NICKEL SOLVENT EXTRACTION FROM DILUTE ACIDIC SULPHATE SOLUTIONS USING OCTYL PHENYL ACID PHOSPHATE (OPAP)

by:

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Montreal, Quebec, Canada
August 1993

A Thesis submitted to the Faculty of Graduate Studies
and Research in partial fulfillment of the
requirements for the degree of
Master of Engineering in Metallurgical Engineering

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From Indje O. Mihaylov Date 17 August 1993

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Appendix A: Separation of mono-OPAP and di-OPAP; from page 225 to page 230.

Indje O. Mihaylov, Ph.D.
Research Chemist, Hydrometallurgy

..\CARM_PRM.FAX

One never notices what has been done; one can only see what remains to be done...

Marie Curie, letter to her brother
March 18, 1894

Abstract

The subject of this work is nickel extraction from dilute, acidic sulphate solutions through the use of organophosphorous acid reagents. The focus is primarily on OPAP, a mixed extractant consisting of mono- and di-octyl phenyl phosphoric acids, as well as on di-(2-ethyl hexyl) phosphoric acid (D2EHPA). The effects of certain parameters on the extraction of nickel, both quantitative and qualitative, have been studied. The parameters include: modifier presence, concentration and type; OPAP concentration; phase ratio; aqueous environment; age of organic solution; and mono-/di-OPAP ratio. The ability to strip nickel from the organic solution as well as selectivity and kinetic tests were carried out.

The use of 10 % isodecanol as a modifier was found to be essential for the purpose of OPAP solubility in kerosene and phase separation. Furthermore, the cation exchange reaction proceeds very quickly, attaining equilibrium within 10 minutes. Unlike other phosphoric acid reagents, OPAP is able to extract significant amounts of nickel in the acidic pH range of 1 to 2. As well, nickel is easily stripped using a 1.0 M sulphuric acid solution.

Résumé

Le sujet de ce travaille est l'extraction du nickel des solutions sulphate, acidique et dilué, en utilisant les réactifs acides organophosphoriques. L'intérêt primaire concerne l'utilisation d'OPAP, un extractant composé d'un mélange d'acides phosphoriques mono- et di-octyl phényl, en plus d'acide phosphorique di-2-éthyl héxyl (D2EHPA). L'effet de certains parametres sur l'extraction du nickel ont été étudies, non seulement quantitativement, mais aussi qualitativement. Les parametres comprennent: la présence, concentration et type de modificateur; la concentration d'OPAP; la proportion des phases; l'environnment aqueux; l'âge de la solution organique; et la proportion de mono-/di-OPAP. La capacité de vider le nickel de la solution organique, en plus, des tests concernant la sélectivité et la cinétique, ont été faits.

L'usage de 10 % isodecanol comme modificateur est essentiel à cause des problèmes avec la solubilité d'OPAP en kérosène et la séparation des phases. De plus, la réaction d'échange cation se déroule très rapidement; l'équilibre est atteint à l'intérieur de 10 minutes. Contrairement aux autres réactifs d'acides organophosphoriques, OPAP est capable d'extraire un montant considérable de nickel entre un pH de 1 et 2. Finalement, le nickel est facilement réextracté en utilisant une solution sulphurique de 1.0 M.

Acknowledgements

I must begin by thanking Professor P.A. Distin, whom I regard as a friend and mentor, rather than just a supervisor. His guidance throughout the course of this study, especially during the writing of the thesis, will never be forgotten.

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I would like to thank Synergistics, through Mr. Gupta and Mr. Tomaselli, for supplying the elusive isodecanol reagent, when no one else was willing to spare a precious sample. I would also like to thank the Fonds pour la Fondation de Chercheurs et l'Aide à la Recherche (FCAR), the Canadian Institute of Mining, Metallurgy and Petroleum (CIM) and my supervisor for financial support.

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Honourable mention to: my close friends from the 1991 graduating class; the invigilation patrol unit; my entire family, especially my parents and sister, Alba, who endured the chaotic clutter I call a bedroom without burning it down; and finally, I would like to thank my best friend, colleague and partner, Edwina Bogusz, for enduring me and my unorthodox work schedule.

Table of Contents

List of Figures

List of Tables

Nomenclature

Symbols

A/O	aqueous/organic volume phase ratio
B	modifier
D	distribution coefficient
G_{hyd}	Gibbs free energy of hydration (kcal/mole)
H_{hyd}	enthalpy of hydration (kcal/mole)
HR	organic acidic extractant
K	equilibrium constant
L	ratio of organic phase equilibrium metal concentration to initial extractant concentration
M	metal; also used as concentration unit (molarity)
n	metal charge
$pH_{1/2}$	pH at 50 % metal extraction
R	alkyl (C_nH_{2n+1}) molecule in organic phase
R'	alkyl (C_nH_{2n+1}) molecule in aqueous phase
s	solvation number
U	weighed out nickel content
V_1	volume required to neutralize the first exchangeable hydrogen atom from OPAP

V_2	volume required to neutralize the second exchangeable hydrogen atom from OPAP
V_m	volume of base contributing to mono-OPAP component
V_d	volume of base contributing to di-OPAP component
V_e	volume of organic sample solution
X	titrated nickel content
—	organic phase
[ ]	concentration (mole of solute/L solution)
(II)	all species possessing 2+ charge

Abbreviations

aq	aqueous phase
D2EHPA	di-(2-ethylhexyl) phosphoric acid
di-	di-octyl phenyl phosphoric acid
DOX	decanal oxime
EDTA	ethylenediamine tetra-acetic acid
EHO	ethylhexanal oxime
mono-	mono-octyl phenyl phosphoric acid
hyd	hydration
isodec	isodecanol

mol	mole
n-dec	n-decanol
OPAP	octyl phenyl acid phosphate
org	organic phase
PPT	precipitate
SX	solvent extraction
TBP	tributyl phosphate
TIOA	triisooctylamine
vol	volume (L)

CHAPTER 1

Introduction

Lateritic or oxide nickel ore bodies represent the bulk (75 %) of the world's nickel reserves [1] but only account for about 15 % of the actual nickel produced [2]. The main disadvantage in dealing with nickel oxide ore bodies instead of sulphides is that concentration through flotation is impossible. Therefore, the ore body has to be treated as a low grade mass (1 % to 2.2 %) rather than a high grade concentrate (6 % to 8 %) [2]. Also, the water content of a laterite can be as high as 30 %.

An advantage of aqueous processing is that this avoids the expense of drying a large tonnage of low grade material, as would be required for a smelting route. The first commercial leaching process developed is usually referred to as the Moa Bay process. Here, ore is leached in sulphuric acid at 260°C, giving a highly acidic (pH of 1) dilute nickel solution (0.5 to 10 g/L). The next step involves precipitating nickel as sulphide using hydrogen sulphide, a highly poisonous gas (Eq. 1).

$$NiSO_4 + H_2S \rightarrow NiS + H_2SO_4 \qquad (1)$$

The sulphide product is then shipped to a smelter.

In principle, an attractive alternative to sulphide precipitation is solvent extraction followed by electrowinning. Here, a major obstacle is to find a reagent that extracts nickel from a highly acidic, dilute solution. For nickel solvent extraction using common reagents, it is necessary to maintain much higher pH values than 2. Thus extensive pre-neutralization of the laterite leach solution would be necessary, along with subsequent solid/liquid separation steps. Significant effluent problems would also be created.

The purpose of the present work is to study the ability of OPAP (octyl phenyl acid phosphate) to extract nickel from dilute, acidic sulphate solutions. Although this reagent is known to extract certain other metals (e.g. Ga) from dilute, acidic sulphate media, there are no reported data on its application to nickel.

CHAPTER 2

Solvent Extraction

Solvent extraction can be best understood by separating the organic solution into its main components [3]. The main organic components of interest are the extractant, the modifier and the diluent. The extractant is the most critical element and therefore usually demands the most attention in research.

2.1. Extractant

The extractant is an active substance capable of combining chemically with metal in the aqueous phase to give a complex which is soluble in the organic diluent. To do this the extractant must be able to form an electrically neutral species with the metal because only these are extracted [4]. Although only uncharged complexes are extracted, all complexes in the aqueous phase should be examined because the charged complexes may further combine to become eventually uncharged [5].

An extractant, which may be solid when pure, is a substance with solvent properties and is dissolved in solution in a suitable diluent [6]. The extractant reacts with the metal at the interface in the aqueous phase and extracts it into the organic phase through such means as solvation, chelation, ion-pairing and ion-exchange.

Extractants are not judged solely on their ability to extract metals. There are many factors that come into play. It is not just the equilibrium extraction performance that counts in commercial applications but extraction rate, selectivity and physical properties, such as mixing and phase separation [7]. These factors combined determine an extractant's potential. There is also the question of availability and cost.

Requirements for an extractant to be commercially attractive have been summarized by Ritcey and Ashbrook as follows [8]. The extractant must be inexpensive, possess a low solubility in the aqueous phase, not form stable emulsions with an aqueous phase, have good coalescing properties when mixed with a diluent and modifier and be able to withstand degradation over time [8]. Other positive traits include: possess a high metal loading capacity, be easily stripped of loaded metal, be non-flammable, non-volatile and non-toxic, be highly soluble in aliphatic and aromatic diluents and possess good kinetics of extraction [8]. General features that an extractant should possess have been summarized by Hudson, as shown in table (1) [4,9].

2.2. Solvent Extraction Systems

There are several ways that extractants can be classified. One such way is the process by which metal is extracted. A first group that can be considered is when metal is extracted through the formation of uncharged coordination compounds. Coordination compounds are formed between complexing agents, which have excess electron pairs, and metal ions with electron pair deficiencies [10]. The chelates represent the most important member of this group, which includes oximes and derivatives of quinoline. They are generally insoluble in the aqueous phase but readily soluble in non-polar solvents.

A second group represents metals extracted by an ion-exchange process. There are two major types, namely cation and anion exchange. The cation exchange process (acidic extractant or liquid cation exchanger) involves the exchange of metal cations with hydrogen atoms, from the reagent dissolved in the organic phase [10]. This group represents such extractants as organophosphorous acids and carboxylic acids. The anion exchange process (liquid anion exchanger) involves the exchange of complex metal anions with anions of long-chain alkyl amines [10].

Table 1: Essential characteristics of an extractant.

1. Ability to extract the metal at the required pH.
2. Selective for the required metal only.
3. Acceptable rates of extraction, scrubbing and stripping.
4. Soluble in the organic phase and very restricted solubility in aqueous phase.
5. Stable throughout the 3 principal stages: solvent extraction, scrubbing and stripping.
6. Mutually soluble with the diluent and modifier.
7. High loading capacity.
8. Low volatility and high flash point.
9. Cheap and commercially available.

The third and final group represents metals extracted through solvation with ion association. Solvation extraction involves the replacement of the solvating water molecules, belonging to a cation in the aqueous phase, by organic solvent molecules [10]. The charge neutralisation necessary for extraction is achieved by the association with an ion of opposite charge [10]. Found in this group are ethers, ketones and some organophosphorous compounds.

The divisions can also be arranged differently, according to whether extraction of cations, anions or neutral species occurs. Under this system, the cationic group includes both the chelating and the acidic cation extractants. It is this cation extractant group that is of interest for the study of nickel extraction.

Within this broad group of extractants, the chelates will not be discussed and instead, the stress will be on the acidic cation extractants since these are the main focus of the present work. The main emphasis will be on organophosphorous acids, including phosphoric, phosphonic and phosphinic acids. There will also be some discussion on carboxylic and sulphonic acids.

2.2.1. Acidic Cation Extractants

The acidic cation extractants, also called liquid cation exchangers, operate by interchange of hydrogen atoms of the acidic organic reagent for the cation in the aqueous phase. The metal cations react with the organic acids to form neutral complexes that are preferentially dissolved by the organic phase [11]. The hydrogen atoms are therefore exchanged for the metal ions, making extraction strongly dependent on hydrogen, and thus pH. The extraction of metals by the cation exchange reaction occurs between the extractable metal ion and usually one or two hydrogen atoms belonging to the extractant [6]. The exact ratio is determined by the replacement of one proton in the extractant for every positive charge on the metal (Eq. 2).

$$M^{n+} + n\overline{HR} \rightleftharpoons \overline{MR}_n + nH^+ \tag{2}$$

M^{n+} represents the metal cation and $\overline{HR}$ represents the acidic extractant. Here, the number of molecules of extractant, *n*, involved in the formation of an extracted species depends on the oxidation state or coordination number of the metal ion and the number of places at which bonding can occur to the extractant [8].

Extraction equilibria involving acidic cation extractants, such as carboxylic and phosphorous acids, are difficult to describe by simple distribution law equations. This is due to the non-ideal behaviour of the solutes in the organic phase [6]. The deviation from ideal behaviour stems from both the tendency of the extractants to aggregate and the metal-extractant complex to solvate. The extent that extractant polymerization and metal-extractant complex solvation occurs depends on such factors as extractant concentration, nature of diluent (aliphatic diluents enhance polymerization) and metal loading of the organic phase (saturation lowers the solvation of the complex and even deaggregates the extractant) [6].

The structure for organophosphorous acid extractants in general is a central phosphorous atom connected with an oxygen double bond, a hydroxide single bond, and two single bonds with an R group or derivative. The R group represents an aliphatic or aromatic hydrocarbon group [12].

In cation exchange, equilibrium is usually reached. For determining the precise position of equilibrium, activities should be used instead of concentrations. However for low metal concentrations, concentration can be considered equal to activity. When activities and concentrations are not equal, the experimental results will at least be relative if the ionic strength is held constant. If the ionic strength varies, then the difference between the activity and concentration also changes and the values are no longer comparable [8]. As seen in equation (2), as the pH decreases, the activity/concentration of the protons increase and the equilibrium is shifted to the left, thus decreasing extractable metal.

The above is identical for both acidic and chelating extractants. Although the form of equation (2) is the same for both, the structure of the loaded complex $\overline{MR_n}$ differs according to extractant type. While both ionic and covalent bonds are present in a chelated compound, only covalent bonds appear in complexes formed with acidic extractants. The similarity is in the qualitative aspects, such as the influence of pH, extractant and metal ion concentration and factors affecting the order of metals extraction [8]. Although the overall reaction involving metal extraction has been discussed above (Eq. 2), this involves a reaction path in which a sequence of distinct reactions occur. According to Madigan, the extraction of a cation can be broken down into 4 steps (for the simplest case of only one complex formed) [8,13]. The first step is that the organic extractant is distributed between the aqueous and organic phases at the interface. This is followed by the dissociation of the extractant in the aqueous phase. The dissociated organic extractant complexes with the cationic metal to form a metal complex within the aqueous phase. Finally the metal complex is distributed between the aqueous and organic phases. The four steps are shown in equations (3) to (6), below [13,14]. Note that R′ denotes that the extractant molecule is in the aqueous phase.

$$\overline{HR} \rightleftharpoons HR \tag{3}$$

$$HR \rightleftharpoons H^{+} + R' \tag{4}$$

$$M^{n+} + nR' \rightleftharpoons MR_n \tag{5}$$

$$MR_n \rightleftharpoons \overline{MR_n} \tag{6}$$

Table (2) lists the major solvent extraction reagents that fall in the specific category of acidic cationic extractants [7].

2.3. Structures

2.3.1. Organophosphorous Acids

The three most important types of organophosphorous acids pertinent to solvent extraction differ only by whether or not oxygen atoms are bonded to the R groups, where R usually represents an alkyl (C_nH_{2n+1}). The phosphorous acid group includes esters of phosphoric, phosphonic and phosphinic acids. The active group in all three cases is a phosphorous atom containing a double bonded oxygen and a single bonded hydroxide [8]. The remaining two single bonded R sites determine exactly the type of phosphorous acid extractant. If both R groups have an attached oxygen atom, then the extractant is called a phosphoric acid. If only one of the two R groups has an oxygen atom, then the structure is a phosphonic acid. Finally, the absence of any bonded oxygen atoms yields a phosphinic acid. The generalized structures are shown in figure (1).

These acid extractants and their derivatives are all water-insoluble and contain at least one hydrogen atom (of the phosphoric acid) available for ion-exchange transfer [15]. Phosphoric, phosphonic and phosphinic acids are usually viscous yellowish liquids with high boiling points. The weakest link in the extractant molecule with respect to thermal decomposition is the oxygen-aliphatic carbon bond [6]. Di-(2-ethylhexyl) phosphoric acid, D2EHPA, is the most widely used organophosphorous extractant in commercial solvent extraction, particularly in the separation of cobalt from nickel. As are all the structures in figure (1), D2EHPA is a monobasic extractant. There is a release of one hydrogen ion for every extractant molecule which combines with a metal [8]. Thus, for Co^{2+} and Ni^{2+}, 2 molecules of D2EHPA and 2 molecules of protons are involved in the extraction of 1 molecule of metal.

The reagent of major concern in the present work is octyl phenyl acid phosphate, abbreviated as OPAP. This extractant is not widely used in solvent extraction, and its use has been restricted to gallium and uranium processing. However, it has the general capability of extracting from more acidic solutions than can be achieved by the more familiar extractants, such as D2EHPA. The structure of OPAP does not fit conventionally into the classification of figure (1), which represents the commonly used acidic organophosphorous extractants. This is because OPAP is in reality a mixture of two extractants, each of which possesses an aromatic (phenyl) group. In addition, one component of the mixture (mono-OPAP) contains an additional OH group in place of one of the R groups shown in the structures of figure (1).

Table 2: Acidic cationic extractants.

TYPE	EXAMPLES	COMMERCIAL USE
Alkyl Phosphoric Acids	D2EHPA (Di-2-ethylhexyl phosphoric acid).	U and Eu extraction Ni/Co separation
	OPAP (Octyl phenyl acid phosphate)*.	U from H_3PO_4 [8] Ga from H_2SO_4
Alkyl Phosphonic Acids	PC-88A	Ni/Co separation
	SME 418 (Shell Ltd. trade name).	Ni/Co separation
Alkyl Phosphinic Acids	Cyanex reagents, CNX (Cyanamid Ltd. trade name).	Ni/Co separation
Carboxylic Acids	Naphthenic Acid	Cu/Ni separation
	Versatic Acid (Shell Ltd. trade name).	Y recovery
Aryl Sulphonic Acids	DNNSA (Dinonyl naphthalene sulphonic acid).	Mg extraction

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[*] Conventionally, OPAP is considered an alkyl (i.e. octyl) phosphoric acid, even though an aromatic (i.e. phenyl) group is present.

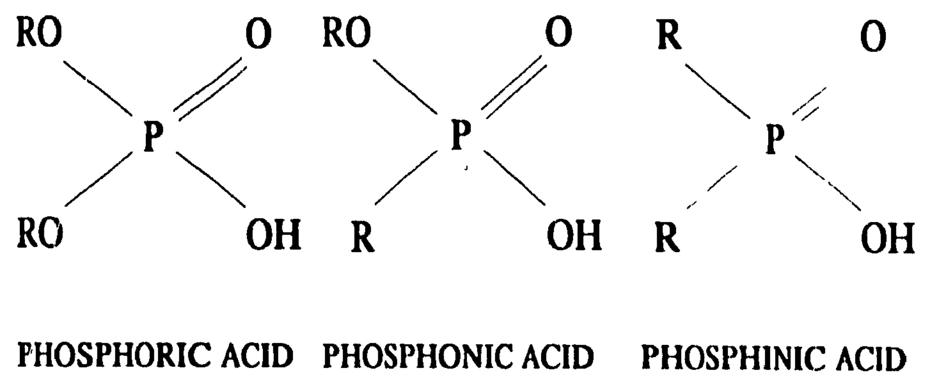

Figure 1: Major types of phosphorous acids.

The detailed structures of both D2EHPA and the two constituents of OPAP (mono- and di-octyl phenyl acid phosphate) are compared in figures (2) and (3). The loading reaction for Ni^{2+} into D2EHPA is shown in figure (4) in a manner that illustrates the structure of the loaded complex. Analogous reactions represent the loading of Ni^{2+} into the OPAP components with appropriate changes to the compositions of the R groups.

2.3.2. Carboxylic and Sulphonic Acids

The main reagents included in this class of acidic cation extractants are the synthetically produced Versatic acids (carboxylic acid derivatives) and naphthenic acids obtained from the distillation of crude petroleum [8]. The structures are shown in figure (5). The variations in the R groups create various different types of similar extractants.

Although not as popular as organophosphorous and carboxylic acids, sulphonic acids are also able to extract metal cations from solution. The most important member in this class is dinonylnaphthyl sulphonic acid, DNNSA [8]. Its structure is shown in figure (6).

