Western Australian School of Mines

Department of Minerals Engineering and Extractive Metallurgy

The Solvent Extraction Behaviour of Chromium with Bis(2,4,4-trimethylpentyl) Phosphinic Acid (Cyanex® 272)

Matthew Derek Lanagan

This thesis is presented as part of the requirements for the award of Degree of Doctor of Philosophy of Curtin University of Technology.

2002

The work contained in the thesis was completed at Curtin University of Technology, Western Australian School of Mines between February 1999 and March 2002. The thesis contains no material that has been accepted for the award of any other degree or diploma in any university. To the best of my knowledge and belief the thesis contains no material previously published by any other person except where due acknowledgment has been made.

ABSTRACT

The bulk of the world's known nickel reserves are contained in laterite ores but sulphidic ores remain the main source of the Western world's nickel production. With the continuing increase in nickel consumption and the depletion of sulphidic ores, the traditional source of nickel, the extraction of nickel from lateritic ores has been the subject of research interest worldwide. Advances in pressure acid leaching (PAL) technology have resulted in significant commercial attempts to extract nickel from these ores.

Leaching the ore with sulphuric acid at elevated temperatures and pressures allows almost complete dissolution of the nickel and cobalt, a valuable by-product of these ores, but yields highly contaminated pregnant leach solutions. Separating and purifying the nickel and cobalt from these solutions remains a hindrance to full commercial production.

Several purifying techniques have been commercialised but all suffer from continuing technical problems. Among them, however, the direct solvent extraction (DSX) technique offers several advantages. Direct solvent extraction involves the separation of the nickel and cobalt directly from the partially neutralised pregnant liquor stream (PLS) by solvent extraction with Cyanex® 272 as the extractant. However certain contaminants adversely affect the solvent extraction process. Among them is chromium and little is known about the solvent extraction behaviour of this metal.

The present work investigated the solvent extraction of chromium with Cyanex® 272. It was found that the solvent extraction behaviour of chromium(III) and chromium(VI), both of which could be found in PAL-generated PLS, are distinctly different. For chromium(III), solvent extraction tests showed that (a) it is extracted in the pH range 4-7; (b) the extraction is partly influenced by diffusion; (c) the apparent equilibration time is significantly longer than most transition metals; (d) increases in temperature from 22 to 40 °C resulted in increases in the

extraction; (e) the $pH_{0.5}$ increases in the order nitrate < chloride < sulphate in the presence of these anions; (f) the presence of acetate depresses extraction of chromium(III) when the solution is allowed to stand before extraction; (g) in the PLS, chromium(III) precipitated at lower pH than that predicted by the solubility product principle; and (h) the $pH_{0.5}$ decreases as the Cyanex® 272 concentration increases.

Chromium(III) is initially extracted by solvation of its inner sphere complex, which then undergoes further reaction in the organic phase leading to the formation of a much more stable species that is difficult to strip. A reaction scheme together with a description of both the initially extracted and resulting stable species is proposed.

Extraction of chromium(VI), on the other hand, (a) occurs at pH less than 2 by solvation of chromic acid; (b) is independent of the aqueous phase composition; (c) does not occur in the pH range (3–6) used in the separation of nickel and cobalt. The latter is irrespective of temperature up to 40 °C, the use of industrial PLS as the aqueous phase or the presence of an anti-oxidant in the organic phase.

The stripping of chromium(III) from a loaded organic phase can be achieved using 1–4 $mol\ L^{-1}$ mineral acids provided the stable organic species have not formed making industrial scale stripping of chromium(III) from Cyanex® 272 difficult. The exact composition of the aqueous phase during extraction affects the stripping efficiency.

PROFESSIONAL ACKNOWLEDGEMENTS

D C Ibana, my supervisor, for his guidance throughout this project.

E J Grimsey, Director of WASM, for his encouragement and support of the project.

P Hosking, G Laing and G Frampton of Bulong Nickel Operation for their interest and support of the project.

W A Rickelton (dec.), C Bourget and M Eichorn of Cytec for discussions on project direction and supply of extractants.

W van Bronswijk of Curtin University for performing and interpretation of IR and Raman measurements.

K Barnard of CSIRO-Bentley for discussions on the crystallisation and chromatography aspects of the project.

This project was carried out under the auspices of the AJ Parker CRC for Hydrometallurgy.

J Avraamides (AJ Parker CRC) and J Hosking (CCWA) for an analytical support grant from CCWA and B Price and S Wilkinson for analytical assistance.

TABLE OF CONTENTS

CHAPTER 4. RESULTS AND DISCUSSION 82

LIST OF FIGURES

LIST OF TABLES

PREFACE

Hydrometallurgical liquid-liquid (solvent) extraction is currently a major research interest particularly of nickel, cobalt and other metals commonly associated with laterite nickel deposits, such as chromium and manganese, in view of the increasing need to process these deposits.

This research project was commenced in 1999 shortly after the commissioning of Bulong Nickel Operation (BNO), a nickel laterite processing operation using pressure acid leaching (PAL) technology and direct solvent extraction (DSX). Cytec (Canada), the manufacturer of Cyanex® 272 approached the WASM Nickel Hydrometallurgy Research Group. They believed that Cyanex® 272 did not extract chromium but early plant data at BNO showed that chromium was extracting with Cyanex® 272 and could not be stripped.

A search of literature revealed that only one study on the extraction of chromium with Cyanex® 272 had been published. Although two other studies on solvent extraction of metals briefly mentioned chromium, the data reported were minimal and seemingly conflicting.

The present study investigated the solvent extraction of chromium with Cyanex® 272 in general and in the DSX processing of PAL-generated leach solutions in particular.

Chapter 1 introduces the topic. It contains a brief description of the occurrence and utilisation of nickel, an overview of nickel laterite formation and the implications that this has on processing nickel from these deposits. The various options for processing nickel laterites, a statement of the problems associated with chromium as well as the project scope, limitations and objectives are discussed.

Chapter 2 reviews the literature on the solvent extraction of chromium with Cyanex® 272. Due to the limited directly relevant literature, the extraction of chromium with other extractants and under a wide range of conditions is also reviewed in order to gain some insight into the general extraction behaviour of chromium.

Chapter 3 details the reagents, experimental procedure and analytical techniques used in the present work.

Chapter 4 discusses the results and observations of the present work on the solvent extraction of chromium with Cyanex® 272. A structure is proposed for the extracted chromium(III) species and the changes observed in the loaded organic phase. The stripping of chromium(III) is also examined.

Chapter 5 summarises the main findings of the present work and Chapter 6 outlines the recommendations for further work.

CHAPTER 1. INTRODUCTION

Chromium as a resource is obtained primarily from mineral deposits containing chromite. However due to its refractory nature, chromium is also found in a variety of other deposits, including economic deposits of other metals. Recent Australian commercialisation of nickel resources from laterite deposits using pressure acid leach (PAL) technology has revealed chromium to be of definite processing significance and one of the major contaminants that adversely affect the performance of a processing facility particularly when using the direct solvent extraction (DSX) technique.

1.1 Occurrence and Utilisation of Nickel

Nickel is the sixth most abundant terrestrial element but is 24th in terms of crustal composition. Natural geological processes increase the local nickel content in suitable locations and commercial deposits may develop. Commercial concentrations of nickel occur in sulphide and laterite deposits. Traditionally the bulk of the nickel supplied to market has originated in sulphide deposits; the nickel being obtained from the original igneous rocks. Recently however an increasing quantity of nickel is being supplied from lateritic sources, the oxidised weathering product of previous deposits. A third type of deposit, deep-sea nodules, contains similar metal concentrations to existing commercial deposits however the in-principle and technical hurdles yet to be overcome means that this type of deposit is yet to be utilised as a commercial resource.

Currently, approximately 60% of world demand for nickel is met from sulphide deposits. However this type of deposit represents a small proportion of world nickel reserves with laterite deposits accounting for approximately 80% of known resources (Roorda & Hermans 1981). A significant, but variable, portion of the demand for nickel is met by recycled materials (Stobart 2001). The vast majority of nickel, approximately 65% of total world demand, is used in stainless steel production (Stobart 2001). Other uses of nickel include the increasing rechargeable battery and superalloy markets (Maurer 2001; Stobart 2001).

The continuing forecasts of increased nickel demand have led to increased interest in the development of lateritic nickel reserves. This may be attributed to the shallow location of these deposits and thus the ease of mining, the potential for lower operating costs, recent advances in the available technology and the lack of new sulphide deposits. The rapid increase in financial commitment to the development of lateritic nickel deposits in Western Australia, at least A$m 1645 (Upton 1999), will focus this discussion.

1.1.1 Overview of Laterite Formation

The history of a nickel deposit has a significant impact both on the formation of a commercially viable resource and the processing route chosen to utilise the resource. An understanding of the history of a deposit is important in assessing possible processing routes to utilising the resource. This discussion provides an overview of laterite formation and the impact that this has on processing options. Much of this discussion is based on the works of Golightly (1973), Roorda and Hermans (1981) and Burger (1996b).

Lateritic reserves show significant changes in structure compared to the parent rock as a result of natural weathering. At shallow crustal depths the ultramafic base rock, commonly peridotite or dunite rocks composed mainly of olivine $(Mg,Fe)_2SiO_4$, will convert in varying amounts to serpentine, $Mg_3(Si_2O_5)(OH)_4$. The weathering of the resulting serpentinic rock results in a volume reduction as magnesia, silica and other soluble components are removed. The deposit becomes enriched in weathering products such as goethite, and limonite and nontronite clays. The goethite and clays contain enriched amounts of relatively insoluble iron, aluminium, nickel, cobalt and chromium. The leaching process results in a horizontally defined deposit with the main zones being unaltered bedrock, saprolite, clays (limonite and nontronite) and caprock (Figure 1-1). The degree of zone development and the transition characteristics are dependent on the local conditions.

The characteristics of the saprolite zone are dependent on the amount of serpentine in the bedrock. Relatively low serpentine levels result in a saprolite zone with substantial remnant bedrock. As the serpentine content increases so does the leachability of the bedrock. Nickel does not occur in distinct minerals but substitutes in the serpentine lattice as magnesium is leached. In locations with arid environments or poor drainage silica enrichment may also occur. Serpentine may be replaced by nontronite clays or silica boxwork. The silica may have associated garnierite (a brilliant green clay, $(Ni,Mg)_3Si_4O_{10}(OH)_2$) or nontronite. Without associated clays the silica will be nickel barren. Magnesite ($MgCO_3$) veinlets and accretions may also occur in the saprolite zone.

The clay zone may be minimal in well-drained locations but will be dominated by nontronite clays in locations with arid environments or poor drainage. Nontronite clays, $Fe(Al,Si)_8O_{20}(OH)_4$, can undergo substantial cation exchange and most of the nickel in this zone is associated with them. This zone will have high moisture content due to the hygroscopic nature of nontronite clays and may also contain goethite inclusions. Manganese oxides may persist in this zone and if so will contain significant adsorbed cobalt and some nickel.

The limonite (ferralite) zone, characteristic of humid, well-drained regions, is dominated by goethite, FeO.OH. There is some substitution of nickel for iron in the newly formed mineral. Limonite is an amorphous form of hydrous ferric oxides. Chromite and manganese oxides may also be found. Laterites formed under arid conditions often contain substantial inclusions of the limonitic clay, kaolin, $Al_4(Si_4O_{10})(OH)_8$, in this zone.

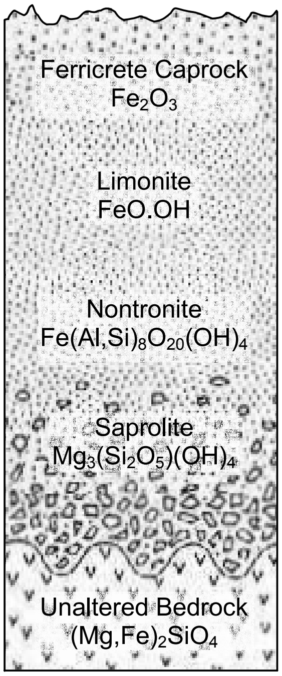


Figure 1-1. The horizontal layer structure developed in lateritic deposits, after Roorda and Hermans (1981).

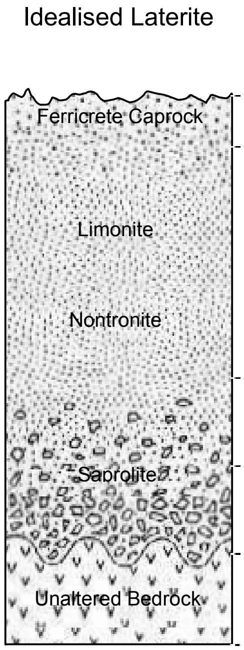
The caprock or ferricrete zone is usually dominated by hematite, Fe_2O_3, with some chromite present. In humid climates the breakdown of this surface layer may have commenced. Many arid zone laterite deposits have an alluvial layer covering the caprock.

1.1.2 Metal Distribution in Laterite Deposits

In humid, well-drained environments the nickel distribution is concentrated in the upper section of the saprolite zone with a bulk concentration approaching 3%. The nickel content steadily decreases towards the caprock. Cobalt values are generally low throughout the profile. Iron content is relatively low in the saprolite zone reaching a maximum of about 25% with a sharp transition to the limonite zone. Silica and magnesia show inverse behaviour compared to iron, increasing in concentration closer to the bedrock.

Laterites that develop in areas of poor drainage or an arid climate have a significantly different metal distribution. In these areas nickel is often concentrated in the nontronite clays along with cobalt and manganese. Significant nickel and cobalt concentrations may also be incorporated in the limonite zone. Silica content also peaks in the clay zone. Iron content increases steadily from the base of the profile reaching a maximum at about 35% in the caprock. Magnesia content decreases from about 35% at the base of the saprolite zone to a minimum of about 2% near the top of the clay zone. This value is maintained through the remainder of the profile. If kaolin is present, usually in the limonite zone, then the alumina content will follow the same profile. The chromium content is 2-3 times greater in the upper levels of the profile than in the saprolite zone.

A summary of the metal distribution in each layer is shown in Figure 1-2.



Approximate Analysis - %				
Ni	Co	Fe	Cr_2O_3	MgO
<0.8	<0.1	>50	>1	<0.5
0.8 to 1.5	0.1 to 0.2	40 to 50	2 to 5	0.5 to 5
1.5 to 1.8	0.02 to 0.1	25 to 40	1 to 2	5 to 15
1.8 to 3		10 to 25		15 to 35
0.25	0.01 to 0.02	5	0.2 to 1	35 to 45

Figure 1-2. Typical variation in metal content with location in laterite profile, after Roorda and Hermans (1981).

Elevated nickel and cobalt values will often be found adsorbed on manganese oxides in the nontronite zone and local concentrations of 5% are common in these areas. Up to 50% of limonitic nickel may be present in manganese oxides (Golightly 1981). Moisture content is dependent on the composition of the profile, especially the clays in the deposit. Alumina-rich clays tend to be hydrophilic with moisture levels up to 35%. Iron-rich limonitic clays are more hydrophobic. The proportions and locations of these phases will determine the overall nature of the deposit.

Lateritic deposits are generally found quite close to the surface and do not extend to great depths however they may cover a large area. The pre-mining deposits at Moa Bay, Cuba extended over approximately 41 km^2 (Chalkley & Toirac 1997). In general the total depth rarely exceeds 100 metres and 20–60 metres is quite common. The caprock may exist to around 5 metres from the surface of the deposit, discounting any alluvial layer. The limonite (ferralite) layer may range in depth from almost non-existent up to 30 metres. A similar depth range exists for the nontronite zone. The saprolite zone, although up to 30 metres deep, usually contains nickel at commercial grades only in the upper 5–15 metres.

Typical bulk compositions of various laterite style nickel deposits and their dominant source of metal values are shown in Table 1-1. The operations detailed have all produced commercial nickel product.

Table 1-1. Elemental composition (%) of the resource for some producing laterite deposits.

	Cawse[1]	**Moa Bay**[2]	**Murrin Murrin**[2]	**Bulong**[1]	**New Caledonia**[2]
Source	Limonite	Limonite	Nontronite	Nontronite	Saprolite
Process	Hydro-metallurgy	Hydro-metallurgy	Hydro-metallurgy	Hydro-metallurgy	Pyro-metallurgy
Ni	1.0	1.3	1.2	1.1	2.5
Co	0.07	0.12	0.08	0.08	0.04
Fe	18	48	22	21	12
SiO_2	42[3]	9.0	42	43	47
Mg	1.6	0.55	3.7	4.6	15
Al	1.7	4.8	2.7	2.8	1.3
Mn	0.17	0.8	0.4	0.36	0.6
Cr	0.92	2.0	1.0	0.6	1.4
H_2O[1]	Up to 10	> 20	About 30	Up to 35	

---

[1] (Kyle 1996)
[2] (Motteram, Ryan & Weizenbach 1997)
[3] Contains significant free silica.

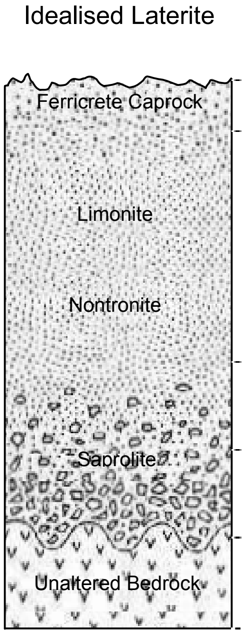
1.2 Processing Options for Nickel Laterites

The composition of a given laterite deposit will be dependent on the type of parent rock, the climate in which the deposit was formed and the weathering history. This gives rise to an almost infinite number of deposit specific relationships between components and consequent processing options and constraints. There are several processing routes available for nickel laterites and these can be classified as shown in Figure 1-3 (Roorda & Hermans 1981).

On the basis of magnesia content and nickel to iron ratio a choice is made between a hydro- or pyrometallurgical extraction process. The degree of inherent homogeneity within a deposit will also have an impact on process choice with hydrometallurgical routes generally requiring a more homogeneous feed (Roorda & Hermans 1981).

The processing of nickel laterites via pyrometallurgical routes (Roorda & Hermans 1981; Reid 1996) is favoured by a low iron to nickel ratio and low moisture content. These requirements limit this processing route to predominantly saprolitic type ores. Nickel content needs to be greater than about 2% for profitable operation. Pyrometallurgical treatment of lateritic ores involves drying, reduction and smelting stages. This produces a ferronickel with 20 to 50% nickel content. Nickel sulphide matte can also be produced but the sulphur required must be purchased and introduced at some point in the process. This allows recovery of some cobalt as a by-product.

Pyrometallurgical treatment, although seen as a relatively robust process for its ability to treat heterogeneous silicates, must have a controlled feed in order to maintain suitable slag chemistry. In particular, the iron, magnesia and silica content must be regulated to control the slag melting point, viscosity and electrical conductivity. Pyrometallurgical treatment cannot be utilised for laterites containing less than 2% nickel and more than 25% iron. This restriction



Approximate Analysis - %					Extraction Procedure
Ni	Co	Fe	Cr_2O_3	MgO	
<0.8	<0.1	>50	>1	<0.5	Overburden to stockpile
0.8 to 1.5	0.1 to 0.2	40 to 50	2 to 5	0.5 to 5	Hydrometallurgy
1.5 to 1.8	0.02 to 0.1	25 to 40	1 to 2	5 to 15	Hydrometallurgy or Pyrometallurgy
1.8 to 3		10 to 25		15 to 35	Pyrometallurgy
0.25	0.01 to 0.02	5	0.2 to 1	35 to 45	Not recovered

Figure 1-3. An idealised laterite profile showing the general processing routes available with variation in composition, after Roorda and Hermans (1981).

excludes pyrometallurgical processing as an option for a significant portion of known laterite reserves.

In order to treat the reserves of material not amenable to pyrometallurgical processing, projects have turned to hydrometallurgical processing options. Nickel not found in the saprolitic region of a lateritic deposit will usually be associated with limonite or nontronite clays. Limitations imposed by the chemistry of this environment have restricted the number of commercial processing routes to two general options:

- Caron Process, and
- Sulphuric Pressure Acid Leach.

Based on the 1995 production data presented by Reid (1996) world nickel production from laterite deposits can be broken down as shown in Figure 1-4. In addition it is worth noting that less than 3% of the corresponding cobalt production (total 3500 t) comes from pyrometallurgical processing.

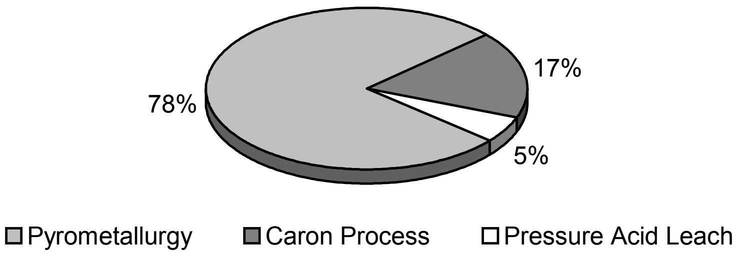


Figure 1-4. Percentage of nickel laterite production by process type, total 344 kt (Reid 1996).

1.2.1 Caron Process

Although developed in the 1920s the Caron process was not commercialised until 1944 (Reid 1996). In this process the ore is dried and milled, then roasted in a reducing atmosphere to convert nickel and cobalt to their metallic form. The resulting product is selectively leached with an ammonia-ammonium carbonate solution at low temperature and atmospheric pressure. Removal of ammonia causes precipitation of nickel carbonate that can be calcined to produce nickel oxide.

Production of pure nickel requires removal of cobalt which, if integrated with the process as described, will occur before nickel carbonate precipitation. Separation of nickel and cobalt in order to achieve the production of pure nickel can be achieved using solvent extraction. The use of solvent extraction also allows the recovery of cobalt. A simplified flowsheet of this modified Caron process, as operated by Queensland Nickel Industries (QNI) Limited nickel and cobalt refinery in Yabulu, Queensland, Australia, is shown in Figure 1-5.

The solvent extraction process uses a modified LIX 84 reagent in ammoniacal solution. This reagent was later designated LIX 87QN (Bhaskara Sarma & Nathsama 1996). The nickel ammine complex is extracted and cobalt(III) remains in the raffinate. The nickel is stripped with an ammonia solution that has a higher ammonia concentration than the extraction solution (Price & Reid 1993). Although recoveries in the solvent extraction circuit are good, overall metal recovery for the process is only approximately 84% for nickel and 45% for cobalt (Reid 1996) depending on the feed material.

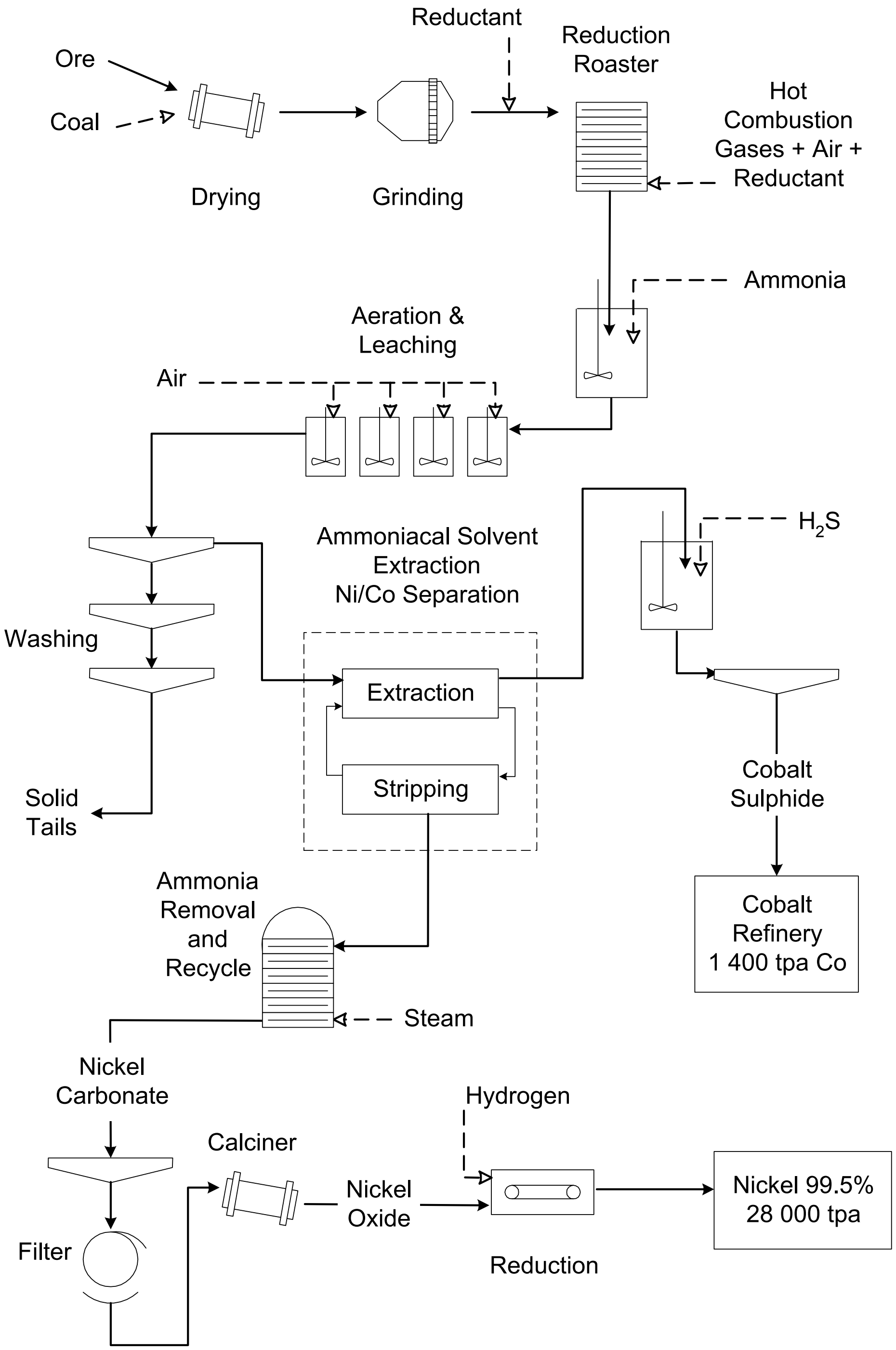


Figure 1-5. Simplified QNI Refinery flowsheet after Fittock (1997). Production data: Reid (1996).

1.2.2 Pressure Acid Leach

The first and, for more than 35 years the only, commercial pressure acid leach (PAL) operation was constructed at Moa Bay, Cuba, in 1959 (Simons 1988). The PAL process involves leaching the slurried ore with sulphuric acid at elevated temperatures and pressures causing almost total dissolution of the feed material. The use of PAL achieves much higher nickel and cobalt dissolution with only half to one third of the energy requirements of the Caron process (Reid 1996). However acid consumption is a major cost component, downstream processing is more complex and effluent disposal can pose difficulties.

Once the nickel and cobalt are in solution a wide variety of processing options are available. These include a range of intermediate precipitation products which may be redissolved and various applications of solvent extraction technology. A range of processing routes have been shown to be technically and commercially viable and those recently implemented are discussed below.

1.3 Pressure Acid Leach Operations in Australia

The recent commissioning of three significant nickel-cobalt operations in Western Australia has resulted in increased interest in the commercial application of PAL technology to lateritic ores. The use of PAL at the front of the processing circuit is common to all three of the new operations. Of interest is the choice of different processing routes following leaching. These fall into two groups: direct and indirect separation. Direct separation involves the application of solvent extraction to separate nickel and cobalt directly from the pregnant liquor stream (PLS). Indirect separation uses an intermediate precipitation and re-leach step to remove impurities before solvent extraction to separate nickel and cobalt. The differences in process selection arise due to differences in the ore mineralogy and behaviour, production philosophy, perceived technical risk and financial considerations. The chosen process routes are discussed below.

1.3.1 The Murrin Murrin Process

The largest of the new operations with an identified resource of 116 million tonnes of ore grading 1.10% nickel and 0.08% cobalt, Murrin Murrin also has the most conservative process flowsheet as identified by technical, start-up and financial risk analysis (Motteram, Ryan & Weizenbach 1997). The process route is shown in Figure 1-6. The ore is leached with sulphuric acid, produced on site by a sulphur burning acid plant, at 255 °C and 4300 kPa for 90 minutes. The leached slurry is fed to a counter-current decantation (CCD) circuit for washing and pH adjustment to 2.4–2.6 with locally available calcrete (calcium carbonate). Adjustment to a higher pH (3.5–4.0) in order to remove iron, aluminium and chromium was attempted but caused unacceptable loss of nickel and cobalt through coprecipitation and/or adsorption (Motteram *et al.* 1996).

The solution at pH 2.4–2.6 then undergoes sulphide precipitation at 90 °C and 105 kPa hydrogen sulphide, also produced on site. Sulphide precipitation rejects a large proportion of the impurities such as aluminium, magnesium and manganese found in the liquor. The relatively mild sulphide precipitation conditions, compared to Moa Bay at 121 °C and 1034 kPa (Chalkley & Toirac 1997) are made possible by using seed recycle and solutions containing high levels of magnesium. A clean water wash is used to remove chlorides from the mixed sulphide precipitate, which is then ready for treatment in the independent on-site refinery.

The mixed sulphide precipitate is slurried in water and leached under oxygen pressure of 400 kPa (total pressure 1100 kPa) at 165 °C giving near total dissolution of the precipitate. Iron is removed via pH adjustment with ammonia. Copper and most zinc are removed by atmospheric sulphide precipitation.

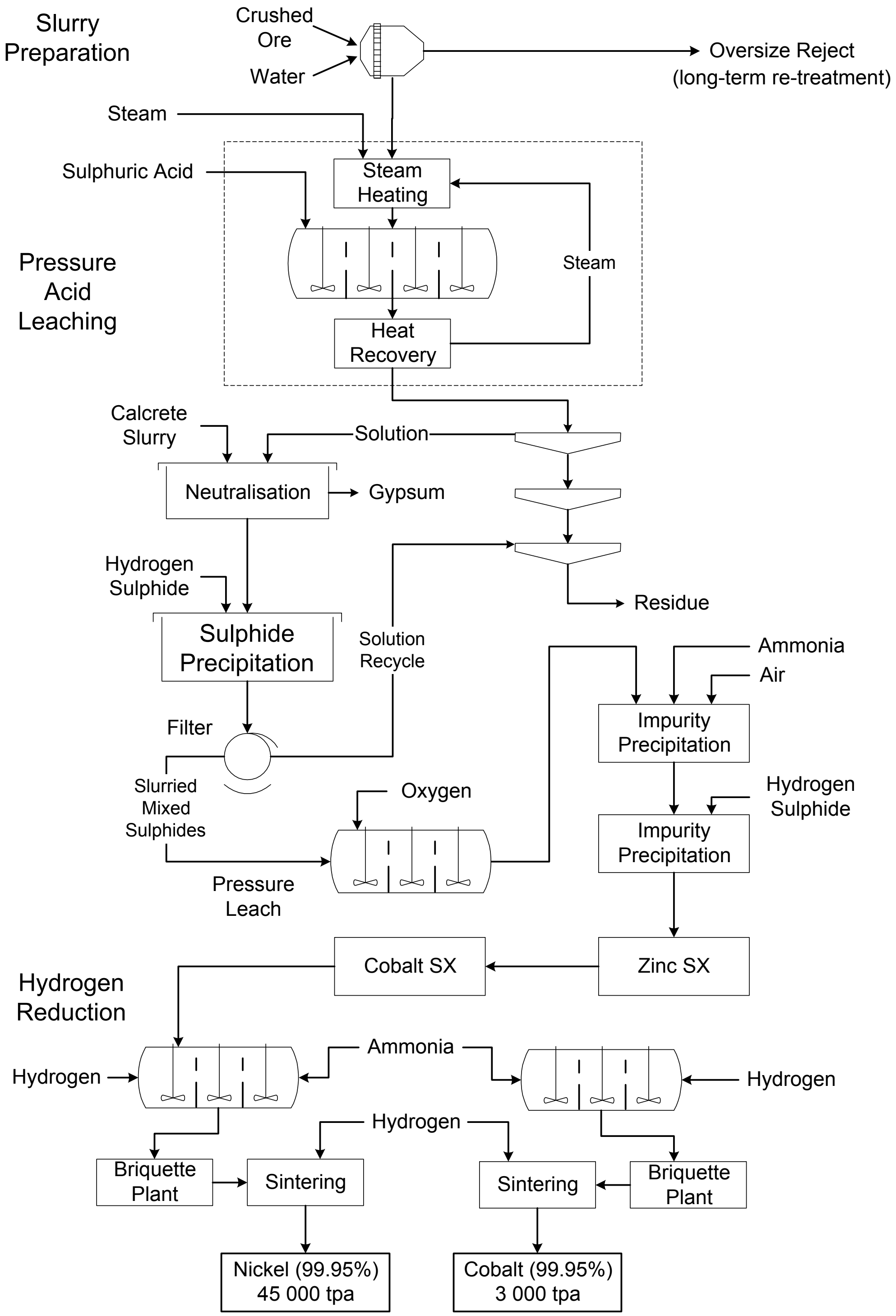


Figure 1-6. Flowsheet of the Murrin Murrin process after Motteram, Ryan and Weizenbach (1997).

The remaining zinc is removed by solvent extraction with Cyanex® 272. After adjusting the pH, Cyanex® 272 is used in a second extraction circuit to remove cobalt. Cobalt is stripped and further refined before hydrogen reduction and briquetting to produce 99.8% cobalt briquettes. The raffinate from cobalt solvent extraction is treated by conventional hydrogen reduction, briquetting and sintering to produce 99.95% nickel briquettes. Design output is approximately 45 000 tpa nickel and 3 000 tpa cobalt.

1.3.2 The Cawse Process

The Cawse Nickel Project is utilising a resource of 52.8 million tonnes of ore grading 1.0% nickel and 0.07% cobalt (Hellsten & Lewis 1996). The process flowsheet is shown in Figure 1-7.

The Cawse resource is the only example of the three Western Australian laterites discussed here which is amenable to physical upgrading of the ore feed before PAL. Removal of the coarse silica fraction (+212 μm) increases the nickel and cobalt feed grade by 30–50% while retaining 70–80% of the metal value (Hellsten & Lewis 1996; Kyle & Furfaro 1997). After removal of the coarse silica fraction, the thickened slurry is fed to the leach autoclave where conditions are 250 °C, 3800 kPa and a residence time of 75–105 minutes.

The leach liquor is adjusted to pH 3.5 with limestone slurry. Air addition is used to aid oxidation of iron(II) to iron(III), which is subsequently precipitated. The resulting slurry is washed and separated through a CCD circuit before a second stage of iron removal by adjustment to pH 6.0. The second stage solids are recycled back to first stage pH adjustment to recover co-precipitated nickel and cobalt. The nickel and cobalt are then removed from the neutralised liquor by hydroxide precipitation. Hydroxide precipitation recovers most of the nickel and cobalt as well as many other metals such as copper, zinc and manganese which are in solution.

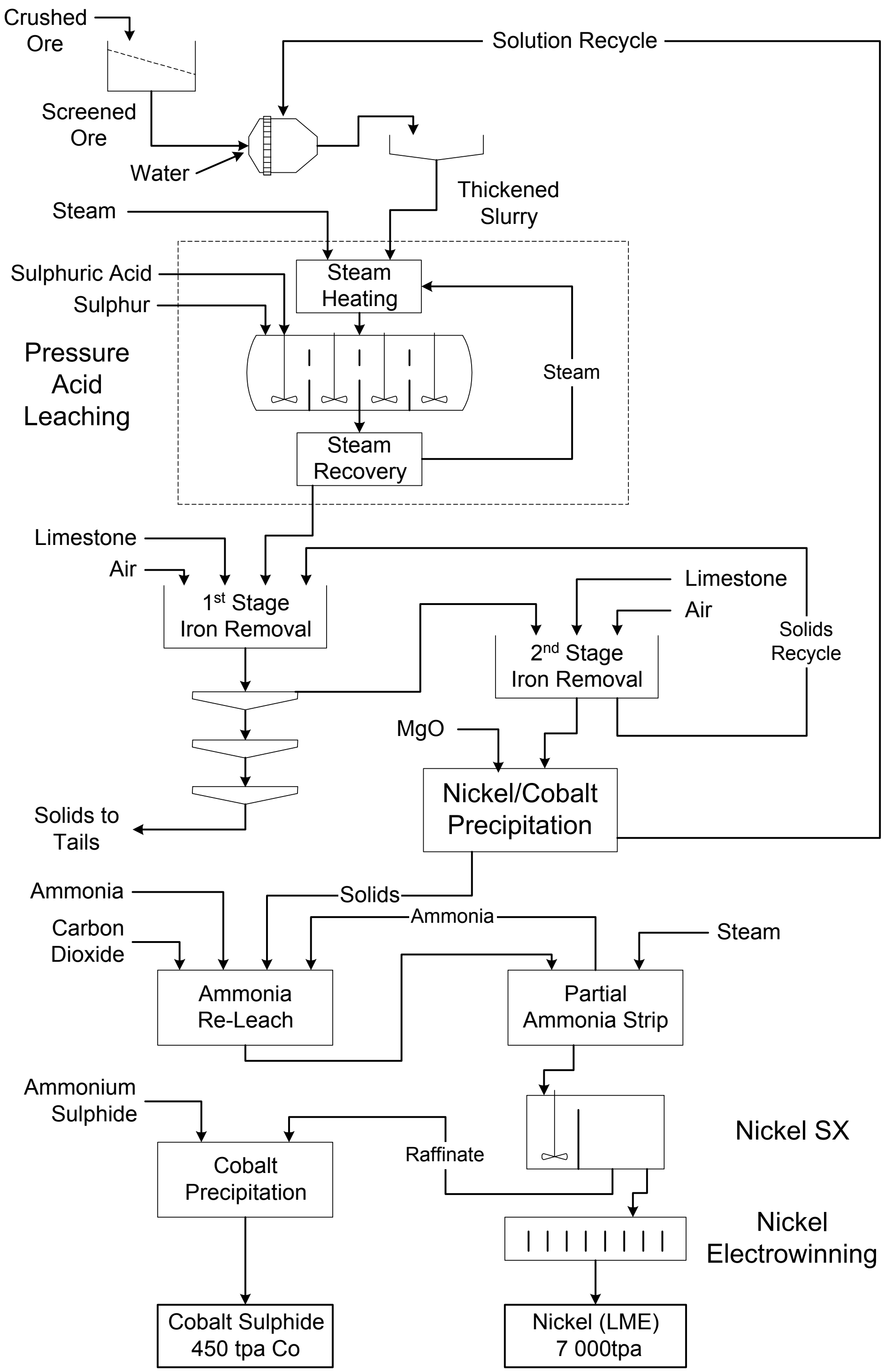


Figure 1-7. Flowsheet of the Cawse process after Kyle and Furfaro (1997).

The processing of a mixed hydroxide precipitate is then carried out in a similar way to the previously proven operation at QNI Limited. That is, the mixed hydroxide precipitate is selectively re-leached with an ammonia-ammonium carbonate solution producing a solution containing nickel, cobalt, copper and zinc with some manganese, magnesium and iron.

Cobalt(II) oxidation to cobalt(III) occurs readily under the conditions present in the re-leach liquor. The change in oxidation state of cobalt prevents its co-extraction in the nickel solvent extraction circuit.

Partial ammonia stripping results in re-precipitation of weak amine complexes such as those formed by zinc and manganese impurities. Nickel solvent extraction is carried out with LIX® 84I in kerosene. This process is selective for nickel under these conditions. The organic phase is scrubbed to remove ammonia and then stripped using sulphuric acid.

Nickel is recovered from the strip liquor by electrowinning to produce nickel cathode. Cobalt is precipitated from the raffinate as a sulphide. It was originally planned to incorporate production of cobalt metal. Initial design output was 8500 tpa nickel and 2000 tpa cobalt by means of selective mining of high-grade zones. The life-of-project design output was 7000 tpa nickel and 450 tpa cobalt (Hellsten & Lewis 1996).

Recent changes in ownership of this operation has seen the solvent extraction circuit and refinery shut down and a mixed hydroxide precipitate as the final on-site product. The mixed hydroxide is refined at an off-site location.

