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"STUDIES INTO THE SEPARATION OF THE COMPONENT METALS OF CHROME RESIDUE"

A Thesis submitted
for the degree of
Doctor of Philosophy

by

Peter Andrew Clarke
B.Sc. [Dunelm]

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September, 1991

Peter A. Clarke

16 OCT 1992

DEDICATION

This thesis is dedicated to my parents for their continual love, support and encouragement.

ABSTRACT

Chrome residue, the disposal product of a chrome ore pyrometallurgical extraction process, contains a number of valuable metals in oxide form. The bulk extraction of the main metals in residue is investigated by acid dissolution, followed by solvent extraction techniques for the selective recovery of the metals from solution. Efforts have been focused on screening for Cr(III) extractants, and parameter optimization for maximizing extraction efficiency and selectivity of suitable extractants. The implications for a potential process are discussed.

This thesis presents laboratory results of studies to determine optimum dissolution and selective metal extraction conditions and reagents.

ABBREVIATIONS

DEHPA = Di–(2 ethyl, hexyl) phosphoric acid
OPAP = Octyl phenyl acid phosphate
DBBP = Di–butylbutyl phosphonate
DBPPA = Dibutyl pyrophosphoric acid
DMPA = Dimethyl pentanoic acid
EMBA = Ethyl methyl butanoic acid
PJMT = Primene JMT
TOA = Tri–n–octyl amine
MIBK = Methyl iso–butyl ketone
TBP = Tri–butyl phosphate
TPP = Tri–phenyl phosphate
TOPO = Tri–n–octyl phosphine oxide

Conc. = Concentration
Temp. = Temperature
pH_i = Initial pH
pH_f = Equilibrium pH
ppm = Parts per million = mgl^{-1}
g = Grammes
l = Litre
mg = Milligrammes
w = Weight
v = Volume
^{o}C = Degrees centigrade/celsius
PR = Phase Ratio = $\frac{\text{Volume of organic phase}}{\text{Volume of aqueous phase}}$ at time = 0
T = CT = Contact Time
[M] = Metal concentration
B.C.C. = British Chrome and Chemicals Limited
mins. = Minutes
Ker. = Kerosene
aq. = Aqueous
org. = Organic
extr. = Extraction

CONTENTS

CHAPTER ONE

AN INTRODUCTION TO CHROME ORE PROCESSING AND SOLVENT EXTRACTION

1.1 Introduction

Chrome residue, the disposal product of a chrome ore pyrometallurgical extraction process, contains a number of valuable metals in oxide form. It is the purpose of this thesis to investigate the separation of the component metals from chrome residue, with the aim of offering a number of separation processes for potential industrial exploitation. The products of the pyrometallurgical extraction of chromite ore are Cr(VI) chemicals. Also, current hydrometallurgical technology regarding chrome ore involves, in every case, the recovery of chromium in the +6 oxidation state. A particular objective of this thesis is to explore possibilities for extracting chromium in the +3 oxidation state.

Chapter 2 is concerned with techniques for the bulk extraction of the component metals from solid residue by acid digestion and chlorination techniques.

In Chapter 3 efforts have been focused on screening for Cr(III) extractants, and in Chapter 4 the optimization of experimental parameters for maximizing extraction efficiency and selectivity is discussed, for promising extractants. In Chapter 5, stripping and scrubbing characteristics have been examined regarding their viability in a schematic flowsheet. The implications for a potential process are discussed in Chapter 6.

The remainder of this chapter is devoted to the discussion of chromite ore and residue in terms of their nature and current processing technology. Hydrometallurgy is compared to pyrometallurgy, and hydrometallurgy is further discussed with a view to its application in the separation of the component metals of chrome residue and ore. Equilibria involved in extraction are discussed with reference to the different classes of extractants. Extractions of the component metals of chrome residue and ore from single metal systems are also discussed.

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1.2 Chrome Ore and Residue

1.2.1. Occurence and Chemical Processing of Chromite Ore

Chromite[1,2] (or chrome ore) is the sole source of chromium for the chrome chemicals and metal alloys industries. This spinel group mineral of composition $(Fe^{II},Mg^{II})O.\ (Cr^{III},Al^{III},Fe^{III})_2O_3$ exists with Cr(III) occupying octahedral sites and Fe(III) occupying tetrahedral sites. Commercial chromites are usually of the composition outlined in Table 1.1.

	Percentage Composition	
	Commercial Chromites	Chromite from the Bushveld Complex in South Africa
Cr_2O_3	28-56	48.9
Al_2O_3	10-32	10.5
Fe (Total)	12-26	14.1
MgO	9-18	14.6
SiO_2	-	4.3
CaO	-	0.3
MnO	-	0.3
TiO_2	-	0.2
V_2O_5	-	0.1

Table 1.1 Commercial Chromite Composition[3]

South Africa has the world's largest reserves of chromite (Table 1.2), with the Bushveld complex being a principal supplier to the British chrome and chemicals industry.

Country	Production (10^6 tonnes)	Estimated reserves (10^6 tonnes) (Cr_2O_3 30-50% values)
South Africa	3.012	2000
U.S.S.R. and other Eastern Bloc countries, and Albania	3.87	51.5
Zimbabwe	0.456	600
Turkey	0.608	10
Philippines	0.276	7.5
Finland	0.257	7.5
Others	1.0	24.4
Total	9.5	2701

Table 1.2 World Chromite Production (1984) and Estimated Resources[2,3]

Chromium chemicals have a wide range of applications, principally used as pigments, organic oxidants, dyes, for leather tanning, corrosion protection, electroplating and in magnetic information storage. Historically, the main user of chromite has been the metallurgical industry, where ferrochromium products are produced from pyrometallurgical smelting in an electric arc furnace.

Upgrading of the ores can be accomplished by beneficiation[4]. Initial physical beneficiation 'cleans' the ore of gangue and clays, the usual techniques being flotation, and magnetic or gravity separation. Liberation of the mineral by these processes is determined by grain size and the nature of the mineral complex.

Chemical beneficiation of iron rich ores can be achieved in a number of ways. Iron may be partially removed in the +3 state by acid leaching, or in the +2 state by selective iron reduction followed by leaching. Chlorination in the presence of reducing agents, and sulphatizing roasting can also improve the Cr:Fe ratio, removing iron as the gaseous chloride or soluble sulphate, respectively.

In the industrial process, ground chromite ore is roasted at high temperatures (~1100°C) in large rotary kilns with soda ash, in the presence of oxygen. A frit is produced containing sodium chromate which is extracted with water. The resultant solution is reacted with sulphuric acid to give a commercially pure solution of sodium dichromate. The solid residue is recycled to the kiln to be used as a filler before disposal in a landfill site.

For chromite deposits with a high silica content, this method of processing is unsatisfactory, as silica forms molten sticky reaction products with the sodium carbonate. An alternative for high silica chromite has been proposed by the U.S. Bureau of Mines[5], where chromite is reacted with molten NaOH under oxidizing conditions to form Na_2CrO_4, as in Equation 1.

$$\text{Ore}(FeCr_2O_4) \xrightarrow[550^{\circ} - 650^{\circ}C]{\text{Excess NaOH, Air}} Na_2CrO_4 \qquad (1)$$

The sodium chromate is solidified, crushed and leached with methanol in a countercurrent procedure. The methanol leach removes the majority of the excess NaOH while removing only a trace of the Na_2CrO_4. The residue is then water leached to recover the remainder of the NaOH, and the Na_2CrO_4 product. The solution is purified of Si and Al by sponging with CO_2 which reduces the pH and thus allows Al and Si compounds to precipitate. The carbonate ion formed during the CO_2 sponge is removed by adding lime to the solution to precipitate $CaCO_3$. The final Na_2CrO_4 product is recovered from the solution by evaporative crystallization. The mother liquor leaving the crystallizer is evaporated and the solids are recycled to the fusion reactor. Chromium extraction, on a pilot plant scale, ranges from 92.5–98.9%, compared to approximately 75% for the higher temperature process involving sodium carbonate.

The process of leaching can be categorized[6] by mechanism (chemical or microbiological e.g. bacterial oxidation of iron sulphides for improving uranium ore dissolution), methods (*insitu*, heap or dump, or percolation or vat), and reagents. The reagents may be (i) acids (usually H_2SO_4 or HCl, but sometimes HNO_3 or HF are used), (ii) bases (NH_4OH or NaOH), (iii) salts ($FeSO_4$, $FeCl_2$, Na_2CO_3, NaCl, NaCN, Na_2S), and (iv) gases (NH_3, SO_2, Cl_2 O_2).

In the following sections various methods for chromite ore extraction are reviewed. Many of the principles outlined in these systems have been used in the investigations described in subsequent chapters.

1.2.2. Chlorination of Chromite

Chlorination[7] and hydrochlorination[8] have been investigated for their application to chromium extraction from chromite. Chlorination of the oxides when in a mixed metal oxide lattice were found to be less efficient than for the pure oxides. For a synthetically prepared sample of $(MgO.FeO)(Al_2O_3.Cr_2O_3)$, under reducing conditions, the maximum chlorination efficiencies of the metal oxides are as shown in Table 1.3.

Metal Oxides	Boiling Point of chlorides (°C)	Percentage efficiency of chlorination
FeO	$FeCl_3$ 315	48.3
Cr_2O_3	1300	31.8
MgO	1412	30.1
Al_2O_3	177.8[a]	5.3

[a] Sublimation temperature.

Conditions : 1 hour, 600°C, Cl_2 flow rate of 3 l g^{-1} hr^{-1}

Table 1.3 Percentage Efficiency of Chlorination

Partial hydrochlorination[8] of chromite ore is possible at temperatures of approximately 1000°C, under a carbon reducing atmosphere. Iron and chromium are removed in the form of a mixed iron–chromium carbide, (90 – 100%, Fe; 6 – 23%, Cr) at 870 – 1060°C.

1.2.3. Chromite Leaching

It has been shown that acid leaching can be selective, e.g. the Falconbridge matte leach process (a matte is a sulphide mixture)[9a] selectively dissolves Ni from a Cu–Ni matte using strong hydrochloric acid. Due to the high corrosiveness of hydrochloric acid, special "acid proof" equipment typically must be used; rubber lined vessels may be employed but only at temperatures less than 70°C.

Chromite ore acid leaching has been studied by Pinto and Boas[4], Wylie[10], and Bruen and Wamser[11]. Pinto and Boas proposed oxidative preroasting of the ore for breakdown of the ferrous spinel.

$$FeO + FeO.Cr_2O_3 + \frac{1}{2}O_2 \xrightleftharpoons{900^{o}C,\ 1hr} Fe_2O_3.Cr_2O_3 \qquad (2)$$

$$2FeO.Fe_2O_3 + \frac{1}{2}O_2 \xrightleftharpoons{900^{o}C,\ 1hr} 3Fe_2O_3 \qquad (3)$$

This increases the porosity of the ore matrix allowing iron leaching by hydrochloric acid. In experiments at 70°C, up to 50% iron was removed. Leaching rates were found to be most significantly affected by temperature, followed by percentage of solids in the mixture, and acid concentration. This same conclusion (with leaching duration as another factor) was reached by Rosenbaum and Dannenberg[12] in studies of the sulphuric acid leaching of beryllium ores.

Preroasting of the ore was found to be beneficial, 6 hours digestion of original ore giving 39% dissolution, but preroasted ore under the same conditions giving 53% dissolution. 24 hours digestion led to 60% dissolution of the original ore and 76% dissolution of preroasted ore. Experimental conditions involved the following: Chromite ore [170g, >200 mesh] and chromic acid [50% $^{W}/w$, 1120g] at a reflux temperature of 110°C. Two hours roasting at 1000°C in air results in 90% conversion of the FeO to Fe_2O_3[11].

Wylie has studied the sulphuric acid dissolution of chromite[10] and concluded that the addition of an oxidant (e.g. CrO_3) was required for oxidative breakdown of the spinel.

$$6FeO + 2CrO_3 \rightleftharpoons Cr_2O_3 + 3Fe_2O_3 \qquad (4)$$

Reflux temperature was found to be important in chromite dissolution efficiency. 75% $^{W}/v$ was found to be the optimum acid concentration in these experiments; considerable amounts of insoluble sulphates separated out at higher acid concentrations. It was suggested that particle size and contact duration were also important factors. An experiment involving the treatment of ore [80g, 200 mesh], CrO_3 [9.8g] and H_2SO_4 [70% $^{W}/v$, 400ml], at 150°C, for 4 hours, filtration at 100°C, gave 92% extraction of chromium for a high grade ore [52% Cr_2O_3], and 89% extraction of chromium for a lower grade ore. At 168°C, using 75% $^{W}/v$ acid, these figures were increased to 96–98%, and 94% chromium extraction respectively.

For the determination of Cr in chromite samples, phosphoric acid solutions containing potassium permanganate have been used[9b]. Phosphoric acid (85%, 15ml), was used to dissolve 0.50g of chromite ore at of 250°–300°C.

1.2.4. Treatment of Chromite Ore Solution

Acid dissolution of chromite ore[10] has been shown to be a non–selective process. Selective metal recovery from solution can be achieved, however, using techniques such as crystallization, electrolysis, dialysis, solvent extraction, and ion exchange resins. Wylie[10] found the fractional crystallization of ore liquors to be non–practicable, due to the formation of a solid solution of chromium(III) in the iron complex.

However, electrolytic oxidation of ore liquor at 45°C yielded 95% conversion of Cr(III) to Cr(VI), giving a solution which may be fractionally crystallized. Initial bulk crystallization of iron and aluminium sulphates leaves a Cr(VI) rich solution. The solution is filtered and washings from the filter cake are added to the mother liquor which is subsequently crystallized yielding substantially uncontaminated CrO_3. (Product composition: CrO_3, 90% [85% yield], H_2O, 5%, H_2SO_4, 5% [removable].)

Oxidation of chromic acid solutions of chromite ore[11], have been studied by Bruen and Wamser. Electrochemical conversion of Cr(III) to Cr(VI) is preferred to chemical oxidation by persulphuric acid, as the former does not introduce foreign ions, e.g. HSO_4^-, into the solution. The resultant solution consists essentially of chromic acid and the cationic dichromates of iron, aluminium, and magnesium; these may be subjected to ion exchange techniques for chromium removal. (See section 1.5.)

1.2.5. <u>Chrome Residue</u>

Typical composition values[13] of residue are outlined in Table 1.4. The presence of highly toxic, water soluble Cr(VI) in residue makes safe disposal a problem. Alternative ideas for residue disposal usually involve an expensive detoxification step, using Fe(II), carbon or sulphur compounds, to reduce Cr(VI) to Cr(III). Ideas for usage of residue have ranged from roadstone to the manufacture of refractory bricks[14,15], and decorative facing materials[16]. Residue solution has also been considered for use as an aid to sewage flocculation[17].

Metal Oxide	Percentage Composition
Cr_2O_3	16.6
Na_2CrO_4	0.6
Al_2O_3	26.5
Fe_2O_3	40.4
MgO	13.8
SiO_2	0.9
V_2O_5	0.4
CaO	0.2
Total	99.4

Table 1.4 Residue Composition

In the event of unforeseen shortages of chromite ore, chrome residue would exist as a readily available source of low grade chromium ore.

Investigations by B.C.C. into metal extraction from residue have focused upon acid digestion. Sulphuric acid and hydrochloric acid digestion studies[17,18,19,20] indicated potential for such a process, but optimized conditions had not been established (see appendix 1). The problem of iron removal from solutions is usually addressed using either the precipitation of iron oxides or complex salts, or by using solvent extraction or ion exchange techniques. The recovery of the components of residue solutions has been investigated using;

(i) Electrolytic oxidation of Cr(III) to chromic acid followed by iron, aluminium, and magnesium precipitation[19].

(ii) Fractional crystallization, which gave unsatisfactory salt separation[18]. Contamination of fractions was due to adsorption, occlusion, and coprecipitation of salts.

Further analysis involved the appraisal of techniques suitable for the economical recovery of saleable products from residue[21]. Ion exchange and solvent extraction[22] have similar objectives in metal separation, extraction and purification. Selectivity in ion exchange resins is determined by metal valency, the hydrated ionic radius, and for special resins, pH control. Ion exchange resins exhibit problems with unfavourable kinetics, resin loss by elutriation, and poor selectivity. Their use is considered too expensive in relation to the value of the end–products. The investigation of solvent extraction techniques was deemed appropriate. If successful, the process should be more economical to operate than those previously considered, as fewer operations would be involved.

1.3 Hydrometallurgy and Pyrometallurgy

Hydrometallurgy[24,25] is defined as a combination of unit processes whereby metal or metal salts may be produced from primary sources (ores and concentrates) or secondary sources (scrap and waste materials), by means of chemical reactions involving aqueous solutions. Pyrometallurgy involves the high temperature roasting, smelting, converting and refining of metal ores and concentrates. Hydrometallurgy is kinetically controlled, whereas pyrometallurgy is thermodynamically controlled. Over the past thirty years the trend towards the use of hydrometallurgical processing has resulted in the considerable use of solvent extraction techniques[23]. Its success has been attributable to its ability to produce pure metal solutions. Industrial use of solvent extraction methods began in the 1950's with uranium in the nuclear reprocessing industry, and spread to the copper industry in the 1960's. The increase in energy and capital costs of pyrometallurgical processing, the cost of minimizing the environmental problems heightened by stricter legislation and the inability to recover economically metals for low grade ores, led to increased interest in hydrometallurgy as an economically acceptable alternative.

In response to these economic and environmental challenges, the pyrometallurgical industry developed process technology to reduce their capital costs and wastes, and improve their treatment of off gases (e.g. electrical smelting developments reduced off gas SO_2 volumes, resulting in reduced equipment requirements and treatment costs. The development of SO_2 scrub catalysts also offered improvements in SO_2 emissions).

Sulphide ore hydrometallurgical processes, being energy intensive, were deemed only applicable to the processing of lower grade ores which are not amenable to pyrometallurgical techniques. However, the mineralization of ore bodies will become more complex as sulphide ore grades decline. Mining, milling, and beneficiation processes in pyrometallurgy must reach a point where they become economically less attractive and therefore are eventually likely to be superseded by hydrometallurgy.

For non sulphide ores, i.e. oxides and silicates, energy costs have favoured hydrometallurgy. Some metals (e.g. Al, Au, Cd, Co and U) are only extractable by hydrometallurgical means, whilst other (e.g. Cu, Ni, Mo, V, W, Zn and the rare earths) have become more predominantly extracted by hydrometallurgical processes.

Research activity has made hydrometallurgical processes for metal recovery into technologically (if not always economically) feasible alternatives to pyrometallurgical processing. However, the gap between research activity, technology transfer, and final implementation has been criticized as limiting the potential for the advantages offered by solvent extraction techniques[26].

