the solvent extraction of nickel and cobalt from a nitrate solution, the chemical stability of the extractant is a major consideration given the known oxidising properties of nitric acid. Indeed the degradation of solvent extraction reagents, i.e. diluent and extractant, when treating nitric acid solutions has been experienced such as in the PUREX process for purifying plutonium and uranium. This process involves the separation of uranium and plutonium from each other and from fission products contained in irradiated uranium fuel elements using tri-n-butyl phosphate (TBP). The extraction process depends on the solvation of uranyl nitrate with TBP, which means this process is carried out at an appreciably high nitric acid concentration ( $>2$  mol/L). Also, this process operates at elevated temperature ( $>70$  °C). Despite the concern of organic degradation, this process along with other commercialised solvent extraction processes that use high concentration of nitric acid solution such as the solvent extraction for purifying zirconium and hafnium with TBP ( $>3$  mol/L  $\text{HNO}_3$ ), and rare earth metals with alkyl phosphoric acids or TBP ( $>1.5$  mol/L  $\text{HNO}_3$ ), remain in operation today. It is therefore fair to suggest that oxidative degradation of the organic reagents used under these conditions is manageable both technically and economically.

The current study, is aimed to develop a solvent extraction process for treating nitric acid leach solutions of nickel laterite ores at the mildest possible conditions, i.e. pH >2.0 at the lowest practical temperature. There is little to no information on the stability of solvent extraction reagents in the presence of dilute nitric acid except for a few reports on oxime degradation in copper solvent extraction in the presence of nitrate ion (Bart et al. 1990, Virnig et al. 2003). The degradation of oximes, however, is well known as they degrade also when used in sulphuric acid media in the presence of redox active metal ions such as, for example, cobalt, copper and manganese. Given the viability of the use of solvent extraction in treating nitric acid media at much more oxidising conditions, it is fair to assume that dealing with much milder conditions is likely to be manageable.

It is worth pointing out that the degradation of solvent extraction reagents that is induced by nitric acid is owing to the formation of the electrophiles nitronium ion ( $\text{NO}_2^+$ ) and nitric acidium ion ( $\text{H}_2\text{NO}_3^+$ ) or free-radicals, which then attack the organic reagents other than alkane chains, which are known to be inert to nitric acid degradation (Bachman et al. 1952, Olah 1973, Olah et al. 1978, Titov 1963). These species, however, form only at certain vigorous conditions. That is, nitric acid generates nitronium and nitric acidium ions through self-dehydration reactions when it is highly concentrated. This is therefore not an issue when using dilute nitric acid. The formation of free radicals, on the other hand, is caused by intense thermal energy that triggers thermal decomposition of the nitric acid vapour. This can be circumvented by operating at temperatures below the boiling point of nitric acid (<83 °C).

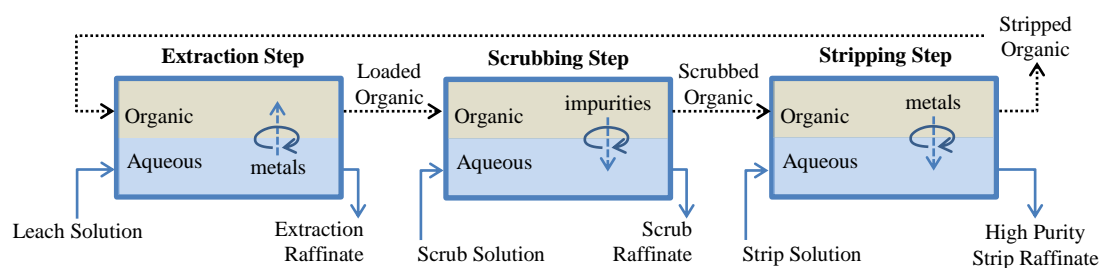
Based on these information, it can be concluded that the use of solvent extraction for purifying nickel and cobalt directly from dilute nitric acid solutions (<1 mol/L) at low temperatures (<83 °C) is worth investigating.

### **2.3 Overview of Hydrometallurgical Solvent Extraction**

It is helpful to begin the search for an extractant that is suitable for purifying nickel and cobalt directly from dilute nitric acid solutions with an overview of hydrometallurgical solvent extraction process. The process involves extraction, scrubbing and stripping steps as illustrated schematically in Figure 2. The three steps may comprise several contactors, and hence stages, in each step and the aqueous and



organic phases are usually fed into the contactor in a counter-current manner in which the two phases are mixed.



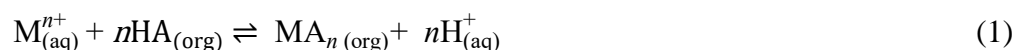
**Figure 2. A simplified solvent extraction process for the purification of base metals.**

In order to achieve extraction, the metal ion, which usually exists as a hydrophilic hydrated ion, must be neutralised and some or all of its water of hydration has to be replaced by hydrophobic molecules or ions. These can be achieved via three basic mechanisms: (i) formation of a neutral compound, (ii) formation of an ion-association complex or (iii) solvation of the metal ion. These mechanisms are not mutually exclusive.

Primarily, the extraction step is aimed to extract the metal of interest selectively to achieve separation, the scrubbing step is aimed to remove co-extracted impurities and the stripping stage is aimed to recover the extracted metal in pure form that is suitable for product recovery such as, for example, electrowinning. Each of these steps, however, can also be used to achieve separation. For example, it may be possible to use the extraction stage to extract two metals simultaneously separating them from all other components of the impure feed solution and then separate one of the two metals by either scrubbing or stripping. This makes solvent extraction a versatile separation and purification technique.

### 2.3.1 Extraction Involving Compound Formation

This mechanism involves cation-exchange reactions as represented in equation (1) for the extraction of metal ion  $M^{n+}$  by an extractant HA. As such, this mechanism applies to both chelating and acidic extractants.



Clearly, the extraction process is pH dependent. The metal extraction is increased as the pH increases and thus, the hydrogen ion that is produced in the extraction reaction must be neutralised to achieve high metal loading of the extractant. This is limited by the hydrolysis pH of the metal, beyond which the precipitation of the metal starts to occur and results in metal loss.

### **2.3.2 Extraction Involving Ion Association**

Ion association, which is also known as outer-sphere complexation, arises from electrostatic forces between ions of opposite charges. The extraction process essentially depends on the ability of metal ions to form anionic species in the aqueous phase, which are then extracted by extractants via anion-exchange reactions. This mechanism thus favours more concentrated aqueous feed solutions, i.e. with ionic strength greater than 0.1 mol/L, as considerable ion pairing between metal complexes with other ions can occur. Diluents with lower dielectric constant, which are usually those with high aromatic content, also favour the extraction process as they minimise the dissociation of the extracted species in the organic phase.

In commercial solvent extraction processes for the separation of cobalt from nickel, the basic extractants that can be used are limited to amines. The separation process exploits the ability of cobalt to form  $\text{CoCl}_4^{2-}$  while nickel cannot form any stable chloro complex in a chloride solution. Since neither nickel nor cobalt forms stable anionic complexes with nitrate ion, this type of extractant is not suitable for treating a nitrate solution.

### **2.3.3 Extraction Involving Solvation of the Metal**

Metal extraction by solvation is based on the ability of the electron-donor containing organic extractant to solvate inorganic molecules or complexes. It occurs by replacing the waters of hydration of the inorganic species with the solvating agent rendering the complex that is formed soluble in organic phase. It is therefore possible to extract both acids and metal complexes by means of solvation. The major solvating extractant groups include ethers, esters, alcohols, ketones and alkyl phosphate esters.

There is very little theoretical basis for this mechanism and there is no general equation for metal extraction that can be used. This is mainly due to the non-ideal nature of the

extracted species and their often nonstoichiometric composition. Nonetheless, it is accepted that the metal extraction using solvating extractant increases with increase in the acidity of the aqueous phase until a certain point beyond of which the extraction starts to fall off.

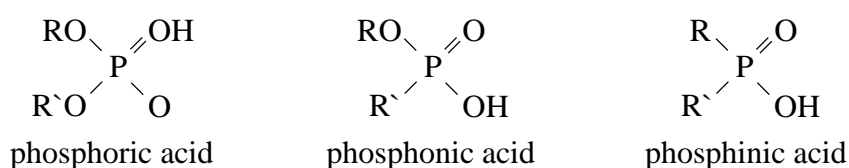
## 2.4 Extractants for Purifying Nickel and Cobalt from a Nitrate

### Solution

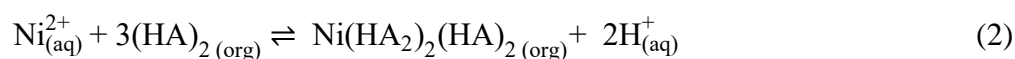
Since the use of anionic or solvating extractant is not suitable for treating a mildly acidic nitrate solution, this review thus focused on the use of cation exchange extractants. There are four types of cationic (acidic) extractant that are being used in commercial operation for purifying nickel and cobalt: alkyl phosphorus acids, thiophosphorus acids, carboxylic acids and hydroxyoximes. Structures of some common acidic extractants for use in base metal hydrometallurgy are tabulated in Appendix B. The use of synergistic mixtures of two or more extractants for this application is also reviewed.

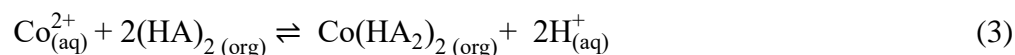
#### 2.4.1 Alkyl Phosphorus Acids

Alkyl phosphorus acid extractants can be classified into three structural groups namely phosphoric-, phosphonic- and phosphinic acids. The structures of these acids are as follows:



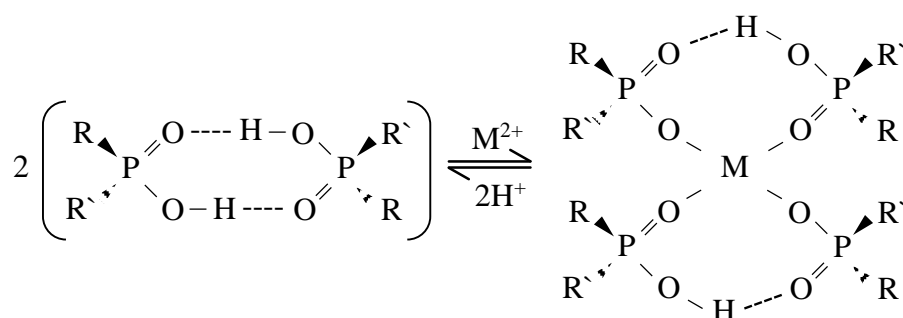
These extractants are known for their ability to separate cobalt from nickel in a weakly acidic solution. The high degree of separation between cobalt and nickel is attributed to the preferential tetrahedral coordination geometries of the former with the extractant while the latter are much more stable as octahedral ones (Danesi et al. 1985, Preston 1982). The extraction of nickel and cobalt may therefore be represented by equations (2) and (3):





where  $(\text{HA})_2$  is a dimeric form of the extractant.

Self-association of the monoacidic organophosphorus compounds, as most of acidic extractants, in non-polar solvents has been well established (Danesi et al. 1985, Kolarik 1982, Peppard et al. 1957, Walmsley 1984). This reaction leads to the formation of 8-membered pseudo chelate rings that provides the metal complexes a very hydrophobic exterior as shown Figure 3, for example.



**Figure 3. Formation of 8-membered pseudo chelate rings from the extraction of metal M with an alkyl phosphorus acid extractant.**

The high degree of separation is attributed to the fact that octahedral nickel complexes may retain some water molecules making them much more hydrophilic compared to the tetrahedral cobalt complexes that are not associated with any water molecules (Danesi et al. 1985, Neuman et al. 1990, Preston 1982, Yuan et al. 1988). As such, the composition of the extracted nickel complex vary from  $\text{Ni}(\text{HA}_2)_2(\text{HA})_2$  at high extractant concentration to  $\text{Ni}(\text{HA}_2)_2(\text{H}_2\text{O})_2$  at low extractant concentration when there is insufficient amount of  $(\text{HA})_2$  for the coordination ligands.

#### 2.4.1.1 Commercial development of alkyl phosphorus acids

The high separation factor between cobalt and nickel that can be achieved by the use of alkyl phosphorus acids has understandably generated considerable research interests. These led to the development of improved versions of an alkyl phosphorus acid that were made commercially available to the industry within only a relatively short period.

Di(2-ethylhexyl) phosphoric acid (D2EHPA) was the first alkyl phosphorus extractant that was used in commercial operation for the separation of cobalt from nickel. The

first D2EHPA process was developed in the 1960s by Eldorado Nuclear Ltd. and Mines Brach (now CANMET) in Canada (Ritcey et al. 1975) and was licensed to Nippon Mining in Japan. Another process using D2EHPA was also developed around the same time by Warren Spring Laboratory in the UK and was adopted at the Rustenburg refinery in South Africa (Bacon and Mihaylov 2002).

Daihachi chemicals and Nippon Mining developed 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester (EHPNA) under designation PC-88A in the early 1970s. This extractant is a poorer nickel extractant than D2EHPA and thus provides better cobalt-nickel separation. As such, Nippon Mining changed to PC-88A for its cobalt-nickel separation circuit after only a year since it was commissioned using D2EHPA in 1975.

In 1982, Cyanamid Canada Inc. (now Cytec) introduced bis(2,4,4 tri-methylpentyl) phosphinic acid (BTMPPA) under designation Cyanex 272. Following its market introduction, this extractant has been the popular choice for the cobalt-nickel separation as it provides much better selectivity than the other two extractants albeit the most expensive. To date, this extractant has been in use in at least 13 hydrometallurgy plants across the world (Flett 2005) including Tocantins plant in Brazil, Kokkola and Harjavalta plants in Finland, Metallurgie Hoboken plant in Belgium and Bulong, Cawse and Murrin Murrin plants in Australia although some of these are no longer in operation.

These extractants are also now available commercially under different tradenames. D2EHPA is also available as DP-8R (Daihachi Chemicals), EHPNA as Ionquest<sup>®</sup> 801 (Rhodia) and SME 418 (formerly known as RD577 by Shell Chemicals), and BTMPPA as PIA-8 (Daihaci Chemicals), Ionquest<sup>®</sup> 290 (Rhodia) and LIX<sup>®</sup> 272 (Cognis).

#### *2.4.1.2 Metals extraction behaviour with alkyl phosphorus acids*

The cobalt-nickel separation factor for the three extractants increases in the order phosphoric < phosphonic << phosphinic acids (Table 2). This has been ascribed to the destabilisation of the octahedral nickel complexes by branching on the alkyl chains and substitution of the oxyalkyl group with alkyl one (Danesi et al. 1985). The former is obvious as the larger the bulk of the component, the greater the steric hindrance effects. The latter enhances the steric hindrance effects by shortening the distance between the group and the phosphorus atom. These effects are more pronounced in

reducing the extractability of the more crowded hexacoordinated nickel complexes than the tetraordinated cobalt complexes and hence, the greater separation factor.

**Table 2. Comparison of separation factor for the three alkyl phosphorus acids (Preston et al. 1984).**

| <b>Extractant</b>            | <b>Co/Ni separation factor</b> |
|------------------------------|--------------------------------|
| D2EHPA (phosphoric acid)     | 14                             |
| PC-88A (phosphonic acid)     | 280                            |
| Cyanex 272 (phosphinic acid) | 7000                           |

Binghua et al. (1996) compared the extraction behaviour of some base metals using the three alkyl phosphorus acids under comparable conditions (Figure 4). Iron, zinc, cobalt and nickel extraction follow the same order for the three extractants, while the order of manganese and copper extraction are shifted but still very close to each other.

There is a noticeable shift of the magnesium extraction, which is in between cobalt and nickel for PC-88A and PIA-8, but is more preferred than the two metals by DP-8R. Others, on the other hand, reported that magnesium extraction is slightly less preferred than both metals with D2EHPA (Cheng 2000, Ritcey et al. 1975). In either case, the separation of either cobalt or nickel from magnesium is difficult using alkyl phosphoric acids. It is interesting to note that the extraction of the three metals by DP-8R is incomplete even at a pH as high as 7.0 and there is no report that shows otherwise.

The three extractants have excellent zinc to cobalt selectivity. The extractant DP-8R is the most selective with  $\Delta\text{pH}_{50}$  (i.e. difference of pH at which 50% of the metal extracted) of 2.66, while PIA-8 and PC-88A follow after with  $\Delta\text{pH}_{50}$  of 2.42 and 2.35, respectively. Having the best selectivity and being the cheapest among the three, D2EHPA is obviously the most preferred choice for zinc extraction processes (Kongolo et al. 2003, Lum et al. 2014, Mellah and Benachour 2006, Owusu 1998, Pereira et al. 2007, Sole et al. 2005).