1.3.3 The Bulong Process

Bulong Nickel Operations are operating from a proven and probable resource of 41 million tonnes at 1.14% nickel and 0.09% cobalt (Burger 1996a). The flowsheet (Figure 1-8) is the only example of nickel production from a lateritic

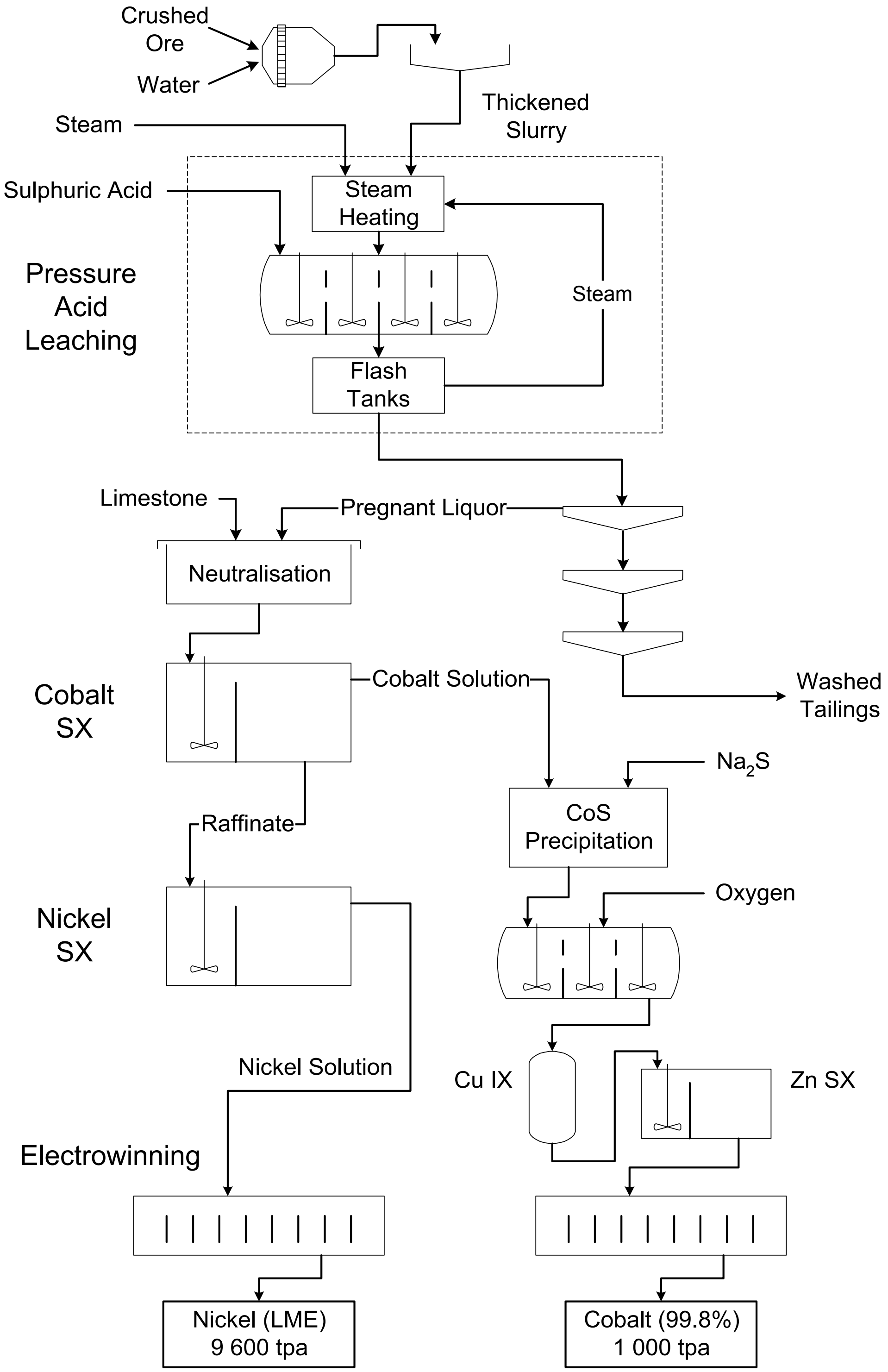


Figure 1-8. Flowsheet of the Bulong process after Kopejtka (2000).

source using direct solvent extraction i.e. without intermediate precipitation and re-leach steps.

The thickened ore is leached at 250 °C and 4000 kPa with a residence time in the autoclave of 75 minutes. A seven stage CCD circuit clarifies the pregnant liquor prior to partial neutralisation. Suspended solids are removed and the liquor pumped to a storage pond ready for treatment in the separate solvent extraction and electrowinning section of the plant.

The clarified pregnant leach liquor is fed directly to the cobalt solvent extraction circuit. The extractant is Cyanex® 272 in Shellsol® 2046 as the diluent. Tributyl phosphate was used as a third phase inhibitor during testwork (Soldenhoff, Hayward & Wilkins 1998) but was not incorporated into the operating plant. At pH 5.5, the cobalt circuit removes cobalt and scavenges impurities such as copper, zinc, manganese and any remaining iron and aluminium from the liquor. After stripping, cobalt is precipitated as sulphide. The cobalt sulphide undergoes a pressure oxygen re-leach, the copper is removed by ion exchange and the zinc is removed by solvent extraction before electrowinning the resulting solution to produce cobalt metal.

The raffinate from cobalt solvent extraction, containing predominantly nickel, magnesium and calcium, is sent to the nickel solvent extraction circuit where Versatic® 10 is used to preferentially extract the nickel. After scrubbing and stripping, nickel metal is recovered by electrowinning. Design output is 9600 tpa nickel and 1000 tpa cobalt.

The output of these three new producers at nameplate capacity will constitute approximately 9% of Western world nickel output based upon 1998 data (Hellsten 1999). This production essentially replaces that forecast from the start-up of Inco's operation at Voisey's Bay in Canada up to 2004 and possibly longer, so it has little impact on forecast supply levels over this period.

1.4 Background of the Research Project

Chromium is an inherent contaminant of nickel laterite ores. It dissolves during PAL but provided appropriate ore blending and process control is maintained it can be completely removed by precipitation. The standard removal process for chromium(III) is precipitation as the hydroxide, together with iron(III) and aluminium(III). Chromium(III) is therefore the preferred form of chromium for downstream processing. At the expected ionic strength of a typical leach liquor precipitation of chromium(III) occurs at a pH of about 4 (Ritcey, Hayward & Salinovich 1996).

Pressure acid leaching using sulphuric acid and elevated temperatures yields near complete dissolution of lateritic ore. The greatest contribution to chromium in the liquor is derived from the dissolution of clays containing chromium(III) (Kyle 1996). Despite its refractory nature, some chromite is also dissolved making a direct contribution to chromium(VI) in the leach liquor (Das *et al.* 1995). Chromium(VI) is undesirable as it cannot be removed from the leach liquor by precipitation and so enters the solvent extraction circuit.

Chromium(VI) is also formed by redox reaction with manganese, so to prevent further formation of chromium(VI) in the leach liquor the manganese(IV) level must be carefully controlled. The manganese(IV) level in turn is controlled by the amount of iron(II) in the leach liquor. These relationships are demonstrated by the reactions shown in Equations 1-1 to 1-3.

The oxidation of chromium(III) to chromium(VI) by manganese(IV):

$$2Cr^{3+} + 3MnO_2 + 2H_2O \rightleftharpoons 2H_2CrO_4 + 3Mn^{2+} + 4H^+ \qquad (1\text{-}1)$$

The reduction of manganese(IV) to manganese(II) by iron(II):

$$MnO_2 + 2Fe^{2+} + 4H^+ \rightleftharpoons Mn^{2+} + 2Fe^{3+} + 2H_2O \qquad (1\text{-}2)$$

The reduction of chromium(VI) to chromium(III) by iron(II):

$$H_2CrO_4 + 3Fe^{2+} + 6H^+ \rightleftharpoons Cr^{3+} + 3Fe^{3+} + 4H_2O \qquad (1\text{-}3)$$

Much of the residual soluble iron is present as iron(II) due to its presence in clays or the activity of reducing agents such as sulphides in the leach liquor. Iron(II) can cause downstream processing problems but is easily oxidised to iron(III) in solution at atmospheric conditions allowing it to be removed by precipitation as the hydroxide.

If chromium(VI) is not controlled in the leach liquor then a reduction step is required as chromium(VI) does not precipitate as the hydroxide. The reduction step is an additional unit process that needs to be incorporated into the process route, with the associated capital and operating expenses.

A chromium(VI) reduction step, incorporated after leaching, may use sodium meta-bisulphite ($Na_2S_2O_5$), sulphur dioxide or iron(II) sulphate. The reaction for sodium meta-bisulphite is shown in Equation 1-4.

The reduction of chromium(VI) to chromium(III) with sodium meta-bisulphite:

$$4H_2CrO_4 + 3Na_2S_2O_5 + 6H^+ \rightarrow 4Cr^{3+} + 6SO_4^{2-} + 6Na^+ + 7H_2O \qquad (1\text{-}4)$$

This reagent has several advantages in nickel laterite processing. These include relatively low reagent consumption (Freeman 1989), the reaction being acid consuming and the reagent not contributing more iron to the system, which in turn would need removal before nickel and cobalt recovery.

The precipitation of chromium(III) as chromium hydroxide effectively removes chromium from the solution provided proper pH control is maintained and sufficient equilibration time allowed (Equation 1-5).

$$Cr^{3+} + 3OH^- \rightarrow Cr(OH)_3 \downarrow \qquad (1\text{-}5)$$

In the absence of ideal process control, it is probable that chromium will enter the solvent extraction circuit either as chromium(VI), which has been formed in the leach and not reduced, or as chromium(III) which has not been fully precipitated during neutralisation. This has been observed in at least one operating plant.

The control of chromium, together with most metals, starts with the mining process. This needs to be controlled to provide a relatively constant blend of material to the ore stockpile. This provides homogeneity of the feed material and consequently better control of leaching variables such as required acid addition and oxidation potential. Ore blending aims to utilise the ore composition to control the chemistry during leaching. In practice, appropriate ore blending is difficult to achieve.

The risks associated with leaving chromium(VI) in solution are varied. The chromium(III)/chromium(VI) couple is able to oxidise iron(II) to iron(III) removing iron(II) from the system before it can consume manganese(IV). This may lead to loss of recoverable metal due to the association of high nickel and cobalt grades with MnO_2 particles.

The effect of chromium(VI) on the organic phase during solvent extraction is not known but chromium(VI) is suspected as a possible oxidant leading to organic decomposition. The degradation of components of the organic phase is a major problem in hydrometallurgical solvent extraction but it is not fully understood. It is known (Cotton & Wilkinson 1988) that chromium(VI) in acidic conditions is a strong oxidising agent and under the right conditions would be able to oxidise susceptible components of the organic phase. This may result in loss of selectivity of metal extraction and/or decrease the phase separation clarity depending on the oxidation products.

The degradation of organic components is not the only hazard associated with chromium(VI). The presence of chromium(VI) in an electrolyte solution is known to decrease current efficiency and even prevent plating of cobalt during electrowinning (Pradhan, Dash & Das 2001). If the chromium(VI) exits the process in the tail stream then it presents a disposal hazard (Bretherick 1986; Freeman 1989; Petura, James & Vitale 1999).

The presence of metals such as cobalt and manganese, which can exist in multiple oxidation states, is a known risk in solvent extraction (Ritcey & Ashbrook 1979; Cheng *et al.* 2000). The unknown behaviour of chromium, another metal that can exist in multiple oxidation states, therefore presents a possible risk to a solvent extraction operation.

1.5 Project Scope and Limitations

The effect of contaminant chromium on solvent extraction has received little attention under anything but ideal conditions during flowsheet development. Nor could the behaviour be reasonably obtained from the literature, as will be shown in the next Chapter 2. Specifically the behaviour of chromium under conditions which separate cobalt from nickel using solvent extraction will be examined.

Chromium poses the greatest risk to a direct solvent extraction processing route, as operated at Bulong Nickel Operation (BNO). In this circuit design cobalt solvent extraction is the first contact for the leached, partially neutralised and clarified feed solution. The cobalt solvent extraction circuit is designed to extract cobalt and contaminant metals leaving a raffinate containing predominantly nickel, magnesium and calcium.

The reagent of choice for this circuit is Cyanex® 272. This phosphinic acid has shown a superior nickel-cobalt separation factor compared to other acidic extractants and is commonly used world-wide for separating these two metals. Efficient nickel–cobalt separation occurs at pH near 5.5 in the BNO cobalt circuit.

The general conditions chosen for this investigation reflect actual operating conditions at BNO. Included in the choice of these conditions is the knowledge that Cyanex® 272 is the predominant reagent for nickel–cobalt separation and therefore the results may have wider applicability.

The organic phase will normally contain Cyanex® 272 in Shellsol® 2046. The aqueous phase normally will be an acidic solution of pH 0-7, or more specifically pH 4-6. Additionally the aqueous phase will contain a range of salt components both singularly and in combinations such as those found in industrial process liquors, especially liquors as encountered in mineral processing operations. The extraction behaviour of chromium from such solutions will be investigated.

1.6 Objectives of the Study

The following objectives have been chosen in order to gain the most generally useful understanding of the behaviour of chromium during solvent extraction. Each objective is addressed in detail in Chapter 4.

The present study was aimed to understand the solvent extraction behaviour of chromium with Cyanex® 272 in general and in relation to the processing of nickel from laterite deposits by pressure acid leach (PAL) direct solvent extraction (DSX) in particular. Specifically it was aimed to:

a) determine the effect of experimental variables:
- contact time;
- stirring speed; and
  - temperature.

b) determine the effect of aqueous phase variables:
- anion type (nitrate, chloride, sulphate, acetate);
- anion concentration;
- chromium oxidation state; and
  - chromium concentration.

c) determine the effect of organic phase variables:
- extractant type (Cyanex® 272, Cyanex® 301, D2EHPA);
- extractant concentration; and
  - diluent type.

d) investigate the stripping of chromium(III).

e) determine the nature of the extracted species.

CHAPTER 2. REVIEW OF CHROMIUM SOLVENT EXTRACTION

2.1 Overview of the Aqueous Chemistry of Chromium

Before considering the solvent extraction behaviour of chromium it is worthwhile to provide a brief overview of the relevant aqueous chemistry.

When present in the aqueous phase chromium commonly exists in both the (III) and (VI) oxidation states. These oxidation states should have a significant effect on the extraction behaviour with Cyanex® 272 due to the different metal species which may form.

Chromium(III) exists in a range of forms at varying levels of hydration (Deltombe, de Zoubov & Pourbaix 1966; Baes & Mesmer 1976). In highly acidic conditions the hexaaqua form, $Cr(H_2O)_6^{3+}$ predominates. Increases in pH from 4 to 7 results in successive hydrolysis reactions occur producing a range of species of the form $[Cr(OH)_x(H_2O)_{6-x}]^{(3-x)+}$ where x = 1, or 2. The log K values, where K is the ratio of reaction products to reactants, for x = 1 and 2 may be estimated as -4.0 and -9.7 respectively. The formally neutral species $Cr(OH)_3$ may exist in solution as well as precipitating as a poorly defined, hydrated solid. Under alkaline conditions the solid may re-dissolve to produce $Cr(OH)_4^-$. Although multinuclear chromium(III) species have been identified these are slow to form and may generally be neglected. Other species have been reported with their respective log K values such as $Cr(SO_4)^+$ (3.9) and $Cr(Ac)^{2+}$ (5.4) (Appendix 3).

Chromium(VI) has a more defined distribution (Deltombe, de Zoubov & Pourbaix 1966; Baes & Mesmer 1976). Under acidic conditions the predominant form is dependant on the concentration of the metal. At concentrations less than 0.01 mol L^{-1} the $HCrO_4^-$ anion is predominant whereas above this concentration the $Cr_2O_7^{2-}$ ion is the preferred form. Under alkaline conditions CrO_4^{2-} is the only significant species. The neutral chromic acid, H_2CrO_4, is proposed at strongly acidic conditions.

2.2 Solvent Extraction of Chromium Related to Mineral Processing

Very few studies on the solvent extraction of chromium, particularly chromium(III) have been reported and only one study on the solvent extraction of chromium(III) with Cyanex® 272 has been published. Two other studies briefly mentioned chromium(III) extraction with Cyanex® 272 however these are limited in the range of conditions that they use as the focus was on other metals. The limited amount of data available on chromium(III) extraction with Cyanex® 272 has inevitably led to some seemingly conflicting reports on the behaviour of the system.

This chapter reviews studies on the solvent extraction behaviour of chromium. Although only the sections on extraction with Cyanex® 272 were directly related to the present work there was little information that could be included. The reported behaviour of chromium with other extractants is therefore included so as to gain some understanding of the general solvent extraction behaviour of chromium that may be applicable to the present work.

2.3 Extraction of Chromium(III) with Acidic Organophosphorus Extractants

2.3.1 Extraction of Chromium(III) with Cyanex® 272

Cyanex® 272 has developed as the extractant of choice for the separation of cobalt and nickel. The active component, bis(2,4,4-trimethylpentyl) phosphinic acid, is shown in Figure 2-1. The supplied commercial product contains approximately 85% active component.

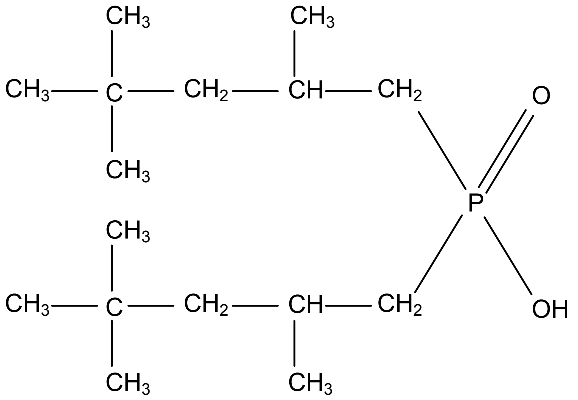


Figure 2-1. The structure of bis(2,4,4-trimethylpentyl) phosphinic acid, the active component of Cyanex® 272.

Little work has been reported on the application of Cyanex® 272 to the solvent extraction of chromium(III) (*Cyanex® 272 Extractant*; Ohki *et al.* 1986; Gandhi, Deorkar & Khopkar 1993; Pandey, Cote & Bauer 1996). The product information (*Cyanex® 272 Extractant*) indicates that chromium(III) is not extracted with Cyanex® 272 from acidic sulphate solutions. Transfer of chromium(III) to the organic phase has been reported in only one paper, that of Pandey, Cote and Bauer (1996).

Pandey, Cote and Bauer (1996) studied the extraction of chromium(III) from a synthetic tanning effluent. The aqueous phase contained chromium(III) (4.41 g L^{-1}), sulphate (12.0 g L^{-1}), sodium chloride (60.0 g L^{-1}), acetic acid (3.90 g L^{-1}) and iron(III) and aluminium(III) at approximately 0.1 g L^{-1} each. The organic phase consisted of Cyanex® 272 (0.48 mol L^{-1}, 15 vol%) and *p*-nonylphenol (0.43 mol L^{-1}, 10 vol%) in kerosene. The Cyanex® 272 was partially ammoniated to control pH during extraction. The contact time of the phases was 5 minutes at an aqueous to organic (A:O) volume ratio of 1. Dispersion of the two phases, 40 mL total, was effected by a mechanical shaker operated at a speed of 250 min^{-1}.

The extraction curve reported by the authors is shown in Figure 2-1. This was the only published solvent extraction curve for chromium(III) and Cyanex® 272.

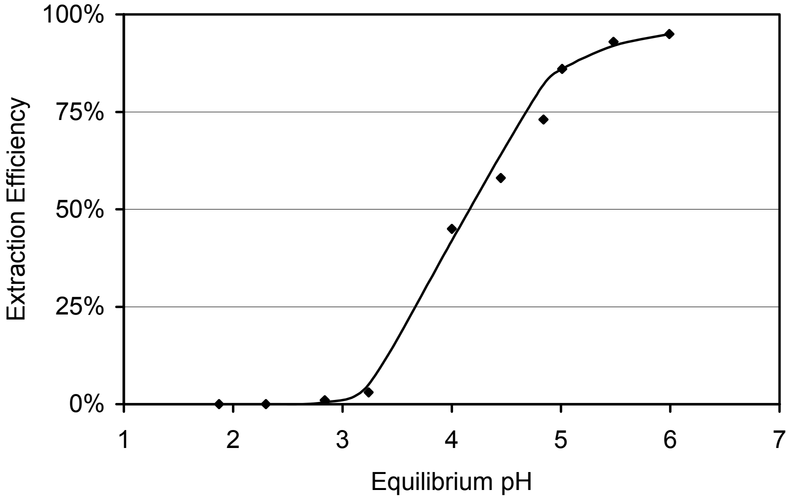


Figure 2-2. Extraction of chromium(III) with Cyanex® 272 as reported by Pandey, Cote and Bauer (1996).

Aqueous phase: Cr(III) 8.5×10^{-2} mol L^{-1}, other components as described in text;

Organic phase: Cyanex® 272 (0.48 mol L^{-1}), *p*-nonylphenol (0.43 mol L^{-1}) in kerosene.

In contrast two other studies (Ohki *et al.* 1986; Gandhi, Deorkar & Khopkar 1993) reported that chromium(III) does not extract with Cyanex® 272.

The work of Ohki *et al.* (1986) examined the extraction of chromium(III) under dark and ultra-violet (UV) irradiated conditions. The aqueous phase contained chromium(III) (2×10^{-4} mol L^{-1}) as chloride, adjusted to pH 2 with hydrochloric acid. The organic phase contained bis(2,4,4-trimethylpentyl) phosphinic acid (5×10^{-2} mol L^{-1}) in toluene. No extraction was reported either in dark or UV irradiated conditions. As this was a screening study only a single pH value was considered. Under the same conditions no extraction of chromium(III) was observed with other extractants including di(2-ethylhexyl) phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A®), trioctyl phosphine oxide (TOPO) and tributyl phosphate (TBP).

The study of Gandhi, Deorkar and Khopkar (1993) on behaviour of cobalt with Cyanex® 272 included chromium(III) in a sequential separation of three metals. The aqueous phase contained 25 μg/10 mL each of iron(III), cobalt(II) and chromium(III). The organic phase contained Cyanex® 272 (5×10^{-3} mol L^{-1}) in chloroform. Iron(III) was extracted at pH 3. Cobalt(II) was extracted at pH 8. The authors stated that chromium(III) remained in the aqueous phase. Under the same conditions nickel(II) showed the same behaviour as chromium(III). The authors do not indicate whether any precipitation and/or re-dissolution of chromium(III) was observed as would be expected as the pH is raised from 3 to 8. At pH 8 chromium(III) may exist as the anionic $Cr(OH)_4^-$ unable to be extracted by Cyanex® 272.

These reports were consistent with the investigation of Pandey, Cote and Bauer (1996) who showed extraction of chromium(III) in the pH range 3–6. The reports discussed above work outside this pH range.

The work of Navarro Mendoza *et al.* (2000) on ion exchange resins provide some useful insights into the behaviour of chromium(III) with Cyanex® 272, even though such work would normally be excluded from a review of liquid-liquid exchange (solvent extraction) literature. The paucity of reported work pertaining to chromium(III) and Cyanex® 272 requires the inclusion of this resin-based ion-exchange process to obtain as much information as may be applicable.

In this work equilibrium was attained in approximately 4 hours although a 24-hour contact time was used throughout. The chromium(III) concentration in the aqueous phase was 2×10^{-4} mol L^{-1}. The resin phase contained Cyanex® 272 (0.30-0.85 mol per kg of resin). The resin density was 0.01 kg resin per L.

The sorption curve of chromium(III) from a nitrate solution onto the impregnated resin is shown in Figure 2-3.

When the Cyanex® 272 concentration was varied the sorption curve shifted to lower pH with increased Cyanex® 272 concentration on the resin. This behaviour is the same as the behaviour expected with solvent extraction systems.

Two different sorption reactions were proposed based on calculated species distribution diagrams. Below pH 3.8 the predominant reaction was:

$$\mathrm{CrL^{2+} + HL_r + H_2O + 2NO_3^- \rightleftharpoons Cr(OH)(HL)_2(NO_3)_{2,r}} \qquad (2\text{-}1)$$

(where HL is Cyanex® 272 and r represents the resin phase). Above pH 3.8 the predominant reaction was given as:

$$\mathrm{CrL^{2+} + HL_r + H_2O \rightleftharpoons Cr(OH)L_{2,r} + 2H^+} \qquad (2\text{-}2)$$

The existance of $\mathrm{CrL^{2+}}$ in the aqueous phase was not examined other than by calculation. In addition the pH values proposed for the sorption reactions are inconsistent with the authors' proposed predominance diagram of the extracant, HL. The same work of these authors (Navarro Mendoza *et al.* 2000) provides some insights into the chemistry of chromium(III) extraction by Cyanex® 272. Whether this information transfers to a system containing two liquid phases cannot be determined from the available data.

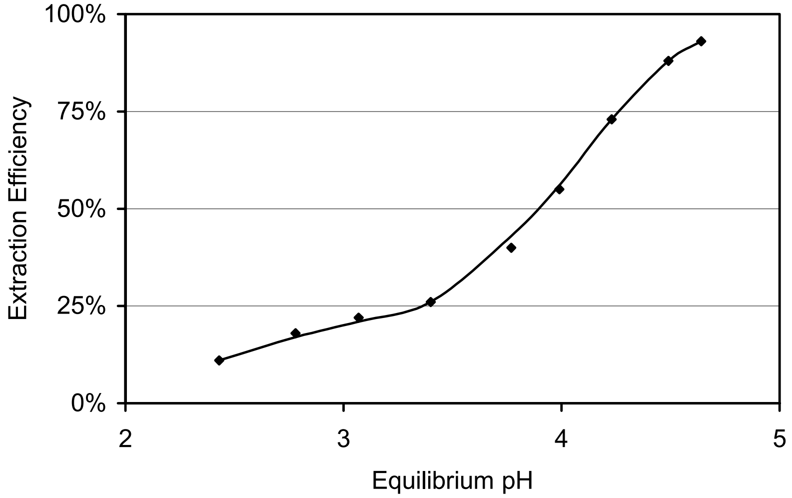


Figure 2-3. The sorption of chromium(III) on resin impregnated with Cyanex® 272 as reported by Navarro Mendoza *et al.* (2000).

Aqueous phase: Cr(III) 2×10^{-4} mol L^{-1}, NO_3^- 0.1 mol L^{-1};

Resin phase: Cyanex® 272 0.53 mol/kg resin, 0.01 kg resin/L.

The literature discussed in this section was the only literature which examined the extraction of chromium(III) by Cyanex® 272. The reported data to date fail to address several key points with respect to the system in question:

a) no attempt was made to determine the structure and thus the nature of the extracted species when dealing with the solvent extraction of chromium(III);

b) the experimental conditions used do not allow sensible comparison with the bulk of other available literature, e.g. there was no work on the use of single anion solutions to allow separation of the effects of the aqueous matrix; and

c) no solvent extraction work with solutions containing relatively low chromium concentrations within a relevant pH range has been reported, which would allow a more theoretical treatment of the data and easier comparison with behaviour in other extraction systems.

The inclusion of resin ion-exchange data provides an indication of behaviour with respect to both the structure and low chromium(III) concentration. The long equilibration times and relatively fixed position of the extractant molecules limit the applicability of these findings to solvent extraction.

The separation of cobalt and nickel was cited (Rickelton, Flett & West 1984) as the principal application of Cyanex® 272 yet the conditions used in many of the above papers do not approach the operating conditions required to effect this separation. Consequently they do not provide data that could be reliably applied to the behaviour of chromium(III) in a system designed for nickel-cobalt separation.

Due to a lack of data on the extraction of chromium with Cyanex® 272, studies on the solvent extraction of chromium with other extractants are also reviewed to gain an insight into its general behaviour in solvent extraction.

2.3.2 Extraction of Chromium(III) with Cyanex® 301 and Cyanex® 302

Cyanex® 301 and Cyanex® 302, the di- and mono-thio analogues of Cyanex® 272 respectively, generally show stronger extraction of metals than Cyanex® 272. This has been used by Mihaylov *et al.* (1995) in the development of a patented process for the separation of nickel and cobalt. Chromium(III) was not extracted from a mixed metal sulphate feed solution between pH 1.5 and 2.5 by an organic phase containing Cyanex® 301 (0.44 mol L^{-1}) in Isopar® M.

Similar results were found by Saily *et al.* (1996) during examination of molybdenum extraction by Cyanex® 301 and Cyanex® 302. The extraction of chromium(III) was reported as less than 5% with either extractant. The extractant concentration was 0.10 mol L^{-1} in toluene. The acid concentration varied from 1×10^{-3} to 5 mol L^{-1} using hydrochloric, nitric and sulphuric acids with little difference in the results. Contact of equal phase volumes was at 25 °C for 5 minutes.

Extraction of chromium(III) by Cyanex® 301 in the pH range –1 to 4.3 was also reported as less than 5% in other literature (Singh *et al.* 1999; Khwaja, Singh & Tandon 2000b). The aqueous phase contained 1×10^{-4} mol L^{-1} metal and the organic phase contained Cyanex® 301 (0.1 mol L^{-1}) in toluene.

It is apparent that the thio analogues of Cyanex® 272 do not extract chromium(III) under commonly used experimental conditions in the pH range –1 to 4.3.

2.3.3 Extraction of Chromium(III) with Di(2-Ethylhexyl) Phosphoric Acid

Di(2-ethylhexyl) phosphoric acid (D2EHPA) is available commercially as a 97% pure liquid. It has been widely used in the extraction of a range of metals including nickel, cobalt, zinc and chromium. The structure of the extractant is shown in Figure 2-4.

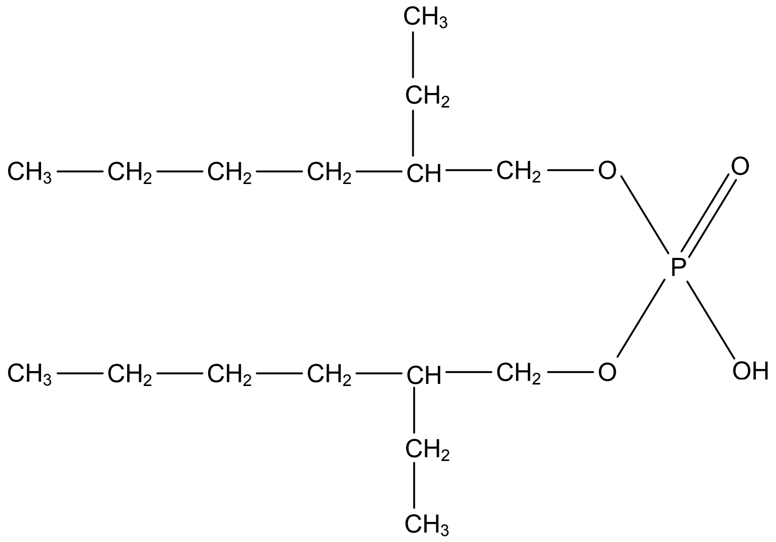


Figure 2-4. The structure of di(2-ethylhexyl) phosphoric acid (D2EHPA).

The extraction of chromium(III) with D2EHPA has received the most attention in the literature of any chromium(III) extraction system although this is still paltry compared to the available data on metals such as nickel and cobalt.

A range of equilibration times for chromium(III) solvent extraction with D2EHPA have been reported dependent upon the pH at which the equilibration time was determined. The chromium hexaaqua ion is known to be kinetically, relatively inert to substitution (Cotton & Wilkinson 1988). However, the hydrolysis reaction:

$$Cr(H_2O)_6^{3+} + H_2O \rightleftharpoons Cr(H_2O)_5OH^{2+} + H_3O^+ \qquad (2\text{-}3)$$

is much faster than water molecule exchange (Baes & Mesmer 1976) and produces a hydroxy species which is more reactive than the hexaaqua ion.

An equilibration time of two minutes was reported by Kimura (1960) and Pandey, Cote and Bauer (1996). Pandey, Cote and Bauer (1996) used an experimental contact time of 5 minutes to ensure attainment of equilibrium. This was the shortest reported equilibration time for chromium(III) and D2EHPA. The only other specified equilibration time was 15 minutes with 30 minutes used as the contact time (Islam & Biswas 1979b). Contact times between 15 and 35 minutes were reported by various workers (Beneitez & Ayllon 1987; Hepworth & Beckstead 1989; Rao & Hariharan 1992; Schügerl, Segelken & Gudorf 1996) although without specifying the actual equilibration time or conditions used in its determination.

The extraction efficiency of a D2EHPA system was governed by the operating pH. The choice of an appropriate operating pH was principally dependent upon the concentration of the extractant with contributions also from the anion type and concentration.

The pH required for maximum extraction of chromium(III) with D2EHPA is 4.5–5 (Islam & Biswas 1979b; Hepworth & Beckstead 1989; Rao & Hariharan 1992; Pandey, Cote & Bauer 1996; Schügerl, Segelken & Gudorf 1996) although significant extraction occurs at pH values as low as three (Rao & Hariharan 1992; Pandey, Cote & Bauer 1996). The early work of Kimura (1960) showed extraction at a relatively low pH although complete extraction was not observed and higher pH values were not reported. Most of these studies used relatively complex aqueous solutions to simulate the real solutions found in waste treatment, a common stimulus for the investigation of chromium solvent extraction.

The work of Beneitez and Ayllon (1987) made no mention of a maximum extraction efficiency but focussed on the nature of the extracted species. The extracted species was reported in the pH range 0.85–1.20 as $CrX_3(H_2O)_2Y$ where Y is D2EHPA and X is the de-protonated form of D2EHPA. The structure suggested by these authors was similar to the CrX_3 reported by Islam and Biswas (1979b) for the pH range 2.5–5.5. Islam and Biswas (1981b) further support this structure by means of phosphorous:chromium ratio analysis. Molecular weight analysis of the complexes suggested to the authors that the structure consisted of trimerised CrX_3 units at higher loadings although the structure could not be determined.

Several groups reported similar effects of anions on the chromium(III) distribution coefficient. Increasing concentrations up to 1 mol L^{-1} of nitrate, perchlorate and acetate ion did not effect the distribution coefficient (Islam & Biswas 1979b; Rao & Hariharan 1992). The presence of sulphate and chloride ions decreased the extraction efficiency (Islam & Biswas 1979b; Rao & Hariharan 1992; Schügerl, Segelken & Gudorf 1996). The work by Schügerl, Segelken and Gudorf (1996) suggested the depression of chromium(III) extraction by sulphate was due to complex formation but provided no supporting details or data.

The work of Islam and Biswas (1979a; 1979b) also demonstrated the effect of anion type and concentration on the rate of extraction of chromium(III) with D2EHPA. The rate of extraction was decreased by sulphate and nitrate while acetate ion did not affect the rate of extraction. The presence of phosphate anion (Islam, Biswas & Biswas 1981) appeared to exert little influence on the chromium(III) extraction however it did prevent increased sulphate concentration depressing the extraction of chromium(III).

Only one study attempted to determine the effect of temperature on the extraction of chromium with D2EHPA. Islam and Biswas (1979a) observed an increase in the distribution coefficient with increasing temperature in the range 30–60 °C but provided no explanation for this behaviour.

The choice of organic diluent has been shown to have a significant effect on the behaviour of some solvent extraction systems. The choice of diluent for the extraction of chromium(III) with D2EHPA has received some attention but the results are conflicting. Islam and Biswas (1979b) concluded that aliphatic diluents produced higher extraction at a given pH than aromatic diluents whereas Rao and Hariharan (1992) concluded that the most efficient extraction occurred with benzene as diluent. The extraction efficiency does not seem to follow any identifiable physical property of the diluent, e.g. dielectric constant or viscosity. There were some differences in the experimental conditions between these two studies such as the use of a chloride vs. sulphate/acetate matrix, different D2EHPA concentration and different pH of extraction (3.06 vs. 3.40) but nothing that would account for the vastly differing results.

The work of Preston (1983) examined the effect of the non-chelating 2-ethylhexanal oxime (EHO) on the extraction of base metals including chromium. The addition of EHO (0.5 mol L^{-1}) to an organic phase containing D2EHPA (0.50 mol L^{-1}) in xylene provided no synergistic advantage as measured by $pH_{0.5}$ value (approximately 3) for the extraction of chromium(III). A significant change in extraction behaviour with pH was noted for the unstable chromium(II). This trend was consistent with the other metals studied, with the synergism observed for divalent but not trivalent metals. This was attributed to the requirement for a formally neutral species to be extracted and the divalent metals requiring only two D2EHPA units for neutrality leaving coordination positions available for the EHO.

The alternative approach of adding non-aqueous solvents such as *N,N*-dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO) to the aqueous phase was studied by Kamitani *et al.* (1988). The aqueous phase contained chromium(III) (2×10^{-2} mol L^{-1}) and the organic phase contained D2EHPA (0.5 mol L^{-1}) in hexane. The presence of DMF and DMSO resulted in a decrease in the extraction of chromium(III) with an increase in non-aqueous solvent concentration. For instance, the extraction was reduced from 80% to less than 30% by the addition of 90 vol% DMF or DMSO to the aqueous phase. The addition of 70 vol% acetonitrile (AN) to the aqueous phase also resulted in a decrease in the chromium(III) extraction but only marginally.

The effect of competing cations was only evident in works that contain several cations in the aqueous solution. Cations that extract at a lower pH than chromium(III) will extract preferentially and if this results in a significantly loaded organic phase then chromium(III) extraction will be depressed. Iron(III) and zinc(II) were common interfering cations in chromium(III) extraction by D2EHPA as evidenced by the work of Schügerl, Segelken and Gudorf (1996). The presence of 1 mg L^{-1} of either iron(III) or zinc(II) decreased the chromium(III) extraction from 80% to 15 and 56% respectively as these cations were preferentially extracted.

The work examining the behaviour of chromium(III) with D2EHPA as the organic extractant was more extensive than that for Cyanex® 272. The metal is generally extracted in the pH range 3–5 and shows similar behaviour to commonly investigated transition metals such as nickel and cobalt. The presence of sulphate and chloride anions appears to depress the extraction while acetate and nitrate have no effect. Some significant differences exist between the various studies. Many of these appear to be due to different experimental conditions but some seem too great to be accounted for in this way.

Although part of the same family as Cyanex® 272, the direct transfer of D2EHPA results may not be possible due to the different pH ranges expected for extraction and the effect that this may have on the aqueous form of chromium(III). However the similarity of the extractant and the relatively large amount of data probably provides the best indication of the expected behaviour of chromium(III) with Cyanex® 272.

2.3.4 Extraction of Chromium(III) with Mono(2-Ethylhexyl) Phosphoric Acid

The use of mono-(2-ethylhexyl)phosphoric acid (M2EHPA) as an extractant for various transition metals has been reported (Yadav, Singh & Tandon 1991; Schügerl, Segelken & Gudorf 1996; Rao & Hariharan 1997; Khwaja, Singh & Tandon 2000a). The structure of the extractant, mono(2-ethylhexyl) phosphoric acid, is shown in Figure 2-5.

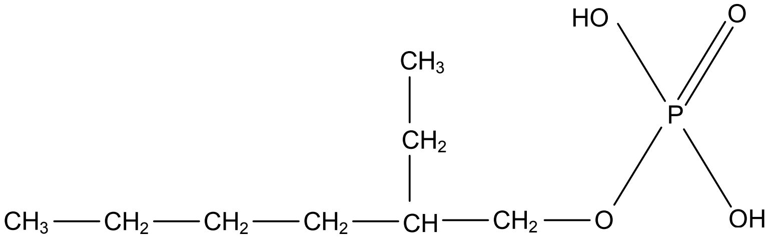


Figure 2-5. The structure of mono-(2-ethylhexyl)phosphoric acid (M2EHPA).

The aqueous phase acidity significantly affected the extraction efficiency, which decreased from near 90% at pH greater than 1 to less than 5% at pH 0.3. Rao and Hariharan (1997) reported slightly different behaviour with maximum extraction not being reached until pH 3.4.