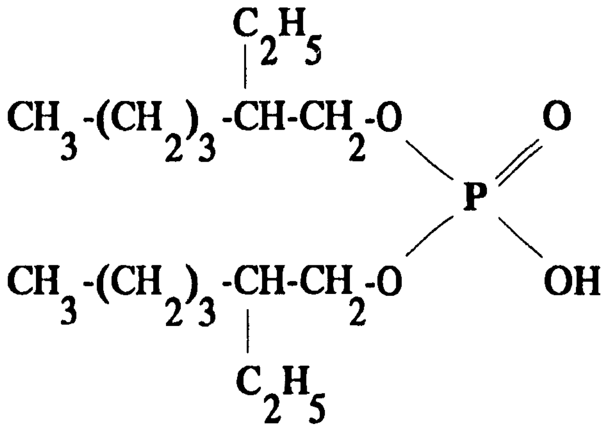

Figure 2: D2EHPA structure.

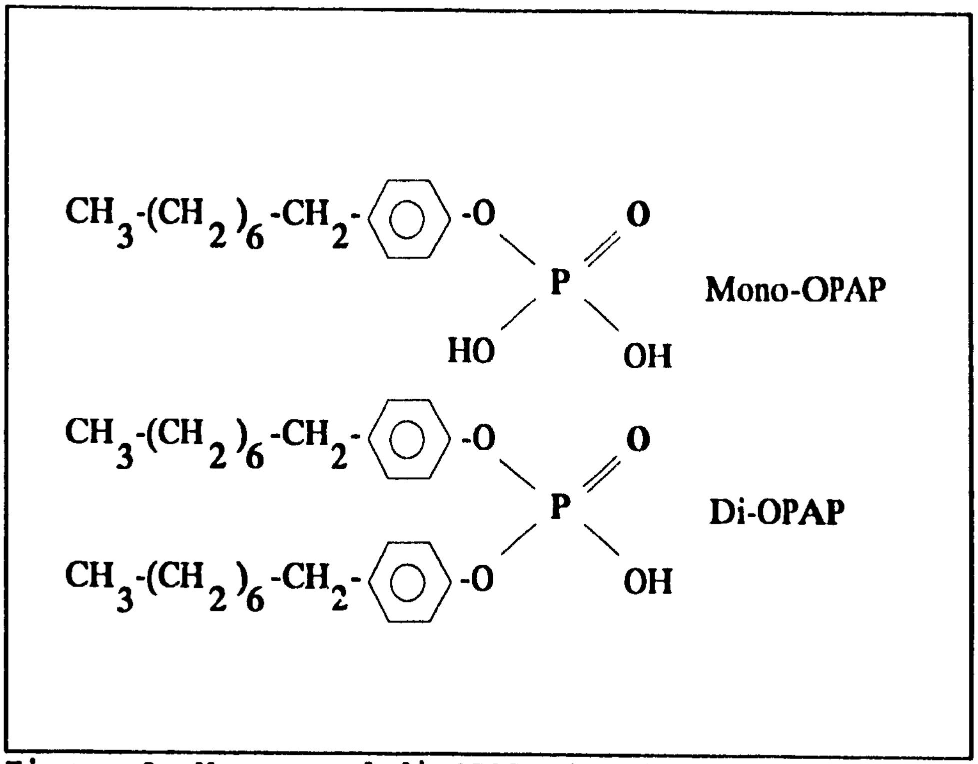

Figure 3: Mono- and di-OPAP structure.

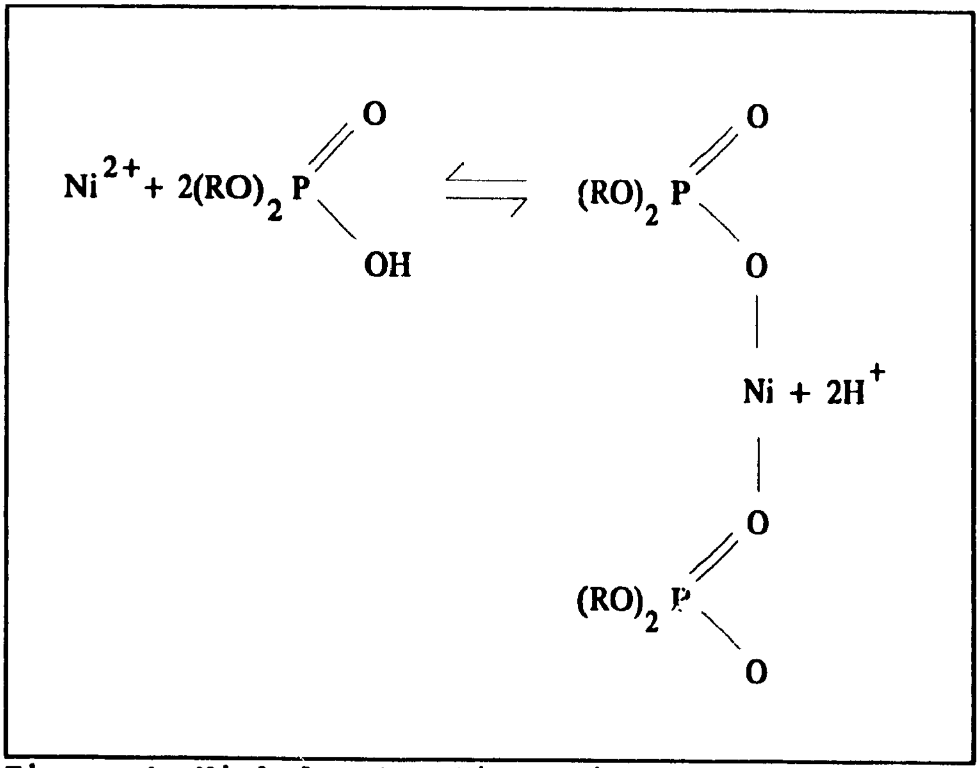

Figure 4: Nickel extraction using D2EHPA.

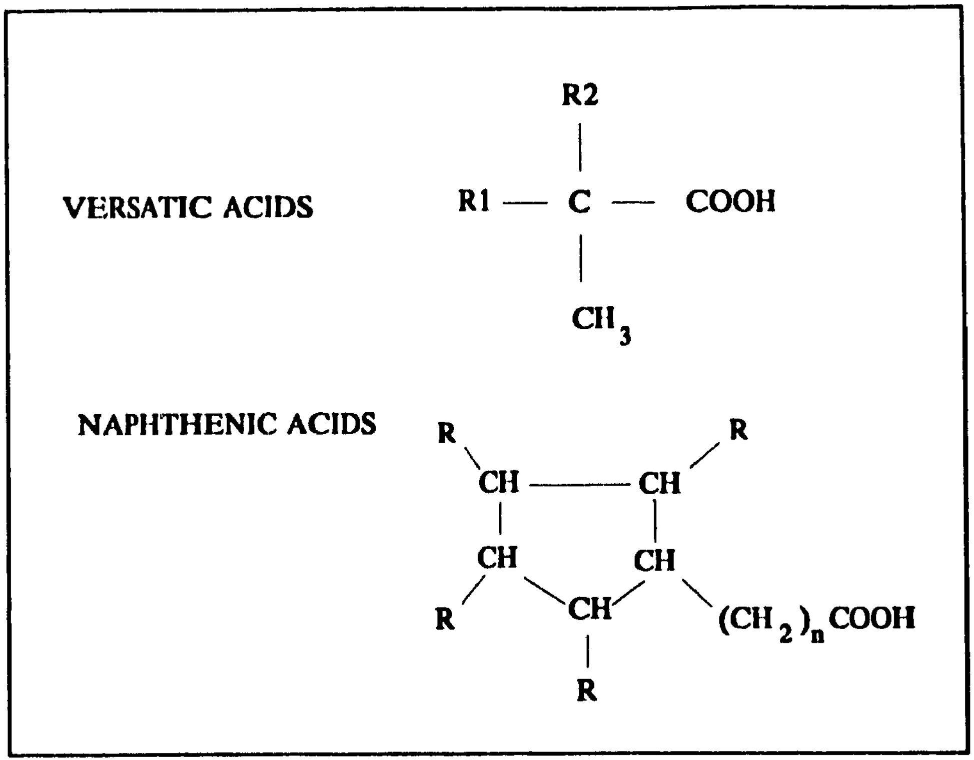

Figure 5: Carboxylic acids.

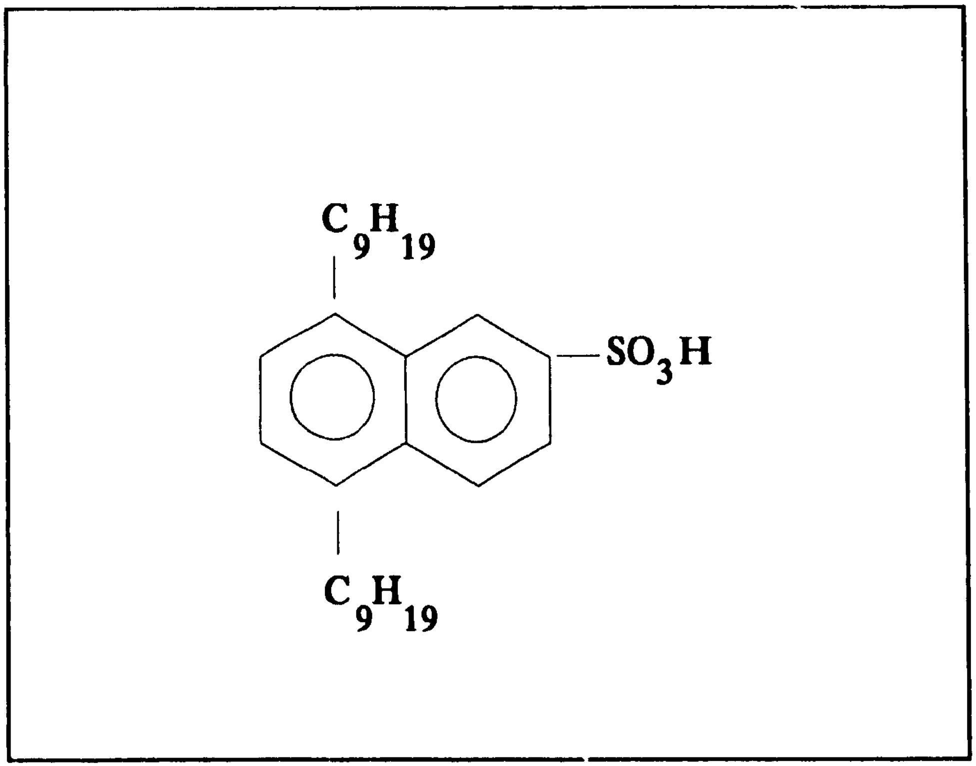

Figure 6: Sulphonic acids.

2.4. Diluents

The diluent, also referred to as the carrier, is an inert organic solvent in which an active organic extractant is dissolved [16]. The main role a diluent serves is to dilute the extractant concentration to an appropriate level for extraction and stripping [17]. Diluents are hydrocarbons and may be either aliphatic, aromatic or a mixture of both. An aliphatic diluent has a structure of C_nH_{2n+2} and possesses low solvency power. Kerosene is an example of an aliphatic diluent. An aromatic diluent has a benzene ring structure and possesses a high solvency power. A diluent which strongly solvates the extractant will tend to remove this reagent from the aqueous/organic interface. This would have an adverse effect on the rate of attainment of equilibrium [4]. However, a diluent which does not sufficiently solvate the extractant will probably be unable to dissolve enough of the reagent for a commercial extraction process [4]. There is a compromise between the two extremes.

There is a large choice of diluents, but, as in dealing with extractants, there are certain characteristics that it should possess. The diluent should be a readily available commercial reagent and enhance selectivity, which is a function of the separation factor [18]. Diluents should be insoluble in the aqueous phase and chemically inert with respect to it. The diluent's desirable characteristics and goals are shown in tables (3) and (4) [9].

Table 3: Diluent characteristics.

1. Mutually soluble with extractant and modifier.
2. Ability to retain in solution the extracted metal complex.
3. Low solubility in water to minimise organic losses (cost and environmental concern).
4. Low viscosity and high flash point.
5. High chemical stability so recycling is possible.
6. Inexpensive and commercially available.

Table 4: Diluent goals.

1. Decrease the viscosity of the extractants.
2. Provide a solvent of suitable extracting power.
3. Improve dispersion and coalescence properties, and thus phase separation characteristics.

The choice of diluent greatly affects the degree of extractant polymerization. Monobasic phosphoric, phosphonic and phosphinic esters are dimeric in non-polar diluents, such as hexane, cyclohexane, benzene and carbon tetrachloride diluents. However, they remain monomeric in polar diluents, such as methanol and acetic acid [6].

Both monomer and dimer species are present in acetone and chloroform diluents for a solute concentration range of 0.01 M to 0.06 M [6]. The extent of extractant polymerization is related to the extent of extractant-diluent interaction. This interaction then in turn affects the extraction of metallic species.

Nickel/cobalt separation is enhanced as the aromatic content in the diluent increases [19]. This improvement is greater at lower pH values. Varying the aromatic content from 0 to 100 %, the separation factor increased from 1.4 to 2 at a pH of 7, marking an increase of 43 %. At a lower pH of 6, the separation factor increased from 2.2 to 4, marking an increase of 82 % [19].

2.5. Modifiers

Modifiers are used to improve the chemical or physical performance of the solvent extraction system [17] and serve two specific purposes. The first is to prevent third phase formation and the second is to improve phase separation [9]. Modifiers accomplish these tasks through their long chain alcohol or phenol structures. The long chain is necessary to prevent water miscibility, which is common to short chain alcohols [9].

Modifiers, such as isodecanol and tributyl phosphate (TBP), have the positive effect of inhibiting emulsions, and are therefore commonly called emulsion inhibiting modifiers. Emulsion formation inhibits clean phase separation. Although these modifiers accomplish the additional task of preventing third phase formation, they unfortunately also lower the ability to separate cobalt from nickel [20]. According to Preston, the use of third phase modifiers has a negative influence on the nickel/cobalt separation capability of extractants, and should therefore be avoided if possible [20]. For example, the presence of isodecanol causes a decrease in cobalt extraction [19]. This decrease is steeper than with other modifiers, such as TBP. Unfortunately, third phase formation commonly occurs at high metal loadings, making the use of modifiers necessary.

Test results compiled by Bouboulis indicate that as the aromatic content of diluents increase, the volume of isodecanol required to eliminate the third phase decreases and the extraction of cobalt increases [19].

2.6. Aqueous Phase

Many metals and their salts are highly soluble in aqueous solutions but are generally much less soluble in organic solvents. Metal salts are highly ionic and are strong electrolytes, existing in aqueous solutions as distinct ions. Water, as a solvent, enhances this effect because of its large dielectric constant. The large dielectric constant reduces the work required to separate oppositely charged ions, allowing metal salts to dissociate freely [5]. Therefore, electrolytes dissociate into ions and water enhances the separation of positive from negative ions.

Another important factor is the tendency of water to solvate ions (hydration). It is important because in essentially all metal extraction systems, the water of hydration must be removed before metal species can enter the organic phase [5]. Also, in order for metal species to enter the organic phase through cation exchange, the formation of an uncharged species must occur. At equilibrium, the concentrations of the components of the system in both the aqueous and organic phases have values independent of the initial presence of the species in one or the other of the phases. Therefore, this equilibrium state should be termed distribution or partition rather than extraction since the metal is distributed between phases and not physically extracted [6].

To favour extraction, or biased distribution towards the organic, the metal species must possess a low affinity for the aqueous phase and conversely a high affinity for the organic phase. There are many factors that promote extraction due to the low affinity of a species for the aqueous phase, such as charge, size, polarity and water activity [6]. As the charge increases, the hydration of the ions also increases, which in turn increases the metal species' affinity for the aqueous phase. Therefore a low charge promotes better extraction. The size of the species also plays an important role. As the size of the species increases, the tendency for hydration decreases, therefore increasing extraction. Also, as the degree of polarity within the aqueous phase decreases, the extent of hydration also decreases, which encourages extraction. Finally, a low water activity can also improve extraction. Salting out agents decrease the availability of water around the metal ion, therefore suppressing hydration (and causing precipitation).

The hydrogen ion concentration plays a very important role in acidic cation extraction. If the equilibrium pH is increased indefinitely, the metal will eventually precipitate as hydroxide and therefore cannot be extracted. A decrease in pH discourages extraction due to the equilibrium of the loading reaction (Eq. 2). Additionally, a decrease in pH may result in the formation of non-extractable metal species as a result of complexation with components of the aqueous phase.

CHAPTER 3

Polymerization and Solvation

3.1. The Organic Phase

The extraction reaction is rarely as straight forward as the simple stoichiometry represented in equation (2). Therefore, the experimental data only occasionally fit the mass action equation of a simple exchange equilibrium [6]. There are essentially two reasons for this deviation. The first is due to the state of the extractant in the organic solution. Unlike chelate acid extractants which do not tend to associate in the organic phase, organophosphorous acids have a strong tendency toward polymerization [6]. The second reason for deviations is due to the solvation of the metal-extractant complex by one or more additional extractant molecules [6].

The two deviation factors, namely the extent of polymerization of the extractant and the degree of solvation of the metal species are governed by many parameters. For instance, the nature of the diluent can affect the polymerization tendency of the extractant [6]. An aliphatic hydrocarbon based diluent enhances the polymerization tendency [6]. D2EHPA, for example, exists almost entirely as dimers, $(\overline{HR})_2$, in alkane (aliphatic) solutions. According to Sastre and Muhammed, D2EHPA possesses a rather large dimerization constant of $10^{4\ 7}$ in n-octane solutions [21]. Polymerization may also occur in solutions with aromatic diluents [22] but the extent is lower. The effect of polymerization can be seen structurally in a D2EHPA dimer, shown in figure (7) [22], which results from hydrogen bonding [8].

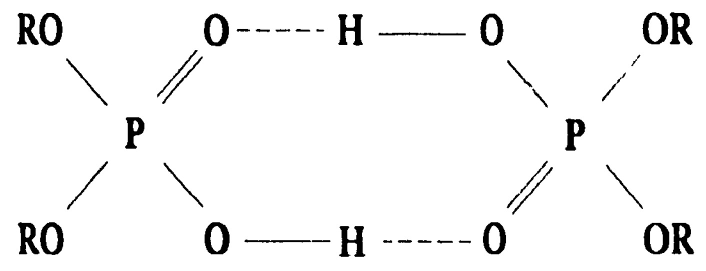

Figure 7: D2EHPA dimer.

Parameters affecting both the polymerization and the degree of solvation are the concentration of the extractant and the metal loading in the organic phase. Under conditions where the saturation of the organic phase with metal occurs, there is a decrease in the solvation of the complex and even depolymerization of the extractant [6]. That is, as the maximum loading capacity is approached, there is less free extractant available, either for polymerization or solvation.

Polymerization and solvation affect the complexation of the species and the reactions taking place and thus, the mass action equation must be modified into equation (7), written for a divalent metal [8].

$$M^{2+} + n\,(\overline{HR})_2 \rightarrow \overline{MR_2\cdot(HR)}_{2n-2} + 2H^{+} \qquad (7)$$

Equation (7) represents a typical situation in which a dimerized extractant reacts to give a solvated monomer complex. Therefore, the chemistry of metal extraction when using acidic extractants is strongly dependent on the solvent phase [8] (i.e. extractant concentration, metal loading and nature of diluent). Although the mass action equation experiences a considerable modification, the amount of hydrogen ions generated is still the same as would be produced in the case where polymerization and solvation do not occur, as seen in equation (2) [8].

3.2. The Aqueous Phase

Equation (2) is the simple reaction showing an exchange of metal for protons. Equation (7) shows that in reality, polymerization of the extractant and solvation of the loaded complex often occur. Although this latter depicts the extraction process more accurately, there is still one important concept missing. The metal, which has been shown as a free ion, is usually found hydrated in the aqueous phase. Here, hydration is equivalent to solvation with water. Therefore, crucial to the extraction of the hydrated metal ion is the removal of the surrounding water molecules [23]. The extractant ligands must be able to complex with the metal ions, which will cause the metal to lose some or all of its hydration [23]. Only then is metal extraction feasible.

The replacement of solvated water molecules by extractant molecules is referred to as ligand exchange. The conventional representation of a loading reaction usually does not show ligand exchange. The reason being that a given number of moles of solvated water shown on the reactant side appears as the same number of moles of *free* water on the product side. If the metal has a strong tendency to hold hydrated water molecules, they will tend to prevent ligand exchange from occurring. Usually a metal ion in aqueous solution holds several solvated water molecules. Thus it is possible for the ligand exchange process to be incomplete. This would result in the formation of mixed complexes of the form $M^{n+} \cdot xH_2O \cdot yR$, where R is the ligand from the extractant. Therefore, the greater the ratio x:y, the more hydrophillic will the metal species be, thus resulting in a lower extraction.