It is interesting to note that major commercial exploitation of solvent extraction processes[27] for metal recovery from secondary sources was initially in evidence in those countries with the most rigorously enforced pollution laws. Conservation of energy and capital resources, and environmental concerns will continue to have important influences on future developments in pyro– and hydro–metallurgical processing.

1.4 Solvent Extraction Technology

1.4.1. General Introduction

Solvent extraction[28,29] is a separation procedure for isolating and concentrating substances from aqueous solution, by means of an immiscible organic solvent. Metal extraction involves the formation of a stoichiometric metal–extractant compound, which has a high relative organic solubility. This process can be made selective for one metal over another, under suitable conditions. The aqueous feed solution is mixed with the solvent (extractant, diluent and if required a modifier) resulting in metal extraction. Undesired coextracted metal can be removed by scrubbing with water, or dilute acid or base. The loaded organic phase is mixed with an aqueous strip solution to cleave the metal–extractant species, providing an aqueous solution of the metal. On going from a dilute feed solution to the strip solution the concentration of the metal may be substantially increased.

An integrated solvent extraction scheme[27] (see Figure 1) might be expected to operate in a countercurrent manner. The 'closed loop' operation produces only the metal of interest, the leached residue and the final aqueous raffinate. The solvent and the strip reagent (usually an acid) are recycled, often the acid being diverted to the acid leaching process. In some systems the metal may be recovered as the hydroxide precipitate which may be a suitable form for recycling through the furance.

In physical solvent extraction processes, when an aqueous solution is mixed with an organic solution into which the solute is extracted, the solute will be distributed between the two phases such that the ratio of the activities (Partition constant, $P^o = a_B/a_A$) and the concentrations (Partition coefficient, $P^i = [i]_B/[i]_A$) are constants[26,30]. The value of the partition constant and coefficient depends on the nature of the solute, the solvents involved, and the temperature, and refers to only one chemical type of solute species. Other forms of the solute species are not included in the partition law. This is applicable only to physical processes of extraction where simple uncharged covalent molecules such as the halides of As(III) and Sb(III) are extracted into organic solvents such as carbon tetrachloride.

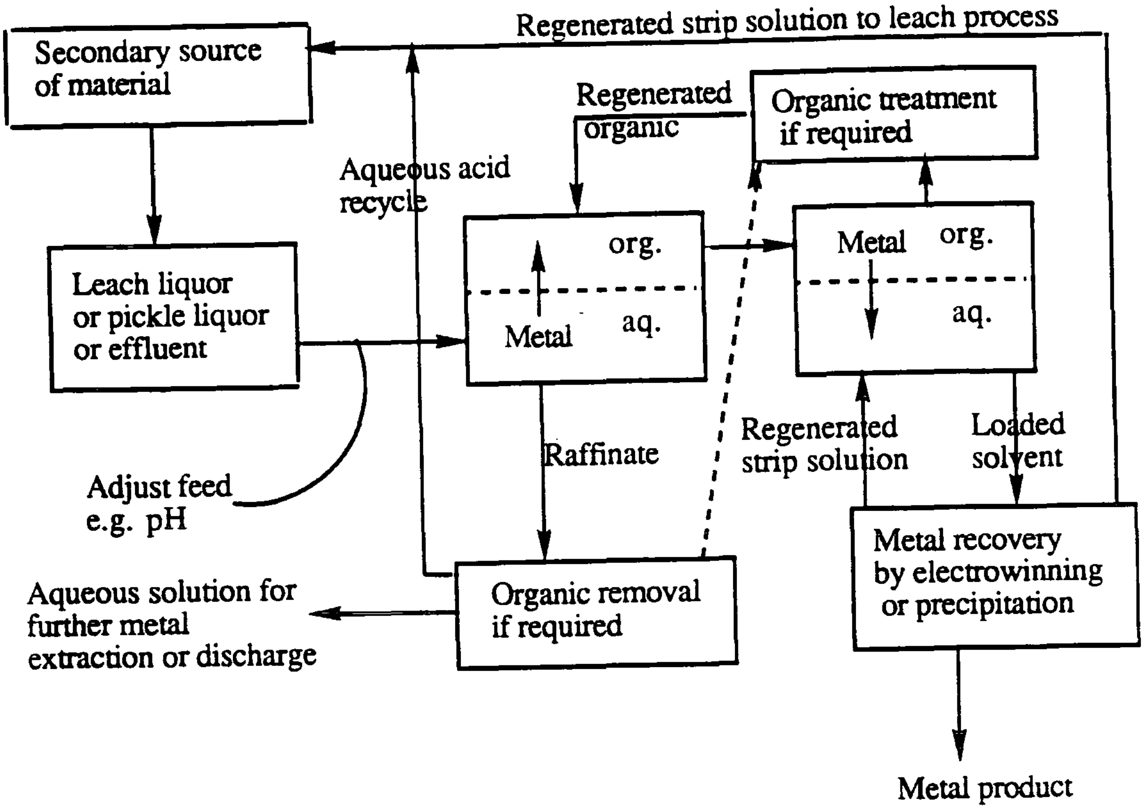


Figure 1.1

An integrated solvent extraction process for metal recovery from secondary sources

In hydrometallurgical systems, chemical interactions are usually in metal extraction, and the distribution law is more applicable. The distribution coefficient (D) in Equation 5;

$$D = \frac{\Sigma \ [M]_{org}}{\Sigma \ [M]_{aq}} \qquad (5)$$

is the ratio between the total metal concentration in the organic phase divided by the total metal concentration in the aqueous phase with the fraction of metal extracted into the organic phase being given by Equation 6.

$$\text{Fraction extracted} = \frac{D}{D + {}^{vaq}/_{vorg}} \qquad (6)$$

This recovery factor may also be expressed as a percentage.

A measure of the separation of two metals, under identical experimental conditions, is given by the separation factor (S.F.) as in Equation 7.

$$\text{S.F.} = \frac{M_1}{M_2} \qquad (7)$$

Metal ions exist as aquo–cations, e.g. $Al(H_2O)_6^{3+}$ in aqueous solution, the waters of hydration causing the complex to exhibit hydrophilic behaviour. For the metal to be soluble in the organic phase, it must change its character to become hydrophobic, which is effected by ligand substitution. In Appendix 2, the theory of metal solvent extraction (from dilute metal solutions) is discussed in greater depth. There are three fundamental types of metal extraction systems which involve[26,30];

(i) Stable complex formation

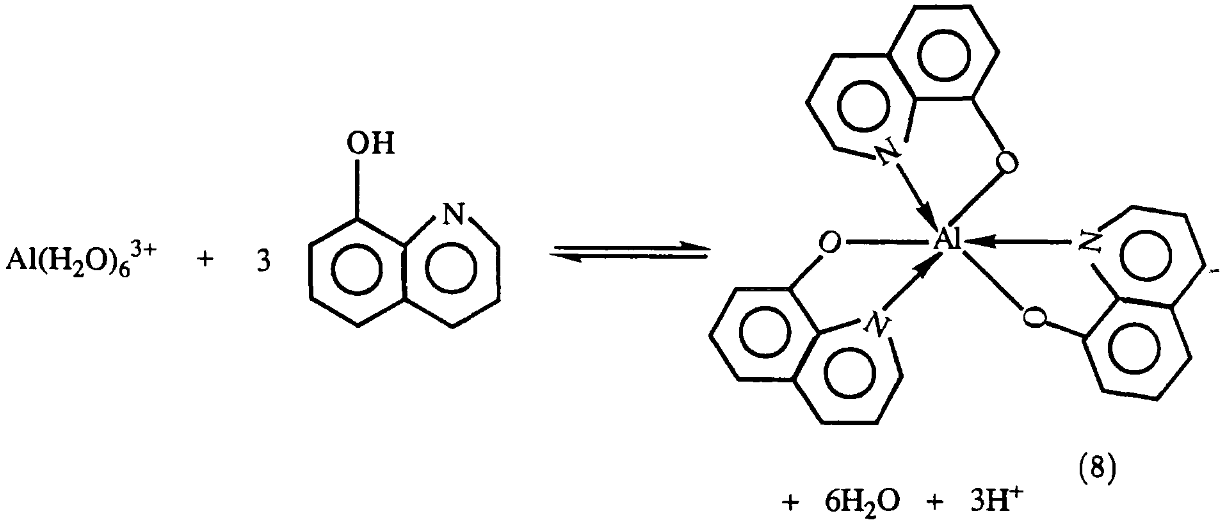
(ii) Ion association

(iii) Solvation

Some extractants, however belong to more than one class.

1.4.2. Chelating Extractants

These have at least two donor atoms in the molecule and thus give rise to ring formation. Five and six membered rings tend to be the most stable. An example of a hydroxyquinoline complex with aluminium is shown in Equation 8.



(8)

The resulting complex is soluble in the organic phase.

The general case may be represented as shown in Equation 9.

$$M^{n+}{}_{aq} + nHA_{org} \rightleftharpoons MA_{norg} + nH^{+}{}_{aq} \qquad (9)$$

where M = metal

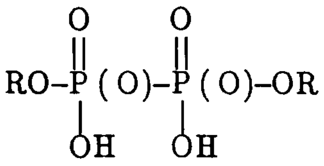
HA = extractant

Commercially available chelating extractant are basically of two types; the 2–hydroxybenzophenone oximes (LIX from Henkel, Acorga from ICI, SME from Shell), and the 8–hydroxyquinolines (Kelex and Sherex, and LIX 26 and 34 from Henkel). Also, available are the β diketones LIX 54 (Henkel) and Hostarex DK16 (Hoechst). The structural formulae for these are illustrated overleaf.

Most of these extractants were designed with the specific aim of selectively extracting copper from leach liquors. Some of the LIX and Kelex reagents are able to selectively remove copper from copper–ferric iron solutions, due to the slow kinetics of iron extraction. However, impurities in Kelex 100 from the starting materials (oximes) may lead to coextraction of the iron, since iron–oxime complexation is a rapid process.

Chelating phosphorus extractants offer potential[32], but commercial use has been limited.

e.g.



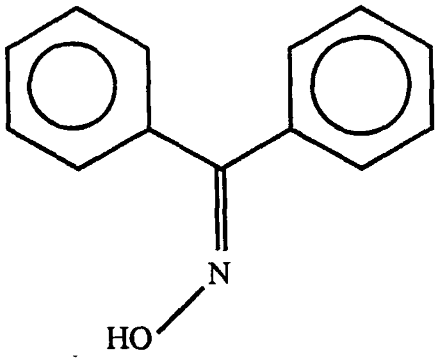
$$RO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}(O)-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}(O)-OR$$

Dialkyl pyrophosphoric acids,

e.g. R = ethyl hexyl, Bis–ethyl, hexyl pyrophosphoric acid, (BEHPPA)

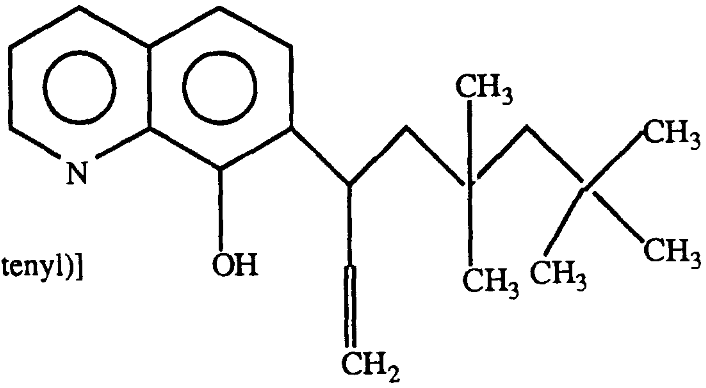
LIX 64

Substituted
o-hydroxybenzophenone



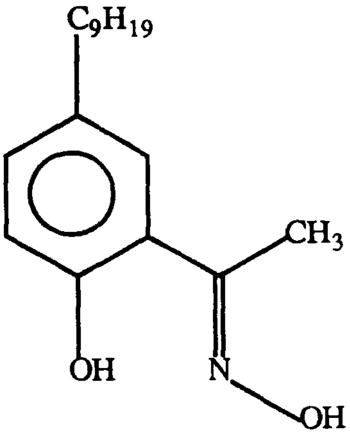
Kelex 100

7-[3-(5,5,7,7-tetramethyl-1-octenyl)]
-8-hydroxyquinoline

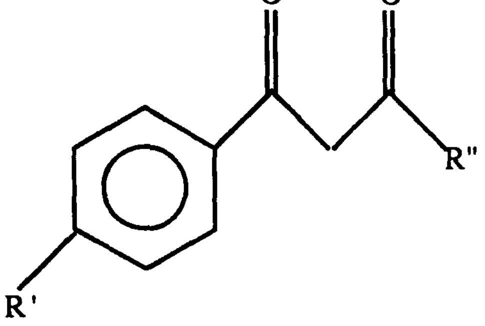


SME 529

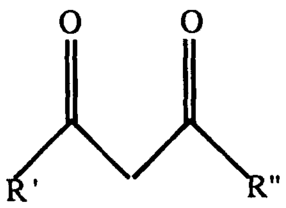
2-hydroxy-5-nonyl
acetophenone oxime



LIX 54



Hostarex DK 16

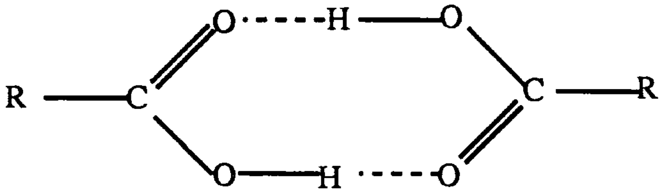


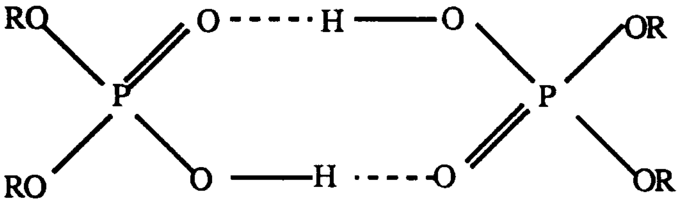
1.4.3. Acid Extractants

Extraction by acid extractants is similar to chelating extractants in that the basic extraction equilibrium is as expressed in Equation 9, though extraction is affected more by solvent phase properties than for chelating extractants, e.g. self association to form dimers and polymers by hydrogen bonding is common, though this does not occur at high metal loading. Acid extractants operate by a cation exchange mechanism, where the extractant proton is substituted by a metal. As well as the equilibria existing for chelating agents, additional equilibria are in existence in these systems, namely extractant dimerization and partition.

Dimers of a) carboxylic acids

b) organophosphoric acids





The qualitative considerations for chelating extractants still apply i.e. pH, extractant concentration, metal concentration, and the factors affecting the order of extraction. The main types of acid extractants are discussed below.

a) Phosphorus acids[32].

This group includes difunctional acids (I and II), the monofunctional acids (III, IV, and V), and the acid phosphates which are mixtures of the monoesters and diesters (I and III).

I	$RO-P(O)(OH)_2$	Phosphoric acid monoesters
II	$R-P(O)(OH)_2$	Alkyl phosphinic acids
III	$(RO)_2P(O)OH$	Diesters of phosphoric acid

IV R–P(O)(OR)OH Alkyl phosphonic acid monoesters

V $R_2P(O)OH$ Dialkyl phosphinic acids

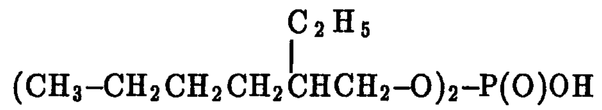
The acid phosphates and monofunctional acids have been used commercially[33]. With divalent metals, DEHPA acts as a bridging ligand in the organic phase forming polymeric complexes. Co(II) extraction by DEHPA is thermochromic[33].

$$Co(DEHP)_2(H_2O)_2 \xrightleftharpoons[\text{Cool}]{\text{Heat}} Co(DEHP)_2 + 2H_2O \qquad (10)$$

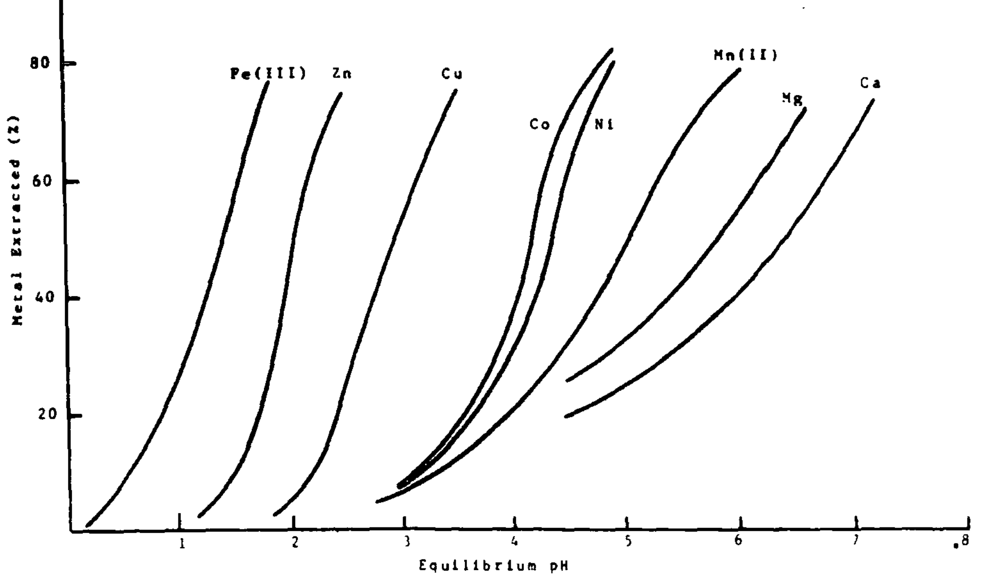
Pink , Octadedral Blue , Tetrahedral

DEHPA has been used in application with a broad range of metals and conditions, lending itself to the tag of '*universal extractant*'. Examples of its use include uranium extraction from phosphoric acid, in conjunction with either TOPO or DBBP, and uranium from uranium ore with TBP as a coextractant. Zinc separation from cobalt and nickel in ore leach solutions by DEHPA, has been used in Japan and Brazil. Other processes using DEHPA include the extraction of iron, beryllium, gallium, vanadium, molybdenum, and the rare earths.

DEHPA



$$(CH_3{-}CH_2CH_2CH_2\underset{}{\overset{C_2H_5}{\overset{|}{C}}}HCH_2{-}O)_2{-}P(O)OH$$



Extraction of some metals by DEHPA from sulphate solution[26].