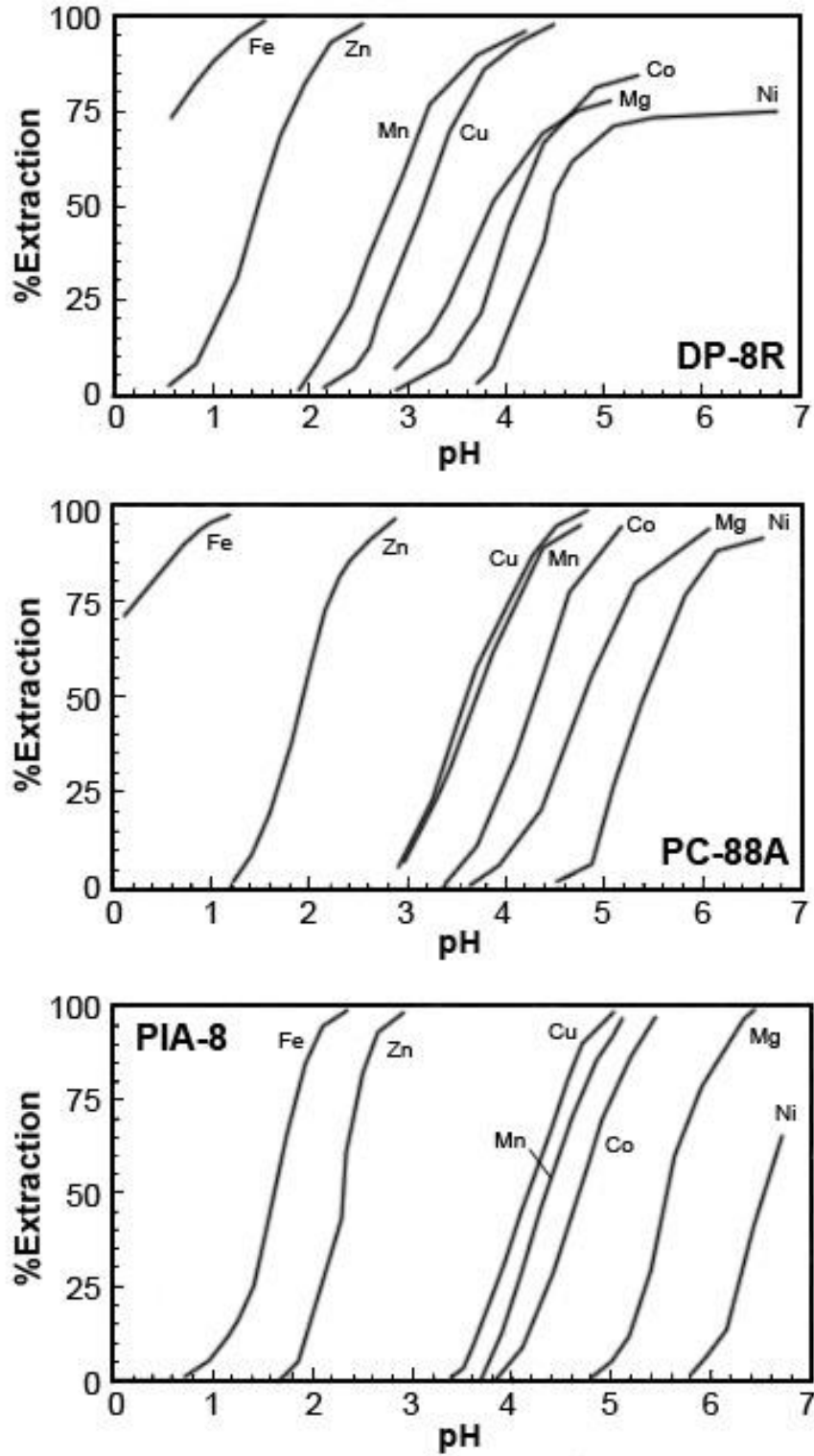


Figure 4. Effect of pH on metals extraction using DP-8R, PC-88A and PIA-8 (Binghua et al. 1996).

The reagent D2EHPA is the only extractant that provides considerable manganese to cobalt selectivity among the three with  $\Delta\text{pH}_{50}$  of about 1.0 to 1.3 (Binghua et al. 1996,

Cheng 2000). As the pH window for manganese extraction and scrubbing of the co-extracted cobalt are quite narrow, rigorous pH control in both circuits is thus required. Despite this difficulty, many researchers have reported that high manganese extraction with very low cobalt losses can be achieved from bench to plant-scale tests. These reports are as summarised in Table 3.

The extractant BTMPPA is the only extractant among the three that extracts cobalt preferentially over calcium (Figure 5). This is an important advantage when the extractant is used in treating sulphate-based liquor as less calcium co-extraction means less scaling problems that can be generated by means of gypsum precipitation in later extraction stage. This is due to the crowding of the co-extracted calcium by cobalt owing to the increasing cobalt tenor in the later extraction stage. While this is not critical for nitrate systems, less calcium co-extraction may lead to less neutralisation agent costs which is the highest reagent cost component in a solvent extraction operation (Donegan 2006).

#### *2.4.1.3 Extraction of aluminium by alkyl phosphorus acids*

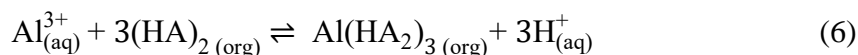
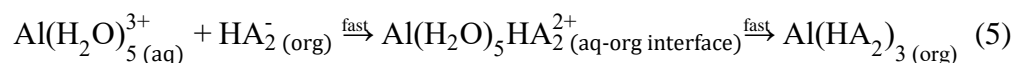
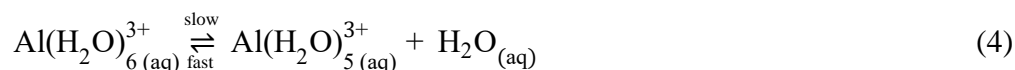
Aluminium, like other trivalent base metal ions, is extracted in preference to divalent metal ions. This makes its separation from cobalt and nickel using alkyl phosphorus acids is possible. Difficulties, however, have been reported in extracting aluminium from the aqueous phase using D2EHPA and EHPNA due to the slow extraction kinetics. The time for equilibration for aluminium extraction with either extractant at 20 to 30 °C was reported to be in the order of hours to days (Matsui and Era 1983, Mihaylov and Distin 1992, Sato and Nakamura 1975, Sato et al. 1978, Sato et al. 1979, Tanaka et al. 1970, Zhang et al. 1995), although two reports indicated higher than 80% extraction can be achieved within 5 minutes of mixing (Mohapatra et al. 2007, Phalke et al. 1996).

It is postulated that the slow aluminium extraction is caused by the fact that most of the aluminium species in sulphuric, nitric or hydrochloric acid solutions exist as hexaaqua ion  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ . Sato et al. (1979) proposed unimolecular nucleophilic substitution ( $\text{S}_{\text{N}}1$ ) mechanism as shown in equations (4) and (5):

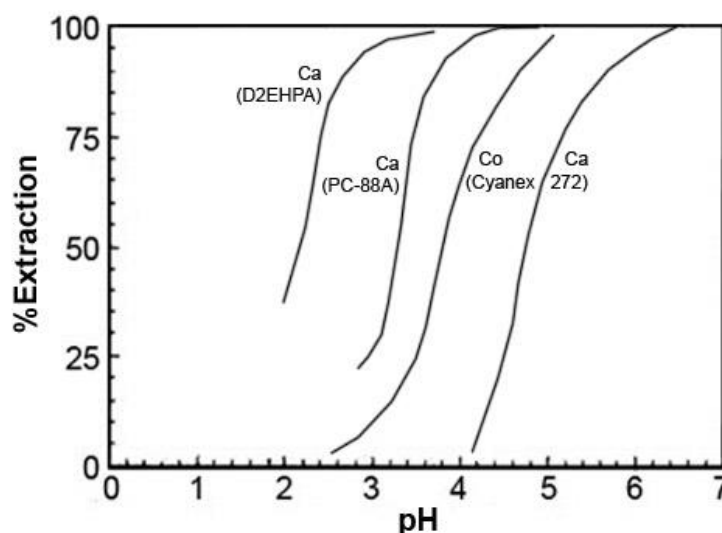


**Table 3. Summary of manganese separation from cobalt and the corresponding cobalt losses from sulphate solutions using D2EHPA.**

| <b>Extraction System</b> | <b>Remark</b>   | <b>Mn separation</b> | <b>Co loss</b> | <b>Reference</b>                             |
|--------------------------|---|----------------------|----------------|--|
| Na-D2EHPA                | Pilot-plant trial to separate 8.5 g/L Mn from a synthetic solution containing 50.4 g/L Co. The process comprises five extraction stages and a scrubbing stage.  | 99.76%               | <1.0%          | Cook and Szmokaluk (1971)                    |
| NH <sub>4</sub> -D2EHPA  | One stage batch extraction test to separate up to 10.0 g/L Mn from a synthetic solution containing 10.0 g/L Co. Note that the unusual term of organic pH was introduced.  | 82.00%               | 10.0%          | Hoh et al. (1984)                            |
| D2EHPA                   | Pilot-plant trial to separate 1.1-1.3 g/L Mn from real PLS containing 3.0-3.2 g/L Co. The process comprises three extraction stages and a scrubbing stage.  | 75-80%               | <0.5%          | Dry et al. (1998); Feather et al. (1999)     |
| D2EHPA + TBP             | Semi continuous counter-current SX test to separate 2.0 g/L Mn from a synthetic PLS containing 0.3 g/L Co. The process comprises two extraction stages and a scrubbing stage.   | 99.90%               | 1.0%           | Cheng (2000)                                 |
| Na-D2EHPA                | Semi continuous counter-current SX test to separate 0.6 g/L Mn from synthetic solution containing 0.6 g/L Co. The process comprises two extraction stages.  | 99.60%               | 1.4%           | Devi et al. (2000)                           |
| D2EHPA                   | Plant trial to separate 0.1 g/L Mn from real PLS containing 7.4 g/L Co. The so-called impurity-removal plant comprises three extraction stages and z scrubbing stage.   | 98.00%               | ~0.0%          | Cole (2002)                                  |
| D2EHPA + TBP             | Semi-continuous counter-current SX test to separate 3.0 g/L Mn from concentrated synthetic leach solutions containing 61.5 g/L Ni and 1.2 g/L Co. The process comprises four extraction stages and a scrubbing stage. | 99.90%               | <0.2%          | Cheng et al. (2004)                          |
| Co-D2EHPA                | One stage batch extraction test to separate 0.8 g/L Mn from real electrolyte solutions containing 55.7 g/L Co with cobalt-loaded D2EHPA as the extractant.  | 71.30%               | 0.5%           | Hossain et al. (2009); Hossain et al. (2011) |



wherein the release of a water molecule from the hexaaquo aluminium(III) ion (4) determines the rate at which the complete process can proceed. Once the water molecule is released, the 5-coordinated species  $\text{Al}(\text{H}_2\text{O})_5^{3+}$  that is formed reacts with an anion dimer of the extractant almost instantly (5). The overall extraction reaction still follows the cation exchange reaction with the extractant (6), which ultimately forms the 6-coordinated aluminium-extractant complex and releases three hydrogen ions.



**Figure 5. Cobalt and calcium extraction using the three alkyl phosphorus acids (Rickelton et al. 1984).**

Aluminium extraction using BTMPPA, on the other hand, does not follow the same trend. Although no study on kinetics is available in the literature, studies on aluminium extraction using Cyanex 272 (Mantuano et al. 2006, Santanilla et al. 2012, Tsakiridis and Agatzini-Leonardou 2005) indicate that equilibrium extraction can be reached within 20 minutes of mixing; two studies (Mohapatra et al. 2007, Park et al. 2007) even reported that this can be reached in less than 3 minutes. There was, however, no significant difference in the experimental conditions which these studies used that might explain the significant differences in the extraction rates observed. In fact, the

solvent extraction tests by Santanilla et al. (2012), Tsakiridis and Agatzini-Leonardou (2005) and Mantuano et al. (2006) were performed at higher temperatures with similar or higher ratios of extractant to aluminium concentrations than those performed by Mohapatra et al. (2007) and Park et al. (2007). Nonetheless, the rate of aluminium extraction with Cyanex 272 is still significantly faster than with D2EHPA or EHNPA and hence, it is safe to assume that aluminium extraction using Cyanex 272 is straightforward similar to those of divalent metal ions (Mohapatra and Park 2008).

#### 2.4.1.4 Organic Stability in Oxidative Environment

Although nitration of the solvent extraction reagents is unlikely to occur given the required vigorous conditions required for such reaction, the presence of nitrate increases the oxidation potential of the system and may affect the stability of the reagents. The increase in oxidation potential was reported to be linear with the rate of diluent degradation for a solvent containing an alkyl phosphorus acid extractant (Flett and West 1986). The rate of diluent oxidation of a solvent containing D2EHPA was found to be slower than that with PC-88A but significantly faster than that with Cyanex 272. Solvents that contain Cyanex 272 are thus significantly more resistant to oxidation than those containing either of the other two extractants.

The diluent degradation is catalysed by the loaded metal ions such as cobalt and manganese to produce carboxylic acids (Flett and West 1986, Rickelton et al. 1991) that would adversely affect the cobalt-nickel selectivity. The mechanism of the metal catalysed degradation for an aliphatic diluent was suggested to be from the alkane ( $RCH_3$ ) to the hydroperoxide ( $RCH_2OOH$ ) to the alcohol ( $RCH_2OH$ ) to the aldehyde ( $R(C=O)H$ ) and finally to the carboxylic acid ( $RCO_2H$ ) (Rickelton et al. 1991). In the absence of such metal ions, most diluents that contain less than 25% aromatic content are generally resistant to oxidation, i.e. degradation rate is negligible even at a highly oxidising environment, provided the operating temperature does not exceed 50 °C (Young et al. 1990).

Phenolic antioxidants such as 2,6-di-tert-butyl-4-methylphenol (BHT) were shown to be effective in preserving the diluent stability by destroying the hydroperoxide radical that forms into a stable phenoxyl radical (7) and thus stopping the oxidation sequence (Rickelton et al. 1991).



Today, the addition of BHT as the antioxidant in a Cyanex 272 circuit appears to be a standard practice at levels of 0.5–1.0 g/L.

While there is no information on the stability of the three extractants, they seem to be resistant to oxidation as there is no report that shows otherwise.

#### **2.4.2 Thiophosphorus Acids as Extractants**

The sulphur-substituted analogue of alkyl phosphorus acids have been known to provide excellent rejection for aluminium, iron, chromium, magnesium and manganese. This is consistent with the theory of hard and soft acids and bases. Hard metal ions (acids) include small, high positive charge ions with few *d* electrons such as  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Co}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{H}^+$  while soft metal ions include large, low positive charge ions with 6 or more *d* electrons such as  $\text{Cu}^+$ ,  $\text{Ag}^+$ ,  $\text{Pd}^{2+}$  and  $\text{Pt}^{2+}$ .  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  are rather soft metal ions albeit in borderline. According to Pearson (1963), hard acids prefer to coordinate with hard bases and soft acids prefer to coordinate with soft bases. Since sulphur is a soft base, it will form more stable complexes with soft metal ions and thus, this type of extractant is able to quantitatively extract nickel and cobalt at very low pH. For example, bis(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex® 301) is able to extract nickel and cobalt simultaneously at pH 2.0 with negligible magnesium, manganese and calcium co-extraction (Figure 6).

Thiophosphorus acids, however, are also known to be highly susceptible to metal poisoning and oxidation. The extraction of zinc and copper are particularly deleterious as they are not readily stripped. The latter also causes extractant degradation via oxidation/reduction reactions resulting in the formation of  $\text{Cu}^+$  and a disulphide compound that is unable to extract metals (Kholkin et al. 1988, Mihaylov et al. 2000). This degradation can also occur in the presence of ferric ion and consequently, rigorous elimination of both copper and iron is required prior to the solvent extraction step. In addition, it is reported that the extracted  $\text{Co}^{2+}$  is readily oxidised in the loaded organic phase by atmospheric oxygen to  $\text{Co}^{3+}$ , which then forms a very stable complex in the organic phase that cannot be stripped (Kholkin et al. 1988).

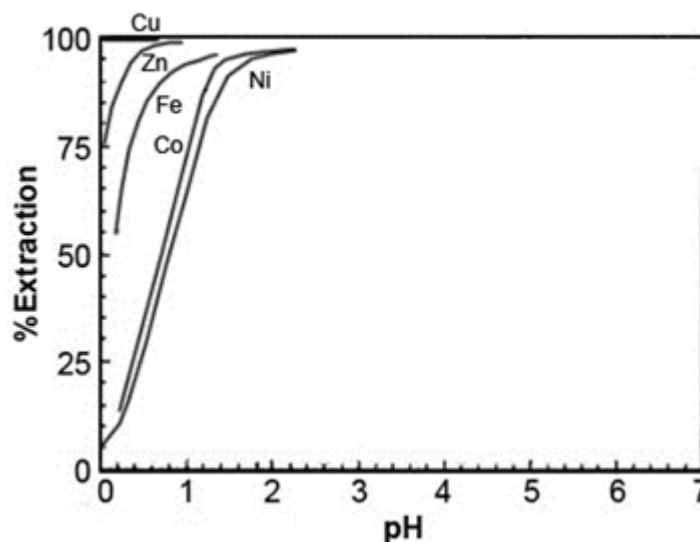


Figure 6. Effect of pH on metals extraction using Cyanex 301 (Sole and Hiskey (1992)).

In spite of these drawbacks, the use of Cyanex 301 in the solvent extraction of nickel and cobalt from HPAL liquors has been implemented a few years ago at Goro, New Caledonia. Its commercialisation appears to be motivated by the fact that reduction of the disulphide back into its dithiophosphinic acid form can be achieved. Rickelton et al. (1998) proposed a regeneration process by contacting the degraded organic with a strong acid, such as sulphuric acid, and an active metal such as metallic zinc. The reaction between a strong acid and an active metal generates nascent (atomic) hydrogen that breaks the S—S bond of the disulphide to form the dithiophosphinic acid as illustrated in Figure 7.

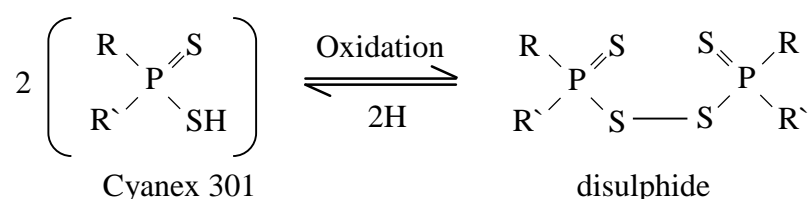
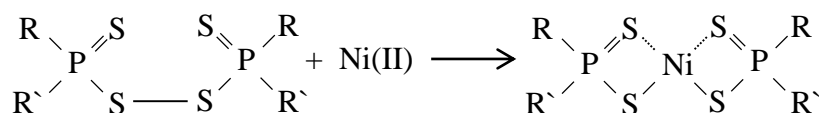


Figure 7. Cyanex 301 oxidation to disulphide and its regeneration with nascent hydrogen.