One method of measuring the tendency for water molecules to remain solvated to the metal ion is through values of free energy and heats of hydration. By comparing these values for seven common divalent metals (Mg, Mn, Fe, Co, Ni, Cu and Zn), a relative bond strength between the metal ion and its hydrated complex can be obtained. Table (5) shows that the hydration tendency is similar for Ni, Cu, Co and Zn ions, and slightly higher than that for Fe, Mg and Mn ions [6]. It should be noted that the Ni^{2+} ion exists in aqueous solution in the hydrated form as $Ni(H_2O)_x^{2+}$ [24], where x is usually quoted as being either 1, 6 or 7.

3.3. Nickel/Organophosphorous Extractant Systems

Several studies of polymerization phenomena involving nickel extraction by acidic reagents have been reported. Some tests were conducted by Preston using phosphonic acid extractants to study the occurrence of polymerization [20]. As the extractant concentration was increased, there was also an increase in the number of neutral $(\overline{HR})_2$

ligands bound to the nickel ion at the expense of coordinated water molecules [20]. At a low extractant concentration, there was insufficient $\overline{(HR)_2}$ extractant present for the total displacement of coordinated water molecules. The resulting complex was represented by Preston as $\overline{Ni(HR_2)_2(H_2O)_2}$, which is conventionally written as $\overline{NiR_2 \cdot (HR)_2 \cdot (H_2O)_2}$. At medium extractant concentration, the resulting complex was $\overline{Ni(HR_2)_2(H_2R_2)(H_2O)}$. Finally, at high concentrations, the complex formed was $\overline{Ni(HR_2)_2(H_2R_2)_2}$. The general formula is therefore $\overline{Ni(HR_2)_2(H_2R_2)_x(H_2O)_{2-x}}$, where x=0,1 or 2. Thus as the extractant concentration increases, both the value of x and the degree of solvation and polymerization in the organic phase increases [20].

Table 5: Heats of hydration [6].

METAL ION	H_{hyd} kcal/mole	G_{hyd} kcal/mole
Ni^{2+}	-703.7	-718.7
Cu^{2+}	-702.3	-712.8
Co^{2+}	-691.4	-706.2
Zn^{2+}	-689.0	-698.7
Fe^{2+}	-659.3	-670.9
Mg^{2+}	-659.8	-669.6
Mn^{2+}	-641.4	-650.4

When organophosphorous acidic extractants are used, such as D2EHPA, Daihachi PC-88A, Cyanamid CNX, carboxylic acids (Shell Versatic 10) or naphthenic acids, relatively weak complexes are formed with nickel, as reported by Preston [25]. In the pH range between 4 and 7, nickel extraction takes place according to equation (7) [20,25], written here for Ni^{2+} as equation (8).

$$Ni^{2+} + n(\overline{HR})_2 \rightarrow \overline{NiR_2 \cdot (HR)_{2n-2}} + 2H^+ \tag{8}$$

For simplicity, water of hydration is ignored and $(\overline{HR})_2$ is the dimerized extractant. Here, over a wide range of metal loading, the extractant dimerizes while the loaded complex, although solvated, remains a monomer. The value of *n* increases with decreased metal loading level (i.e. more free extractant is present) [8].

Conversely, at high metal loading, extraction occurs according to equation (9) [8]. Under these conditions, there is insufficient free extractant available to permit either extractant dimerization or solvation of loaded complex. Subsequent dimerization of $\overline{NiR_2}$ may then occur at high concentrations of this complex.

$$Ni^{2+} + 2\overline{HR} \rightarrow \overline{NiR_2} + 2H^+ \tag{9}$$

The solvent extraction of several cationic metals was carried out by Brisk and McManamey at 25°C using D2EHPA dissolved in kerosene [26]. Two mechanisms of extraction were observed. When the ratio (L) of organic phase equilibrium metal concentration to initial D2EHPA concentration was less than 0.1 (low metal loading), the metals were extracted according to equation (7) [26]. For L greater than 0.1, polymers were formed both by the unloaded extractant and the loaded metal complex [26]. In the latter case, a simple depolymerization or further polymerization of $\overline{MR_n}$ must be expected if the total concentration of the compound $\overline{MR_n}$ is decreased or increased, as the case may be [11].

It can be seen from the foregoing that polymerization of both the extractant and the loaded complex, $\overline{MR_n}$, can occur. Polymerization of the extractant is enhanced by an increase in free (i.e. uncomplexed) extractant molecules while that of the complex is sometimes promoted by an increase in metal loading or extraction. With D2EHPA, extensive polymerization of loaded complexes may occur at high metal loadings and the limiting ratio of metal to D2EHPA of 1:2 is approached for divalent metals [20]. Under these conditions, of course, there is no free extractant available for solvation. According to Dreisinger, extensive polymerization of the metal-extractant species at high cobalt loading is especially noticeable in the cobalt-D2EHPA system [18].

Under most conditions (excluding high metal loading), the proportion of the monomer $\overline{MR_n}$ is much lower than that of the dimer $\overline{MR_n \cdot (HR)_n}$ because the monomer-dimer equilibrium of the extractant strongly favours extractant dimerization and subsequent solvation [6]. In general, extractant monomers tend to occur in polar, aromatic diluents, with a high metal loading in the organic phase. Dimers prefer non-polar (or low polar), aliphatic diluents, with a low metal loading in the organic phase [6].

CHAPTER 4

Loading Selectivity

4.1. General

Different organophosphorous extractants possess comparable extractability values for particular metals over different acidity ranges, but the metal selectivity order remains approximately the same within an extractant group. The extraction power increases as the extractant structure changes from phosphoric to phosphonic to phosphinic [27]. More importantly is the order in which metals are extracted, that is, the selectivity for metals as pH changes. The order for metal extraction is often defined in terms of $pH_{½}$, which is the pH value at which 50 % extraction is achieved [7,8]. For a phosphoric acid, such as D2EHPA [7], the general order for $pH_{½}$ is $Ni^{2+} > Co^{2+} > Mg^{2+} > Cu^{2+} > Ca^{2+} > Zn^{2+} > Fe^{3+}$. For a phosphonic acid, such as SME418 [7], the order changes slightly to $Ni^{2+} > Mg^{2+} > Co^{2+} > Ca^{2+} > Cu^{2+} > Zn^{2+} > Fe^{3+}$. Finally, for a phosphinic acid, such as Cyanex 272 [8], the order becomes $Ni^{2+} > Ca^{2+} > Co^{2+} > Mg^{2+} > Cu^{2+} > Zn^{2+} > Fe^{3+}$. The carboxylic acids (Versatic 9) [8] follow a general pattern of $Co^{2+} > Ni^{2+} > Zn^{2+} > Cu^{2+} > Fe^{3+}$. Finally, sulphonic acids (alpha-bromo lauric acid) [8] $pH_{½}$ follow $Ca^{2+} > Co^{2+} > Zn^{2+} > Ni^{2+} > Cu^{2+} > Fe^{3+}$.

The order of metal extractability by acidic (and chelating) extractants almost always follows the order of the metal hydrolysis constants, controlled by conditions existing in the aqueous phase [8]. This constant represents the equilibrium shown in equation (10) and is defined by equation (11).

$$M^{n+} + nOH^{-} \rightleftharpoons M(OH)_n \qquad (10)$$

$$K = \frac{1}{[M^{n+}]\ [OH^{-}]^{n}} \qquad (11)$$

Deviations may occur due to varying ionic strength which may reverse the order of the hydrolysis constants of two metals which are very similar. Other factors affecting extractability include ionic charge and radius. Extractability of metals increases with increasing charge on the ion, while within a group of equally charged ions the distribution coefficient varies inversely with respect to the ion radius [6].

4.2. Nickel/Cobalt Separation

4.2.1. Sulphate Solutions

The separation of cobalt from nickel receives much attention in research and industry. The problem is not only that they readily occur together in ore bodies but that these two metals are chemically similar and therefore difficult to separate from each other. A common route involves extracting Co (II), leaving Ni (II) behind in the aqueous phase. This is employed by nickel refineries such as INCO, Outokumpu and Matthey Rustenburg [28].

Preston noted that nickel/cobalt separation was possible with essentially all of the acidic cation extractants, including phosphoric acids (D2EHPA), phosphonic acids (Shell RD 577) and phosphinic acids (Cyanex CNX) [20]. In all three cases, cobalt was extracted at a lower pH value than nickel and thus cobalt can be separated from a nickel solution, but not vice versa. What does vary between the acidic extractants is the separation factor. As extraction tests progressed from phosphoric to phosphonic to phosphinic acids, the separation factor between cobalt and nickel improved [20]. Preston obtained separation factors of 0.78, 1.49 and 2.05 pH units respectively, carried out without modifier and at 50°C.

Another way that the separation factor was increased was through temperature. Using a temperature range of 20°C to 50°C, Preston noted that cobalt was always extracted at lower pH values than nickel. However, as temperature was increased, the gap between the cobalt and nickel extractions also increased, thus increasing the separation factor [20].

Although separation could be increased by changing organic type and increasing temperature, the explanations are slightly different. The improvement on separation due to temperature was caused essentially by a shift *to the left* of the cobalt curve showing percent extraction vs pH. However, the improvement on separation due to the type of acidic extractant used was essentially due to a shift *to the right* of the corresponding nickel curve. Thus the best separation of cobalt from nickel occurred at the highest tested temperature of 50°C and using a phosphinic acidic extractant, such as CNX.

Flett and West showed that a rise in temperature enhances selectivity of D2EHPA for cobalt [29]. According to Dreisinger and Cooper, as temperature increases, the coordination number of cobalt changes and the new compound is more extractable [18]. Nickel does not follow the same change and thus, the overall effect is to increase the separation factor with increasing temperature. This phenomenon was tested for several acidic organophosphorous extractants and the same result occurred [18]. However, spectra analysis by Dreisinger did not detect a change in the coordination number of cobalt with increasing temperature. That is, there was no octahedral to tetrahedral conversion of the cobalt species, and thus this reasoning cannot explain the improved extractability observed [18]. Electronic spectra of the organic extracts done by Preston show that phosphorous acids form complexes of tetrahedral structure with cobalt and octahedral with nickel [20].

Modifiers, such as isodecanol and tributyl phosphate, had the positive effect of inhibiting emulsion but unfortunately, also lowered the ability to separate cobalt from nickel [20]. This was explained using equation (12).

$$\begin{gathered}(\overline{HR})_2 + \overline{B} = \overline{(HR)_2 \cdot B} \\ (\overline{HR})_2 + \overline{2B} = \overline{2HR \cdot B}\end{gathered} \tag{12}$$

The organic phase additive or modifier is represented by $\overline{B}$ in equation (12). The modifier $\overline{B}$ may interact with the dimerized extractant $(\overline{HR})_2$ through hydrogen bonds. These interactions compete with the metal extraction of equation (7) and therefore exhibit a damaging influence upon the extraction equilibrium [20].

A synergistic effect was found for a D2EHPA-EHO mixture, which extracts nickel at a lower pH than with D2EHPA alone. The addition of EHO (ethylhexanal oxime), a non-chelating oxime, improved the extraction of nickel. The nickel extraction range, according to Preston, was lowered from an initial pH range of 4 to 7 to the synergistic range of 2 to 3 [25]. The conditions for solvent extraction used were an initial content between 2 and 24 g/L Ni^{2+}, a 20 g/L ammonium sulphate solution and a phase ratio (A/O) of ½. Finally, stripping was carried out using a 1 M perchloric acid solution. All tests were carried out at 20°C [25].

Stripping was unfavourable in Escaid 110, an aliphatic diluent. When Solvesso 150, an aromatic diluent, was used, stripping was favoured at the expense of extraction [25]. Many other extractant combinations cause synergism, such as LIX 63 with either D2EHPA, carboxylic acids, sulphonic acids or KELEX 100, as well as KELEX 100 combined with carboxylic acids (Versatic 911) [30,31].

Tests done by Brisk and McManamey involved using D2EHPA dissolved in kerosene to attempt nickel/cobalt extraction from sulphate solutions at 25°C. Although ionic strength was not controlled, pH control was accomplished through additions of ammonium hydroxide and sodium hydroxide [26]. The importance of this work lies in the similarity with the present tests using OPAP. The results showed that an emulsified third phase appeared when cobalt extraction was high, which occurred at relatively high pH values. If these mixtures were allowed to stand for a long time, an opaque white third phase separated out, possibly because of formation of the ammonium salt of D2EHPA [26].

The most widely used process for nickel/cobalt separation in acid sulphate solution involves D2EHPA, which, according to Ritcey et al., is more selective for cobalt than for nickel [32]. Over the years, new reagents have been developed for this separation. For instance, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester was developed by Daihachi Chemical Industry Company Ltd. and marketed by Shell as SME 418 and by Chugai Chemicals as PC 88A. Kasai reports that this phosphonic acid derivative has improved the nickel/cobalt selectivity over that with phosphoric acids and is used by Nippon Mining Co. for Ni/Co separation [18]. Other phosphonic acid type reagents (e.g. Cyanex 272) have been developed which produce similar results, i.e. improved selectivity between cobalt and nickel. An example of the extraction characteristics of a phosphoric acid derivative is given by the performance of 20 % PC 88A in the diluent Varsol DX3641. From 1 M Na_2SO_4, the extraction order with increasing pH is Fe^{3+}, Zn, Cu/Mn, Cd, Ca/Pb/Fe^{2+}/Co, Mg and finally Ni. Thus nickel/cobalt separation is possible.

No solvent extraction reagent is designed specifically for the selective recovery of nickel. The practice, according to Suetsuna et al., is to first extract other metals, such as copper and cobalt [33]. The nickel content of these raffinates, typically present as 12 g/L, is usually too low for electrowinning. Therefore, a solvent extraction step is required to concentrate the electrolyte to suitable levels, typically 70 g/L to 100 g/L nickel [25].

A comparison of commercial nickel/cobalt separation processes from a sulphate solution is listed in table (6) [7].

4.2.2. Chloride Solutions

From a chemistry stand point, a simple way to separate cobalt from nickel is to use the fact that cobalt forms an anionic chloride complex while nickel does not [7]. In a chloride solution, Co^{2+} reacts with 4 chloride anions to form an anionic chloride complex, $CoCl_4^{2-}$, which can be extracted by anion exchange. There is no equivalent reaction for Ni^{2+} and this forms the basis of separation, as demonstrated by Thornhill

[34] using the anionic extractant triisooctylamine (TIOA). The separation of cobalt from nickel is more difficult in sulphate solutions because both cobalt and nickel extract cationically [18]. Thus in a chloride medium, the separation is facilitated.

Table 6: Comparison of commercial nickel/cobalt separation processes from sulphate solutions.

COMPANY	LOCATION	FEED MATERIAL	SX PROCESS
Nippon Mining Co.	Hitachi, Japan	Mixed Ni/Co sulphides from Australia	Co extraction with alkyl phosphonic acid mono alkyl ester
Sumitomo Metal Mining Co.	Niihama, Japan	Mixed Ni/Co sulphides from Philippines	Bulk Ni/Co extraction with Versatic 10, HCl stripping and Ni/Co separation with trialkyl amine
Matthey Rustenburg Refiners (Pty) Ltd.	Rustenburg, South Africa	Co retreatment cake from Ni-Cu-Co-S matte treatment process for sulphides	Cobalt nickel separation with di 2-ethyl hexyl phosphoric acid (D2EHPA)

Many processes based on this principle have been developed, such as the Falconbridge Matte Leach process, the Societé Le Nickel process, the process operated by Metallurgie Hoboken Overpelt and part of the Sumitomo process (see Table 6 for the latter case).

Studies involving organophosphorous extractants in a chloride environment have been restricted to nickel extraction, since cobalt forms an anionic complex extractable only by anion exchange. Thus, in principle, it is possible to extract nickel selectively over cobalt with an organophosphorous reagent.

In studies of nickel extraction into D2EHPA-EHO mixtures, synergistic effects have been experienced [35]. A 0.5 M D2EHPA and 0.1 M EHO mixture was used at pH 2, A/O of 1 and an initial nickel feed of 12 g/L. EHO, by itself, can extract significant amounts of nickel. The advantage in D2EHPA additions is not only to increase the extraction values but also to increase significantly the extraction rate. D2EHPA on its own, however, is unable to extract any appreciable amounts of nickel [35]. Sodium hydroxide was used to alter the pH in a 1 M EHO-0.5 M D2EHPA test to extract nickel at 25 g/L. Varying the pH value did not affect the nickel extraction, which ranged between 13 g/L and 14 g/L for a pH range of 0.8 to 2.2 [35]. The chloride to nickel ratio ranged from 1.81 to 2.09, averaging a value of 1.96. Thus nickel seems to be extracted as an ion pair or neutral complex with the stoichiometric composition of $NiCl_2$ [35].

One of the main drawbacks of combining organophosphorous compounds with aliphatic oximes to create synergistic mixtures is their instability. The EHO-D2EHPA mixture degraded to form ammonium ions, due to ammonium hydroxide additions for pH control. The resulting ammonium salts are insoluble and precipitate as a mixture of NH_4Cl and $NH_4H_2PO_4$ crystals [35]. Since the stability of the organic extractant is such a crucial criterion, other aliphatic oximes were tested in combination with organophosphorous compounds to improve on the stability characteristics. Of the aliphatic oximes tested (i.e. heptanal, octanal, decanal and dodecanal), decanal (or DOX) possessed the highest stability in the presence of organophosphoric acids.

Although the DOX-D2EHPA mixture possessed the highest stability of the mixtures tested, it is characterized by a relatively slow extraction and strip [35]. A 90 % extraction was achieved in 5 minutes but 60 minutes was required to reach equilibrium. Similarly, it took 5 minutes for a 50 % strip, 40 minutes for a 90 % strip but 240 minutes to reach equilibrium.

Thus it may be concluded that in chloride solution, it is easier to extract selectively cobalt over nickel via anion exchange than to extract nickel over cobalt using organophosphorous reagents. All commercial processes involving chloride solutions use the former approach.

CHAPTER 5

Experimental Methodology

5.1. Reagents

The reagents can be divided as either belonging to the aqueous or to the organic phase. In the aqueous phase, the nickel solution was generated from either $NiSO_4 \cdot 6H_2O$ or $Ni(NO_3)_2 \cdot 6H_2O$ powder. The nickel sulphate compound was supplied from Fisher Scientific, with a 99.8 % purity. The nickel nitrate compound was supplied from Aldrich Chemical Company Inc. A magnesium sulphate solution was generated from $MgSO_4 \cdot 7H_2O$, supplied by BDH, with a minimum purity of 98 %.

A base and an acid were required to alter and control the pH of the aqueous solutions. Sodium hydroxide was the chosen base, supplied by American Chemicals Ltd, with a minimum purity of 97 %. The chosen acid was sulphuric acid, supplied by ACP with a 35.5 N concentration.

The octyl phenyl acid phosphate extractant was supplied by Albright & Wilson Americas Inc. This reagent was supplied as a solid, physical mixture of mono- and di-octyl phenyl phosphoric acids. From potentiometric titrations, the average results were found to be 59.9 mol % mono-OPAP and 40.1 mol % di-OPAP. Mihaylov reported that this same mixture was found to comprise between 61.5 and 62.0 mol % mono-OPAP, the remainder di-OPAP [36]. Since the extractant is composed of two distinct compounds, a method of separating mono- from di-OPAP was required to study their individual effect. This method was developed by Mihaylov [36] and is described in appendix (A).

Di-2-ethyl hexyl phosphoric acid is the other extractant used in the experiments and was purchased from BDH Inc. Potentiometric titrations, when applied to the supplied D2EHPA, yielded essentially 100 % D2EHPA and 0 % M2EHPA, the mono-variety of the extractant. Mihaylov reported 97.5 % to 98.0 % D2EHPA from the same extractant solution [36].

Kerosene was the diluent, or solvent, used for all the organic solutions and was supplied by Fisher Scientific. Due to solubility and third phase formation problems involved with OPAP experiments, the use of modifiers was necessary. These phenomena were also experienced by Mihaylov [36]. The modifiers used were n-decanol, supplied by Eastman Kodak Co. and isodecanol, supplied by Exxon Chemical Company (through Synergistics) under the trade name of Exxal 10 alcohol.

A leach liquor was supplied by INCO Ltd. to carry out a selectivity of extraction test on nickel and manganese. This solution contained 3.9 g/L Ni^{2+}, 2.2 g/L Mn^{2+}, 1.5 g/L Mg^{2+}, 0.5 g/L Ca^{2+} and 17.7 g/L SO_4^{2-}.