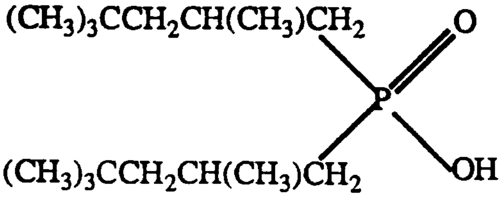
EHEHPA, a derivative of DEHPA, is used for the separation of cobalt from nickel, and some of the more difficult rare earth separations, as it is a very selective extractant. Also known as Ionquest 801[34], it extracts Cr(III) from sulphate solutions, though the distribution coefficients quoted are very poor[34b].

OPAP is another extractant which has found application in uranium extraction from phosphoric acid. However, problems with phase disengagement, the precipitation of ferric complexes, and difficulties in removing impurities from the extractant resulted in the discontinuation of these plants in Canada and the U.S.A. OPAP is still manufactured on a small scale in the U.S.A.

DBBP has properties intermediate between those of TBP and TOPO, and has been used in americium 241 recovery from plutonium solutions, and with DEHPA in uranium recovery. Interest in the use of DBBP for gold, silver, titanium, and zinc processes may result in more widespread use of DBBP.

Cyanex 272 has been used in cobalt extraction from both sulphate and chloride solutions.

Cyanex 272

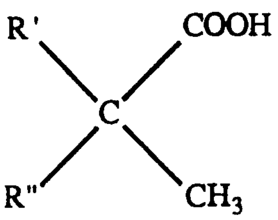


The pH required for >97% metal extraction by Cyanex 272, for Fe^{3+}, Al^{3+}, and Mg^{2+} were 2.3, 3.1, and 5.8 respectively.

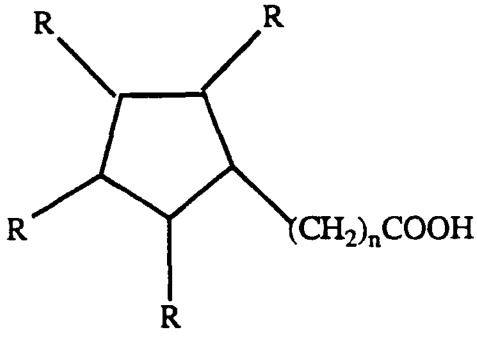
b) Carboxylic acids[26,35,36,37,38].

These are not as widely used as phosphorus acids. The most common carboxylic acids in use are the Versatic acids (Shell), and naphthenic acids which are produced as a distillation fraction of crude oil. Naphthenic acids have a molecular weight range of about 170–330, resulting in a significant variation in extraction character.

Versatic acids

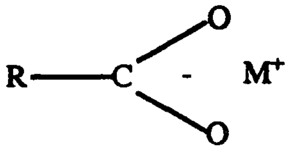


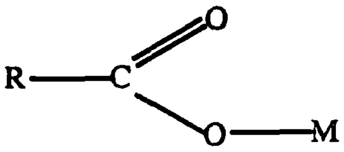
Naphthenic acids

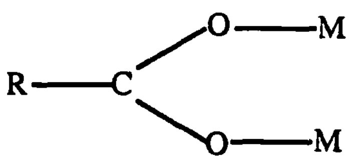


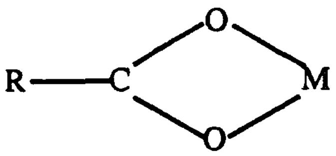
Versatic 10 consists of a mixture of highly branched C_{10} isomers, the greater branching than in linear acids offering improvement in thermal stability, chemical stability, and organic solubility of the extracted metal species.

Carboxylic acids exist in the organic phase as undissociated monomers or dimers, and in the aqueous phase as dissociated anions, dimeric anions, molecule–anion dimers, and undissociated acids, the equilibria of which is pH dependent. Carboxylate anions can bond to metals in any of the following ways;









Formation of carboxylic acid–metal species involving charge neutralization does not occur simultaneously with coordination saturation of the metal, as with chelating agents. To satisfy the coordination number of the metal ion, neutral ligands (such as carboxylic acid molecules) are added, or polymerized species are formed (by oxo–hydroxo bridging) where metal ions share edges or apices with one other. In non–polar diluents, the extracted species of carboxylic acid dimers are solvated by one or more carboxylic acid molecules. An interesting exception is the aluminium–decanoic acid species which exists in the hydrolysed form; $(AlR_2(OH)_6)$.

Polymerization increases with chain length due to a hydrophobic interaction arising from intertwining of the alkyl chain. In this way, metal coextraction can occur, and the scrubbing of metal impurities may not be possible. The stoichiometry of mixed metal complexes is dependent upon the aqueous solution composition. Diluent characteristics are important, an increase in polarity decreasing the extent of polymerization.

The reason for the relative unpopularity of carboxylic acids in solvent extraction flowsheets is attributable to their limited extraction power with respect to pH, aggregate formation, and problems with solvent loss. Also, the presence of water in the organic phase (hydrogen bonded to acid monomers and dimers) can cause complications. Therefore, much of their study has been limited to analytical scale investigations. These studies indicate that extraction is influenced by the alkyl chain length of the acid. On an analytical scale, the C_7–C_9 acids have been shown to extract the component metals of chromite residue with the following order of efficiency: iron(III) > chromium(III) > aluminium(III) > magnesium, while naphthenic acid gives iron(III) > aluminium(III) > chromium(III) > magnesium. Naphthenic acid has also been reported to extract Fe(II), Ni, Ca, Cu, Zn, Mn, Th, Ga, In, U, Co and the rare earths. 2–bromodecanoic acid, being halo–substituted, is more acid than analagous non halo–substituted acids. This allows metal extraction at lower pH's, as exemplified in Table 1.5.

However, problems with emulsification of the 2–bromodecanoic acid system restricts its practical use to elevated temperatures. Salicylic acids have also been investigated for their extractive properties, which include UO^{2+} and $Th(IV)^-$ extractions.

	$pH_{1/2}$			
Carboxylic acid	Iron(III)	Chromium(III)	Magnesium(II)	Aluminium(III)
Versatic 10	1.8	-	8.1	3.5
Naphthenic acid	1.8	-	7.4	3.4
2-bromodecanoic acid	1.2	2.6	5.4	2.7
3,5-diisopropyl salicylic acid	1.2	2.6	6.2	2.7

Metals [0.05M] extracted by carboxylic acids [0.50M] in xylene at 20^{0}C.

Table 1.5 Carboxylic Acid Extraction Data

Preston[37] has found that the practical application of iron(III), aluminium, and chromium(III) extractions from sulphate solutions by carboxylic acids is limited due to their slow extraction rates. Carboxylic acids, although cheap and readily available, have found limited commercial application. Processes for yttrium extraction (U.K.), and cobalt/nickel separation (USSR), were in operation in the 1970's.

Sulphonic and alkyl sulphuric acids have not been used as extractants in commerical solvent extraction processes, since like carboxylic acids, they tend to have a high solubility in the aqueous phase and aggregate in the organic phase.

1.4.4. Ion Association Complexes

Ion association systems are necessarily of high ionic strength, and are therefore not subject to quantitative mathematical analysis. Traditionally their study has been purely empirical. Long chain aliphatic primary, secondary, and tertiary amines are often used as ion association extractants.

Amine cations are formed with an acid as part of an ion association complex, and are soluble in the organic phase.

$$R_3N_{org} + HA_{aq} \rightleftharpoons R_3NH^+ A^-_{org} \qquad (11)$$

$$(A = HSO_4^-, Cl^-)$$

The amine salt is the extracting agent, not the free amine. Aqueous solubility of amine salts depends on the chain length and the degree of branching, and can be significant if the molecular weight is below 250. The molecular weight of amines tends to be in the range 250 – 400. Primary, secondary, and tertiary amines are all good metal extractants for sulphate systems, the efficiency of extraction generally being in the order, $3^o > 2^o > 1^o$. This order is due to the increase in cation–anion interaction caused by the increased number of hydrogens on the nitrogen, and the decreasing number of alkyl groups sterically hindering the approach of the anion to the hydrogen of the ammonium ion. Quaternary ammonium salts characteristically extract metals only from neutral and alkaline solutions. The anion type plays an important role in this reaction. Extraction increases in the order, $ClO_4^- > NO_3^- > Cl^- > SO_4^{2-} > F^-$. Large excesses of sulphate[26] have been reported as inhibiting the distribution coefficient, due to the formation of blocked amine bisulphate.

$$\underset{\text{Bisulphate}}{(R_3NH^+ \cdot HSO_4^-)} \rightleftharpoons \underset{\text{Sulphate}}{[(RNH_3^+)_2SO_4^{2-}]} + H_2SO_4 \qquad (12)$$

Increasing ammonium sulphate concentrations is also known to depress extraction by the formation of relatively stable aqueous ammines.

As amines are colloidally dispersed in solution, activity is fairly constant over a range of concentrations. Amine concentrations are usually kept quite low

(~10% $^{v}/_{v}$) due to emulsification problems which result from the use of high concentrations.

There are two types of extraction mechanism;

(i) Anion exchange, which results in the formation of an association complex, e.g. with anionic chloro–metal species:

$$MA_m{}^{M-N\,-} + [(m-n)(R_3N.HA)]_{org} \rightleftharpoons (R_3NH^+{}_{m-n}.MA_m{}^{M-N\,-}) + (m-n)A^- \qquad (13)$$

e.g. $[Fe(SO_4)_2]^-$

(ii) Adduct formation, where a neutral metal sulphate species forms an extractable adduct with the amine complex.

$$(R_3NH)_2SO_{4\,org} + MSO_{4\,aq} \rightleftharpoons (R_3NH)_2.M(SO_4)_2 \qquad (14)$$

M = divalent metal species

$$(R_3NH)_2SO_{4\,org} + M'OHSO_{4\,aq} \rightleftharpoons (R_3NH)_2.M'OH(SO_4)_{2\,org} \qquad (15)$$

M' = trivalent

$$\text{e.g. } (RNH_3{}^+)_2SO_4{}^{2-} + n[Fe_2(SO_4)_3] \rightleftharpoons (RNH_3{}^+)_2SO_4{}^{2-}.n[Fe_2(SO_4)_3] \qquad (16)$$

Amine aggregation is prevalent, and is affected by the nature of the diluent. Larger aggregates are promoted by diluents with very low dielectric constants and little chemical solvating ability.

$$R_3NH^+ + A^- \rightleftharpoons (R_3NH^+A^-)_{1-n-1} \rightleftharpoons (R_3NH^+A^-)_n \quad (17)$$

Amine aggregation starts at 10^{-7}–10^{-6} M, but is also affected by aqueous phase conditions.

Ion association involving sulphate depends upon sulphate concentration and pH. At high pH and high sulphate concentrations the amine does not easily form the sulphate salt and exists predominantly as free amine, which limits metal extraction. Conversely, at low pH the bisulphate species is predominant and the required form of the metal species for ion association/adduct formation limits extraction. Also, the excess sulphuric acid converts the amine sulphate to the bisulphate, thus reducing the sites available in the organic phase.

Akzo Chemie[39] and Rohm and Haas are the major producers of commercial amine extractants. The number of carbons in the alkyl chains range from 12 to 22, and when protonated or alkylated the nitrogen is hydrophilic. Molecules containing groups with hydrophilic and hydrophobic components are known as ampiphilic. The molecules arrange themselves so as to achieve the lowest energy state, which involves micellization or a particular orientation at a surface.

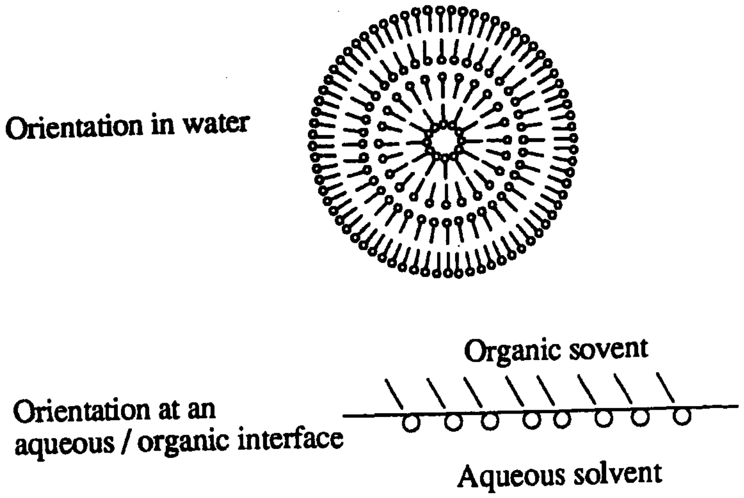


Figure 1.2 Orientation of Ampiphilic Ammonium Compounds in Water and at an Aqueous/Organic Interface

1.4.5. Solvating Extractants[26]

Neutral species may be solvated by extractants with electron donor properties. The chemical form of the metal species is the same in the two phases. The two types of extractant employed are;

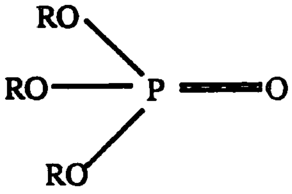
a) **Those involving oxygen bonded to carbon.**

Examples include ethers and ketones which require water as an integral part of the complex, and thus a high degree of metal hydration is observed in the organic phase species. Metal halides are commonly extracted by these extractants, but not metal sulphates. Commercial exploitation has been restricted to alcohols and MIBK; MIBK is used in the separations of niobium and tantalum, and zirconium and hafnium, while e.g. gold(III) is extracted with dibutyl carbitol.

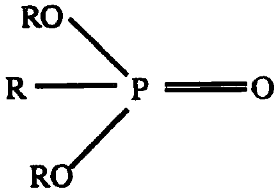
b) **Those involving oxygen bonded to phosphorus.**

Organophosphorus compounds are strongly polar and easily undergo substitution reactions with water in the first coordination sphere of metal ions. Examples in this class include trialkyl phosphates(I) (e.g. TBP), dialkyl alkylphosphonates(II) (e.g. Tributyl butylphosphonate), alkyl dialkylphosphinates(III), and trialkyl phosphine oxides(IV) (e.g. TOPO).

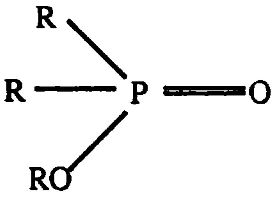
I



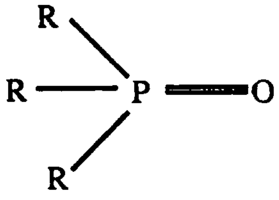
II



III



IV



Their extractive power is found to decrease in the order (IV) > (III) > (II) > (I), correlating with the number of electron withdrawing groups attached to the phosphorus.

TBP is widely used in commercial processing. Examples include uranium extraction from a nitrate–nitric acid system, zirconium/hafnium separation, chromic acid recovery, and iron removal from chloride solutions containing cobalt and nickel.

TOPO has been used in vanadium recovery from phosphate solutions. Sulphur analogues are softer extractants, and are therefore more suitable to softer metals, e.g. Cyanex 471 (Tri–isobutyl phosphine sulphide) extracts silver from sulphate, chloride and nitrate solutions.

1.4.6. Scrubbing

No extractant is entirely specific for one metal, thus scrubbing of the unwanted coextracted species may be required to obtain purer products. Coextraction can be physical or chemical in nature. Aqueous physical entrainment in the organic phase, especially with high metal concentrations, will show up as coextraction, but can be overcome by scrubbing the loaded solvent with water. Chemical coextraction requires the use of a scrub solution whose pH is just sufficient to remove the unwanted metal and leave behind the metal of interest in the organic phase. The pH of the scrub solution is based on the distribution data for the metals.

1.4.7. Stripping[26]

Stripping of a metal from a loaded solvent is essentially the reverse of extraction (as shown in Equation 9). The loaded solvent is contacted with an acid solution sufficiently acid to drive the metal into the aqueous phase. The number of stripping stages can be obtained by stage to stage calculations. The type and concentration of the strip solution is governed by the stability of the extracted species. If the stability of the extracted species is great, acid stripping may prove ineffective.

The extraction of a metal does not mean that it will be stripped easily e.g. Cobalt(III), though extracted at pH 6, can not be stripped by even concentrated acids. However, Co(III) may be removed as the sulphide by sparging the solution with hydrogen sulphide.

Selective stripping of Co from loaded Fe/Co solvating solvents, (produced from a nickel matte solution) has been achieve using 0.2 M HCl[39b] Iron(III) is subsequently stripped using the same strength HCl strip solution, with selectivity being controlled by the phase ratios used. Also, Cl^- may be stripped with good selectivity from Al/Fe – TOPO solutions (produced from chloride leach liquors), although an iron scrubbing stage is required to obtain high purity products.[39b]

Alternatively, coextraction and co–stripping followed by iron precipitation from the chloride strip solution, has been used in the separation of iron and zinc.[39b]

Grunding and Anderson have coextracted Fe and Al from sulphate and chloride solutions by bis(3–5–dimethyl phenyl hydrogen phosphate) at pH 1.0 – 3.5 Al and Fe were then co–stripped with 28% HCl, and a tertiary or quaternary amine was used to selectivity extract Fe from the chloride strip solution.

Alternatives (for carboxylic acids) include hydrolytic stripping[40] and precipitation stripping[41]. Hydrolytic stripping involves reacting a loaded carboxylic acid at elevated pressures with water at 150°–200°C, with iron precipitating as haematite, Equation 18.

e.g.

$$(RCOO)_3Fe_{org} + 3H_2O_{aq} \xrightleftharpoons{150^\circ\text{–}200^\circ C} Fe_2O_3 + 6RCOOH_{org} \qquad (18)$$

In precipitation stripping, the loaded carboxylic acid (usually iron) is heated with sulphuric acid [0.05 – 0.4 molar], for two hours at 100°C, at atmospheric pressure, yielding goethite, (FeOOH), (see Equations 19 and 20). If the initial sulphate: iron ratio is high, basic sulphates such as glockerite, $Fe_4SO_4(OH)_{10}$ and jarosite, $H_3OFe_3(SO_4)_2(OH)_6$ are also formed.

1. Stripping $(RCOO)_3Fe_{org} + 3H^+_{aq} \rightleftharpoons Fe^{3+}_{aq} + 3RCOOH_{org}$ (19)

2. Precipitation $Fe^{3+}_{aq} + 2H_2O_{aq} \rightleftharpoons FeOOH_{ppt} + 3H^+_{aq}$ (20)

In both cases the carboxylic acid is regenerated and is available for recycling for further metal extraction. Alkyl phosphoric acids and alkyl sulphonic acids do not have the required thermal stability for hydrolytic stripping. Studies on the application of precipitations stripping for DEHPA–Fe indicate that the extractant is too acid for this method to be viable. DEHPA[32] forms strong ferric complexes which are difficult to strip. In processes involving uranium extraction from phosphoric acid, iron has been removed by prior reduction to the ferrous state. A Japanese plant recovers high purity iron from steel pickling acids by DEHPA extraction, followed by efficient stripping with ammonia and hydrofluoric acid.