The effect of diluent was discussed by Rao and Hariharan (1997) and Khwaja, Singh and Tandon (2000a). From chloride solutions, toluene as diluent gave the least efficient extraction while benzene and nitrobenzene were the most efficient of those tested. They concluded that commercial grade diluents could usually be substituted for reagent grade without detriment to the extraction behaviour. Extraction increased with increased extractant concentration, e.g. in the work of Schügerl, Segelken and Gudorf (1996) extraction increased from 70% at 5 vol% M2EHPA to 100% at 20 vol% M2EHPA.

The extracted species was proposed to be $Cr(HR)_3$ where H_2R is M2EHPA (Rao & Hariharan 1997; Khwaja, Singh & Tandon 2000a). This structure was based on slope analysis of the various parameters and was suggested to apply irrespective of the hydrolysis state of the extracted chromium(III).

Khwaja, Singh and Tandon (2000a) observed no decrease in loading up to 10^{-2} mol L^{-1} of chromium(III) whereas Schügerl, Segelken and Gudorf (1996) observed a 50% reduction in loading with an increase from 1.5 to 3.5 mg L^{-1} (approximately 5×10^{-5} mol L^{-1}) initial chromium(III) concentration in the aqueous phase.

The presence of perchlorate, nitrate and acetate anions up to 1 mol L^{-1} did not interfere in the extraction. Increases in the concentration of sulphate or chloride anions up to 1 mol L^{-1} resulted in decreases in the extraction efficiency.

The extraction behaviour of chromium(III) with M2EHPA appears quite similar to the behaviour with D2EHPA although the investigations have generally been focussed on different problems. This has led to a divergence of investigated conditions.

2.3.5 Use of Other Phosphoric Acid Extractants for Extraction of Chromium(III)

The extraction of chromium(III) with di-*o*-tolyl phosphoric acid has been investigated by Islam, Begum and Mustafa (1985). The contact time required to reach equilibrium was found to be about 20 minutes at pH 2.2. This was similar to some of the equilibration times reported above for other extractants in this pH range. The maximum extraction of 91% was observed at pH 2.55 from an aqueous solution containing chromium(III) (0.6 g L^{-1}) by an organic phase containing 0.4 mol L^{-1} extractant in benzene with hexanol as modifier. The extraction efficiency increased with increase in pH in the range 1.2–2.6 and with increase in extractant concentration in the range 0.06–0.4 mol L^{-1}. The extracted species was suggested to be a 1:1 metal:extractant complex at low loading in the pH range 1.55–2.55. This was postulated to change to a 1:3 complex at high loading with each extractant molecule acting as a bi-dentate ligand. The extraction increased with increases in temperature up to 50 °C but further increases in temperature resulted in decreases in extraction. The overall behaviour of this extractant appeared quite similar to D2EHPA.

Mellah and Bauer (1995) reported the extraction of chromium(III) from phosphoric acid solutions by *p*-(1,1,3,3-tetramethylbutyl) phenyl phosphoric acid in kerosene. The distribution coefficient (D) for chromium peaks (9.0) at an aqueous acid concentration of 5 mol L^{-1} H_3PO_4. The extraction efficiency was dependent on the metal ion concentration and acid strength of the aqueous phase. Maximum extraction of almost 90% occurred at 0.1 mol L^{-1} Cr(III) from 7 mol L^{-1} H_3PO_4 with 0.2 mol L^{-1} extractant. The effect of extractant concentration was insignificant in the range 0.2–0.4 mol L^{-1} (85 cf. 80% extraction respectively) although only 65% extraction occurred at 0.1 mol L^{-1} extractant. The level of extraction does not appear to be reproducible (cf. extraction for H_3PO_4 5 mol L^{-1}, chromium(III) 0.01 mol L^{-1} and extractant 0.2 mol L^{-1} in Figures 1 and 3 of the reported work).

2.4 Extraction of Chromium(III) with Other Extractants

2.4.1 Extraction of Chromium(III) with Tributyl Phosphate

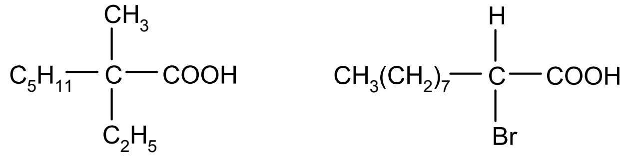
The extraction of chromium(III) with tributyl phosphate from perchloric acid solutions was investigated by Aggett and Udy (1970). The aqueous phase usually contained chromium(III) (1×10^{-4} mol L^{-1}) in perchloric acid. The extraction increased with decreases in acidity in the pH range from -1 to 3 and was not dependent on the chromium(III) concentration up to 10^{-2} mol L^{-1}.

Attempts to determine the nature of the extracted species by examining the visible absorption spectra failed to reveal anything other than the absence of hydrolysed species as predicted by the chemistry of the system. The reported spectra for $[Cr(H_2O)_6]^{3+}$ and $[Cr(ClO_4)(H_2O)_5]^{2+}$ were very similar to each other and the spectrum for the extracted species did not, according to the authors, correspond precisely with either. The visible spectrum of the loaded organic phase showed a marked change on heating which the authors suggested may be due to the formation of polymers in the organic phase.

The extraction of chromium(III) appeared anomalous for trivalent cations based on the expected behaviour of similar ions found in the literature, however the behaviour resembled that of divalent cations in moderately concentrated perchloric acid solutions. The authors suggested that $[Cr(ClO_4)(H_2O)_5]^{2+}$ was the predominant species extracted under these conditions.

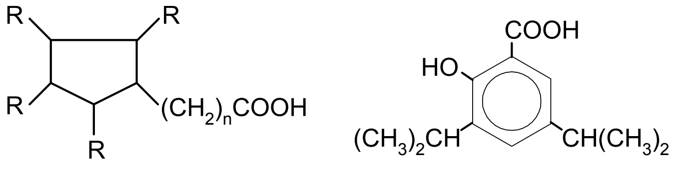
2.4.2 Extraction of Chromium(III) with Carboxylic Acids

The extraction behaviour of a range of metals, including chromium(II) and (III), with a number of carboxylic acids was reported by Preston (1985). The aqueous phase consisted of 0.05 mol L^{-1} $Cr(NO_3)_3$ in 1.0 mol L^{-1} $(Na,H)NO_3$. An aqueous phase containing chromium(II) was prepared by reacting chromium metal with sulphuric acid and used under a nitrogen atmosphere. The organic phase contained carboxylic acid (0.50 mol L^{-1}) in xylene. The carboxylic acid extractants are shown in Figure 2-6.



Versatic 10 Acid

2-Bromodecanoic Acid (BDA)



Naphthenic Acid

3,5 - Diisopropylsalicylic Acid (DIPSA)

Figure 2-6. Carboxylic acid extractants as used by Preston (1985).

Chromium(II) was only extracted by 3,5-diisopopylsalycylic acid (DIPSA) with a $pH_{0.5}$ of 3.2. Chromium(III) was extracted by 2-bromodecanoic acid (BDA) and DIPSA with $pH_{0.5}$ values of 2.56 and 2.50 respectively but required up to 150 hours to reach equilibrium in the these systems. Chromium(III) was not extracted by either Versatic® 10 or naphthenic acid. This was attributed by the author to hydrolysis of the metal in the aqueous phase at pH values below those required for extraction and is in contrast to the work of Doyle-Garner and Monhemius (1985).

An investigation into hydrolytic stripping of the extractant Versatic® 10 was reported by Doyle-Garner and Monhemius (1985). An obvious requirement of stripping metal from Versatic® 10 is that the metal could be loaded onto the organic extractant. The report indicated that 15.6 g L^{-1} Cr(III) was loaded onto Versatic® 10 (33 vol%) in Escaid® 110 diluent from either a sulphate or chloride solution.

The use of hexanoic acid has been reported for the extraction of chromium(III) from chloride-containing solutions (Apostoluk & Bartecki 1985). These workers found that a contact time of 48 hours was required to reach equilibrium in a system containing chromium chloride (1.09×10^{-3} mol L^{-1}) and sodium chloride (0.10 mol L^{-1}) in the aqueous phase with hexanoic acid (0.104 mol L^{-1}) in carbon tetrachloride as the organic phase.

These authors observed that increases in chloride ion concentration from 0.10 to 3.00 mol L^{-1} increased the chromium(III) extraction. An increase in the initial chromium(III) concentration from 2×10^{-4} to 1×10^{-2} mol L^{-1} resulted in increased chromium extraction. They argued that this dependence on initial chromium(III) concentration indicated the formation of polynuclear chromium(III) complexes in the organic phase. An increase in the extractant concentration in the range 0.1–1.0 mol L^{-1} shifted the extraction curve to lower pH values. Based on these data they concluded that $[Cr(OH)R_2{\cdot}HR]_3$ was the extracted species where HR is hexanoic acid.

The same authors also compared a range of straight and branched carboxylic acids as extractants. They concluded that for straight chain carboxylic acids, molecules with a longer chain length were better extractants due to changes in the solubility of the acid in the aqueous phase. Branched chain carboxylic acids were more effective than the corresponding straight chain extractant although no explanation was offered for this observation.

The use of a natural rosin, being primarily carboxylic acids, has been reported for the extraction of chromium(III) from aqueous solutions (Jimenez Gomez *et al.* 1990). The aqueous phase contained chromium(III) (1 g L^{-1}) as its nitrate salt. The extractant consisted of natural clear rosin (being the non-volatile fraction of pine resin) dissolved in toluene. The rosin contained over 90% acid matter, primarily abietic acid ($C_{20}H_{30}O_2$), and was tested in the concentration range 0.1–0.5 mol L^{-1}. The extraction curve moved to lower pH with increasing extractant concentration as expected for an ideal solvent extraction system. Complete extraction was achieved at a pH of approximately 2.5. A scheme for separating iron(III), chromium(III), manganese(II), cobalt(II) and nickel(II) was demonstrated. Although extraction using this reagent appeared generally efficient several of the details presented in this literature were conflicting.

The use of carboxylic acids appears to require long contact times for apparent equilibrium to be established possibly due to the lower pH values reported for extraction. This is in contrast to the reported times and extraction pH with Cyanex® 272 or D2EHPA.

2.4.3 Extraction of Chromium(III) with Long Chain Amines

The report of Coleman *et al.* (1958) represented several year's work of the Oak Ridge National Laboratory on the extraction properties of organic solutions of amines. A wide variety of primary, secondary and tertiary amines were studied at a concentration of 0.1 mol L^{-1} in an aromatic hydrocarbon diluent. Uranium extraction was the main focus of the study, however 22 other metal species were included at various stages. From an aqueous phase at pH 1 containing 1 mol L^{-1} sulphate anion there was less than 10% extraction of chromium(III) regardless of the extractant. This placed chromium(III) in the same group of behaviour as aluminium(III), vanadium(IV) and divalent metals such as cobalt, nickel, copper and zinc on the basis of extraction efficiency.

2.4.4 Extraction of Chromium(III) with Primene JMT™

The solvent extraction of chromium(III) from sulphate systems with Primene JMT™, a primary amine, was reported by Flett and West (1970). The aqueous phase contained chromium(III) (1×10^{-2} mol L^{-1}) in sulphate (1.5 mol L^{-1}) from sulphuric acid and sodium sulphate. The organic phase contained Primene JMT™ (5-20 vol%) in xylene.

Results were found to be dependent on the solution history and age. A stock solution was allowed to age at room temperature until there was no change in the extent of extraction. This was a solution age of approximately 500 hours at which time approximately 47% extraction occurred. An increase in the extraction temperature from 60 to 80 °C resulted in increases to the rate and extent of extraction over the first 300 minutes after which the results were the same.

The extent of extraction increased with decreasing acidity of the aqueous phase. The UV-visible spectra of the aqueous and loaded organic phases were not similar however no suggestion was made to explain this observation. It was found that chromium(III) and iron(III) could be separated as extraction of iron(III) depressed the extraction of chromium(III). Chromium(III) could also be separated from copper(II) as the divalent metal was not extracted.

Seeley *et al.* (1981), as part of a purification process for the recovery of aluminium, also investigated the extraction of various trace metal impurities. The aqueous phase contained chromium(III) in the range 10^{-4}–1 mol L^{-1} and ammonium sulphate (2 mol L^{-1}) at a pH of 1.5. The organic phase contained Primene JMT™ sulphate (0.435 mol L^{-1}) in toluene. Kinetics of extraction were poor with significant differences in extraction being noted between equilibration times of 15 minutes, 1 hour and 20 hours. The distribution coefficient was less than 0.1 indicating both poor extraction as well as poor kinetics.

2.4.5 Extraction of Chromium(III) with Trioctylamine

The extractants trioctylamine (TOA) and the commercial product Alamine® 336 are chemically similar. Trioctylamine contains only C_8 chains whereas the commercial extractant Alamine® 336 contains a mixture of C_8–C_{10} chains (*Alamine® 336* 2000). The choice of extractant by resective authors were retained in this review with the understanding that the results are normally comparable.

Florence and Farrar (1969) investigated the changes in extraction behaviour of chromium(III) with the straight chain tertiary amine, Alamine® 336 from concentrated halide media. The organic phase contained Alamine® 336 (0.3 mol L^{-1}) in cyclohexane. This diluent gave the best results of the seven diluents tested. Extraction from an aqueous phase containing chromium(III) (5×10^{-3} mol L^{-1}), zero free acid and various concentrations of lithium chloride reached a maximum of approximately 90% at 13 mol L^{-1} LiCl. The extraction decreased rapidly if acid was present in the system. Extraction was reported to increase in the order $Cl^- < Br^- < I^-$ with respect to the halide ion type, although the extent of extraction was not given. When extraction of chromium(III) was undertaken from methanolic solutions, equivalent extraction efficiency occurred at lower lithium chloride concentrations than from aqueous solutions.

The work of McDonald and Bajwa (1977) examined the extraction of chromium(VI) with Alamine® 336 and this is discussed in Section 2.6.1. In the course of their experiments low total chromium extraction results were found to occur due to the presence of chromium(III), which was not extracted under the experimental conditions used. Oxidation of the solutions prior to extraction in order to convert chromium(III) to chromium(VI) restored the extraction efficiency clearly indicating that long-chain tertiary amine reagents are poor extractants of chromium(III).

2.4.6 Extraction of Chromium(III) with Triisooctylamine

Selmer-Olsen (1966) examined the extraction of various metal ions, including chromium(III), from hydrochloric acid solutions. The organic phase contained triisooctylamine (TIOA) (20 vol%) in carbon tetrachloride. The aqueous phase contained chromium(III) (0.1 mol L^{-1}) and various concentrations of hydrochloric acid (1, 2 or 6 mol L^{-1}). The two phases were mixed for 2 minutes at an A:O ratio of 5:1. Chromium(III) was not extracted from these solutions.

Consistently, Brooks, Potter and Martin (1970), working to recover metal values from superalloy scrap, found that chromium[4] was not extracted by TIOA. The aqueous phase contained 35 g L^{-1} Cr, 19 g L^{-1} Co and 76 g L^{-1} Ni at pH 0. The organic phase contained TIOA (0.5 mol L^{-1}) in aromatic naphtha.

2.4.7 Extraction of Chromium(III) with Trioctyl Methylammonium Chloride

Irving and Al-Jarrah (1975) reported the use of trioctyl methylammonium chloride (Aliquat® 336) to extract the anionic ethylene diamine tetraacetic acid (EDTA) complex of various metals including chromium(III). A solution of Aliquat® 336 (0.2 mol L^{-1}) in 1,2-dichloroethane extracted up to 67% of the chromium(III) at pH 4.86 from an aqueous phase containing chromium(III) (4×10^{-3} mol L^{-1}) and EDTA (4.4×10^{-3} mol L^{-1}). The phase ratio was set to unity. The extracted species at pH 8 was found to be $CrY(OH)^{2-}$ where Y is the deprotonated EDTA species.

---

[4] The oxidation state of the chromium was not specified, but on the basis of it being recovered by precipitation as the sulphate salt, it was probably present in the (III) state.

In their work on the purification of plating solutions, Carstens *et al.* (1981) investigated the behaviour of chromium(III) when removing iron(II) and (III) as a thiocyanato complex with Aliquat® 336. Chromium(III) extraction did not occur under any of the investigated conditions. This was attributed to the slow rate of ligand exchange for chromium(III) and an extraction process that lasted only 15 minutes. No work with a longer contact time was reported.

2.4.8 Extraction of Chromium(III) with Other Amine Extractants

Irving and Al-Jarrah (1971) reported the use of quaternary *n*-hexylammonium chloride in 1,2-dichloroethane to extract chromium(III) from solutions containing an excess of EDTA. The extracted species was the $NR_4^+CrY(H_2O)^-$ ion pair (R = *n*-hexyl; Y is the deprotonated EDTA species) between pH 3.6 and 6.0 (maximum extraction at pH 4.7). The extraction constant, *K*, was determined as 0.062.

2.4.9 Extraction of Chromium(III) with Oxime Extractants

Brooks (1987) reported the use of single stage extractions for the recovery of metals from finishing wastes. From a synthetic solution containing 1 g L^{-1} each of Cr(III), Fe(III), Co(II), Cu, Ni, and Zn, less than 20% of the chromium was extracted at pH 1.75. The organic phase contained LIX® 622 (10 vol%) in naphtha.

A sequential solvent extraction scheme was investigated with an aqueous solution as above with metal concentrations of 0.2 g L^{-1}. A mixture of LIX® 63 and dinonyl naphthalene sulphonic acid (SYNEX DNO-52) extracted 99.8% of the chromium at pH 7.

Brooks (1993) also examined a binary mixture of LIX® 63 and D2EHPA. This organic combination extracted 76% of the chromium(III) from a solution containing 1.3 ppm[5] Cr (2864 ppm total metals) in a single contact at pH 5.

Mahmoud and Barakat (2001) reported the use of the extractant Acorga® M5640, which contains an aromatic oxime. The aqueous phase contained chromium(III) (6×10^{-3} mol L^{-1}). The organic phase contained Acorga® M5640 (10 vol%) in kerosene. Contact was at 30 °C for 10 minutes using a horizontal shaker. Chromium(III) was not extracted in the pH range 0.5–10.

The use of oxime extractants does not seem to provide efficient extraction of chromium(III). The extraction reported using mixed extractants is probably attributable to the non-oxime extractant.

2.4.10 Extraction of Chromium(III) with Acetylacetone

Extraction of chromium(III) was achieved at room temperature with acetylacetone (AA) by changing the nature of the aqueous phase (Kiba, Imura & Honjo 1977). In an attempt to modify the pH of a solution buffered with acetic acid-sodium acetate, the use of chlorinated acetic acid was investigated. The addition of these materials enhanced the extraction of chromium(III) in the order mono- < di- < tri-chloro acetic acid. Compared to extraction from solutions containing the acetate ion, extraction from solutions containing tri- and mono-chloroacetates and perchlorate all indicated a decrease in $pH_{0.5}$ (up to 5 pH units in the case of trichloroacetate). The extracted species was defined as $Cr(AA)_3$. In the absence of AA, chromium(III) was extracted into organic solvent provided chloroacetic acid, especially tri-chloro, was present in the aqueous phase. During this process the authors believe that the inner solvation sphere of the metal cation did not appear to be altered. The organic solvent must have a donor oxygen atom.

---

[5] Insufficient data provided to convert to SI units.

2.5 Extraction of Chromium(VI)

Chromium(VI), the other common oxidation state of chromium, is also known to exist in PAL generated industrial liquors. It has significantly different behaviour to chromium(III) due to its preference for forming neutral and anionic species in aqueous solutions (Cotton & Wilkinson 1988).

The speciation of chromium(VI) is dependent on the acidity and chromium(VI) concentration of the aqueous solution (Deltombe, de Zoubov & Pourbaix 1966). At pH less than about 1, chromic acid (H_2CrO_4) is the predominant form. Within the pH range 1–7 the predominant form is determined by total chromium(VI) concentration. If the chromium concentration is greater than 0.02 mol L^{-1} (≈1 g L^{-1}) then the dichromate ion ($Cr_2O_7^{2-}$) is predominant. At lower chromium(VI) concentrations, i.e. less than 0.02 mol L^{-1} the bichromate ion ($HCrO_4^-$) is predominant. At pH greater than about 7, the chromate ion (CrO_4^-) is predominant.

2.5.1 Extraction of Chromium(VI) with Acidic Organophosphorus Extractants

2.5.2 Extraction of Chromium(VI) with Cyanex® 272

The work of Ohki *et al.* (1986) examined chromium(VI) extraction with the use of a mercury lamp ultra-violet (UV) radiation source to assist solvent extraction. The aqueous phase contained sodium dichromate (2×10^{-4} mol L^{-1}) and hydrochloric acid (1×10^{-2} mol L^{-1}), pH 2. The organic phase contained bis(2,4,4-trimethylpentyl) phosphinic acid (5×10^{-2} mol L^{-1}) in toluene. An equal volume of each phase was mixed for 30 minutes in both dark and UV irradiated conditions.

Chromium(VI) showed 6% extraction in the dark and 56% extraction following phase contact under UV lamp irradiation. The author's interpretation was the photo-reduction of chromium(VI) to an activated state that reacts with the extractant prior to formation of an inert hexaaqua chromium(III) species. The extraction in the dark was attributed to reducing impurities in the organic phase that have the same effect as the UV irradiation.

The work of Ohki *et al.* (1986) is unique in its use of UV irradiation to assist solvent extraction and this makes it difficult to compare to other studies. A comparison by the authors of the extraction of chromium(VI) with Cyanex® 272 and a variety of other extractants is shown in Table 2-1. As this was a screening study no other details were provided.

Table 2-1. The extraction of chromium(VI) from an aqueous phase containing chromium(VI) (2×10^{-4}mol L^{-1}) in hydrochloric acid at pH 2 in dark and UV irradiated conditions. The organic phase contained the indicated extractant in toluene. The phase ratio was one and the contact time was 30 minutes.

Extractant (mol L^{-1})	UV Extraction (%)	Dark Extraction (%)
Bis(2,4,4-trimethylpentyl) phosphinic acid (5×10^{-2})	56	6
PC-88A® (5×10^{-2})	37	0
D2EHPA (5×10^{-1})	31	12
TOPO (2×10^{-2})	91	26
TBP (5×10^{-2})	56	0

Effective extraction of chromium(VI) was reported by Rao and Prasad (1988) and Nahar *et al.* (1995) with Cyanex® 272 in approximately 30 minutes. The acidity of the aqueous phase was more important than the acid type with similar results observed with hydrochloric, hydrobromic, sulphuric, perchloric and nitric acids (Rao & Prasad 1988). This is consistent with the suggestion of Nahar *et al.* (1995) that the extracted chromium(VI) species is chromic acid, H_2CrO_4. Efficient extraction therefore requires pH less than two and preferably the aqueous phase contained 1.5–3 mol L^{-1} acid. The extracted species was suggested to be a 1:1 metal:extractant complex by both groups of authors. Nahar *et al.* (1995) found this to be supported by shifts for the P=O vibration of the IR spectrum. The addition of the corresponding sodium salt to the aqueous phase was observed to decrease the chromium(VI) extraction by Rao and Prasad (1988) although no details or data were provided.

The extraction coefficient increased with increasing temperature between 21 and 50 °C indicating to the authors an endothermic extraction reaction (Nahar *et al.* 1995).

The extraction of chromium(VI) with Cyanex® 272 occurs at low pH irrespective of the components of the aqueous phase. The extraction mechanism appears to be the formation of a 1:1 extractant:chromic acid species.

2.5.3 Extraction of Chromium(VI) with 2-Ethylhexyl Phosphonic Acid Mono-2-ethylhexyl Ester

John *et al.* (1999) investigated the extraction of iron(III) and titanium(IV) from acidic chloride solutions with 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A®, EHEHPA). Chromium(VI) was included as a metal found in waste chloride liquors of the titanium minerals industry. The extraction of chromium(VI) was found to be moderate, 8–20%, with hydrochloric acid concentrations between 0.03 and 1 mol L^{-1}. Other conditions were chromium(VI) (1×10^{-4} mol L^{-1}), EHEHPA (5×10^{-2} mol L^{-1}) in xylene, A:O 1, temperature 303±1 K and a contact time of 15 minutes.

2.6 Extraction of Chromium(VI) with Other Extractants

2.6.1 Extraction of Chromium(VI) with Tributyl Phosphate

The extraction and recovery of chromium(VI) from industrial effluents has been reported by Cuer, Stuckens and Texier (1974). Tributyl phosphate (TBP) was used undiluted to extract chromium(VI) from a solution containing chromium(VI) (7.7 g L^{-1}) and sulphuric acid (2 mol L^{-1}). An organic phase containing 23.6 g L^{-1} Cr(VI) was produced and after 24 hours only 0.3% of the metal had been reduced to chromium(III). On this basis TBP appeared more stable to acidic, oxidising conditions than trioctyl amine (TOA) and di-lauryl amine (LA 2). This difference was probably due to the higher purity of TBP and the absence of diluent when this extractant was used. The other amine extractants, TOA and LA 2, showed no loss of amine function indicating that the chromium(VI) reduction was due to the presence of the diluent when these extractants were used. At 1 mol L^{-1} acid concentration and an aqueous chromium(VI) concentration of 0.2 g L^{-1} the distribution coefficient was 6.0 and the maximum loading was 30.0 g L^{-1} Cr(VI). These values could be increased to 12.5 and 55.0 respectively by doubling the acidity of the aqueous phase, a useful property of TBP as an extractant for chromium as many of the effluents were of an acidic nature. Increasing the initial concentration of chromium depressed the concurrent loading of the sulphate ion.

A process for the recovery of pure metal salts from waste hydroxide sludges has been patented (Bolt, Tels & Van Gemert 1984). Following dissolution of the mixed hydroxide sludge and removal of iron, the solution was oxidised at pH 3 with liquid bleach to convert all chromium to chromium(VI). The chromate anion was then extracted (99.9%) with a mixture of TBP and TOA in 2 stages at pH 3.5 and A:O of 2. The loaded organic was stripped with caustic at pH 8, and the chromium precipitated as sodium chromate, $\mathrm{Na_2CrO_4}$.

2.6.2 Extraction of Chromium(VI) with Trioctyl Phosphine Oxide

Huang, Huang and Chen (1997) studied the extraction of chromium(VI) with trioctyl phosphine oxide (TOPO) after calculating the chromium equilibria in aqueous solution. The aqueous phase containing chromium(VI) (3.9×10^{-3} mol L^{-1}) was contacted with a solution of TOPO (0.1 mol L^{-1}) in kerosene. In the pH range 2.2–4 both bichromate, $\mathrm{HCrO_4^-}$, and dichromate, $\mathrm{Cr_2O_7^{2-}}$, (the predominant species in this pH range) transferred to the organic phase. The predominant species in both the aqueous and organic phase were chromium concentration dependent as would be expected from earlier work on aqueous equilibria (Deltombe, de Zoubov & Pourbaix 1966). The extracted species were given as $\overline{\mathrm{H_2CrO_4\cdot(TOPO)}}$ and $\overline{\mathrm{H_2Cr_2O_7\cdot(TOPO)_3}}$. The first structure is similar to the 1:1 metal:extractant ratio proposed by Murty, Rao and Sastri (1981) for the extraction of chromium(VI) from solutions of orthophosphoric acid.

2.6.3 Extraction of Chromium(VI) with Trioctylamine

The extraction of chromium(VI) with trioctylamine (TOA), or Alamine® 336, has been studied by several groups of workers.

The extraction of chromium(VI) with TOA is relatively well studied particularly in relation to its application in waste-water treatment. Davis *et al.* (1988) used the existing body of work in a comparison of methods for removing chromium from wastewater concluding that liquid ion exchange (solvent extraction) had a role to play.

The transfer of chromium(VI) to an organic phase that contained Alamine® 336 appears to be quite fast with reported extraction times in the range 1–3 minutes (Deptula 1968; McDonald & Bajwa 1977; Horn *et al.* 1994; Duan, Li & Zhuang 1998).

Chromium(VI) is extracted by TOA over a range of pH values with maximum extraction occurring in the range 0–2 and extraction decreasing as the pH exceeds this range (Deptula 1968; Zumer, Modic & Zupan 1974; Horn *et al.* 1994; Duan, Li & Zhuang 1998). Deptula (1968) found that extraction also decreased at higher acid concentration due to competitive extraction of sulphate and bisulphate. The work of Horn *et al.* (1994) found no evidence for competition by sulphate ion for extraction sites in the organic phase as was earlier reported by Cuer, Stuckens and Texier (1974).

The control of pH is important in controlling the metals extracted by a reagent. The combination of proton producing and consuming reactions has been proposed by Chilukuri, Yang and Sirkar (1998) to control the pH of the aqueous phase. The aqueous phase contained copper, chromium(VI) and sometimes zinc. The organic phase contained TOA and LIX 84 in kerosene. Simultaneous extraction of cationic species (Cu^{2+}, Zn^{2+}) by LIX 84 and anionic species ($HCrO_4^-$) by TOA resulted in improved pH control and hence extraction efficiency. The system was very sensitive to the metal concentration in the feed solution and the ratio of extractants in the organic phase.

The extraction efficiency of chromium(VI) did not appear to be affected by the initial chromium concentration (and hence initial chromium(VI) speciation) provided the correct pH was maintained and sufficient extractant was available. Compare for example the work of Cuer, Stuckens and Texier (1974) and McDonald and Bajwa (1977). Both these research groups reported near complete extraction of chromium(VI), one with $7.6\ g\ L^{-1}$ Cr(VI) and the other $1.2\times10^{-3}\ g\ L^{-1}$. The extracted species may change as discussed by Duan, Li and Zhuang (1998) who proposed a 1:1 trioctyl amine (TOA):Cr complex for singly charged chromium(VI) species and a 2:1 complex for doubly charged chromium(VI) species.

There were several reports of chromium(VI) being reduced to chromium(III). Deptula (1968) reported that the loaded organic solutions changed from orange to green on exposure to sunlight for several days or UV light for one hour. No change took place when solutions were stored in the dark. Despite storing solutions in the dark, Cuer, Stuckens and Texier (1974) found 12% of the chromium(VI) to be reduced to chromium(III) in 144 hours. This was attributed to reaction with impurities in the solvent as no loss of amine functionality was reported. Reduction of chromium(VI) to chromium(III) can cause problems due to the inability of TOA to extract chromium(III) (McDonald & Bajwa 1977) and the possible stabilisation of emulsions by organic degradation products (Cuer, Stuckens & Texier 1974).

The extraction efficiency of chromium(VI) was observed to increase with increasing trioctylamine (TOA) concentration in the range 0.01–0.1 mol L^{-1} (Deptula 1968). The effect of extractant concentration was not reported by other authors.

A number of organic diluents have been used in the organic phase during chromium(VI) extraction. Deptula (1968) compared the extraction behaviour of chromium(VI) when hexane, cyclohexane, nitrobenzene, chloroform, carbon tetrachloride, benzene, toluene and xylene were used as diluent. Hexane and cyclohexane were found to be unsuitable due to the formation of a third phase. The extraction coefficient of the other diluents was found to lie between that of nitrobenzene (highest) and carbon tetrachloride (lowest). Kerosene (Zumer, Modic & Zupan 1974), Exxsol® D-60 (Horn *et al.* 1994) and octane (Duan, Li & Zhuang 1998) have also been successfully used as a diluents.

The synergistic and antagonistic effects of alkylphosphoric acids (HX) on extraction of chromium(VI) with trioctylamine (TOA) have been examined (Deptula 1971). The alkylphosphoric acids interact only with complexes as described above to form complexes of the type $(R_3NH)_2Cr_2O_7(HX)_n$ or $R_3NH_2Cr_2O_7(HX)_n$ where R_3N is TOA and the alkylphosphoric acids were hydrogen bonded to the dichromate anion. The synergistic effect observed with alkylphosphoric acids compared to extraction by TOA alone was attributed to the formation of these strongly organophilic ion pairs. The extraction mechanism was independent of the mineral acid concentration and the appearance of synergistic or antagonistic effects.

The extraction of chromium(VI) with TOA is fast and occurs from aqueous solutions at pH less than 4, preferably less than 2. The composition of the organic phase with respect to the extractant concentration and diluent appears to have little effect on the efficiency of extraction provided sufficient extractant is available and phase separation occurs.

2.6.4 Extraction of Chromium(VI) with Triisooctylamine

The extraction of various metal ions, including chromium, from hydrochloric acid solutions has been studied with triisooctylamine (TIOA) as the extractant (Selmer-Olsen 1966). An organic phase containing TIOA (0.57 mol L^{-1}) in carbon tetrachloride was used at an A:O ratio of 5:1 to extract metals from an aqueous solution containing chromium(VI) (0.1 mol L^{-1}) and hydrochloric acid. Complete extraction of chromium(VI) from 1 or 2 mol L^{-1} HCl was observed in 2 minutes.

Attempting to clarify the mechanism for extraction, Huang, Chen and Kuo (1992) examined the species extracted from a solution containing chromium(VI) (1.92×10^{-2} mol L^{-1}) with TIOA (0.025 mol L^{-1}) in *o*-xylene at various hydrogen and chloride ion concentrations. They concluded that the extracted species were $\overline{\text{(TIOAH)HCrO}_4}$ or $\overline{\text{(TIOAH)HCrO}_4\cdot\text{HCl}}$ dependent on the product of the hydrogen and chloride ion activities. It was stated that within the confines of this system, dichromate species were not transferred into the organic phase even though the dominant chromium species in aqueous solution were the $Cr_2O_7^{2-}$ and $HCrO_4^-$ anions (pH 1 to 5).

2.6.5 Extraction of Chromium(VI) with Other Amine Extractants

The extraction of chromium(VI) with di-lauryl amine (LA 2) has been studied (Cuer, Stuckens & Texier 1974). The aqueous phase contained chromium(VI) (3.8 g L^{-1}) and sulphuric acid (1 mol L^{-1}). The organic phase contained LA 2

(0.1 mol L^{-1}) in xylene. A loaded organic phase containing 5.43 g L^{-1} Cr(VI) was produced. In 170 hours 6% of the extracted chromium(VI) had been reduced to chromium(III), which was attributed to oxidation of the diluent as the amine functionality was unchanged. The distribution coefficient was increased by decreasing the acidity in the aqueous phase from 1 to 0.01 mol L^{-1}. The sulphate ion was interpreted to be extracted together with the dichromate ion.

A metal recovery process from plating rinse water has been developed that includes chromium recovery (Magdics & Stain 1989). An aqueous phase containing traces of chromic and sulphuric acids (pH 6 to 8) was contacted with an organic phase containing trioctyl methyl ammonium hydroxide in kerosene. Chromium(VI) was extracted selectively over nickel and cobalt.

2.6.6 Extraction of Chromium(VI) with Other Extractants

The use of 2-hexylpyridine (HPy) to selectively extract chromium(VI) has been reported (Iqbal & Ejaz 1978). The extraction of trace (<10^{-5} mol L^{-1}) and macro (0.05 mol L^{-1}) amounts of chromium was examined. The organic phase contained HPy (0.1 mol L^{-1}) in chloroform. Aromatic hydrocarbons were found to depress chromium(VI) extraction and a precipitate formed at the aqueous/organic interface. Alcohol based organic phases underwent an increase in turbidity and volume during extraction experiments.

Maximum extraction of chromium(VI) occurred in the pH range 0–1 irrespective of the acid used. The extracted species contained a 1:1 metal:extractant ratio as found for other amine extractants in this pH range. The addition of neutral chloride and sulphate anions did not affect the extraction. The presence of nitrate, ascorbate, acetate, citrate, oxalate, thiosulphate and thiocyanate ions decreased the extraction of chromium(VI).

The use of 5-(4-pyridyl)nonane *N*-oxide (P_yNO_x) for the extraction of chromium(VI) was reported (Gashgari, Al-Yobi & Ejaz 1990). The extractant was dissolved in benzene to give a concentration of 0.1 mol L^{-1}. The chromium(VI) concentration was varied from trace ($<10^{-6}$ mol L^{-1}) to 1 g L^{-1}. The predominant mode of extraction was through ionic association i.e. complexes of the form $P_yNO_xH^+ \cdot HCr_2O_7^-$. Extraction of chromium(VI) was studied from sulphuric, hydrochloric and nitric acids. The use of hydrochloric acid gave lower distribution coefficients than sulphuric acid. The use of nitric acid inhibited the reduction of chromium(VI) to chromium(III) as reported with the other mineral acids. Similar effects of masking anions and metal comparisons were made as for extraction by HPy.

The relatively specific extraction of chromium(VI) by a crown ether has been reported in the development of an analytical method (Yakshin, Vilkova & Makarova 1998). Extraction efficiency was dependant on the type of acid used in the aqueous phase. The sequence was represented by:

$$H_3PO_4 < H_2SO_4 < HNO_3 < HCl$$

In the case of orthophosphoric and nitric acids the addition of the corresponding salts decreased the extraction. The addition of sulphate or chloride salts to sulphuric and hydrochloric acid solutions respectively increased the extraction efficiency. The use of chloroform or dichloroethane as organic solvent was suggested. The ability to extract chromium(VI) from sulphate solutions with a crown ether was reported as novel.

It was recommended that the concentration of sulphuric acid not be allowed to exceed 3 mol L^{-1} in order to prevent reduction of chromium(VI) to chromium(III), which did not extract. The extracted complex exhibits a 1:1 ratio of metal:crown ether and the analytical method could be used for analysis of material containing up to 2.5 g L^{-1} chromium(VI).

2.7 Stripping of Chromium

When solvent extraction is used in hydrometallurgical processing, where purification and/or concentration of specific components is the aim, it is essential that the extractant can be easily stripped to allow recycling of the organic phase without loss of efficiency.

Unlike most first-row transition metals such as copper, nickel and cobalt(II), stripping of chromium from a loaded organic phase appears to be highly dependent not only on the stripping conditions but also on the conditions in which the organic phase was loaded. Factors such as stripping agent, amount of chromium loaded on to the organic phase and the organic phase components all affect stripping performance whereas for many metals stripping is governed only by the concentration of the strip solution (Ritcey & Ashbrook 1984).

2.8 Stripping of Chromium(III) from Acidic Organophosphorus Extractants

2.8.1 Stripping of Chromium(III) from Cyanex® 272

Pandey, Cote & Bauer (1996) examined the stripping of chromium(III) from Cyanex® 272 following extraction from a synthetic leather tannery effluent. The loaded organic phase contained chromium(III) (7×10^{-2} mol L^{-1}), Cyanex® 272 (0.48 mol L^{-1}, 15 vol%) and *p*-nonylphenol (0.43 mol L^{-1}, 10 vol%) in kerosene. Experiments were performed at 22 °C and a phase ratio of 1.

The stripping of chromium(III) from Cyanex® 272 was incomplete. In 20 minutes, hydrochloric acid (8 mol L^{-1}) stripped 80% of the loaded chromium. Kinetic studies indicated that 77% of loaded chromium(III) was stripped within 2 minutes with increased contact time having little effect. With four individual five minute contacts, stripping reached 84%. Hydrochloric acid concentrations of less than 6 mol L^{-1} did not achieve more than 70% stripping even with multiple contacts. This incomplete stripping was attributed by the authors to the extraction of some hydrolysed or polymeric species although further work was suggested as no evidence was provided.

The same study showed that the removal of low levels of chromium(III) from the organic phase appears to go to completion under relatively mild conditions. A loaded organic phase containing chromium(III) (8×10^{-4} mol L^{-1}) was completely stripped with hydrochloric acid (3 mol L^{-1}) with a contact time of 5 minutes.

The stripping of low concentrations of chromium(III) from Cyanex® 272 impregnated resin has been reported by Navarro Mendoza *et al.* (2000). The chromium(III) concentration was 2×10^{-4} mol L^{-1} and the stripping of chromium(III) was dependent on the strength of hydrochloric acid used. The highest acid concentration tested (6 mol L^{-1}) gave the best result of 95% stripping efficiency.

These results clearly show that both the amount of loaded chromium(III) in the organic phase and the acidity of the stripping solution have significant effect on the stripping efficiency.

2.8.2 Stripping of chromium(III) from Di(2-Ethylhexyl) Phosphoric Acid

Islam and Biswas (1979a) reported chromium(III) could not be stripped from an organic phase of di(2-ethylhexyl) phosphoric acid (D2EHPA) in benzene although no details were given.