5.2. Nickel Titrations

5.2.1. Titration Procedure

An integral part of the experimental set-up is the nickel analysis carried out through a titration using EDTA, *e*thylene*d*iamine *t*etra-*a*cetic acid, as the titrant (figure 8) [37]. It was supplied by Aldrich as a 0.0499 M solution, with a formula weight of 336.21. The indicator used was murexide, $C_8H_8O_6N_6 \cdot H_2O$, and was supplied by Fisher

Scientific as a powder. It was later supplied by Aldrich in the unhydrated form, with a formula weight 284.19.

In order for any complex formation titration to be successful, certain requirements must be fulfilled [37]. The foundation of the titration requires that complex formation be stoichiometric so a basis for calculation exists. To ensure a sharp endpoint, the titration must also possess a fast rate of reaction, a high complex stability and an endpoint that is achieved in as few steps as possible. Other requirements include that locating the endpoint be simple, accomplished through indicators, and that no precipitation occur. The stoichiometry in the formation of a nickel-EDTA complex is 1 to 1. Virtually all complexes between EDTA (-4 valency) and metals occur in a ratio of 1 to 1, regardless of the valency of the metal ion [37].

Only rarely are all requirements met in a titration application. In using EDTA to titrate for nickel using a murexide indicator, the above requirements are satisfied except for fast rate of reaction. The titration procedure involves using 10 ml to 20 ml, exactly measured, of nickel solution. To this, 5 ml of buffer pH 10 is added and then diluted to about 50 ml. Several drops of murexide indicator are added and the titration proceeds until the colour changes from yellow to a deep violet. The endpoint is very sharp but the complexing of nickel is slow. Therefore, the titration must be done slowly, particularly if carried out at room temperature. At higher temperatures, the reaction rate is faster but the stability of the murexide indicator is much lower [37].

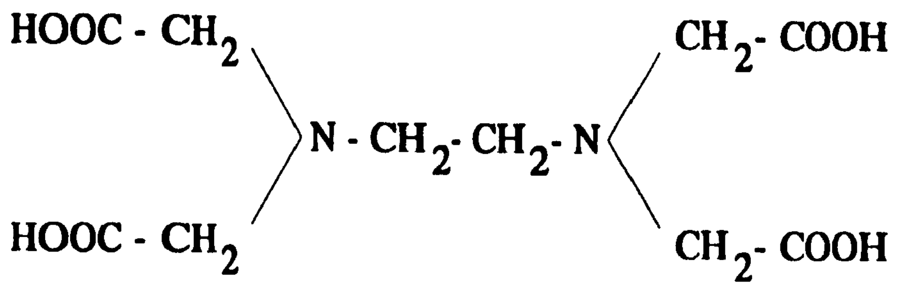

Figure 8: EDTA structure.

The nickel titration procedure using EDTA is accurate as long as the pH of the entire solution is kept high, above a pH value of about 8. Care must therefore be taken with very acidic (pH 1 to 2) nickel solutions and/or high nickel content solutions. In both cases, the initial buffer pH 10 addition is not sufficient to keep the pH value elevated in the desired range. In the first case, the nickel solution is too acidic for the buffer pH 10 solution to raise the pH significantly. In the second case, the problem is caused by the larger volume of EDTA required to complex all the available nickel. EDTA, an acid, has the effect of lowering the pH of the solution. Under normal circumstances, this effect is minimal. If large amounts of EDTA are used, then the effect is no longer negligible and the pH of the solution is lowered significantly.

Allowing the pH to drop causes the colour change to occur prematurely, therefore distorting the results. The problem is solved through periodic base (NaOH) additions, which allow the pH to be manually controlled and kept between pH values of 8 and 9.

The addition of titrant was done using a 10 ml ABU 80 autoburette, from Radiometer Copenhagen. It offers a reading with three decimal digits and a precision of ±2.5 μl [36].

5.2.2. Titration Accuracy

The nickel titrations using EDTA are an essential part of the experimental procedure. The results were dependant on the titration being both accurate and reliable. To control continuously the precision of the nickel titrations, control samples of known concentration were included among the test samples. These control samples were titrated under exactly the same conditions as the regular samples, to prevent bias. In the titration, bias has been reduced through two means. The first is that the control sample of known nickel content is labelled and mixed in with the other samples. The titrations are then carried out in a random order, to avoid the human tendency of obtaining desirable results. Secondly, the digital display of the titrator representing the volume of titrant added to the sample is hidden from view until the titration is officially over. Only at this time is the display looked at and the value recorded.

The titrated nickel content of the control samples were continuously compared with the weighed out nickel content to ensure that the titration was producing results that were both reliable and accurate. The results of the control sample titrations are shown in figures (9) and (10). Figure (9) displays both the titrated and weighed out nickel

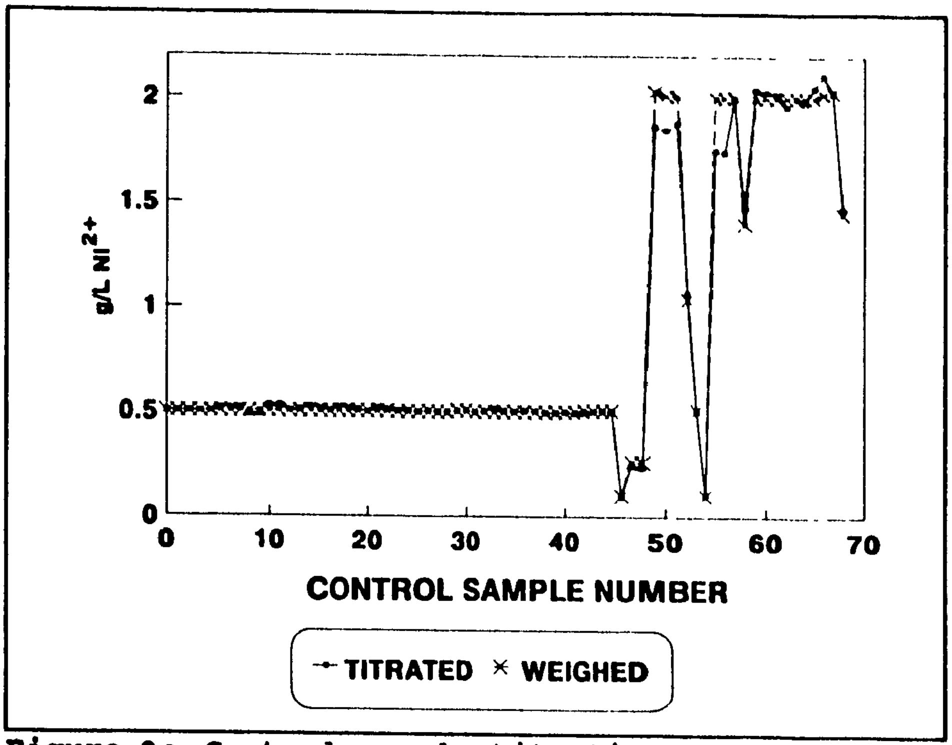

Figure 9: Control sample titrations.

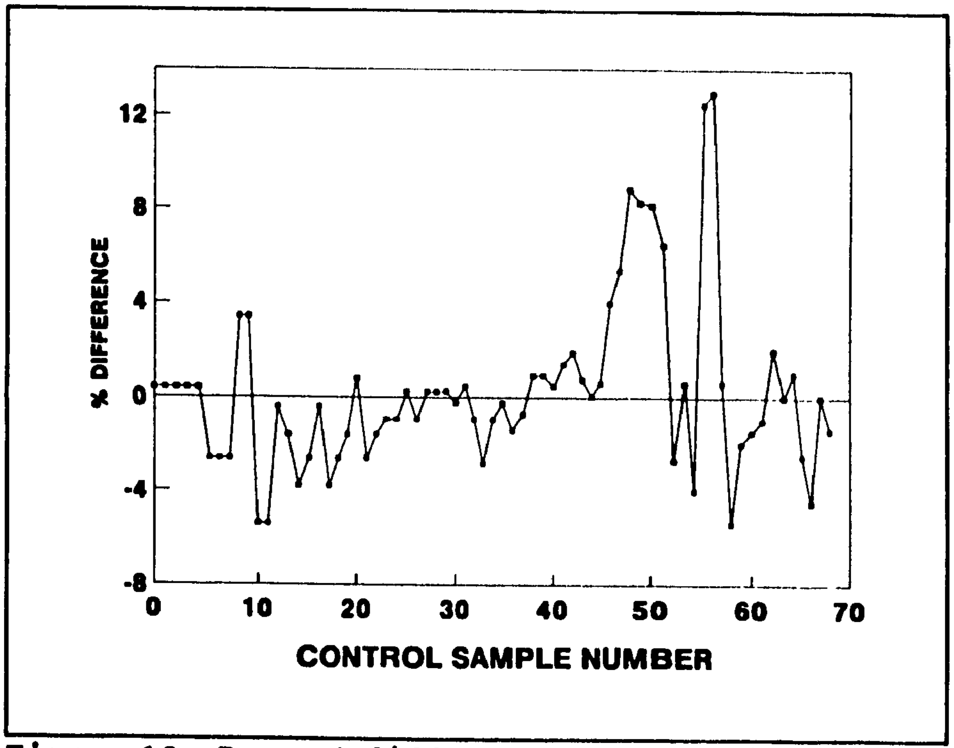

Figure 10: Percent difference between titrated and weighed-out nickel contents.

content of the control samples. Over the entire period of testing, control samples have contained between 0.10 g/L and 2.0 g/L Ni^{2+}. To better compare the values, figure (10) plots the percent difference between titrated and weighed out values. The percent difference is defined in equation (13).

$$\% \ DIFFERENCE = \frac{[U - X]}{U} \times 100 \tag{13}$$

U = Weighed out nickel content

X = Titrated nickel content

There is a sharp increase in the percent difference for sample numbers 55 and 56. These represented samples of high nickel content in an acidic solution. The uncharacteristic large deviation signalled a problem was occurring in the titrations. As outlined in section 5.2.1., when dealing with acidic and/or high nickel content solution, the initial amount of buffer used is no longer sufficient to maintain the pH of the solution above 8. It was as a result of figure (10) that this effect was noticed and that periodic base additions were used to counter this effect. As a consequence, the percent difference was lowered from 9.7 % (no pH adjustment) to -0.8 % (pH adjustment) for acidic, high nickel content solutions.

5.3. Other Analytical Methods

5.3.1. pH Meter

The acidity of the aqueous solutions was determined with a pH electrode. The pH was measured using a PHM 84 Research pH meter from Radiometer Copenhagen and an ORION ROSS combination pH electrode. Minimizing drift and obtaining accurate and reproducible readings were critical to minimizing the low accuracy of measurements in the region of pH 1 [36]. Calibrations of the electrode were carried out with standard buffer solutions, using pH values of either 7.00 and 4.01 or 1.00 and 4.01. No significant difference was noted using either calibration combinations, even at low pH values.

5.3.2. Atomic Absorption Spectrometry

The titration procedure of section 5.2.1. applies to single metal solutions [37], specifically outlined for Ni^{2+} (also applicable to either Cu^{2+} or Co^{2+}). In some tests, multi-metal solutions were used and therefore another method was required for metal analysis. The chosen method was flame atomic absorption using hollow cathode lamps and air-acetylene. This was applied to solutions containing several metals and analysed for Ni^{2+}, Mg^{2+} and Mn^{2+}. The linear range exists up to 5.0, 0.4 and 3.0 μg/L, respectively.

5.3.3. Potentiometric Titration for As-Received Extractant

A potentiometric titration was required to determine the ratio of mono- to di-components of both OPAP and D2EHPA within the supplied reagents. When the separating procedure was applied to the supplied OPAP to isolate the mono- from the di-OPAP structures, the potentiometric titration was used to determine the newly created ratios of the fresh solutions. This procedure not only provides information on mono- to di- ratios of the acidic extractants but also on the extractant concentration.

The mono- to di-OPAP ratios and the extractant concentrations were determined by potentiometric titration using NaOH solutions, varying from 0.1 M to 0.5 M. The procedure begins with a prepared test organic solution, made up of either OPAP or D2EHPA dissolved in a kerosene-modifier solution. A small sample, V_e, of this organic solution (1 ml to 3 ml) is then further dissolved in 100 ml acetone (reagent grade) and subsequently diluted with 25 ml water. The only important detail to note is that a large amount of acetone is required, relative to the initial organic sample, to act as a mutual solvent for both kerosene and water [36]. The titrant base was then slowly added in small volume intervals. After each volume addition, both the pH value and base volume were recorded.

Figure (11) shows the results of a typical potentiometric titration applied to *as-received* OPAP, producing the standard S-shape titration curve. The first peak (V_1) represents the volume required to neutralize the first exchangeable hydrogen atom encountered in the OPAP structures, present in both the mono- and di-OPAP components. Similarly, the second peak (V_2) represents the second exchangeable hydrogen atom in the OPAP structures, present in only the mono-OPAP component. Therefore, the volume of base contributing to the mono-OPAP component is $V_m=V_2-V_1$, and that contributing to the di-OPAP component is $V_d=V_1-V_m$ (Table 7).

As was previously mentioned, the concentration of the organic extractant sample can also be determined. What is required is the initial organic sample volume, V_e, the concentration of the base used as titrant and the value for the first equivalence point, V_1. The moles and the concentration of extractant used in that sample can be determined from equation (14).

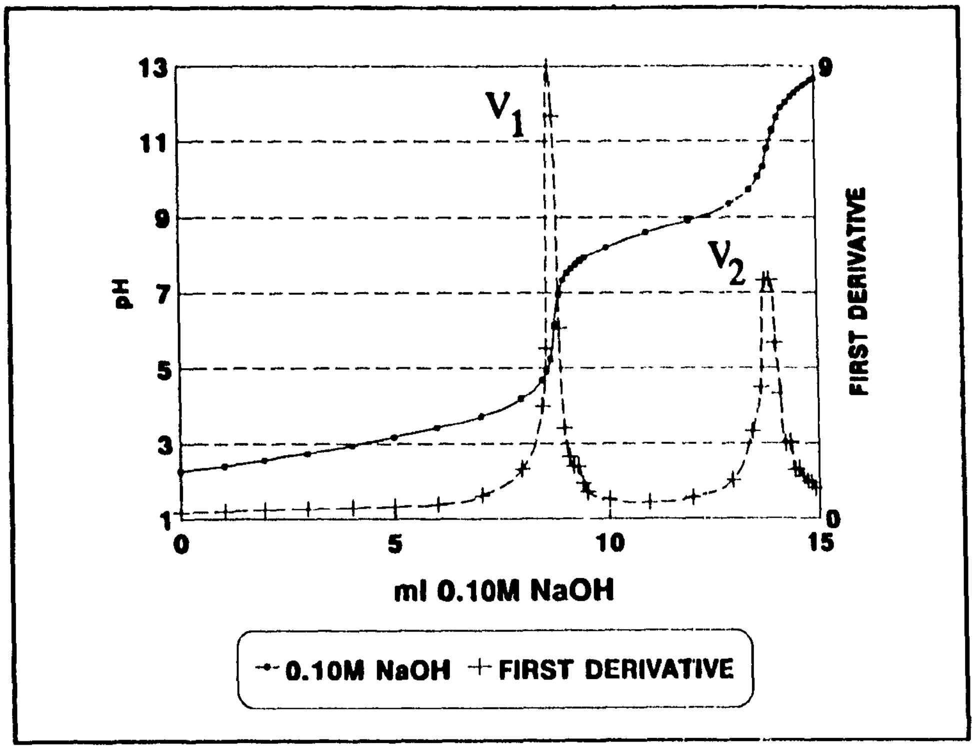

Figure 11: Potentiometric titration of mono- and di-OPAP.

Table 7: Typical potentiometric titration results for *as-received* OPAP.

PARAMETER	VALUE	PARAMETER	VALUE
V_1	8.75 ml	V_2	13.95 ml
V_m	5.20 ml	V_d	3.55 ml
% MONO	59.4 %	% DI	40.6 %

$$[OPAP]\ (moles/L) = \frac{V_1\ (L) \times [NaOH]\ (moles/L)}{V_e\ (L)} \qquad (14)$$

5.3.4. Potentiometric Titration Results for Separated OPAP Fractions

The average mono-OPAP content of the supplied OPAP extractant is 59.9 %, with a sample standard deviation of 3.6 %. Although the measured mono-OPAP values range from 56.1 % to 65.3 %, the actual mono-OPAP value, using a 95 % confidence level, lies between 56.6 % and 63.2 %.

The supplied OPAP extractant was separated and produced three distinct organic samples. According to Mihaylov [36], the first precipitate is high in mono-OPAP, the separated organic *third phase* is low in mono-OPAP, and the second precipitate has a mono- to di-OPAP ratio of approximately 1. Results from our tests showed reversed outcomes for the two precipitates. The first precipitate averaged 61.0 % mono-OPAP with a standard deviation of 5.3 % while the second precipitate averaged 80.1 % mono-OPAP with a standard deviation of 4.2 %. The third phase remained consistent with Mihaylov's results, with a 20.0 % mono-OPAP and a standard deviation of 4.0 %.

In section 5.3.3., it was mentioned that the potentiometric titration curves yield information not only on mono-/di-OPAP ratios but also on extractant concentrations. To be certain that the extractant concentration values can be determined accurately from the titration curves, tests were first carried out using known concentrations. The calculated extractant concentrations consistently fell short of the actual weighed out values. On average, the calculated concentration was 6 % less than the prepared value. The difference is within acceptable experimental error and therefore the calculation of concentration from titration curves is reasonable.

Being able to carry out concentration calculations is crucial, particularly in analysing the organic samples of the separated extractants. The separated solid extractants (PPT #1, #2 and third phase) often appear to be viscous liquids, signifying the inability to evaporate completely the ether content. This therefore has the effect of altering the density of the separated extractant sample. Being able to calculate the concentrations through titration analysis is superior to relying on values based on weighed quantities where the assumption is that all the ether has evaporated.

5.4. Shake Out Tests

Contact between the aqueous and organic phases was enhanced using a Burrell wrist action shaker (Model 75). Using Pyrex 125 ml flasks, 20 ml of both the aqueous and the organic phase were shaken together, typically for 10 minutes to ensure equilibrium. All tests were carried out at room temperature (23±2°C).

CHAPTER 6

Results

6.1. Nickel Extraction Using D2EHPA.

Before beginning testwork using the OPAP extractant, two series of extraction tests were carried out using D2EHPA on a nickel sulphate solution with pH as the variable. The purpose was to gain confidence and credibility in the experimental procedure by carrying out testwork on a system which had been previously studied by others.

Two separate series were carried out, both involving D2EHPA in a kerosene diluent. In the first series, a 0.20 M D2EHPA solution, approximately 6.7 % by volume, was applied to a 0.50 g/L nickel solution. The second series consisted of a 0.60 M D2EHPA solution, approximately 20.1 % by volume, applied to a 2.0 g/L nickel solution. In both cases the shaking time applied was 20 minutes within which equilibrium is reached (section 6.2.2). The tests were carried out with a phase ratio (A/O) equal to 1 and the initial pH was modified using various additions of NaOH.

The results of both series can be seen in figure (12). The first series, involving the lower extractant and metal concentration, yielded a $\text{pH}_{1/2}$ of 3.7 (curve A). The second series, involving the higher extractant and metal concentration, yielded slightly better extraction results, with a $\text{pH}_{1/2}$ of 3.1 (curve B). These $\text{pH}_{1/2}$ values agree closely with the data of Slater [38].

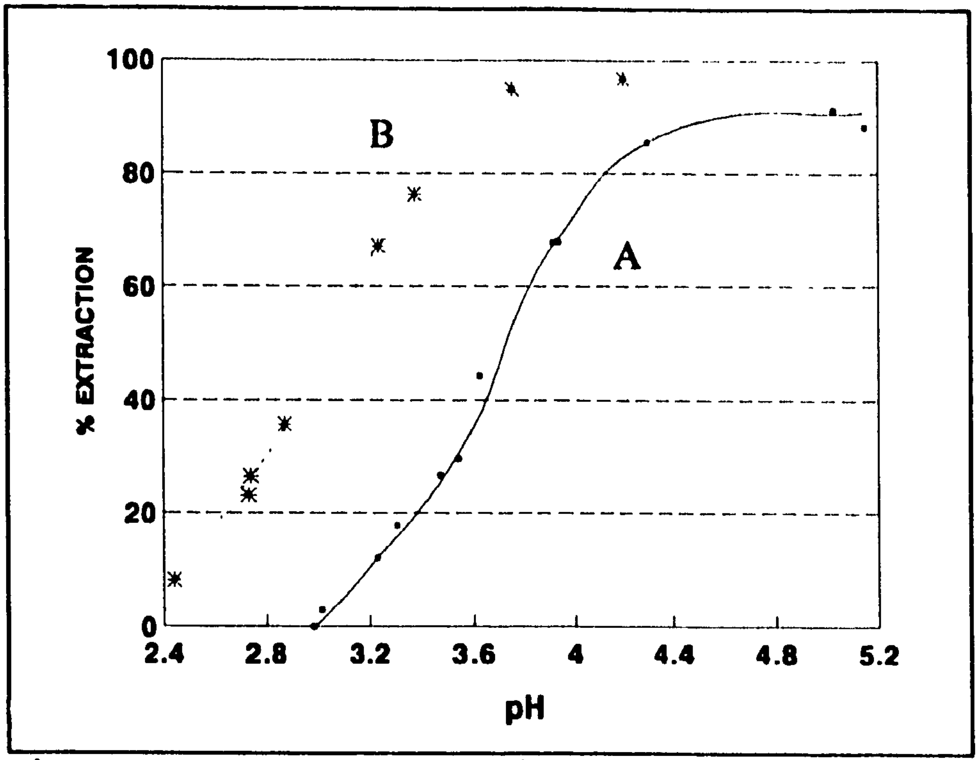

Figure 12: Percent extraction vs pH using D2EHPA.