Later, Perraud et al. (2000) improved the regeneration process by directly reducing the S—S bond by the addition of an active metal such as nickel in an environment that is essentially free of water and acid as illustrated in Figure 8. This avoids the risk of explosion from the generation of hydrogen with the former process as well as the need for and disposal of acidic reagents. The dithiophosphinic acid can then be either directly recycled into the Cyanex 301 SX circuit or recycled after the loaded metal is

stripped. Both regeneration processes, however, proceed rather slowly. The former process requires about 3 hours of reaction time to regenerate the degraded extractant capacity to 95% at 60 °C (Rickelton et al. 1998) while the latter process requires about 4 hours of reaction time to do so at 65°C (Perraud et al. 2000).



**Figure 8. Cyanex 301 regeneration by the addition of nickel.**

The contact of Cyanex 301 with nitric acid solutions is obviously undesirable. Rapid degradation of this extractant was reported even at low acidity and mild conditions and therefore the use of Cyanex 301 for treating a nitrate solution is not recommended (Sole et al. 1993).

### 2.4.3 Carboxylic Acids as Extractants

This type of extractant is not as widely accepted as their organophosphorus counterpart despite being known to have excellent resistant to chemical attack and much less expensive than the three alkyl phosphorus acids. This is because they are much less capable for separating nickel and cobalt and also exhibit a rather high aqueous solubility especially at high pH.

So far, carboxylic acid extractant that has found true commercialisation in nickel and cobalt hydrometallurgy is only Versatic™ 10, a mixture of highly branched isomers of C<sub>10</sub> monocarboxylic acid. Indeed it has a very limited separation factor for nickel and cobalt but it has much better selectivity for separating nickel and cobalt from magnesium and calcium than the three alkyl phosphorus acids (Figure 9). This makes Versatic 10 useful for such application.

While the equilibrium for nickel and cobalt extraction can still be attained within a few minutes, equilibrium times for aluminium extraction using Versatic 10 is reported to take up to 15 hours (Preston 1985). This is not surprising as extraction of metals by carboxylic acids is generally slower than those by D2EHPA (Ritcey 2006b), which also exhibits slow aluminium extraction. This extractant also forms a very stable complex with ferric ion that cannot be stripped under normal conditions. Hence, the

use of Versatic 10 is not suitable for a feed solution that contains or susceptible to aluminium and iron contamination.

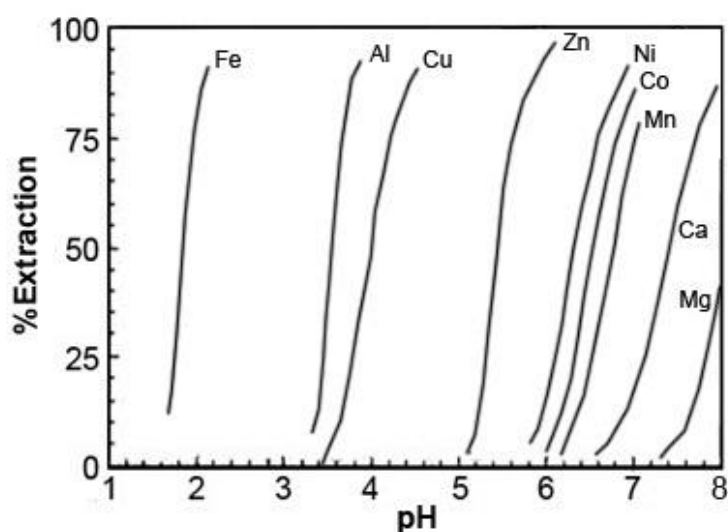


Figure 9. Effect of pH on metals extraction using Versatic 10 (Preston 1985).

#### 2.4.4 Hydroxyoximes as Extractants

Hydroxyoximes are widely known as copper-selective chelating extractants. This type of extract has been used commercially to extract nickel from ammonium sulphate or carbonate solutions since the 1970s and still continues in operation for at least one major refinery at Yabulu, Australia.

Hydroxyoximes do not have a particularly good nickel and cobalt separation but magnesium, manganese and calcium are not extracted from an acidic solution. This has been shown for LIX<sup>®</sup> 63, an aliphatic  $\alpha$ -hydroxyoxime with the active component 5,8-diethyl-7-hydroxydodecanone-6 oxime (Figure 10). This extraction characteristic, however, has never been exploited commercially due to the organic degradation owing to cobalt oxidation. The oxidised cobalt in the loaded organic phase cannot be easily stripped.

As such, the refinery at Yabulu oxidises cobalt to its trivalent state in the ammoniacal phase before feeding it to the solvent extraction circuit. As a trivalent ion, cobalt is not extracted with LIX<sup>®</sup> 84-I, a specially produced extractant for nickel extraction from ammoniacal solutions with the active component 2-hydroxy-5-nonylacetophenone

oxime, and thus nickel and cobalt can be separated effectively and organic degradation is minimised.

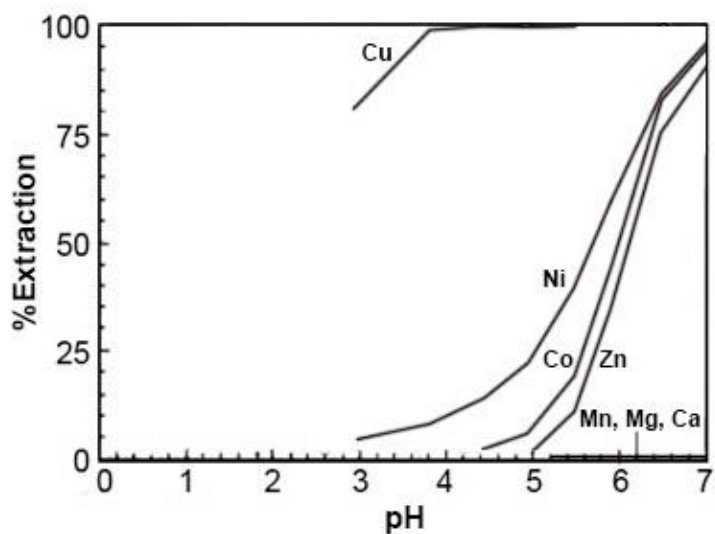


Figure 10. Effect of pH on metals extraction using LIX 63 (Cheng 2006).

Hydroxyoximes are not only prone to oxidative degradation but also nitration. This is due to the presence of aromatic ring in the oxime making it susceptible to electrophilic attack. Nitration of oxime was reported in copper solvent extraction processes where nitrate ion was present in the sulphate-based liquor (Virnig et al. 2003) or when the oxime was contacted with a dilute nitric acid solution (Bart et al. 1990). Despite the several measures that have been developed to overcome these problems, e.g. reductive stripping, reoximation of the degraded oxime and redox potential control (Mackenzie et al. 2006, Virnig et al. 2003, Virnig et al. 2002, Virnig et al. 2004), the use of hydroxyoximes is not suitable for treating a nitrate solution as their rates of degradation make their use uneconomical.

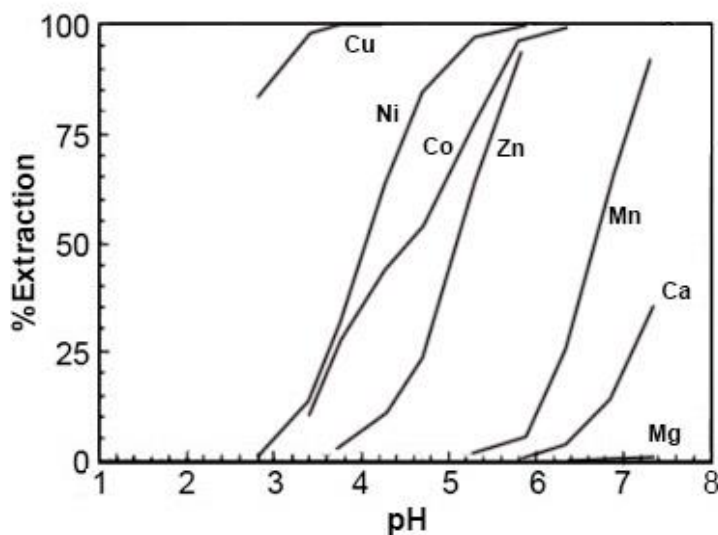
#### 2.4.5 Synergistic Systems

The combination of two or more extractants in an extraction system may provide better metal selectivity than each of the component individually. This phenomenon is attributed to the synergistic extraction of certain metal ions upon addition of adduct former resulting in higher extraction than that of any of the extractant alone.

The use of synergistic solvent extraction (SSX) for purifying nickel and cobalt has generated a considerable interest in the last decade. This is driven by the limited



selectivity of the current commercially-available extractant to purify nickel and cobalt especially for the separation of manganese since Cyanex 301 is prone to degradation. Synergistic mixtures of hydroxyoximes and carboxylic acids are of particular interest such as combination of LIX 63, Versatic 10 and a phase modifier TBP that provides good rejection for manganese, magnesium and calcium (Figure 11).



**Figure 11. Effect of pH on metals extraction using synergistic mixture LIX 63/Versatic 10/TBP (Cheng 2006).**

These mixtures, however, are prone to oxime degradation as well. In addition to the concern of degradation by cobalt oxidation and nitration, the presence of acidic extractant in the system such as Versatic 10 can also disrupt the oxime stability (Barnard and Moyer 2008, Barnard and Tsuntsaeva 2013, Barnard et al. 2010). Thus, Hutton-Ashkenny et al. (2015) proposed the use of synergistic mixture containing Versatic 10 and nonyl-4-pyridine carboxylate which is potentially more resistant to degradation for application to nitrate solutions, although having a slightly less manganese rejection than the LIX 63 containing system.

Nonetheless, the use of SSX struggles with complexities. The chemistry of an SSX system is complex and often not well understood especially for a newly developed system such as Versatic 10 and nonyl-4-pyridine carboxylate. It is also difficult to maintain the desired synergistic mixture due to differential losses of each extractant owing to their different solubilities in water. This is clearly a major concern since the effectiveness of an SSX system is sensitive to the proportion of each extractant in the mixture. Owing to these complexities, the use of SSX is not promising for purifying

nickel and cobalt from a nitrate solution. This is not surprising given commercial application of SSX systems is yet to be realised despite the numerous research and development on the technique since the early 1970s.

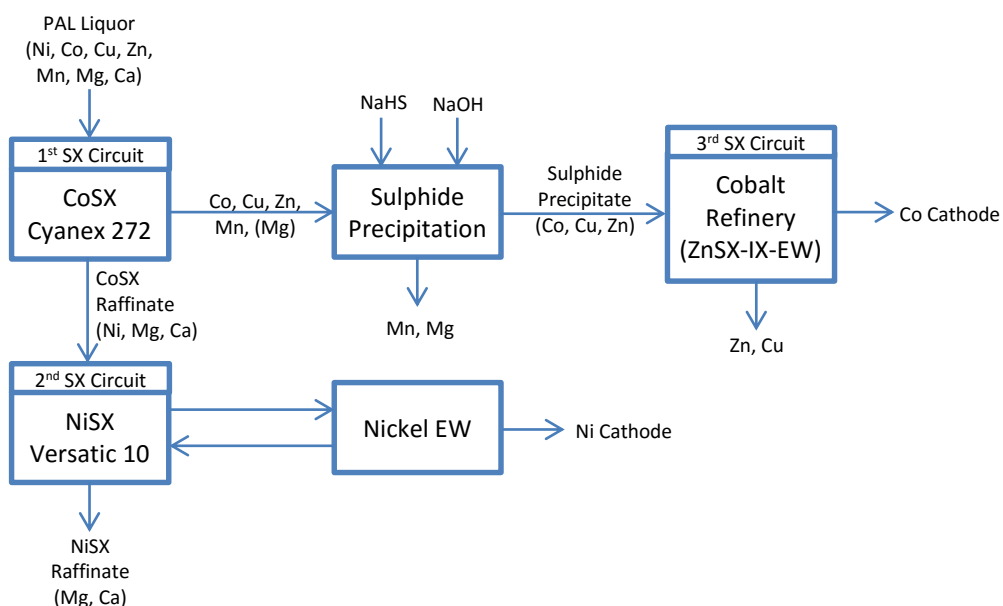
## **2.5 Direct Solvent Extraction Processes for Sulphate Solutions**

There are two commercialised DSX processes for purifying nickel and cobalt from sulphate-based liquors: Bulong process and Goro process. The former involves the use of three extractants, *viz.* Cyanex 272, Versatic 10 and D2EHPA, while the latter involves the use of Cyanex 301 for separating nickel and cobalt from major impurities and a tertiary amine extractant for separating cobalt from nickel. Since the use of either Cyanex 301 or tertiary amine is not suitable for treating a nitrate solution, the following discussion is focused only on the the Bulong process as it has relevance to the development of an SX process for nitrate-based liquors.

Bulong Nickel Operation (Bulong) pioneered the use of a DSX route to produce nickel and cobalt cathodes from HPAL liquor of nickel laterite ores. The plant consisted of three SX circuits as illustrated in Figure 12. The first circuit (Co SX) was to separate cobalt along with copper, zinc, manganese and some magnesium from nickel using Cyanex 272, whereas the second circuit (Ni SX) was to extract nickel over magnesium and calcium from the Co SX raffinate using Versatic 10. The nickel-containing stripped liquor from Ni SX circuit was then electrowon to produce nickel cathode with 99.5% purity. The cobalt, copper and zinc from the Co SX stripped liquor were separated from manganese and magnesium via sulphide precipitation, which was re-leached in an autoclave. The generated leach solution was then fed into the third circuit (Zn SX) where zinc was separated using D2EHPA. The remaining copper was separated from Zn SX raffinate using the ion exchange resin Purolite 5950 before the cobalt-rich raffinate was fed into the cobalt electrowinning circuit (Flett 2004, Ritcey 2006a).

Bulong suffered serious ramping-up retardation soon after its commissioning in 1998 due to numerous issues especially with severe gypsum formation in the Ni SX circuit (Donegan 2006, O'Callaghan 2003b, Ritcey 2006a). The circuit consisted of four extraction stages (Figure 13) wherein the pH profile was staggered to allow good nickel recovery while minimising the co-extraction of calcium. The calcium was

extracted in E3 and E4 (pH 6.8-6.9), when the barren organic was contacted with the calcium-saturated feed solution, but then crowded out by nickel in E1 and E2 (pH 6.5-6.6). This crowding out effect was responsible for the significant formation of gypsum in the Ni SX circuit by supersaturating an already calcium-saturated solution due to the use of limestone and lime in the upstream neutralisation.



**Figure 12. Simplified Bulong flowsheet**

The scaling problem was worsened by Cyanex 272 contamination of nickel-containing raffinate from the cobalt extraction circuit as it was an effective calcium extractant at the Ni SX extraction pH. Calcium extraction in Ni SX therefore increased with increases in the concentration of Cyanex 272 in the Ni SX solvent. The presence of Cyanex 272 also reduced the selectivity of Versatic 10 for nickel over Mg and, consequently, reduced the extraction efficiency in terms of ammonia consumption and organic loading. While gypsum formation will not be a problem in treating nitrate-based liquors, extractant cross-contamination remains among the major challenges for such DSX application.

As control measures for Cyanex 272 entrainment, a diluent wash (DW) process, a Cyanex 272 recovery circuit (C272-R) and crud filters were installed in May-June 2001. Such modifications are depicted schematically in Appendix C. The Co SX raffinate, which contained about 150 mg/L of entrained 16% Cyanex 272, was contacted with a recirculating stream of diluent in the DW stage. Cyanex 272 was then

recovered from DW organic with dilute ammonia stream at pH 10 that converted the Cyanex 272 into an aqueous-soluble salt form. This Cyanex 272-rich aqueous stream was then transferred to the stripped organic wash stage where the high salt content and acidity of the aqueous phase resulted in complete recovery of Cyanex 272 to be reused in the Co SX circuit. Some Cyanex 272 was also recovered by periodically transferring the DW organic to Co SX circuit as make-up organic.

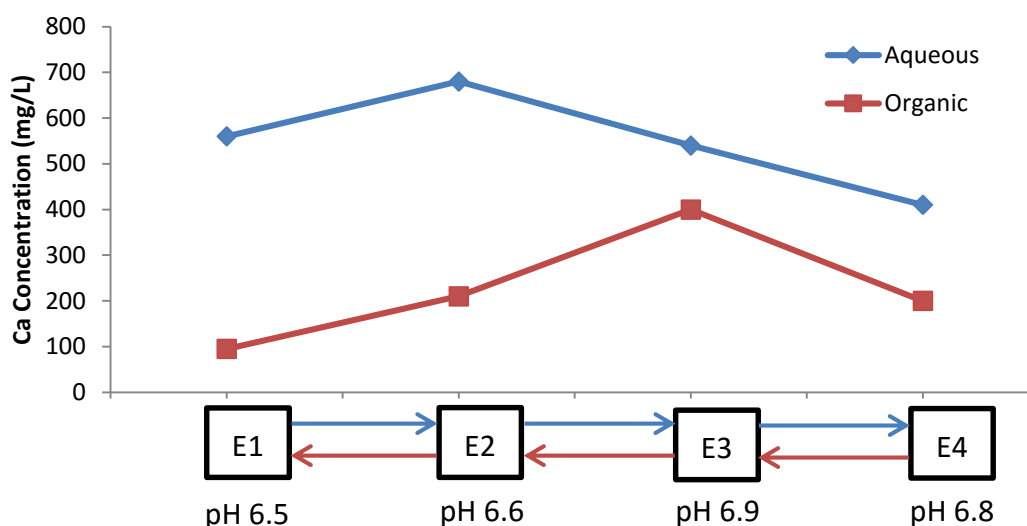


Figure 13. Distribution of calcium in Ni SX circuit (Ibana 2002).

The use of DW process is more desirable for recovering Cyanex 272 rather than precipitating the reagent out of the organic phase as in C272-R at a higher cost. Unfortunately, the amount of Cyanex 272 that could be recovered via DW process while still maintaining wash efficiency was not been determined (Ritcey 2006a). The DW raffinate still contained about 150 mg/L of organic entrainment; about one third of this was removed in a Jameson cell (J-Cell, a flotation cell) and overall Cyanex 272 recovery from Co SX raffinate was >99%. This recovery allowed acceptable Ni SX performance. Crud filters were also installed owing to the significant contribution of crud to Cyanex 272 contamination in the Ni SX circuit.