In contrast Pandey, Cote and Bauer (1996) found that some chromium(III) could be stripped from an organic phase containing D2EHPA. The loaded organic phase contained chromium(III) (approximately 4 g L^{-1}), D2EHPA (0.45 or 0.75 mol L^{-1}) and isodecanol (0.53 mol L^{-1}) in kerosene. Experiments were performed at 22 °C and a phase ratio of 1.

They found that stripping of chromium(III) from the organic phase with hydrochloric acid was dependent on the acid strength. A contact time of 30 minutes yielded maximum recovery of approximately 50% with up to 3 mol L^{-1} acid. This is a poor metal recovery when complete stripping of nickel could be achieved with 1 mol L^{-1} acid solutions as shown for instance in the study by Preston and Fleming (1983).

An increase in the acid concentration to 8 mol L^{-1} resulted in 80% recovery and a further increase in the acid strength to 11 mol L^{-1} gave 1-2% more recovery. An increase in the contact time from 24 to 72 hours improved the stripping efficiency with 8 mol L^{-1} hydrochloric acid from 85 to 87%. Improved recovery of 90% could be achieved in 20 minutes with 12 mol L^{-1} acid but it was felt by the authors that this may lead to decomposition of the extractant. The use of nitric or sulphuric acid, 6 mol L^{-1}, yielded only 45% recovery of chromium(III) in 10 minutes and 10 mol L^{-1} nitric acid resulted in 65% recovery in 20 minutes.

An increase in the temperature of the stripping experiments to 40 °C with hydrochloric acid (8 mol L^{-1}) showed approximately 70% stripping in one five-minute contact and 85% recovery in five contacts.

The authors (Pandey, Cote & Bauer 1996) noted that a much lower concentration of chromium(III) (2×10^{-3} mol L^{-1}), could be completely stripped from an organic phase containing D2EHPA (0.45 mol L^{-1}) and isodecanol (0.53 mol L^{-1}) in kerosene with hydrochloric acid (1.0 mol L^{-1}) at room temperature using a 5 minute contact time.

This is similar to the independent finding of Schügerl, Segelken & Gudorf (1996) who reported near-complete stripping of organic phases that have low chromium(III) loading. In their study, the loaded organic phase contained chromium(III) ($\sim4\times10^{-5}$ mol L^{-1}) and D2EHPA (1.5 mol L^{-1}) in kerosene. Stripping reached 98% with sulphuric acid (0.5 mol L^{-1}) and 74% with hydrochloric acid (1 mol L^{-1}). When using sulphuric acid the stripping A:O ratio could be reduced to 1:4 while maintaining the stripping recovery. These authors noted that allowing the loaded organic phase to stand before stripping led to a marked decrease in stripping recovery.

The stripping of chromium(III) from a loaded organic phase containing D2EHPA appears difficult. Low levels of chromium(III) may be completely stripped however higher loadings or complete stripping from an organic phase that has been allowed to age was not possible. The use of concentrated acids or higher temperatures did not significantly improve the stripping efficiency.

2.8.3 Stripping of Chromium(III) from Mono-(2-Ethylhexyl) Phosphoric Acid

Schügerl, Segelken & Gudorf (1996) reported a near-complete stripping of organic phases containing chromium(III) loaded onto mono-(2-ethylhexyl) phosphoric acid (M2EHPA). The loaded organic phase contained chromium(III) (~4×10^{-5} mol L^{-1}) and M2EHPA (20 vol%) in kerosene. Stripping reached 98% with sulphuric acid (0.5 mol L^{-1}) and 86% with hydrochloric acid (1 mol L^{-1}). The stripping A:O ratio could not be reduced without reducing the stripping recovery. They observed, similar to the behaviour with D2EHPA, that allowing the organic phase to stand before stripping reduced the stripping efficiency although no explanation was offered.

2.9 Stripping of Chromium(III) from Other Extractants

2.9.1 Stripping of Chromium(III) from Tributyl Phosphate

Ohki *et al.* (1986) observed that stripping of chromium(III) from TBP reached only 16% with hydrochloric acid (6 mol L^{-1}) in one hour under UV irradiation but no chromium(III) could be stripped in the absence of UV irradiation. Neither further details nor explanation for these observations was offered.

2.9.2 Stripping of Chromium(III) from Trioctyl Phosphine Oxide

The work of Ohki *et al.* (1986) on extraction of chromium(VI) concluded that trioctyl phosphine oxide (TOPO) was the most efficient extractant for chromium(VI) (Chapter 2.6.1). Although extraction experiments were carried out using chromium(VI) the authors concluded that chromium(III) was the stable oxidation state in the organic phase. The stripping of chromium from TOPO was therefore considered assuming stripping of chromium(III). Stripping efficiency of 94% was achieved with hydrochloric acid (6 mol L^{-1}) and contacting the two phases for two hours under UV irradiation. Reducing the acid concentration, the contact time or operating without UV irradiation all decreased the amount of stripping.

2.9.3 Stripping of Chromium(III) from Primene JMT™

The stripping of chromium(III) from Primene JMT™ was reported by Flett and West (1970). The loaded organic phase contained chromium(III) in the range 24–110×10^{-3} mol L^{-1} and 10 vol% extractant in xylene. Hydrochloric acid was a more effective stripping agent than sulphuric acid with complete stripping always possible using hydrochloric acid. Although it was always possible to remove all the chromium(III) from the organic phase with hydrochloric acid, harsher conditions in the form of higher temperatures (up to 60 °C), higher acid strengths (up to 6 mol L^{-1}) or longer contact times (up to 180 minutes) were required as the chromium(III) concentration increased from 0.02 to 0.1 mol L^{-1}.

2.9.4 Stripping of Chromium(III) from Oxime Extractants

Brooks (1987) reported complete extraction of chromium(III) (2×10^{-2} mol L^{-1}) by a mixture of LIX® 63 and dinonyl naphthalene sulphonic acid (SYNEX DNO-52) but attempts to strip this loaded organic phase using two contacts of sulphuric acid (1.9 mol L^{-1}) were not successful.

2.9.5 Stripping of Chromium(III) from Carboxylic Acids

An investigation into hydrolytic stripping of the extractant Versatic® 10 was reported by Doyle-Garner and Monhemius (1985). The report indicated that 15.6 g L^{-1} Cr(III) loaded onto Versatic® 10 (33 vol%) in Escaid® 110 diluent could not be hydrolytically stripped from Versatic® 10. Instead polymerisation occurred and a viscous organic phase formed.

The stripping of chromium(III) from a natural rosin dissolved in toluene has been reported (Jimenez Gomez *et al.* 1990). Total stripping of chromium(III) (2×10^{-2} mol L^{-1}) was obtained using a stoichiometric amount of sulphuric acid.

2.10 Stripping of Chromium(VI)

The recovery of chromium(VI) from the organic phase appears easier than the recovery of chromium(III). Provided chromium(VI) is not reduced during extraction, or on standing of the loaded organic phase, it is usually completely recovered. There were however no reports on the stripping of chromium(VI) from acidic organophosphorus extractants.

2.10.1 Stripping of Chromium(VI) from Tributyl Phosphate

The recovery of chromium(VI) from an organic phase consisting of undiluted tributyl phosphate (TBP) was investigated by Cuer, Stuckens and Texier (1974).

The organic phase was loaded with chromium(VI) (0.4 mol L^{-1}). They found that chromium could be stripped as sodium chromate from TBP using two moles of sodium hydroxide for each mole of chromium(VI). Chromium(VI) could also be stripped as sodium dichromate by reducing the pH of the aqueous phase to 4 prior to sodium hydroxide addition. A 1:1 ratio of sodium hydroxide to chromium was then sufficient for complete stripping.

2.10.2 Stripping of Chromium(VI) from Trioctylamine

Several of the groups of researchers who investigated the extraction of chromium(VI) with trioctylamine (TOA) also reported the conditions used to remove chromium(VI) from the loaded organic phase. Deptula (1968) used sodium hydroxide (0.5 mol L^{-1}) to strip chromium(VI) with a phase ratio of unity. The required contact time was 10 minutes. Zumer, Modic and Zupan (1974) found that a mixture of sodium chloride and sodium hydroxide provided the most effective stripping solution. McDonald and Bajwa (1977) used sodium hydroxide (4 mol L^{-1})to strip chromium(VI) (0.1 mol L^{-1}) from TOA. This was a more effective stripping medium than sulphuric acid, ethylenediamine or ethylene diamine tetraacetic acid (EDTA).

2.10.3 Stripping of Chromium(VI) from Other Amine Extractants

Cuer, Stuckens and Texier (1974) considered the stripping of chromium(VI) from the secondary amine di-lauryl amine (LA 2). They found that an organic phase containing chromium(VI) (2×10^{-3} mol L^{-1}) and LA 2 (0.1 mol L^{-1}) could be completely stripped by using two moles of sodium hydroxide for each mole of chromium(VI). Any sulphate in the organic phase was preferentially stripped. Chromium(VI) was recovered primarily as the chromate ion, CrO_4^{2-}.

A patent application of Magdics and Stain (1989) for treating plating rinse water used trioctyl methylammonium hydroxide in kerosene as the organic phase. Accordingly, this organic phase loaded with trace amounts of chromium(VI) could be stripped with ammonium hydroxide but no further details were provided.

2.11 Summary of Related Literature

Little work on the extraction of chromium(III) with Cyanex® 272 has been reported with seemingly conflicting results. These studies used limited experimental conditions especially with respect to the pH range reported. The single study that deals primarily with the extraction of chromium(III) with Cyanex® 272 found that chromium(III) could be extracted with Cyanex® 272 over a certain pH range which is in apparent contrast to other reports dealing primarily with other metals or extractants. However this paper used a complex aqueous phase limiting the application of the generated data to other systems. The shortage of studies on this system mean that several key variables have not been investigated nor comparative behaviour been determined.

The shift to lower extraction equilibrium pH when di(2-ethylhexyl) phosphoric acid (D2EHPA) was used as the extractant suggested that the data generated in this system, although more extensive, cannot be extended to its extraction with Cyanex® 272 because the change in the predominant chromium(III) species. With decreased hydrolysis occurring at lower pH, the nature of the metal species involved in extraction may change as the pH changes. The extraction behaviour of chromium(III) appeared more typical of first-row transition metals than is often predicted. This suggests that extraction of chromium(III) with Cyanex® 272 should be possible if the contact conditions can be optimised.

Although it has been shown that various extractants could be used to extract chromium(III), the wide variation in experimental conditions required for each extractant clearly indicated that those data cannot be extended to Cyanex® 272.

The extraction of chromium(VI) with Cyanex® 272 occurred at lower pH and by a different mechanism to extraction of chromium(III). Although again there is little work on this system it appeared less conflicting than the collective work on chromium(III).

A greater amount of work has been published on the extraction of chromium(VI) as the anionic species, which predominate in aqueous solution, than on any other aspect of chromium solvent extraction. Cyanex® 272 does not extract anionic species and so this information could not be transferred to the system used in the present work.

The stripping of chromium from a loaded organic phase has received less attention than its extraction. Chromium(III) was difficult to strip from the organic phase, especially at higher metal concentrations or if the loaded organic phase was allowed to age before stripping. Due to the different extraction mechanism, stripping of chromium(VI) appeared easier and more effective than stripping of chromium(III).

CHAPTER 3. EXPERIMENTAL PROCEDURE

3.1 Preparation of Aqueous Phase Test Solutions

The aqueous solutions were prepared from analytical grade (Univar®) salts, sourced from Ajax Chemicals unless noted. Water used in the preparation of synthetic solutions was distilled deionised water. Chromium(III) solutions were prepared from chromium nitrate nonahydrate ($Cr(NO_3)_3.9H_2O$, Unilab®). Chromium(VI) solutions were prepared from sodium dichromate ($Na_2Cr_2O_7$). The matrix components were added as sodium sulphate (Na_2SO_4) and sodium chloride (NaCl, BDH, AnalaR®). The ionic strength was adjusted with sodium nitrate ($NaNO_3$) as nitrate is generally non-complexing and does not interfere in analysis of chromium by atomic absorption spectroscopy. The ionic strength (I) of the solutions was maintained at 0.7 mol L^{-1} calculated using the formula $I = 0.5\sum c_i z_i^2$ where *c* is the concentration of the ion and *z* is its formal charge (Vogel 1962).

To simulate real operating conditions some experiments used solutions obtained from Bulong Nickel Operation. A 20 L sample of cobalt feed solution (PLS) was collected and the analysis is shown in Table 3-1. This solution was spiked with the appropriate chromium ion, i.e. chromium(III) as chromium nitrate or chromium(VI) as sodium dichromate to provide the desired concentration of chromium in the test solution. Although the sample of plant solution did not contain detectable levels of chromium, this metal has been detected in the PLS as a function of upstream plant performance (Personal Communication: S. Allen 1999, W. Rickelton 1999).

Table 3-1. Elemental composition of Bulong Nickel Operation cobalt feed solution (PLS).

	Ni	Co	Fe	Al	Cr	Ca	Mn	Mg	Zn
Conc. mg L^{-1}	4650	352	1	0.07	0	463	1031	1520	42

All aqueous test solutions were prepared using standard glass pipettes and volumetric flasks. This included the transfer of aliquots of the test solution to the mixing vessel.

3.2 Preparation of the Organic Phase Test Solutions

The extractants Cyanex® 272 and Cyanex® 301 were used as supplied by Cytec (Australia). Di(2-ethylhexyl) phosphoric acid (D2EHPA) was sourced from BDH Laboratory Supplies (minimum assay 98%) and used as supplied. The primary diluent, Shellsol® 2046, was supplied as a sample by the Shell (Australia) Ltd. Shellsol® 2046 is a narrow-cut kerosene containing 20% aromatics and 80% alkanes (paraffins) and cycloalkanes (naphthenes). The boiling range was given as 198–240 °C. Other diluents used were obtained from Ajax Chemicals and were hexane (Unilab®), cyclohexane (Univar®) and xylene (Univar®). All organic reagents were used without further purification.

The supplied batch of Cyanex® 272 contained approximately 92% active component, bis(2,4,4-trimethylpentyl) phosphinic acid. This was assessed by acidimetric titration as described in the product information (*Cyanex® 272 Extractant*).

An aliquot of the organic phase to be analysed was washed with sulphuric acid and the two phases separated using Whatman® 1PS phase separation paper. A 25 mL aliquot was diluted to 200 mL with the appropriate diluent. The analyte sample, 25 mL, was diluted to approximately 50 mL with 75 vol% 2-propanol solution and a pH electrode placed in the solution. The analyte was titrated against standard 0.1 mol L^{-1} NaOH in 75 vol% 2-propanol. The pH was recorded as a function of added volume of NaOH to determine, potentially, three endpoints corresponding to neutralisation of any remaining sulphuric acid, neutralisation of the phosphinic acid and the first replaceable hydrogen in any phosphonic acid impurity and the third endpoint being the replacement of the final phosphonic acid proton.

The presence of 2,4,4–trimethylpentyl phosphonic acid, an impurity known to be present in Cyanex® 272 (*Cyanex® 272 Extractant*), was only occasionally detected suggesting very small quantities of this impurity were present. This was consistent with Sole and Hiskey (1992) who reported <0.1% diacid impurity.

The purity of the supplied batch of Cyanex® 272 extractant was higher than that used by Sole and Hiskey (1992) who suggested that the major impurity in Cyanex® 272 was tris-(2,4,4-trimethylpentyl) phosphine oxide, which is not accounted for using acidimetric titration. The extractant was used as received as the generated results have greater applicability to commercial operation.

When necessary *p*-nonylphenol was used as a phase modifier.

Ionol®, a trade-name for butylated hydroxy toluene (BHT), was added to the organic phase in some experiments. It is added to the organic phase in many operating plants to act as a sacrificial reducing agent (anti-oxidant) in order to consume oxidants before they react with other components of the organic phase.

To remove water-soluble components and saturate the organic phase with the aqueous solution, the organic portion was washed prior to contact with aqueous test solutions. A wash solution containing sodium nitrate (0.7 mol L^{-1}) and adjusted to pH 2 with nitric acid was contacted with an equal volume of organic phase. The removal of water-soluble components by washing the organic phase was shown to have no effect on the extraction behaviour during batch experiments and was discontinued.

All organic test solutions were prepared by weighing the appropriate mass of extractant and making to volume using the organic diluent in standard glass volumetric flasks. The transfer of aliquots of the test solution to the mixing vessel was carried out using standard glass pipettes.

3.3 Contact Method

The efficient transfer of metal between phases within a reasonable time frame is dependent on the two phases being intimately mixed. Several apparatus were tested to achieve this. Preliminary extraction tests were undertaken to establish appropriate experimental parameters. This was necessary to ensure reproducible results were obtained over the course of the experimental program.

3.3.1 Extraction Experiments

A magnetic stirrer and 20 mm spin bar were initially used to mix the two phases, with some success. The solutions, 20 mL of each phase, were mixed in a 100 mL conical flask. However some problems with the formation of an unidentified phase were observed. This phase was apparent in the aqueous portion after separation and could be collected at the interface by gentle mechanical action. The existence of this unidentified material was probably due to the existence of local concentration effects during mixing (Hughes 1998). It could not be removed by long separation times or centrifugation of the sample.

Subsequent experiments were carried out using an impeller driven by an overhead motor, IKA Labortechnik RW20. When the total solution volume was less than 60 mL a two-blade, stainless steel paddle stirrer of 34 mm diameter was used (IKA part R 1001) at 500 r.p.m. If greater solution volumes were in use a 3-blade propeller style mixer made of polypropylene with a diameter of 50 mm was used (Cole-Parmer Cat. No. U–06370–00) at 350 r.p.m. This visibly reduced the formation of the unidentified third phase. The use of a motor driven impeller also allowed greater consistency and accuracy in calibration of the stirring speed. Appropriate sized mixing vessels were used in different extraction tests depending on the total volume of the solution: a 100 mL tall form beaker for 40 mL solution volume; a standard 100 mL beaker for 50 mL solution volume; or a standard 250 mL beaker for 100 mL solution volume.

All experiments used a contact time of 10 minutes unless otherwise specified. After mixing, the solution was transferred to a 250 mL separatory funnel and the phases allowed to separate. The aqueous phase was withdrawn, filtered through Whatman® 541 filter paper and analysed for final pH and chromium content. When organic phase analysis was required, the sample was filtered through Whatman® 1PS phase separation paper or dried over magnesium sulphate.

3.3.2 Stripping Experiments

Stripping experiments were carried out differently to extraction experiments in order to reduce entrainment of the aqueous strip solution in the organic phase. The loaded organic phase was prepared as in the extraction experiments. Phase separation was allowed for 5 minutes. The loaded organic phase was dried over magnesium sulphate and a portion withdrawn for analysis. Portions of the loaded organic phase (2.5 mL) were placed in centrifuge tubes together with the strip solution. The sealed tubes were shaken on a flask shaker for 60 minutes then transferred immediately to a centrifuge. Separation was carried out at 3000 r.p.m. for 10 minutes. The organic phase was withdrawn and sent to the Chemistry Centre of Western Australia for independent chromium analysis.

3.4 Temperature, Phase Ratio and pH Control

Experiments were performed at room temperature of 22 ± 2 °C or in a water bath fitted with a thermostatic temperature controller. All analytical measurements were made at room temperature.

All experiments were performed with a phase (A:O) ratio of 1, i.e. equal volume of aqueous and organic phase.

Due to the precipitation of chromium(III) with high aqueous phase pH and to more accurately simulate real conditions it was often necessary to add a basic solution to the vessel during mixing. Small or known volumes of ammonia were added to maintain or adjust the pH to the desired value. The maximum feed pH when using chromium(III) solutions was approximately 5.2 in synthetic solutions. When using spiked PLS the precipitation pH reduced to approximately 4. The reduction in the pH of precipitation was due to the higher activity of chromium(III) and hydroxide in the high ionic strength PLS. The addition of base during extraction enabled a wider range of equilibrium pH values to be studied. No precipitation problems occurred when using chromium(VI) solutions as chromium(VI) does not form an insoluble hydroxide.

A second approach to the control of pH during extraction was the conversion of the phosphinic acid to its ammonium salt by reaction with an aqueous ammonia solution (Ritcey & Ashbrook 1984). Although this description was for di(2-ethylhexyl) phosphoric acid (D2EHPA) the principle is the same for bis(2,4,4-trimethylpentyl) phosphinic acid. Conversion of the extractant to its ammonium salt gives a metal-salt exchange during extraction which does not release protons to the aqueous phase and hence does not drive down the pH with the consequent effect on extraction efficiency.

3.5 Analytical Determinations

The determination of pH was carried out with instruments purchased from TPS Australia. A TPS 900 P was used for raffinate pH measurement throughout the experimental work. This instrument was used with either a standard combination pH electrode (model PBFC) or an Intermediate Junction Electrode (IJ44) supplied by Ionode Pty Ltd. Dispersion pH was measured with an IJ44 electrode and TPS MC-80 instrument.

Chromium determination was performed using atomic absorption spectroscopy (AAS) on a SpectrAA-50 purchased from Varian Australia. Chromium(III) standards were prepared by diluting a 1000 mg L^{-1} stock solution (BDH, Spectrosol®). Standard solutions contained nitric acid (0.5%) to reduce adsorption onto the container walls prior to aspiration of the sample (Shendrikar & West 1974). Chromium(VI) standards were prepared by diluting a 2000 mg L^{-1} stock solution that had been prepared from primary standard sodium dichromate ($Na_2Cr_2O_7$, Ajax, Analar®). Where possible, AAS standards contained the same matrix as the samples. An oxidising, fuel-rich flame was used for all chromium AAS analysis.

The analysis of chromium in the organic phase was performed by external laboratories. The organic samples from extraction experiments were analysed by Bulong Nickel Operation (BNO) by directly volatilising the organic phase using graphite furnace AAS. The organic samples from stripping experiments were analysed by the Chemistry Centre of Western Australia (CCWA) by dry-ashing and acid re-dissolution of the sample prior to determination using inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Ultraviolet-visible spectroscopy was carried out using a Varian DMS 70. The samples were placed in 10 mm path length cuvettes and the wavelength scanned from 350–800 nm in 10 nm intervals. The lower limit was set by the UV cut-off of the diluent (Shellsol® 2046) and the upper wavelength was the instrument limit. The reference was the corresponding unloaded solvent.

The errors associated with all analytical determinations were mainly due to volumetric measurements and instrumental variations. In total these errors produce a calculated range of ± 3.5% of the reported extraction efficiency. The errors associated with determining the pH of extraction are estimated to be ± 0.025 pH units.

CHAPTER 4. RESULTS AND DISCUSSION

4.1 Effect of Contact Conditions on Extraction of Chromium(III)

The efficiency of solvent extraction is partly determined by the efficiency of contact between the two immiscible phases. The conditions used to bring these two phases into contact will therefore have some effect on the process. The individual nature of solvent extraction processes and differences in experimental design require determination of the appropriate contact conditions for each system. Hence as the first step of this investigation, a suitable method of contact, stirring speed and contact time were determined for the present system.

4.1.1 Effect of Stirring Speed

The effect of the stirring speed is shown in Figure 4-1. The initial increase in the extraction efficiency with an increase in stirring speed from 100 to 300 r.p.m. indicated that the extraction process was at least partly influenced by diffusion. Partial diffusion control would be expected for solvent extraction as it is a heterogenous reaction (Ritcey & Ashbrook 1984). The stirring speed required varies with experimental design resulting in meaningless comparison with other data unless conditions were identical.

These results indicate that, for the method of contact chosen for the present study, 300 r.p.m. was the minimum stirring rate required to minimise the effect of diffusion. A higher stirring speed (500 r.p.m.) was used to ensure sufficient mixing at lower pH where larger droplets are produced. A further increase in stirring speed would not have any beneficial effect but could adversely effect phase separation.

The rate and method of agitation is an important consideration in the development of a commercial operation. The chosen conditions will impact both the operating costs due to power consumption and the separation time due to the droplet size produced. Energy needs to be input to the system to provide mixing however a further increase in stirring speed does not necessarily increase the extraction efficiency and may lead to increased formation of cruds and stable emulsions which inhibit phase separation.

4.1.2 Effect of Contact Time

The results from a range of contact times are shown in Figure 4-2. The apparent equilibrium in this system was reached with contact times between 5 and 10 minutes. To ensure that apparent equilibrium was reached, 10 minutes was chosen as the contact time for experiments using chromium(III) and Cyanex® 272. No data exists in the literature for comparison as no other study of the extraction of chromium(III) from a simple solution with Cyanex® 272 has been reported.

This apparent equilibration time is longer than that for most transition metals. Sole and Hiskey (1992) reported that equilibrium was usually obtained in 2-3 minutes for iron, cobalt, nickel, copper and zinc cations. Similar times were reported by Preston (1982) for cobalt and nickel cations with phosphoric, phosphonic or phosphinic acids. No attempt was made to investigate the actual equilibration time.

Islam and Biswas (1979b) reported 15 minutes as the time required to reach equilibrium for extraction of chromium(III) with D2EHPA at pH 3.1. Pandey, Cote and Bauer (1996) reported 2 minutes as sufficient time to reach equilibrium for the extraction of chromium(III) (approximately 4 g L^{-1} in complex solutions) with Cyanex® 272 (0.48 mol L^{-1}) as 50% ammonium salt when the equilibrium pH was 4.0.

The result of the present study indicated that the extraction of chromium(III) was slower than the extraction of heavier first-row transition metals and that the

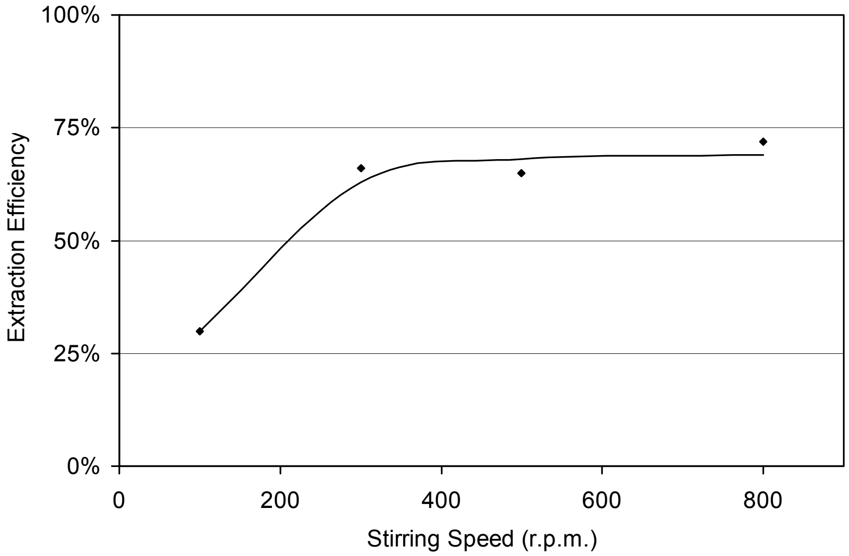


Figure 4-1. The effect of stirring speed on the extraction efficiency of chromium(III) with Cyanex® 272.

Aqueous phase: Cr(III) 1×10^{-3} mol L^{-1}; NO_3^- 0.7 mol L^{-1}, pH 4.4;

Organic phase: Cyanex® 272 0.32 mol L^{-1} in Shellsol® 2046.

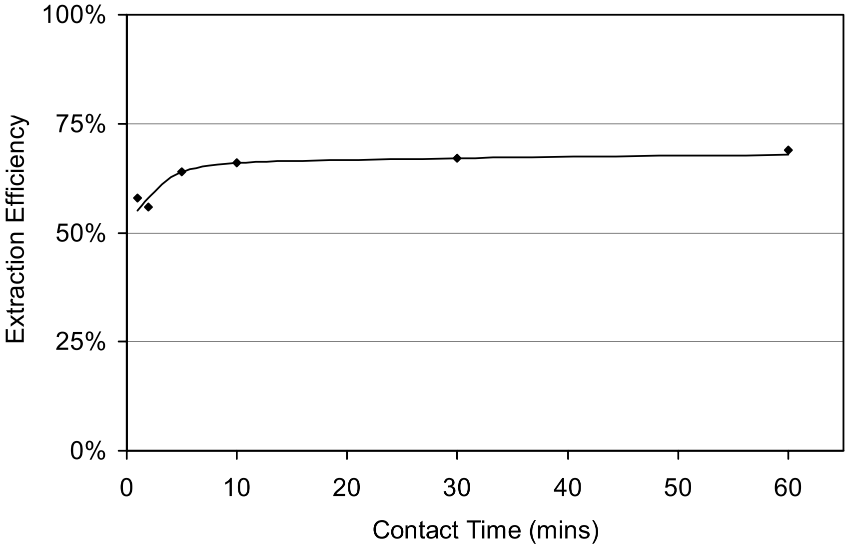


Figure 4-2. The effect of contact time on the extraction efficiency of chromium(III) with Cyanex® 272.

Aqueous phase: Cr(III) 2×10^{-4} mol L^{-1}; NO_3^- 0.7 mol L^{-1}, pH 4.2;

Organic phase: Cyanex® 272 0.32 mol L^{-1} in Shellsol® 2046.

experimental conditions, especially the pH, used in determining the equilibration time have a significant effect on the reported value. The range of hydrolysed chromium(III) species that exist at different pH values are known to react at different rates (Islam & Biswas 1979a; Cotton & Wilkinson 1988) so that the equilibration times reported in the literature for D2EHPA for instance (Islam and Biswas 1979b) appears to be due to the different pH values used by these investigators.

At higher pH the chromium(III) extraction was much faster than would be predicted on the basis of the behaviour of the hexaaqua chromium(III) ion and suggested the involvement of the hydrolysed species in the reaction mechanism. This indicated that the behaviour of chromium(III) may not be accurately predicted from the literature by the behaviour of other transition metals or even a single chromium species.

The present results indicated that for extraction of chromium(III) by Cyanex® 272 a contact time of 10 minutes and a stirring speed of 500 r.p.m. provided sufficient time and energy for extraction of chromium(III) to occur. These conditions were therefore used throughout the current work unless otherwise indicated.

4.2 Effect of Temperature on Extraction of Chromium(III)

The choice of laboratory operating temperature in the range 22–50 °C had a negligible effect on the extraction curves (Figure 4-3), the $pH_{0.5}$ values differing by only 0.07 units (4.54 to 4.61). A slight increase in distribution coefficient (D) with an increase in temperature is suggested in Figure 4-4 however the magnitude of this change at a given pH value is small. No comparable data exists in the literature. No further increase in extraction was observed once the temperature exceeded 40 °C.

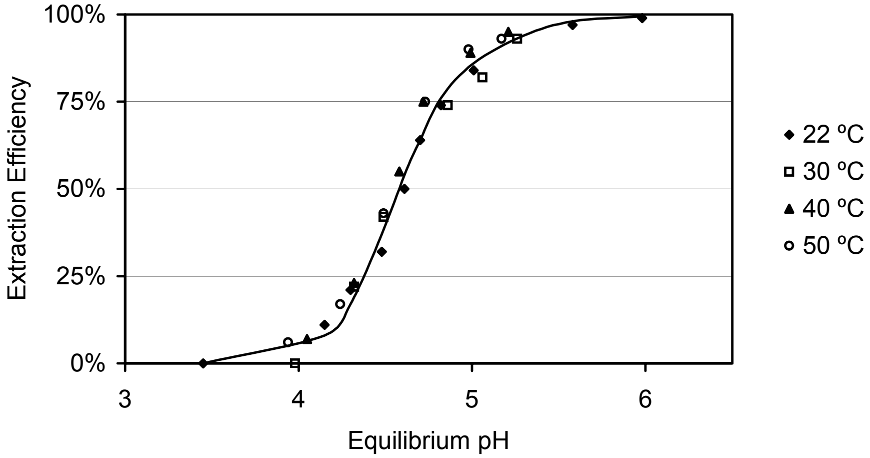


Figure 4-3. The effect of temperature on the extraction of chromium(III) from sulphate solution with Cyanex® 272.

Aqueous phase: Cr(III) 2×10^{-4} mol L^{-1}, SO_4^{2-} 0.1 mol L^{-1};

Organic phase: Cyanex® 272 0.32 mol L^{-1} in Shellsol® 2046.

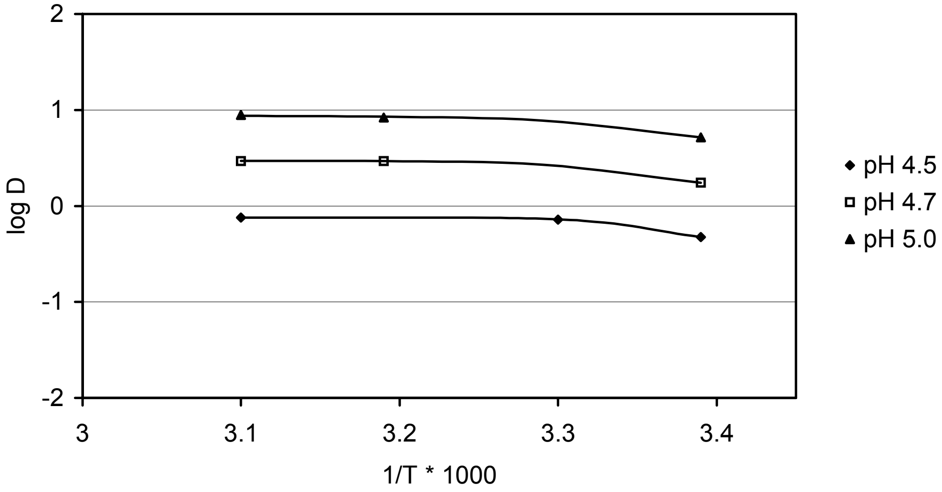


Figure 4-4. The effect of temperature on the distribution coefficient (D) for extraction of chromium(III) from sulphate solution with Cyanex® 272.

Aqueous phase: Cr(III) 2×10^{-4} mol L^{-1}, SO_4^{2-} 0.1 mol L^{-1};

Organic phase: Cyanex® 272 0.32 mol L^{-1} in Shellsol® 2046.

It was noted that the plot of log D vs. 1/T (Figure 4-4) was non-linear. Islam and Biswas (1979b) noted in their work with D2EHPA that non-linearity occurred in the absence of acetate. The present work extends the non-linear behaviour in the absence of acetate to extraction of chromium(III) with Cyanex® 272. This trend appears to be an indication that the extraction reaction is at least partially diffusion controlled although kinetic investigation was not part of the aims of this work.

4.3 Effect of Chromium Concentration on Extraction of Chromium(III)

The effect of initial chromium(III) concentration in the range 10^{-4}–10^{-2} mol L^{-1} (5 to 500 mg L^{-1}) is shown in Figure 4-5. There was little difference in the behaviour of aqueous solutions containing 10^{-2} mol L^{-1} and 10^{-3} mol L^{-1} chromium(III). However solutions containing less chromium(III) (10^{-4} mol L^{-1}) showed a significantly higher extraction at a given pH.

Two possible causes for this behaviour were considered: chromium(III) was extracted in hydrolysed forms and the lower metal to extractant ratio in the system. The extraction of chromium(III) in hydrolysed form appeared more likely as it is known that, unlike most transition metal ions, chromium(III) exists in various hydrolysed forms (Deltombe, de Zoubov & Pourbaix 1966) as shown in Equations 4-1 and 4-2. The extent of hydrolysis increases with increases in pH. At the same time, the percentage of hydrolysed forms increases with decreases in initial chromium(III) concentration.

$$\mathrm{Cr}^{3+} + \mathrm{H_2O} \rightleftharpoons \mathrm{Cr(OH)}^{2+} + \mathrm{H}^{+} \qquad (4\text{-}1)$$

$$\mathrm{Cr(OH)}^{2+} + \mathrm{H_2O} \rightleftharpoons \mathrm{Cr(OH)}_2^{+} + \mathrm{H}^{+} \qquad (4\text{-}2)$$

The lower ratio of metal to available extractant, i.e. thermodynamic equilibrium, as an explanation for the change in behaviour at lower initial chromium(III) concentration appeared unlikely as the extractant was much in excess of all the metal concentrations investigated.

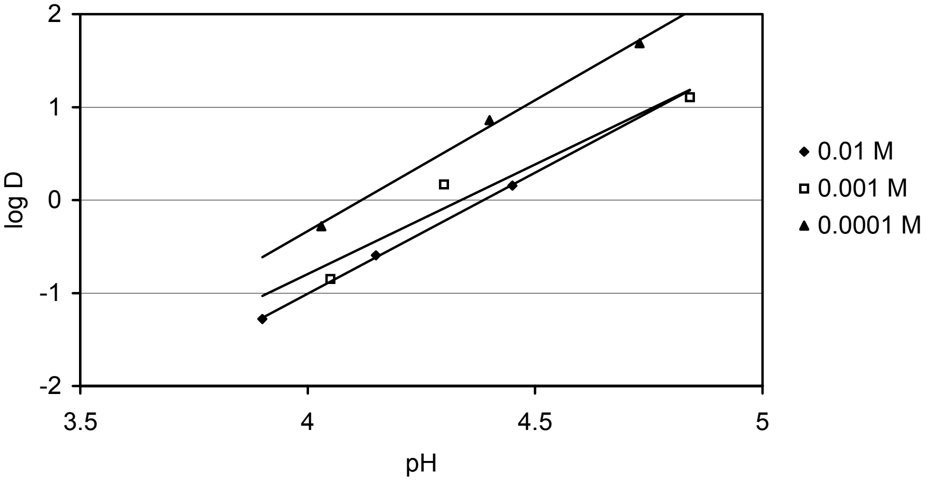


Figure 4-5. The effect of initial chromium(III) concentration in the aqueous phase on the distribution coefficient (D) of extraction of chromium(III) with Cyanex® 272.

Aqueous phase: [Cr(III)] as shown;

Organic phase: Cyanex® 272, 0.32 mol L^{-1} in Shellsol® 2046.

The results of the present study on the effect of temperature (Chapter 4.2) are consistent with this suggestion that hydrolysed forms are important in the extraction behaviour of chromium(III). There was no previously reported study

on the effect of initial chromium(III) concentration on the extraction behaviour with Cyanex® 272 so no data exists for comparison. Although no explanation was offered, a decrease in extraction with increased initial chromium(III) concentration was observed with D2EHPA as the extractant (Islam & Biswas 1979b).

4.4 Effect of Anion Type and Concentration on Extraction of Chromium(III)

The effect of various anions and their concentration on the extraction of chromium(III) was investigated. For other metals it is known that the common anions found in process solutions affect solvent extraction. When D2EHPA is the extractant the anion affect is in the order nitrate < chloride < carbonate < sulphate (Ritcey & Ashbrook 1984). The increasing effect on solvent extraction efficiency indicates that metal-sulphate complexes are more stable than metal-nitrate complexes.

These observations are consistent with the behaviour observed for metal ligand interaction in coordination chemistry. The generation of a spectrochemical series indicating increasing complex stability has been undertaken by Huheey (1983). A portion of this generated series is:

$$S^{2-} < SCN^- < Cl^- < NO_3^- < OH^- < H_2O < NH_3 << CN^-$$

This spectrochemical series indicates the relative weakness of nitrate and chloride complexes as suggested by Ritcey and Ashbrook (1984).

The solvent extraction of chromium(III) from aqueous solutions containing nitrate, chloride and sulphate anions was investigated. The extraction behaviour from solutions containing a mixture of chloride and sulphate anions as commonly found in processing solutions was also considered as it is of significant practical importance.

4.4.1 Extraction of Chromium(III) from Nitrate Solutions

The extraction curve obtained for the extraction of chromium(III) from a nitrate solution with Cyanex® 272 is shown in Figure 4-6. No comparable curve was available in the literature. However the shape of the curve is typical of extraction curves for first-row transition metals with acidic organophosphorus extractants. This is exemplified by the extraction of cobalt(II) with Cyanex® 272 (Sole & Hiskey 1992). The comparison of these curves is shown in Figure 4-7.

The presence of nitrate should have little effect on chromium(III) extraction as both the hydroxide and aqua complex are more stable than the nitrate complex as indicated by the position of these anions in the spectrochemical series. With D2EHPA as the extractant, Islam and Biswas (1979b) found that increasing the concentration of nitrate ions from 0.05 to 2 mol L^{-1} had no effect on the extraction of chromium(III), which they later suggested was due to the limiting reaction being the formation of $Cr(OH)_2^+$ (Islam & Biswas 1979a).