6.2. Extraction Using OPAP - No Modifier.

6.2.1. Solubility of OPAP.

The first test using the OPAP extractant was without modifier. It was immediately clear that OPAP dissolves very slowly in kerosene. Initially, a solution of 0.20 M OPAP was desired but it was obvious after 24 hours of room temperature stirring that only a small fraction of the solid organic extractant had dissolved. One option was to experiment with smaller amounts of OPAP until complete dissolution was encountered but that would lead to a needless waste of large amounts of extractant and organic solution. Instead, kerosene was added to the initial undissolved OPAP solution until all the extractant was dissolved.

A 9.1 g sample of OPAP was placed in 100 ml of kerosene. Then, a small volume of kerosene was added, followed by a period of stirring. This was continued until all the solid OPAP extractant had dissolved. Eventually, a solution was obtained with complete OPAP dissolution, with an approximate concentration of 0.03 N. This value should by no means be interpreted as the solubility of OPAP in kerosene without modifier. It is the maximum amount of OPAP that could be conveniently dissolved in kerosene within a reasonable time. The exact reason for the slow dissolution of OPAP was not investigated, neither the nature of the undissolved precipitate.

6.2.2. Extraction Tests.

A simple kinetic test was carried out to determine the time required to attain equilibrium. A 0.50 g/L nickel solution was shaken in a flask, along with the 0.03 N OPAP solution at A/O of 1, for 1, 5, 10, 15, 20 and 30 minutes. Although some fluctuation did occur, the extraction remained essentially constant (between 20 % and 30 % extraction) throughout the time range. Using linear regression, the points yielded a slope of -0.08 for the percent extraction vs time plot. This value is very close to 0, which represents a true horizontal line and therefore complete independence of extraction from shaking time. Since equilibrium was reached very quickly, shaking the samples for a few minutes is sufficient. The equilibrium pH for the kinetic tests was attained naturally (no pH control), with an average value of 2.3. The next step was to study the effect of pH under otherwise the same conditions. Equilibrium pH values were varied between 2.3 and 5.5 by initial NaOH additions at various concentrations. Amounts added were never more than 1.0 ml so as not to alter significantly the total aqueous volume. Since equilibrium is achieved very quickly, a 15 minute shaking time was deemed sufficient to guarantee equilibrium. The results are seen in figure (13). Nickel extraction gradually increases as the pH increases from 2.3 to 5.5, as expected.

In addition to the solubility problem noted above, a further difficulty was third phase formation at high pH values where the best extractions were obtained. This third phase broke down eventually, the time required varying between minutes and days, depending on pH.

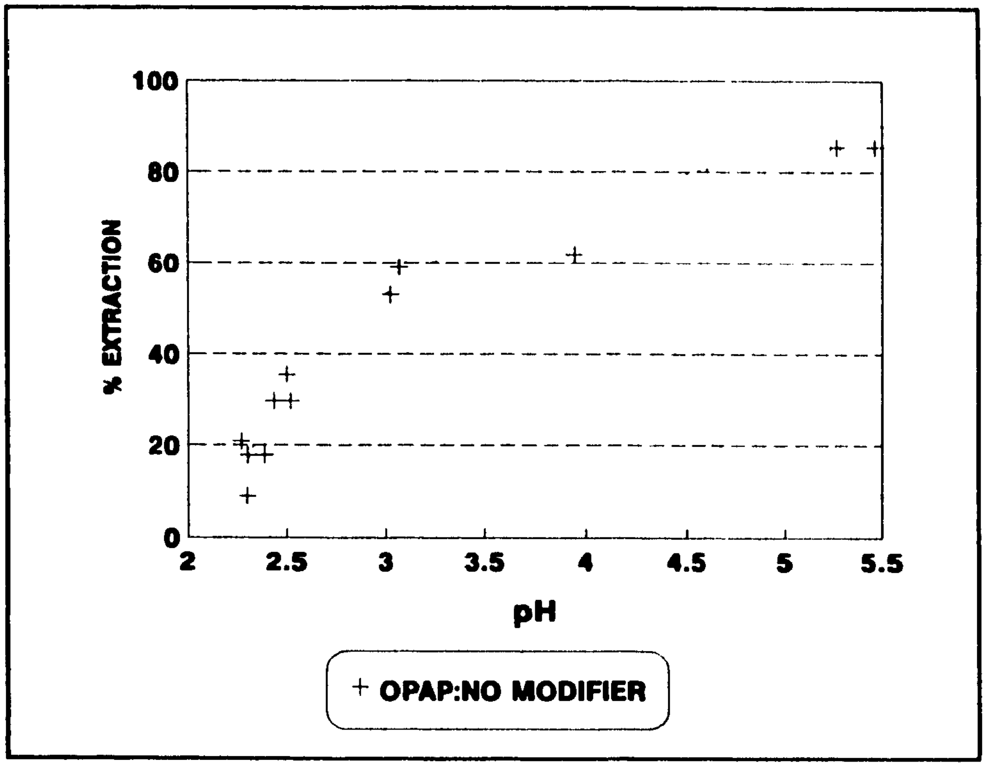

Figure 13: Percent extraction vs pH using OPAP without modifier.

6.3. OPAP (With Modifier) Concentration

At this point, it was clear that a modifier addition was necessary, both to improve OPAP solubility and to reduce the tendency for third phase formation at high pH. Thus in the next tests, the solvent was composed of 85 vol % kerosene diluent and 15 vol % n-decanol, this latter being a common modifier in solvent extraction systems. It was immediately found that major increases in the amounts of dissolved OPAP could be readily obtained. Tests were carried out to determine if rapid loading was still obtained with modifier addition. Here, the 15 vol % n-decanol/kerosene solvent contained 0.15 M to 0.31 M OPAP and nickel was extracted from a 0.50 g/L Ni^{2+} solution at A/O of 1.

The results (Fig. 14) showed that equilibrium was reached within 10 minutes, so in subsequent tests, a 10 minute contact time was used. It should be noted that in figure (14), extraction does not follow the order of OPAP concentration. This is because pH was not controlled and set to a common value. The pH equilibrium values range between 1.9 and 2.5.

The results of figure (14) are encouraging in that major recovery (up to 90 %) was obtained under high acidity conditions, for which extraction into D2EHPA would be essentially zero. However, recoveries above 90 % can be obtained only by increasing the pH, thus creating the possibility of third phase formation and phase separation problems.

The next tests were carried out under controlled pH, with various OPAP concentrations in 15 vol % n-decanol/kerosene. Sodium hydroxide was added during the

10 minute shaking time to produce the desired final pH. Again, the aqueous phase initially contained 0.50 g/L Ni^{2+}. As expected, extraction increased with both increasing pH and OPAP concentration (Fig. 15), maximum recovery reaching 100 % above a pH of 2.75.

In terms of phase separation quality, a general observation made was that as extraction increased, the phase separation became worse. At lower extractions, the phases separated quickly, giving a clear organic top layer and a murky translucent aqueous bottom layer. For higher extractions, the aqueous phase was filled with a webbed third phase which eventually broke up. Finally, for essentially 100 % extraction regimes, the phase separation was slow due to the quality of the aqueous region. The organic region was still clear but reduced in volume since most organic was still physically tied up with the aqueous solution. The aqueous region was characterized by a milky, dense texture. With time, the milky aqueous region became initially spongy, then commenced webbing until the web broke up, leaving two distinct phases.

Others have also found a connection between extraction and phase separation properties when using organophosphorous extractants. Bouboulis found that at high concentrations of D2EHPA (and therefore high extraction levels), a third phase is formed which requires a modifier to eliminate it [19]. Brisk and McManamey report that at high pH values, cobalt extraction into D2EHPA is plagued by emulsification although given enough time, the opaque white third phase separated out [26].

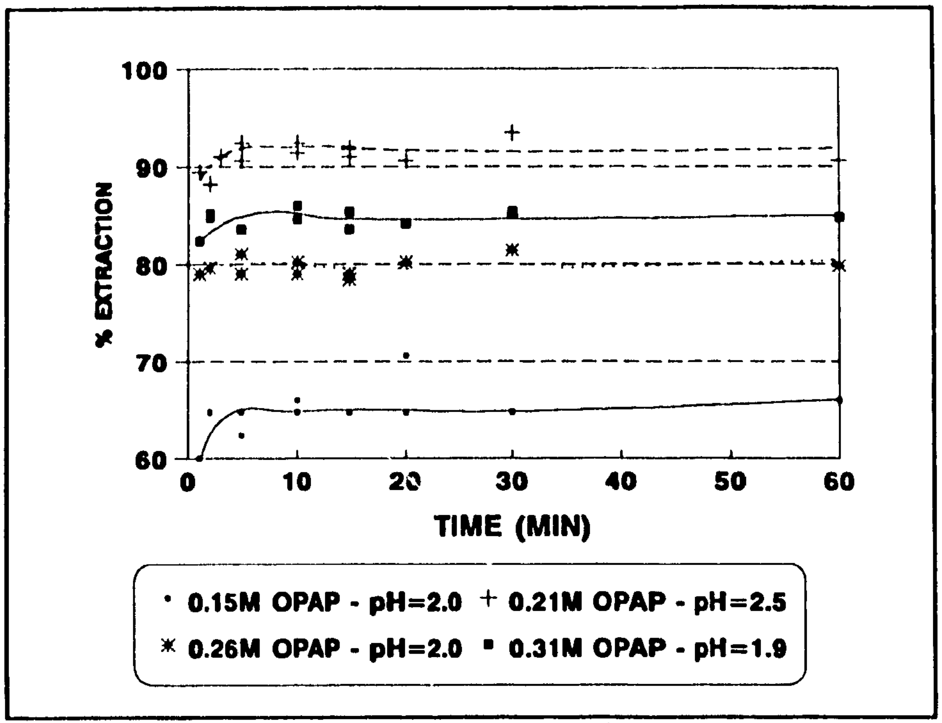

Figure 14: OPAP concentration effect on extraction kinetics.

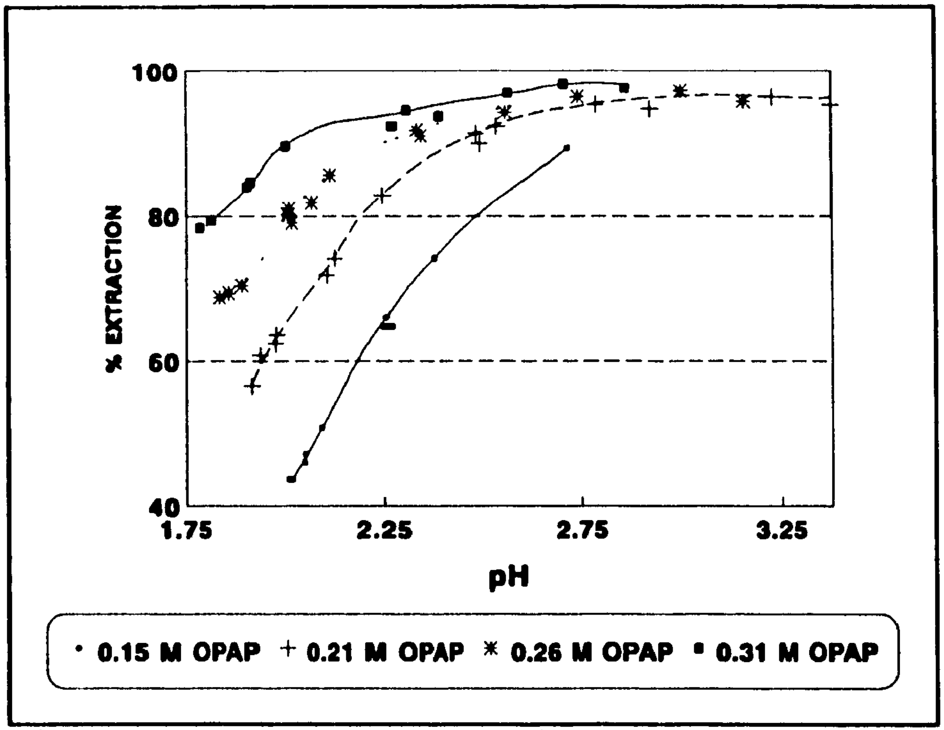

Figure 15: OPAP concentration effect on nickel extraction.

6.4. Modifier Content

The 15 vol % n-decanol addition for the tests shown in figures (14) and (15) was an arbitrarily chosen value. Further experiments were then carried out with three progressively decreasing modifier additions, under otherwise same conditions (0.30 M OPAP, 0.50 g/L Ni^{2+} and A/O=1). Figure (16) shows that, as expected, equilibrium was reached rapidly, regardless of degree of modifier. It can also be seen that extraction is significantly reduced when the n-decanol addition is at levels above 10 %. This latter effect was further explored in tests where the equilibrium pH was also varied (Fig. 17). Here, 10 minute shaking times were used and the equilibrium pH was controlled between 1.8 and 1.9.

The extraction curves for the 4 different modifier contents are shown in figure (17). The 5 vol % and 7.5 vol % n-decanol solutions yield very strong extraction curves while the 10 vol % and 15 vol % n-decanol solutions yield weaker curves. The 5 vol % modifier solution suffered from extremely slow separation times and rather poor separation characteristics, especially at high pH values. The shaken solution remained very milky in texture and separation progressed at a slow rate, in the order of days. Even after a long wait, the separation was poor in quality, as residue was left clinging to the walls of the shaken flask. However, a high extraction was readily obtained. The 7.5 vol % modifier solutions produced similar results for both extraction and separation properties.

Both the 10 vol % and 15 vol % modifier tests offered a much faster and better quality separation but at the expense of extraction. The separation time decreased from a magnitude of days to that of minutes.

It was also noticed that separation characteristics deteriorated with increased shaking time. Table (8) shows some approximate separation times required following different shaking times at each modifier level studied. Here, final pH was set in the 1.9 to 2.0 range, where extractions varied from above 95 % (for 5 vol % and 7.5 vol % modifier) to below 85 % (for 10 vol % and 15 vol % modifier). It is important to note that, since equilibrium is reached within 10 minutes, further shaking time will damage phase separation characteristics without improving extraction.

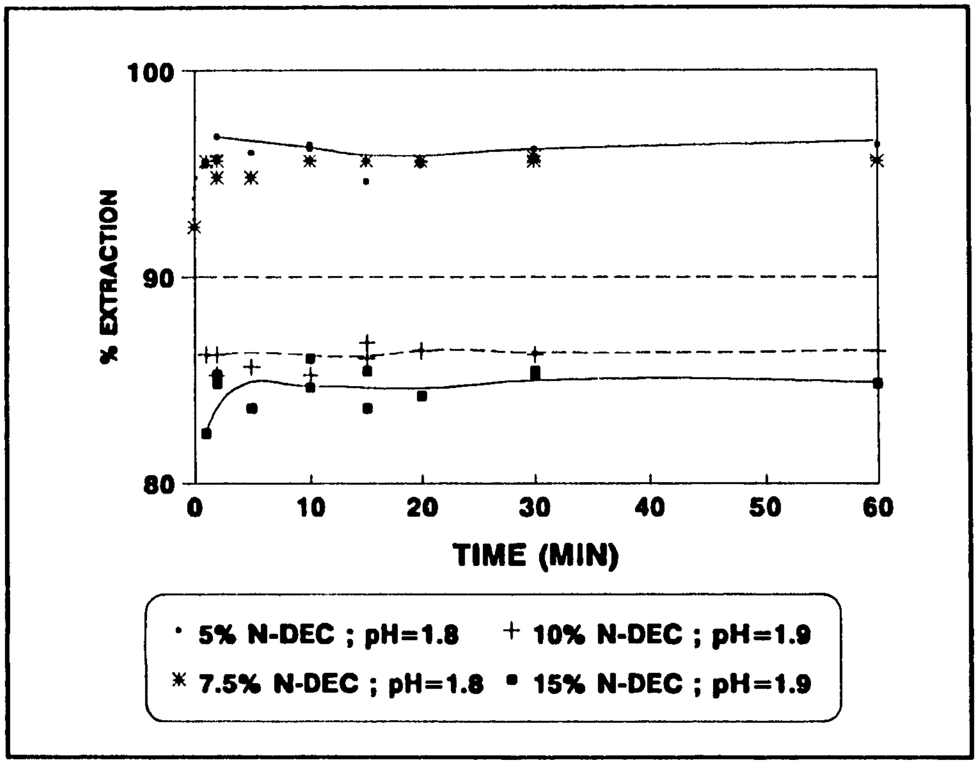

Figure 16: The effect of modifier content on kinetics.

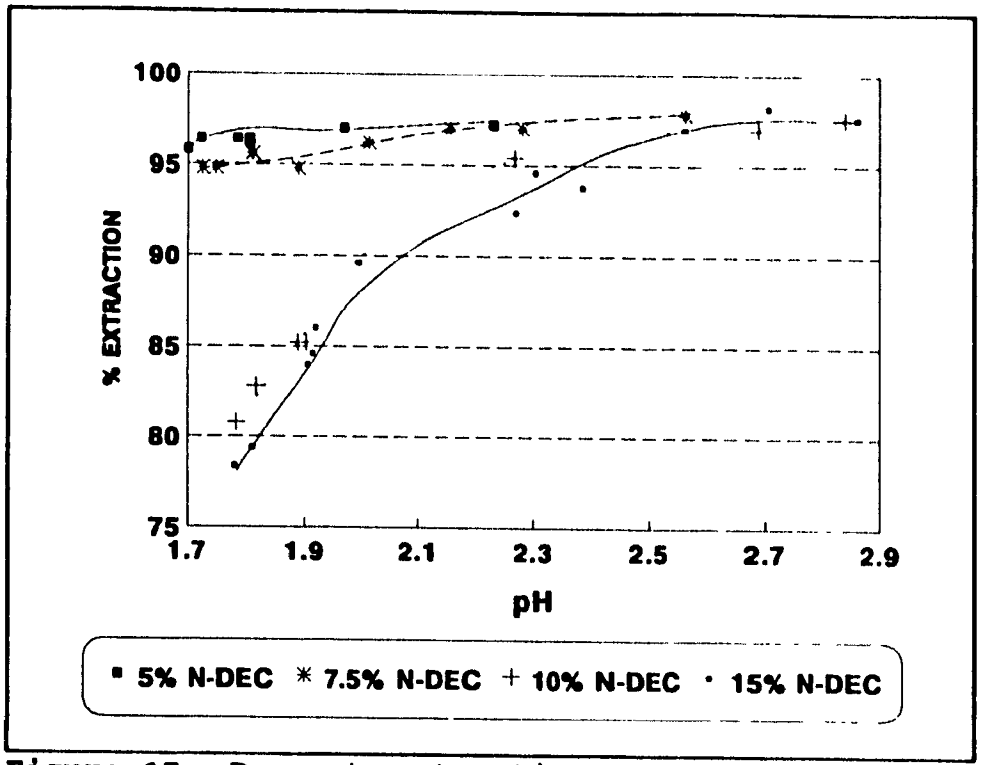

Figure 17: Percent extraction vs pH for various modifier contents.

In summary, a 5 vol % modifier addition will increase OPAP solubility in kerosene to at least 0.3 M, which is a commercially useful level. While high extractions can be maintained over a wide pH range, phase separation properties are unacceptable. As the modifier content increases, phase separation becomes rapid and clean while extraction decreases, until the final pH is above 2.5. Thus, there is a compromise between ease of phase separation and extraction.

Table 8: Phase separation time as a function of modifier content and shaking time (pH=1.9-2.0).