Stripping of iron[42] from alkylphosphoric acids, alkyl or aryl dithio phosphoric acids and hydroxyoximes by one or more of HF, NH_4F, NH_4HF_2 (>40 gl^{-1}) yields an aqueous solution of iron fluoride or ammonium fluoride.

$$R_3Fe + 3NH_4NF_2 \rightleftharpoons 3RH + (NH_4)_3FeF_{6\,ppt} \qquad (21)$$

$$R_3Fe + 6NH_4F \rightleftharpoons 3RNH_4 + (NH_4)_3FeF_{6\,ppt} \qquad (22)$$

$$R_3Fe + 3NH_4NF_2 \rightleftharpoons 3RH + (NH_4)_3FeF_{6\,ppt} \qquad (23)$$

The iron products are filtered off leaving recyclable acid. Purity can be improved by repeated dissolution and crystallization of the crystalline iron species. Iron oxide is obtained by thermal decomposition of ammonium fluoride or iron fluoride in a water or oxygen containing gas stream.

$$(NH_4)_3FeF_6 + \frac{3}{4}O_2 \rightleftharpoons 3NH_4F + 3F + \frac{1}{2}Fe_2O_3 \qquad (24)$$

$$(NH_4)_3FeF_6 + \frac{3}{2}H_2O \rightleftharpoons 3NH_4F + 3HF + \frac{1}{2}Fe_2O_3 \quad (25)$$

$$FeF_3 + \frac{2}{3}O_2 \rightleftharpoons 3F + \frac{1}{3}Fe_3O_4 \quad (26)$$

$$FeF_3 + \frac{3}{2}H_2O \rightleftharpoons 3HF + \frac{1}{2}Fe_2O_3 \quad (27)$$

Studies have shown this stripping method to be successful with DEHPA and OPAP, e.g. experiments at 28.5°C, for 10 minutes with a phase ratio of 1.0, showed that 97.1% of the iron was stripped by 50% OPAP in a paraffin based diluent with 100% NH_4HF_2. After stripping the iron concentration in the organic phase was 0.2 gl^{-1}.

Stripping of DEHP–Fe solutions with HF yields an FeF_3 product. Stripping efficiencies of DEHPA and OPAP and DEHPA/OPAP mixtures by HF and H_2SO_4 are outlined in Table 1.6.

Solvent + (acid)	Stripping Efficiency
DEHPA 30% + (HF [50gl^{-1}]^a)	61.4%
DEHPA 30% + (HF [75gl^{-1}]^a)	96.8%
DEHPA 30% + (HF [100gl^{-1}]^a)	100%
DEHPA 30%^{b}	56.4%
DEHPA 20% & OPAP 30%^{b}	50.3%
OPAP 50%^{b}	54.7%

[a] Initial iron concentration of 2.0 gl^{-1}.

[b] Strip solution of H_2SO_4 [300gl^{-1}] and an initial iron concentration of 18.1-18.4 gl^{-1}.

Table 1.6 Efficiencies of Iron Stripping using Sulphuric Acid and HF

1.4.8. Commercial Considerations

There are many considerations to be made in the development of a commercial extraction system, including the experimental parameters which may be controlled. These include extractant concentration, phase ratio, pH and temperature. Solvent pretreatment, and selection of diluents and modifiers may also be used to improve extraction characteristics such as extraction rate and solvent losses. These aspects of solvent extraction are discussed below.

a) Extractant Concentration

The formation of a stoichiometric metal–extractant compound, will obviously be dependent upon extractant concentration as the expression in Equation 28 indicates. The loading capacity of the solvent increases linearly with concentration of the extractant, until extractant aggregation occurs. At higher extractant concentrations the loading capacities increase only slightly.

$$D = K_D \frac{[HA_{org}]^n}{[H^+]_{aq}} \tag{28}$$

An increase in extractant concentration will increase metal extraction.

Dimerization and polymerization of the extractant may occur at high extractant concentrations, which will have a negative effect upon extraction. Similarly, the $pH_{1/2}$ of extraction will decrease with increasing extractant concentration, as shown in Equations 29 and 30.

$$pH = {}^1/_n \log D - {}^1/_n \log K_D - \log[HA]_{org} \tag{29}$$

$$pH_{1/2} = -{}^1/_n \log K_D - \log[HA]_{org} \tag{30}$$

The qualitative mathematical treatment of systems expressed here is for dilute solutions, but holds qualitatively for concentrated solutions.

b) Phase Ratio and Loading Capacity

The amount of extractant available for metal extraction is also dependent upon the phase ratio ("PR") (Equation 31);

$$PR = \frac{\text{Volume of organic phase}}{\text{Volume of aqueous phase}} \qquad (31)$$

High viscosities of loaded solvents can be a problem in some solvent extraction systems, so lower extractant concentrations with correspondingly higher phase ratios are used to provide equivalent amounts of extractant. Maximum utilization of the extractant requires the loading of the solvent to be as near as possible to its capacity. Under the relevant experimental conditions of pH, temperature, etc., the extractant concentration and phase ratios are optimized to achieve high solvent loading. Too high levels of free extractant may give coextraction of an unwanted metal, or such high extraction that the extracted species exceeds it solubility in the organic phase and is observed as a third phase. In a process, the use of a minimum solvent flow rate is economically important. Loading capacity depends upon the amount of free extractant available and the organic solubility of the metal–extractant species, which is affected by the diluent and modifier.

c) Diluents and Modifiers[26,43]

The diluent is the organic liquid in which the active agent (the extractant) and modifier are dissolved to form the solvent. In early solvent extraction processes the diluent was thought to be inert, but since has been accepted as having an important bearing on the solvent mixture. Choice of diluent is determined by a number of factors. The extractant, modifier, and metal–extractant species need to have high solubilities in the diluent. A low aqueous solubility of the diluent is essential. The density and viscosity of the diluent need to be low to aid dispersion and also coalescence for phase disengagement. The surface tension must be low to reduce the emulsion forming tendencies of a system. For safety reasons diluents must have high flash points, and of considerable importance is their low cost and easy availability. Generally, oil fractions, such as kerosene are used.

The diluent and modifier can affect the extraction, separation, scrubbing and stripping characteristics of a system. The polarity, aromaticity and dielectric constant of the diluent can affect the extraction properties.

Amine salts[44] have a high tendency for aggregation, which is reduced on going from an aliphatic hydrocarbon diluent, to one with a relatively high dielectric constant. (e.g. in aromatic hydrocarbons where single non–aggregated ion pairs are stabilized.) An increase in the polar nature of a diluent can cause an increase in diluent–extractant interactions with the resultant formation of a diluent–extractant species. Diluents with a high dielectric constant generally supress extraction by removal of free extractant in this way. Acid organophosphorus metal complexes exist as $M(AHA)_n$ in aliphatic hydrocarbons, but in more polar solvents are in the monomeric form MA_n.

The amount of aromatic or aliphatic component in the diluent can affect extraction, and is dependent on the mechanism of extraction. Cationic exchange mechanisms (applicable to DEHPA, LIX, Kelex reagents) exhibit decreased extraction efficiencies with increased aromatic content of the diluent, whereas for solvation and ion–association mechanisms the reverse is true. The separation of Co from Ni by DEHPA is improved by a decrease in the aromatic content of the diluent. The differing solvation abilities of aromatic and aliphatic hydrocarbons is exhibited in their effect upon third phase formation. Evidently, the choice of diluent for any system needs to be tailored to its individual characteristics.

Third phase formation is essentially the splitting of the organic phase into two, the new phase being of intermediate density between that of the solvent and the aqueous phases. It is caused by the limited organic solubility of the metal–extractant species, under conditions of high metal loading. Its temperature dependence is illustrated by the disappearance of the third phase with an increase in temperature. Third phase formation is greater when the diluent is an aliphatic hydrocarbon, especially where an amine is employed as the extractant. The tendency for third phase formation with amines and DEHPA is affected by the anion type, increasing in the order, nitrate < chloride < sulphate. Generally, acid phosphorus extractants are free from third phase formation problems[44]. The addition of a polar modifier depolymerizes aggregates, forming stronger hydrogen bonds than those of self association. This effectively inactivates the reaction sites, severely reducing extraction efficiencies.

Inorganic branched amine salts have limited compatibility with organic solvents which is observed in many severe cases of third phase formation. Straight chain amines, however, show little tendency towards third phase formation.

Modifiers are used to alleviate third phase problems. These reagents are usually alcohols (e.g. isodecanol, 2–ethylhexanol, p–nonyl phenol), or TBP, in 2–5% $^{v}/_{v}$ concentration. They increase the solubility of the extracted species in the solvent phase by changing some of the physical and chemical properties of the extractant, and also inhibit the formation of stable emulsions. However, some modifiers, such as the alcohols, depress the metal distribution ratios, the mechanism being the same as in the case of polar diluents.

The modifier is thought to be an important constituent of the extracted complex, with all types of organic phase species, though its mode of action changes with extractant type. In extractions involving separation or compound formation its solubilizing power is due to a secondary solvation of the surface, whereas in amine extractions, the modifier penetrates the interior of the complex, by forming solvent shared ion pairs. When sufficient modifier has been added, further additions have little effect on metal extractability.

Fungal growths have been known to occur in solvent extraction systems, using the modifier as a source of nutrients e.g. the Buffelsfontein uranium circuit in South Africa[26] used a tertiary amine as the extractant and isodecanol as the modifier, and had problems with fungi.

The selection of the best modifier for a system is more difficult than for diluents, as a definite pattern is not followed, and has to be done by testing in actual feed solutions.

d) pH

In dilute systems, pH varies according to the expression shown in Equation 32.

$$pH = {}^{1}/_{n} \log D - {}^{1}/_{n} \log K_D - \log[HA]_{org} \qquad (32)$$

The point where logD = O is termed $pH_{1/2}$, i.e. 50% extraction, as shown in Equation 33.

$$pH_{1/2} = -{}^{1}/_{n} \log K_D - \log[HA]_{org} \qquad (33)$$

$pH_{1/2}$ values are useful in determining the relative acidities of extractant under identical conditions. For a particular metal, the most acid extractant will have the lowest $pH_{1/2}$ values, and the most stable metal–extractant complex.

Increasing acidity will drive the equilibrium shown in Equation 34 to the left.

$$M^{n+}{}_{aq} + nHA_{org} \rightleftharpoons MA_{n\,org} + nH^{+}{}_{aq} \qquad (34)$$

i.e. the formation of the extracted species is less favoured at higher acidity.

pH readings are dependent upon the concentrations of all the metals and anions in solution, the vast array of equilibria involved affecting the overall H^+ concentration. In Equation 9, H^+ is released, thus increasing the concentration H^+ in aqueous solution. As metal is removed from the aqueous solution, re–equilibration of metal hydrolysis reactions occurs. The greater the amount of metal complexed, the greater will be the drop in pH, which will have a consequent effect on the distribution coefficient. The limitations of pH measurement in such complex systems are discussed in the experimental section.

e) Temperature[28a]

Temperature will have a significant effect upon the extractive and stripping properties of a solvent extraction system. The equilibrium constant for metal–extractant interactions will be affected by temperature, with a consequent effect on the distribution coefficient.

$$M^{n+}{}_{aq} + nHA_{org} \rightleftharpoons MA_{norg} + nH^{+}{}_{aq} \qquad (35)$$

The equilibrium in Equation 35 being endothermic will move to the right with an increase in temperature. This is used to advantage in metal extraction, but for metal stripping higher temperatures will have a detrimental effect on the equilibrium position. Raising the temperature will increase the rate at which equilibria are obtained, and can considerably improve contact times. It will reduce phase viscosity which will improve coalescence and promote the rate of phase transfer.

f) Solvent Pretreatment[26]

Solvent impurities (resulting from reagent starting materials or by–products) can lead to deviations in extractant data. Impurities can cause the production of cruds, can change phase separation characteristics, and can alter the distribution coefficient. They are usually more soluble in the aqueous phase than the extractant, and will therefore eventually be lost to the raffinates with recycling. Therefore, solvents should be washed of aqueous impurities before bench scale tests are undertaken, e.g. tertiary amines often contain small quantities of primary amines, and DEHPA may contain 2–ethylhexanol or some monoacid. Typically, washing is carried out with an aqueous solution of comparable ionic strength to the aqueous solution to be contacted.

The formation of an ion association complex involves the amine salt. Equilibration of amine solvents may be accomplished before extraction, or during the extraction stage. Pre–extraction equilibria is common, but equilibria of the amine with its salt form may be favourable with aqueous feed solutions with a high salt concentration, e.g. some leach liquors. Base addition is usually required to obtain the desired aqueous pH for extraction. Addition of base can be reduced by achieving the desired pH_{eq} by using the amine extractant to remove protons, which also equilibrates the solvent, as in Equation 36.

$$R_3N_{org} + H^+_{aq} + HSO_4{}^-_{aq} \rightleftharpoons R_3NH^+.HSO_4{}^-_{org} \qquad (36)$$

Acid extractants undergo proton–metal exchange, decreasing solution pH which has a negative effect upon extraction. To maintain aqueous pH during extraction, the sodium salt of the extractant may be used, with extraction becoming a metal–metal substitution reaction, as in Equation 37. However, this requires an extra contact stage, and the extraction characteristics (e.g. selectivity) may be altered.

$$2NaOPO(OR)_2 + Co^{2+} \rightleftharpoons Co(OPO(OR)_2)_2 + 2Na^+ \quad (37)$$

Stripped solvent may be needed to be treated to convert the extractant to the desired form. The removal of impurities from solvents is essential, whereas the requirement for pre–equilibration is dependent upon the system under study.

g) Rate of Extraction[26,30,31,45]

Extractant rate dictates the residence time in the contactor and for a continuous flow process, the contactor size. The determining factors controlling the rate of metal extraction are mass transfer and complex formation. Important experimental parameters include agitation, temperature and phase viscosity. In metal chelate solvent extraction processes, under conditions of high agitation and low metal concentrations, the mass transfer rates may be faster than the chemical reaction rates.

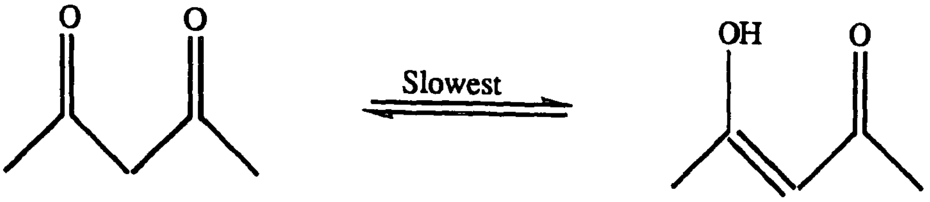
Ionic processes forming metal–extractant species are usually rapid, but chelate formation is often slow and regarded as the rate determining step, (especially if the extractant concentration is relatively low). (See Equations 38 and 39.)

$$M^{n+}{}_{aq} + nHA_{aq} \overset{\text{Slow}}{\rightleftharpoons} MA_{aq} + nH^{+}{}_{aq} \qquad (38)$$

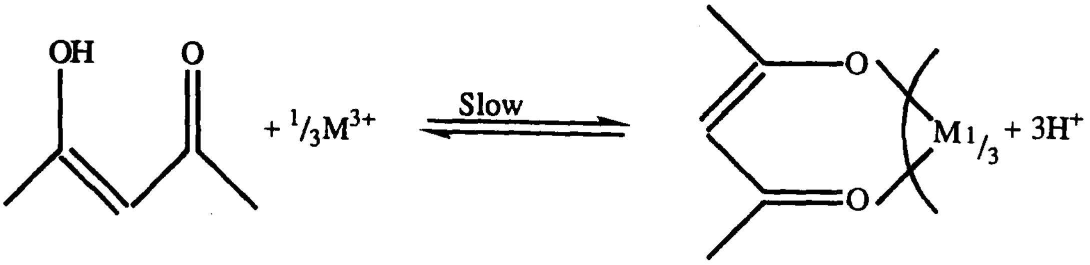
$$MA_{naq} \overset{\text{Fast}}{\rightleftharpoons} MA_{norg} \qquad (39)$$

Chemical conversion of the extractant to a suitable form for complexation (e.g. enol formation) is generally slow and may be the rate determining step.

Steric rearrangement to provide the suitable isomeric form of the extractant for complexation may be rate determining. E.g. in acid solution the LIX anti isomer may complex but the syn may not, as shown below. The rate of inversion and therefore of extraction will depend on the energy inversion barrier.

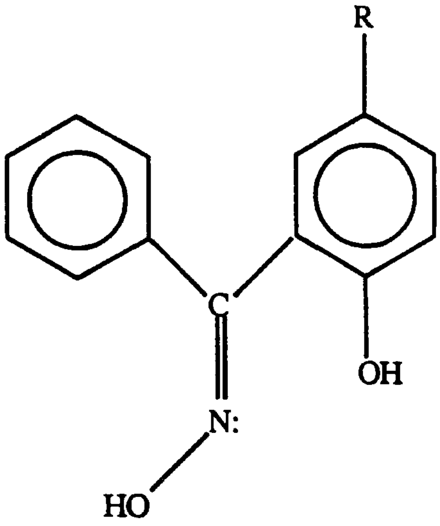


(40)

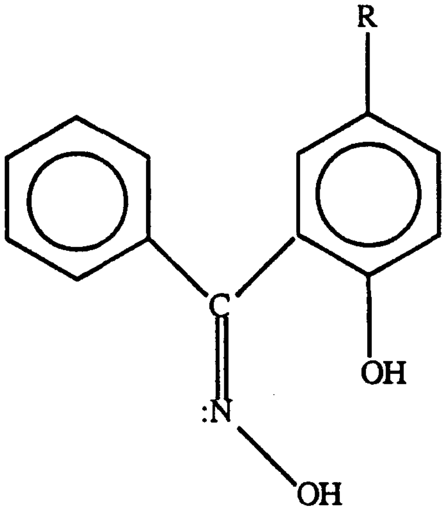


(41)

The isomeric forms of the LIX reagents



anti isomer



syn isomer

The rate of metal extraction is also affected by the form of the aqueous species tending to be a function of the rate of hydrated metal ion substitution, which for a series of divalent and trivalent ions decreases in the order;

$$Cu^{2+} > Mn^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+} > Fe^{3+} > Cr^{3+}$$

This metal–ligand substitution is a kinetic effect and may be useful in determining metal selectivity. Aqueous ammine metal complexes have high stability constants, causing the rate of the ammine–extractant substitution process to be slow. For this reason, in some systems, sodium hydroxide may be a better choice than ammonium hydroxide for pH adjustment.