The presence of varying amounts of nitrate ion should therefore not affect the extraction of chromium(III) and this was consistent with the observations of the present study. The data on the effect of chloride ion concentration (Chapter 4.4.2) provides corollary evidence of the effect of the nitrate ion. The nitrate anion was used to maintain a constant ionic strength in the aqueous phase and its concentration varied from 0.4 to 0.7 mol L^{-1}. There was no observable change in the extraction behaviour of chromium(III) as the nitrate and chloride ion concentrations changed.

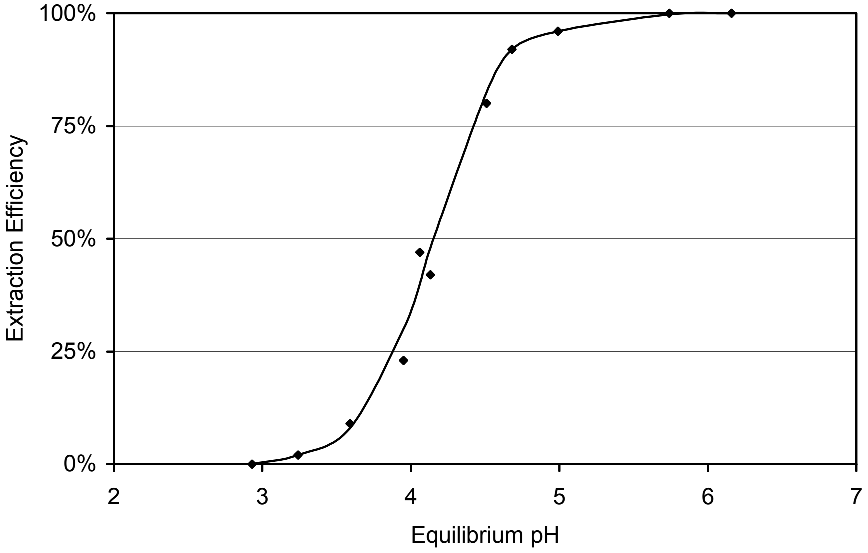


Figure 4-6. The extraction of chromium(III) from nitrate solution with Cyanex® 272.

Aqueous phase: Cr(III) 1×10^{-2} mol L^{-1}, NO_3^- 0.66 mol L^{-1};

Organic phase: Cyanex® 272, 0.32 mol L^{-1} in Shellsol® 2046.

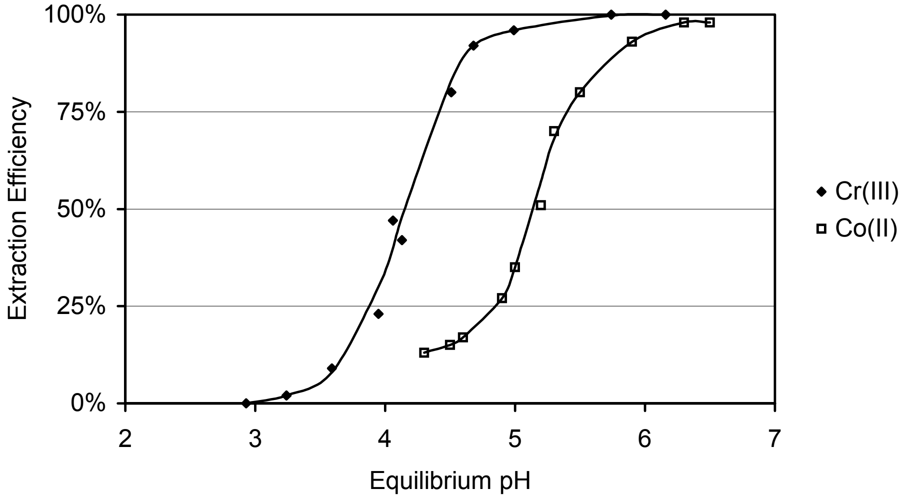


Figure 4-7. The extraction of chromium(III) with Cyanex® 272 from nitrate solution compared to the extraction of cobalt (Sole & Hiskey 1992).

Aqueous phase: Cr(III) 1×10^{-2} mol L^{-1}, NO_3^- 0.66 mol L^{-1}.

Organic phase: Cyanex® 272, 0.32 mol L^{-1} in Shellsol® 2046.

4.4.2 Extraction of Chromium(III) from Chloride Solutions

The extraction curve for the extraction of chromium(III) from a chloride solution with Cyanex® 272 is shown in Figure 4-8. There was no literature curve for comparison. However as with extraction of chromium(III) from nitrate solutions the shape of the curve was typical of the extraction of transition metals with acidic organophosphorus extractants. The extraction of chromium(III) from chloride solutions was expected to be similar to extraction from nitrate solutions based on the relative positions of chloride and nitrate in the spectrochemical series as discussed in Chapter 4.4.1.

The earlier study of Gandhi, Deorkar and Khopkar (1993) concluded that chromium(III) is not extracted by Cyanex® 272 from a chloride solution at pH 3 or 8. The lack of extraction at pH 3 is consistent with this work. The lack of extraction at pH 8 was probably due to the amphoteric nature of chromium(III) and its tendency to form $Cr(OH)_4^-$ in alkaline conditions. Anionic species are generally not extracted by Cyanex® 272. The inability of Cyanex® 272 to extract anionic species was also observed for chromium(VI) as discussed in Chapter 4.9.1.

The effect of chloride ion concentration in the range 0–0.25 mol L^{-1} on the extraction of chromium(III) with Cyanex® 272 is shown in Figure 4-9. The change in the chloride ion concentration in this range had little effect on the extraction behaviour. The formation of weak complexes between transition metals and chloride anion is predicted from the spectrochemical series discussed in Chapter 4.4. The present study is the first attempt to determine the effect of chloride ion concentration on the extraction of chromium(III) with Cyanex® 272.

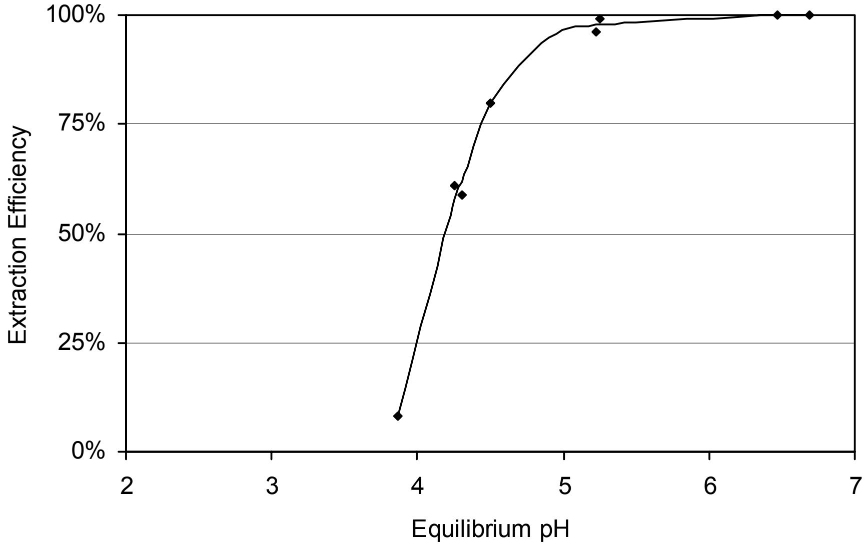


Figure 4-8. The extraction of chromium(III) from chloride solution with Cyanex® 272.

Aqueous phase: Cr(III) 9.6×10^{-3} mol L^{-1}, Cl^{-} 0.1 mol L^{-1};

Organic phase: Cyanex® 272, 0.32 mol L^{-1} in Shellsol® 2046.

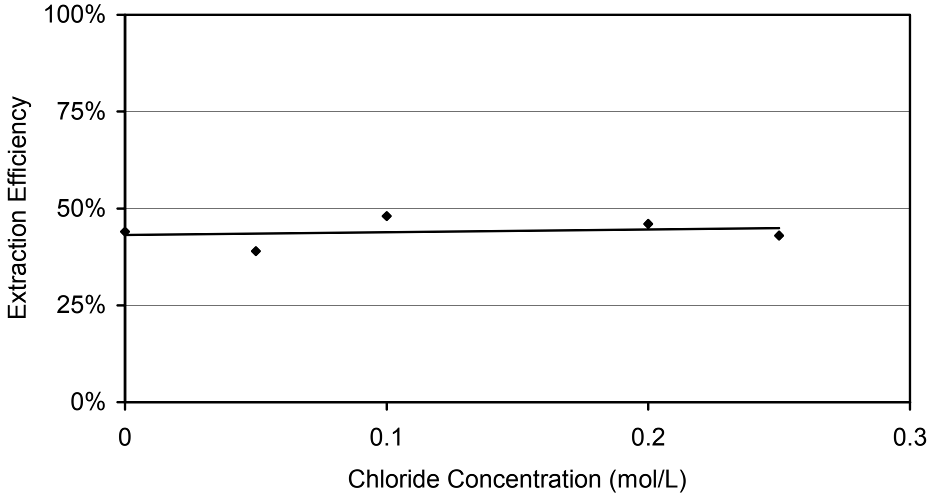


Figure 4-9. The effect of chloride concentration on extraction of chromium(III) with Cyanex® 272.

Aqueous phase: Cr(III) 1×10^{-3} mol L^{-1}, Cl^{-} variable, pH 4.4;

Organic phase: Cyanex® 272, 0.32 mol L^{-1} in Shellsol® 2046.

4.4.3 Extraction of Chromium(III) from Sulphate Solutions

The extraction curve for extraction of chromium(III) from a sulphate solution with Cyanex® 272 is shown in Figure 4-10. There was no literature curve for comparison. However as with extraction from nitrate solutions the shape of the curve was typical for extraction of transition metals with acidic organo-phosphorus extractants. It was noted that the pH of extraction was higher from sulphate solutions than from nitrate or chloride solutions. This is discussed in Chapter 4.4.5. The use of sulphate solutions to test solvent extraction systems for the separation of cobalt and nickel is important because processing of these metals frequently requires purification of these metals from sulphuric acid solution.

The few papers that mention chromium(III) extraction with Cyanex® 272 reported that the metal was not extracted from sulphate solutions (*Cyanex® 272 Extractant*; Nahar *et al.* 1995). The conditions used in these literature relate to extraction at pH less than 2. There was no literature for the extraction of chromium(III) from sulphate solution in the pH range 2.5–6.5. This is the pH range of interest in nickel-cobalt separation, a major use for Cyanex® 272.

The transfer of chromium(III) to an organic phase containing Cyanex® 272 from sulphate solution reported in the present work therefore represents a break from the previously reported data. This is not entirely unexpected as at pH 2 the only first-row transition metals to show significant extraction are iron(III), zinc and vanadium(IV). Many metals such as nickel and cobalt are known to be extracted at higher pH yet pH 2 is the highest pH in a previously reported study on extraction of chromium(III) with Cyanex® 272 from a sulphate solution (*Cyanex® 272 Extractant*; Ritcey & Ashbrook 1984; Sole & Hiskey 1992).

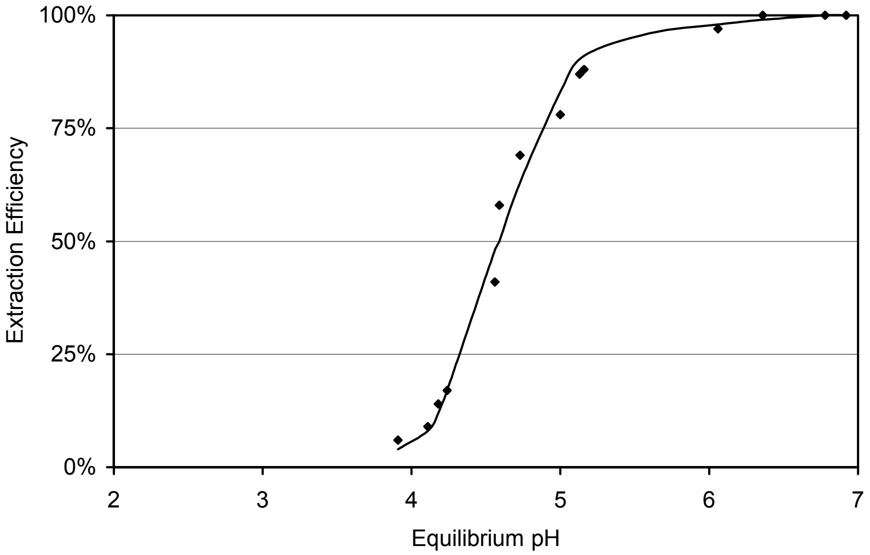


Figure 4-10. The extraction of chromium(III) from sulphate solution with Cyanex® 272.

Aqueous phase: Cr(III) 9.6×10^{-3} mol L^{-1}, SO_4^{2-} 0.1 mol L^{-1};

Organic phase: Cyanex® 272, 0.32 mol L^{-1} in Shellsol® 2046.

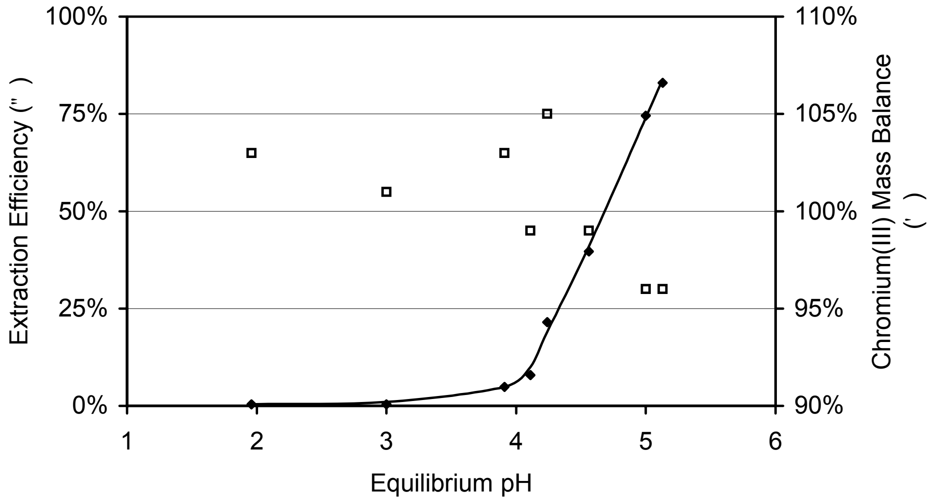


Figure 4-11. The extraction of chromium(III) from sulphate solution with Cyanex® 272 (organic phase analysis).

Aqueous phase: Cr(III) 9.6×10^{-3} mol L^{-1}, SO_4^{2-} 0.1 mol L^{-1};

Organic phase: Cyanex® 272, 0.32 mol L^{-1} in Shellsol® 2046.

A further observation made in all cases when chromium(III) was extracted was the development of a coloured organic phase and the loss of colour from the aqueous phase. To confirm that the observed colour development in the organic phase was due to chromium(III), this phase was directly analysed for chromium. The results with an acceptable mass balance are shown in Figure 4-11. The shape of the curve and $pH_{0.5}$ value were similar (aqueous 4.62, organic 4.64) to the curve generated by analysis of the aqueous phase data (Figure 4-10).

These reported results clearly showed that chromium(III) was extracted from sulphate solution with Cyanex® 272. More importantly, this extraction occurred within the pH range of cobalt extraction. The pH range at which chromium(III) was most likely to be extracted by Cyanex® 272 has not been reported by previous investigators. This may be due to the type of solutions, e.g. tanning effluents, hydroxide sludges, which were the focus of previous investigations.

The concentration of sulphate ion in the aqueous phase affects the extraction behaviour as shown in Figure 4-12. Increases in sulphate concentration from 0 to 0.33 mol L^{-1} resulted in decreases in the chromium(III) extraction.

With D2EHPA as the extractant, a decrease in extraction with increasing sulphate concentration has been reported previously (Islam & Biswas 1979b). The depression of extraction was attributed to the formation of $Cr(SO_4)^+$ and $Cr(SO_4)_2^-$ in preference to the formation of the chromium(III)-D2EHPA complex. Schügerl, Segelken and Gudorf (1996), also using a chromium(III)/sulphate/ D2EHPA system made similar observations although the depression of extraction was not attributed to a specific complex.

There is no published information regarding the relative strength of the chromium(III)-sulphate and chromium(III)-Cyanex® 272 complex. The sulphate anion was not reported in the spectrochemical series as discussed by Huheey (1983). Ritcey and Ashbrook (1984) suggested that the sulphate anion had the greatest effect of the common anions on extraction behaviour with D2EHPA.

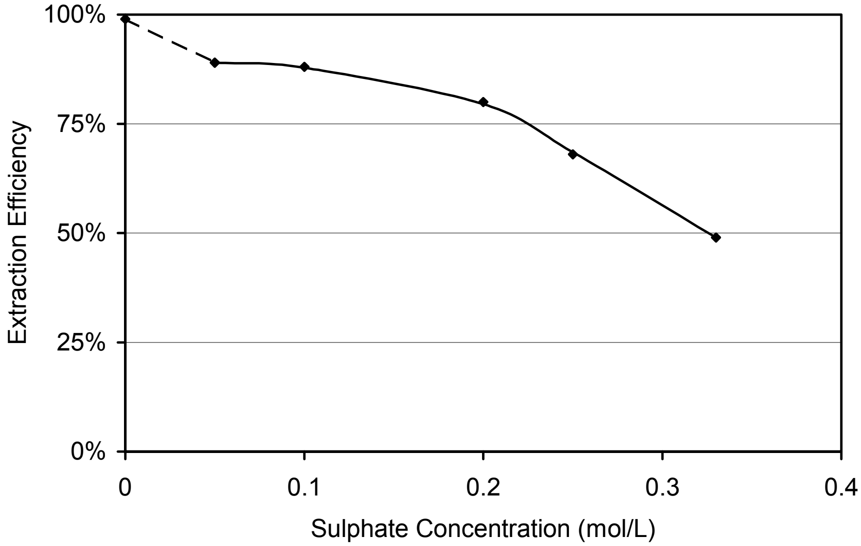


Figure 4-12. The effect of sulphate concentration on extraction of chromium(III) with Cyanex® 272.

Aqueous phase: Cr(III) 1×10^{-3} mol L^{-1}, pH 5.2;

Organic phase: Cyanex® 272 0.32 mol L^{-1} in Shellsol® 2046.

The present work suggested that the sulphate complex is stronger than the $Cr(OH)_2^+$ complex and the Cyanex® 272 complex. The only experimental conditions available to compare the strengths, as log K values, of such complexes is at infinite dilution which is not directly applicable to the test solutions used in the present study. In addition no work has been completed on the formation of complexes with solvent extraction reagents. Nonetheless the available data (Appendix 3) indicates log K for sulphate complex $Cr(SO_4)^-$ as 3.9 and for the $Cr(OH)_2^+$ complex as -4.0 suggesting the sulphate complex is preferred.

This is consistent with the literature which suggested that the sulphate complex is stronger than the D2EHPA complex on the basis that sulphate anion depressed extraction with D2EHPA. In turn the chromium(III)-D2EHPA complex is expected to be stronger than the chromium(III)-Cyanex® 272 complex on the basis of the lower pK_a of D2EHPA. The pK_a of D2EHPA is 1.72 (Smelov & Lanin 1969) compared to 6.37 for Cyanex® 272 (Sole & Hiskey 1992) indicating that D2EHPA will generally form stronger complexes than Cyanex® 272.

4.4.4 Extraction of Chromium(III) from Mixed Sulphate/Chloride Solutions

The extraction of chromium(III) from a mixed sulphate/chloride solution (Figure 4-13) shows behaviour analogous to that from single anion solutions and was most similar to extraction from sulphate solution. This suggested that the sulphate ion has the greatest effect on the extraction behaviour with chloride acting primarily as a non-complexed spectator ion. This is consistent with the relative strengths of the chromium(III)–anion interaction as discussed in Chapter 4.4.2 and 4.4.3.

The only previously published study that reports the successful extraction of chromium(III) with Cyanex® 272 also used a mixed anion solution. Pandey, Cote

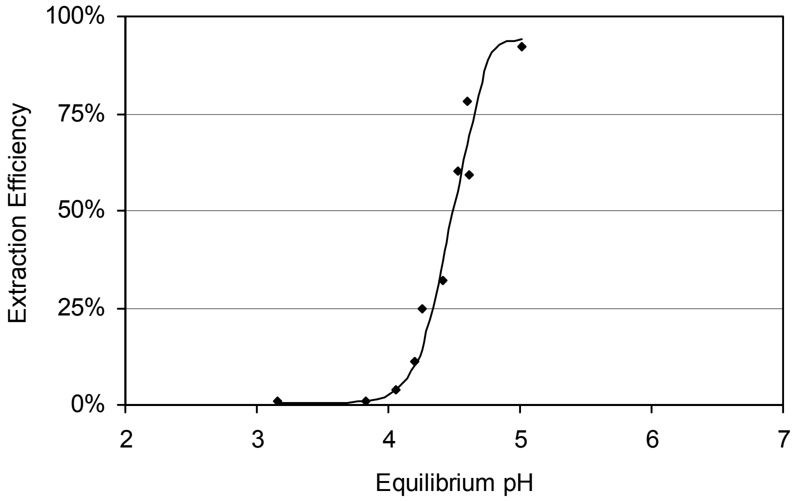


Figure 4-13. Extraction of chromium(III) from solutions containing sulphate and chloride anions with Cyanex® 272.

Aqueous phase: Cr(III) 9.6×10^{-3} mol L^{-1}, SO_4^{2-}, Cl^- each 0.1 mol L^{-1};

Organic phase: Cyanex® 272, 0.32 mol L^{-1} in Shellsol® 2046.

and Bauer (1996) investigated the extraction of chromium(III) with Cyanex® 272 from synthetic spent tanning solutions which contained both sulphate and chloride anions.

A simplified solution similar to that used in the work of Pandey, Cote and Bauer (1996) was used in the present study to demonstrate that the extraction was due to the interaction between chromium(III) and Cyanex® 272 as opposed to a side reaction due to components of the tanning effluent. The conditions used in thepresent work and by Pandey, Cote and Bauer (1996) are compared in Table 4-1. The differences in experimental conditions used would not be expected to have any significant effect on the result, unless specific interactions with minor components exist. The similarity of the extraction curves in Figure 4-14 indicate that the extraction of chromium(III) with Cyanex® 272 is due to the reaction between metal and extractant and is independent of the minor components in the synthetic tanning liquor.

4.4.5 Comparison of Anion Effects on the Extraction of Chromium(III) with Cyanex® 272

The data of chromium(III) extraction from aqueous solutions containing various anions with Cyanex® 272 are shown in Figure 4-15. The data indicated that there was no difference in the achievable extraction between the different solutions.

The difference in the $pH_{0.5}$ values for nitrate (4.16) and chloride (4.28) containing solutions showed some difference to those solutions containing mixed sulphate–chloride (4.50) and sulphate (4.63) anions. The extraction from sulphate and sulphate–chloride solutions was similar indicating the predominance of sulphate type behaviour due to the stronger complexing nature of this anion.

Table 4-1. Comparison of the experimental parameters used in the present work and by Pandey, Cote and Bauer (1996).

Parameter	This Work	Pandey, Cote and Bauer (1996)
Cr(III)	0.5 g L^{-1}	4.41 g L^{-1}
Other metals	None	Fe(III) 0.09 g L^{-1}
		Al(III) 0.12 g L^{-1}
Acetic Acid	None	1.56 g L^{-1}
SO_4^{2-}	12.0 g L^{-1}	12.0 g L^{-1}
NaCl	60.0 g L^{-1}	60.0 g L^{-1}
Contact Method	Magnetic Stirrer	Flask Shaker
pH control	Added base	Ammoniated extractant

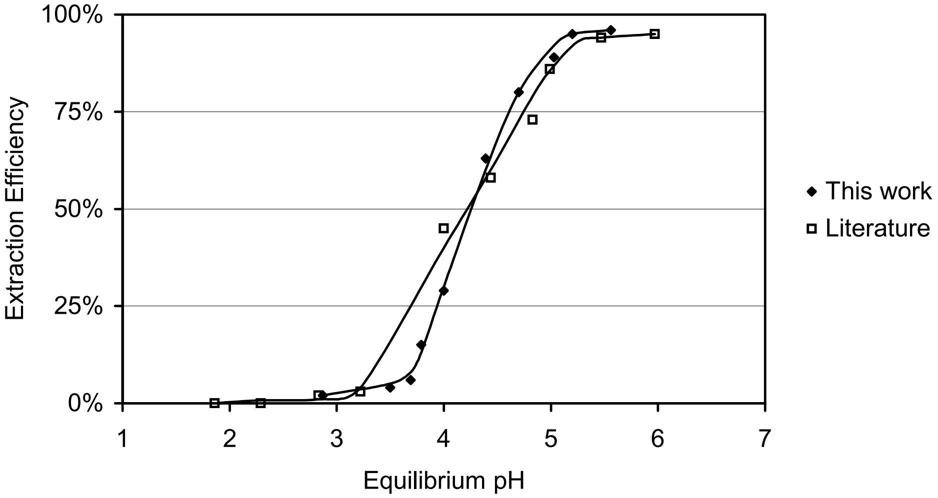


Figure 4-14. Comparison of the present work and the existing data (Pandey, Cote & Bauer 1996) for extraction of chromium(III) from sulphate/chloride solutions with Cyanex® 272. Aqueous phase: as in Table 4-1 above;

Organic phase: Cyanex® 272, 0.48 mol L^{-1}, *p*-nonylphenol 0.43 mol L^{-1} in kerosene.

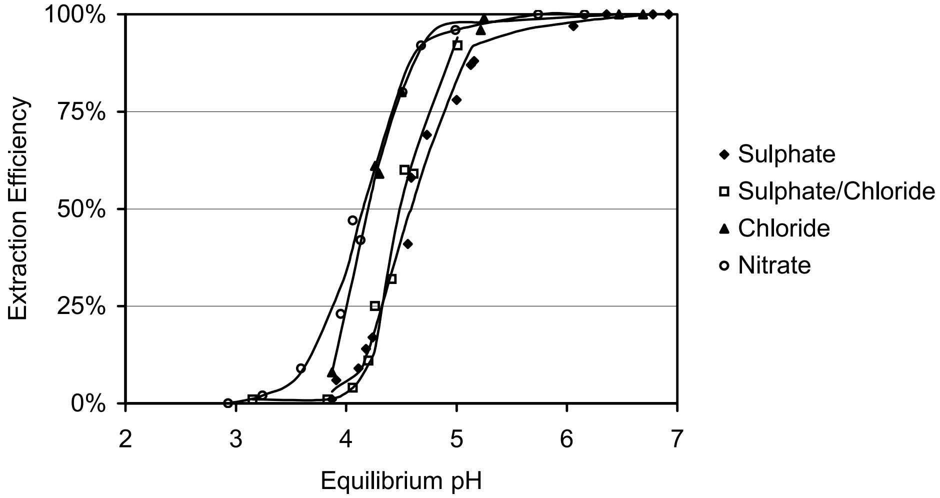


Figure 4-15. Comparison of chromium(III) extraction with Cyanex® 272 from aqueous solutions containing various anions.

Aqueous phase: Cr(III) 9.6×10^{-3} mol L^{-1}, anion 0.1 mol L^{-1};

Organic phase: Cyanex® 272, 0.32 mol L^{-1} in Shellsol® 2046.

Sole and Hiskey (1992) suggested that cobalt extraction occurred at higher pH values as the sulphate concentration increased. This was attributed, at least partially, to the existence of the sulphate-bisulphate equilibrium:

$$SO_4^{2-} + H_2O \rightleftharpoons HSO_4^- + OH^- \qquad (4\text{-}3)$$

The present work indicated that the presence of sulphate in the aqueous phase and the resulting sulphate-bisulphate equilibrium also caused extraction of chromium(III) to occur at higher pH values than in the absence of sulphate.

The present results add to those reported by Preston (1982) on the difference in extraction behaviour from sulphate and non-sulphate solutions. The previous work studied nickel and cobalt extraction with a dialkyl phosphonic acid while the present work adds data for the extraction of chromium(III) with a dialkyl phosphinic acid. The data for these three first-row transition metals are summarised in Table 4-2. The larger difference for extraction of chromium(III) compared to nickel and cobalt may be attributed to the different extractant. The higher charge on the metal centre in the present work may also effect the reported difference as a higher charge on the central metal generally results in a stronger complex due to an increase in the electrostatic attraction between the ions that make up the complex (Huheey 1983).

Table 4-2. The difference in $pH_{0.5}$ values for cobalt, nickel and chromium(III) extraction from nitrate, chloride and sulphate solutions.

Metal	$NO_3^- - Cl^-$	$NO_3^- - SO_4^{2-}$	$Cl^- - SO_4^{2-}$	Source
Co	0.07	0.32	0.25	Preston (1982)
Ni	0.08	0.33	0.25	Preston (1982)
Cr	0.12	0.47	0.35	This work

The present work both extends the previously published literature and simplifies the data available. The hydrometallurgical separation of cobalt and nickel with Cyanex® 272 occurs in the pH range 3–6. The addition of the present work indicated that chromium(III) was extracted by Cyanex® 272 in this pH range from a variety of aqueous solutions. This requires that the flowsheet design process ensures adequate pH control for chromium(III) precipitation as well as consideration of the implications that the presence of chromium(III) may have on downstream processes such as solvent extraction.

The use of sulphate solutions for assessing the behaviour of PAL generated liquors appears to have some justification when examining the behaviour of chromium(III) on the basis of the similar behaviour observed with sulphate and sulphate–chloride solutions. The use of solutions not containing sulphate may provide advantages in some processing situations, e.g. a reduction in the amount of neutralising media required to obtain a suitable pH for solvent extraction following an acidic leach. It is more likely however that the choice of anion system will be determined by other process requirements, e.g. a suitable solution for electro-winning of metal.

The addition of the present work to the existing literature provides data for chromium(III) extraction under comparable conditions to that published for other first-row transition metals. This allows some confidence in the preparation of comparative extraction curves, which is not reasonable unless the experimental conditions were similar due to the effect of the various experimental parameters on the extraction behaviour. A comparison of the extraction conditions for some available literature is shown in Table 4-3. The data demonstrate that the conditions were quite similar. The difference in metal concentration and temperature is expected to have little effect, while decreasing the sulphate concentration during chromium(III) extraction would move this curve to lower pH as discussed in Chapter 4.4.3, i.e. closer to the cobalt curve in this example.

The comparison of chromium(III) extraction with Cyanex® 272 and the existing data in the literature is shown in Figure 4-16. Data as shown in this figure is considered a vital starting point for the development of an solvent extraction process yet chromium(III) was never previously included as it was believed that it was not extracted from sulphate solutions.

The effect of changes in extraction conditions is shown in Figure 4-17 where extraction of copper by Cyanex® 272 under three sets of experimental conditions (Table 4-4) is shown. The observed shift in the extraction pH is consistent with suggestions that increasing the sulphate concentration increases the extraction pH (Chapter 4.4.3) and increasing the extractant concentration decreases the extraction pH (Chapter 4.5.2).

To obtain the best comparative data extraction should be undertaken under identical conditions. If the composition of the actual solvent extraction feed solution can be approximated then this should be used to generate data which more accurately represents the behaviour that would be encountered during industrial operation.

Table 4-3. A comparison of the experimental conditions used in extraction of first-row transition metals with Cyanex® 272 (Figure 4-16). The aqueous:organic ratio was 1 in all experiments.

Aqueous Phase	$[\mathrm{M}^{n+}]$ (mol L^{-1})	$[\mathrm{SO}_4^{2-}]$ (mol L^{-1})	Temperature (°C)	Contact Time (minutes)
(Rickelton, Flett & West 1984)	0.015	0.015 (Fe 0.022)	50	5
This work: Cr(III)	0.001	0.1	22	10

Organic Phase	[Cyanex® 272] (mol L^{-1})	Diluent	Modifier
(Rickelton, Flett & West 1984)	0.6	Kermac 470B	*p*-nonylphenol
This work: Cr(III)	0.5	Shellsol® 2046	none

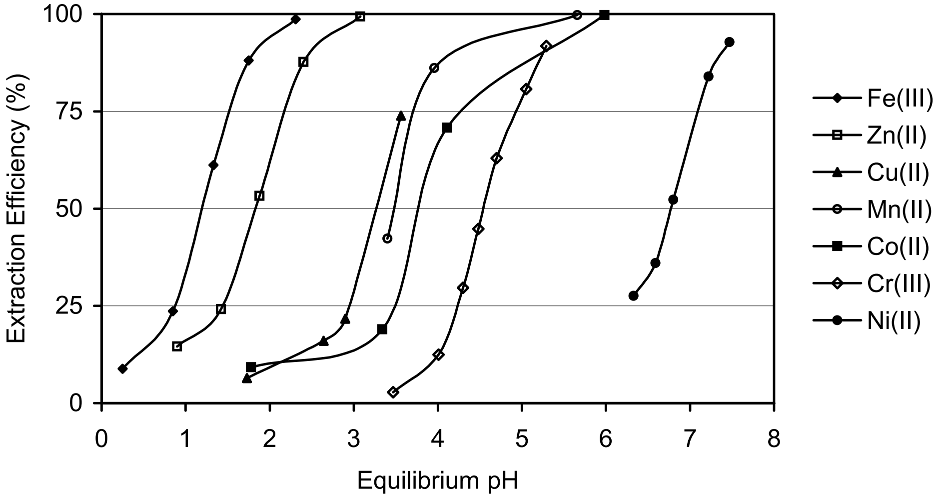


Figure 4-16. The extraction of chromium(III) from sulphate solution compared to some other first-row transition metals. The experimental conditions are shown in Table 4-3.

Table 4-4. A comparison of experimental conditions for extraction of copper with Cyanex® 272 (Figure 4-17). The aqueous:organic ratio was 1 in all experiments.

Aqueous Phase	$[\mathrm{Cu}^{2+}]$ (mol L-1)	$[\mathrm{SO}_4^{2-}]$ (mol L-1)	Temperature (°C)	Contact Time (minutes)
(Rickelton, Flett & West 1984)	0.015	0.015	50	5
This work	0.001	0.1	22	10
Sole and Hiskey (1995)	0.001	0.5	23	15

Organic Phase	[Cyanex® 272] (mol L-1)	Diluent	Modifier
(Rickelton, Flett & West 1984)	0.6	Kermac 470B	*p*-nonylphenol
This work	0.3	Shellsol® 2046	none
Sole and Hiskey (1995)	0.1	Xylene	none

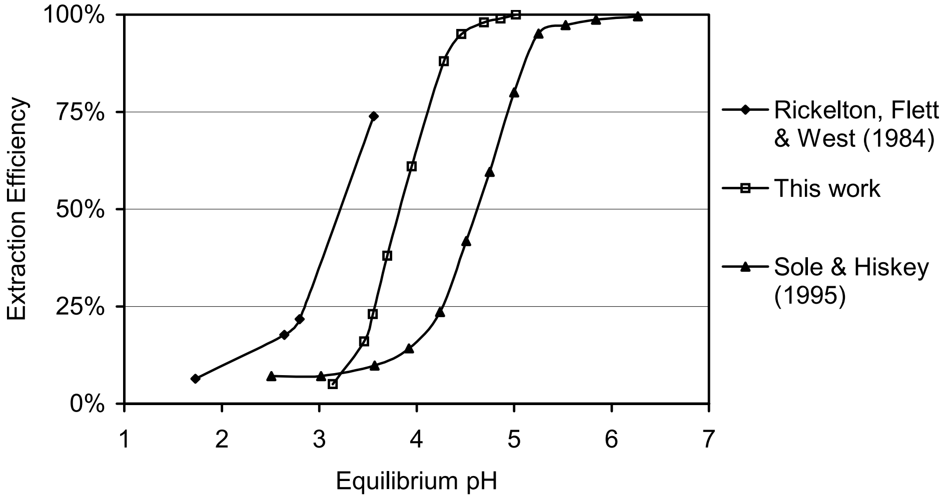


Figure 4-17. The extraction of copper from sulphate solution with Cyanex® 272. The experimental conditions are shown in Table 4-4.

4.4.6 Effect of Acetate on Extraction of Chromium(III)

The presence of acetate in the aqueous phase caused a curious and previously unreported effect on the extraction of chromium(III) with Cyanex® 272. In freshly prepared aqueous solutions the presence of acetate anions (0.1 mol L^{-1}) had no effect on the extraction of chromium(III) with Cyanex® 272. However if the aqueous phase was allowed to stand, producing an aged aqueous phase, prior to contact with the organic extractant a marked decrease in extraction was observed (Figure 4-18). This effect of aging appeared to be due to the formation of a chromium(III)-acetate complex.

The decrease in extraction suggested that the chromium(III)-acetate complex was stronger than either the hydrolysed chromium(III) species, the chromium(III)-sulphate species or the chromium(III)-Cyanex® 272 complex. If the hydrolysed chromium(III) was the stronger species then chromium(III) would still be available to react with the extractant. Similarly if the complex with Cyanex® 272 was stronger it could break up the acetate complex forming an extractable species. As compared to the earlier stated log K value of the $Cr(SO_4)^-$ species of 3.9 the $Cr(acetate)^{2+}$ species is stronger with a log K value of 5.4. These values are consistent with the observations of the present work although it is again noted that no values are available for the chromium(III)-Cyanex® 272 complex.

In solutions containing chromium(III) as the only trivalent metal, acetate is known to prevent the precipitation of chromium(III) hydroxide (Svehla 1996) indicating that a strong interaction between chromium(III) and the acetate anion may be possible in the present system. Investigations that use industrial solutions (e.g. Pandey, Cote & Bauer 1996) rarely meet these conditions as they contain a range of metals in solution.

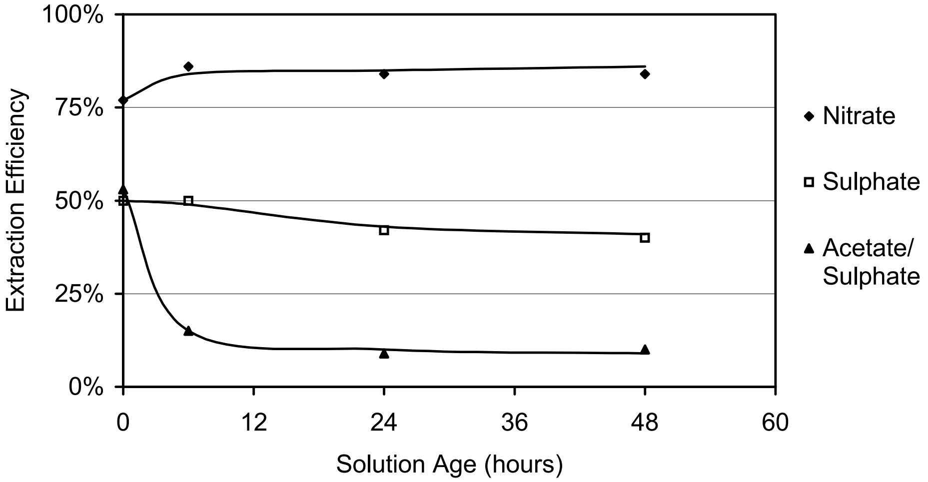


Figure 4-18. The effect of aqueous solution age and composition on the extraction of chromium(III) with Cyanex® 272.

Aqueous phase: Cr(III) 5×10^{-3} mol L^{-1}, anions as shown 0.1 mol L^{-1}, pH 4.7;

Organic phase: Cyanex® 272 0.32 mol L^{-1} in Shellsol® 2046.

An earlier report indicated that, on the basis of increased acetate concentration not influencing the extraction efficiency, acetate did not effect extraction of chromium(III) when D2EHPA was the extractant (Islam & Biswas 1979b). However this report did not consider the effect of the age of the aqueous phase before contact with the extractant.

In the present study, examination of the aging effect of acetate on chromium(III) extraction with D2EHPA as the extractant is shown in Figure 4-19. This indicated that the solution age also affects extraction of chromium(III) with D2EHPA. This has not been noted previously in the literature and indicated that the chromium(III)-acetate complex, once formed, was also stronger than the chromium(III)-D2EHPA complex.