SHAKING TIME	5 vol % MODIFIER	7.5 vol % MODIFIER	10 vol % MODIFIER	15 vol % MODIFIER
2 MIN	1 DAY	1 DAY	3 HOURS	30 MIN
10 MIN	3 DAYS	3 DAYS	20 MIN	20 MIN
30 MIN	4 DAYS	4 DAYS	3 HOURS	3 HOURS

6.5. Effect of Contact Time After Shaking

In tests designed to establish the time required to reach equilibrium (Figs. 14 and 16), a maximum shaking time of 1 hour was used. Due to the long separation times involved under some conditions, it was necessary to verify that equilibrium had in fact been reached within the shaking time and no further extraction occurred, especially if the subsequent separation time extended for several hours.

An organic solution comprising of 0.27 M OPAP in 15 vol % n-decanol/kerosene was shaken with a 0.50 g/L Ni^{2+} aqueous phase for 10 minutes, at which point, according to figures (14) and (16), equilibrium is reached. After shaking, the solutions were left in contact for an additional 10, 90, 190 and 480 minutes to check if additional extraction was occurring. The results are listed in table (9). The difference in extracted nickel between the 10 minute and the 480 minute separation contact time was only 0.7 %. Considering experimental error, this difference is negligible. This ensures that all results can be compared, regardless of the time required to separate the aqueous from the organic phase (since no further extraction takes place).

Table 9: Contact time effect.

CONTACT TIME *AFTER* SHAKE	EXTRACTION (%)
10 MIN	81.2
1.5 HOURS	81.2
3.2 HOURS	80.5
8 HOURS	81.9

6.6. Modifier Type

Although n-decanol is highly effective in increasing OPAP solubility and improving phase separation properties, there is a tendency for loss of nickel extraction, as noted above. It was decided to compare n-decanol with isodecanol, the latter also being commonly used as a modifier in solvent extraction [39].

In the initial tests, 0.30 M OPAP in 10 vol % isodecanol/kerosene was contacted with 0.50 g/L Ni^{2+} aqueous phase for times between 2 minutes and 60 minutes. In each case the equilibrium pH was 1.90. Directly comparable experiments had been carried out earlier but with n-decanol in place of isodecanol (Fig. 14). As shown in table (10), equilibrium was again achieved rapidly, but the use of isodecanol gave an additional 5

% nickel extraction.

Table 10: Effect of modifier type on nickel extraction (pH 1.9).

SHAKE TIME	ISODECANOL (% Ni Extracted)	N-DECANOL (% Ni Extracted)
2 MIN	90.4	85.2
5 MIN	90.6	85.6
10 MIN	90.4	85.2
60 MIN	90.6	86.4

Further experiments were carried out to compare the behaviour of n-decanol and isodecanol when extractions were performed under equilibrium conditions (10 minute shaking time) at different pH levels (Fig. 18). The results again show that isodecanol provided the higher nickel extraction. The improvement was greater at lower pH values, with the curves approaching equilibrium and each other at pH values above 2.3.

Although isodecanol produced higher nickel extraction values, the phase separation quality was similar to that when using n-decanol. For extractions above 95 %, aqueous/organic separation took between 20 minutes and 40 minutes. For extractions below 95 %, separation time was on average 10 minutes. It should also be noted that both modifiers were equally effective in promoting OPAP dissolution in kerosene.

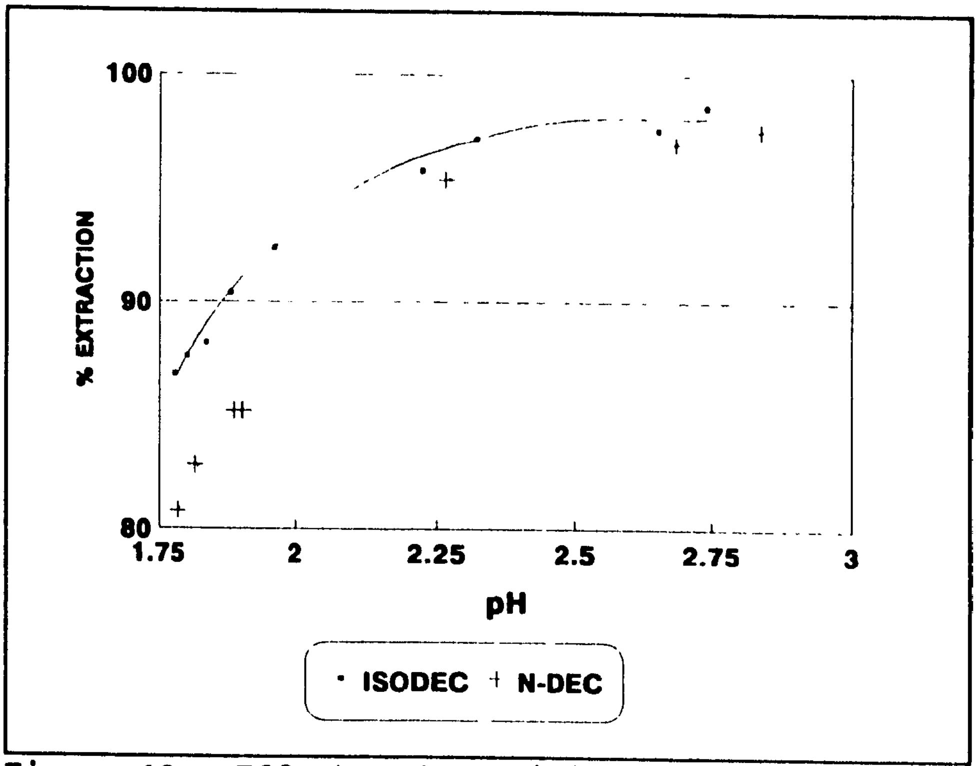

Figure 18: Effect of modifier type on nickel extraction.

6.7. Phase Ratio

For all our batch tests described above, the phase ratio or volume aqueous/volume organic (A/O) was 1.0. When designing a commercial counter-current operation, it is necessary to have equilibrium data from batch tests at several phase ratios. Thus some tests were carried out in which A/O was varied from 1/5 to 5/1. Conditions were chosen based on the best results obtained at A/O of 1, namely 0.30 M OPAP, 10 vol % isodecanol/kerosene, 0.50 g/L initial nickel in aqueous and 10 minute shake. Figure (19) shows percent extraction vs equilibrium pH at each of the phase ratios studied. As expected, extraction increased with decreasing A/O. Clearly, it would be economically impractical to operate at high phase ratios.

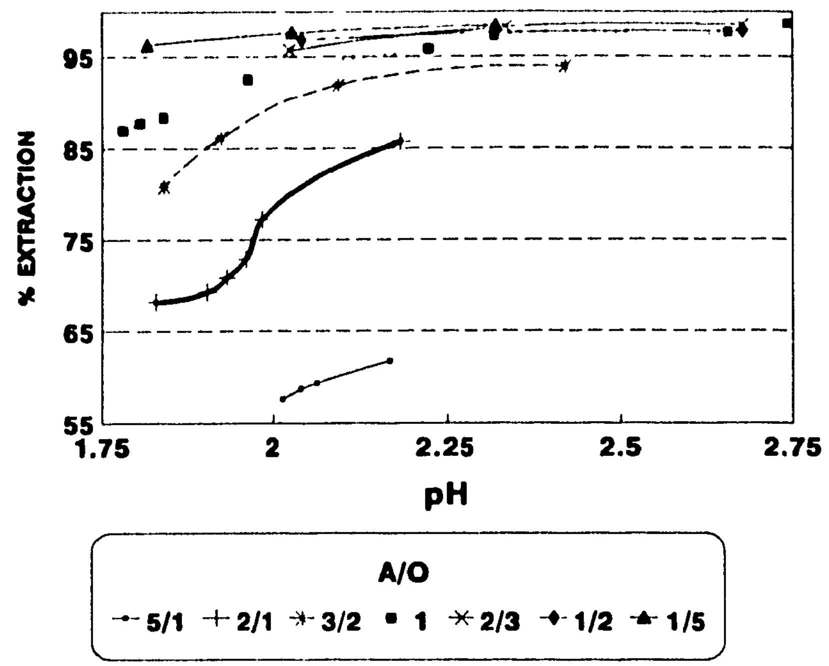

Figure 19: Effect of phase ratio on nickel extraction.

6.8. Initial Nickel Content

In all tests described so far, the aqueous phase initially contained 0.50 g/L Ni^{2+}. Since leach solutions from different sources have differing nickel contents, it is important to obtain data covering a range of initial nickel levels in the aqueous feed. Using 0.30 M OPAP in 10 vol % isodecanol/kerosene and 10 minute shake-outs, tests were carried out with initial aqueous nickel contents of 0.10, 0.25, 0.50, 1.0 and 1.5 g/L Ni^{2+}. Extractions are shown as a function of equilibrium pH in figure (20).

In analysing the results of figure (20), it is convenient to refer to the loading reaction in its simplest form, seen previously in equation (9). $\overline{HR}$ represents OPAP, while possible solvation and polymerization effects in the organic are neglected. From equation (9) and at a given pH under equilibrium conditions, percent nickel extraction would be expected to decrease with increasing initial nickel content in the aqueous phase such that an equilibrium position is maintained. This trend is observed in figure (20), although the effect is obscured at low nickel levels by the scatter of points at 0.25 g/L Ni^{2+} and especially, at 0.10 g/L Ni^{2+}. In these latter two cases, the amounts of nickel remaining in the raffinate are extremely small, and it is difficult to obtain precise analyses with the titration procedure used.

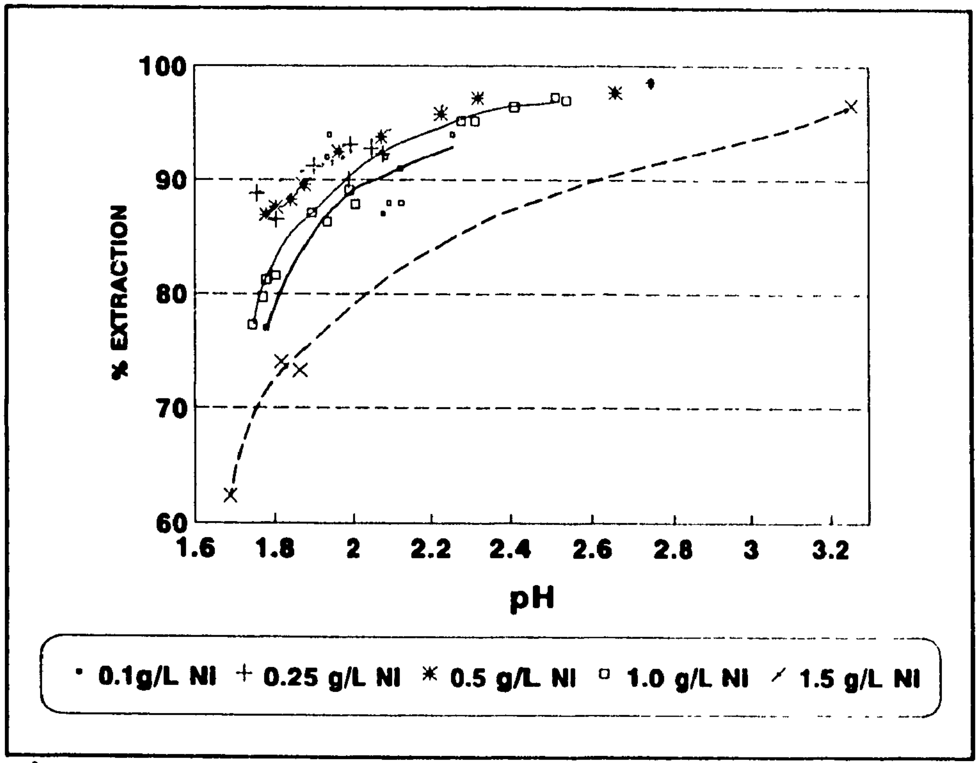

Figure 20: Effect of initial nickel content on extraction.

It should also be noted that the amount of available extractant greatly exceeds that required to load the nickel at all concentrations studied. The maximum OPAP consumption corresponds to complete extraction of 1.50 g/L Ni^{2+} (0.026 M), which would consume 0.052 M OPAP or 17 % of the total OPAP available. The assumption is that 2 moles of OPAP are consumed for every mole of nickel complex formed.

6.9. High OPAP and Nickel Concentrations

Up to this point, the maximum OPAP concentration used had been 0.30 M. Solubility tests showed that extractant amounts giving about 1.0 M OPAP could be dissolved reasonably quickly in 10 vol % isodecanol/kerosene. In solvent extraction, it is commonly observed that the viscosity of the organic phase increases with increasing extractant concentration such that phase mixing and subsequent separation become problematic. Tests were therefore run with 0.60 M OPAP in 10 vol % isodecanol/kerosene to check physical and chemical performance at relatively high extractant concentration. The initial aqueous feed contained 2.0 g/L Ni^{2+} and the phases were contacted for 10 minutes at A/O of 1.0.

The results are presented in figure (21) as percent extraction vs equilibrium pH. Usually sodium hydroxide was used to control pH. However, for the high OPAP concentration used, significant extraction was observed at low pH values (between 1.1 and 1.5), for which sulphuric acid addition was necessary. From a physical viewpoint, the phases mixed readily and subsequent separation was reasonably quick and clean.

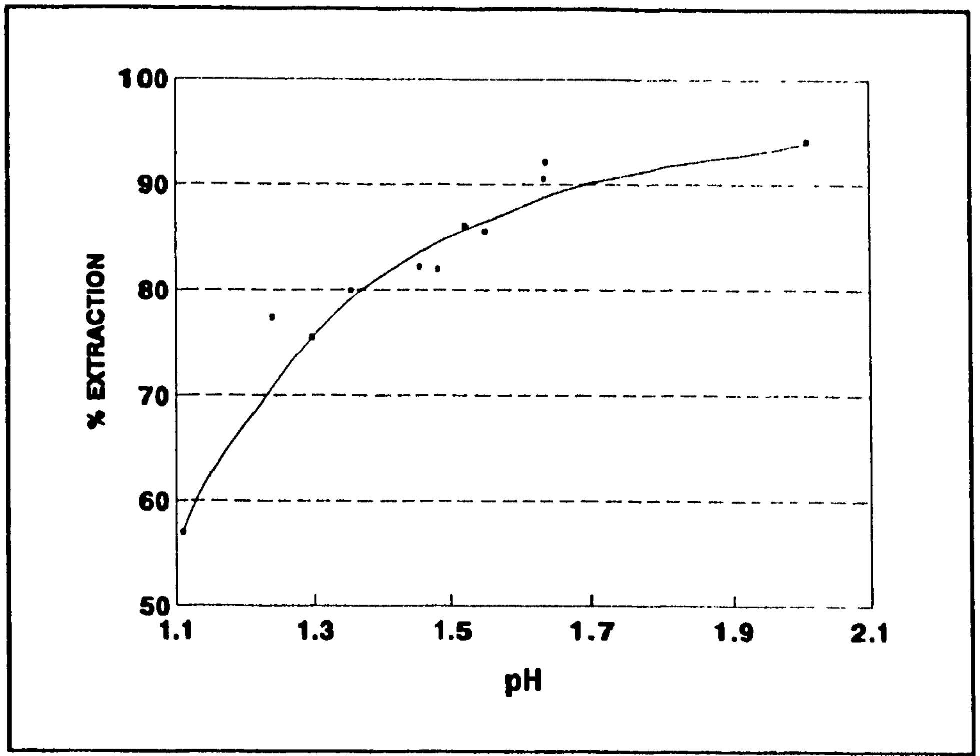

Figure 21: Percent extraction vs pH for 0.60 M OPAP and 2.0 g/L Ni^{2+}.

6.10. Nitrate Environment Extraction

From a practical viewpoint, nickel extraction from an acidic sulphate solution has more industrial relevance than from other acidic media. However, it is sometimes found that complexation between a metal ion and the sulphate anion produces unextractable species and reduced recoveries. It is also generally recognised that the nitrate ion has a lower complex-forming tendency with most common metal ions than does the sulphate ion. In the present work, the influence of nickel-anion complexation was tested by comparing extraction performance in sulphate and nitrate media. Conditions used for this comparison were 0.60 M OPAP in 10 vol % isodecanol/kerosene contacted for 10 minutes with an aqueous phase containing 2.0 g/L Ni^{2+} either as sulphate or nitrate.

Recoveries as a function of equilibrium pH are shown in figure (22). The results show that extractions from a nitrate medium are slightly better than in the sulphate system. Thus, while there is evidence of formation of unextractable complexes in the latter case, this is not a major problem. It should also be noted that phase separation characteristics were generally better in the nitrate than in the sulphate system. Third phase formation was rare and separation time varied from 20 minutes to 115 minutes, roughly increasing with increasing pH value.

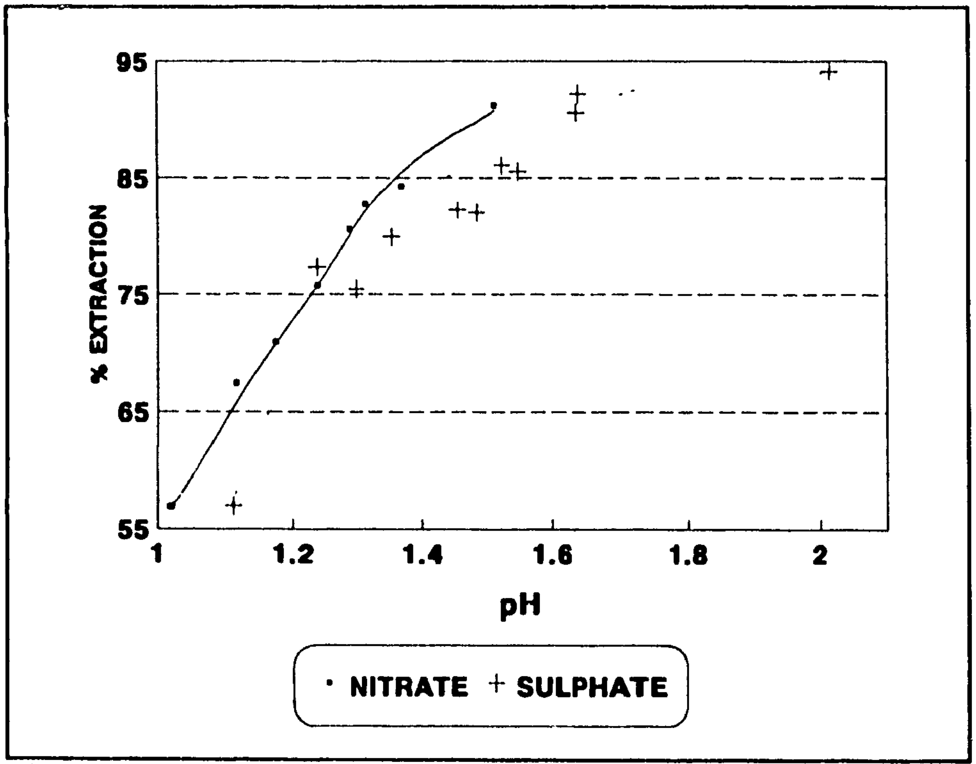

Figure 22: Extraction as a function of sulphate and nitrate media.

6.11. Extraction Using Separated Mono-/Di-OPAP

As described in the Experimental section (Chapter 5) of this thesis, the composition of *as-received* OPAP was determined by potentiometric titration to be 59.9 weight % mono-OPAP and 40.1 weight % di-OPAP.

A series of tests were carried out to determine the relative importance of the mono- and di-OPAP components as extractants. Here, *as-received* OPAP was first separated according to the procedure outlined in appendix (A). The goal was then to compare extraction performance at a constant overall OPAP level, but at different mono-/di-OPAP ratios. The conditions were set at 0.60 M OPAP (targeted level), 10 vol % isodecanol/kerosene, 2.0 g/L Ni^{2+} (initial) aqueous and a 10 minute shake. Extractions obtained for different mono-/di-OPAP ratios vs equilibrium pH are shown in table (11).

First, it can be seen that only a rough idea of the effect of mono-/di-OPAP ratio can be deduced from table (11). It was experimentally difficult to prepare a series of solutions with different mono-/di-OPAP proportions but with a constant overall OPAP level. The actual OPAP contents varied from 0.43 M to 0.71 M. Nevertheless, the general trend is to improve extraction with increasing mono-/di-OPAP ratio. This implies that mono-OPAP is more *acidic* than its di-OPAP counterpart. Therefore, for mono-OPAP, the exchangeable hydrogen atom is replaced more readily by nickel and the position of equilibrium in the extraction reaction lies more in the direction of the products. In fact, optimum composition is approximately that of the *as-received* material (59.9 % mono-OPAP), so that no significant benefit is to be gained by changing the mono-/di-OPAP ratio before nickel extraction. Table (11) shows the expected increase in extraction with increasing pH, at a fixed mono-/di-OPAP ratio.