In ion association systems[46], the rate at which equilibrium is reached is affected by the slow rate of desorption of surface active agents from the interface, especially if a large interface is created by excessive agitation. Non–extracting surfactants can "mechanically block" the transfer of metallic species, and therefore reduce reaction rates.

Increases in the aqueous electrolyte concentration have been reported to decrease the rate at which equilibrium is achieved. Usually, the rate is determined by both mass transfer and the chemical reaction, but high aqueous metal concentrations may place mass transfer as the more important rate determining factor. The mechanism of interfacial mass transfer is different for different types of systems, and even for the same systems there is often ambiguity as to the precise mechanism. For highly surfactant type extractants and low metal concentrations, the transfer site is probably at the interface of phases, whereas for more aqueous soluble extractants (e.g. MIBK) the site is more likely to be within the aqueous phase. For extractants falling into an intermediary category, the reaction probably occurs in a film adjacent to the interface on the aqueous side. Estimations of the depth of the film range from 10 – 100 μm.

The mass transfer of a metal from the aqueous to an organic phase intially involves the diffusion of extractant and metal species from the bulk of their respective phases to the reaction zone. This occurs by two independent mechanisms.

(i) Slow molecular diffusion arising from thermal motion

(ii) Rapid turbulent diffusion arising from the random motion of small packets of fluid.

The latter is the most important mechanism once agitation is introduced.

The adsorption of the extractant into the aqueous film (dependent upon the electron releasing and withdrawing properties of the extractant substituents) is followed by extractant dissociation and formation of the metal extractant species. The extractant species and the released counter ions are desorbed from the film and diffused into their respective phases.

The rate of mass transfer increases with the interfacial contact area which is promoted by increasing agitation. The phase ratio determines which of the phases are continuous or dispersed. Generally, the minority phase is the dispersed phase. Droplet size is dependent upon the phase densities and ratios, the interfacial energy and the nature and degree of agitation. High agitation energies cause break down of drops, yielding large interfacial areas, but this advantage is offset by the reduction in internal motion. Excessive agitation can reduce the droplet size so much that they resemble rigid spheres, leading to the formation of stable emulsions. Obviously, the degree of agitation must represent a compromise between an efficient extraction rate and efficient phase separation.

An emulsion is classified as a dispersed phase within a continuous phase. The use of surfactants as extracting agents can cause problems with the formation of stable emulsions.

Also the formation of dense, viscous surfactant films on the surface of aqueous solutions will lead to the trapping of air bubbles upon high agitation. Closely packed aqueous layers may be hydrogen bonded between surfactant chains. The tendency for hydrogen bond formation between water molecules and the surfactant determines the characteristics of the film on the aqueous phase. Low viscosity, and mobile, open surface films form areas of weakness in the bubble surface eventually leading to bubble rupture. In systems where phase separation is a problem (due to emulsification and/or low phase density differences) centrifugation or the application of an electric field may be used to accelerate coalescence.

h) Solvent Losses[26]

Loss of solvent can have severe implications for the economics of a process. There are essentially five solvent loss categories.

(i) Solvent stability in the aqueous phase
(ii) Physical entrainment
(iii) Evaporative losses
(iv) Degradation
(v) Crud loss

The loss of solvent due to aqueous solubility must be very small. Solvent stability increases with increased temperature and decreased aqueous salt concentration. pH variation also affects the solubility of polar solvent components.

Entrainment losses are quite variable and are usually as a result of poor equipment design, or poor choice of extractant concentration of diluent. The formation of micelles can lead to aqueous components being carried through the organic phase in the core of micelles, which is a route for the physical extraction of impurities[45]. Evaporation of solvent is dependent upon the temperature relative to the boiling range of the solvent, but use of an enclosed system can usually alleviate this problem. Degradation of the solvent is conditional upon the stability of the extractant to temperature and the aqueous phase conditions. Oxidizing agents, e.g. chromate or nitric acid, may oxidatively breakdown the extractant. Tertiary amines are susceptible to oxidation. TBP is oxidized to dibutyl and monobutyl phosphates, which have high aqueous solubilities. Crud formation arises from the stabilization of emulsions and fine solid particles, the most common constituents of crud being Si, Fe, Mg, Ca and Al with the extractant. Agitation and the type of solvent and aqueous feed all affect crud formation. Precipitation of hydrolysed compounds and even bacterial growth have been known to cause problems with solids in the solvent extraction circuit. Filtering, neutralization, acidification and centrifugation are some of the ways of removing crud.

Activated carbon offers an effective means for the removal and recovery of solvent in the aqueous phase. The absorbed organic material on the carbon may be removed by caustic stripping, steam stripping, or carbon reduction in a furnace, though often it is cheaper to discard the loaded carbon. Biochemical treatment, or the use of flotation cells for solvent containing raffinates in activated sludge plants are alternatives. Washing of the aqueous raffinate with an organic solvent (of negligible aqueous solubility), will remove entrained solvent, e.g. TOA has been suggested as an agent to remove organophosphates from aqueous solution. A coalescing device[47] fitted to the raffinate discharge line collects organic droplets, passing them out through a separate organic discharge line. Peroxygens may also be used for the oxidative destruction of organic components in the aqueous phase.

The presence of organic solvents in aqueous effluents is a matter of considerable environmental concern. Although effluent treatment may be expensive, it will become more prevalent as environmental legislation becomes increasingly stringent. Effluents from different plants although seemingly similar may be unique in their required treatment. Biodegradability may even become a significant factor in solvent selection. An alternative to large scale effluent treatment is water reuse which has gained in popularity over recent years.

Due to commercial and environmental pressures it is likely that the added stage (with its duly incurred cost) for solvent recovery from aqueous raffinates will become more common in solvent extraction flowsheets.

i) Synergism[26,48]

This is observed when a mixture of extractants is used, and the overall extraction is greater than the sum of the extractions when the extractants are used individually. The mechanism for metal chelate formation usually involves the displacement of water molecules from solvent extractable metal species (with a low distribution coefficient) by a neutral organic species with electron donor properties. The hydrophobicity of the metal species is increased and is extracted at a far greater efficiency. However, mixed extractant systems are yet to be used commercially.

1.4.9. Structure Versus Reactivity[32]

The array of chemical equilibria involved in a solvent extraction system demonstrates the potential for optimizing the metal separation process by adjustment of the various chemical parameters. The differing abilities of metal ions to form metal chelates is due to (i) changes in Lewis acidity associated with their position in the periodic table, and (ii) differences in oxidation state. Altering the nature of the bonding atoms of the chelating agent and the ring size will affect β and K_a values. The acidity, hydrophilic and steric characteristics of the chelate are all important e.g. thorium extraction by $(RO)_3P$ is adversely affected by an increase in the size of the alkyl substituents. The branching of substituents and their electronic contribution can also influence metal selectivity.

Sulphur analogues of oxygen containing chelating agents are generally more selective for softer metal ions.

However, little work has been carried out on examining the effect of structural effects upon selectivity[31]. i.e. on the ratio of β_n values for given pairs of metal ions. Extractants with (i) a significant steric factor or (ii) special d–pi bonding possibilities can achieve improved selectivity, as demonstrated in the separation of the lanthanides.

1.5 Review of Extractants for the Component Metals of Chrome Residue and Ore

1.5.1. Introduction

Reviews of extractants are given in the following articles[26,52,53]. In addition to the industrial applications discussed, an appraisal of extractants which have been used in the extraction of chromium(III) and (VI), iron(III), magnesium(II) and aluminium(III) is outlined below. Available extraction distribution data covers a wide range of conditions, so valid comparisons cannot be made. Often the conditions are for analytical operations (e.g. very low metal concentrations) and the data cannot be extrapolated to leach liquor concentrations.

The economical removal of iron from solution is one of the more difficult problems facing hydrometallurgy. Zinc production involves use of one of the controlled hydrolytic precipitation processes (jarosite, goethite and haematite) for iron removal[54]. The main reason for iron removal is to prevent its interference with the recovery of the other metals. However, if recovered in a pure form it may be sold; e.g. ferric chloride can be used in the removal of phosphates from waste effluents. The low purity of the iron product generally makes it unsuitable for reuse, and also safe disposal is a problem. Alternative solvent extraction processes tend to be far more expensive. The problems associated with the solvent extraction of Fe(III) tend to be slow extraction rates, the occurrence of precipitates in the settlers, and more importantly poor stripping characteristics.

An alternative to the extraction of Cr(VI) is its reduction to Cr(III) and subsequent precipitation as the hydroxide[49]. Cheap reagents would be sulphurous acid for the reduction step and lime for solution neutralization. However, the $Cr(OH)_3$ formed is gelatinous, difficult to filter and is usually very impure, such that it is uneconomical for reuse.

1.5.2. Chelating Agents

Chromium(III) in the aqueous phase is fairly inert, existing in the hydrated form $[Cr(H_2O)_6]^{3+}$, but at elevated temperatures it reacts with many organic reagents. Reaction times usually vary between 20 minutes and two hours. In analytical extraction procedures, the slow kinetics of chromium extraction at room temperature is used to obtain good metal separations.

Examples of analytical procedures involving Cr(III) extraction by chelating agents are outlined below.

N–methyl piperazine–4–carbodithioate[55] is used to extract Cr(III) from the nitrate solutions of steels and alloys. Interference from coextracted elements (e.g. iron(III)) is eliminated by the addition of masking agents (e.g. hydroxylamine). 8–hydroxyquinoline and 2–methyl–8–hydroxyquinoline[56] are used to extract Cr(III) into molten naphthalene. Phenanthrene monoximate[57] will extract Cr(III) from chloride solutions into molten naphthalene. Thenoyltrifluroacetone extracts Cr(III) from chloride and sulphate media.

4–(2–pyridylazo) resorcinol(PAR) extracts Cr(III)[58] into chloroform at pH 4.0–5.5 with xylometazolonium EDTA. The composition of the complex is Cr(PAR)3XMH.EDTA where XMH is xylometazolonium. Heating 1–(2–trizolylazo)–2–naphthol in the presence of sodium benzoate and sodium dodecyl sulphate for 5 minutes extracts Cr(III) in a 1:1 complex[59]. Cr concentrations are typically 0.2–2.4 ppm Phenylarsenazo[60] forms a blue 1:1 complex with Cr(III) after heating the mixture for 15 minutes at pH 2.2. This procedure has been successfully applied to the determination of Cr in alloy steel. Sunchromine Blue R[60] and Arsenazo III[60] also form extractable Cr(III) complexes. 2–(5–Bromo–2–pyridylazo)–5–diethylaminophenol extracts Cr(III) and Cr(VI) sequentially[61].

Compared to other metals, Mg is fairly difficult to extract from aqueous solution, i.e. the aqueous pH required to form extractable Mg complexes is a great deal higher than for other metals.

The $pH_{1/2}$ of the extraction of Mg by lauric acid ($C_{12}H_{24}O_2$) from nitrate solutions is dependent upon the extractant concentration. 0.5M and 0.05M extractant concentrations give $pH_{1/2}$ values of 6.4 and 7.0 respectively. The $pH_{1/2}$ of Mg in lauric acid decreases slightly with an increase in Mg concentration. At 1.0×10^{-3}M Mg, the $pH_{1/2}$ is 6.9, but at 6.0×10^{-3}M Mg, the $pH_{1/2}$ is 6.7.

At pH 8, 99.8% extraction is achieved at all the above Mg concentrations. The extracted complex is in the form $(MgA_2HA)_2$.

The use of synergists to improve Mg extraction has been demonstrated[62]. Normally Mg forms non–extractable magnesium oxinate dihydrate with 8–hydroxyquinoline (Q). Substitution of the coordinated water molecules by n–butylamine, butylcellulose, pyridine, or tetradecylbenzylammonium chloride (zephiramine) coordinately saturates the metal, resulting in the formation of an extractable complex such as $Mg(Q)_3(zeph)$. Mg concentrations are typically in the order of 10^{-2}.

5, 7–dinitro–8–hydroxyquinoline and rhodamine B[63a] extract Mg in the form $Mg(DNH_q)_3(Rho)$, when Mg is present at levels ~20 ppm. Benzoyltrifluroacetone[63b] in carbon tetrachloride extracts Mg. The dioctyl ester of phenylsulphonylamidophosphoric acid[64] extracts Mg as MgA_2.

Acetyl acetone is a well used chelating agent in analytical laboratories. The commerical extractant, Hostarex DK 16, is a derivative of acetyl acetone. It has an appreciable solubility in aqueous solution which increases with acidity. This allows extraction in more acid solutions as it minimizes the effects of hydrolysis and also increases the rate at which equilibrium is obtained. Studies into the extraction of metals depends on the chemical form of the metal[65]. If the metal originates in the organic phase, >99% extraction of Cr(III) acetylacetonate over the pH range –0.3–2.0, is observed. But, if the experiment involves the extraction of Cr(III) as the hydrated ion from the aqueous phase at 25°C, negligible extraction occurs even up to pH 6. For Al and Fe(III) the equilibrium is the same either way, with extraction of Al 10–90% over the pH range 0.95–4.4, and the extraction of Fe 10–99.9% over the pH range –0.3–1.5. This may be attributed to the nature and strength of bonding. Cr(III) acetylacetonates are all essentially covalent, whereas the Fe(III) species are ionic. Also, polynuclear Cr(III) complexes exist in the aqueous phase, in the form $[Cr_2(OH)_2]^{4+}$, $[Cr_2(OH)_3]^{3+}$, $[Cr_2(OH)_4]^{2+}$. The extent of the formation of these polymeric species is dependent upon the age of the chromium solution. Studies of the extraction of Cr(III) from perchlorate and chloride solutions by acetyl acetone in carbon tetrachloride at 25°C for 24 hours, showed very low extraction coefficients.

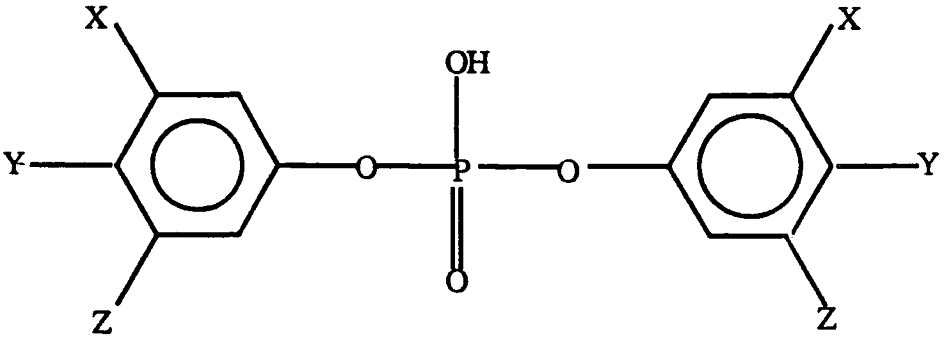
Iron and aluminium acetylacetonates have been observed to undergo exchange in carbon tetrachloride solutions[66]. The exchange rate is dependent upon aqueous pH, temperature, and iron and aluminium concentrations. Stripping studies at 30°C showed no back extraction of Cr(III) even at very high acidities.

1.5.3. Organophosphorus Compounds

a) Acids

DEHPA selectively extracts Fe(III) from sulphate solutions containing Cr(III)[67]. The conditions involve a sulphuric acid concentration of >50 gl^{-1}, at 55°–60°C to prevent crystal formation. Iron concentrations are reduced from ~30 gl^{-1} to ~5 ppm. The molar ratio of iron to DEHPA in the organic phase must not exceed 0.2 at any extraction stage, otherwise the organic phase becomes pulpy due to the aggregation of polymers. The preferred method of stripping is with 6 M hydrochloric acid. For recycling, spent acid requires enriching with HCl gas or concentrated hydrochloric acid. Iron is extracted from the concentrated iron–HCl solution by a solution comprising TBP (40% $^v/_v$), isodecanol (25% $^v/_v$) and kerosene (35% $^v/_v$). The extracted species, $HFeCl_4.TBP$, is washed with water to obtain $FeCl_3$ in dilute hydrochloric acid. Iron is obtained from roasting as Fe_2O_3, or from fractional distillation, as $FeCl_3$. All of the organic reagents are recyclable. Chloride is simply removed from the extractant solution by washing with dilute sulphuric acid.

The purification of iron and aluminium ions is typically obtained by extraction with an alkyl substituted phosphoric acid $HRR'PO_4$, where R is a straight chain or branched alkyl containing >7 carbon atoms, and R' is a hydrogen or alkyl (e.g. dioctyl phosphoric acid). Also, symmetrical bis(3,5–C1–C10 alkylsubstituted phenyl) hydrogen phosphates in the hydrogen (acid) form can used for the extraction of aluminium[68].



An example of an alkylsubstituted phosphoric acid is bis(3,5–dimethylphenyl) hydrogen phosphate.

X $= C_1–C_{10}$ alkyl group.

Z $= C_1–C_{10}$ alkyl group.

Y $= H, C_1–C_5$ alkyl group.

if $Y > C_1$, then X and Z are $> Y + 3$.

Typically an alcohol modifier is used in a kerosene diluent. At ambient or slightly elevated temperatures aluminium extraction (with iron coextracted) is observed at pH 1–3.5. The preferred stripping method is with 6M hydrochloric acid. Iron removal from the aluminium is accomplished from this stage by extraction with an extractant such as a tertiary aimine, to leave a pure aluminium chloride solution. Aluminium is recovered as $AlCl_3$ or alumina.

Cyanex 272 extracts magnesium at pH 5–6 and iron(III) at pH2. Cyanex 923 extracts Cr(VI) at pH~2.

Chromium(III) and aluminium are extracted by the mono–2–ethylhexyl ester of 2–ethylhexyl phosphonic acid from sulphate solutions[34a,69]. Aluminium is extracted as $AIR_3.2RH$, and has a quoted $pH_{1/2}$ value of 1.5. Aluminium is also extracted by monododecylphosphoric acid[26].

Mono–2–ethylhexyl phosphoric acid has been shown to selectively extract iron(III) (as $Fe(HA)_3$, or $(FeHSO_4(HA)_2H_2A)$) from zinc sulphate solutions (H_2SO_4 <150 gl^{-1})[54]. Extraction efficiencies ranged from 85% to 99% from H_2SO_4 concentrations of 180 gl^{-1} to 50 gl^{-1}, (at 20°C, PR1, with a contact time of 5 minutes). 6M HCl stripped 60% of the metal in 5 minutes.

DEHPA in toluene or n–hexane has been shown to extract Cr(III), Fe(III), Al(III) and Mg as in Table 1.7[70]. From sulphate solutions, Cr(III) is extracted in the form $Cr(OH)^{2+}.A_2$[71].