A comparison of chromium(III) extraction from solutions containing acetate anions with Cyanex® 272 and D2EHPA is shown in Figure 4-20. The depression of extraction due to the presence of acetate anion occurred faster and was greater (within 48 hours) when Cyanex® 272 was used as the extractant.

The rapid depression of extraction with Cyanex® 272 compared to D2EHPA represents a major shift in behaviour with decreasing phosphate character of the extractant. The lower pK_a of D2EHPA, due to its greater phosphate character, also causes extraction of most metals to occur at lower pH when D2EHPA is the extractant, which in the case of chromium(III) may significantly change the aqueous species present in solution. The increased presence of hydrolysed species at higher pH (Chapter 1.1) as required for extraction with Cyanex® 272 probably allows faster formation of the chromium(III)-acetate complex and this was reflected in the faster depression of extraction efficiency with Cyanex® 272.

The variable behaviour with solution age, especially when using Cyanex® 272, inhibits the use of an acetate buffer for pH control in laboratory experiments on this system. The slower depression of extraction when using D2EHPA should

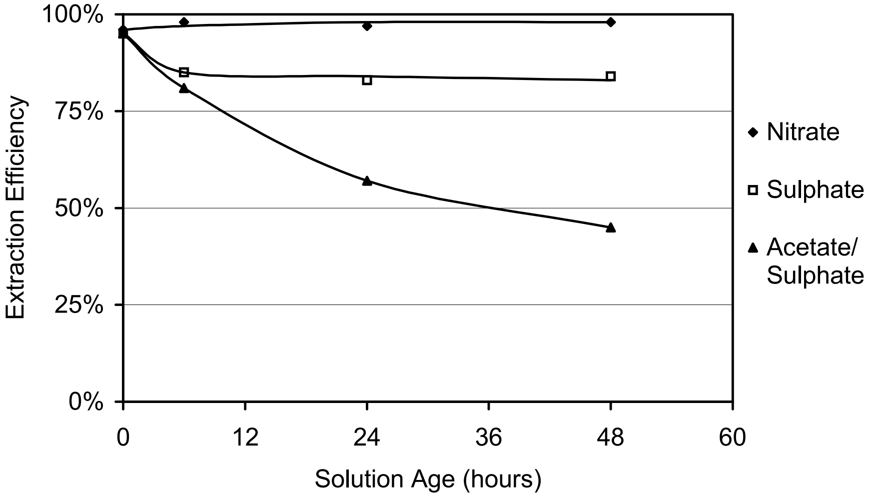


Figure 4-19. The effect of aqueous solution age and composition on the extraction of chromium(III) with D2EHPA.

Aqueous phase: Cr(III) 5×10^{-3} mol L^{-1}, anions as shown 0.1 mol L^{-1}, pH 4.1;

Organic phase: D2EHPA, 0.3 mol L^{-1} in Shellsol® 2046.

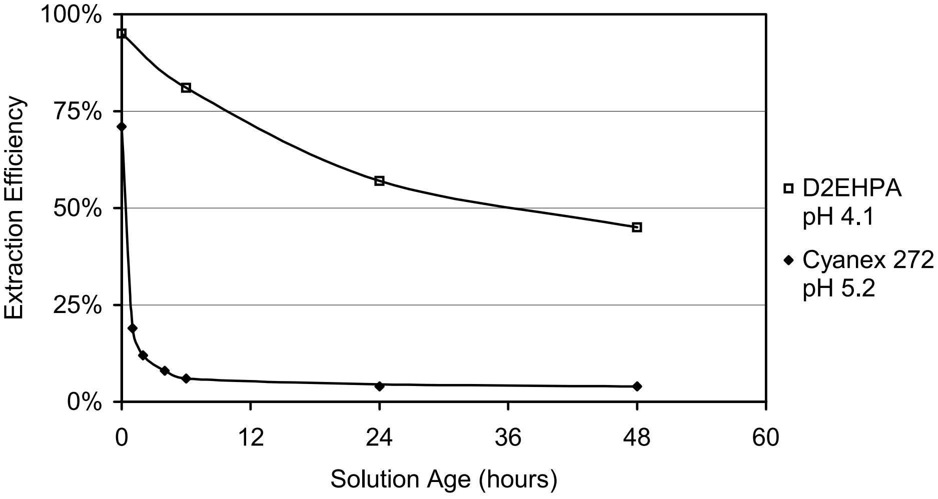


Figure 4-20. A direct comparison of the effect of solution age on the extraction of chromium(III) when using different acidic organophosphorus extractants.

Aqueous phase: Cr(III) 5×10^{-3} mol L^{-1}, Ac^{-}/SO_4^{2-} each 0.1 mol L^{-1};

Organic phase: Extractant 0.3 mol L^{-1} in Shellsol® 2046.

allow experiments with an acetate buffer to be reproducible provided experimental conditions with respect to solution age were constant.

The change in behaviour with solution age may also influence the industrial application of solvent extraction as solutions are often not processed as soon as they are generated. The time lag in processing may have unforeseen consequences on the extraction behaviour dependent upon solution composition.

4.4.7 Extraction of Chromium(III) from Industrial PLS

A sample of cobalt pregnant liquor stream (PLS) from the feed to Bulong Nickel Operation's cobalt solvent extraction circuit (see Figure 1-8) was spiked with chromium(III) (1×10^{-4} mol L^{-1}, 5 mg L^{-1}). Extraction tests were undertaken with Cyanex® 272 in Shellsol® 2046 in the pH range 4–6.5. The results are shown in Figure 4-21. Chromium(III) is shown only at pH 4.3 as at higher pH values the mass balance showed incomplete recovery of the metal. Ritcey, Hayward and Salinovich (1996) demonstrated that the level of chromium(III) was reduced from 22 mgL^{-1} to < 1 mgL^{-1} by the adjusting the pH of the PLS solution to 4.3.

The minor differences in extraction order such as the nickel showing higher extraction than calcium and cobalt showing generally higher extraction than zinc could be attributed to the relative concentrations of these metals in solution (Table 3-1).

The precipitation of chromium(III) during solvent extraction from PLS, which has an ionic strength between 4 and 4.5 mol L^{-1}, calculated from published data (Soldenhoff, Hayward & Wilkins 1998) indicated a change in chromium(III) behaviour to a more reactive species as the ionic strength of the solution increased.

In the present work the chromium(III) species that precipitated, probably a hydroxide, was an insoluble, fluffy white mass with no obvious crystalline structure. Chromium(III) hydroxide is known to form amorphous precipitates which were relatively inert to acid addition after a short period of time (Spiccia *et al.* 1987).

The precipitate was observed throughout the aqueous phase, although with gentle agitation it could be collected at the aqueous/organic interface. This suggested that a significant amount of organic was trapped within the structure or adsorbed onto its surface as a purely inorganic precipitate would be expected to settle out of solution. The presence of a precipitate at the A/O interface may interfere with phase separation.

The high ionic strength of the PLS caused precipitation of chromium(III) to occur at a lower pH than predicted by solubility product calculations. This is understandable considering that existing theories describing the behaviour of ions in solution apply only to dilute solutions and include the approximation of species concentration for actual species activity. As the ionic strength of a solution increases the activity of the species moves further from its concentration, and its real behaviour moves further from that predicted by ideal chemistry rules. In addition, rules describing the behaviour of aqueous solutions are formulated in the absence of organic components, which is obviously not the case during solvent extraction. The changes observed in behaviour of chromium(III) at high ionic strength reinforce the need for the testing of a proposed circuit with solutions of equivalent composition to those expected to be generated during continuous operation.

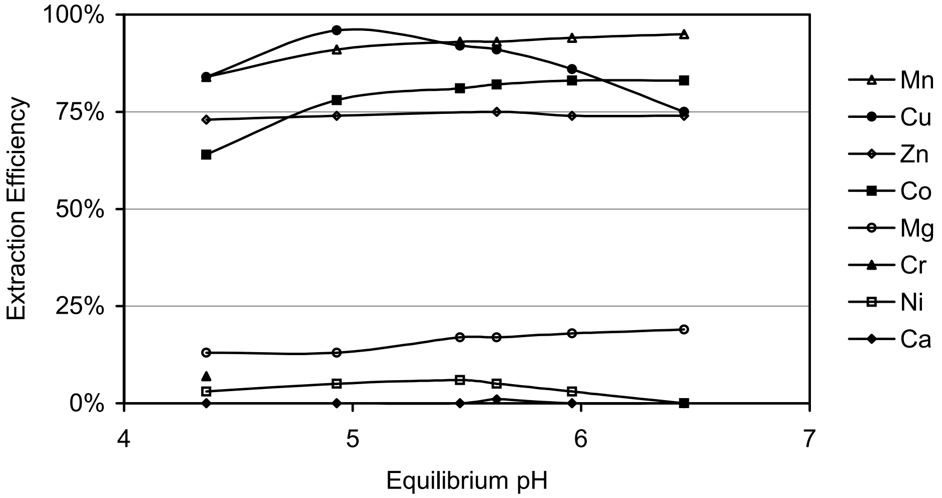


Figure 4-21. The extraction behaviour of Bulong PLS spiked with chromium(III), (1×10^{-4} mol L^{-1}, 5 mg L^{-1}). The organic phase contained Cyanex® 272 (0.3 mol L^{-1}) in Shellsol® 2046.

4.5 Effect of Organic Phase Composition on the Extraction of Chromium(III)

The composition of the organic phase is of primary importance in determining the behaviour of a solvent extraction system. The most important component of the organic phase is the extractant. This is the organic component that actively forms an extractable species with the component of the aqueous phase being extracted. The choice of extractant will determine the conditions under which extraction of the desired species occurs and the separation that may be achieved from other species in solution. The extraction behaviour of chromium(III) with a range of acidic organophosphorus extractants is examined in Chapter 4.5.1. The concentration of the extractant also affects the extraction behaviour. This is considered in Chapter 4.5.2.

Other components of the organic phase also have a role to play. The diluent, which is normally the largest constituent by volume, often determines the physical properties of the organic phase. The diluent may also affect the stability of the organic phase during continuous operation. The effect of diluents with different organic characteristics is discussed in Chapter 4.5.3.

In some instances a phase modifier may be used. This component often serves to increase the solubility of the extractant in the diluent and may also decrease the time required for phase separation. Phase modifiers were not used, except when it was necessary to match the conditions used by previous workers, in order to keep the system under investigation as simple as possible. No significant solubility or phase separation problems due to the organic phase were noted during extraction experiments.

The extractant, diluent and any modifier required may all degrade during continuous operation. This may be due to exposure to entrained oxygen during mixing, oxidising agents in the aqueous phase, UV irradiation or the action of micro-organisms. The presence of degradation products commonly produces a reduction in the effective separation of metals.

To minimise the formation of degradation products, a sacrificial reductant (anti-oxidant) may also be added to the organic phase. Solvent extraction systems involving acidic extraction of metals often use butylated hydroxytoluene (BHT or the trade name Ionol®) as the anti-oxidant. This chemical has the advantage that its degradation products are soluble in the aqueous phase, so may be washed out of the system. As no continuous experiments were performed, Ionol® was not used during experiments on extraction of chromium(III).

4.5.1 Effect of Acidic Organophosphorus Extractant on Extraction of Chromium(III)

Extraction with D2EHPA required a longer contact time to reach apparent equilibrium. A contact time of 30 minutes was used for all experiments where D2EHPA was the extractant. A contact time of 30 minutes was also used for extraction experiments with Cyanex® 301 to ensure sufficient time for extraction was allowed.

The effect of the chosen extractant within the family of acidic organophosphorus extractants is shown in Figure 4-22. The extraction of chromium(III) with D2EHPA occurs, as expected on the basis of its lower pK_a value, at lower pH than extraction with Cyanex® 272. The extent of extraction was the same. Cyanex® 301 did not extract chromium(III) in the pH range 2–5. This was consistent with the finding of Singh *et al.* (1999) up to pH 4.3. However the conditions used in the present study were the first to use a sulphate-containing aqueous phase and also used a higher extractant concentration than previous work.

Cyanex® 302 was not considered as it is unstable in industrial solutions limiting its commercial use (Personal Communication, G. M. Ritcey March 2001). It has been reported that less than 5% of chromium(III) was extracted by Cyanex® 302 at pH less than 3 (Saily *et al.* 1996).

The extraction of chromium(III) with D2EHPA reported in the present work was the first under these experimental conditions. Extraction of chromium(III) with D2EHPA has previously been reported from a range of solutions (see e.g. Kimura 1960; Islam & Biswas 1979b; Pandey, Cote & Bauer 1996). The range of experimental conditions used has led to a range of results being published. The general behaviour of chromium(III) reported under comparable conditions was similar to that reported in the present work.

Despite the effective extraction of latter first-row transition elements by Cyanex® 301, the lack of extraction of chromium(III) was plausible when considered from a hard-soft acid-base viewpoint (Huheey 1983). Chromium(III) is considered a hard acid and as such would prefer contact with a hard base. The functional group of Cyanex® 301 containing sulphur is soft, certainly much softer than the oxygen that the aqueous chromium(III) is surrounded by (Huheey 1983). The preference of chromium(III) to form a complex with oxygen-containing rather than sulphur-containing ligands is also shown by the hexaaqua chromium(III) complex being stronger than the chromium(III) diethyldithiophosphate complex (Huheey 1983).

A previous study on the extraction of first-row transition metals between chromium(III) and zinc(II) with Cyanex® 301 indicated that chromium(III) and manganese(II) do not show significant extraction whereas heavier metals all showed at least 80% extraction (Singh *et al.* 1999). This is also consistent with the product information for Cyanex® 301, which suggests that this extractant be used for the extraction of zinc, (a soft, late-transition metal) from calcium (a hard, alkaline-earth metal) (*Cyanex® Extractants*).

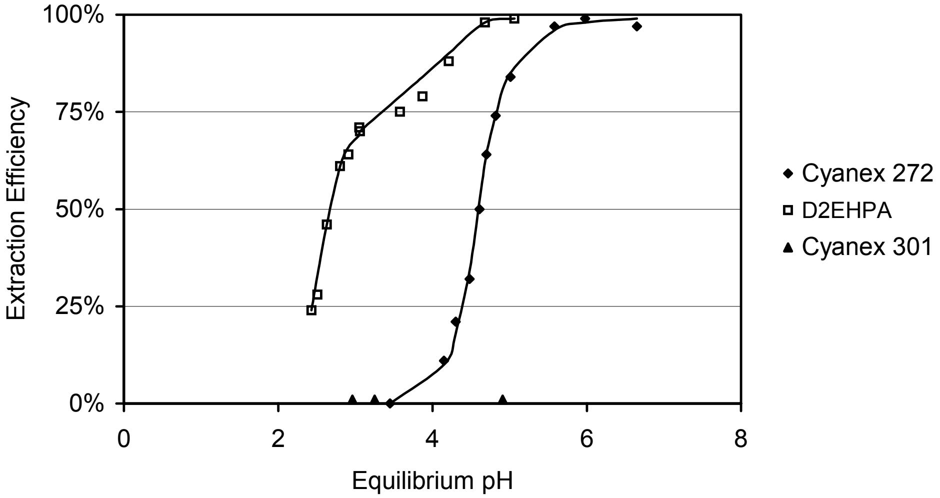


Figure 4-22. The extraction of chromium(III) from sulphate solution with various acidic organophosphorus extractants.

Aqueous phase: Cr(III) 2×10^{-4} mol L^{-1}, SO_4^{2-} 0.1 mol L^{-1};

Organic phase: Extractant as shown, 0.3 mol L^{-1} in Shellsol® 2046.

4.5.2 Effect of Extractant Concentration on the Extraction of Chromium(III)

The effect of Cyanex® 272 concentration on the distribution coefficient of chromium(III) in the absence of sulphate is shown in Figure 4-23. The data shown in the figure indicates that increasing the extractant concentration caused a decrease in the pH of chromium(III) extraction. These results were in general agreement with Equation 4-4 proposed by Ritcey and Ashbrook (1984):

$$D = K_D \frac{(\overline{HA})^n}{(H^+)^n} \tag{4-4}$$

This equation indicates that the distribution coefficient, *D*, is dependent on the extractant concentration in the organic phase and the pH of the aqueous phase, where K_D is an extraction constant. When plotted as the logarithmic function (Figure 4-23), a ten-fold increase in extractant concentration should move the $pH_{0.5}$ value by 1 pH unit. The shift in pH shown in Figure 4-23 was 1.2 pH units, close to the expected value of unity but indicative of other influences on the extraction behaviour of chromium(III).

The change in observed slope of the lines in Figure 4-23, from 2.6 to 1.6, with increasing pH indicated the involvement of several species, probably hydrolysed chromium(III), in the extraction. The behaviour averages that of $Cr(OH)^{2+}$, which would produce a slope of 2. However the active species is better represented as $Cr(OH)_j^{(3-j)+}$ where *j* is 0, 1 or 2, which would produce a range of slope values.

The application of Equation 4-4 requires a number of assumptions which may not be satisfied in the present system. Unlike many metals, chromium(III) undergoes significant hydrolysis reactions without forming an insoluble precipitate. This behaviour violates one of the assumptions underlying Equation 4-4, that no significant metal hydrolysis occurs(Ritcey & Ashbrook 1984).

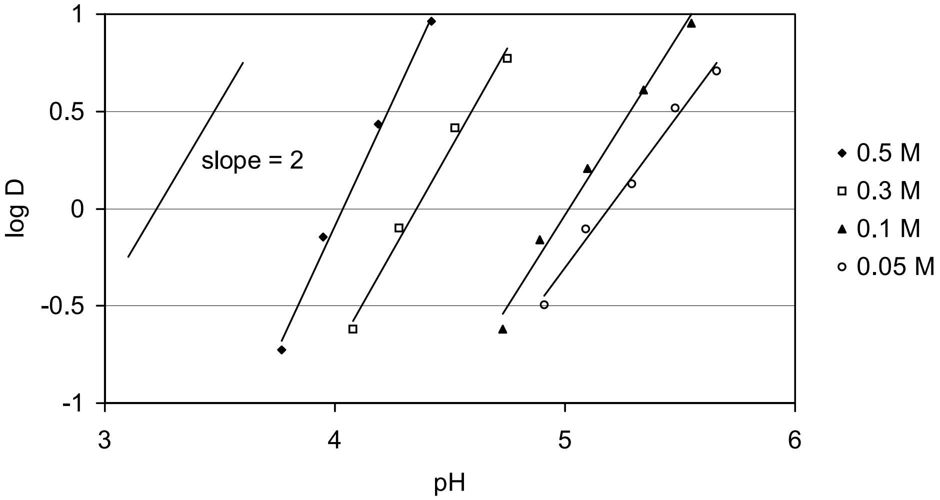


Figure 4-23. The effect of Cyanex® 272 concentration on the distribution coefficient (D) of chromium(III) in the absence of sulphate.

Aqueous phase: Cr(III) 1×10^{-3} mol L^{-1};

Organic phase: Cyanex® 272 (concentration as shown) in Shellsol® 2046.

The observed shift in $pH_{0.5}$ value and the change in the slope of the lines indicated non-ideal behaviour, although still in general agreement with the predicted behaviour, a higher extractant concentration results in a lower extraction pH.

In the presence of sulphate anions there was noticeable curvature in plots showing the effect of extractant concentration on the distribution coefficient of chromium(III) (Figure 4-24). The existence of this curvature indicated a more complex system for chromium(III) than has been previously observed for other metals. The curvature was more pronounced at higher extractant concentrations and therefore was unlikely to be due to saturation of the organic by the metal. The sulphate concentration did not affect the curvature as shown in Figure 4-25 where the same curvature is observed from solutions containing 0.1 and 0.3 mol L^{-1} sulphate anions.

These data suggest that the presence of sulphate anion was required for the curvature to be observed but the curvature was especially notable at higher extractant concentration. The requirement of the sulphate anion for the curvature to be observed may be due, as was suggested in Chapter 4.4.3, to the formation of chromium(III) sulphate species.

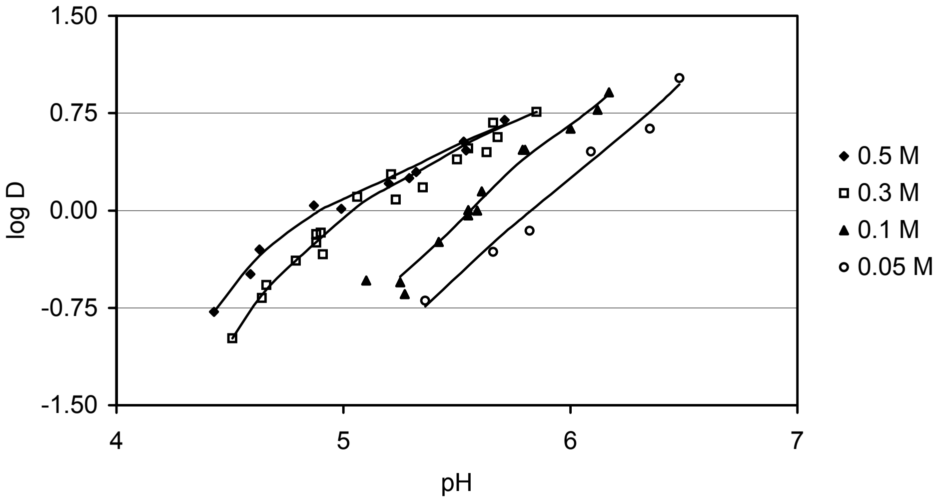


Figure 4-24. The effect of Cyanex® 272 concentration on the distribution coefficient (D) of chromium(III) in the presence of sulphate.

Aqueous phase: Cr(III) 1×10^{-3} mol L^{-1}, SO_4^{2-} 0.33 mol L^{-1};

Organic phase: Cyanex® 272 (concentration as shown) in Shellsol® 2046.

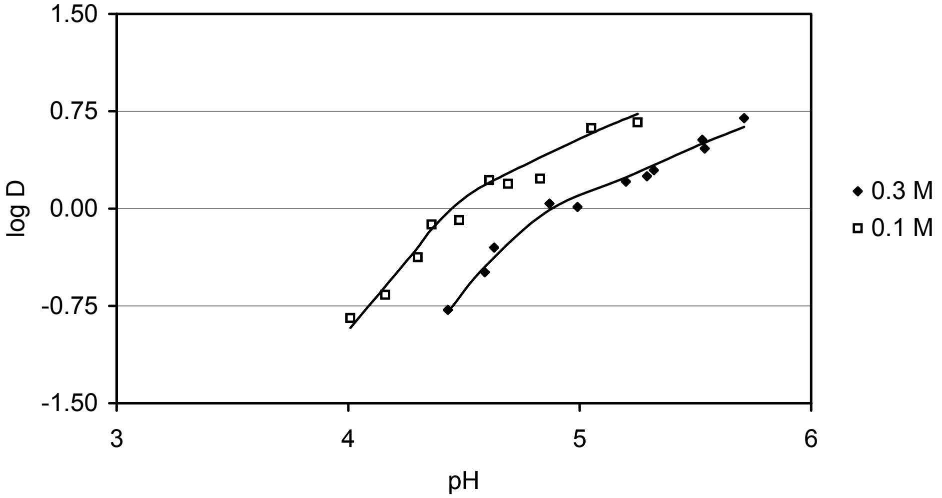


Figure 4-25. The effect of sulphate concentration on the distribution coefficient (D) of chromium(III) at high constant Cyanex® 272 concentration.

Aqueous phase: Cr(III) 1×10^{-3} mol L^{-1}, SO_4^{2-} concentration as shown;

Organic phase: Cyanex® 272 0.5 mol L^{-1} in Shellsol® 2046.

4.5.3 Effect of Organic Diluent on Extraction of Chromium(III)

The choice of an aliphatic or aromatic organic diluent had a minor effect on the extraction behaviour. This is shown in Figure 4-26. The extent of extraction was similar and the $pH_{0.5}$ values differ by only 0.2 units (hexane 5.36 to Shellsol® 2046 5.56).

At constant pH the distribution coefficient for chromium(III) was higher when hexane, a pure aliphatic, was used as the diluent. This is shown in Figure 4-27. The behaviour of Shellsol® 2046 which contains 20% aromatics and xylene, a pure aromatic diluent was similar. Preston (1982) found that heptane, an aliphatic diluent, gave higher extraction than xylene for cobalt and nickel and the higher extraction for aliphatic diluents is now extended to chromium(III) by the present work.

Although the choice of diluent has only a small effect on the chemical behaviour of chromium(III) with Cyanex® 272, the physical properties of the extraction system may be altered significantly by the choice of diluent as it is the largest volume component of the organic phase. In the present system a slightly better phase separation was observed with hexane, an aliphatic diluent. Continuous testing is necessary to assess the stability of the diluent in contact with the aqueous phase and the effect of any degradation products on either the physical or extraction properties of the system. There is some agreement that an aliphatic diluent is preferable with respect to stability, however the capital and operating costs also need to be considered in a commercial operation.

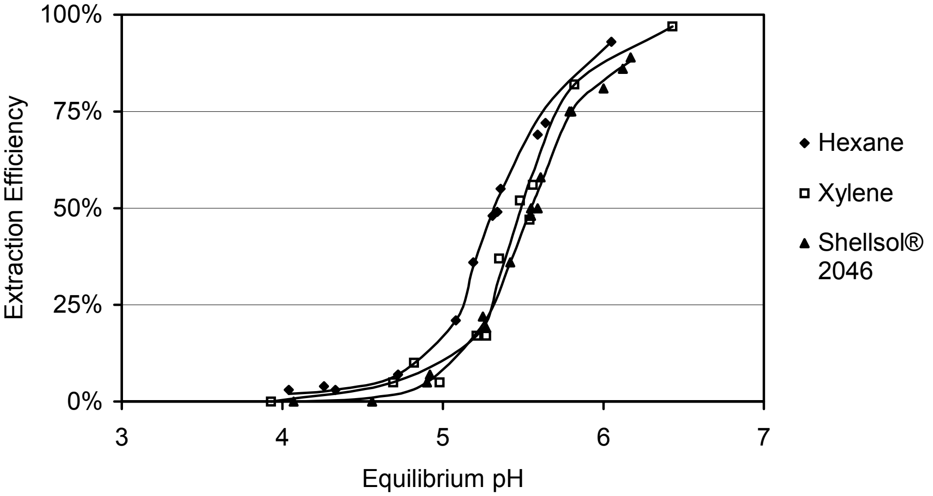


Figure 4-26. The effect of organic diluent on the extraction of chromium(III) from sulphate solution with Cyanex® 272.

Aqueous phase: Cr(III) 1×10^{-3} mol L^{-1}, SO_4^{2-} 0.33 mol L^{-1};

Organic phase: Cyanex® 272 0.32 mol L^{-1} in diluent as shown.

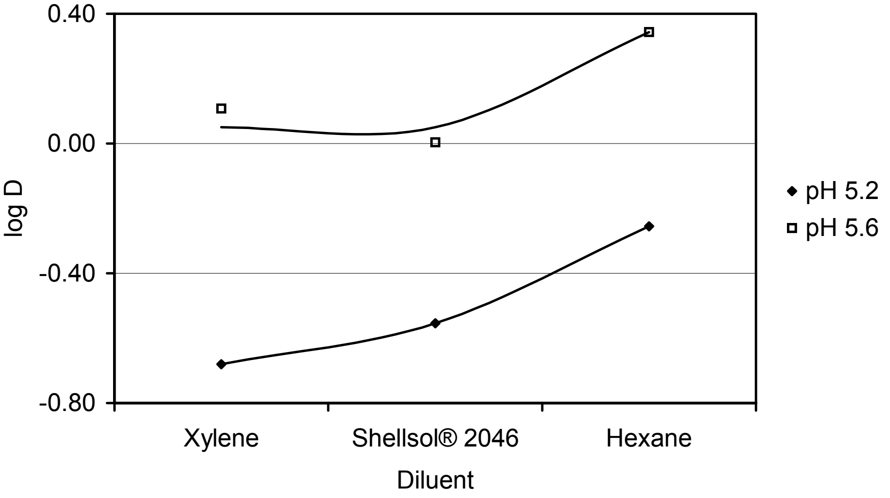


Figure 4-27. The effect of organic diluent on the distribution coefficient (D) of chromium(III) from sulphate solution with Cyanex® 272.

Aqueous phase: Cr(III) 1×10^{-3} mol L^{-1}, SO_4^{2-} 0.33 mol L^{-1};

Organic phase: Cyanex® 272 0.32 mol L^{-1} in diluent.

4.6 Changes in an Organic Phase Loaded with Chromium(III)

The organic phase takes on the blue colour of the chromium(III) (1×10^{-2} mol L^{-1}) feed solution when initially loaded. Observation of the same colour in both the aqueous and freshly loaded organic phase indicates that the inner coordination sphere of the metal is unchanged. If the organic phase was allowed to stand for approximately 24 hours a green organic solution was observed. This colour is characteristic of octahedrally coordinated chromium(III) (Nannelli, Gillman & Block 1971). The UV-Visible spectra of the initial and aged solutions are shown in Figure 4-28. There was a clear shift in the wavelength of the peak maxima from 410-20 to 450 nm and from 580 to 620 nm. The shoulder near 685 nm is also enhanced in the aged spectra. Aggett and Udy (1970) reported a change in the UV-Vis spectrum peaks from 412 nm and 570 nm to 448 nm and 628 nm respectively which are close to the observed values in the present work. These authors attributed the observed changes to a change in the structure of the extracted chromium(III) species in the organic phase.

The same colour change was observed when the organic phase was heated on a steam bath but the colour development was much faster appearing complete in approximately 10 minutes. The UV-Visible spectra of heated solutions was similar those for solutions aged for 24 hours at room temperature indicating the same change in the nature of the extracted species. No study on the extraction of chromium(III) has previously reported a change in the colour of an organic phase containing an acidic organophosphorus extractant with solution age. In the present work the same colour change was observed with Cyanex® 272 or D2EHPA as the extractant although UV-Visible spectra were only recorded for Cyanex® 272.

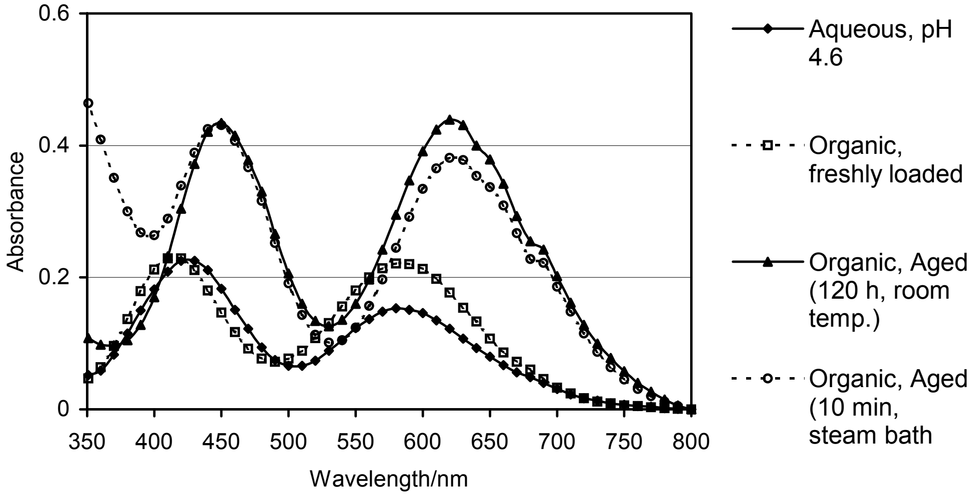


Figure 4-28. UV-Visible spectra of chromium(III) in the aqueous and organic phase under various aging conditions.

Cr(III) 1×10^{-2} mol L^{-1}, Cyanex® 272 0.32 mol L^{-1} in Shellsol® 2046.

At room temperature a noticeable cloudiness in the loaded organic phase developed as the solution aged. The cloudiness could be removed by passing the organic phase through Whatman® 1PS phase separation paper suggesting that the cloudiness was due to water in the organic solution. The appearance of water in the organic phase suggested that water was expelled from the extracted chromium(III) species as the solution aged.

These observations clearly indicate that after extraction of chromium(III) with an acidic organophosphorus extractant, either Cyanex® 272 or D2EHPA, a slow reaction takes place in the organic phase resulting in a different form of the extracted species. The transition to a different species is also suggested by the change in stripping behaviour discussed in Chapter 4.10.4 where complete stripping of a freshly loaded organic phase is achieved but no stripping could be achieved with an aged organic phase.

Previous work on the extraction of chromium(III) with other extractants has also reported a change in the UV-Visible spectrum: Aggett and Udy (1970) with TBP as the extractant; and Flett and West (1970) with Primene JMT™ as the extractant. Aggett and Udy (1970) also found that the change in colour of the loaded organic phase made chromium(III) inert to stripping. A change in the nature of the extracted species may explain the reported difficulty in stripping loaded chromium(III) from a range of extractants. The age of the organic phase used in stripping experiments was rarely specified.

The change in the spectra of the organic phase indicated a change in the ligand structure or type surrounding the metal centre. Chromium(III) shows almost exclusively octahedral coordination in the aqueous phase (Cotton & Wilkinson 1988) and the same would be expected in organic solutions. The change in the structure of the extracted species could account for the change in UV-Visible spectra.

4.7 Nature of the Extracted Chromium(III) Species

Direct determination of the extracted species in the organic phase was not possible even though a variety of techniques were utilised. Attempts to crystallise a sample by evaporation of solvent produced only a viscous or semi-solid mass unsuitable for X-ray crystallography. A spectrum could not be obtained using Fourier transform-Raman spectroscopy due to self-absorption in the highly coloured solutions. Spectra could be obtained using near infra-red spectroscopy however the extracted species could not be separated from the excess extractant either in the observed spectra nor using silica-gel chromatography. Nuclear magnetic resonance (NMR) spectroscopy could not be used due to the paramagnetic properties of chromium.

Thus the determination of the extracted chromium(III) species is dependent on indirect methods of analysis drawn from the literature.

It is evident from the preceding discussions on the effect of anion type, especially sulphate, that the presence of complexing anions has some effect on the complex transferred to the organic phase. In the absence of sulphate and at low chromium(III) concentration the slope of the log D vs. pH curves (Figure 4-23) was approximately 2 as summarised in Table 4-5.

Table 4-5. Slope and $pH_{0.5}$ data extracted from Figure 4-23, the extraction of chromium(III) from nitrate solutions with Cyanex® 272.

[Cyanex® 272]	0.5 mol L^{-1}	0.3 mol L^{-1}	0.1 mol L^{-1}	0.05 mol L^{-1}
$pH_{0.5}$	4.03	4.35	5.02	5.19
Slope	2.56	2.08	1.86	1.60

The decrease in the observed slope with increase in $pH_{0.5}$ is consistent with increasing involvement of hydrolysed chromium(III) species in the extraction reaction. The predominant form of chromium(III) in the aqueous phase changes as the pH of the solution changes with higher concentrations of $Cr(OH)^{2+}$ and

$Cr(OH)_2^+$ cations existing at higher pH, especially at low metal concentration (Baes & Mesmer 1976).

The hydrolysed chromium(III) species appear similar to the form suggested by Islam and Biswas (1979b) for the extraction of chromium(III) with D2EHPA as the extractant. This is shown in Equation 4-5:

$$Cr(OH)_j^{(3-j)+} + 1.5H_2A_2 \rightleftharpoons CrA_3 + jH_2O + (3-j)H^+ \qquad (4\text{-}5)$$

where j = 0, 1 or 2 and H_2A_2 is dimerised D2EHPA. In another paper Islam and Biswas (1979a) proposed the involvement of hydrolysed species in the extraction mechanism due to the significantly faster kinetics of $Cr(OH)^{2+}$ compared to Cr^{3+}. The same authors also suggested that the mononuclear chromium(III) species was involved in the rate-determining step of the reaction despite the probable formation of Cr-O-Cr bridged structures in the aqueous phase (Islam & Biswas 1979a; Cotton & Wilkinson 1988). The higher pH required for extraction of chromium(III) with Cyanex® 272 compared to extraction with D2EHPA increases the importance of hydrolysed chromium(III) species.

An additional consideration in the determination of the extracted species is the unchanged nature the metal coordination sphere suggested by the similar spectra of the aqueous and freshly loaded organic phase (Figure 4-28). This suggests that the hydrolysed species $[Cr(OH)_x(H_2O)_{(6-x)}]^{(3-x)+}$ (where x is 0, 1 or 2) is transferred to the organic phase without undergoing any change. This requires that the extractant is acting in the outer coordination sphere of the metal to form an organophilic ion pair.

The unchanged nature of the inner coordination sphere also suggests that the extraction reaction is much faster than exchange of ligands in the inner coordination sphere of chromium(III). This is consistent with the known inert nature of the chromium(III) cation in aqueous solution (Cotton & Wilkinson 1988).

The nature of the extractant as it exists in the organic phase may also affect the nature of the extracted species. Di-alkyl organophosphorus extractants (HA) have been shown to exist as the dimer in organic solutions (Ritcey & Ashbrook 1984; Sole & Hiskey 1995) and this was assumed to be carried through to the extracted species at low metal loadings (Ritcey & Ashbrook 1984) as shown in Equation 4-6:

$$\mathrm{M}^{n+} + n\overline{(\mathrm{HA})_2} \rightleftharpoons \overline{\mathrm{M}(\mathrm{A}\cdot\mathrm{HA})_n} + n\mathrm{H}^+ \tag{4-6}$$

At high metal loadings the simpler form of the equation (Equation 4-7) is generally assumed to dominate.

$$\mathrm{M}^{n+} + n\overline{\mathrm{HA}} \rightleftharpoons \overline{\mathrm{MA}_n} + n\mathrm{H}^+ \tag{4-7}$$

There is little agreement about which equation applies. Preston (1982) extends the low loading assumption (Equation 4-6) to metal loadings of 0.1 mol L^{-1} whereas Islam and Biswas (1979b) assumed high metal loading (Equation 4-7) at a metal loading of 4×10^{-3} mol L^{-1} even though the concentration of the extractant was nearly the same in both works.

On the basis of the known strong interaction between Cyanex® 272 molecules (Tokhadze *et al.* 1997; Gonzalez *et al.* 1998) and the known existence of Cyanex® 272 dimers in the organic phase (Sole & Hiskey 1992) it seemed reasonable to adopt a dimerised extractant model in the present study. Additionally, the low metal to extractant ratio used throughout the present study meant that excess extractant was always available for dimer formation.

The equations describing metal extraction outlined by Sole and Hiskey (1992) were used to calculate the dependence of the extracted species on the extractant concentration (Equation 4-8 and 4-9):

$$\mathrm{M}^{n+} + m\overline{(\mathrm{HA})_2} \rightleftharpoons \overline{\mathrm{M}(\mathrm{HA}_2)_n(\mathrm{HA})_{2(m-n)}} + n\mathrm{H}^+ \tag{4-8}$$

$$n\mathrm{pH}_{0.5} = -m\log\overline{(\mathrm{HA})_2} - \log\mathrm{D} \tag{4-9}$$

From Equation 4-9 a plot of $\mathrm{pH}_{0.5}$ against $\log\overline{(\mathrm{HA})_2}$ should give a straight line of slope –*m*/*n*. This plot is shown in Figure 4-29 from which the slope is determined as –1.2. The calculated matrix of *m* and *n* values are shown in Table 4-6.

Table 4-6. Calculated values of *m* using data from Figure 4-29. The *x* and *n* values are equivalent methods of establishing the species M^{n+}.

x	Species M^{n+}	n	m
0	$[Cr(H_2O)_6]^{3+}$	3	3,4
1	$[Cr(OH)(H_2O)_5]^{2+}$	2	2,3
2	$[Cr(OH)_2(H_2O)_4]^{+}$	1	1,2

A value of *n* equal to 1 or 2 was most likely in this pH range as discussed in Chapter 1.1. However at the highest reported extractant concentration (0.5 mol L^{-1}) the large excess of extractant and the lower pH of extraction enable the formation of extractable species with $n = 3$. This is demonstrated by the intermediate slope value of 2.6 observed at this extractant concentration (Table 4-5). When the extractant concentration was 0.3 mol L^{-1}, the most commonly used experimental conditions, an *n* value of 2 was predominant.