The Nickel Hydrometallurgy Research Group at the WA School of Mines developed a technique involving the use of an anti-scalant to further minimise gypsum formation in the Bulong SX circuits<sup>1</sup>. This resulted in a dramatic reduction in the rate of scale formation throughout the extraction circuits without causing any adverse impact on

<sup>1</sup> D Ibana, Head of Nickel Hydrometallurgy Research Group, Personal Communications, December 2013

the chemical or physical performance of the SX circuits or any other part of the Bulong operation (Donegan 2006, Helm 2004, O'Callaghan 2003b). The primary advantage of this is that it allows higher average flow-rates of wash water, by reducing hydraulic restriction in pipes and valves, through the counter-current decantation (CCD) circuit since Ni SX raffinate was used as wash. This is important because poor SX flow-rates directly translates into poor CCD metal recovery (O'Callaghan 2003b). This also allows extended operation before cleaning shutdowns were required leading to a significant increase in productivity and reduction in maintenance and descaling costs.

The abovementioned modifications in the Bulong refinery significantly improved its metallurgical performance. Despite this, Bulong was closed in October 2003 due to financial pressures and has not been re-commissioned since. Several major process deficiencies encountered during the early operation were largely addressed and Bulong SX circuits were able to meet or exceed most design parameters at the time of plant closure. It was capable for producing nickel electrolyte suitable to produce nickel cathode with >99.8% purity and a concentrated liquor suitable for recovering a saleable cobalt products which was only cobalt sulphide at the time. The typical recoveries of nickel and cobalt from the Co SX feed tank to product liquor were 98.2% and 98.5%, respectively, which were exceeding their designed recoveries of 98% each (Donegan 2006).

## **2.6 Summary of the Review**

The major findings of this review may be summarised as follows:

- The extraction selectivity for base metals from sulphate, chloride and nitrate matrices using cationic extractants are the same but shifted to lower pH values in this order such that the  $pH_{50}$  from sulphate media is approximately 0.5 pH units higher than the corresponding  $pH_{50}$  from nitrate media. This is owing to the weaker complexing nature of the nitrate ligand compared to the sulphate or chloride.
- The degradation of solvent extraction reagents in a mildly acidic nitrate solution at moderate temperatures is unlikely since the generation of electrophiles or free radicals from nitric acid is unlikely under such conditions.

- Cationic extractants including alkyl phosphorus acids, thiophosphorus acids, carboxylic acids and hydroxyoximes are the only of type of extractants that may be suitable for treating a mildly acidic nitrate solution as anionic and solvating extractants require much higher acidity for an effective extraction to occur.
- Among these cationic extractant, bis(2,4,4 tri-methylpentyl) phosphinic acid (BTMPPA) is the most suitable for separating aluminium, nickel and cobalt in terms of selectivity, chemical stability to withstand oxidation and metal poisoning, and kinetics of both extraction and stripping of aluminium, nickel and cobalt. Thiophosphorus acids and hydroxyoximes are not suitable for this application as they are susceptible to degradation in the presence of nitrate ion. Versatic 10, D2EHPA and EHPNA are only suitable for treating an aqueous solution that is free of aluminium and iron.
- Based on Bulong experience, Cyanex 272 is an effective extractant for DSX applications as it allows the production of high purity nickel and cobalt products with high recoveries.

## Chapter 3

### MATERIALS AND METHODS

#### 3.1 Reagents

The inorganic reagents used in the experimental work are listed in Table 4. All inorganic reagents used were of Analytical Reagent (AR) grade.

**Table 4. Inorganic reagents used in the experimental work.**

| Reagent                        | Formula  | Purity | Supplier                               |
|--------------------------------|--|--------|--|
| Nickel nitrate hexahydrate     | $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ | 98%    | Scharlau                               |
| Cobalt nitrate hexahydrate     | $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ | 97%    | BDH Laboratory                         |
| Aluminium nitrate nonahydrate  | $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ | 98%    | Chem-Supply                            |
| Zinc nitrate tetrahydrate      | $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ | 99%    | Chem-Supply                            |
| Manganese nitrate tetrahydrate | $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ | 98%    | Chem-Supply                            |
| Magnesium nitrate hexahydrate  | $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ | 99%    | Chem-Supply                            |
| Calcium nitrate tetrahydrate   | $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ | 99%    | Univar <sup>®</sup> Ajax<br>Finechem   |
| Sodium hydroxide pellet        | NaOH   | 99%    | Rowe Scientific                        |
| Nitric acid                    | $\text{HNO}_3$                                       | 99%    | RCI Labscan                            |
| Sulphuric acid                 | $\text{H}_2\text{SO}_4$                              | 98%    | EMSURE <sup>®</sup> Merck<br>Millipore |

The extractant, Cyanex 272 (industrial grade, Cytec Australia), diluent, ShellSol 2046 (industrial grade, Shell Chemicals), and phase modifier, TBP (AR, Merck Millipore), were used in this study as supplied. ShellSol 2046 was selected as diluent based on its low aromatic content (8% v/v), availability and commercial experiences in nickel and cobalt refineries.

#### 3.2 Preparation of Synthetic Aqueous Feed Solutions

Synthetic nitrate solutions that simulated those produced in the DN<sub>i</sub> process post iron and aluminium precipitation steps, were prepared by dissolving the respective nitrate salts of the metals in minimum amount deionised water to dissolve them completely. The volume of the solutions was then made close to those of the volumetric flasks.

The solution pH was adjusted by adding nitric acid (1 mol/L) and then made to the volume. The actual concentrations of the metal ions were determined by inductively coupled plasma spectrophotometer (ICP). A typical solution composition is shown in Table 5.

**Table 5. Typical synthetic feed solution composition**

| <b>Element</b>     | Ni   | Co   | Al   | Zn   | Mn   | Mg   | Ca   | NO <sub>3</sub> <sup>-</sup> |
|--------------------|------|------|------|------|------|------|------|------------------------------|
| <b>Conc. (g/L)</b> | 4.43 | 0.15 | 0.14 | 0.03 | 0.63 | 85.0 | 1.64 | ~452*                        |

\*Nominal nitrate concentration calculated based on the assumption of 1:3 and 1:2 metal to nitrate ligand ratio for the trivalent and divalent metals at pH 2.0.

Aqueous feed solutions used for the subsequent extraction steps were prepared in similar manner to simulate the aqueous raffinates with compositions and pH that were found experimentally in this study.

### **3.3 Preparation of Organic Solutions**

The organic solutions were prepared by dissolving the required volume of the extractant Cyanex 272 and the modifier, TBP, when required, in ShellSol 2046. The concentrations of the extractant and phase modifier are in volume percentage (% v/v). The organic solutions were pre-treated by manually shaking them with an equal volume of acidified deionised water (pH ~5) in a separatory funnel for 10 minutes at 20 to 30°C to remove any water soluble constituent as has been suggested by Ritcey (2004). This acidified deionised water was prepared by adding a single drop (~0.03 mL) of sulphuric acid solution (1 mol/L) for every 500 mL of deionised water used. The addition of acid and the control of temperature to higher than 20 °C were found to be essential to avoid any emulsion formation. The organic phase was then filtered through Whatman® 1PS phase separator paper to avoid any water entrainment.

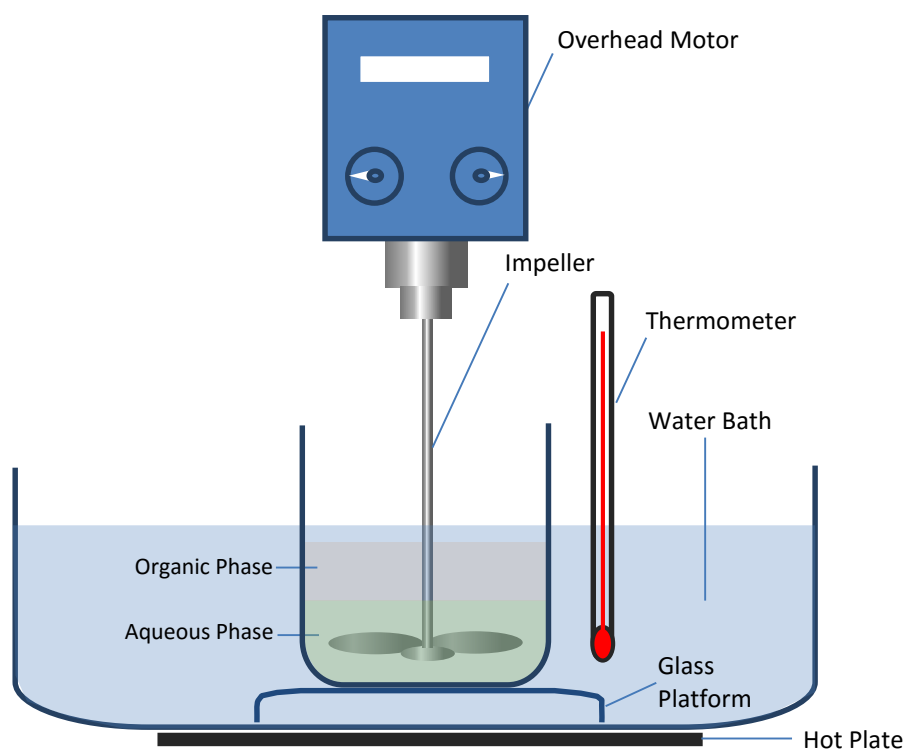
### **3.4 Experimental Set-up**

All extraction, scrubbing and stripping experiments were carried out in a 150-mL glass beaker as the extraction cell sitting in a glass water bath. A hollow-glass platform was fixed at the bottom of the water bath to promote a more even temperature profile around the extraction cell. Mixing was facilitated using a mechanical stirrer (Heidolph RZR 2020 Mixer System) equipped with a four-bladed impeller (35 mm diameter).



The stirring speed was set at 350 rpm for all extraction tests. An alcohol thermometer was clamped in position to allow the monitoring of the bath temperature. The temperature was maintained at a certain value by manually adjusting the temperature controller of the hot plate. A diagram of the experimental set-up is depicted in Figure 14.

All experiments were performed in a fume hood to control exposure to hazardous or toxic fumes or vapours.



**Figure 14. Experimental set-up for the solvent extraction tests.**

### 3.5 Solvent Extraction Test Procedure

Solvent extraction tests were carried out by transferring the required volumes of the aqueous (feed) and organic solutions into separate beakers. The pH of the feed solution was adjusted to required value with a known volume of sodium hydroxide solution (5 mol/L) or nitric acid solution (1 mol/L). The use of a more concentrated nitric acid solution is not desirable given its oxidising nature. The beakers were immersed in the water bath to equilibrate to the desired temperature. Once equilibrated, both solutions were transferred in to the extraction cell and mixing was started. After mixing, the

phases were allowed to disengage and then an aqueous sample (10 mL) was withdrawn using a syringe for pH measurement, which was carried out using a pH meter (TPS WP-90) equipped with an Ionode IJ44-C pH probe. If necessary, the pH was adjusted and the process was repeated until the desired equilibrium pH was reached. The mixture was then transferred into a separatory funnel, allowed to disengage and the phases were separated. All pH measurement was carried out at  $21 \pm 2$  °C.

When the total volume of the organic and aqueous phases used was below 60 mL, such as for experiments at various organic to aqueous phase ratio (O/A), the extraction equilibria were carried out in a 100-mL glass beaker by the same experimental procedure but using magnetic stirrer for mixing.

To ensure apparent equilibrium was reached in all experiments, the two immiscible phases was mixed for 15 minutes. This mixing duration was found to be sufficient based on the exploratory extraction tests that showed the apparent equilibrium for aluminium extraction using 20% Cyanex 272 at 40 °C was reached between 10 and 12 minutes while for other metals, it was reached within 5 minutes only.

### **3.6 Scrubbing and Stripping Tests**

The loaded organic solutions for scrubbing and stripping tests were collected from extraction tests at the determined operating conditions. A number of extraction tests were carried out to obtain a certain volume of loaded organic phase that was sufficient for a series of scrubbing or stripping test. The loaded organic phase that was collected in each test was filtered through a Whatman® 1 PS phase separation paper to avoid any aqueous entrainment.

The concentrations of the metals in the loaded organic phase was determined by stripping the loaded organic phase with sulphuric acid solution (0.5 mol/L) at 40 °C and O/A = 1. These stripping conditions were determined to yield complete stripping of the loaded metals from the exploratory stripping tests using various sulphuric acid concentrations (0.05, 0.1, 0.25, 0.5, 1, 2 and 5 mol/L).

The stripping tests were carried out in similar manner as the extraction tests described in Chapter 3.5 but using sulphate-based solutions as the aqueous phase.

### 3.7 Multi-stage Extraction Tests

In each extraction stage, the feed aqueous phase used was collected from the preceding extraction stage. Similar to the scrubbing and stripping tests, multiple extraction tests were carried out to obtain a certain volume of raffinate that was sufficient for multiple extraction stages in the following stage. In each extraction test, 30 mL of the raffinate as the feed and 30 mL of fresh organic solution were used.

### 3.8 Assay of Metals

The concentrations of the metal ions in all aqueous phase were analysed by an independent analytical laboratory (Bureau Veritas Australia) using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo Fisher iCAP 6000). Metal detection limits of the instrument for the solution analysis are shown in Table 6. Dilution factor of 5 and 2.5 were mostly used for aqueous samples taken from the extraction and stripping tests, respectively. Given the low concentration of aluminium and its instrumental detection limit, standard deviations from the aluminium analysis of the duplicated experiments were up to 15% but mostly below 5%.

**Table 6. Elemental detection limits of the ICP-AES used by the analytical laboratory**

| <b>Element</b>                | Ni  | Co  | Al  | Zn  | Mn  | Mg  | Ca  |
|-------------------------------|-----|-----|-----|-----|-----|-----|-----|
| <b>Detection Limit (mg/L)</b> | 0.5 | 0.5 | 1.0 | 0.5 | 0.5 | 1.0 | 1.0 |

## **Chapter 4**

### **RESULTS AND DISCUSSIONS**

#### **4.1 Development of a Direct Solvent Extraction Concept for Purifying Nickel and Cobalt from Nitrate Solutions**

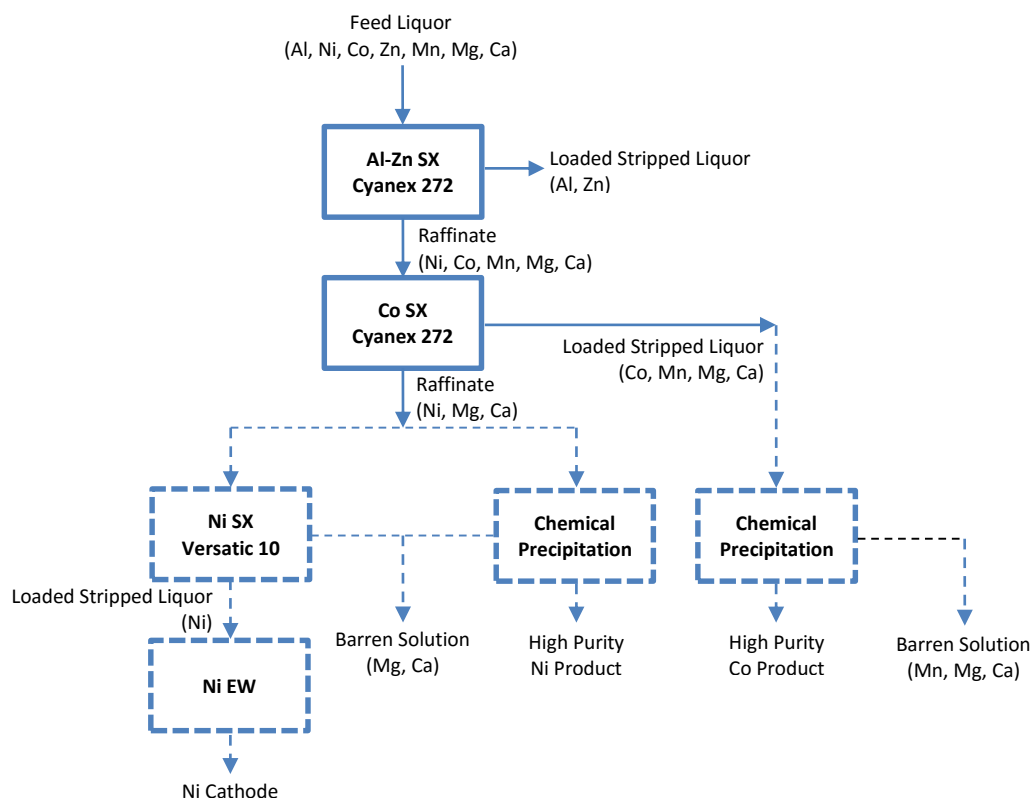
It was clear at this stage of the study that a DSX technique for the purification of nickel and cobalt from the nitric acid leach solution of the DNi process is highly desirable but it requires one that allows the removal of aluminium (Chapter 1.5) prior to the separation of cobalt and nickel. This is because unlike sulphate-based liquors, which allow complete aluminium removal in the upstream neutralisation step (partial neutralisation), a high concentration of aluminium remains in the partially neutralised nitrate-based liquor.

The review of extractants indicated that based on selectivity, kinetics of extraction and stripping, and stability against oxidative degradation, the use of bis(2,4,4 trimethylpentyl) phosphinic acid such as Cyanex 272 may allow the removal of aluminium from this liquor prior to the separation of nickel and cobalt. Subsequently, the nickel and cobalt can then be separated using the same extractant. Hence, a DSX process involving two sequential solvent extraction circuits but using Cyanex 272 in both circuits was conceived. The first circuit is to remove aluminium along with zinc and the second circuit is to separate cobalt along with manganese from nickel. If any copper or iron(II) remain in the feed aqueous solution, they should also be separated in the second circuit leaving only nickel along with calcium and magnesium in the raffinate. The proposed DSX route is illustrated schematically in Figure 15.