Table 11: Effect of mono-OPAP content on nickel extraction.

% MONO - M OPAP	pH 1.0	pH 1.2	pH 1.4	pH 2.0
15.1 % - 0.43 M	18 %	30 %	42 %	54 %
56.0 % - 0.55 M	68 %	78 %	85 %	92 %
59.6 % - 0.71 M	72 %	84 %	90 %	96 %
65.9 % - 0.60 M	79 %	89 %	92 %	95 %
69.3 % - 0.56 M	80 %	90 %	95 %	98 %
84.4 % - 0.56 M	76 %	84 %	88 %	93 %

6.12. Stripping

Before nickel can be recovered as metal, the loaded organic must be stripped. This would give a pure nickel-containing aqueous solution from which metal would be obtained, most probably by electrowinning. In the cation exchange system of present interest, the conventional stripping method is to contact the loaded organic with a sulphuric acid solution of sufficient concentration to reverse the loading reaction.

The stripping behaviour of nickel-loaded OPAP was tested by first loading 0.60 M OPAP in 10 vol % isodecanol/kerosene from a 2.0 g/L Ni^{2+} aqueous phase. Different extraction levels were obtained through pH control. Loaded organic was stripped with

0.5 M, 1.0 M or 2.0 M H_2SO_4 at A/O of 1. It was assumed that equilibrium would be reached as rapidly in stripping as in loading since both steps involve the same reaction, but proceeding in opposite directions. Thus, a 10 minute contact time was considered sufficient.

The results are shown in table (12). Here, the percent stripped values are based on the amount loaded as representing 100 %. At the 90 % extraction level, loaded organic can be completely stripped with only 0.5 M H_2SO_4. This is compatible with electrowinning, because many base metal (Cu, Ni, Co, Zn) electrolytes contain about 1.5 M H_2SO_4. It should also be noted that nickel concentration in the electrolyte would have to be higher than either the loaded organic or aqueous feed. Thus, in a commercial process, the A/O in stripping would have to be less than 1.0. However, the ease with which OPAP could be stripped in the present tests suggests that A/O values below 1.0 would readily give acceptable recoveries.

Table 12: Stripping results

EXTRACTION	STRIPPING		
	0.5 M H_2SO_4	1.0 M H_2SO_4	2.0 M H_2SO_4
80 %	84 %	95 %	96 %
85 %	88 %	95 %	100 %
90 %	100 %	100 %	100 %

Phase separation following weak (0.5 M) acid strips was slower (30 to 120 minutes) than for more strongly acidic conditions (5 to 15 minutes). Although 0.5 M H_2SO_4 may be adequate for high recoveries, more concentrated acid is required for rapid phase separation.

6.13. Age of Organic Solution

From the experience gained during the tests leading to table (12), it was suspected that the age of the organic solution was affecting its performance. Organic solutions that were made and used immediately behaved differently from those which were stored and then used later. The extraction/stripping tests were initially carried out with some leftover aged organic solution and then repeated and continued using a fresh organic solution. The older organic solution, when compared to the fresh solution, yielded similar extraction values but with lower quality separations. For example, following 85 % extraction (Table 12) with aged organic, separation required about 3 hours. The same test required only about 50 minutes (between 25 and 75 minutes) for separation when using fresh organic solution. This phenomenon was the driving force behind answering the following two questions. Is nickel extraction and phase separation affected by (1) the age of the organic solution and (2) the environment of the aged organic during storage?

To answer these questions, the performance of three solutions of identical composition, were compared following storage under different conditions. Each solution was made up as 0.60 M OPAP in 10 vol % isodecanol/kerosene. The first was stored for 2 months in a dark and closed container. The second was stored for 2 months but left out in regular light and occasional sunlight. The third represented a fresh solution with immediate usage. All three were then contacted with a 2.0 g/L nickel aqueous solution. The results are seen in figure (23), which shows percent extraction vs equilibrium pH.

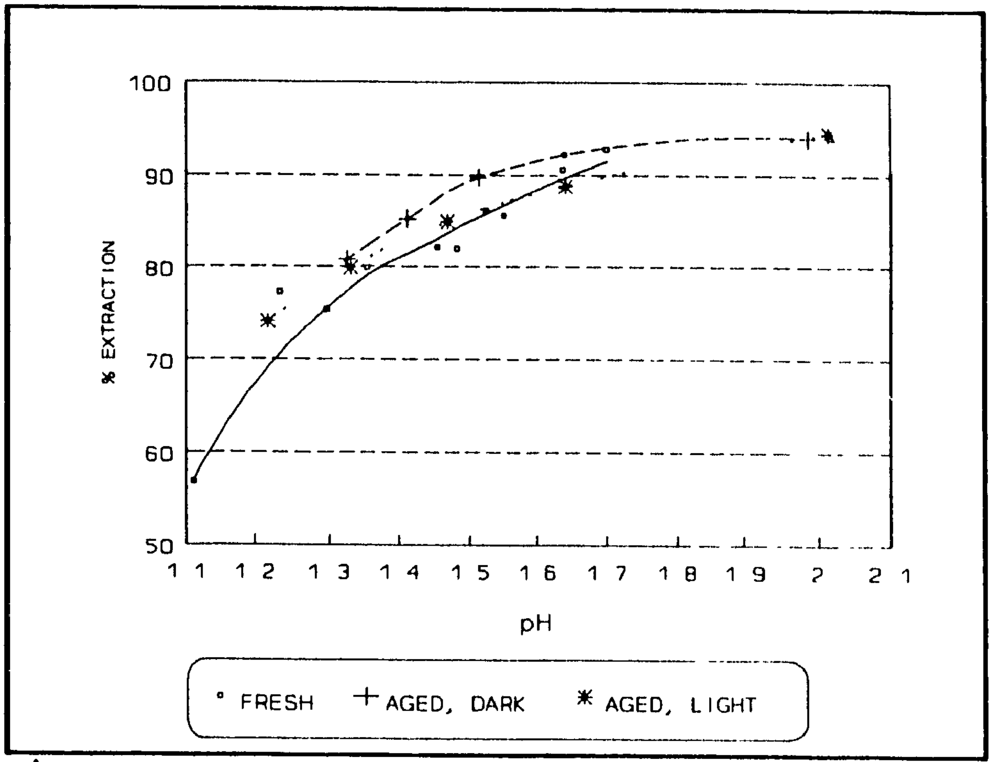

Figure 23: Effect of organic age on nickel extraction.

As expected, extraction values at fixed pH are approximately the same for all three solutions. The solution stored in darkness gave the highest extraction, but only about 5 % more at any given pH. The effect of both aging and light had no beneficial or detrimental effect on nickel extraction. The differences arose in phase separation characteristics after contact. With fresh organic, the phases separated after about 10 minutes when nickel extraction was low (< 85 %), and after 2 hours at high extraction

(> 95 %). The aged solutions, regardless of environment, took much longer to separate: between 2 and 7 hours depending on extraction level. The passage of time weakens the positive effect isodecanol has on improving phase separation, but the reasons for this are not immediately apparent.

6.14. Reaction Stoichiometry (*Slope Analysis*)

The distribution coefficient, D, is defined as the concentration of metal in the organic phase divided by the concentration of metal in the aqueous phase at equilibrium [8,16]. It can be expressed as both an extraction or a stripping coefficient. The value of D is increased with increasing extractant concentration and increasing pH. For extraction, the reaction can be expressed as equation (15).

$$M^{n+} + (n+s)\overline{HR} \rightarrow \overline{MR_n\cdot sHR} + nH^{+}$$

$$\text{Thus} \quad K = \frac{[\overline{MR_n\cdot sHR}]\,[H^{+}]^{n}}{[M^{n+}]\,[\overline{HR}]^{(n+s)}} \qquad (15)$$

$$\text{and} \quad \log D = (n+s)\log\,[\overline{HR}] + \log K + n\,pH$$

The calculation of D assumes that a mass balance between the metal in the aqueous and organic phase exists. This assumption is not held under certain conditions [8]:

(i) If a volume change occurs upon shaking of the two phases. This does not occur in the present work as the volumes of both phases were measured before and after shaking and no difference existed.

(ii) If a third phase is formed. This occurred at times, particularly at low modifier contents and extractions close to 100 %, where separation quality suffered.

(iii) If crud or precipitate is formed. This only occurred in situations where pH values unintentionally rose above a value of 6.

A plot of log D vs pH (constant $\overline{HR}$) yields a slope equal to the number of molecules of extractant, n, associated with a metal atom in the extracted species [8]. Alternatively, a plot of log D vs log $\overline{HR}$ (constant pH) gives a slope equal to (n+s), where s is the solvation number. This form of slope analysis provides a simple and quick way of obtaining the stoichiometry of the extracted species. The analysis fails if the slope deviates, which occurs if [11]:

(i) Species other than Ni^{2+} are extracted. Speciation diagrams have shown that Ni^{2+} is the predominant cation for nickel sulphate systems, as discussed in appendix B.

(ii) Activity is not equal to concentration. This is important because the equilibrium constant should be derived using activities instead of concentrations. The assumption holds well when dealing with dilute metal content solutions but worsens as the metal concentration increases [8]. Activities can change substantially with increasing metal concentration. This is why fundamental studies are normally done at low metal concentrations, as in the present work.

To minimize this deviation, the total ionic strength of the aqueous phase is often maintained at a constant value, irrespective of the metal concentration. This is accomplished by the addition of an electrolyte, usually a sodium salt, which is not extracted, thus maintaining a constant metal ion activity coefficient. According to Brisk and McManamey [40], maintaining a constant ionic strength through the separate addition of an electrolyte is unnecessary. The authors maintain that the alkalis (NH_4OH and NaOH) added to adjust the hydrogen ion concentration (pH) tended to keep the ionic strength approximately constant for any particular initial metal and D2EHPA concentration [40]. Therefore, the NaOH used for pH control in the present tests ensures an ionic strength that is approximately constant, therefore minimizing the effect of activity/concentration difference.

(iii) Equilibrium is not reached. Kinetic tests have shown that equilibrium is achieved within minutes.

(iv) Extractant concentration drops significantly. Excess extractant concentration was used for all extraction tests to prevent this from occurring. For example, in using 2.0 g/L nickel (or 0.034 M), twice this amount, or 0.068 M, of extractant is required for complete extraction. Since in this test 0.60 M extractant was added, at most only 11.4 % of the organic extractant can be used up.

(v) Non-extractable species form due to polymerization, complex formation or hydrolysis. The formation of these nonextractable complexes will reduce the distribution coefficient and thus give rise to a curved plot instead of a line. As shown in appendix (B), there is the possibility of some unextractable $NiSO_4$ forming in the present system.

6.14.1. Sulphate Media Slope Analysis

Slope analysis was applied to log D vs pH curves where $\overline{HR}$ was in large excess. This was carried out on the D2EHPA tests for nickel extraction values falling between 5 % and 85 %. Points outside this range causes the slope to distort due to analytical uncertainty beyond these two extremes. The 0.20 M D2EHPA/0.5 g/L nickel tests yielded a slope of 1.66 with a correlation of 0.9944. The 0.60 M D2EHPA/2.0 g/L nickel tests yielded a slope of 1.63 with a correlation of 0.9970. Although the values fall short of the expected slope of 2, they are very consistent with each other, producing essentially the same slope values (figure 24). The deviation from the value of 2 is common for sulphate systems where complex formation or polymerization occurs [26]. Brisk studied the distribution of Ni^{2+} between an aqueous sulphate solution and a kerosene organic solution of D2EHPA. Brisk reported that the deviation in slope was attributed to the hydrolysis of metal in the aqueous phase [40].

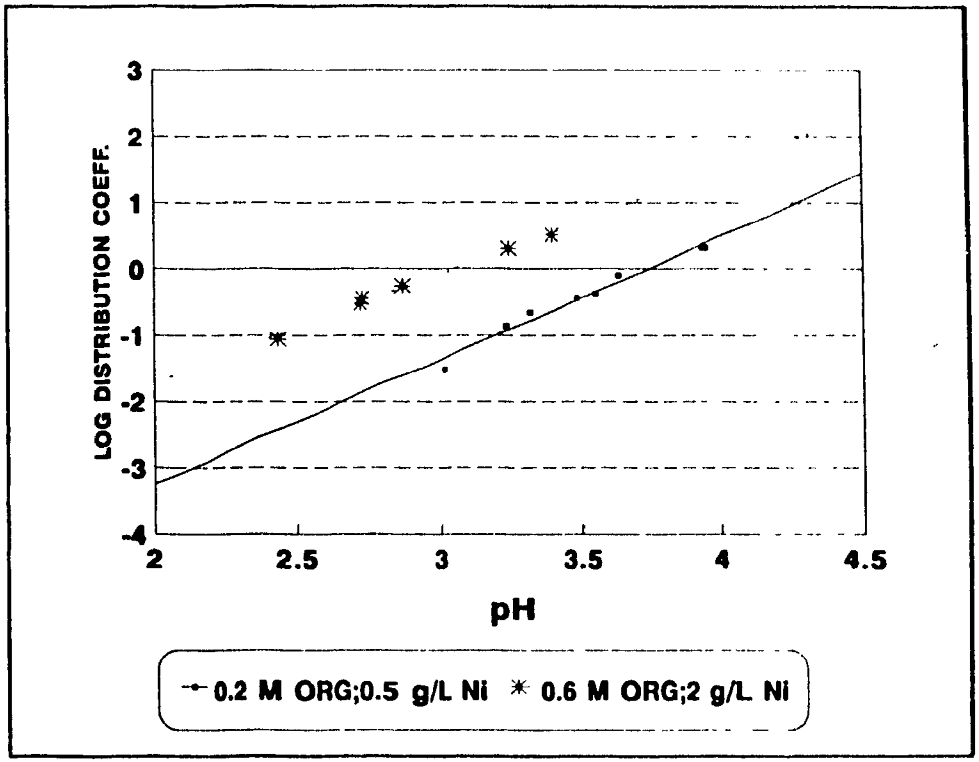

Figure 24: Log D vs pH for different D2EHPA concentrations.

Turning our attention to OPAP, slope measurements were carried out using the data from percent extraction vs pH at various excess extractant concentrations. Using only points below 85 % extracted nickel, the slopes obtained were 1.56, 1.61, 1.58 and 1.39 for the 0.15 M, 0.21 M, 0.26 M and 0.31 M OPAP tests respectively (Fig. 25). In each case, the calculated correlation was above 0.985. Except for the slope obtained at 0.31 M OPAP, the slope values are very similar to those obtained from the D2EHPA tests.

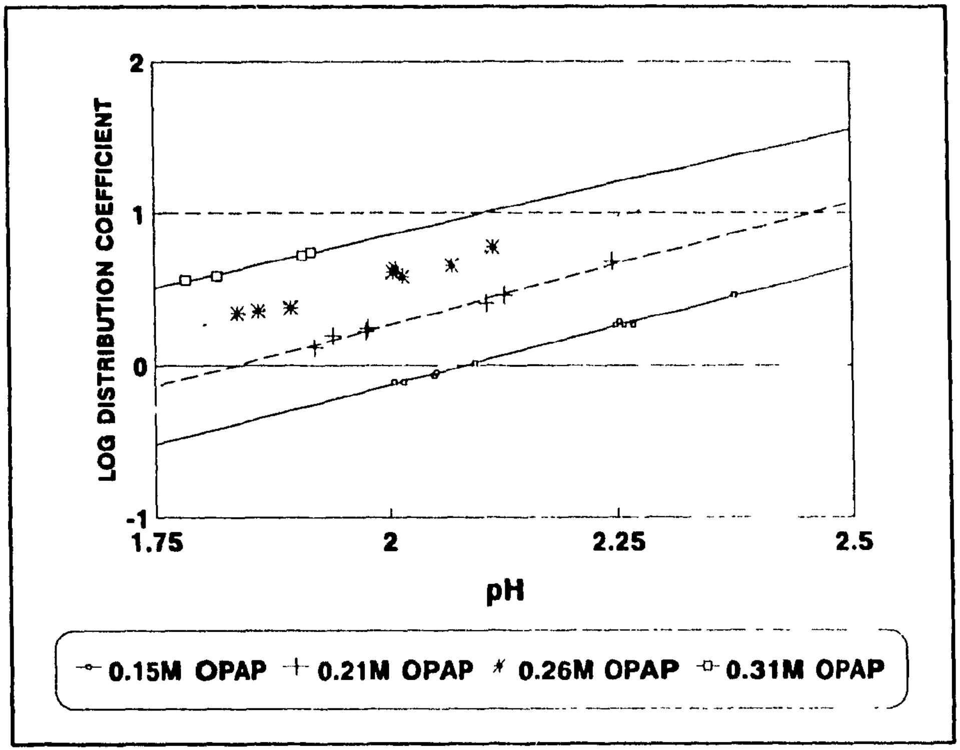

Figure 25: Log D vs pH.

The second slope analysis carried out was by plotting distribution coefficient against OPAP concentration, both on a logarithmic scale (Fig. 26). Using the 4 OPAP concentrations defined above, the plot was prepared for a fixed pH value of 2 where the slope represents $n+s$. Ideally, n should be 2 and the solvation number also an integer. The slope obtained from figure (26) is 3.34. This would imply a solvation number of

1.7 (=3.3-1.6) or approximately 2. The value of *s* has not been measured previously for nickel sulphate/OPAP extraction, but s=2 has been frequently observed in other metal/organophosphorous extractant systems.

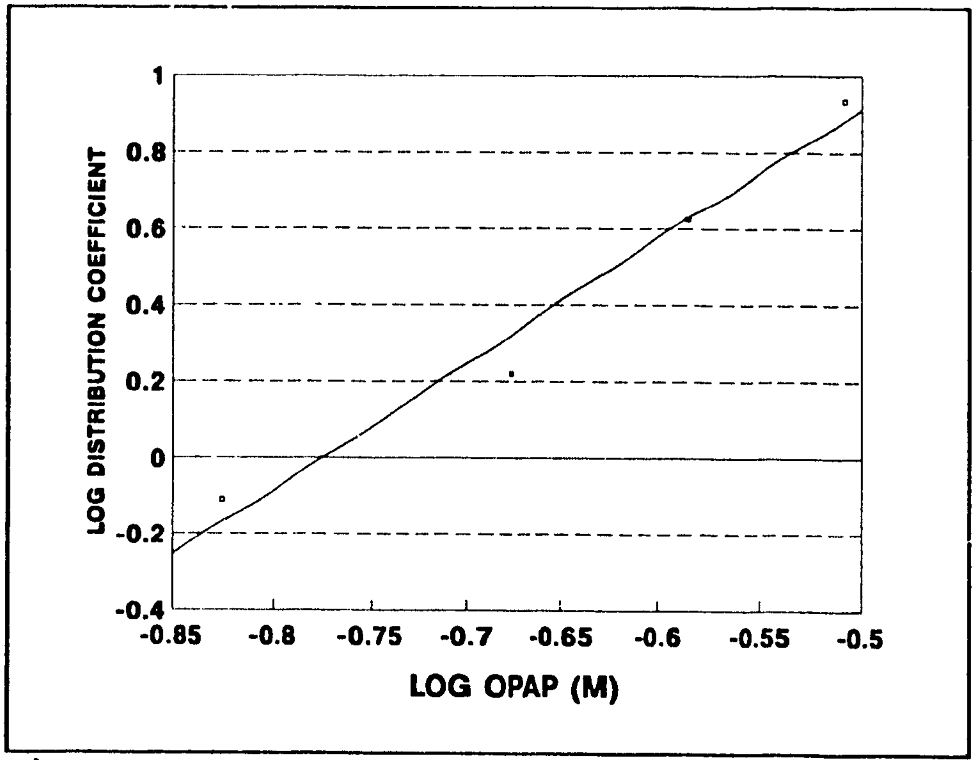

Figure 26: Log D vs OPAP concentration at pH 2.

6.14.2. Nitrate Media Slope Analysis

All slopes derived from log D vs pH plots obtained from sulphate media produced values well below the expected value of 2. The slopes varied between 1.39 and 1.61, averaging 1.54. There are several factors that can cause a slope to deviate, as outlined in section 6.14. All the factors listed, except for the effect of non-extractable species forming, can be dismissed. To verify if non-extractable species due to complex formation in the aqueous phase is the cause of the deviation in slope, nickel extraction tests were carried out in a nitrate environment instead. It is generally recognized that simple ions, such as Ni^{2+}, are less prone to complexation by NO_3^- than by SO_4^{2-} ion. According to Sekine and Hasgawa [41], polymerization of the extractant is minimized in the presence of nitrate solutions.