The metal species, M^{n+}, in Equation 4-8 is the hydrolysed chromium(III) species $[Cr(OH)_x(H_2O)_{(6-x)}]^{(3-x)+}$ (where *x* is 0, 1 or 2) as discussed earlier. Substituting the metal species formed (Table 4-6) and the matrix of *n* and *m* values into Equation 4-8 results in the species shown in Figure 4-30. For a given *n* value the only difference in structure with a higher *m* value, is the inclusion of an intact Cyanex® 272 dimer in the extracted species. An intact dimer would probably be lost from the outer coordination sphere once the extracted species was in the bulk organic solution.

The species suggested in Figure 4-30 provide a different interpretation of the nature of the extracted chromium(III) species than the formation of CrA_3 as the extracted complex with D2EHPA suggested by Islam and Biswas (1979b). In fact, the extracted species suggested in the present work is novel, providing an alternative view on the development of the extracted chromium(III) species with Cyanex® 272 as the extractant.

Given the range of experimental slope values obtained for chromium(III) and known presence of a range of chromium(III) species it was reasonable to assume that a mixture of species formed in the organic phase. Additionally changes in experimental conditions, especially the amount of available extractant, may change the complexes formed. As the total loading of the organic phase increases the presence of unreacted dimers decreases, as does the available excess extractant needed to form an extractable species with deprotonated dimers.

This may lead to the simpler extracted species proposed by many workers at higher loadings.

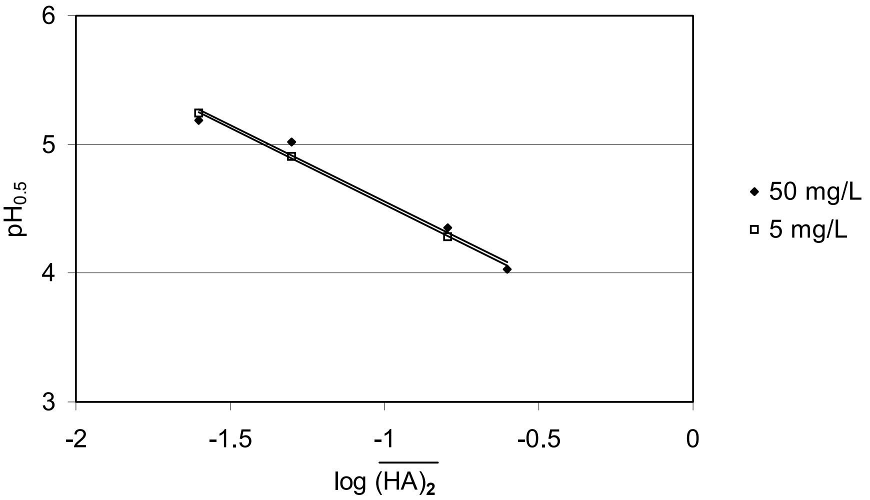


Figure 4-29. Plot of $pH_{0.5}$ for extraction of chromium(III) with Cyanex® 272 against extractant concentration.

Aqueous phase: Cr(III) concentration as shown;

Organic phase: Cyanex® 272 in Shellsol® 2046.

(I) $[Cr(H_2O)_6]^{3+}\cdot[(HA_2)^-]_3$

(II) $[Cr(H_2O)_6]^{3+}\cdot[(HA_2)^-]_3\ldots(HA)_2$

(III) $(HA_2)^-\cdot[Cr(OH)(H_2O)_5]^{2+}\cdot(HA_2)^-$

(IV) $[(HA_2)^-\cdot[Cr(OH)(H_2O)_5]^{2+}\cdot(HA_2)^-]\ldots(HA)_2$

(V) $[Cr(OH)_2(H_2O)_4]^{+}\cdot(HA_2)^-$

(VI) $[[Cr(OH)_2(H_2O)_4]^{+}\cdot(HA_2)^-]\ldots(HA)_2$

Figure 4-30. Possible structures of the extracted chromium(III) species, by substitution of generated data into $\overline{M(HA_2)_n(HA)_{2(m-n)}}$.

(I) n = 3, m = 3; (II) n = 3, m = 4; (III) n = 2, m = 2; (IV) n = 2, m = 3; (V) n = 1, m = 1; (VI) n = 1, n = 2.

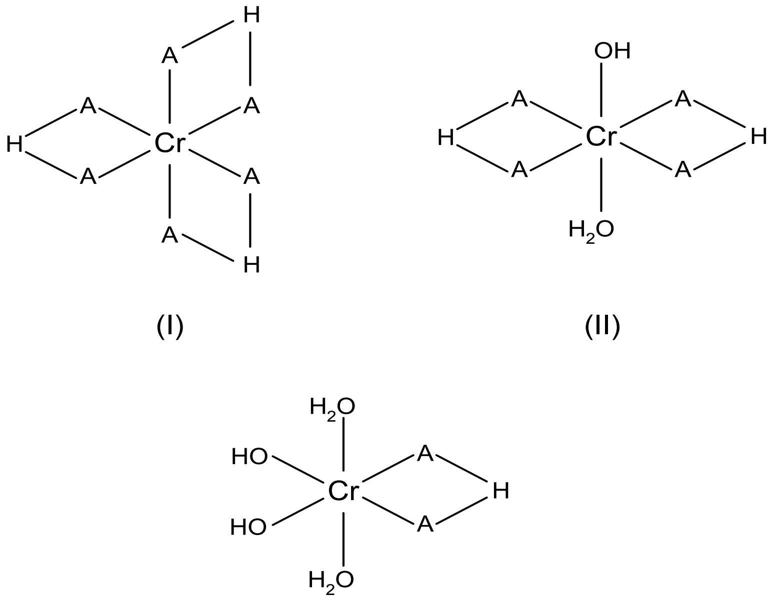
4.8 Nature of the Stable Organic Chromium(III) Species

The present work suggested that the extracted species usually incorporates a monomeric, hydrolysed chromium(III) centre, unchanged from the aqueous phase, with sufficient extractant to form an ion pair soluble in the organic phase (Figure 4-30). A dimer model for the extractant behaviour has been assumed as described in Chapter 4.7. The evidence presented in Chapter 4.6, that a species with different UV–Visible spectra forms when the loaded organic phase is allowed to stand or is heated, suggests that a stable chromium(III) species was formed in the organic phase that was different to the extracted species.

The expulsion of water during the formation of the stable organic species suggests that the inner coordination sphere of the chromium(III) metal centre is being exchanged for components of the organic phase. The nature of the change from the initially extracted to the stable organic species will be postulated from the known behaviour of chromium(III).

The immediate suggestion is the attachment of the extractant molecules from the outer coordination sphere of the extracted species directly to the chromium(III) centre. The intact dimers associated with some of the extracted species are thought to be lost once the extracted species enters the bulk organic solution so are not incorporated in the stable species. This rearrangement would produce the species shown in Figure 4-31.

A further possibility is the formation of tightly bound CrA_3 species with the extractant acting as a bi-dentate ligand (Figure 4-32), either directly from the extracted species or via the structures shown in Figure 4-31. The tris-bidentate



(I)

(II)

(III)

Figure 4-31. Possible stable species in the organic phase formed by extractant molecules in the outer coordination sphere attaching directly to the chromium(III) centre. (I) $x = 0$; (II) $x = 1$; (III) $x = 2$.

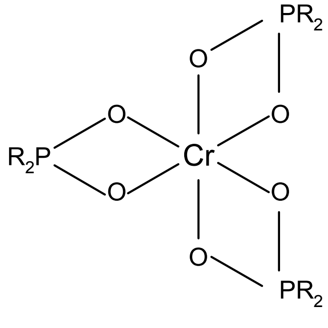
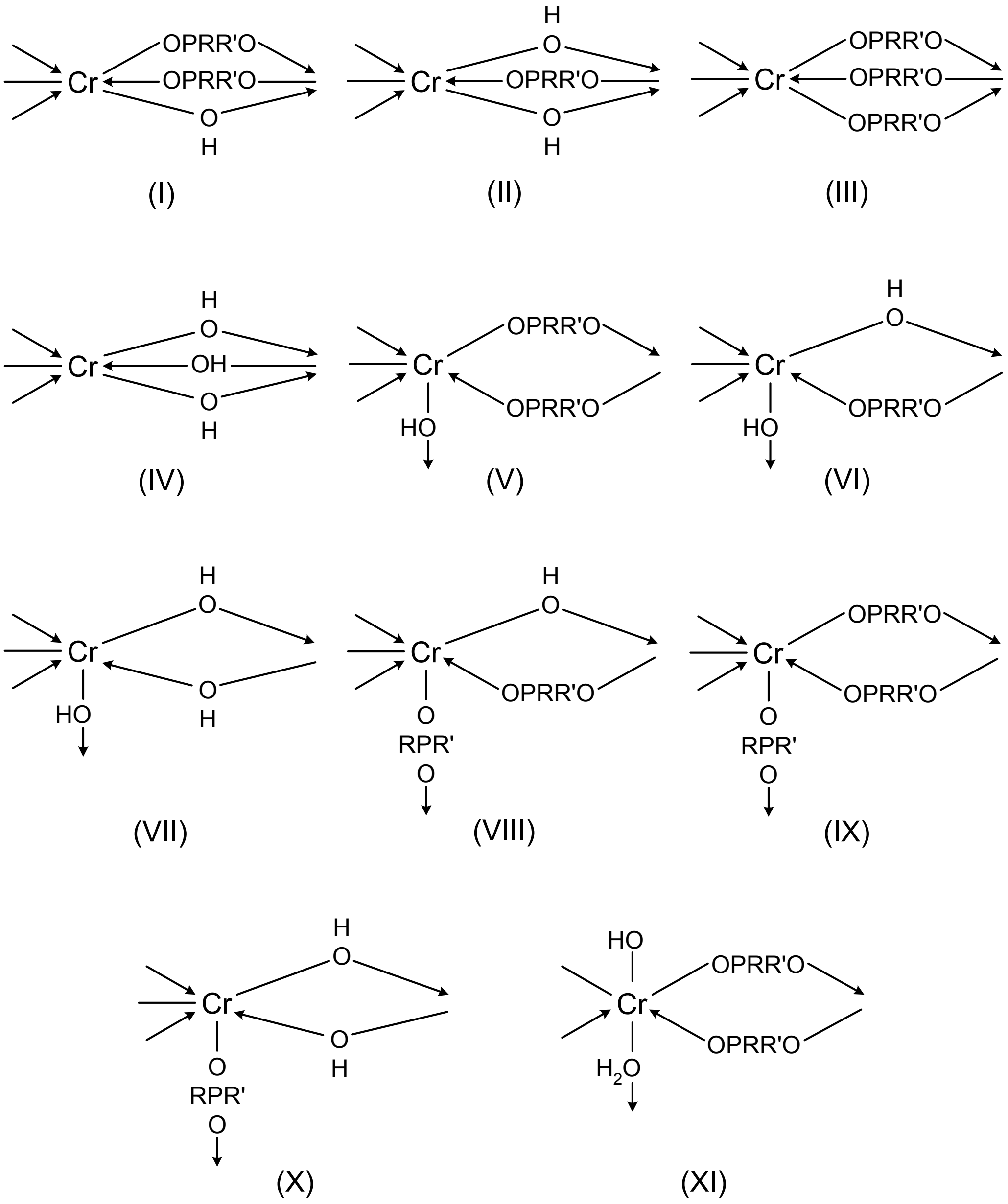


Figure 4-32. The structure of tris-bidentate CrA_3 where A is de-protonated bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex® 272).

structure CrA_3 is the previously suggested form of the extracted chromium(III) species with D2EHPA (Islam & Biswas 1979b; Pandey, Cote & Bauer 1996). There is no previously published extracted species for solvent extraction of chromium(III) with Cyanex® 272. However the work of Navarro Mendoza *et al.* (2000) suggested that during ion exchange of chromium(III) the extracted species after 24 hours was $Cr(OH)(H_2O)A_2$ where A is a bi-dentate Cyanex® 272 molecule. Given the long contact time used in this work the defined extracted species may be similar to the stable species in the present work. The likelihood of forming stable species containing bi-dentate ligands increases as the total extractant loading increases.

A different option is the formation of a range of polymeric chromium(III) species. Chromium(III) is known to form multinuclear species in the aqueous phase (Laswick & Plane 1959) and polymeric species of other metals and extractants are known to exist in the organic phase (Crabtree & Rice 1974; Sato & Ueda 1974). It was therefore plausible that polymeric chromium species form in the organic phase. This has been suggested by some previous workers (Aggett & Udy 1970; Pandey, Cote & Bauer 1996) to explain a variety of observations although without experimental data.

Nannelli, Gillman and Block (1971) proposed that a range of chromium(III) phosphinate polymers could be formed. Earlier work (Block *et al.* 1962) suggested that a bridging rather than a bi-dentate structure was favoured while linear chains without significant cross-linking were also more likely (Nannelli, Gillman & Block 1971). The range of structures, shown in Figure 4-33, were produced under harsher conditions than those used in the present work, although production under mild conditions in inert solvents has been observed (Block *et al.* 1962). The production of such species appears consistent with the observations of the present work, in particular the maxima in the visible spectra at 450 and 620 nm are similar. The most recent work by this group suggested that structure (I) may be predominant (Gillman & Nannelli 1977).



(I) (II) (III)

(IV) (V) (VI)

(VII) (VIII) (IX)

(X) (XI)

Figure 4-33. The structures proposed for chromium(III) phosphinic acid polymers by Nannelli, Gillman and Block (1971). Similar species to some of these may be inferred in the current work.

The available evidence does not directly identify the nature of the stable chromium(III) species in a loaded organic phase containing Cyanex® 272 for the reasons discussed previously. Thus the proposed changes draw on the understanding of the behaviour observed in the present work and the previously published literature. The formation of a mixture of all the suggested stable species cannot be ruled out, especially the transition from the species formed from attachment of the outer coordination sphere components (Figure 4-31) to a polymeric structure (Figure 4-33). Conversely the bi-dentate extractant model (Figure 4-32) has been proposed previously and is consistent with the generally accepted model of extracted species formation.

4.9 Extraction of Chromium(VI)

It is reasonable to suggest that chromium(VI) in the pH range 0–7 would show different behaviour to chromium(III). In particular the neutral or anionic species formed by chromium(VI) in this pH range would be expected to produce different reactions to the cationic species formed by chromium(III). This was confirmed in this part of the present work.

4.9.1 Extraction of Chromium(VI) from Sulphate or Chloride Solutions

The extraction curve of chromium(VI) from sulphate or chloride-containing solutions with Cyanex® 272 is shown in Figure 4-34. There was no difference in the extraction behaviour between the sulphate and chloride solutions. This confirmed some of the observations of Rao and Prasad (1988) who found that the extraction of chromium(VI) from acid solution was independent of the acid type.

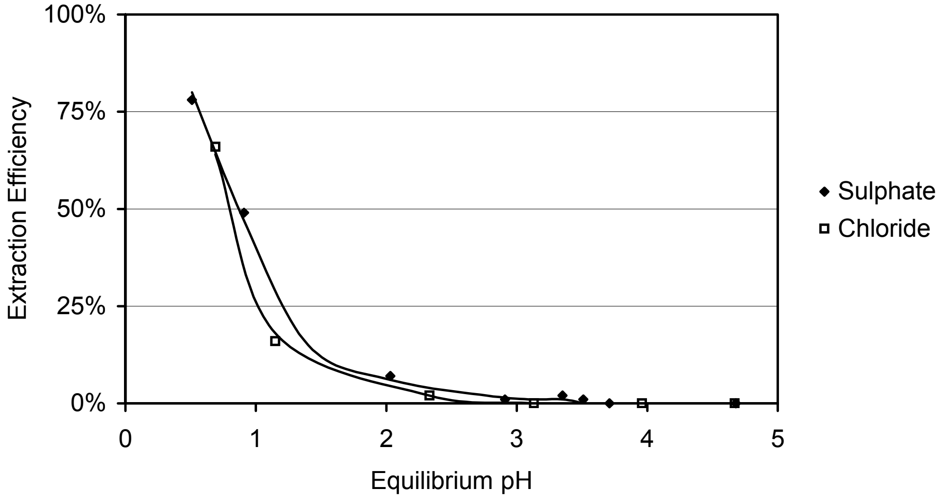


Figure 4-34. Extraction of chromium(VI) from sulphate and chloride solutions with Cyanex® 272.

Aqueous phase: Cr(VI) 0.01 mol L^{-1}, anion as shown 0.1 mol L^{-1};

Organic phase: Cyanex® 272 0.32 mol L^{-1} in Shellsol® 2046.

Unlike chromium(III), significant extraction of chromium(VI) does not occur at pH greater than 2 suggesting that the neutral chromic acid, H_2CrO_4, was involved in the transfer. The acid/base equilibria shown in Equations 4-10 and 4-11 establish that the neutral species becomes significant at about pH 2 and increases in concentration as the pH decreases. This was consistent with the modelling of Huang, Huang and Chen (1997) where chromic acid was proposed to exist in the pH range –1 to 2. The extraction of chromium(VI) with Cyanex® 272 increases with increasing acidity of the aqueous phase due to the increasing proportion of chromic acid present in the system.

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+ \qquad K_a\ 1.8\times10^{-1} \qquad (4\text{-}10)$$

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+ \qquad K_a\ 3.2\times10^{-7} \qquad (4\text{-}11)$$

The extraction of the neutral molecule was consistent with the independence of the extraction behaviour on anion type in the aqueous phase. At pH 2, despite the low levels of chromic acid naturally present in the system, significant extraction of this species was possible with long contact times as transfer of chromic acid to the organic phase caused the aqueous equilibrium of the system to produce more of the neutral species as shown in Equation 4-10.

The extraction of neutral metal species by bis(2,4,4-trimethylpentyl) phosphinic acid is not generally accepted. However Cyanex® 272 contains a significant amount of phosphine oxide impurity (Sole & Hiskey 1992) and neutral organophosphorus extractants have been shown to extract chromium(VI) under a range of conditions (Cuer, Stuckens & Texier 1974; Murty, Rao & Sastri 1981; Bolt, Tels & Van Gemert 1984; Ohki *et al.* 1986; Huang, Huang & Chen 1997).

The yellow/orange colour of the aqueous phase was transferred to the organic phase during extraction suggesting that, similar to the extraction of chromium(III), the inner coordination sphere of the metal was unchanged. This is consistent with workers using neutral organophosphorus extractants who suggested a solvation mechanism for the extraction of chromium(VI) (Huang,

Huang & Chen 1997) and the strong oxo species of chromium(VI) (Cotton & Wilkinson 1988).

The inability of Cyanex® 272 to extract anionic species and the previously observed extraction of chromium(VI) by species similar to an impurity found in the commercial extractant, suggest that extraction of chromium(VI) with Cyanex® 272 may be due to the presence of the neutral phosphine oxide impurity in commercially supplied Cyanex® 272. Attempts to purify the extractant according to the method of Hu, Pan and Fu (1995) were unsuccessful. Although it would be interesting to know the component responsible for extraction, from an operational viewpoint it is not normally relevant as it is not practical to use a purified extractant, i.e. if the commercially supplied product extracts the metal then metal extraction is considered to occur regardless of the molecule involved.

4.9.2 Effect of Temperature on Chromium(VI) Extraction at High pH

To determine whether chromium(VI) could be extracted under conditions used in the cobalt extraction circuit at Bulong Nickel Operation (BNO), a series of experiments were performed at 40 °C to assess the effect of temperature on chromium(VI) extraction. These experiments were limited to a pH range of 3–5.8 i.e. the designed operating pH of BNO's cobalt extraction circuit. The aqueous phase contained chromium(VI) (1×10^{-2} mol L^{-1}) and 0.1 mol L^{-1} of both sulphate and chloride ions. The organic phase contained Cyanex® 272 (0.32 mol L^{-1}, 10 vol%) in Shellsol® 2046. No extraction of chromium(VI) was observed under these conditions. This supports the earlier suggestion that chromium(VI) speciation determined by aqueous phase pH is the dominant factor in determining the extraction efficiency.

4.9.3 Extraction of Chromium(VI) from Industrial PLS

To further assess whether chromium(VI) could be extracted under conditions used in the cobalt extraction circuit at BNO, a sample of cobalt pregnant liquor stream (PLS) was spiked with chromium(VI) (5×10^{-3} mol L^{-1}, 250 mg L^{-1}). The organic phase contained Cyanex® 272 (0.32 mol L^{-1}) and Ionol® (1 g L^{-1}) in Shellsol® 2046. Ionol® is used as an anti-oxidant in the industrial organic phase which contacts the PLS. These experiments were performed at 40 °C in the pH range 2.6–6.5. These conditions provided the most accurate batch replication of the cobalt extraction circuit at BNO. Within the pH range investigated no extraction of chromium(VI) was observed. This clearly demonstrated the inability of Cyanex® 272 to extract chromium(VI) during normal operation of the BNO cobalt solvent extraction circuit.

The results of the present study extend the published data for the extraction of chromium(VI) with Cyanex® 272 in the range of conditions frequently utilised for the commercial application of this extractant. Previously published studies did not investigate extraction of chromium(VI) at pH values greater than 2. The present study newly examined the pH range 2–6.5 and reports no extraction of chromium(VI). The present work was in agreement with previous studies in the pH range 0.7–2, where extraction of chromium(VI) was found to occur.

4.9.4 Effect of UV Irradiation on Chromium(VI) Extraction

The effect of UV irradiation, as encountered in a windowed laboratory, was examined by carrying out a series of experiments in a darkened room. No difference in extraction behaviour between samples of chromium(VI) exposed to UV during extraction and extracted under darkened conditions was noted near pH 2 in sulphate solution. This is shown in Figure 4-35. The offset between the two curves is at the upper end of the estimated error range but is approximately the correct magnitude for the difference in pH at which they were obtained. The

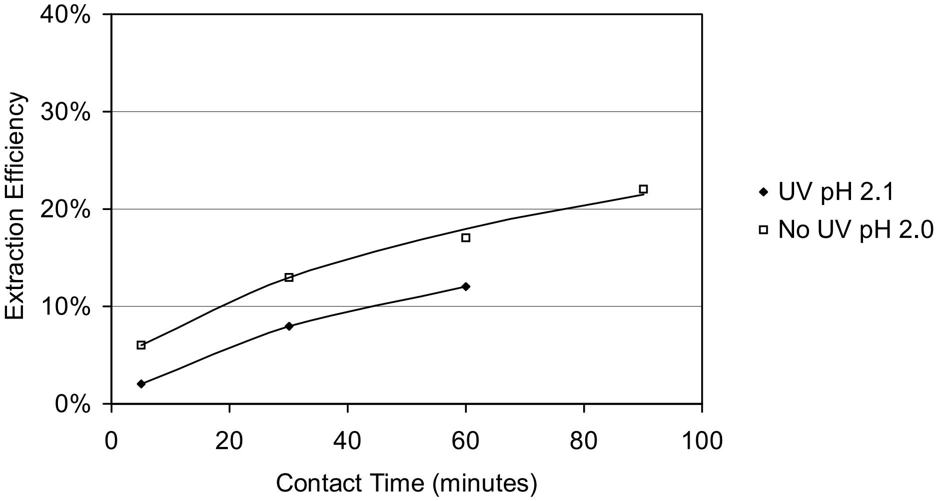


Figure 4-35. The effect of contact time on the extraction efficiency of chromium(VI) with Cyanex® 272 in the presence and absence of UV radiation.

Aqueous phase: Cr(VI) 0.01 mol L^{-1}, SO_4^{2-} 0.1 mol L^{-1};

Organic phase: Cyanex® 272 0.32 mol L^{-1} in Shellsol® 2046.

absence of a plateau in the extraction efficiency was due to the driving of the chromic acid equilibrium by removal of H_2CrO_4 as discussed previously (Equation 4-10). The effect of UV irradiation is relevant to the operation of many solvent extraction circuits as very few are closed systems. The cobalt extraction circuit at BNO has mixer units that are open to atmosphere and exposed to direct sunlight.

4.9.5 Oxidation of the Organic Phase by Chromium(VI)

On the basis of solution colour, it appeared that an organic phase loaded with chromium(VI) and allowed to stand for 24–48 hours reduced chromium(VI) to chromium(III). This suggested that at least one of the organic phase components was oxidised. There was no available method of confirming the chromium oxidation state in the organic phase. The UV-Visible spectra of freshly loaded and aged organic phases, initially containing chromium(VI) and chromium(III), are shown in Figure 4-36 and Figure 4-37. Despite the differences between spectra of chromium(VI) and chromium(III) in the freshly loaded samples (Figure 4-36), the spectra of the aged samples (Figure 4-37) were barely distinguishable with respect to peak position and shape.

Oxidation of the organic phase was dependent on chromium(VI) being loaded onto the organic phase and being allowed to remain there i.e. no colour change was observed in the aqueous phase when extraction did not occur. The conditions required for extraction of chromium(VI) should not occur when Cyanex® 272 is being used for nickel–cobalt separation. The determination of oxidation products in the organic phase is an analytical problem which has generated research projects on its own account (Hughes 2000).

A variety of techniques were attempted in order to determine the presence of oxidation products in the organic phase in the present work. Gas chromatography was used to separate the organic components. Mass

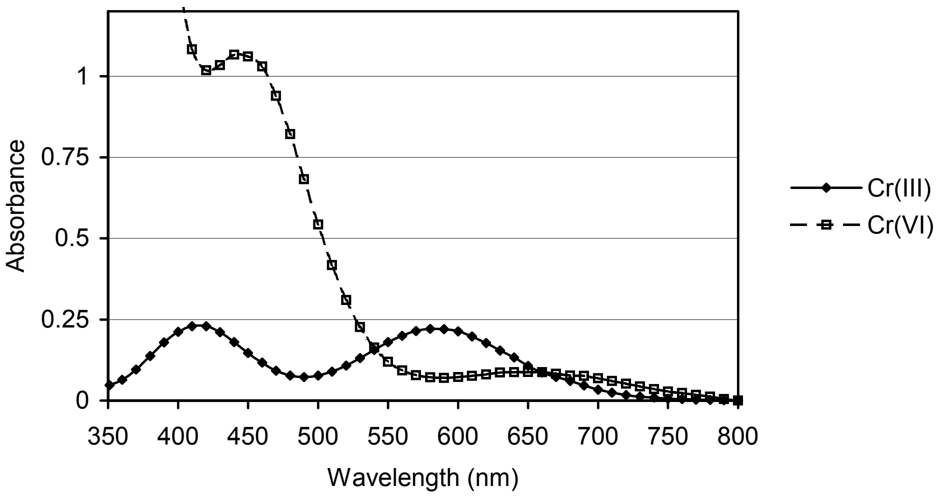


Figure 4-36. The UV-Visible spectra of a freshly loaded organic phase containing chromium. Cr 1×10^{-2} mol L^{-1}, Cyanex® 272 0.32 mol L^{-1} in Shellsol® 2046.

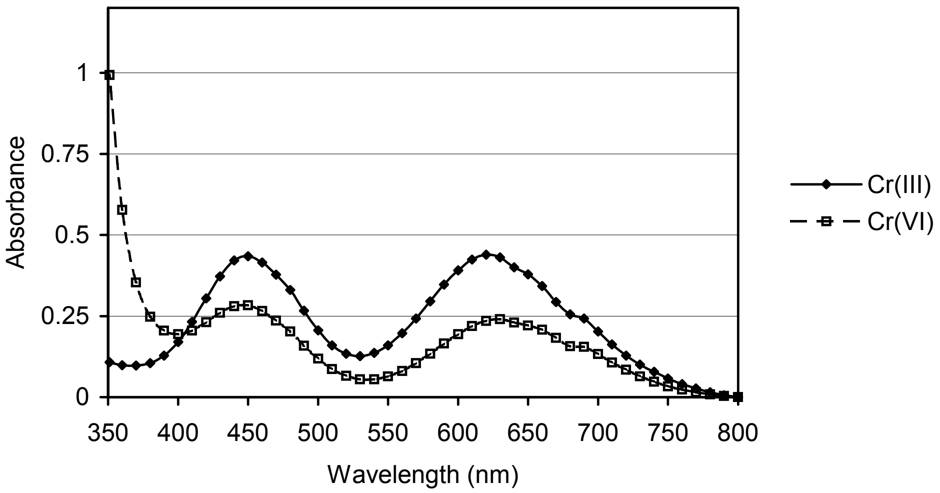


Figure 4-37. The UV-Visible spectra of an aged (48 h) loaded organic phase containing chromium.
Cr 1×10^{-2} mol L^{-1}, Cyanex® 272 0.32 mol L^{-1} in Shellsol® 2046.

spectrometry and atomic emission spectroscopy were used to try and identify the separated components. The presence of the major components could be identified but quantitative determination was not possible. Minor components, such as extractant impurities or oxidation products, could not be identified. The relatively low concentration of these products was further complicated as they have received insufficient attention to be included in analytical spectra libraries making their identification extremely difficult. As a result of the analytical difficulties and in the absence of operational problems directly attributable to the presence of oxidation products due to chromium(VI), further work was not carried out on their presence or identification.

4.10 The Stripping of Chromium(III) from Cyanex® 272

The stripping of chromium(III) from Cyanex® 272 has received little attention in the published literature despite the necessity for any commercial operation to be able to recycle the organic phase without significant loss of extractant activity. Pandey, Cote and Bauer (1996) reported incomplete stripping of high chromium(III) loadings but complete stripping of low loadings. Nearly complete stripping of low chromium(III) loadings was also reported by Navarro Mendoza *et al.* (2000) from Cyanex® 272 impregnated resin.

4.10.1 Effect of Stripping Contact Method

When stripping chromium(III) from Cyanex® 272 was attempted using the same contact method as that used for extraction, the phase separation time significantly affected the calculated stripping efficiency. The variation in stripping efficiency with separation time was found to be due to entrainment of the stripping solution in the organic phase. Entrainment gave the organic phase a milky appearance that cleared only over a period of days to months. If both phases were filtered, i.e. organic removed from the aqueous and discarded and vice versa, the chromium mass balance was unacceptably low due to removal of entrained chromium-containing components.

The method described in the experimental section (Chapter 3.3.2) for stripping experiments eliminated the long and incomplete phase separation observed when stripping experiments were conducted using the same contact method as extraction experiments.

The effect of the stripping contact time on stripping efficiency is shown in Figure 4-38. The stripping efficiency did not increase with increased contact time in the range 10–120 minutes. This suggested that the stripping reaction was quite fast. Pandey, Cote and Bauer (1996) also found that the stripping reaction was effectively complete within 10 minutes although only 79% of the loaded chromium(III) was removed from the organic phase by hydrochloric acid (8 mol L^{-1}). Although they tried longer contact times, significantly more chromium(III) could not be removed from the loaded organic phase.

The stripping of chromium(III) from an organic phase containing D2EHPA has conflicting reports. Pandey, Cote and Bauer (1996) found similar behaviour to Cyanex® 272 while Islam and Biswas (1979a) found that the chromium(III) could not be stripped from the organic phase. The difference in behaviour observed by these groups may be attributable to the change in the nature of the extracted species as discussed in Chapter 4.8 as the age of the solution was not specified in either report.

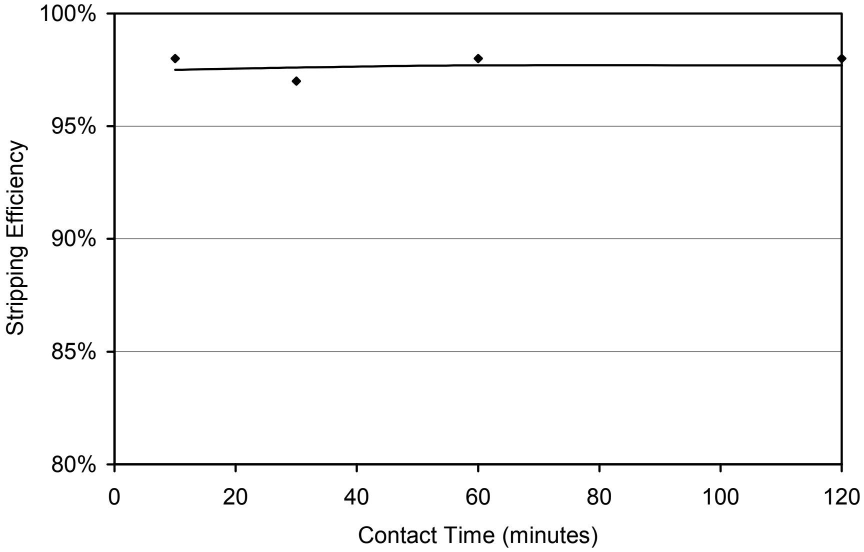


Figure 4-38. The effect of contact time on the stripping of freshly loaded chromium(III) from Cyanex® 272.

Strip solution: Hydrochloric acid, 2 mol L^{-1};

Organic phase: Cyanex® 272 in Shellsol® 2046 containing freshly loaded chromium(III) (1×10^{-2} mol L^{-1}).

4.10.2 Effect of Aqueous Phase Composition

The composition of the aqueous feed solution containing chromium(III) appeared to have an effect on the stripping efficiency as shown in Figure 4-39. The presence of sulphate (0.1 mol L^{-1}) in the feed solution appeared to depress the stripping efficiency when hydrochloric acid was used as the stripping agent.

It was previously noted (Chapter 4.4.3) that the presence of sulphate anions decreased the extraction of chromium(III) due to the formation of chromium(III) sulphate complexes. The formation of such complexes may also play a role in the decreased stripping efficiency.

At this time it was not possible to rule out a contribution to this observation due to analytical variations. The initial organic sample may contain extracted sulphate that depresses the analytical result. The stripped organic phase will present a different matrix for analysis as any sulphate will probably be removed by the stripping operation.

4.10.3 Effect of Acid Type and Concentration on Stripping Efficiency

The effect of the acid type, hydrochloric, sulphuric or nitric, on stripping efficiency is shown in Table 4-7. There was little difference in the stripping efficiency between the acids used. The stripping of chromium(III) from Cyanex® 272 has only previously been reported with hydrochloric acid. The present work suggested that any mineral acid may be used with similar results on a freshly loaded organic phase.

The data in Table 4-7 also shows that the choice of acid concentration in the range 1–4 mol L^{-1} has little impact on the stripping efficiency. However if incorrect contact conditions were used, then the use of 4 mol L^{-1} acid produced greater entrainment during stripping. So even though the chemical behaviour of

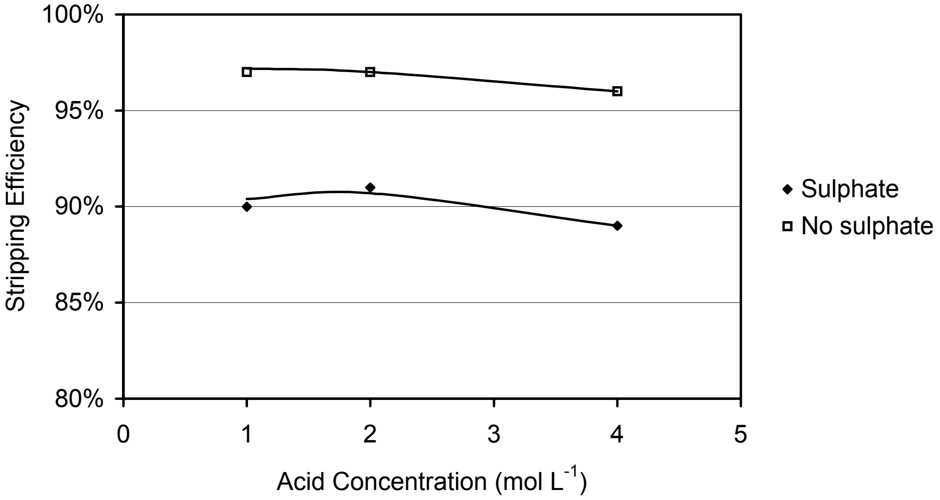


Figure 4-39. The effect of sulphate in the aqueous phase during loading of the organic phase on the stripping of chromium(III) from Cyanex® 272.

Strip solution: Hydrochloric acid;

Organic phase: Cyanex® 272 0.32 mol L^{-1} in Shellsol® 2046 containing 1×10^{-2} mol L^{-1} chromium(III), fresh.

Table 4-7. The effect of acid type and concentration on stripping of chromium(III) (1×10^{-2} mol L^{-1}, fresh) from Cyanex® 272 (0.32 mol L^{-1}) in Shellsol® 2046.

Strip Solution		Stripping Efficiency (%)
HCl	1 mol L^{-1}	96
HCl	4 mol L^{-1}	96
H_2SO_4	1 mol L^{-1}	98
H_2SO_4	4 mol L^{-1}	98
HNO_3	1 mol L^{-1}	98
HNO_3	4 mol L^{-1}	99

different acids may be similar, the use of a lower strength acid may have lower associated risk as the physical behaviour of the system was more stable.

4.10.4 Effect on Stripping Efficiency of Loaded Organic Aging

The change in the loaded organic species as the organic phase ages, described in Chapter 4.6, also affects the stripping efficiency. If an organic phase loaded with chromium(III) was permitted to stand until the changes occurred, stripping became low and was not reproducible. The use of hydrochloric or sulphuric acid up to 8 mol L^{-1} did not strip loaded chromium(III) after the organic phase had been allowed to age. The same effect would be expected if the loaded organic phase was heated as the same change in UV-Visible spectrum was observed. The study of Aggett and Udy (1970) on the extraction of chromium(III) with tributyl phosphate (TBP) as the extractant reported that a loaded organic phase heated for 4 hours on a steam bath was inert to stripping.

The difference in stripping behaviour between fresh and aged Cyanex® 272 solutions containing chromium(III) has not been reported previously. This observation may explain some of the conflicting reports in the literature as the age of the organic phase is not specified. The same observations with respect to changes in the organic phase as it aged were made with either Cyanex® 272 or D2EHPA as the extractant. Thus the application of the present study may also apply to stripping of chromium(III) from D2EHPA.

The suggested changes on the loaded organic phase as it ages (Chapter 4.6) may all produce a species that is more difficult to strip than the extracted species. This is especially true of a tightly bound (bi-dentate) or polymeric structure. The change in stripping efficiency as the loaded organic phase ages suggests that stripping of chromium(III) is only possible while the chromium(III) retains the inner coordination sphere of the extracted species. Once components of the organic phase have entered the inner coordination sphere of the metal stripping is no longer possible.

4.10.5 Use of Alternative Stripping Solutions

The present work found that chromium(VI) is not extracted by Cyanex® 272 at pH values greater than 2 (Chapter 4.9.1). It was thought therefore that oxidising the chromium(III) to chromium(VI) would strip the chromium from the organic phase and this was attempted.

A standard method for oxidising chromium(III) to chromium(VI) is the use of ammonium persulphate (Vogel 1962). The use of a strip solution containing this reagent failed to remove any chromium(III) from the organic phase.

The number of oxidants to choose from for the oxidation of chromium(III) is limited by the required oxidising strength. The search for a suitable oxidant of chromium(III) to chromium(VI) was discontinued due to the lack of appropriate literature to serve as a starting point and also the risk of oxidative degradation of the organic phase.

The risk of organic oxidation is especially pertinent, as the oxidative power of chromium(VI) is the primary industrial concern about the presence of this metal in the aqueous phase. Addition of another strong oxidant that will oxidise chromium(III) to chromium(VI) therefore introduces a further risk to the organic phase and hence the attempt to oxidatively strip chromium(III) was abandoned.

CHAPTER 5. SUMMARY AND CONCLUSIONS

A significant portion of the world's known nickel reserves occur in laterite deposits. The majority of these deposits may only be economically utilised using hydrometallurgical processing with the focus currently on pressure acid leaching due to the higher achievable metal recoveries. However the relatively recent commercialisation of this technology means that the downstream processing has had little opportunity for development. The outcome of this is the high incidence of previously unconsidered interactions between metals found in this type of deposit and downstream processes. This is of particular significance in the direct solvent extraction (DSX) approach where nickel and cobalt are separated from the leach solution without intermediate precipitation and re-leach stages. The use of DSX poses some downstream risk as, even with metals that are inherent in nickel laterite deposits such as chromium, little work has been reported.