The use of two Cyanex 272 circuits upfront is versatile as it would allow the production of high purity nickel and cobalt products such as cathodes, sulphides or hydroxides since the major impurities that remain in the solution after the first solvent extraction circuit would only be manganese, magnesium and calcium. The amount of these impurities are much less than the feed solutions in Bulong, the pioneering commercially proven DSX process that allowed the production of these high purity products. If high purity nickel cathode is desired as the final product, Versatic 10, for example, can then be used to separate the nickel from magnesium and calcium to produce a sufficiently pure nickel electrolyte. Otherwise, chemical precipitation

processes such as sulphide or hydroxide precipitation can be used to produce high purity products as both are selective over manganese, magnesium and calcium.

The scrubbing and stripping steps of this proposed DSX route will utilise sulphuric acid to take advantage of the more well-understood chemistry as well as process metallurgy recovery technologies such as chemical precipitation and electrowinning in sulphate media. This is also to avoid the use of high concentration of nitric acid to minimise the risk of oxidative degradation of the solvent extraction reagents.



**Figure 15. Proposed DSX route for the recovery of nickel and cobalt from nitric acid leach solution. Dashed lines are the options for the nickel and cobalt recovery.**

The proposed DSX route has a number of advantages over that of Bulong. The use of only one extractant in these adjoining solvent extraction circuits circumvents the need to remove any residual extractant from the raffinate of the first circuit to avoid contamination of the second circuit via, for example, organic entrainment and consequently adversely affect its chemistry as discussed previously. Unlike Bulong, which suffered from severe gypsum precipitation, this DSX route has no susceptibility to gypsum precipitation being nitrate-based.

## **4.2 Determination of the Operating Temperature**

As the first step of the experimental program, the appropriate operating temperature for the extraction, scrubbing and stripping was explored by carrying out exploratory solvent extraction tests. It was found that 40 °C was most suitable based on a compromise between the apparent rate of aluminium extraction, phase separation and minimum temperature to minimise the possibility of oxidative degradation, which high temperature favours. For comparison, Bulong was operated at 45 °C in its Co SX circuit (Donegan 2006) and most studies that indicated equilibrium of aluminium extraction was reached within 20 minutes were carried out at 40 to 50 °C (Mantuano et al. 2006, Tsakiridis and Agatzini-Leonardou 2005). In addition to this, it was mentioned previously that the solvent extraction reagents are generally resistant to oxidation provided the aromatic content in the diluent is below 25% and the operating temperature does not exceed 50 °C (Young et al. 1990).

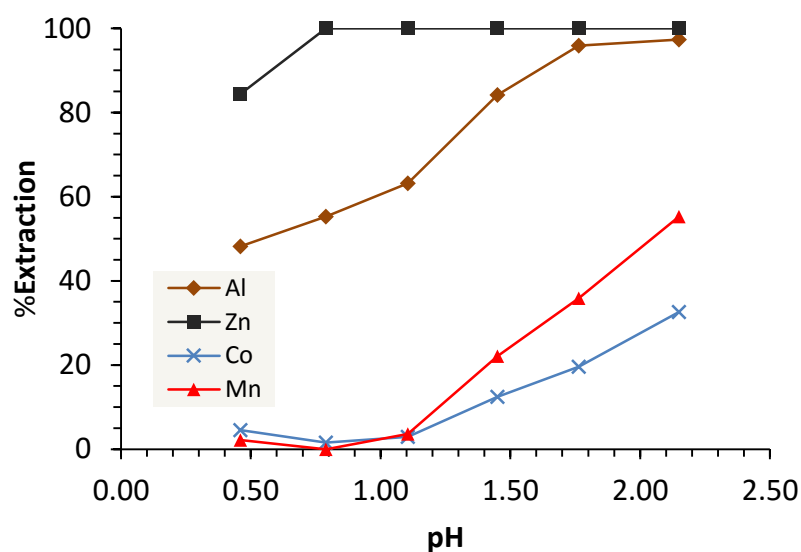
It was noted that operating temperature in the range of 25 to 50 °C had little effect on the extraction curves. For example, in a study of solvent extraction and stripping of chromium from a sulphate solution with Cyanex 272, Lanagan (2002) reported that the increase of operating temperature provides a slight increase in the extraction. The change in extraction efficiency at any given pH values is almost negligible and there is no further increase in extraction once the temperature exceeds 40 °C. This is also supported by Santanilla et al. (2012) who studied the solvent extraction of aluminium, nickel, zinc and iron with Cyanex 272 from sulphate solutions. They compared the effect of temperature and the results show that variation of temperature over the range of 25 to 50 °C provides insignificant changes in the extraction efficiency of the four metals.

## **4.3 Metal Extraction Behaviour using Cyanex 272**

The metal extraction behaviour using Cyanex 272 was investigated to evaluate the extraction selectivity for the major components of the nitrate feed solutions. To achieve this, a series of extraction tests following the procedures outlined in Chapter 3.5 using 20% Cyanex 272 at pH range of 0.5 to 2.2 was carried out. The results, summarised in Figure 16, showed that the order by which the metals were extracted is comparable to those obtained from sulphate systems (Donegan 2006, Mantuano et al.

2006) except that they are shifted toward lower pH values. These are consistent with the observations of earlier investigators such as Preston (1982), Lanagan and Ibane (2003) and Hutton-Ashkenny et al. (2014) who attributed this to the weaker complexing nature of the nitrate ion compared to the sulphate ion.

Nickel, calcium and magnesium co-extraction did not exceed 1% over the pH range investigated. This is favourable to the industrial application of the technique. Good phase separation was also observed over this pH range, with both phases disengaging almost instantly.



**Figure 16. Effect of pH on the extraction of metals using 20% Cyanex 272.**

Aqueous phase: 0.14 g/L Al, 0.03 g/L Zn, 0.63 mg/L Mn, 0.15 g/L Co, 4.4 g/L Ni, 1.6 g/L Ca and 85.0 g/L Mg; initial aqueous pH = 2.0; T = 40 °C; O/A = 1. See Table D-1 in Appendix D for the experimental data.

Zinc extraction showed excellent selectivity over cobalt. Complete zinc extraction was achieved at pH as low as 0.8 wherein cobalt co-extraction was negligible.

Complete aluminium extraction, on the other hand, was achieved only at pH 2.2, which was accompanied by appreciable amount of cobalt co-extraction (33%). A similar trend, although in sulphate media, has been reported previously by Orive et al. (1992) who studied the recovery of cobalt and nickel from acidic sulphate solutions in the presence of aluminium. Their extraction curves for aluminium, cobalt and nickel with Cyanex 272 show quantitative aluminium extraction accompanied by more than 50% of cobalt co-extraction. This is also apparent in the extraction curves plotted by

Mantuano et al. (2006) in their investigation of the recovery of base metals from sulphuric acid leaching of spent rechargeable batteries with Cyanex 272. Lesser cobalt co-extraction (3.2 to 17.9%) were reported by Mohapatra et al. (2007) in their study of the solvent extraction of aluminium from sulphate solutions using the sodium salt of Cyanex 272. These cobalt co-extraction values, however, are still too high to be lost in the waste and therefore must be recovered.

The separation of manganese from cobalt was, however, difficult as their extraction curves were close together. Manganese would therefore continue to contaminate cobalt in the aqueous phases but this is not an issue as their subsequent separation is well established as done, for example, in the Bulong process.

#### **4.4 Aluminium and Zinc Separation from Cobalt**

Orive et al. (1992) and Mohapatra et al. (2007) also reported that the co-extracted cobalt was able to be scrubbed out easily using only mildly acidic solutions. This indicates that it may be possible to achieve effective separation of aluminium and zinc from cobalt via selective extraction of aluminium and zinc and scrubbing of the co-extracted cobalt. Hence, this was pursued.

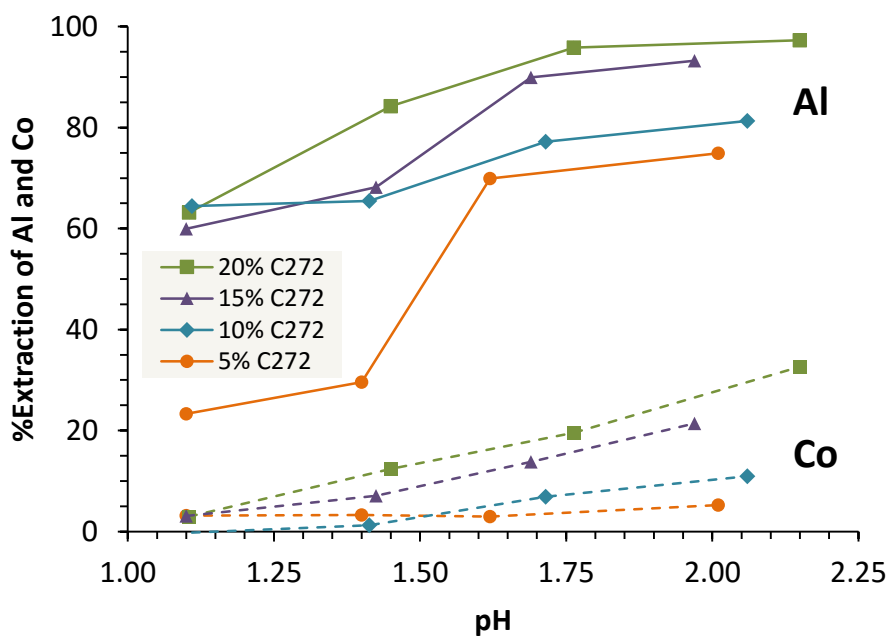
To optimise the separation process, the effect of various experimental variables in the extraction, scrubbing and stripping steps were investigated. The extraction step was optimised by investigating the effect of extractant concentration and pH on the separation of aluminium from cobalt. The scrubbing and stripping steps were optimised by investigating the effect of aqueous phase acidity on the process efficiency. The nature of the extracted species was investigated via slope analysis to verify if the extraction of metals from the current nitrate system proceeded via similar mechanism to those from sulphate systems.

##### **4.4.1 Effect of Extractant Concentration and pH on Aluminium and Cobalt Separation**

The variation of extractant concentration was investigated to explore whether higher separation factor for aluminium and cobalt ( $\beta_{Al-Co}$ ) can be achieved by limiting the free-extractant in the organic phase so that the co-extraction of the metals that have lower distribution coefficients ( $D$ ) is inhibited.



It was found that decreases in extractant concentration resulted in decreases in cobalt co-extraction but also the aluminium extraction (Figure 17). The relative decrease of aluminium, however, was higher than cobalt. That is, the separation factor between cobalt and aluminium ( $\beta_{Al-Co}$ ) decreased with decreases in extractant concentration except when using 10% Cyanex 272 at pH below 1.4 wherein the  $\beta_{Al-Co}$  were higher than 149 (Table 7). At such low pH and extractant concentration, however, aluminium extractions were below 66% requiring many extraction stages to achieve complete aluminium removal compared to only one or two extraction stages when using 20% Cyanex 272 at pH about 2.1. This is supported by the McCabe-Thiele diagram of aluminium extraction (Figure 18) showing that a single extraction stage is theoretically sufficient for removing aluminium completely using O/A as low as 1/2 and only two stages is required when using O/A of 1/3. As there was no merit in using lower extractant concentration, the use 20% Cyanex 272 and pH 2.1 was optimal for the aluminium and zinc extraction step.



**Figure 17. Effect of extractant (Cyanex 272) concentration on aluminium and cobalt extraction.**

Aqueous phase: 0.14 g/L Al, 0.03 g/L Zn, 0.63 mg/L Mn, 0.15 g/L Co, 4.4 g/L Ni, 1.6 g/L Ca and 85.0 g/L Mg; initial aqueous pH = 2.0; T = 40 °C; O/A = 1. See Table D-1 in Appendix D for the experimental data.

The effect of variation of pH (1.9 to 2.3) was investigated by undertaking a series of extraction tests using 20% Cyanex 272. The raffinate from these tests were assayed and it was found that their aluminium contents were consistently less than 5 mg/L. An

upset condition, wherein 10 mg/L of aluminium remained in the raffinate, was subjected to a second extraction stage using fresh organic solution. The use of pH 1.9 reduced the residual aluminium to below 5 mg/L. The use of pH 2.4 yielded complete aluminium removal. This clearly showed that satisfactory aluminium removal from nitric acid leach solutions can be achieved using Cyanex 272 although with appreciable amount of cobalt co-extraction, which was addressed by scrubbing.

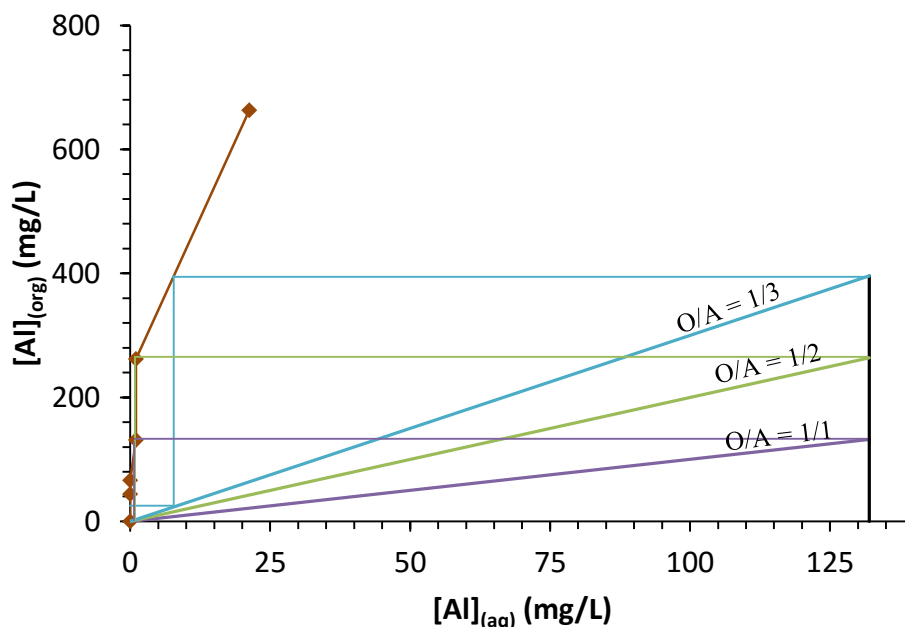
**Table 7. Distribution coefficient and separation factor for aluminium and cobalt at various Cyanex 272 concentration and pH.**

| <b>Extractant Concentration</b> | <b>pH</b> | $D_{Al}$ | $D_{Co}$ | $\beta_{Al-Co} = \frac{D_{Al}}{D_{Co}}$ |
|---------------------------------|-----------|----------|----------|---|
| 5%                              | 1.40      | 0.42     | 0.03     | 12.3                                    |
|                                 | 1.62      | 2.32     | 0.03     | 76.0                                    |
|                                 | 2.01      | 2.98     | 0.06     | 54.0                                    |
| 10%                             | 1.41      | 1.90     | 0.01     | 149.1                                   |
|                                 | 1.72      | 3.39     | 0.07     | 46.0                                    |
|                                 | 2.06      | 4.36     | 0.12     | 35.4                                    |
| 15%                             | 1.43      | 2.14     | 0.08     | 28.2                                    |
|                                 | 1.69      | 8.91     | 0.16     | 55.8                                    |
|                                 | 1.97      | 13.77    | 0.27     | 50.6                                    |
| 20%                             | 1.45      | 5.33     | 0.14     | 37.6                                    |
|                                 | 1.76      | 23.19    | 0.24     | 95.3                                    |
|                                 | 2.13      | 36.11    | 0.48     | 74.6                                    |

#### **4.4.2 Cobalt Scrubbing**

The loaded organic solutions from the extraction tests that were determined to be at the optimum conditions for the aluminium removal were subjected to scrubbing tests using acidified (H<sub>2</sub>SO<sub>4</sub>) deionised water. The composition of the loaded organic phase was determined by stripping with 0.5 mol/L sulphuric acid solution at phase ratio of unity as described in Chapter 3.6.

The results, summarised in Table 8, showed that the cobalt scrubbing step was particularly sensitive to pH. For example, the amounts of co-scrubbed aluminium were markedly different with only 0.2 to 0.3 pH unit difference at pH values below 1.4.



**Figure 18. McCabe-Thiele diagram for aluminium extraction with various operating lines (O/A).**

Aqueous phase: 0.13 g/L Al, 0.03 g/L Zn, 0.61 mg/L Mn, 0.14 g/L Co, 3.9 g/L Ni, 1.6 g/L Ca and 85.0 g/L Mg; initial aqueous pH = 2.0; T = 40 °C. See Table D-2 in Appendix D for the experimental data.

The use of lower extractant concentration at the extraction stage to improve the scrubbing selectivity was explored. This was carried out in a series of scrubbing tests using loaded organic phase from extraction tests wherein only 10% Cyanex 272 was used and carried out at 40 °C and pH 1.7. The scrubbing tests were then carried out, also with acidified deionised water as scrub solution.

The results, summarised in Table 9, showed that the scrubbing raffinate would still be susceptible to aluminium contamination. This reinforced the finding in the previous section that the use of extractant concentration lower than 20% provides no merit for the aluminium removal step prior to the subsequent cobalt recovery step. It however highlighted the need to explore a suitable approach for dealing with the co-extraction of cobalt in the aluminium removal step or the co-scrubbing of aluminium with cobalt in the cobalt scrubbing step.

**Table 8. Effect of pH on the scrubbing of cobalt and manganese from 20% Cyanex 272 loaded organic phase using acidified deionised water.**

| pH   | %Scrubbing |     |    |    |
|------|------------|-----|----|----|
|      | Co         | Mn  | Al | Zn |
| 1.20 | 100        | 100 | 69 | 63 |
| 1.35 | 100        | 100 | 46 | 50 |
| 1.38 | 100        | 100 | 19 | 18 |
| 1.40 | 79         | 51  | 0  | 0  |
| 1.70 | 3          | 1   | 0  | 0  |

Organic phase: 0.14 g/L Al, 0.03 g/L Zn, 0.04 g/L Co and 0.35 g/L Mn; T = 40 °C; O/A = 1.