	Concentration (moles.l^{-1})	pH	% extraction
Cr(III)	0.039	12.6	80
Fe(III)	1.0	0.0	100
Mg	0.018	12.3	30
Al(III)	0.38	0.4	18

Table 1.7 DEHPA Extraction of Cr(III), Fe(III), Al and Mg[70]

The $pH_{1/2}$ for magnesium extraction by DEHPA is 3.5[72]. The distribution coefficient is said to increase with temperature and slightly decrease with an increase in sodium sulphate concentration. Extraction is according to the following equation;

$$Mg^{2+} + 2(R_2H_2) \rightleftharpoons (MgR_2.2RH) + 2H^+ \qquad (42)$$

b) Neutral Compounds

The extraction of iron(III) by neutral organophosphorus compounds (e.g. TBP) from chloride solutions is in the form $FeCl_3.A_2(H_2O)$[73,74]. Chromium(III)[75], ferric[76] and magnesium[77] thiocyanate complexes are extracted by TBP. Chromium extraction (at pH 1–3 and 100°C) significantly decreases from 99.9% when the metal concentration is greater than 10^{-2} gl^{-1}, because of the formation of polymeric chromium species in the aqueous phase. Chromium(III) is also extracted from perchlorate solutions by TBP, as an ion pair[78]. Magnesium extraction (80% at pH 4) occurs as shown in the following equation.

$$Mg^{2+} + 2SCN^- + 4TBP \rightleftharpoons Mg(SCN)_2.4TBP \qquad (43)$$

Similarly, magnesium may be extracted as the iodide by TBP. Aluminium perchlorates and aluminium hydroxoperchlorates ($Al(OH)_2ClO_4$) are extracted by TBP[79] as polymerized species. Tri–iso–amylphosphate (TAP) is used analytically in the extraction of Cr(III), Fe(III), and Al(III)[80,81]. In all these cases an increase in the anion concentration causes an increase in extraction.

Cr(VI) is extracted from sulphuric acid media by TBP[49,50,82] and TOPO[83] as H_2CrO_4. Stripping is achieved with; (i) caustic soda with the Na:Cr ratio 2:1, and (ii) water at pH 4, and (iii) base[49,50]. No amines stable to Cr(VI) oxidation are known, so stripping must soon follow the extraction stage.

1.5.4. Amines

The four classes of amines (primary, secondary, tertiary and quaternary) are all used in solvent extraction, their selectivity increasing in that order. The extraction of Cr(III), Fe(III), Mg and Al(III) (at 0.01M) by one amine out of each class is shown in Table 1.8[84]. All showed a minor dependence upon sulphate concentration.

Of particular relevance is a study of the solvent extraction of Cr(III) from sulphate solutions by Primene JMT, (by Flett and West[85]). They decided that the best chance of success for a useful solvent extraction system for Cr(III) was with using a primary amine and a sulphate solution of low acidity. Primene JMT (5–10% in xylene) was pretreated with a sulphuric acid/sodium sulphate solution, and reacted with a solution of Cr(III) (500 ppm), in 1.4M Na_2SO_4/0.1M H_2SO_4. Extraction was shown to be highly dependent upon temperature. Equilibrium (90% extraction) was reached in 30 minutes at 80°C, and in almost 5 hours at 60°C. At 25°C, under the same conditions, only 50% extraction was achieved after 5 hours, equilibrium being reached after 20 days. This trend is attributed to the non labile nature of the aqueous Cr(III) ion in complex formation. The extraction of the component metals of chrome residue by some amines are outlined in Table 1.8. The primary amine, PJMT, is observed to extract Fe(III) more efficiently than the other amines.

	$\log D_{max}$.			
Amine	Cr(III)	Fe(III)	Mg	Al(III)
1° Primene JMT	-1	2.5	No extraction	<-1
2° Amberlite LA-1	~-2	-0.5	No extraction	<-2
3° Adogen 364	~-2	-2	No extraction	<-2
4° Adogen 464	~-2	-1	No extraction	<-1

Amine concentration = 0.1 M, Metal concentration = 0.01 M, Contact time = 10 minutes, H_2SO_4 concentration = 0.15-2.5 M

Table 1.8 Metal Extraction by Amines

Due to its characteristic non–lability, Cr(III) is difficult to strip from liquid cation exchangers. They observed that the age of their aqueous chromium solutions affected extraction, the percentage of chromium extraction increasing with age up to ~5–6 hours after which no change was observed. At 60°C , using 10% Primene JMT, and with an equilibration time of 7 hours, sulphuric acid concentrations of 0, 0.5 and 1.0M gave extraction efficiencies of 100, 50 and 10% respectively. Stripping studies showed that hydrochloric acid is superior to sulphuric acid, and that stripping is more efficient at 60°C than at 25°C. However, sulphuric acid is recommended if stripping is at an elevated temperature, such as 60°C. At pH 2 in aqueous solution the species $Cr(OH)(SO_4)(H_2O)_4$ and $Cr(H_2O)_4{}^{3+}$ are present, but there is no proof that the chromium is extracted in the ion association complex in these forms. Studies regarding Fe(III) extraction by Primene JMT, showed that Fe(III) has a depressant effect on Cr(III) extraction, and that the separation of Fe(III) from Cr(III) sulphate solutions is feasible.

Chromium(III) oxalate (metal concentration = 5×10^{-5}M) is extracted by high molecular weight amines (amine concentration = 0.1M) in chloroform, as $(R_3NH^+)_3Cr(C_2O_4)_3{}^{3-}$[86]; e.g. Primene JMT – 94.6%, Amberlite LA–2 – 93.8%, Alamine 336 – 90.8% and Aliquat 336 – 88.6%.

Amine extraction of Cr(VI) is usually greater with low concentrations of metal. Chromium(VI) is extracted from alkaline solutions by the trioctyl–methylammonium salt (TOMAC, commercially known as Adogen 464) in benzene[87,88], and by Aliquat 336[88]. Tri–n–octylamine [89], tri–iso octylamine (Adogen 382)[90], and di–tridecylamine (Adogen 283)[90] all extract Cr(VI) from acidic sulphate solutions. Quaternary t–butyl amine chloride [91] extracts Cr(III) and Cr(VI) under all levels of HCl and is recommended for use in separating Cr(VI) from Cr(III) by selectively extracting the Cr(VI). Decomposition problems are associated with systems involving amine–Cr(VI) complexes.

The extraction of Fe(III) (0.012M Fe, in 0.096M H_2SO_4) at pH 1.5 by amines (0.2M in chloroform and benzene) has been studied (Table 1.9)[92].

	D	
Amine	In chloroform	In benzene
Primene 81-R	250	500
Primene JMT	250	250
2,2-diethylhexyl	15	39
Amberlite LA-2	2.6	12
di-n-decyl	6.4	2.8
XE-204	0.004	-

Table 1.9 Amine Extraction of Fe(III)

Under identical conditions, aluminium (2.60 gl^{-1}) and magnesium (0.32 gl^{-1}) had distribution coefficients of 0.10 and 0.057 respectively.

The amine Primene JMT has been described as one of the most effective extractants of iron(III) from sulphate solutions[93]. Fe(III) is thought to enter the organic phase in the form of hydroxy complexes, and thus, aqueous pH must be sufficiently high for these species to be stable. The distribution coefficient of Fe(III) (1.29 gl^{-1}) was found to be 500, with Primene JMT (30% in toluene). Formation of iron(III) extractable complexes in chloride solutions occurs at lower chloride concentrations than other metals allowing selectivite extraction[94]. The forms of Primene JMT extracted complexes from sulphate solutions are different in different diluents;

Benzene of trichloroethylene or hexane

$[FeOH(SO_4)_2]^{2-}$

Amsco + Alcohol

$[Fe_2(OH)_2(SO_4)_3]^{2-}$

Trioctylamine in kerosene and octanol extracts Fe(III) in the form $[Fe(SO_4)_2]^{2-}$. Adogen 382 is suggested as a suitable reagent to extract Fe(III) from highly acidic sulphate solutions containing Cr(III)[67]. For satisfactory phase separations the amine concentration needs to be <0.3M. Hydrochloric acid stripping is suggested as the method for Fe removal from the loaded solvent. The separation factor for iron and aluminium from bauxite solutions achieved by Primene JMT is higher than 10000[21]. Stripping of iron from Primene JMT is improved with a modifier (e.g. octanol); stripping with 2.5 M sulphuric acid achieving up to 60% of the iron stripped[95].

Aluminium is extracted from fluoride solutions by di–n–decylamine in chloroform as $(R_2NH_2^+)_3(AlF_6)^{3-}$ [94]. Alamine 336 in diisopropylbenzene (0.59M), and Aliquat 336 poorly extract Al(7.2M) and Mg(5.2M)[94]. The distribution coefficients for Alamine 336 are 2.3×10^{-6} and $1.1. \times 10^{-5}$, and for Aliquat 336 are 1.3×10^{-4} and 8.1×10^{-3} for Al and Mg respectively.

1.5.5. Carboxylic Acids

The extraction of Cr(III), Fe(III), Al and Mg by some carboxylic acids is given in Table 1.10[36,37,38,96].

	$pH_{1/2}$ values (Metal conc.= 0.1 M)				
	Versatic 10	Naphthenic acid	2-bromo decanoic acid	3,5-diisopropyl salicylic acid	C_7-C_9 aliphatic monocarboxylic acids
Cr(III)	-	-	2.6	2.5	2.64
Fe(III)	1.8	1.8	1.2	1.2	0.99
Mg	8.0	9.5	5.5	6.5	4.93
Al	3.5	3.4	2.7	2.7	3.19

Table 1.10 $pH_{1/2}$ Values of the Extractant Cr, Fe, Mg and Al by Carboxylic Acids.

The $pH_{1/2}$ value for Fe(III) extraction by Versatic 9 is quoted as 2.4[38] and 2.5[97], and by neodecanoic acid is 2.8, 2.0 and 1.7 from sulphate, chloride and nitrate media respectively[98].

Table 1.11 shows the form of the extracted metal complexes from different carboxylic acids.

Metal	Solvent	Complex composition	Reference
Fe(III)	Octanoic acid in benzene	$Fe_3A_9(H_2O)_3$	99
Fe(III)	Decanoic acid in benzene	Fe_3A_9	99
Fe(III)	Naphthenic acid	$Fe(OH)A_2$ $Fe(OH)_2A$	100
Fe(III)	Capric acid	$(FeA_3)_3$ $(Fe(OH)A_2)_2$ $(Fe(OH)_2A.HA)$	100
Fe(III)	Versatic acid	$(FeV_3.3HV)_2$ $(FeV_3.2HV)_2$ $(FeV_3.HV)_2$ $(FeV_3)_2$	100
Fe(III)	Oleic acid	$(FeA_3.HA)_2$	101
Al	Decacarboxylic acid in benzene	$Al_6A_{12}(OH)_6$	99
Mg	Naphthenic acid in kerosene	MgA_2	99
Mg	C_7-C_9 aliphatic monocarboxylic acid in octane	$MgA_2(HA)_4$	99

Table 1.11 Composition of Carboxylic Acid–Metal Extracted Species

1.6 Industrial Applications

A few examples of relevant industrial applications of solvent extraction are outlined here. The application of hydrometallurgical techniques[25] has been known for over three hundred years. Copper was leached from the Rio Tinto ores in Spain as early as 1670, though not until ionic theory appeared at the end of the 19th century did hydrometallurgical extraction processes become possible for a range of metals. Some important landmarks in hydrometallurgy are outlined below[25,103].

1700	Copper leaching is followed by precipitation from solution with iron, at Rio Tinto, Spain.
1900	Aluminium Bayer process. Alumina is leached from bauxite by caustic soda, followed by crystallization.
1900	Gold and silver ores leached with cyanide. Gold precipitation with zinc powder.
1920	Zincblende ore is roasted and leached with sulphuric acid to provide a solution for an electrolytic zinc process.
1940	Selective reduction and ammoniacal leach for removal of nickel from oxidic ores.
1953	Acid leaching and ion exchange to obtain uranium from low grade ores.
1956	Amine solvent extraction for uranium recovery from solution.
1958	Pressure leach with sulphuric acid for nickel oxide ore, Cuba.
1960	Bacterial leaching of low grade copper ore dumps, USA.
1964	Iron removal as jarosite from zinc sulphate leach liquors, Spain.
1968	Sulphuric acid dump leaching of oxide copper ore, followed by solvent extraction and electrowinning.
1968	Falconbridge matte leach process for copper, nickel and cobalt recovery from hydrochloric acid solutions by solvent extraction.
1975	Ammoniacal leach of copper sulphide concentrate, followed by solvent extraction and electrowinning.
1981	Hydrometallurgical extraction of zinc and other metal values from highly pyritic ores.

1982	Cobalt leaching with ferric sulphate/sulphuric acid solution.
1983	Simultaneous leaching and cementation of gold.
1986	The first copper solvent extraction plant to use a new matte leaching process was erected in Port Pirie, South Australia.
1990	High temperature solvent extraction of Mn from its ferroalloy, by liquid bismuth.

A good example of an industrial application of hydrometallurgy is the solvent extraction processing of beryllium ores[12]. The ore is initially leached with sulphuric acid, with the beryllium subsequently separated from iron, aluminium and magnesium by solvent extraction. The solvent is comprised of DEHPA in kerosene with $2\%^{v}/_{v}$ isodecanol as modifier. The major difficulty is the effective separation of beryllium from the other metals, (this is directly analogous to the separation of chromium(III), from iron, aluminium and magnesium, in the present study). The order of metal extraction is Fe > Be > Al > Mg. DEHPA removes iron and beryllium together, and iron is separated by precipitation resulting from caustic stripping. However, entrained or coextracted beryllium levels may be too high and the mixed Fe–Be hydroxides may need to be reprocessed. The beryllium in the strip solution is hydrolysed to obtain beryllium as the hydroxide. There is a range of alternatives for iron removal. These include prior solvent extraction, usually with a primary amine, followed by reduction of ferric iron to the ferrous state with sulphur dioxide or sodium hydrosulphide. Prior removal of iron by solvent extraction, though technically viable is not so economical. Complexation of Fe(III) with HF has been used, followed by extraction of the complex with TBP. Studies on solutions of reduced iron concentration, showed that high yields could be maintained. This is probably due to air oxidation of Fe(II) to maintain the equilibrium of reduced–oxidized species, as Fe(III) is continually being removed by DEHPA. Fe(II) may be maintained, however, by keeping the leach solution under an atmosphere of nitrogen.

Aluminium coextraction with beryllium may be reduced by high loading of beryllium in the solvent, as beryllium displaces aluminium. Excellent Be–Al separation is afforded when Be in the strip solution is hydrolysed, leaving the aluminium in solution.

In the development of this system, metal selectivity was observed to be dependent upon the form of the extractant. At pH 2, Mg and Ca were effectively extracted by the sodium form of DEHPA, but negligibly extracted by the hydrogen form. Thus, to reduce co–extraction of metals with beryllium, it was necessary to use the hydrogen form of the extractant. The acid requirements were found to be 1.5 to 2 times greater than the stoichiometric equivalent, due to entrained sodium hydroxide in the organic solution. These findings bear relevance to the development of chrome residue solvent extraction systems, and will be discussed later. The form of the desired end product often determines the chosen scheme, caustic stripping in this case leading to production of a high grade of beryllium hydroxide.

Interesting applications of solvent extraction to the processing of metals from secondary sources are outlined in Table 1.12[27]. Of particular relevance is the recovery of chromate from effluents arising from plating solutions and from the manufacture of sodium chromate(VI).

This process[49,50] was operated by "Produits Chimiques Ugine Kuhlmann" in France during the 1970's, to recover industrial acid effluents, usually sulphochromic acids containing impurities of Cr(III), Fe(III), Co(II) and Ni(II). The processes involved the use of TBP as the extraction agent, removing anionic chromium(VI) from highly acidic (2 to 4 molar) aqueous solutions.

Extraction efficiency was ~99.5% and so only one extraction stage was required. TBP was found to have acceptable stability to the oxidizing media, in tests where TBP was contacted with sulphochromic acid (4N), at 25°C in the dark. At equilibrium with an aqueous chromate solution (2N) the saturated loading capacity of TBP was observed as 30 gl^{-1} of chromium.

Process Nature	Extractant Type
(i) Gullspang process. Electrolytic leach solution of metal scrap containing Mo, W, Cr, Co, and Ni	25% Alamine 15% decanol 60% Kerosene
(ii) Fe, Co, Ni slag residues. Chlorine treatment of a matte transfers metals into a sodium chloride slag which can be leached.	Tertiary amines LA2, Adogen 381. Metals extracted as chloride complexes.
(iii) Copper bearing scrap. Ammonia and ammonium carbonate are used to leach copper as the amine complex. Ammonia is recovered in the extraction stage and recycled to the leach section.	LIX 64N
(iv) Cu, Zn scrap. The scrap is dissolved in sulphuric acid.	Ca salt of DEHPA (though problems with $CaSO_4$ precipitates is common).
(v) Zn, Cd fume condensate. The residue is dissolved in hydrochloric acid.	TBP to form $ZnCl_2$.TBP.
(vi) Acidic chromate effluents from plating solutions.	TBP
(vii) Alkali chromate effluents arising from sodium chromate manufacture.	Aliquat 336

Table 1.12 Solvent Extraction Processes for Metal Recovery from Secondary Sources

Sulphuric acid extraction by TBP (resulting in an inhibition of Cr(VI) extraction) was dependent upon the Cr/SO_4^{2-} ratio in the aqueous phase. Stripping of Cr(VI) from the loaded TBP ([Cr(VI)] = 5–30 gl^{-1}) was also a one stage process, operated at

60–65°C. A strip solution of sodium chromate ([Cr] = 250 gl^{-1}) was used, producing a sodium dichromate solution. It was found to be operable without the use of sodium hydroxide in the strip solution.

$$H_2Cr_2O_7n.TBP_{org} + 2NaCrO_{4aq} \rightleftharpoons nTBP_{org} + 2Na_2Cr_2O_{7aq} + H_2O_{aq} \quad (44)$$

The raffinate, which contains <150 ppm of Cr(VI), if still sufficiently acidic was recommended for use in another manufacturing process not requiring a pure acid. The solvent TBP was recycled for further extraction.

A patent concerning the dissolution of chromite ore and the subsequent separation of chromium from iron, aluminium and magnesium is of considerable relevance to this thesis[11]. The dissolution process, previously discussed, shows a maximum of 76% ore dissolution, in 24 hours with chromic acid at 110°C. Cr(III) in the solution is oxidized electrochemically to Cr(VI). Electrochemical oxidation is preferable to chemical oxidation, e.g. by persulphuric acid, as the former does not introduce foreign ions into the solution.

The resultant ore liquor consists essentially of chromic acid and the dichromates of Fe(III), Al and Mg. The cations Fe^{3+}, Al^{3+} and Mg^{2+} ions are extracted by ion exchange techniques, e.g. either by the resin Amberlite 200 which was found to be resistant to strong chromic acid solutions, or acid liquid cationic exchangers such as DNSA (dinonyl naphthalene sulphonic acid), or DEHPA.