The interaction of chromium and Cyanex® 272, the predominant extractant for nickel–cobalt separation in acidic solutions, has only been rarely mentioned in the literature with seemingly conflicting results. The solvent extraction of chromium(III) with Cyanex® 272 has been reported from a synthetic industrial solution but no other studies confirm this result. Further this study did not provide data which could be logically compared with the solvent extraction behaviour of other metals.

The literature on the solvent extraction behaviour of chromium with extractants other than Cyanex® 272, especially other acidic organophosphorus extractants, was also reviewed in order to gain a general understanding of chromium solvent extraction behaviour. For various reasons however, the information obtained could rarely be applied to the system being investigated.

The present work investigated the solvent extraction of chromium with Cyanex® 272. The oxidation state of the metal was found to have the greatest influence on the extraction behaviour. They behave so differently that, for clarity, chromium(III) and chromium(VI) need to be discussed separately. For the extraction of chromium(III) with Cyanex® 272 it has been observed that:

- the apparent equilibration time was slower (2–5 minutes) than most first-row transition metals. The pH at which the equilibration time is determined may affect the reported time owing to the change in chromium(III) species associated with change in the extraction pH.
- the rate of stirring affects the extraction so that good control is necessary to generate data that would be meaningfully compared. This parameter is only comparable with identical experimental arrangements and so little is gained by comparison with other studies.
- an increase in the extraction temperature from 22 to 50 °C had negligible effect on the extraction efficiency.
- a lower initial concentration of chromium(III) produced slightly better extraction at a fixed pH.
- extraction from simple solutions occurred in the pH range 3-7. This was the first report of chromium(III) extraction from simple solutions with Cyanex® 272.
- complete extraction could be achieved from all dilute solutions (ionic strength less than 1 mol L^{-1}).
- the $pH_{0.5}$ increased in the order nitrate < chloride < sulphate when these anions were present in solution. Solutions containing a mixture of anions including sulphate show similar behaviour to solutions containing only sulphate.

- the extraction of chromium(III) from concentrated solutions, in this instance an industrial PLS, was ineffective due to precipitation of the metal at lower pH than that required for extraction.

- the presence of acetate anion in the aqueous solution inhibits extraction of chromium(III), particularly if the aqueous solution was allowed to stand prior to extraction.

- chromium(III) could be completely extracted from the aqueous phase with either Cyanex® 272 or D2EHPA as the extractant but no extraction was observed when Cyanex® 301 was used as the extractant.

- the $pH_{0.5}$ decreases as the concentration of Cyanex® 272 in the organic phase increases.

- the choice of diluent, aliphatic or aromatic, has a small effect on the chemical behaviour but has a greater effect on the physical properties of the extraction system. An aliphatic diluent yielded slightly better chemical and physical behaviour.

- The UV-Visible spectrum of a freshly loaded organic phase is the same as the aqueous phase.

- The UV-Visible spectrum of an aged organic phase is significantly different to a freshly loaded organic phase.

Based upon these observations, conclusions on the behaviour of chromium(III) during extraction with Cyanex® 272 have been drawn and are summarised as follows.

- The pH at which equilibration times are determined may affect the equilibration time due to a change in the hydrolysis of the chromium(III) species with pH and the different kinetic behaviour of the different species.

- Chromium(III) forms sulphate and acetate species and the formation of these species reduces the extraction of the metal at a given pH.
- The extracted species formed during extraction of chromium(III) with Cyanex® 272 can be represented by the general formula:
  $[Cr(OH)_x(H_2O)_{6-x}]^{(3-x)+}[(HA_2)^-]_{(3-x)}\ldots[(HA)_2]_y$
  where x = 0, 1 or 2 and y = 0 or 1 and $(HA)_2$ is a Cyanex® 272 dimer.
- The extracted species undergo further reaction in the organic phase yielding a much more stable species that could not be easily stripped. This is probably due to the expulsion of water from the inner coordination sphere of the metal and its replacement by components of the organic phase, most likely the extractant.

The behaviour of chromium(VI) is significantly different to that of chromium(III). For the extraction of chromium(VI) with Cyanex® 272 it was found that:

- the extraction efficiency is independent of the anions (sulphate or chloride) in the aqueous phase.

- the speciation of the metal in the aqueous phase has the greatest influence on the extraction efficiency and is governed by the pH of the solution. Extraction occurs in the pH range 0.7 to 2.

- within the pH range (3–6) used for nickel–cobalt separation chromium(VI) is not extracted from the aqueous phase irrespective of the temperature up to 40 °C. This was observed in both pure and industrial liquor. The presence of an anti-oxidant in the organic phase has, similarly, no effect.

- The UV-Visible spectrum of a loaded organic phase changes as the organic phase ages.

These observations indicate that:

- chromium(VI) is extracted by solvation of chromic acid, H_2CrO_4.
- if a loaded organic phase is allowed to age then the chromium(VI) is reduced to chromium(III) and a component of the organic phase is oxidised.
- No significant oxidation of the organic phase was observed within the pH range (3–6) used for the separation of nickel and cobalt.

As chromium(VI) was not extracted within the pH range of nickel–cobalt separation only the stripping of chromium(III) from Cyanex® 272 was investigated. The present work observed that:

- the composition of the aqueous phase used to load the organic for stripping experiments and the contact method of the stripping experiments significantly affected the stripping efficiency.
- complete stripping with 1–4 mol L^{-1} mineral acids was obtained up to 10 minutes after extraction.
- the age of the loaded organic phase affects stripping due to the change in the nature of the metal bonding. Once the aged chromium(III) species was formed it could not be removed from the organic phase.

In general the behaviour of chromium(III) in these solutions was found consistent with it being a first-row transition metal. Although a range of chromium(III) hydroxy species extract within the pH range useful for nickel–cobalt separation, the extracted species can be approximated as $Cr(OH)^{2+}$ under the general conditions of the present work.

The observed behaviour indicates that control of chromium during industrial processing could be achieved by controlling the oxidation potential and pH of the solution. Such control is essential as it has been demonstrated that chromium(III) is an extractable metal and that stable chromium(III) species in the organic phase cannot be stripped. The inability to strip chromium that was loaded in either oxidation state will lead to poisoning of the organic phase if chromium, especially chromium(III), levels are not controlled in the solvent extraction feed material. With proper control of oxidation potential and pH, the presence of chromium in an exploitable nickel laterite resource should not hinder processing of the deposit. Chromium(VI) does not extract with Cyanex® 272 within the pH range used in the separation of nickel–cobalt.

CHAPTER 6. RECOMMENDATIONS

The results and observations of the present work have contributed significantly to understanding of the solvent extraction behaviour of chromium with Cyanex® 272. Like any research work, however, these results and observations have led to further questions that are outside the scope of the present work and are recommended for further study.

- Determination of the exact nature of the extracted and stable species during solvent extraction by direct measurement.
- Explore the use of acetate for inhibiting chromium(III) extraction in industrial operation.
- Determine the contribution of chromium(III) precipitation to crud formation and increased phase separation times in industrial processing liquors.
- Determination of the exact component of the commercially supplied extractant that is active during extraction of chromium(VI).
- Assess the risk of chromium(VI) induced oxidation of the organic phase during continuous operation especially if entrained chromium(VI) is carried through to the stripping circuit where more acidic conditions exist.
- Explore the oxidation of chromium(III) to chromium(VI) in the organic phase as a means of stripping the stable chromium(III) species from the organic phase. This approach needs to be balanced against the risk of damage to the organic phase.

- Attempt the stripping of chromium(III) from the organic phase using a concentrated solution of a better extracted metal e.g. cobalt, which has known stripping behaviour.

- Assess the use of acetic acid as a stripping agent for the stable organic species.

CHAPTER 7. REFERENCES

Aggett, J. & Udy, D. J. 1970, 'Solvent extraction of chromium(III) from aqueous perchloric acid solutions by tributyl phosphate', *Journal of Inorganic and Nuclear Chemistry,* vol. 32, pp. 2802-05.

Alamine® 336 2000, Available: [http://www.cognis-us.com/cognis/mining/et/prodinfo/BlueLineAlamine336.pdf] (9 April 2002).

Apostoluk, W. & Bartecki, A. 1985, 'Extraction of chromium(III) from sodium chloride solutions by means of carboxylic acids', *Hydrometallurgy,* vol. 15, pp. 191-202.

Baes, C. F., Jr & Mesmer, R. E. 1976, *The Hydrolysis of Cations*, John Wiley & Sons, New York.

Beneitez, P. & Ayllon, S. 1987, 'Extraction studies in the system between bis(2-ethylhexyl) phosphoric acid and chromium(III) in several aqueous solutions', *Solvent Extraction and Ion Exchange,* vol. 5, no. 4, pp. 597-609.

Bhaskara Sarma, P. V. R. & Nathsama, K. C. 1996, 'Extraction of nickel from ammoniacal solutions using LIX 87QN', *Hydrometallurgy,* vol. 42, pp. 83-91.

Block, B. P., Roth, E. S., Schaumann, C. W. & Ocone, L. R. 1962, 'Inorganic coordination polymers. III. Substitution-addition leading to dimer formation', *Inorganic Chemistry,* vol. 1, no. 4, pp. 860-63.

Bolt, A., Tels, M. & Van Gemert, W. J. T. 1984, 'Recovery of pure metal salts from mixed heavy metals hydroxides sludges', in *Fourth International Recycling Congress*, ed. Thome-Kozmiensky, K. J., EF-Verlag fur Energie und Umwelttechnik, Berlin, pp. 1025-31.

Bretherick, L. (ed.) 1986, *Hazards in the Chemical Laboratory,* 4th edn, The Royal Society of Chemistry, London.

Brooks, C. S. 1987, 'Applications of solvent extraction in treatment of metal finishing wastes', *Metal Finishing,* vol. 85, no. 3, pp. 55-60.

Brooks, C. S. 1993, 'Recovery of nonferrous metals from metal finishing industry wastes', *Separation Science and Technology,* vol. 28, no. 1-3, pp. 579-93.

Brooks, P. T., Potter, G. M. & Martin, D. A. 1970, 'Processing of superalloy scrap', *Journal of Metals,* vol. 22, no. 11, pp. 25-9.

Burger, P. A. 1996a, 'The Bulong, Western Australia, Ni/Co laterite deposits-a case history', in *Nickel '96 Mineral to Market*, eds. Grimsey, E. J. & Neuss, I., The Australasian Institute of Mining and Metallurgy, Melbourne, pp. 37-41.

Burger, P. A. 1996b, 'Origins and characteristics of lateritic nickel deposits', in *Nickel '96 Mineral to Market*, eds. Grimsey, E. J. & Neuss, I., The Australasian Institute of Mining and Metallurgy, Melbourne, pp. 179-83.

Carstens, P. A. B., Du Preez, J. G. H., Van Vuuren, C. P. J. & Bartlett, H. 1981, 'Some aspects of the solvent extraction of iron(II) and iron(III) from an aqueous acidic medium containing chromium(III)', *Journal of Inorganic and Nuclear Chemistry,* vol. 43, no. 9, pp. 2105-8.

Chalkley, M. E. & Toirac, I. L. 1997, 'The acid pressure leach process for nickel and cobalt laterite. Part I: Review of operations at Moa', in *Nickel-Cobalt '97*, vol. 1, eds. Cooper, W. C. & Mihaylov, I., Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, pp. 341-53.

Cheng, C. Y., Hughes, C. A., Barnard, K. R. & Larcombe, K. 2000, 'Manganese in copper solvent extraction and electrowinning', *Hydrometallurgy,* vol. 58, pp. 135-50.

Chilukuri, R., Yang, Z.-F. & Sirkar, K. K. 1998, 'Batch extraction studies of cationic and anionic heavy metallic species by a mixed solvent extraction system', *Separation Science and Technology,* vol. 33, no. 16, pp. 2559-78.

Coleman, C. F., Brown, K. V., Moore, J. G. & Allen, K. A. 1958, 'Amine salts as solvent extraction reagents for uranium and other metals', in *Proceedings of the 2nd International Conference on Peaceful Uses of Atomic Energy*, United Nations, Geneva, pp. 278-88.

Cotton, F. A. & Wilkinson, G. 1988, *Advanced Inorganic Chemistry,* 5th edn, John Wiley & Sons, New York.

Crabtree, H. E. & Rice, N. M. 1974, 'A spectrophotometric study of the organic complexes formed in the extraction of cobalt(II) with carboxylic acids', in *Proceedings of the International Solvent Extraction Conference (ISEC '74)*, vol. 1, ed. Jeffreys, G. V., Society of Chemical Industry, London, pp. 791-822.

Cuer, J. P., Stuckens, W. & Texier, N. 1974, 'Techniques of solvent extraction applied to the treatment of industrial effluents', in *Proceedings of the International Solvent Extraction Conference (ISEC '74)*, vol. 2, ed. Jeffreys, G. V., Society of Chemical Industry, London, pp. 1185-200.

Cyanex® 272 Extractant, Cytec Industries Inc.

Cyanex® Extractants, Cytec Industries Inc.

Das, G. K., Acharya, S., Anand, S. & Das, R. P. 1995, 'Acid pressure leaching of nickel-containing chromite overburden in the presence of additives', *Hydrometallurgy,* vol. 39, pp. 117-28.

Davis, M. L., Chang, M., Copedge, D. & Strong, M. 1988, 'Is there a role for liquid ion exchange in the recovery of chromium from plating wastewater?' in *42nd Purdue University Industrial Waste Conference Proceedings*, Purdue University, West Lafayette, USA, pp. 803-7.

Deltombe, E., de Zoubov, N. & Pourbaix, M. 1966, 'Chromium', in *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Pergamon Press, Oxford, pp. 256-71.

Deptula, C. 1968, 'Extraction of chromium(VI) from sulfuric acid solutions by means of tri-*n*-octylamine', *Journal of Inorganic and Nuclear Chemistry,* vol. 30, no. 5, pp. 1309-16.

Deptula, C. 1971, 'Synergic and antagonistic effects in the extraction of chromium(VI) with a mixture of tri-*n*-octylamine and alkylphosphoric acids from mineral acid solutions', in *Solvent Extraction, Proceedings of the International Solvent Extraction Conference (ISEC '71)*, vol. 1, ed. Gregory, J. G., Society of Chemical Industry, London, pp. 638-55.

Doyle-Garner, F. M. & Monhemius, A. J. 1985, 'Hydrolytic stripping of single and mixed metal-Versatic solutions', *Metallurgical Transactions B: Process Metallurgy,* vol. 16B, no. 4, pp. 671-7.

Duan, Q., Li, A. & Zhuang, S. 1998, 'Extraction of chromium by tri-*n*-octylamine in sulfuric acid solution', *Shanghai Youse Jinshu,* vol. 19, no. 2, pp. 81-86.

Fittock, J. 1997, 'QNI Limited cobalt refinery: Process development, installation and operation', in *Nickel-Cobalt '97*, vol. 1, eds. Cooper, W. C. & Mihaylov, I., Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, pp. 329-38.

Flett, D. S. & West, D. W. 1970, 'Solvent extraction of chromium(III) from sulfate solutions by a primary amine', *Transactions of AIME,* vol. 247, no. 4, pp. 288-91.

Florence, T. M. & Farrar, Y. J. 1969, 'Liquid-liquid extraction of manganese, chromium, and thorium by long-chain amines from concentrated halide media', *Australian Journal of Chemistry,* vol. 22, no. 2, pp. 473-6.

Freeman, H. M. (ed.) 1989, *Standard Handbook of Hazardous Waste Treatment and Disposal*, McGraw-Hill Book Company, New York.

Gandhi, M. N., Deorkar, N. V. & Khopkar, S. M. 1993, 'Solvent extraction separation of cobalt(II) from nickel and other metals with Cyanex 272', *Talanta,* vol. 40, no. 10, pp. 1535-39.

Gashgari, M. A., Al-Yobi, A. & Ejaz, M. 1990, 'Liquid-liquid phase distribution studies of chromium(VI) between mineral acid solutions and 5-(4-pyridyl)nonane *n*-oxide in benzene, and enrichment by extraction plant with pulsation column', *Separation Science and Technology,* vol. 25, no. 7, pp. 903-20.

Gillman, H. D. & Nannelli, P. 1977, 'Inorganic coordination polymers. XXI. Chromium(III) bis(phosphinate) polymers containing some organic anions', *Inorganica Chimica Acta,* vol. 23, no. 2, pp. 259-62.

Golightly, J. P. 1973, 'Nickeliferous laterites: A general description', in *International Symposium on Hydrometallurgy*, eds. Evans, D. J. I. & Shoemaker, R. S., The American Institute of Mining, Metallurgical, and Petroleum Engineers, pp. 3-23.

Golightly, J. P. 1981, 'Nickeliferous laterite deposits', in *Economic Geology 75th Anniversary Volume*, ed. Skinner, B. J., The Economic Geology Publishing Company, El Paso, pp. 710-35.

Gonzalez, L., Mo, O., Yanez, M. & Elguero, J. 1998, 'Very strong hydrogen bonds in neutral molecules: The phosphinic acid dimers', *Journal of Chemical Physics,* vol. 109, no. 7, pp. 2685-93.

Hellsten, K. 1999, 'Nickel: Reinventing the Australian industry', in *Outlook '99*, vol. 3, Australian Bureau of Agricultural and Resource Economics, Canberra, pp. 287-90.

Hellsten, K. J. & Lewis, C. R. 1996, 'Cawse nickel laterite deposit', in *ALTA Nickel/Cobalt Pressure Leaching and Hydrometallurgy Forum*, ALTA Metallurgical Services, Blackburn South, Australia.

Hepworth, M. T. & Beckstead, L. W. 1989, 'Chromium recovery from electroplating sludge', *Plating and Surface Finishing,* vol. 76, no. 11, pp. 50-2.

Horn, M. W., Fraser, B. G., Pritzker, M. D. & Legge, R. L. 1994, 'Chemistry of chromium(VI) solvent extraction using tri-*n*-octylamine', *Separation Science and Technology,* vol. 29, no. 4, pp. 535-42.

Hu, Z., Pan, Y. & Fu, X. 1995, 'Purification of organophosphorous acidic extractants', *Solvent Extraction and Ion Exchange,* vol. 13, no. 5, pp. 965-76.

Huang, T.-C., Huang, C.-C. & Chen, D.-H. 1997, 'Thermodynamic equilibria of the extraction of chromium(VI) with tri-*n*-octylphosphine oxide from aqueous solutions', *Solvent Extraction and Ion Exchange,* vol. 15, no. 5, pp. 837-62.

Huang, Y.-H., Chen, C.-Y. & Kuo, J.-F. 1992, 'Extraction equilibria of chromium(VI) from hydrochloric acid solutions with triisooctylamine in *o*-xylene', *Hydrometallurgy,* vol. 28, pp. 297-307.

Hughes, C. 1998, *Annual Report 1997/98*, The A J Parker Cooperative Research Centre for Hydrometallurgy, Solvent Extraction Project.

Hughes, C. 2000, *Annual Report 1999/2000*, The A J Parker Cooperative Research Centre for Hydrometallurgy, The control of reagent losses and phase separation problems in solvent extraction.

Huheey, J. E. 1983, *Inorganic Chemistry: Principles of Structure and Reactivity,* 3rd edn, Harper & Row, New York.

Iqbal, M. & Ejaz, M. 1978, 'Selective solvent extraction of chromium(VI) using 2-hexylpyridine. Separation from uranium, thorium, fission products and first transition series elements', *Journal of Radioanalytical Chemistry,* vol. 42, no. 2, pp. 313-21.

Irving, H. M. N. H. & Al-Jarrah, R. H. 1975, 'Extraction of various metals as their anionic complexes with EDTA by solutions of Aliquat-336 chloride in 1,2-dichloroethane', *Analytica Chimica Acta,* vol. 74, no. 2, pp. 321-31.

Islam, F., Begum, D. A. & Mustafa, C. M. 1985, 'Solvent extraction of chromium(III) with di-*o*-tolylphosphoric acid-benzene-hexanol system', *Journal of Bangladesh Academy of Sciences,* vol. 9, no. 1, pp. 55-64.

Islam, F. & Biswas, R. K. 1979a, 'Kinetics of solvent extraction of metal ions with HEDHP. III. The kinetics and mechanism of solvent extraction of Cr(III) from acidic aqueous solutions with bis-(2-ethyl hexyl) phosphoric acid in benzene', *Canadian Journal of Chemistry,* vol. 57, no. 23, pp. 3011-16.

Islam, F. & Biswas, R. K. 1979b, 'The solvent extraction of chromium(III) with bis-(2-ethyl hexyl) phosphoric acid in benzene and other solvents', *Journal of Inorganic and Nuclear Chemistry,* vol. 41, pp. 229-33.

Islam, F. & Biswas, R. K. 1981b, 'Infrared spectra, magnetic moment, and molecular weight data of the complexes of Ti(IV), V(IV), Cr(III), Fe(III) and Mn(II) with bis(2-ethylhexyl) phosphoric acid', *Journal of Bangladesh Academy of Sciences,* vol. 5, no. 2, pp. 19-24.

Islam, F., Biswas, R. K. & Biswas, S. K. 1981, 'Solvent extraction of iron(III), vanadium(IV) and chromium(III) from acidic sulfate-acetate-phosphato media with bis-(2-ethylhexyl) phosphoric acid in kerosene', *Nuclear Science and Applications, Series B: Physical Sciences,* vol. 12-13, no. 6, pp. 35-40.

Jimenez Gomez, S., Lopez Valdivia, L. M., Gonzalez Iglesias, C. & Rico Selas, M. I. 1990, 'Separation and concentration processes of solutions of cobalt(II), nickel(II), chromium(III), iron(III), and manganese(II) by extraction with toluene-dissolved rosin', *Journal of Chemical Technology and Biotechnology,* vol. 49, no. 3, pp. 267-74.

John, K. S., Rao, T. P., Ramamohan, T. R. & Reddy, M. L. P. 1999, 'Solvent extraction of tetravalent titanium from acidic chloride solutions by 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester', *Hydrometallurgy,* vol. 53, pp. 245-53.

Kamitani, M., Shibata, J., Sano, M. & Nishimura, S. 1988, 'Effects of nonaqueous solvents on the extraction of metal ions with D2EHPA', *Nippon Kinzoku Gakkaishi, Journal of the Japan Institute of Metals,* vol. 52, no. 3, pp. 303-9.

Khwaja, A. R., Singh, R. & Tandon, S. N. 2000a, 'Mono(2-ethylhexyl) phosphoric acid as an extractant for Cr(III) and its application to industrial waste', *Separation Science and Technology,* vol. 35, no. 3, pp. 447-55.

Khwaja, A. R., Singh, R. & Tandon, S. N. 2000b, 'Recovery of Cr(III) from tannery spent chrome liquor for reuse', *Journal of Environmental Engineering,* vol. 126, no. 4, pp. 307-12.

Kiba, T., Imura, H. & Honjo, T. 1977, 'Extraction of metal ions from trichloroacetic acid solutions to polar solvents', *Chemistry Letters*, no. 7, pp. 805-8.

Kimura, K. 1960, 'Inorganic extraction studies on the system between bis(2-ethyl hexyl)-orthophosphoric acid and hydrochloric acid (I)', *Bulletin of the Chemical Society of Japan,* vol. 33, no. 8, pp. 1038-46.

Kopejtka, P. 2000, 'Bulong Plant Update', in *New Generation Nickel: Laterites in the Eastern Goldfields*, The Australasian Institute of Mining and Metallurgy/ Curtin University of Technology (WASM), Kalgoorlie, Western Australia.

Kyle, J. H. 1996, 'Pressure acid leaching of Australian nickel/cobalt laterites', in *Nickel '96 Mineral to Market*, The Australasian Institute of Mining and Metallurgy, Melbourne, pp. 245-49.

Kyle, J. H. & Furfaro, D. 1997, 'The Cawse nickel/cobalt laterite project metallurgical process development', in *Nickel-Cobalt '97*, vol. 1, eds. Cooper, W. C. & Mihaylov, I., Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, pp. 379-89.

Laswick, J. A. & Plane, R. A. 1959, 'Hydrolytic polymerisation in boiled chromic solutions', *Journal of the American Chemical Society,* vol. 81, pp. 3564-67.

Magdics, A. & Stain, D. B., *Recovery of metals from electroplating wastewaters by extraction and recycling of metals and of extractants,* Europe EP 332447 A1, UNC Reclamation, Inc., USA, (patent).

Mahmoud, M. H. H. & Barakat, M. A. 2001, 'Utilization of spent copper-pickle liquor for recovery of metal values', *Renewable Energy,* vol. 23, pp. 651-62.

Maurer, A. 2001, 'Nickel: Outlook to 2005-06', in *Outlook 2001*, vol. 3, Australian Bureau of Agricultural and Resource Economics, Canberra, pp. 226-34.

McDonald, C. W. & Bajwa, R. S. 1977, 'Removal of toxic metal ions from metal-finishing wastewater by solvent extraction', *Separation Science,* vol. 12, no. 4, pp. 435-45.

Mihaylov, I. O., Krause, E., Laundry, S. W. & Luong, C. V., *Process for the extraction of nickel and/or cobalt,* USA 5,378,262, Inco Limited, (patent).

Motteram, G., Ryan, M., Berezowsky, R. & Raudsepp, R. 1996, 'Murrin Murrin nickel/cobalt project - project development overview', in *ALTA Nickel/Cobalt Pressure Leaching and Hydrometallurgy Forum,* ALTA Metallurgical Services, Blackburn South, Australia.

Motteram, G., Ryan, M. & Weizenbach, R. 1997, 'Application of the pressure acid leach process to Western Australian nickel/cobalt laterites', in *Nickel-Cobalt '97*, vol. 1, eds. Cooper, W. C. & Mihaylov, I., Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, pp. 391-407.

Murty, M. V. N., Rao, V. M. & Sastri, M. N. 1981, 'Extraction of chromium(VI) from aqueous orthophosphoric acid solutions by tri-*n*-octyl phosphine oxide', in *Nuclear Chemistry and Radiochemistry Symposium*, Indian Department of Atomic Energy, New Delhi, pp. 253-57.

Nahar, M. N., Islam, M. F., Begum, D. A. & Shamsul Islam, M. 1995, 'The solvent extraction of chromium(VI) from aqueous acidic sulphate media with bis-(2,4,4-trimethylpentyl) phosphinic acid (Cyanex-272)', *Journal of the Bangladesh Academy of Sciences,* vol. 19, no. 1, pp. 33-41.

Nannelli, P., Gillman, H. D. & Block, B. P. 1971, 'Inorganic coordination polymers. XI. A new family of chromium(III) bis(phosphinate) polymers, $[Cr(OH)(OPRR'O)_2]_x$', *Journal of Polymer Science, Part A: Polymer Chemistry,* vol. 9, pp. 3027-38.

Navarro Mendoza, R., Saucedo Medina, T. I., Vera, A., Avila Rodriguez, M. & Guibal, E. 2000, 'Study of the sorption of Cr(III) with XAD-2 resin impregnated with di-(2,4,4-trimethylpentyl) phosphinic acid (Cyanex® 272)', *Solvent Extraction and Ion Exchange,* vol. 18, no. 2, pp. 319-43.

Ohki, A., Fujino, Y., Ohmori, K. & Takagi, M. 1986, 'A possible use of photo-reaction in liquid-liquid extraction of substitution-inert metal complexes. Extraction of chromium(III) and cobalt(III) complexes', *Solvent Extraction and Ion Exchange,* vol. 4, no. 4, pp. 639-62.

Pandey, B. D., Cote, G. & Bauer, D. 1996, 'Extraction of chromium(III) from spent tanning baths', *Hydrometallurgy,* vol. 40, pp. 343-57.

Petura, J. C., James, B. R. & Vitale, R. J. 1999, 'Chromium(VI) in soils', in *The Wiley Encyclopedia of Environmental Pollution and Cleanup*, vol. 1, eds. Meyers, R. A. & Dittrick, D. K., John Wiley & Sons, New York, pp. 349-55.

Pradhan, N., Dash, U. N. & Das, S. C. 2001, 'Effect of chromium(VI) on electro-crystallisation of cobalt from sulphate solution', *Hydrometallurgy,* vol. 62, no. 1, pp. 1-10.

Preston, J. S. 1982, 'Solvent extraction of cobalt and nickel by organophosphorus acids. I. Comparison of phosphoric, phosphonic and phosphinic acid systems', *Hydrometallurgy,* vol. 9, pp. 115-33.

Preston, J. S. 1983, 'Solvent extraction of base metals by mixtures of organo-phosphoric acids and nonchelating oximes', *Hydrometallurgy,* vol. 10, no. 2, pp. 187-204.

Preston, J. S. 1985, 'Solvent extraction of metals by carboxylic acids', *Hydrometallurgy,* vol. 14, no. 2, pp. 171-88.

Preston, J. S. & Fleming, C. A. 1983, 'The recovery of nickel by solvent extraction from acidic sulphate solutions', in *Hydrometallurgy: Research, Development and Plant Practice. 3rd International Symposium on Hydrometallurgy*, eds. Osseo-Asare, K. & Miller, J. D., The Metallurgical Society of the American Institute of Mining, Metallurgical, and Petroleum Engineers, Warrendale, USA, pp. 475-89.

Price, M. J. & Reid, J. G. 1993, 'Separation and recovery of nickel and cobalt in ammoniacal systems-process development', in *Solvent Extraction in the Process Industries, Proceedings of ISEC '93*, vol. 1, eds. Logsdail, D. H. & Slater, M. J., Elsevier Applied Science, London, pp. 159-66.

Rao, V. M. & Hariharan, A. V. L. N. S. H. 1992, 'Solvent extraction of chromium(III) from aqueous mineral acid solutions by di-(2-ethylhexyl) phosphoric acid', *Oriental Journal of Chemistry,* vol. 8, no. 4, pp. 324-9.

Rao, V. M. & Hariharan, A. V. L. N. S. H. 1997, 'Solvent extraction of chromium(III) from aqueous mineral acid solutions by mono(2-ethylhexyl) phosphoric acid', *Ultra Scientist of Physical Sciences,* vol. 9, no. 2, pp. 245-50.

Rao, V. M. & Prasad, S. K. 1988, 'Some investigations on the solvent extraction of chromium(VI) by bis-(2,4,4-trimethylpentyl)-phosphinic acid (Cyanex 272)', in *International Solvent Extraction Conference (ISEC '88)*, vol. 1, USSR Acadamy of Sciences, Moscow, pp. 338-40.

Reid, J. G. 1996, 'Laterite ores - nickel and cobalt resources for the future', in *Nickel '96 Mineral to Market*, eds. Grimsey, E. J. & Neuss, I., The Australasian Institute of Mining and Metallurgy, Melbourne, pp. 11-16.

Rickelton, W. A., Flett, D. S. & West, D. W. 1984, 'Cobalt-nickel separation by solvent extraction with bis(2,4,4-trimethylpentyl) phosphinic acid', *Solvent Extraction and Ion Exchange,* vol. 2, no. 6, pp. 815-38.

Ritcey, G. M. & Ashbrook, A. W. 1979, *Solvent Extraction: Principles and Applications to Process Metallurgy, Part II*, Elsevier Science Publishers, Amsterdam.

Ritcey, G. M. & Ashbrook, A. W. 1984, *Solvent Extraction: Principles and Applications to Process Metallurgy, Part I*, Elsevier Science Publishers, Amsterdam.

Ritcey, G. M., Hayward, N. L. & Salinovich, T., *The recovery of nickel and cobalt from lateritic ores,* Australia 40890/96, Resolute Resources Limited, (patent).

Roorda, H. J. & Hermans, J. M. A. 1981, 'Energy constraints in the extraction of nickel from oxide ores (I)', *Erzmetall,* vol. 34, no. 2, pp. 82-88.

Saily, A., Khurana, U., Yadav, S. K. & Tandon, S. N. 1996, 'Thiophosphinic acids as selective extractants for molybdenum recovery from a low grade ore and spent catalysts', *Hydrometallurgy,* vol. 41, pp. 99-105.

Sato, T. & Ueda, M. 1974, 'The complexes formed in the divalent metals-hydrochloric acid - di-(2-ethylhexyl)-phosphoric acid extraction systems: Manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes', in *Proceedings of the International Solvent Extraction Conference (ISEC '74)*, vol. 1, ed. Jeffreys, G. V., Society of Chemical Industry, London, pp. 871-91.

Schügerl, K., Segelken, G. & Gudorf, M. 1996, 'Extractive recovery of chromium(III) from effluents of fur finishing industry', in *Value Adding Through Solvent Extraction, Proceedings of ISEC '96*, vol. 2, eds. Shallcross, D. C., Paimin, R. & Prvcic, L. M., University of Melbourne, Melbourne, pp. 1531-36.

Selmer-Olsen, A. R. 1966, 'Solvent extraction of chlorocomplexes by triisooctyl-amine/carbon tetrachloride from hydrochloric acid medium', *Acta Chemica Scandinavica,* vol. 20, no. 6, pp. 1621-5.

Shendrikar, A. & West, P. 1974, 'A study of adsorption characteristics of traces of chromium(III) and (VI) on selected surfaces', *Analytica Chimica Acta,* vol. 72, pp. 91-96.

Simons, C. S. 1988, 'The production of nickel: Extractive metallurgy - past, present, and future', in *Extractive Metallurgy of Nickel & Cobalt*, eds. Tyroler, G. P. & Landolt, C. A., The Metallurgical Society of the American Institute of Mining, Metallurgical, and Petroleum Engineers, Warrendale, USA, pp. 91-134.

Singh, R., Khwaja, A. R., Gupta, B. & Tandon, S. N. 1999, 'Extraction and separation of nickel(II) using bis(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex 301) and its recovery from spent catalyst and electroplating bath residue', *Solvent Extraction and Ion Exchange,* vol. 17, no. 2, pp. 367-90.

Smelov, V. S. & Lanin, V. P. 1969, 'Dissociation of di-2-ethylhexyl phosphoric acid in aqueous solution', *Radiaokhimiya,* vol. 11, no. 4, pp. 445-47.

Soldenhoff, K., Hayward, N. & Wilkins, D. 1998, 'Direct solvent extraction of cobalt and nickel from laterite-acid pressure leach liquors', in *EPD Congress 1998*, ed. Mishra, B., The Minerals, Metals and Materials Society, Warrendale, USA, pp. 153-65.

Sole, K. C. & Hiskey, J. B. 1992, 'Solvent extraction characteristics of thiosubstituted organophosphinic acid extractants', *Hydrometallurgy,* vol. 30, pp. 345-65.

Sole, K. C. & Hiskey, J. B. 1995, 'Solvent extraction of copper by Cyanex 272, Cyanex 302 and Cyanex 301', *Hydrometallurgy,* vol. 37, pp. 129-47.

Spiccia, L., Stoeckli-Evans, H., Marty, W. & Giovanoli, R. 1987, 'A new "active" chromium(III) hydroxide: $Cr_2(\mu\text{-}OH)_2(OH)_4(OH_2)_4.2H_2O$. Characterization and use in the preparation of salts of the $(H_2O)_4Cr(\mu\text{-}OH)_2Cr(OH_2)_4^{4+}$ ion. Crystal structure of $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(OH_2)_4][(H_3C)_3C_6H_2SO_3]_4.H_20$', *Inorganic Chemistry,* vol. 26, pp. 474-82.

Stobart, C. 2001, 'Outlook for nickel: Short term worries, long term hopes', in *Outlook 2001*, vol. 3, Australian Bureau of Agricultural and Resource Economics, Canberra, pp. 248-53.

Svehla, G. (ed.) 1996, *Vogel's Qualitative Inorganic Analysis,* 7th edn, Longman Group, Harlow, England.

Tokhadze, K. G., Denisov, G. S., Wierzejewska, M. & Drozd, M. 1997, 'First example of the ABC ν(OH) absorption structure for both gaseous and crystalline phase: infrared studies of dimethylphosphinic acid', *Journal of Molecular Structure,* vol. 404, no. 1-2, pp. 55-62.

Upton, D. 1999, 'Nickel: Crunch time for acid leaching', in *Outlook '99*, vol. 3, Australian Bureau of Agricultural and Resource Economics, Canberra, pp. 275-80.

Vogel, A. I. 1962, *A Text-Book of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis,* 3rd edn, Longmans, Green & Co, London.

Yadav, S. K., Singh, O. V. & Tandon, S. N. 1991, 'Mono-(2-ethylhexyl)phosphoric acid as an extractant for Mn(II), Co(II), Ni(II), Cr(III) and Fe(III)', *Indian Journal of Chemistry,* vol. 30A, no. 11, pp. 982-3.

Yakshin, V. V., Vilkova, O. M. & Makarova, L. T. 1998, 'Extraction of chromium(VI) with crown ethers from solutions of mineral acids', *Journal of Analytical Chemistry,* vol. 53, no. 5, pp. 409-11.

Zumer, M., Modic, R. & Zupan, J. 1974, 'Extraction of chromium(VI) by means of Aliquat 336 and Alamine 336', *Vestnik Slovenskega Kemijskega Drustva,* vol. 21, no. 3-4, pp. 105-15.

APPENDIX 1. DEFINITION OF ABBREVIATIONS USED

Abbreviation	Definition
$\overline{x}$	Overlining a chemical species indicates it is present in the organic phase.
A:O	Volume ratio of aqueous to organic phase
CCD	Counter current decantation
D	Distribution coefficient, $\frac{[\text{Metal}]_{\text{Organic}}}{[\text{Metal}]_{\text{Aqueous}}}$
D2EHPA	Di(2-ethylhexyl) phosphoric acid
DMF	*N*,*N*-dimethyl formamide, $H.CO.N(CH_3)_2$
DMSO	Dimethyl sulphoxide, CH_3SOCH_3
EDTA	Ethylene diamine tetra acetic acid, a common complexing agent in aqueous solution.
Extraction Efficiency (%)	$\frac{[\text{Metal}]_{\text{Feed}} - [\text{Metal}]_{\text{Raffinate}}}{[\text{Metal}]_{\text{Feed}}} \times 100$
M	mol L^{-1}
M2EHPA	Mono(2-ethylhexyl) phosphoric acid
PAL	Pressure acid leach
PC-88A®, EHEHPA	2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester
$pH_{0.5}$	The pH value at which equal metal concentration is found in the aqueous and organic phase. If the A:O ratio is 1 then this corresponds to 50% extraction.
PLS	Pregnant liquor stream
ppm	Parts per million defined as the approximation of mg L^{-1}
r.p.m.	Revolutions per minute
TBP	Tributyl phosphate
TIOA	Triisooctyl amine
TOA	Trioctyl amine
TOPO	Trioctyl phosphine oxide
Vol %	Relative volume of a component when mixing two or more liquids e.g. 10 vol % = 10 mL of component in 100 mL total volume.

APPENDIX 2. CONVERSIONS

Chromium Concentration

mol L^{-1}	mol L^{-1}	g L^{-1}	mg L^{-1}
3.85×10-5	4×10-5	0.002	2
1.00×10-4	1×10-4	0.005	5
1.92×10-4	2×10-4	0.010	10
9.62×10-4	1×10-3	0.050	50
4.81×10-3	5×10-3	0.250	250
9.62×10-3	1×10-2	0.500	500
0.019	2×10-2	1	1000
0.038	4×10-2	2	2000
0.072	7×10-2	4	4000

Cyanex® 272 Concentration

mol L^{-1}	g L^{-1}	vol %
5×10^{-3}	1.5	0.16
1×10^{-2}	2.9	0.32
5×10^{-2}	14.5	1.6
0.10	29.0	3.2
0.30	87.0	9.5
0.32	92.0	10.0
0.48	138	15.0
0.50	145	15.8
0.63	184	20.0
0.79	230	25.0
1.0	290	31.5

D2EHPA Concentration

mol L^{-1}	g L^{-1}	vol %
5×10^{-2}	16.1	1.7
0.10	32.2	3.3
0.30	97.00	10
0.60	193	20
0.75	242	25
1.0	322	33
1.5	484	50

Appendix 3: FORMATION CONSTANTS OF SOME CHROMIUM(III) SPECIES

Note: For copyright reasons Appendix 3 has not been reproduced.

Data can be found at: http://jess.murdoch.edu.au

(Co-ordinator, ADT Project (Retrospective), Curtin University of Technology, 1.5.03)