It was decided that the most suitable approach is to allow the small amount of aluminium contamination (25 to 70 mg/L) in the cobalt scrubbing raffinate because this can be removed easily by chemical precipitation given it is in sulphate media. The precipitation of aluminium from sulphate media is well established as it has already been in use in the partial neutralisation step of many commercial processes such as Bulong (O’Callaghan 2003a), Murrin-Murrin (Motteram et al. 1996) and Ravensthorpe (White et al. 2006) in Australia, Coral Bay Project in the Philippines (Tsuchida et al. 2004) and Ambatovy Project in Madagascar (Collins et al. 2004). Hence, the chosen approach was to recycle the cobalt scrubbing raffinate from the aluminium solvent extraction circuit downstream, where there is no nickel present. For example, it can be combined with the stripping raffinate from the cobalt extraction step. Another option is to scrub at lower pH (1.40) but this would require more than one scrubbing stage.

Given these consideration, the most suitable approach in dealing with the poor scrubbing selectivity of cobalt from the aluminium loaded extractant is, therefore, to operate the scrubbing circuit at pH below 1.38 to ensure maximal cobalt recovery and recycle the scrub to the raffinate of the stripping circuit of the cobalt extraction step.

#### **4.4.3 Aluminium and Zinc Stripping**

The metals stripping tests were carried out in a similar manner as the scrubbing tests (Chapter 3.6) to determine the lowest acidity required for complete stripping of the aluminium and zinc. It was found that quantitative stripping of the two metals can be achieved at pH 0.8 indicating that sulphuric acid solution at concentration as low as

0.1 mol/L was sufficient to achieve complete stripping of these metals. This is consistent with the results of the work by Orive et al. (1992) who reported quantitative aluminium stripping from loaded Cyanex 272 that contained 90 mg/L of aluminium using sulphuric acid solution at pH 0.9. Tsakiridis and Agatzini-Leonardou (2005), Park et al. (2007) and Mohapatra and Park (2008) reported that higher sulphuric acid concentrations (2 to 3 mol/L) were required to achieve complete aluminium extraction from loaded Cyanex 272 that contained more than 5 g/L of aluminium. Although they did not report the final acid concentration in the stripping raffinate, the difference is clearly owing to the higher molar requirement to reverse the cation exchange process.

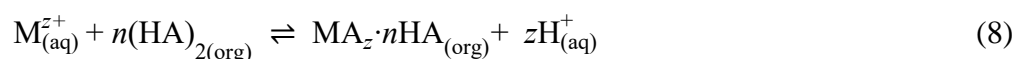
**Table 9. Effect of pH on the scrubbing of cobalt and manganese from 10% Cyanex 272 loaded organic phase using acidified deionised water.**

| pH   | %Scrubbing |     |    |     |
|------|------------|-----|----|-----|
|      | Co         | Mn  | Al | Zn  |
| 1.50 | 100        | 100 | 67 | 100 |
| 1.67 | 100        | 100 | 23 | 38  |
| 1.83 | 100        | 100 | 5  | 3   |
| 2.00 | 20         | 6   | 0  | 0   |
| 2.50 | 0          | 0   | 0  | 0   |
| 3.00 | 0          | 0   | 0  | 0   |

Organic phase: 0.10 g/L Al, 0.03 g/L Zn, 0.01 g/L Co and 0.12 g/L Mn; T = 40 °C; O/A = 1.

#### 4.4.4 Nature of the Extracted Species

The apparent composition of the extracted species was determined indirectly via slope analysis assuming that the extraction reaction was simply cation exchange as shown in the following equation:



The equilibrium constant,  $K$ , of the reaction may be written as:

$$K = \frac{[MA_z \cdot nHA]_{(org)} [H^+]_{(aq)}^z}{[M^{z+}]_{(aq)} [(HA)_2]_{(org)}^n}$$

or,

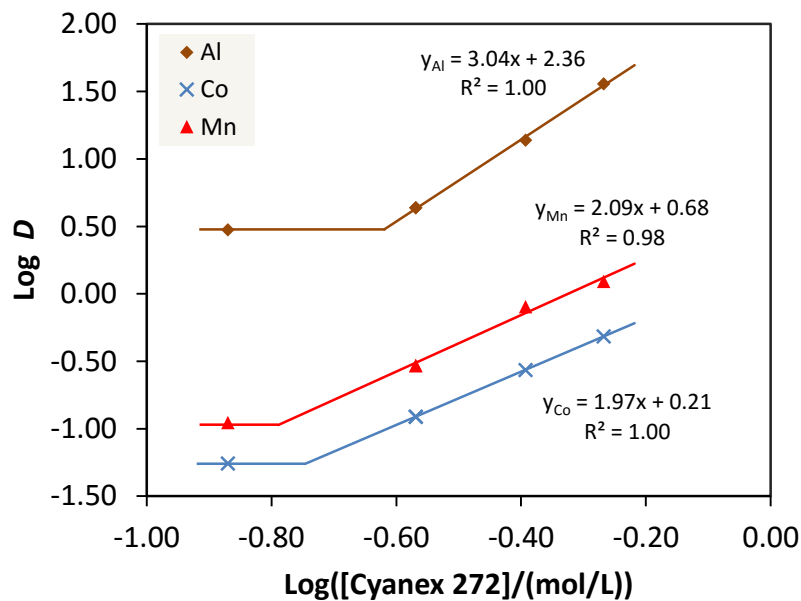
$$K = \frac{D_M [H^+]_{(aq)}^z}{[(HA)_2]_{(org)}^n} \quad (9)$$

where the distribution coefficient of the metal  $D_M = [MA_z \cdot nHA]_{(org)} / [M^{z+}]_{(aq)}$ .

Taking the logarithms and re-arranging yields:

$$\log D_M = \log K + zpH + n \log (HA)_{2(org)} \quad (10)$$

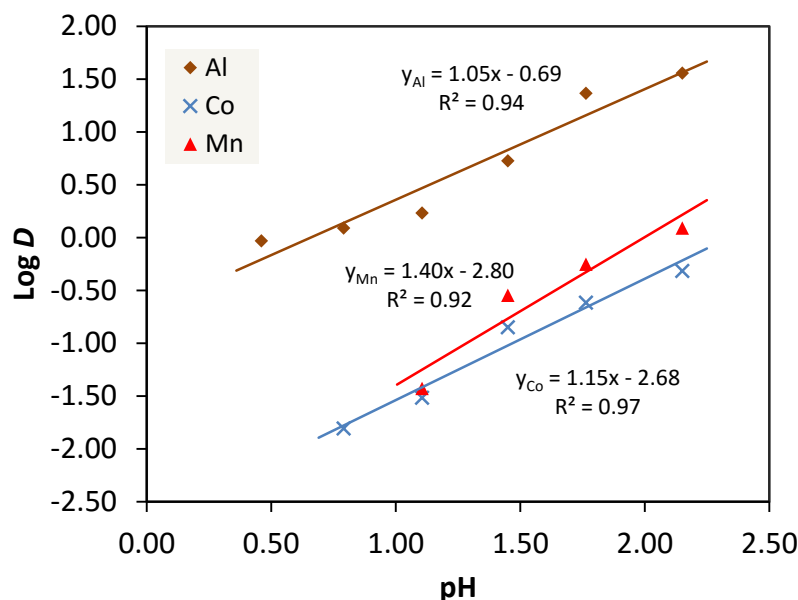
The plots of  $\log D$  versus  $\log [(HA)_2]$ , summarised in Figure 19, showed that the values of  $n$  were 3 for aluminium and 2 for cobalt and manganese. This is consistent with the formation of the extracted species  $AlA_3 \cdot 3HA$ ,  $CoA_2 \cdot 2HA$ , and  $MnA_2 \cdot 2HA$  which is in agreement with the findings of previous studies in either sulphate (Mohapatra and Park 2008, Tait 1993, Tsakiridis and Agatzini-Leonardou 2004, Zhao et al. 2011) or nitrate systems (Preston 1982). The deviations of the plots from linearity at very low Cyanex 272 concentration indicated that there was not enough free extractant (Rydberg et al. 2004) and hence, their corresponding  $K$  values cannot be included in determining the slopes.



**Figure 19. Plot of  $\log D$  versus  $\log [(HA)_2]$  for the extraction of aluminium, cobalt and manganese at pH 2.0.**

Aqueous phase: 0.14 g/L Al, 0.03 g/L Zn, 0.63 mg/L Mn, 0.15 g/L Co, 4.4 g/L Ni, 1.6 g/L Ca and 85.0 g/L Mg; T = 40 °C; O/A = 1.

The slopes of lines from the plot of  $\log D$  versus pH as shown in Figure 20, however, indicated that the overall reactions for each mole of extraction metals released only one mole of  $H^+$  instead of the expected 3 for aluminium and 2 each for cobalt and manganese, if the predominant reaction occurred as shown in equation (8).



**Figure 20. Plot of  $\log D$  versus pH for the extraction of aluminium, cobalt and manganese using 20% Cyanex 272.**

Aqueous phase: 0.14 g/L Al, 0.03 g/L Zn, 0.63 mg/L Mn, 0.15 g/L Co, 4.4 g/L Ni, 1.6 g/L Ca and 85.0 g/L Mg;  $T = 40\text{ }^{\circ}\text{C}$ ;  $O/A = 1$ .

These discrepancies suggested the involvement of monovalent complexes or other extraction mechanisms. Extraction of monovalent complexes such as the hydrolysed form of aluminium,  $Al(OH)_2^+$ , may result in lower pH dependence (lower slope of  $\log D$  versus pH). The involvement of monovalent complexes has been proposed for the extraction of iron(III) with Cyanex 272 in sulphate systems that also showed a pH dependence of about one (Biswas and Singha 2006, Quinn and Soldenhoff 2015). The extraction of the monovalent complexes, however, should also result in lower extractant concentration dependence, which is not in accord with the current findings.

Another possible explanation for these results is the involvement of the formation of outer-sphere complexes, which is also known as solvation, involving nitrate ions. This appeared to be a more likely explanation as solvation of the metals would not generate any hydrogen ion but may still exhibit the same extractant concentration dependence as if extraction occurred via cation exchange reactions. Extraction by means of both

cation exchange and solvation mechanisms would explain both the evident dependence on the extractant concentration and the deviation from expected pH dependence.

Outer-sphere complexes involving nitrate was possible due to the high nitrate ion concentration in the solution, which was about 452 g/L assuming 1:3 and 1:2 metal to nitrate ligand ratio for the trivalent and divalent metals, respectively. This could lead to the formation of solvated  $\text{Al}(\text{NO}_3)_3(\text{HA})_3$  species. A study, for example, by Miralles et al. (1992) on iron(III) extraction from nitrate solution using Cyanex 272 suggested the formation of the species  $\text{FeA}_3$ ,  $\text{FeA}_3(\text{HA})_3$  and  $\text{Fe}(\text{NO}_3)_3(\text{HA})_3$ . The solvation of iron as  $\text{Fe}(\text{NO}_3)_3(\text{HA})_3$  to explain the lower pH dependence was supported by the presence of nitrate ion in the organic phase which was confirmed by using a diphenylamine sulphuric acid solution. The ability of Cyanex 272 to extract metals via cation exchange and solvation reactions has also been demonstrated in uranium extraction from nitrate solution. A study, for example, by Dogmane et al. (2002) showed that uranium extraction mechanism changed from predominantly cation exchange to solvation as the nitric acid concentration increased. Confirmation of the actual reason to explain the current findings would require a more detailed fundamental study of the phenomenon, which was outside the scope of the present study.

## **4.5 Cobalt Separation from Nickel**

The raffinates from aluminium and zinc extraction step at the determined optimum conditions were subjected to the cobalt extraction step using also 20% Cyanex 272 to separate cobalt along with manganese from nickel along with magnesium and calcium in the raffinate discharged. The effect of pH on the extraction behaviour, multi-stage extraction of the metals, nickel and magnesium scrubbing, and stripping behaviour of the metals were investigated.

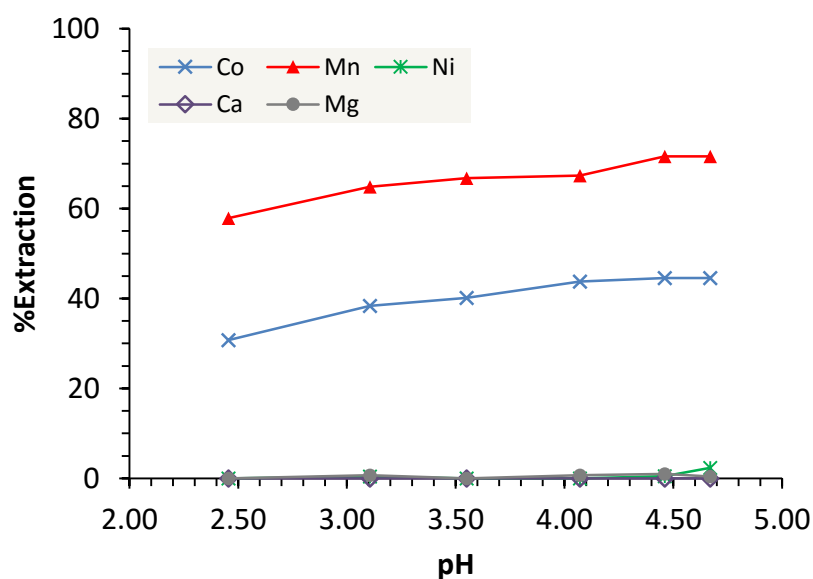
### **4.5.1 Cobalt and Manganese Extractions Behaviour**

This series of extraction tests was carried out under comparable experimental conditions to those of the aluminium and zinc extraction step (20% Cyanex 272, 40 °C, and O/A = 1) except that the pH was varied from 2.5 to 4.7. The results, summarised in Figure 21, showed that, interestingly, the usual S-shaped extraction curves were not observed over the pH range studied. The cobalt extraction increased



from 31% at pH 2.5 to 44% at pH 4.1 but increased only slightly to 45% at pH 4.7. A similar trend was also observed with manganese extraction. Both nickel and magnesium co-extractions were less than 1% at pH below 4.1. Calcium extraction was negligible over the pH range studied.

Increasing the pH of extraction further to increase cobalt extraction was not desirable as significant nickel precipitation and third phase formation were observed. The former was easily apparent from the formation of significant amounts of greenish precipitate (Figure 22 a) and confirmed by the results of the assay of the solutions, which revealed that up to 10% of the nickel precipitated when the extraction was carried out at a pH of 5.6. The cobalt and manganese extractions at this pH were only 58% and 79%, respectively. The latter was visible as a thin gelatinous phase that formed between the aqueous and organic phases, but much better observed when both the organic and aqueous phases were transferred to another container, as this gelatinous phase then adsorbed on the inner surface of the separatory funnel (Figure 22 b).

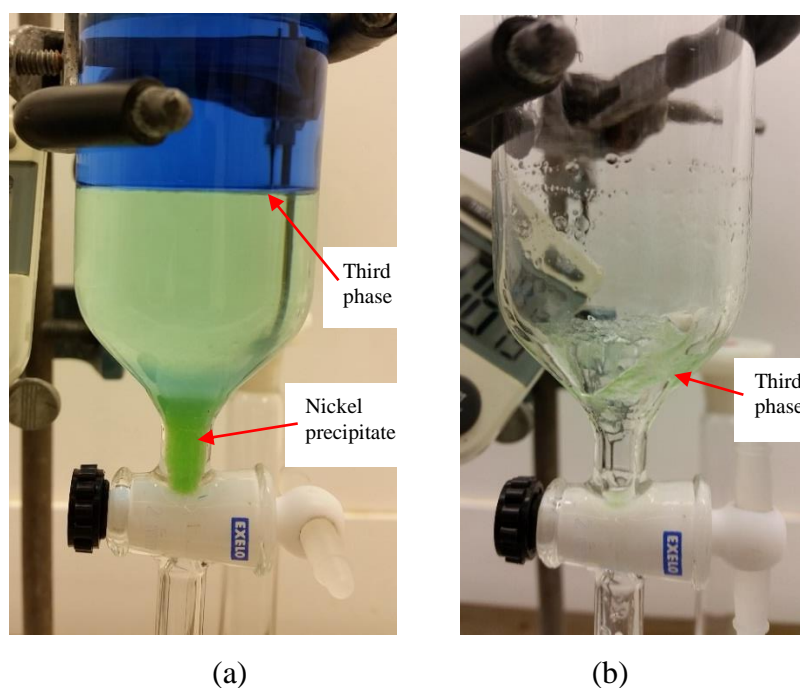


**Figure 21. Effect of pH on the extraction of metals from the aluminium and zinc extraction raffinate using 20% Cyanex 272.**

Aqueous phase: 0.11 g/L Co, 0.30 mg/L Mn, 4.1 g/L Ni, 1.6 g/L Ca and 79.0 g/L Mg; initial aqueous pH = 2.0; T = 40 °C; O/A = 1. See Table D-3 in Appendix D for the experimental data.

Two strategies were attempted to increase the cobalt extraction while avoiding metal precipitation: dilution of the feed solutions and adding a modifier into the organic phase. The former was conducted by adding equal volume of deionised water into the

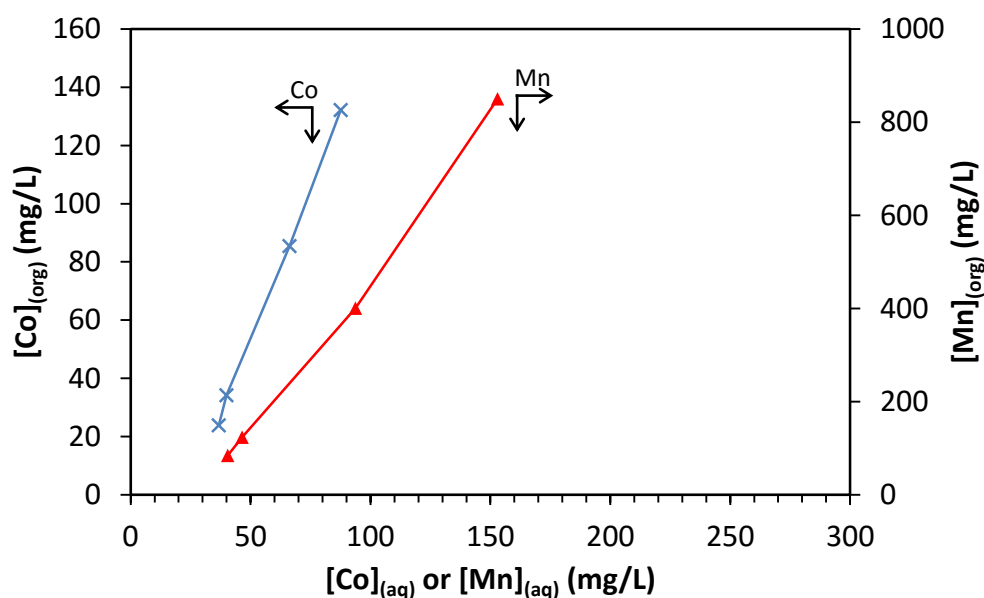
feed aqueous solution while the latter was conducted by adding 5% TBP into the organic phase. The former method yielded 85% cobalt extraction at a pH of 6.1 but 12% of the nickel precipitated. The latter method yielded no noticeable improvement in either nickel precipitation or cobalt extraction. Neither method was therefore adopted and hence, the original experimental conditions (20% Cyanex 272, 40 °C, and O/A = 1) was kept.