Tests in nitrate solution were carried out under conditions that allowed direct comparison with equivalent tests in a sulphate medium (2.0 g/L Ni^{2+} and 0.60 M OPAP). Nickel extractions showed a slight improvement in nitrate over sulphate media (Section 6.10). More importantly however, is a comparison of the slopes of the log distribution vs pH plots (Fig. 27). While the slope for this test in a sulphate medium is 1.34, the test in a nitrate solution yielded a slope of 1.78, using points below 85% extraction.

Although the slope in nitrate media is not exactly 2, the increase from 1.34 to 1.78 by shifting from sulphate to nitrate media suggests that complex formation in the former case is reducing extraction. This deviation is due to the formation of non-extractable species, such as $NiSO_4$ (appendix B). The remainder of the deviation can be attributed to experimental error and the error involved in using concentration instead of activity values in the organic phase.

6.15. Selectivity of Extraction

6.15.1. Nickel and Manganese - Limonite Ore Processing

To simulate a leach liquor obtained from a limonite ore body, an acidic sulphate solution containing nickel and manganese was required. If nickel can be extracted

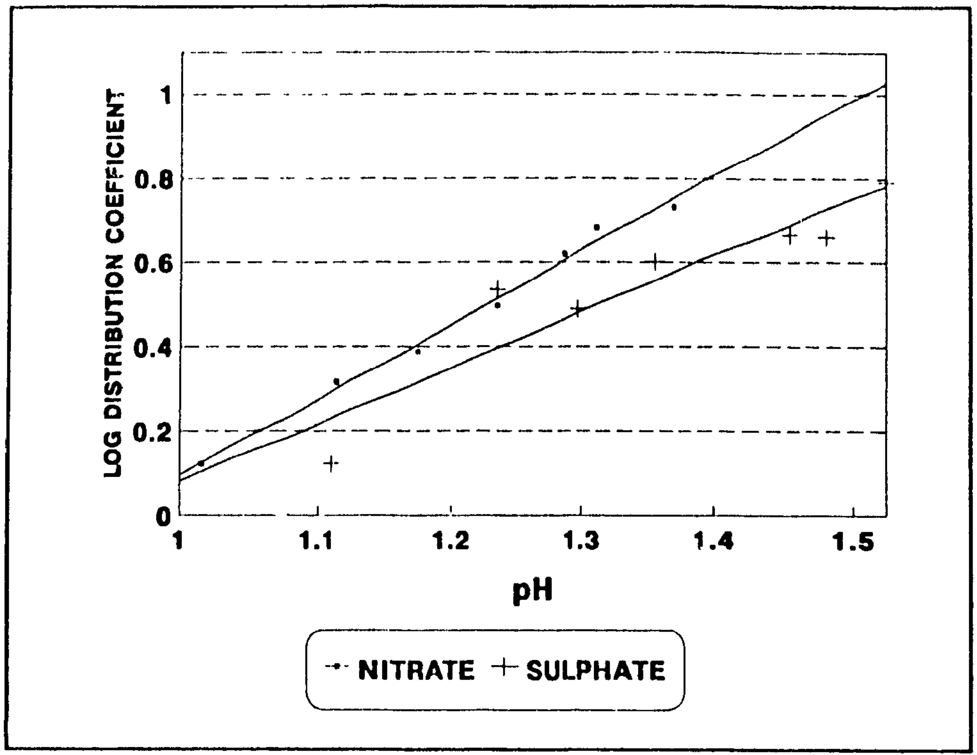

Figure 27: Comparison of log D vs pH for sulphate and nitrate media.

preferentially over manganese, then a direct industrial application exists for OPAP in extracting nickel from limonite leach liquors. An INCO leach liquor, containing many metals, was used to carry out this nickel and manganese extraction study. Since the solution contains many metals, the titration procedure previously used is no longer applicable. Instead, atomic absorption was chosen in the analysis of nickel and manganese contents.

A 0.40 M OPAP - 10 vol % isodecanol solution was prepared and contacted with the leach solution, containing 4.0 g/L Ni^{2+} and 2.0 g/L Mn^{2+}. The reason that the extractant concentration is no longer in large excess of the metal content (48 % unused extractant) is because *slope analysis* is not a concern for these tests. The loaded organic was then contacted with a 4 M HCl stripping solution. Both the raffinate and the stripped solution were analyzed for nickel and manganese content.

The extraction curves for both metals are shown in figure (28) while the stripping results are listed in table (13). Manganese is preferentially extracted over nickel throughout a pH range of 1 to 7. The lone point in figure (28) represents a typical nickel extraction value when metal competition does not exist. Therefore, at pH 1.5, nickel extraction drops from about 82 % to 15 % in the presence of manganese.

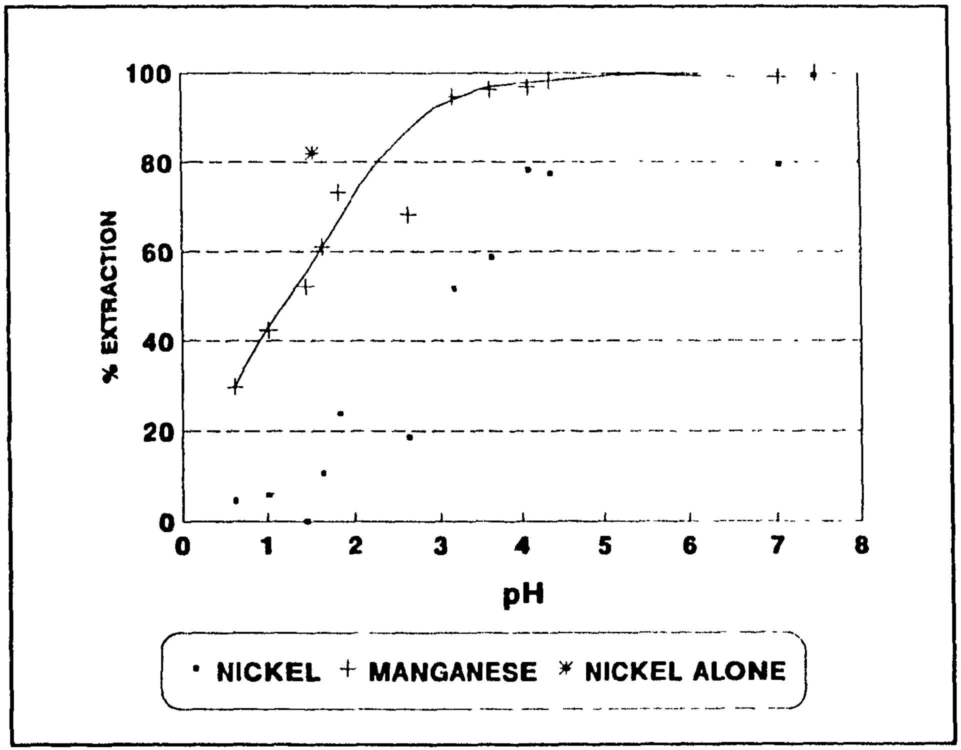

Figure 28: Nickel and manganese extraction from limonite leach liquor.

Table 13: Nickel and manganese stripping results.

EXTRACTION OF RESPECTIVE METAL	Ni STRIPPED: % OF EXTRACTED METAL	Mn STRIPPED: % OF EXTRACTED METAL
30 %	69 %	76 %
50 %	65 %	99 %
70 %	57 %	90 %
80 %	50 %	84 %
90 %	36 %	80 %

In stripping, the metals behave differently in that at a given percent extraction level, manganese is much more readily stripped than nickel. This effect was not further explored since the original objective of selective nickel extraction over manganese was not achieved.

6.15.2. Nickel and Magnesium - Serpentine Ore Processing.

Similar to the limonite test, to simulate a leach liquor obtained from a serpentine ore body, an acidic sulphate solution containing nickel and magnesium was required. If nickel can be extracted preferentially over magnesium, then a direct industrial application exists for OPAP in extracting nickel from serpentine leach liquors. For this purpose, a laboratory solution was made containing only nickel and magnesium sulphate. As before, atomic absorption was used for the nickel and magnesium content measurements.

A 0.40 M OPAP - 10 vol % isodecanol/kerosene solution was prepared and contacted with the leach solution, containing 4.0 g/L Ni^{2+} and 3.0 g/L Mg^{2+}. The extraction curve is shown in figure (29) and the stripping results in table (14). Magnesium was extracted preferentially over nickel. The lone point in figure (29) represents a typical nickel extraction value when no other metal competition exists. Therefore, at pH 1.5, extraction drops from about 82 % to 25 % nickel extraction in the presence of magnesium competition.

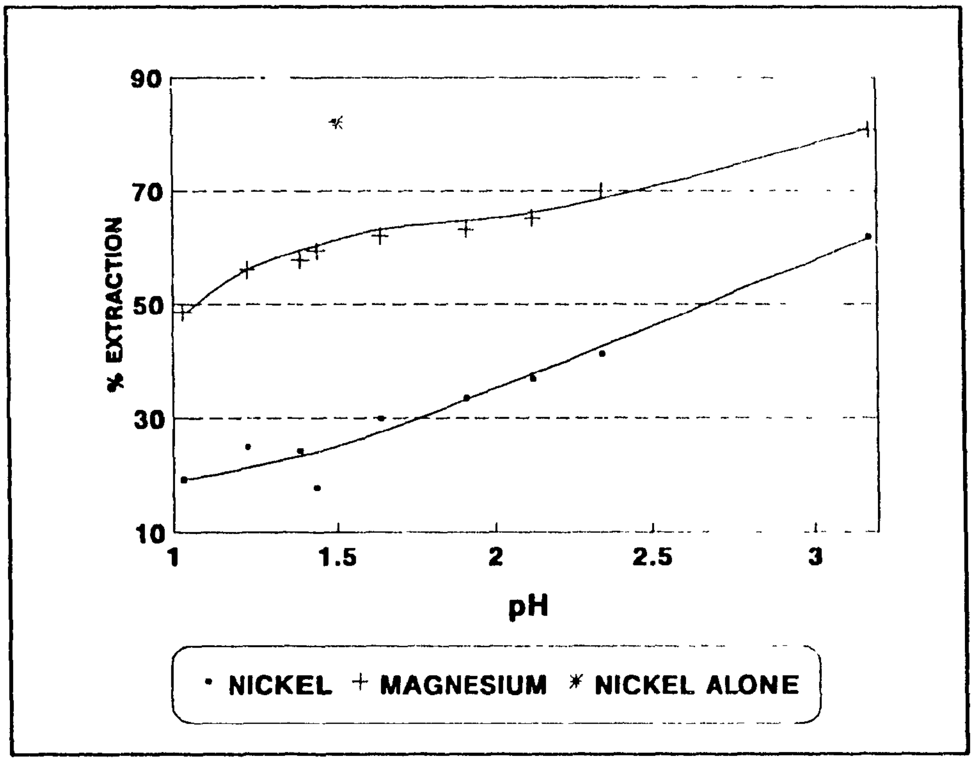

Figure 29: Nickel and magnesium extraction from synthetic serpentine leach liquor.

Table 14: Nickel and magnesium stripping results.

EXTRACTION OF RESPECTIVE METAL	Ni STRIPPED: % OF EXTRACTED METAL	Mg STRIPPED: % OF EXTRACTED METAL
20 %	43 %	---
25 %	30 %	---
30 %	35 %	---
50 %	65 %	25 %
55 %	65 %	20 %
60 %	64 %	25 %
80 %	---	43 %

In stripping, the metals again behave differently. At a given percent extraction level, nickel is more easily stripped than magnesium, this being the reverse behaviour to that experienced with the nickel/manganese pair. Again, further work on stripping behaviour was not worthwhile due to lack of selectivity for nickel extraction.

CHAPTER 7

Conclusion

The purpose of this work was to determine the ability of octyl phenyl acid phosphate (OPAP) to extract nickel from highly acidic, dilute sulphate solutions. First, the presence of a modifier (iso or n-decanol) in the organic phase is essentially for two reasons. This additive raises the solubility of OPAP in the kerosene diluent to levels at which a commercial process would be technically feasible. Also, phase separation characteristics are greatly improved with modifier addition, especially at high extraction levels where third phase formation and its subsequent breakdown seriously impede phase separation if modifier is absent. However, some decrease in extraction results from modifier addition. It was also noted that aged modifier was less effective than fresh modifier in improving phase separation properties.

Nickel is extracted by a cation exchange reaction, in which extraction increases with increasing pH. The reaction is rapid, and equilibrium was reached within 10 minutes for all conditions tested. Typical results are represented by data for extraction from 2.0 g/L Ni^{2+} aqueous phase into 0.60 M OPAP in 10 vol % isodecanol/90 vol % kerosene. After a 10 minute contact at room temperature and phase ratio of 1.0, nickel extraction increased from 65 % at pH 1.2 (i.e. strongly acidic) to 85 % at pH 1.5 and 90 % at pH 2.0. With commonly used organophosphorous reagents, pH values much higher than 2.0 would be needed for 90 % nickel extraction. Nickel can be readily stripped from OPAP using 1.0 M H_2SO_4, a suitable level for electrowinning.

The slope analysis method of determining reaction stoichiometry indicates that the extracted species is an OPAP/nickel complex with molar ratio 1.54. This decrease from the expected value of 2.0 is partially due to formation of an unextractable $NiSO_4$ complex. When the aqueous environment was changed from SO_4^{2-} to NO_3^-, this stoichiometry ratio increased to 1.78, which is consistent with the lower complexing power of the NO_3^- over the SO_4^{2-} ion.

While nickel can be extracted at much higher acidity than previously found possible for organophosphorous extractants, nickel cannot be extracted selectively over the common impurities manganese and magnesium. The potential for selective extraction over other common impurities (e.g. Fe, Cr, Al, Ca, etc.) is a major subject for future work.

APPENDIX A

Separation of Mono-OPAP and Di-OPAP

The separation procedure was developed and reported by Mihaylov [36] and is reproduced here.

> The method is based on the fact that monoalkyl phosphoric esters can be separated from dialkyl phosphoric esters by selective precipitation as barium salts. The procedure, adopted here, differs from the one proposed for D2EHPA and M2EHPA separation in the preparation of the homogeneous OPAP-containing solution before the addition of soluble barium salt solution as well as in treatment of the filtrate after precipitation.
>
> A sample of 27g OPAP is taken and fully dissolved in 300ml acetone (reagent grade) under continuous stirring. Then 180ml distilled water are added. The obtained solution is clear, with pH of 1.3-1.4. Small portions of 2M NaOH are then slowly added under stirring until pH reaches a value of 11.4-11.5. Up to this point, the procedure is, in fact, a potentiometric titration of the OPAP sample, and it is intended to be so, because the purpose is to obtain full dissociation of mono-OPAP. The choice of end pH value here is based on pH of the second equivalent point-for mono-OPAP (i.e., pH 11.0-11.1), as determined from the

titration curve. Both di- and mono-OPAP dissociate, di-OPAP:

$$(CH_3(CH_2)_6CH_2C_6H_4O)_2P(O)OH \rightarrow (CH_3(CH_2)_6CH_2C_6H_4O)_2P(O)O^- + H^+$$

and mono-OPAP-first,

$$CH_3(CH_2)_6CH_2C_6H_4OP(O)(OH)_2 \rightarrow CH_3(CH_2)_6CH_2C_6H_4OP(O)(OH)O^- + H^+$$

and second dissociation:

$$CH_3(CH_2)_6CH_2C_6H_4OP(O)(OH)O^- \rightarrow CH_3(CH_2)_6CH_2C_6H_4OP(O)(O)_2^- + H^+$$

The solution is still visibly clear though with a slight yellowish colour. Under continued stirring (but with pH electrode now removed), a slow addition of 60ml 0.5M $BaCl_2$ solution starts. Immediately a white precipitate of barium mono-OPAP salt forms. The amount of $BaCl_2$ is approximately half that required for full mono-OPAP precipitation based on stoichiometry. If more is added, coprecipitation of the respective di-OPAP salt will become significant.

The precipitate is filtered (preferably with the help of vacuum) and collected (precipitate I). Filtration here is difficult because of slow formation of viscous organic liquid ('third phase'), heavier than water, containing mostly di-OPAP. Its formation is probably due to salting-out effects. It reports into the filtrate and can be then readily separated. After doing so, a new portion of 0.5M $BaCl_2$ solution is added to the filtrate in order to precipitate completely the rest of mono- and di-OPAP. This second precipitate is filtered more easily (precipitate II).

Each precipitate is transferred into a separatory funnel and then di-ethyl ether is added in. Any water, if present, easily separates and is removed. The mixture in the funnel is then contacted with a 1M HCl solution, the white precipitate disappears-barium (and sodium) is stripped and the extractant is thus regenerated. A second contact with HCl solution follows in order to assure complete stripping-the acid solution is then checked for presence of Ba^{2+} by testing with soluble sulphate.

The same procedure is followed for the organic liquid ('third phase'), separated from the first filtrate-it is readily dissolved into di-ethyl ether, and then the extractant is regenerated by contacting with HCl solution.

The ether solutions are then washed several times with distilled water in order to remove any acid remaining. Finally, the ether evaporated to leave the extractant, containing mono- and di-OPAP in different proportions.

APPENDIX B

Nickel Speciation Diagrams

In general, the only oxidation state for nickel of interest is Ni(II). Under certain conditions, other oxidation states are possible, ranging from 0 to 4+. These oxidation states will not be considered in the speciation analysis.

The nickel sulphate-sulphuric acid-water system exhibits species that originate directly from the constituent species such as Ni^{2+}, SO_4^{2-}, $NiSO_4(aq)$, H^+, H_2SO_4, HSO_4^- and OH^-. Once in solution, nickel hydroxides may also be present in the form of $NiOH^+$, $Ni_4(OH)_4^{4+}$, $Ni(OH)_2(aq)$ and Ni_2OH^{3+}. The system is comprised of the above 10 species (OH^- and H^+ are interrelated and therefore count as only one species).

The exact procedure for the construction of a speciation diagram is lengthy and has been studied in detail elsewhere [42]. The result of this study is shown in figure (A). Mathematically, the amount of nickel sulphate was kept constant at 0.01 M while the amount of sulphuric acid was gradually increased. The free nickel ion is the dominant species throughout the entire pH range but 20 % to 30 % of the nickel species formed are in the form of $NiSO_4$, an unextractable nickel complex.

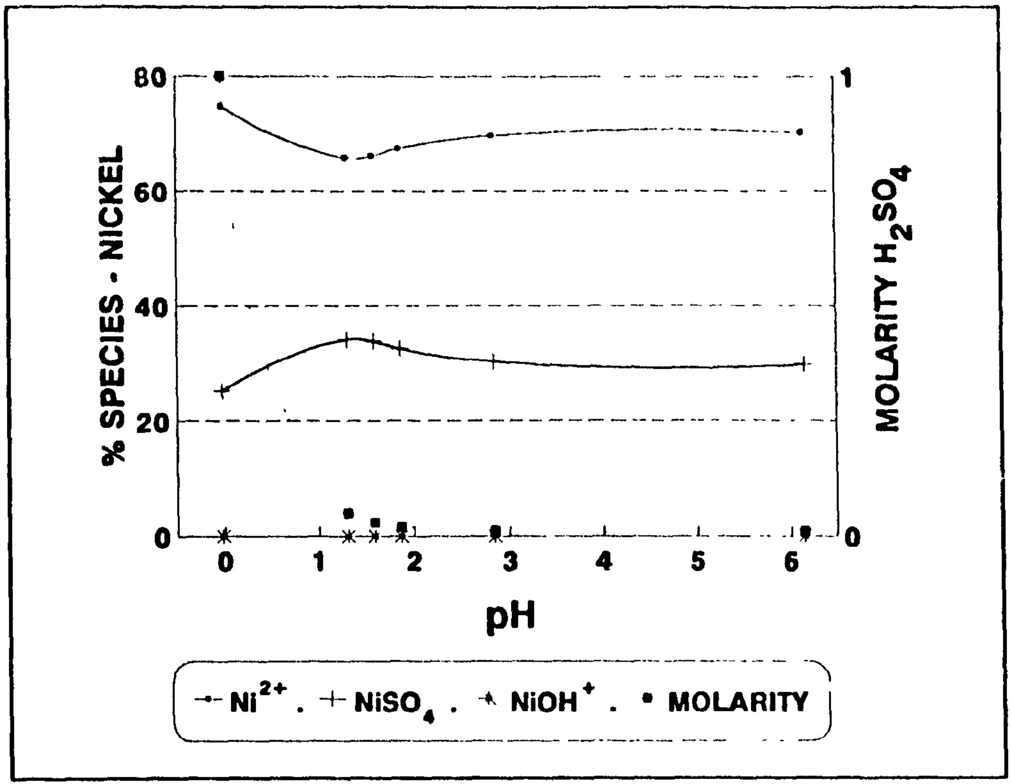

Figure A: Speciation diagram for $NiSO_4$-H_2SO_4 solution.

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