Part of the chromic acid is returned to the digestion step, with the remaining chromic acid processed to give anhydrous chromium trioxide, sodium dichromate, or sodium chromate.

For high purity chromium trioxide, the Fe, Al and Mg extraction stage must be of very high efficiency. Solutions for sodium chromate production may contain small amounts of impurity, as Fe, Al and Mg will be precipitated upon base/sodium carbonate addition and removed by filtration.

1.7 Summary

It is in the interests of the chromium industry to have a range of technologically and economically viable operations to choose from for residue processing. The task of these investigations is to outline potential processes from available technology, and also to probe for new routes for the selective extraction of residue components. A sideways glance at the implications for novel ways of processing chrome ore is also addressed.

Studies into the bulk extractions of residue are based upon previous investigations. Consequently, detailed studies into the optimization of some of the parameters are not undertaken. Instead attempts are made to optimize the limiting conditions of bulk extraction.

Solvent extraction studies have focused on the screening of Cr(III) extractants, and subsequent study of suitable extractants for an optimized flowsheet. Treybal[102] has discussed laboratory scale solvent extraction studies with a view to process development. The objectives for such a study are the evaluation of solvents for separating complex mixtures, and setting conditions to be used in a commercial process prior to pilot plant study. 'Real' mixtures do not usually contain two or three chemically pure substances, but probably contain at least minor amounts of substances whose fate in an extraction process cannot always be foreseen. Their effect will only be observed if they become concentrated in a multi–state process. When considering the separation of complex mixtures, because the distribution of components is interdependent, it is extremely difficult to accumulate meaningful equilibrium distribution data. Standard mathematical treatment of data is valid for dilute solutions (<0.1 molar ionic strength), but not for typical industrial leach liquors where deviation from ideality occurs (due to (i) the inequivalence of activity and concentrations, (ii) high salt concentrations of liquors, (iii) coextraction of other metals, (iv) high metal loading of extractant, and (v) interdependent complex aqueous phase interactions. Therefore, detailed mathematical analysis of distribution data from systems involving leach liquors is not attempted. Also, for the above reasons, distribution data obtained from single metal solutions or 'synthetic' solutions cannot be applied to industrial leach liquors, as deviations can be considerable. For complex mixtures, laboratory extraction investigations must resemble in every way the industrial conditions with respect to phase ratios, numbers of stages, etc. as stage calculations (such as McCabe Thiele diagrams) will not be possible[22b,102]. Therefore, all experimental data has been obtained from residue and ore solutions/raffinates, derived from the dissolution process (unless otherwise specified). Batch simulation techniques to model a multistage cocurrent contact process were used to provide simple and clear data.

The viability of acid stripping and scrubbing metals from the loaded extractants was also examined. The prime objective of this thesis is to provide clear options to the chromium chemicals industry for the processing of chrome residue to obtain pure compounds of the component metals. Chapter 6 assesses the potential for the development of a process from these studies. However, before the metals can be extracted from solution, they must be solubilized, which is the subject of Chapter 2.

CHAPTER TWO

THE BULK EXTRACTION OF CHROME RESIDUE

2.1 Introduction

In this chapter, two approaches to bulk extraction are examined. The first concerns an evaluation of a 'dry' chlorination approach, and the second a 'wet' acid digestion.

Previous studies[10,17] of acid dissolution of chrome ore and residue have shown that digestion is non selective for any of the component metals. The range of parameters influencing residue digestion by reflux or distillation techniques include acid type and concentration, residue mass and particle size, the method and degree of agitation, reaction temperature, and the techniques of dilution and filtration.

Wylie[11] investigated the variation of dissolution of chromite ore with contact time, his results showing little increase in digestion after 2 hours. Agitation was not a limiting factor as long as efficient mixing was maintained.

In the studies herein, the different parameters investigated include: acid type, reflux and distillation techniques, residue mass, reaction temperature, dilution and filtration techniques, and the effect of the addition of an oxidant.

With regard to acid type, Bruen and Wamser[12] have shown that chromic acid can be used quite successfully for chromite ore digestion, but this route leads to the recovery of chromium in the +6 state (the aim of this study is to recover chromium in the +3 state). Perchloric and hydrofluoric acids, although very efficient in residue dissolution, are discounted due to dangers associated with their use.

2.2 Chlorination of Residue and Ore

Partial separation of the component metals of ore and residue is possible by employing chlorination at controlled temperatures. The chlorination process of metal oxides is known to be rather complex in nature.[113] The mechanism, rate, and degree of reaction is influenced by several parameters, including temperature of thermal pretreatment, morphology, particle size distribution of raw materials, heating rate, chlorination temperature, residence time at reaction temperature, and partial pressure of the reacting gases.

Chlorination of predried chromite ore at 400°–500°C, yielded small quantities of pure anhydrous $FeCl_3$ (Table 2.1).

$$2FeO + 3Cl_2 \rightleftharpoons 2FeCl_3 + O_2 \qquad (3)$$

Mass ore (g)	Initial temperature (°C)	Final temperature (°C)	Time (minutes)	Mass residual solid (g)	Mass Product (g)	Observed product	Product
10.0 [a]	448	494	60	9.7	1.2	Red crystals and colourless condensate	$FeCl_3$ [d] and water
9.7[b]	527	471	60	9.7	0.0	-	-
10.0[c]	440	452	15	9.7	0.89	Red crystals	$FeCl_3$ [d]

[a] Not predried.

[b] Residual material from a.

[c] Predried at 120°C for 7 days.

[d] Fe = 26.5%, Cl = 53.5 %, H_2O = 20%; Molar ratio Fe:Cl::1:2.95

Table 2.1 Chlorination of Ore

Overall chlorination efficiency of ore was low possibly due to either the oxide chlorination temperatures, or the boiling points not being reached. At temperatures up to 600°C condensed chromium, aluminium and magnesium products were not observed.

Chlorination of residue at 400°–420°C yielded both iron and chromium products, whose sublimates were separated along a temperature gradient. (Appendix 3) The generation of even smaller quantities of $FeCl_3$ from residue, compared to ore, suggests that the state of iron in the residue may be different to that in ore. Lower oxides are known to be more active towards chlorination.

At 440°C, 5% of chromium in residue was obtained as chromyl chloride (CrO_2Cl_2; identified by infra red spectroscopy). In order to understand why only a small amount of chromium could be released in this manner further chlorination experiments were undertaken with anhydrous Cr_2O_3, hydrated Cr_2O_3, and sodium chromate. These experiments showed that neither anhydrous Cr_2O_3 nor sodium chromate are converted to chromyl chloride suggesting that it is the hydrated form of chromic oxide ($Cr_2O_3.xH_2O$) which reacts with chlorine to form chromyl chloride. This may indicate that a portion of chromium in residue exists in a form chemically bound to H_2O.

$$Cr_2O_3.H_2O + 3Cl_2 \rightleftharpoons 2CrO_2Cl_2 + 2HCl \qquad (4)$$

In the chlorination of ore, chromyl chloride is not released, probably due to its instantaneous aqueous reduction by Fe(II). Residue contains considerably less Fe(II), thus a small amount of chromyl chloride is released upon chlorination. The low yield of chromyl chloride from residue may be due to (i) only a small proportion of chromium(III) oxide molecules being in the hydrated form, or (ii) a substantial proportion of the waters of hydration being driven off at 440°C. As the level of chromyl chloride formation is low, its industrial application is not considered feasible, and therefore was not investigated further.

2.3 Acid Dissolution of Residue

2.3.1. Evaluation of Single Component Acids Under Non–reflux Conditions

Experiments were undertaken to investigate if any other acids, either by themselves or in combination, might provide greater digestion values than sulphuric acid alone. An initial series of experiments consisted of mixing 50 ml acid with 5g residue at ca. 98°C for 30 minutes. For each acid the strength was chosen as 60% of the commercially supplied acid strength. (Commercial acid strengths: H_2SO_4 ~ 98%, HCl ~ 35.5%, HNO_3 70%, H_3PO_4 90%.) Observed dissolution efficiencies were poor, (24% dissolution for 59.1% H_2SO_4, 26% dissolution for 21.6% HCl, and 24% dissolution for 42.0% HNO_3). Under these conditions only a small proportion of metal oxides were readily amenable to acid attack and thus were solubilized.

2.3.2. Evaluation of Single and Dual-acid Compositions Under Reflux Conditions

Experiments using similar experimental conditions to those reported in B.C.C. studies, with refluxing sulphuric acid residue mixtures, gave comparable dissolution efficiencies (~50–70%). It appears that there is an "inert" portion of residue which is less susceptible to digestion by hot acid. These "inert" solids probably remain due to a particle effect and/or their chemical composition. Further studies were undertaken to investigate the potential of acid digestion upon the insoluble solids from an initial acid treatment of residue. The remaining insoluble solids from an experiment which solubilized 64% of the residue, were used to investigate the extractive capabilities of some acids and acid mixtures, as shown in Table 2.2. In each experiment the solid was refluxed in the acid mixture. The residue mixture with sulphuric acid alone had the highest reflux temperature (139°C) with a corresponding dissolution value of 67.1%. Solutions involving sulphuric acid with nitric or hydrochloric acid had lower reflux temperatures and slightly depressed dissolution values (60–64.6%). In the case of a sulphuric/nitric acid mixture, an increase in the proportion of nitric acid had little effect on the dissolution value. Phosphoric acid alone gave similar results to sulphuric acid.

Acid Type	Acid Strength (%w/w)	Acids ratio	B.P. acid(s) (°C)	Final boiling point of mixture (°C)	Dissolution %^{a}
H_2SO_4	59.1	-	139	139	67.1
H_3PO_4	51.0	-	112	110	63.0
H_3PO_4	59.1	-	118	115	65.0
H_3PO_4	70.0	-	128	123	69.6
H_2SO_4 H_3PO_4	59.1 54.3	1:1	124	124	73.6
H_2SO_4 HNO_3	59.1 42.0	1:1	123	123	63.2
H_2SO_4 HNO_3	59.1 42.0	2:1	126	124	64.6
H_2SO_4 HCl	59.1 21.9	2:1	107	114	60.0

Acid mixture [500 ml] + Insoluble solid [10.0g (from an experiment obtaining 64% dissolution)], Contact time = 2 hours

Table 2.2. Digestion of "Insoluble Solids" by Reflux with Different Acids

However, a 1:1 mixture of sulphuric and phosphoric acids showed an increase in dissolution from $\sim$67% to 74%. Although this difference is not large it may possibly arise due to a synergistic effect between the phosphoric and sulphuric acids.

2.3.3. Evaluation of Sulphuric Acid and Sulphuric/Phosphoric Acid Mixtures Under Distillation Conditions

Since sulphuric acid and the sulphuric/phosphoric acid mixture gave the most promising results, these systems were further investigated using a distillation method. This involved distilling water from the mixture leading to a gradual increase in distillation temperature and a progressively more concentrated acid mixture (see Table 2.3).

Acid Type	Acid Strength (%w/w)	B.P. acid(s) (°C)	Final boiling point of mixture (°C)	Volume of distilled water (ml)	Dissolution %
H_2SO_4 H_3PO_4	59.1 60.0 1:1 ratio	121	131	150	87.2
H_2SO_4	59.1	134	147	159	91.1

Acid [500 ml] + Residue [146.5 g], Contact time = 2 hours, Identical heating conditions

Table 2.3 Digestion of Residue by Distillation with Sulphuric Acid and Sulphuric/Phosphoric Acid Mixtures

In this case, the sulphuric acid alone showed the greater dissolution, probably as a result of the higher reflux temperature attained. Thus, it would appear that under these conditions the presence of phosphoric acid in the sulphuric acid mixture does not improve dissolution efficiency.

From a purely practical viewpoint, the use of phosphoric or nitric acid would lead to problems in a solvent extraction circuit, since the disposal of raffinates containing phosphates or nitrates would be environmentally hazardous. Sulphuric acid was therefore selected as the best possible acid to effect residue digestion.

2.3.4. Effects of Acid Concentration, Temperature and Input Mass of Residue

A series of experiments were conducted varying residue input and filtration temperature for reflux operations (see Table 2.4) and also distillate volume for distillations (see Table 2.5). General trends were observed between residue inputs, boiling points, and dissolution efficiencies.

H_2SO_4 used (% of stoichiometric amount)	Final boiling point of mixture (°C)	Mass residue (g)	Temperature of water used for dilution (°C)	Dissolution %
124	128	110.3	80	86.2
93	125	147.1	60	78.9
93	124	147.1	22	78.0
83	123	165.2	90	80.1
83	125	165.2	90	81.2
62	121	220.7	80	63.8

Sulphuric acid [500 ml, 59.1 %w/w], Contact time = 2 hours

Table 2.4 Reflux Residue Digestion Experiments

If the initial acid concentration is too high, the exothermic addition of residue to the acid is quite violent. [This occurred with an experiment with residue (146.5g) and sulphuric acid (500ml, 85% $^{w}/_{w}$), in which the reaction mixture spilled out of the 1 litre reaction flask.] Alternatively, a lower initial acid concentration can be used, and by distillation the acid concentration of the mixture can be maintained or increased throughout the reaction (Table 2.5). The final boiling point of the mixture, can be controlled by the rate of distillation, as observed by the volume of water distilled.

H_2SO_4 used (% of stoichiometric amount)	Final boiling point of mixture (°C)	Mass residue (g)	Volume of water distilled (ml)	Temperature of water used for dilution (°C)	Dissolution %
186	142	73.6	98	80	96.6
93	132	146.5	90	80	91.1
103 (65% acid)	148	146.5	124	80	97.8
93	147	146.5	159	70	87.0
93	146	146.5	146	80	93.2

Sulphuric acid [500 ml, 59.1 %w/w], Contact time = 2 hours

Table 2.5 Residue Distillation Experiments

a) Boiling Point of Mixture

The relationship between final boiling point and % dissolution (in both reflux and distillation experiments) is shown in Figure 1. The lower boiling mixtures (i.e. 121°C–128°C) were achieved using the reflux technique, whilst the higher boiling mixtures (with correspondingly higher dissolution efficiencies) were achieved using the distillation techniques.

In reflux experiments (Table 2.4), the digestion of the metal oxides is accompanied by a decrease in acid concentration due to formation of water. This results in a fall in the boiling point of the mixture. To achieve higher boiling points, water may be removed by distillation (Table 2.5).

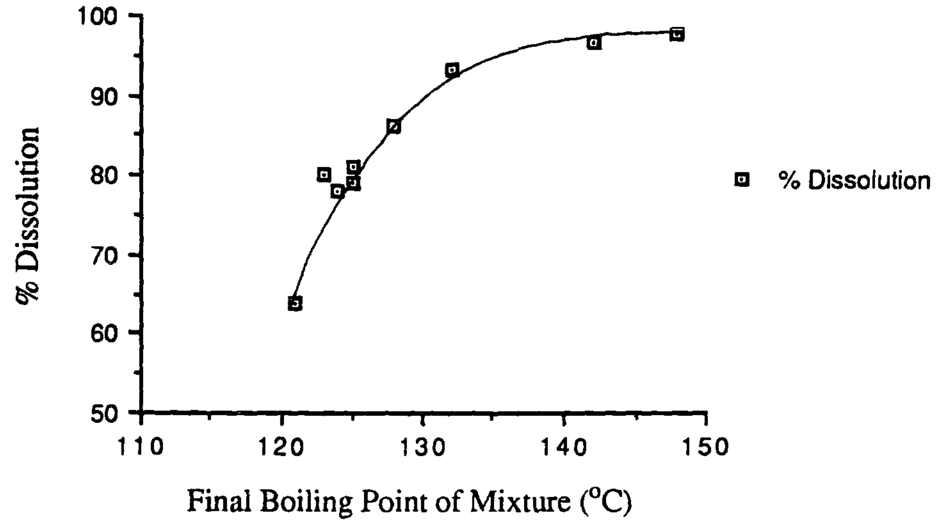
$$M_2O_3 + 3H_2SO_4 \rightleftharpoons M_2(SO_4)_3 + 3H_2O \tag{5}$$

$$M'O + H_2SO_4 \rightleftharpoons M'SO_4 + H_2O \tag{6}$$

e.g. a reflux experiment in Table 2.4, with a residue input mass of 147.1g had a final boiling point of 125°C (79% dissolution), whereas a corresponding distillation experiment in Table 2.5 with a comparable residue mass of 146.5g, had a final boiling point of 147°C (87% dissolution).

The general trend of increased % dissolution with an increase in the final boiling point of the mixture is clearly shown in Figure 1.

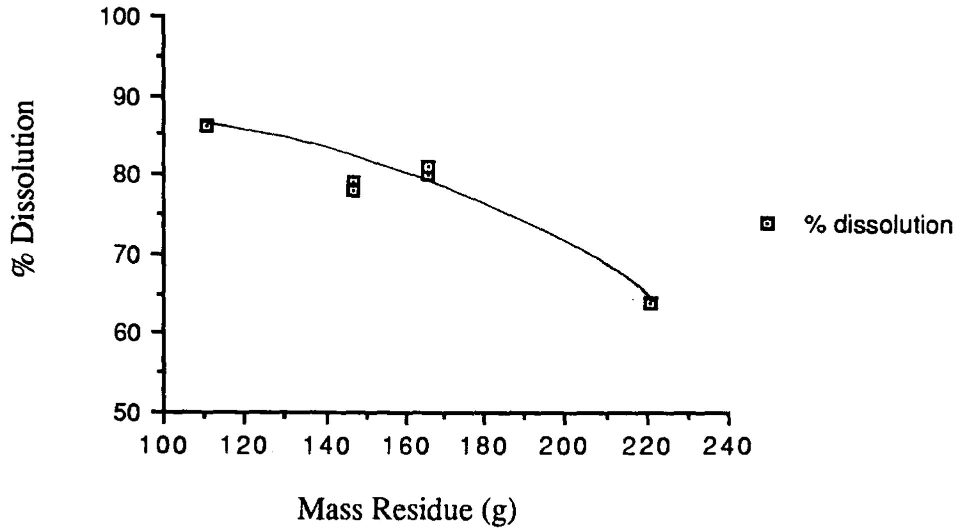
Figure 2.1 Efficiency of digestion vs Final Boiling Point of the Mixture Using Sulphuric acid



b) **Mass of Residue**

In reflux experiments (Table 2.4) the final boiling point of the mixture (and % dissolution) is observed to decrease with an increase in the mass of residue input. As input mass was varied between 110.3g and 220.7g, the value of stoichiometric % H_2SO_4 varied from 124% to 62%, respectively. Consequently, as illustrated in Figure 2, dissolution was observed to be inversely proportional to the mass of residue input (at constant acid input). The points lying above and below the line on Figure 2 illustrate the effect of the temperature of the water used for dilution (i.e. filtration temperature); e.g. in the distillation experiments (Table 2.5) using 146.5g of residue, the temperature of the water of dilution was observed to affect percentage dissolution. Water at 70°C gave 87% dissolution, with a temperature of 80°C resulting in 93% dissolution.