**Figure 22. Visual observation of the phases from the extraction test using 20% Cyanex 272 at 40 °C, pH 5.6 and O/A = 1: (a) greenish precipitation formation and (b) third phase formation.**

The use of more concentrated multi-ion solutions usually results in extraction curves with smaller slopes as the various ions compete for the exchangeable ions of the extractant. It was thought that this might be the main reason for the low cobalt extraction efficiency. Assuming that one mole of divalent metals consumed two moles of dimeric Cyanex 272 ions, however, the metals loading would have been still below 30% of the total Cyanex 272 loading capacity over the pH range of 2.5 to 4.7. The observable property of the organic phase was consistent with the assay results. There was, for example, no noticeable change in the rate of phase disengagement indicating no change in viscosity over this pH range. It is known that the viscosity of Cyanex 272 increase significantly when metal loading exceeds 65-70% (Bourget and Jakovljevic 2008).

The fact that the amount of free extractant did not significantly affect the extraction efficiency was also supported by the relatively low cobalt extraction even at higher O/A values. It was found that cobalt extractions were only 62% and 65% at O/A of 2 and 3, respectively. This was also the case for manganese extractions which were only 82% and 85% at O/A of 2 and 3, respectively. Consequently, extraction raffinates with low metal concentration for the extraction isotherm plots (Figure 23) could not be obtained. Hence, graphical prediction by the use of McCabe-Thiele diagram to estimate the number of extraction stages required to achieve complete extraction could not be made. A series of multi-stage extraction tests was therefore carried out to provide an estimate.



**Figure 23. Cobalt and manganese extraction isotherms using 20% Cyanex 272.**

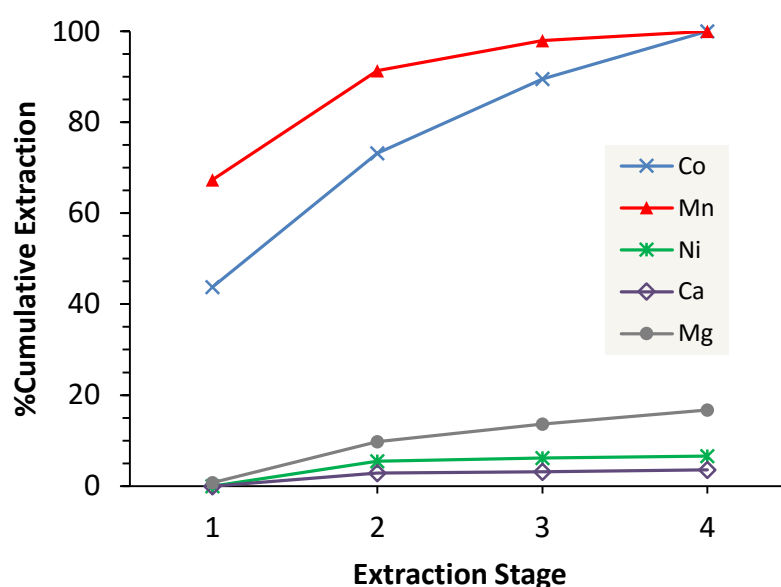
Aqueous phase: 0.11 g/L Co, 0.30 mg/L Mn, 4.0 g/L Ni, 1.6 g/L Ca and 81.8 g/L Mg; initial aqueous pH = 2.0; T = 40 °C; O/A = 1.

#### 4.5.2 Multi-stage Extraction

Despite the low cobalt extraction, good cobalt and nickel separation was achieved at pH 4.0 with negligible co-extraction of nickel. A series of multi-stage extraction tests using 20% Cyanex 272 at 40 °C and O/A = 1 was carried out at staggered pH values to achieve quantitative cobalt and manganese extraction. The experiments were conducted in a semi-batch manner with fresh organic solutions used in each stage as described in Chapter 3.7. The staggered pH values were used to simulate the actual counter-current extraction conditions. In a counter-current operation, the increasing

pH values as the extraction stage increase is aimed to maximise the cobalt extraction but since the organic phase is fed in the opposite direction, the co-extracted nickel may be scrubbed out of the loaded organic phase since the pH values are decreasing.

The cumulative extraction curves, shown in Figure 24, indicated that quantitative cobalt extraction can be achieved in four stages at pH 4.0, 4.4, 4.5 and 4.0 in the first, second, third and fourth stage, respectively. Significant co-extraction of nickel, magnesium and calcium occurred in the second stage but only increased slightly in the latter stages except for magnesium, which still showed appreciable co-extraction. The analysis of the final raffinate then showed that 6%, 16% and 3% of nickel, magnesium and calcium, respectively, from the feed solution were cumulatively co-extracted.



**Figure 24. Representation of the cumulative metals extraction using 20% Cyanex 272.**

Extraction pH: stage 1 = 4.0; stage 2 = 4.4; stage 3 = 4.5; stage 4 = 4.0.

Feed aqueous solution: 0.11 g/L Co, 0.30 mg/L Mn, 4.1 g/L Ni, 1.6 g/L Ca and 79.0 g/L Mg; initial feed solution pH = 2.0; T = 40 °C; O/A = 1. See Table D-5 in Appendix D for the experimental data.

Interestingly, despite the significant changes in cobalt concentration in the feed aqueous solutions for the first, second and third extraction stage, the cobalt extraction behaviour in each circuit remained somewhat consistent with 44%, 52% and 61% extraction, respectively. This finding was consistent with the insignificant effect of free extractant to extractable-metal concentration ratio as discussed earlier. In the fourth stage, wherein the cobalt concentration in the feed was below 11 mg/L, quantitative extraction was achieved.

### **4.5.3 Nickel and Magnesium Scrubbing**

A series of scrubbing tests using acidified deionised water at 40 °C and phase ratio of unity was carried out using the loaded organic phases from the first and fourth extraction stage. The nickel concentrations in the first and fourth loaded organic phases were about 20 mg/L and 3 mg/L, respectively, whereas the magnesium concentrations were 1.9 g/L and 2.8 g/L, respectively. It was found that nickel can be easily scrubbed out at pH 5.0 and below, but magnesium scrubbing could not be easily achieved. Scrubbing from the first loaded organic phase at pH as low as 2.0 showed that less than 20% of magnesium scrubbed out of the organic phase while at lower pH, cobalt started to be co-scrubbed as well. Magnesium scrubbing was even more difficult from the fourth loaded organic phase since the use of sulphuric acid solution at pH 1.0 was only able to scrub less than 80% of magnesium, while more than 10% of cobalt was co-scrubbed. Given that magnesium is not an issue in the downstream process of recovering cobalt through the established method of chemical precipitation from sulphate media, its poor scrubbing behaviour has no significant practical implication. The only main consideration therefore in the scrubbing step was nickel, which was easily scrubbed out quantitatively at pH about 2.0.

### **4.5.4 Stripping of the Metals**

As has been pointed out earlier, higher acidity is required to strip magnesium out of the organic phase. A series of stripping tests was carried out using sulphuric acid solutions. It was found that 0.5 mol/L sulphuric acid was sufficient to completely strip the extracted metals from the first and fourth loaded organic phases. It is then reasonable to conclude that 0.5 mol/L sulphuric acid is able to completely strip the extracted metals from the loaded organic phases in all stages.

## **4.6 Schematic Flow Diagram of the Two Solvent Extraction Steps**

The outputs for the two solvent extraction steps treating the synthetic nitrate solution are tabulated in a schematic flow diagram shown in Figure 25. The diagram shows that aluminium, nickel and cobalt can be separated and a separate nickel and cobalt streams that are devoid of each other can be produced. Hence, it shows that the proposed DSX process is able to generate sufficiently pure nickel and cobalt solutions to produce high purity products of each metal. Essentially complete recoveries of the nickel and cobalt

were also achieved because the co-extracted cobalt from the aluminium and zinc extraction step and the co-extracted nickel from the cobalt extraction step can be scrubbed out completely and recovered back to the process. The concentrations of the metals in the aqueous stream output in each extraction step were slightly lower than those of the input due to the increases in the volumes as a result of addition of either base or acid for pH adjustment.

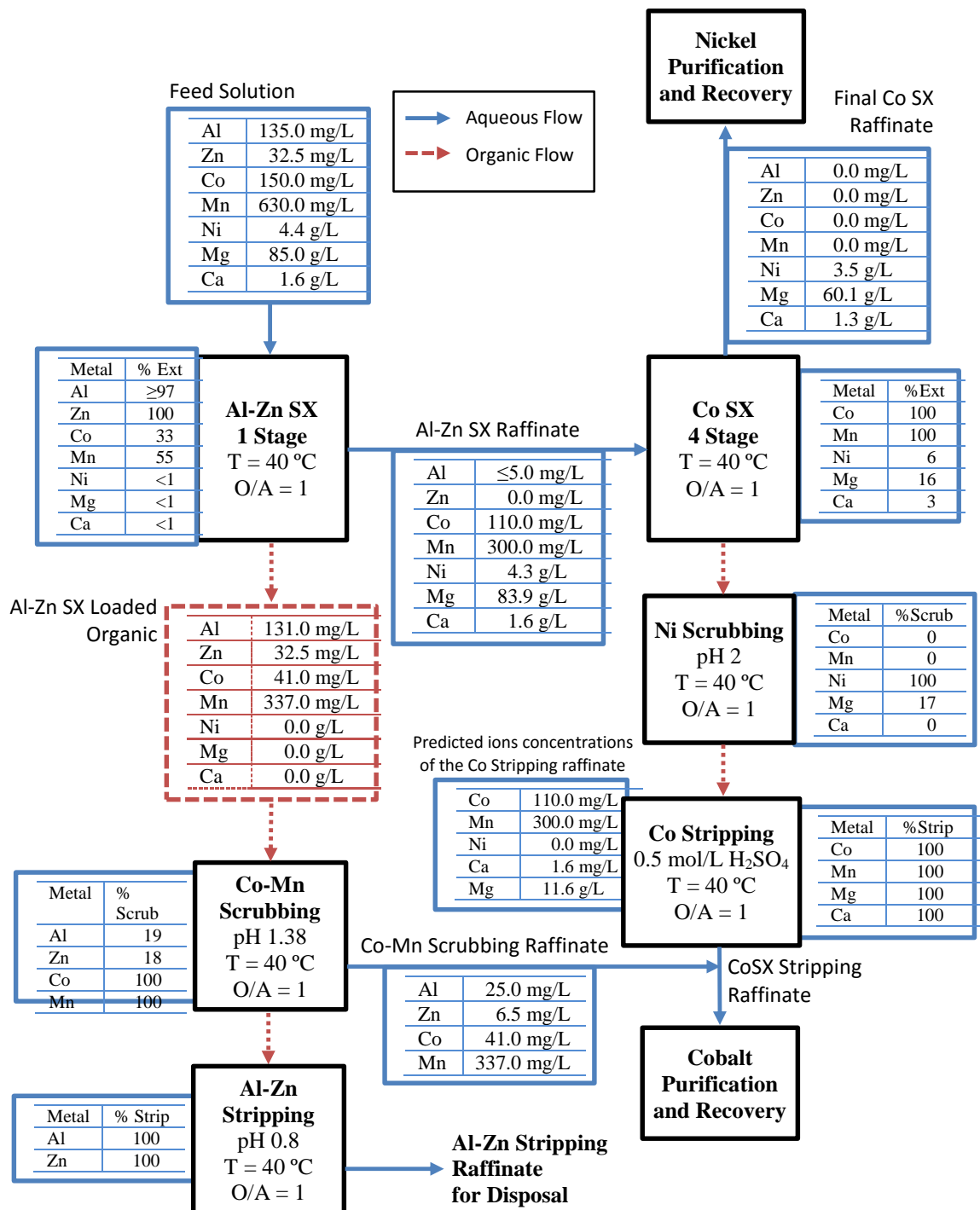


Figure 25. Schematic flow diagram of the two Cyanex 272 extraction circuits for separating aluminium, cobalt and nickel from the synthetic nitrate solution.

## Chapter 5

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 Conclusions

As part of the continuing intense interest in developing a more effective and economical method of processing nickel laterite ores, there has been an increasing interest in nitric acid leaching. This has led to the development of two nitric acid leaching technologies that have recently achieved successful demonstration plant scale testing. A purification technique, however, for the resulting leach solutions is yet to be developed. Both nitric acid leaching technologies have adopted the mixed hydroxide precipitation as the purifying step but this is proving to be difficult. This is because, unlike sulphate systems, that allow complete aluminium removal together with iron and chromium during the partial neutralisation step, the removal of aluminium from nitric acid leach solutions during this step is particularly difficult due to the formation of colloidal aluminium hydroxide leading to separation problems and aluminium contamination of the nickel and cobalt products.

The present study attempted to address this issue by conceiving and developing up to proof-of-concept level a method of removing the aluminium and separating nickel and cobalt directly from the PLS, and hence, a direct solvent extraction (DSX) process. This approach is novel as it has not been previously attempted.

The literature review revealed that there is limited information on the use of solvent extraction for separating aluminium, nickel and cobalt from nitrate solution. There is, however, a good indication that the solvent extraction behaviour and selectivity of metals from a nitrate media is similar to those from a sulphate media except that their  $pH_{50}$  values are shifted slightly to the lower value. Hence, the available data on sulphate media provided some guidance in pursuing the current work.

Although limited, the available information on the use of nitric acid in process metallurgy, such as in uranium industry, as well as the basic chemistry of nitric acid is useful in selecting a suitable extraction system and conditions for treating nitrate-based liquors. It is clear from this information that solvent extraction conditions involving high nitric acid concentrations and high temperatures must be avoided as either favours

degradation of solvent extraction reagents particularly those that are inherently susceptible to oxidation reactions. Consequently, ionic and solvating extractants are better avoided as they require high acidity. This leaves only cationic extractants as possible choices.

Given these considerations, the use of bis(2,4,4 tri-methylpentyl) phosphinic acid (Cyanex<sup>®</sup> 272) appeared to be the most suitable among the current commercially available extractants. It has high selectivity for separating aluminium, cobalt and nickel; it offers fast extraction and stripping kinetics; it is not particularly susceptible to oxidation; and its applications in commercial operations are well established. Thus, a DSX process that consists of two sequential extraction circuits using Cyanex 272 in both circuits was conceived: the first circuit is for the removal of aluminium along with zinc, and the second is for the separation of cobalt along with manganese from nickel.

An experimental program involving bench-scale batch and semi-batch extraction, scrubbing and stripping tests were then developed and implemented, to explore and evaluate the viability of the proposed process up to a proof-of-concept level, using only synthetic solutions that simulated the leach solution of the atmospheric nitric acid leaching technology post partial neutralisation step. The main findings of the research work may be summarised as follows:

- Consistent with the results of previous studies on the extraction of base metals from sulphate media, Cyanex 272 exhibited the selectivity; kinetics for extraction, scrubbing and stripping; and phase disengagement that is suitable for the extraction of aluminium and cobalt from nitrate media.
- The extraction of aluminium, cobalt and manganese from nitrate solutions with high magnesium content (~85 g/L) with Cyanex 272 apparently involved more than one mechanisms, which may be cation exchange and solvation. This was evident in the slopes of  $\log D$  versus  $\log$  [Cyanex 272] concentration and the slopes of  $\log D$  versus pH. It however had no significant practical implication on the proposed process.
- The first extraction circuit allowed complete aluminium and zinc extraction in a single extraction stage using 20% Cyanex 272 in ShellSol 2046 at pH 2.1,



temperature of 40 °C and phase ratio of unity but with appreciable cobalt and manganese co-extraction. The co-extracted cobalt and manganese was able to be scrubbed out completely in a single scrubbing stage from the loaded organic phase using sulphuric acid solution at pH about 1.38 but with some amounts of aluminium contamination. The extracted aluminium and zinc was able to be stripped out completely in a single stripping stage using sulphuric acid solution at pH 0.8.

- The second extraction circuit allowed complete separation of cobalt along with manganese from nickel in four extraction stages using 20% Cyanex 272 at a staggered pH profile of 4.0, 4.4, 4.5 and 4.0 in the first, second, third and fourth stages respectively at a temperature of 40 °C and phase ratio of unity. The cumulative co-extraction of nickel was less than 6% and all can be scrubbed out completely using sulphuric acid solution at pH 2.0. The cumulative co-extraction of magnesium and calcium were 16% and 3% respectively. They could not be scrubbed out easily but this was not an issue as they are soluble and will not interfere in the subsequent precipitation and separation of cobalt from manganese. All metals in the loaded organic phase were able to be stripped out completely in a single stage using 0.5 mol/L sulphuric acid solution.
- The use of sulfuric acid for scrubbing and stripping has the advantage of allowing their downstream processing, either by means of solvent extraction or selective precipitation, to be carried in sulphate media, which is better understood and has abundant relevant literature and plant experience data.
- These results show that the conceived DSX process was effective in separating aluminium, cobalt and nickel from synthetic nitrate solutions that simulated the leach solution of the atmospheric nitric acid leaching of nickel laterite ores post partial neutralisation step and thus, achieved the objectives of the study.

Further investigation of the process using actual PLS from the new nitric acid leaching technologies would provide a significant step toward the development of its application

## 5.2 Recommendations for the Future Research

The limited period and scope of the present study and the novelty of the proposed DSX process have yielded many interesting observations that merit further consideration. Among them are as follows:

- Determine the reason for the anomalous stoichiometry of aluminium, cobalt and manganese extractions using Cyanex 272, which was evident in the deviation from the expected cation exchange reactions. It appeared that this may be owing to the high concentrations of nitrate and magnesium ions in the leach solution.
- Investigate the reason for the low cobalt extraction efficiency from the aluminium and zinc extraction raffinate and thus, requiring four extraction stages at a staggered pH profile.
- Evaluate the performance of the DSX process on actual nitrate-based leach solutions that are generated from either or both existing nitric acid leaching technologies given one is carried out at atmospheric pressure while the other is at elevated pressure. Both batch and continuous testing are desirable.
- Evaluate the long-term stability of organic reagents in simulated and actual PLS of nitric acid leaching.

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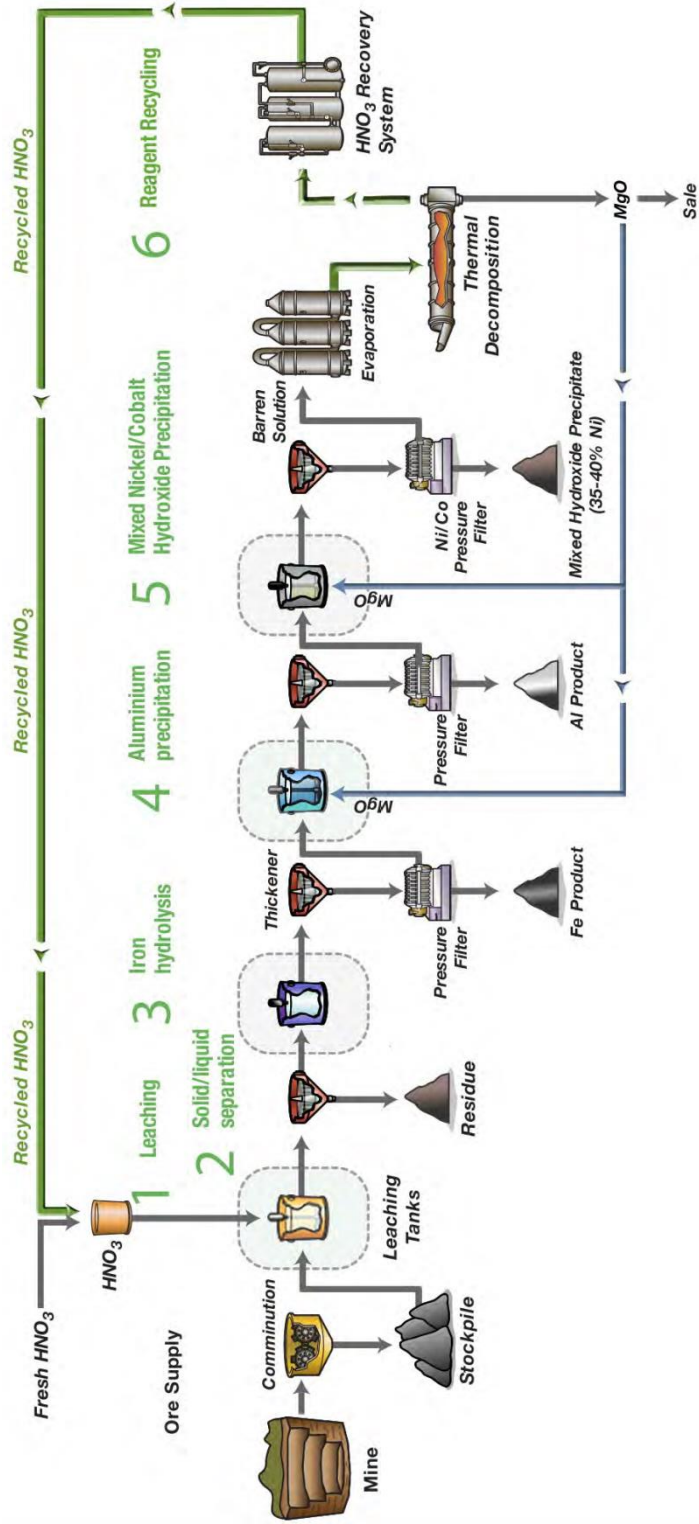
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# APPENDIX A

## THE DNI PROCESS FLOWSHEET

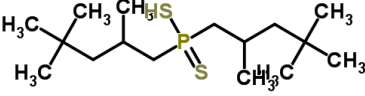
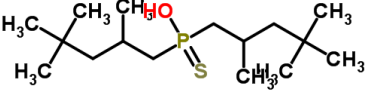
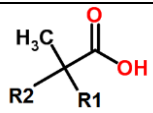
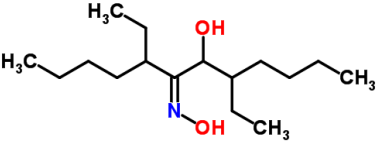
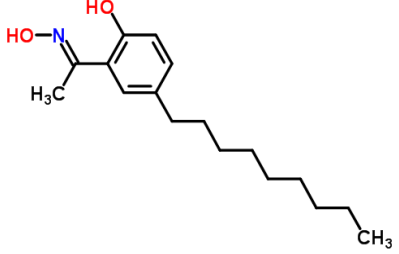
(McCarthy and Brock 2014)



## APPENDIX B

### SOME COMMON ACIDIC EXTRACTANTS FOR USE IN HYDROMETALLURGY OF BASE METALS

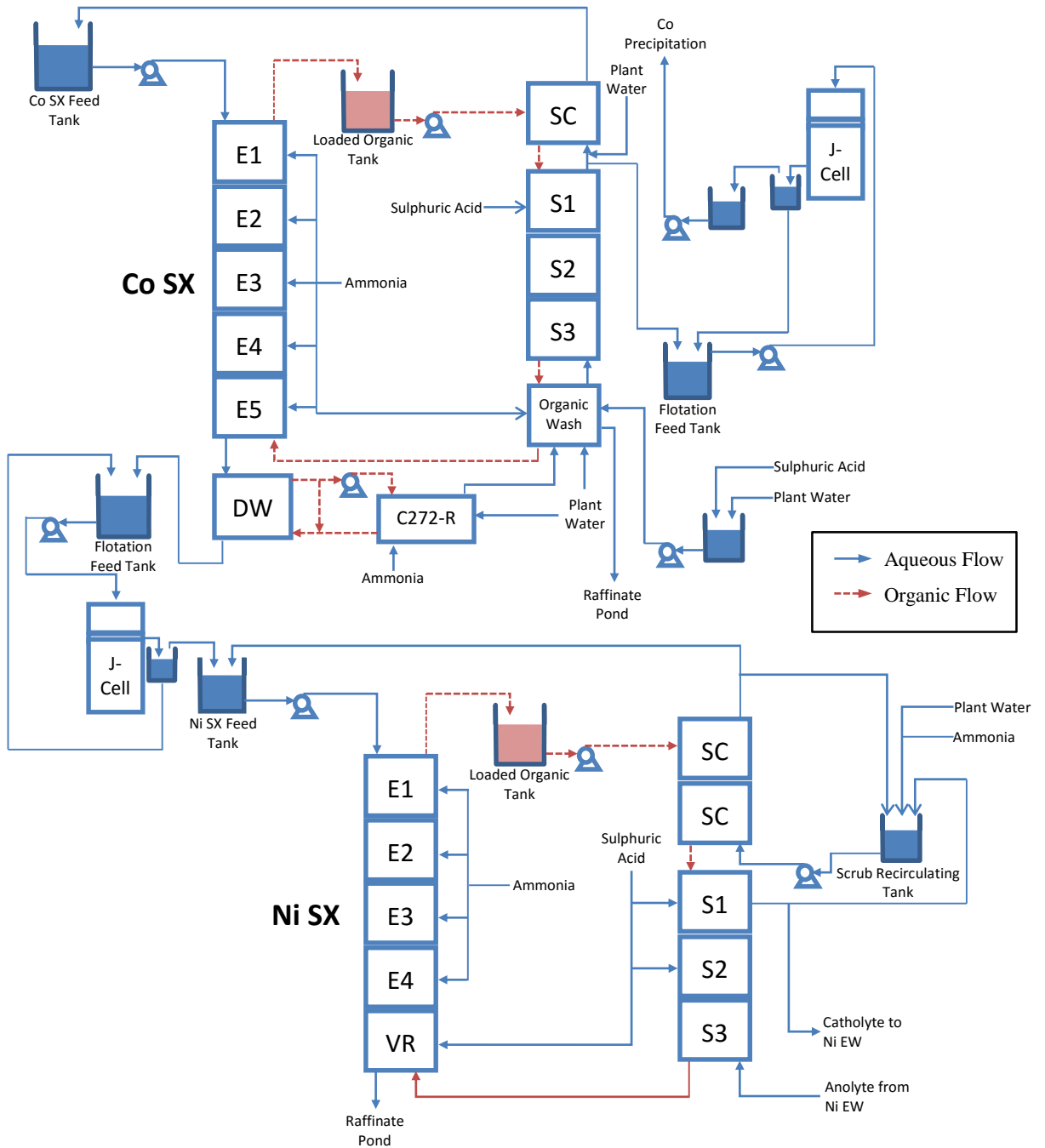
| Class                  | Chemical Name   | Trade Name   | Structure | Manufacturer                         | Common Commercial Use  |
|------------------------|---|--|-----------|--------------------------------------|--|
| Alkyl phosphorus acids | di-2-ethylhexyl phosphoric acid                         | D2EHPA<br>DEHPA<br>EHPA<br>Hostarex PA 216<br>DP-8R  |           | Mobil<br><br>Hoechst<br>Daihachi     |  |
|                        | 2-ethylhexyl phosphonic acid<br>mono 2-ethylhexyl ester | EHPNA<br>PC-88A<br>Ionquest® 801<br>SME 418<br>RD577 |           | Daihachi<br>Rhodia<br>Shell<br>Shell | Cobalt/Nickel Separation,<br>Zinc, Beryllium, Indium,<br>Gallium, Rare earths,<br>Vanadium, etc. |
|                        | bis(2,4,4 tri-methylpentyl)<br>phosphinic acid          | Cyanex® 272<br>Ionquest® 290<br>LIX® 272             |           | Cytec<br>Rhodia<br>Cognis            |  |

|                     |   |                          |  |                      |                                       |
|---------------------|---|--------------------------|--|----------------------|---------------------------------------|
| Thiophosphorus acid | bis(2,4,4-trimethylpentyl)<br>dithiophosphinic acid   | Cyanex 301               |   | Cytec                | Nickel, Cobalt                        |
|                     | bis(2,4,4-trimethylpentyl)<br>monothiophosphinic acid | Cyanex 302               |   | Cytec                |                                       |
| Carboxylic acid     | Neodecanoic acid                                      | Versatic™ 10             |   | Hexion               | Copper, Cobalt, Nickel, Iron,<br>Zinc |
| Hydroxyoxime        | 5,8-diethyl-7-<br>hydroxydodecanone-6 oxime           | LIX® 63                  |   | Cognis               | Copper, Nickel                        |
|                     | 2-hydroxy-5-<br>nonylaceto-phenone oxime              | LIX® 84I<br>Mextral® 84H |  | Cognis<br>KopperChem | Copper, Nickel/Cobalt<br>Separation   |

# APPENDIX C

## COBALT AND NICKEL SOLVENT EXTRACTION CIRCUITS AT BULONG NICKEL OPERATION

(Redrawn from O'Callaghan (2003b))





## APPENDIX D

### SAMPLE EXPERIMENTAL RESULTS

**Table D-1. Extraction of aluminium, zinc, manganese and cobalt at various Cyanex 272 concentrations.**

Aqueous phase: 0.14 g/L Al, 0.03 g/L Zn, 0.63 mg/L Mn, 0.15 g/L Co, 4.4 g/L Ni, 1.6 g/L Ca and 85.0 g/L Mg; initial aqueous pH = 2.0; T = 40 °C; O/A = 1.

| Cyanex 272 Concentration | pH   | %Extraction |     |    |    |
|--------------------------|------|-------------|-----|----|----|
|                          |      | Al          | Zn  | Mn | Co |
| 5%                       | 0.83 | 33          | 85  | 0  | 0  |
|                          | 1.10 | 23          | 92  | 1  | 3  |
|                          | 1.40 | 30          | 100 | 2  | 3  |
|                          | 1.62 | 70          | 100 | 5  | 3  |
|                          | 2.01 | 75          | 100 | 10 | 5  |
| 10%                      | 0.78 | 45          | 86  | 0  | 0  |
|                          | 1.11 | 64          | 100 | 2  | 0  |
|                          | 1.41 | 65          | 98  | 6  | 1  |
|                          | 1.72 | 77          | 96  | 18 | 7  |
|                          | 2.06 | 81          | 100 | 23 | 11 |
| 15%                      | 0.82 | 44          | 92  | 0  | 0  |
|                          | 1.10 | 60          | 100 | 3  | 3  |
|                          | 1.43 | 68          | 93  | 19 | 7  |
|                          | 1.69 | 90          | 100 | 28 | 14 |
|                          | 1.97 | 93          | 100 | 45 | 21 |
| 20%                      | 0.46 | 48          | 84  | 2  | 5  |
|                          | 0.79 | 55          | 100 | 0  | 2  |
|                          | 1.11 | 63          | 100 | 4  | 3  |
|                          | 1.45 | 84          | 100 | 22 | 12 |
|                          | 1.76 | 96          | 100 | 36 | 20 |
|                          | 2.15 | 97          | 100 | 55 | 33 |

**Table D-2. Extraction of aluminium, zinc, cobalt and manganese at various O/A.**

Aqueous phase: 0.13 g/L Al, 0.03 g/L Zn, 0.61 mg/L Mn, 0.15 g/L Co, 3.9 g/L Ni, 1.6 g/L Ca and 85.0 g/L Mg; initial aqueous pH = 2.0; equilibrium pH = 2.0; T = 40 °C.

| O/A  | Al Extraction (%) | [Al] <sub>aq</sub> (mg/L) | [Al] <sub>(org)</sub> (mg/L) | %Co-extraction |    |    |
|------|-------------------|---------------------------|------------------------------|----------------|----|----|
|      |                   |                           |                              | Zn             | Co | Mn |
| 0.17 | 81                | 21.3                      | 663.1                        | 100            | 5  | 17 |
| 0.50 | 99                | 1.0                       | 262.0                        | 100            | 14 | 36 |
| 1.00 | 99                | 1.0                       | 131.0                        | 100            | 26 | 53 |
| 2.00 | 100               | 0.0                       | 66.0                         | 100            | 35 | 63 |
| 3.00 | 100               | 0.0                       | 44.0                         | 100            | 39 | 66 |

**Table D-3. Extraction of cobalt, manganese, nickel, magnesium and calcium at various pH using 20% Cyanex 272.**

Aqueous phase: 0.11 g/L Co, 0.30 mg/L Mn, 4.1 g/L Ni, 1.6 g/L Ca and 79.0 g/L Mg; initial aqueous pH = 2.0; T = 40 °C; O/A = 1.

| pH   | %Extraction |    |    |    |    |
|------|-------------|----|----|----|----|
|      | Co          | Mn | Ni | Mg | Ca |
| 2.46 | 31          | 58 | 0  | 0  | 0  |
| 3.11 | 38          | 65 | 0  | 1  | 0  |
| 3.55 | 40          | 67 | 0  | 0  | 0  |
| 4.07 | 44          | 67 | 0  | 1  | 0  |
| 4.46 | 45          | 72 | 1  | 1  | 0  |
| 4.67 | 45          | 72 | 2  | 0  | 0  |

**Table D-4. Extraction of cobalt, manganese, nickel, magnesium and calcium from each extraction stage using 20% Cyanex 272.**

Aqueous phase: 0.11 g/L Co, 0.30 mg/L Mn, 4.1 g/L Ni, 1.6 g/L Ca and 79.0 g/L Mg; initial aqueous pH = 2.0; T = 40 °C; O/A = 1.

| Stage No. | pH   | Base Addition<br>mL 5 mol/L NaOH<br>mL aqueous phase | %Extraction |     |     |    |    |
|-----------|------|--|-------------|-----|-----|----|----|
|           |      |  | Co          | Mn  | Ni  | Mg | Ca |
| 1         | 4.00 | 0.03   | 44          | 67  | 0.0 | 1  | 0  |
| 2         | 4.40 | 0.04   | 52          | 73  | 5.0 | 9  | 3  |
| 3         | 4.45 | 0.05   | 61          | 77  | 0.5 | 4  | 0  |
| 4         | 4.00 | 0.05   | 100         | 100 | 0.0 | 3  | 0  |

**Table D-5. Cumulative extraction of cobalt, manganese, nickel, magnesium and calcium from the multi-stage extraction test using 20% Cyanex 272.**

Aqueous phase: 0.11 g/L Co, 0.30 mg/L Mn, 4.1 g/L Ni, 1.6 g/L Ca and 79.0 g/L Mg; initial aqueous pH = 2.0; T = 40 °C; O/A = 1.

| Stage No. | pH   | Base Addition                       | %Extraction |     |     |    |    |
|-----------|------|-------------------------------------|-------------|-----|-----|----|----|
|           |      | mL 5 mol/L NaOH<br>mL aqueous phase | Co          | Mn  | Ni  | Mg | Ca |
| 1         | 4.00 | 0.03                                | 44          | 67  | 0.0 | 1  | 0  |
| 2         | 4.40 | 0.04                                | 73          | 91  | 5.5 | 10 | 3  |
| 3         | 4.45 | 0.05                                | 90          | 98  | 6.2 | 14 | 3  |
| 4         | 4.00 | 0.05                                | 100         | 100 | 6.6 | 17 | 4  |