Figure 2.2. Variation of Digestion Efficiency with Residue mass



c) **Filtration temperature**

If the temperature of filtration for particularly viscous solutions is insufficient (e.g. temperature of water for dilution is 70°C) there is a slight decrease in digestion value.

d) **Discussion of parameters**

Assessment of the parameters has established that digestion efficiency is primarily determined by the following;

(i) Final boiling point of the mixture

(ii) Quantity of excess acid

(iii) Dilution

(iv) Filtration temperature

The boiling point of the mixture appears to be the overriding factor in the efficiency of residue dissolution. It is determined by the mass of residue (Figure 2), the quantity and concentration of acid, and for distillation experiments also the volume of distilled water.

The solubilization is also suspected to be affected by frothing of the mixture. At higher acid concentrations (and therefore higher temperatures) frothing of the mixture occurs, which aids aeration of the solution and assists in the breakdown of remaining spinel components. Frothing, however, needs to be carefully controlled with adjustment of the heat source, to ensure that the mixture remains in the containing vessel. Although not shown in Tables 2.4, 2.5 or 2.6 the degree of frothing can have a marked effect upon digestion efficiency. Chrome residue, having been roasted in a kiln at 1100°C, is expected to be more susceptible to acid digestion than chrome ore since the $FeO.Cr_2O_3$ spinel is broken down by air oxidation to Fe_2O_3 and Cr_2O_3. Addition of an oxidant (e.g. CrO_3, see Table 2.6) will also assist in the breakdown of remaining spinel components, and thus aid digestion. Treatment of the insoluble solids showed them to be increasingly insoluble in acid, probably due to both an increased silica content and a particle effect. Analysis of the insoluble solid resulting from 97.6% dissolution (Table 2.6) showed that 40% of the solid was SiO_2.

The treated mixture requires correct dilution and filtration at elevated temperatures to prevent the precipitation of barely soluble sulphates. The particle size of residue determines the available surface area for reaction with the acid. For a commercial process, the stoichiometric ratio of residue to acid may be increased for acid efficiency, though digestion values would inevitably be reduced. The boiling of a sulphuric acid solution, which contains small amounts of Cr(VI), reduces the Cr(VI) to Cr(III) sulphates[112]. Therefore, the 0.6% Na_2CrO_4 present in solid residue is expected to be in the reduced form in residue solution. However, addition of excess CrO_3 oxidant will result in the presence of Cr(VI) in the solution, which would require an extra extraction stage. Thus, addition of CrO_3 needs to be in less than stoichiometric quantities. These experiments have shown significant improvements in the bulk extraction of residue, with digestion efficiencies in excess of 95%, in one step. The principles established in these laboratory scale experiments should prove useful should a pilot plant operation be undertaken.

H_2SO_4 used (% of stoichiometric amount)	93	93	93
Final B.P.of mixture (°C)	140	140	164
Volume of acid (ml)	500	500	1000
Acid concentration %w/w	59.1	59.1	69.3
Mass residue (g)	147.5	146.5	295.0
Mass CrO_3 (g)	10.0	10.0	10.0
Temperature of water used for dilution (°C)	100	80	100
Volume of distilled water (ml)	120	130	244
Dissolution %	96.6	95.8	97.6

Contact time = 2 hours

Table 2.6 Residue Distillation Experiments with the Addition of an Oxidant

2.3.5. Optimized Conditions for Sulphuric Acid Dissolution

The optimized conditions for the sulphuric acid dissolution of residue could be determined by either of two criteria; (i) those conditions giving as high a dissolution efficiency as possible, and (ii) those conditions giving the most cost effective procedure for residue digestion. Working on criteria (i), the final boiling point of the mixture would be maximized by using a high acid concentration, a low input mass of residue, and boiling water for dilution (filtering at 'high' temperature). The conditions outlined in Table 2.5 giving 97% dissolution (with 73.6g residue) appear to be 'sensible' whilst giving very high dissolution. By almost doubling the input residue mass (to 146.5g), dissolution was reduced to 91.1%. The latter would appear to represent a more cost effective alternative. Thus, the following set of conditions represents suitable working conditions to achieve a high efficiency 'cost effective' procedure for residue dissolution. [Note – it is doubtful whether increased severe conditions (e.g. using 65% acid to achieve 98% digestion) would increase the cost effectiveness of the operation. For full assessment of these factors, a detailed study of capital and operating costs versus extremity of conditions would be required.]

Sulphuric acid (500ml, 59.1% $^{w}/_{w}$), Residue (146.5g). Mixed for 2 hours, whilst distilling off water (~90ml). Water (~250ml, 90°C) added, and mixed for 15 minutes. Water (~200ml, 80°C) added during hot filtration (~80°C).

2.4 Acid Dissolution of Chromite Ore

Promising results from acid dissolution of residue suggested consideration of a similar acid extraction of the ore. The major differences between ore and residue are that in the ore the chromium is fully bound in spinels, usually in the reduced form $FeO.Cr_2O_3$, but also as $MgO.Cr_2O_3$. Wetting with acidified solution in an environment where air is the sole oxidant, breaks the ferrous spinel down to the more soluble Fe_2O_3 and Cr_2O_3 rather inefficiently (<35% digestion at 200°C). But, with the addition of CrO_3 as oxidant, the bulk extraction efficiencies of ore are observed at a similar level to residue (>90%, see Table 2.7). The factors affecting ore digestion appear to be the same as for residue.

Thus, the bulk extraction of ore into solution has been shown to be viable in a one step process.

Final B.P. (°C)	Acid Concentration	Mass ore (g)	Mass CrO_3 (g)	Volume of distilled water (ml)	Temperature of water for dilution (°C)	Dissolution %[a]
162	59.1	146.5	0	100	90	9.6
200	70.0	146.5	0	99	80	33.8
196	70.0	73.6	9.8	134	80	97.6
155	70.0	146.5	20.0	73	90	93.2

[a]% dissolution is regarded as the decrease in the % of ore mass, without including CrO_3 as an input solid, as CrO_3 will be fully soluble in the resultant filtrate.

H_2SO_4 volume = 500 ml, Contact time = 2 hours

Table 2.7 Ore Distillation Experiments

2.5 State of Residue and Ore for Further Processing

The solutions produced from such a process will vary according to the nature and precise composition of the solid feed (e.g. the composition of residue batches will vary according to the current efficiency of the chromate extraction process), and the dissolution efficiencies achieved. The composition of the solutions should be within a few thousand ppm of the typical values outlined below.

Dilution of the solutions is required for storage at room temperature to prevent the formation of sulphate precipitates.

	Residue	Ore
Mass input solid (g)	146.5	146.5 + 20g CrO_3
Volume of solution (ml)	1500	1590
Cr ppm	14000	35000
Fe ppm	30000	18000
Mg ppm	8000	4500
Al ppm	12000	6000
H_2SO_4 concentration used %w/w	500ml, 59.1	500ml, 70.0
Sulphate concentration gl^{-1}	~200	~230
Free H_2SO_4 (moles)	0.041 [a]	- [b]

[a] Based upon acid not required for reaction of metal oxides. But, this is a poor indication of acidity as metal sulphates in aqueous solution are acidic.

[b] Calculation is not possible as (i) chromic acid also dissolves metal oxides, and (ii) Proportion of Fe(II) to Fe(III) is not known.

Table 2.8 Typical Solution Composition Values of Residue and Ore

2.6 Summary

The studies into the chlorination of residue and ore, indicate that the bulk extraction of their component metals by this technique would not be commerically viable. However, residue/ore benefication could technically be achieved by chlorination techniques.

The combination of earlier chromite acid dissolution studies enabled the early identification and investigation of the vital parameters for residue and ore digestion. Depending upon the physical and chemical compositions of the material, the following parameters are found to be crucial for efficient dissolution of ore and residue; acid type and concentration, and boiling point of the mixture (a function of the acid/solid ratio). A need for an additional oxidant has been shown to be required for the ore.

It has been demonstrated that >95% acid dissolutions of both chrome residue and ore are technically feasible.

CHAPTER THREE

PRELIMINARY EVALUATION OF POTENTIAL EXTRACTANTS

3.1 Introduction

In this chapter potential extractants are investigated, with a view to assessing their suitability for the extraction of the component metals in residue solution with particular emphasis upon Cr(III). Since Cr(III) is considered to be the most difficult of the component metals to extract much of the work presented in this chapter has focussed on optimizing conditions for Cr(III) extraction.

The selection of the solvent (extractant, diluent and modifier) for a system is determined by the particular characteristics of the aqueous solution. Of primary importance is the choice of extractant, whilst diluent and modifier selection are based upon their suitability for the extractant. Nevertheless, the majority of the necessary characteristics of the extractant are shared by the diluent and modifier. It is improbable that a solvent will exist which exhibits every desirable feature, and compromises may be necessary with less important factors. Thus, the relative importance of the factors must be assessed. At the initial extractant selection stage the phase separation characteristics, and Cr(III) extractability were investigated. Those solvents found to be suitable under these criteria were further examined for their suitability in light of the remaining factors. As the aqueous residue feed solution is highly acidic with high metal and sulphate concentrations a solvent will be required which exhibits high loading in such media. The feed solution will be derived from the acid dissolution, at a temperature in excess of 100°C. Thus, extraction characteristics need to be examined at elevated temperatures as well as at ambient temperature. It could also be advantageous if the chosen solvent has been used in other solvent extraction processes, since information regarding the troubleshooting of any problems could prove to be highly valuable. The range of characteristics which are used to assess the reagents are outlined below.

a) Cost

The extractant must be priced compatibly with the value of the metals in their recovered form, and the cost associated with using that particular extractant, e.g. solvent losses. Extractants may be recovered from raffinates but this represents a significant extra cost, and should be avoided. Many extractants are derived from petroleum, and therefore their price is subject to fluctuations in the price of oil.

b) Extractant Availability

Reagent availability parallels cost, in that readily available extractants are usually less expensive than their rarer counterparts. The designing of an extractant with the exact requirements for a particular system is an attractive proposition to the synthetic chemist. But, even if this was completely successful, the production of a new chemical for a single application would be unlikely to be an attractive alternative to the use of a well established and currently manufactured extractant. Thus, instead of the development of novel extractants, commercially available extractants were selected for initial investigations.

c) Distribution Coefficient

The distribution coefficient determines the number of stages required for extraction, thus a solvent exhibiting high distribution coefficients for the range of feed solution compositions over a wide pH range is desired. In the case of residue solutions, solvents are required which have high distribution coefficients at very low pH. The effect of temperature can be used to increase both the loading capacity and distribution coefficients of a solvent.

d) Selectivity

The selective extraction of metals by an extractant is probably the most important consideration for the problem addressed here. For residue solution, the selective extraction of all of one metal is required, and upon a change in conditions the selective and complete extraction of another metal, and so on. Product purity (which may be improved by scrubbing and stripping) is highly influential in determining the value of the product.

e) Rate of Extraction

Reaction rates must be sufficiently rapid to deal with high throughputs, without the need for too large and expensive equipment. Fe(III) and Cr(III) are usually observed as having slow reaction rates, but these can be improved by using elevated temperatures.

f) Loading Capacity

High loading capacities are preferred so that high organic to aqueous phase ratios can be avoided. At high loading, significant deviation in the physical properties of the solvent are disadvantageous.

g) Stripping

The loaded solvent should be easily stripped by reagents which produce easily recoverable metal species. The stripped extractant should be easily converted to the required form for further extraction.

h) Solvent Stability

The solvent must be stable under the range of process conditions. Decomposition by thermal or light degradation, or by chemical reaction will lead to high solvent costs.

i) Solubility in Hydrocarbon Media

The extractant must be highly soluble in the diluent to give a solution which has reasonable density and viscosity. The addition of a modifier enhances extractant solubility in the diluent, though aqueous phase solubility is also increased. Also, higher temperatures significantly improve solubility.

j) Solvent Density

A large difference in density between solvent and aqueous phase is essential for efficient phase separation. Phase disengagement time is very important as it determines the size of the settlers.

k) Viscosity

Solvent viscosity may be controlled by diluent choice, and extractant concentration. Too high a viscosity tends towards high power requirements for pumping and agitation, slow settling of dispersions, and low heat and mass transfer rates.

l) Interfacial Tension

Interfacial tension, between the two phases, needs to be fairly high for rapid coalescence. However, if it is too high, the mixing of phases requires additional agitation energies. This is preferable to too low an interfacial tension which leads to the formation of stable emulsions. The presence of salts and surfactants usually decreases interfacial tension.

m) Solubility in Aqueous Media

High aqueous solvent solubility may tend to high distribution coefficients, but the associated costs of solvent loss and solvent recovery make this a highly unfavourable characteristic. In strongly alkaline solutions, where extractants are present in salt form, aqueous solubility of the solvent may be greatly increased.

n) Toxicity

Highly toxic materials present handling problems. In particular, reagents should exhibit low toxicity towards the microorganisms responsible for sewage biodegradation of effluents.

o) Vapour Pressure

Low solvent vapour pressures are preferred to keep solvent losses from evaporation to a minimum.

p) Freezing Point

A sufficiently low freezing point is required for convenient storage of the solvent.

q) Flammability

A high flash point, and close concentration limits for explosive mixtures with air, are necessary for safe handling of materials.

r) Corrosiveness

Non–corrosive systems are preferred, but occasions do occur when fairly corrosive systems are justified by their superior efficiency. Plastic and glass lined reactors have been used commercially.

3.2. Extractant Evaluation

3.2.1 Survey of Extractant Features

The Cr(III) extractive capabilities of 32 different extractants, from aqueous residue solutions were investigated at 20°C and 100°C. (Residue solution is a loose term describing (i) solution of sulphuric acid and residue obtained as outlined in Chapter 2, (the solutions used were derived from digestion experiments where >90% dissolution efficiency had been achieved) and (ii) raffinates obtained from the solvent extraction of these initial solutions.)

Iron(III) and aluminium(III) extractions from sulphate solutions are well documented in the literature (see Chapter 1). Iron is extracted at high efficiencies from highly acidic solutions by many extractants. Aluminium may also be extracted by a wide range of extractants, e.g. the separation of Fe(III) and Al from acidic sulphate solutions by Versatic 10 is the subject of a thesis by M.I. Stefanakis[103]. As Fe(III) and Al(III) may be extracted relatively easily, the survey of potentially useful extraction systems has focussed on Cr(III) rather than these metals (comments concerning the extraction of these metals, are made only where relevant).

The pH of solutions have been increased by the addition of NaOH . In most cases these pH's (~3–4) are just below the pH of hydrolysis and precipitation (which is the pH at which extraction is at a maximum). The employed test conditions were at a pH somewhat higher than would be industrially feasible.

The bulk of these extractants are commercially available, although a few were studied for academic interest. The extractant range included chelating agents, acidic extractants, ion association extractants, and solvating agents. Some potential candidates were dismissed because of their high toxicity (e.g. hexamethylphosphoramide), or their lack of availability (e.g. tri–iso–amyl phosphate TAP). In some cases metal complexing agents were added (e.g. thiocyanate). Producers of commercial extractants (see Table 3.1) were contacted for 'industrial quality' samples of potentially useful extractants. The state of the extractants, solvent types employed, and suppliers are quoted in Table 3.1.

	Supplier	Physical State	Solvent Form
Chelating Agents			
8-hydroxyquinoline	Fluka Chemie AG	Solid	5,10% in chloroform/ kerosene/ toluene/ quinoline
Sodium diethyl dithiocarbamate	Fluka Chemie AG	Solid	5,10% in chloroform/ kerosene/ toluene/ quinoline
Salicylaldehyde hydrazone	Fluka Chemie AG	Solid	5% in chloroform 10% in chloroform/ kerosene/ quinoline
N,N'bis salicylidene ethylene diamine	Lancaster Synthesis Ltd.	Solid	10% in chloroform/ kerosene/ quinoline
Salicylaldoxime	Fluka Chemie AG	Solid	10% in chloroform/ kerosene/ quinoline
Acetaldoxime	Fluka Chemie AG	Solid	10% in chloroform/ kerosene
Acetyl acetone	Fluka Chemie AG	Liquid	50% in chloroform/ kerosene
Amines			
N-benzoyl, N-phenyl hydroxylamine (Cupferron)	Fluka Chemie AG	Solid	10% in chloroform
Primene JMT (PJMT)	Rohm and Haas[a]	Liquid	10% in kerosene

Tri-n-octyl amine	Aldrich Chemical Company Inc.	Liquid	10% in kerosene
Armeen 2C	Akzo Chemie[a]	Solid	5,10% in chloroform/ kerosene
Armeen 12 D	Akzo Chemie[a]	Solid	5,10% in chloroform/ kerosene
Armeen 16D	Akzo Chemie[a]	Solid	5,10% in chloroform/ kerosene
Di-octa-decylamine	Fluka Chemie AG	Solid	5,10% in chloroform/ kerosene
Solvating Agents			
Methyl-iso-butyl ketone (MIBK)	BDH	Liquid	100%
Ethanol	J.Burrough (FAD) Ltd.	Liquid	100%
Ethyl acetate	May & Baker	Liquid	100%
Tri-butyl-phosphate (TBP)	Fluka Chemie AG	Liquid	100%
Tri-n-octyl phosphine oxide[b] (TOPO)	Fluka Chemie AG	Solid	10% in kerosene
Tri-phenyl phosphate (TPP)	BDH	Solid	10% in kerosene
Solvating agents with complexing agents			

TBP-thiocyanate	Fluka Chemie AG/ Fluka Chemie AG	Liquid-Solid	Various concentrations in chloroform
TBP-Calcon/Alloxan	Fluka Chemie AG/	Liquid-Solid/ Solid	Various concentrations in chloroform
Acidic Extractants			
Di-2-ethylhexyl phosphoric acid (DEHPA)	Albright and Wilson Ltd[a]./ BDH	Liquid	50% in kerosene
Di-butylbutyl phosphonate (DBBP)	Albright and Wilson Ltd.[a]	Liquid	50% in kerosene
Dibutyl-pyrophosphoric acid (DBPPA)	Albright and Wilson Ltd.[a]	Liquid	50% in toluene
Octyl phenyl acid phosphate (OPAP)	Albright and Wilson Ltd.[a]	Solid	Various concentrations in kerosene
Cyanex 272	American Cyanamid Co.[a]	Liquid	50% in kerosene
Dimethylpentanoic acid (DMPA)	Synthetic Chemicals Ltd.[a]	Liquid	50% in kerosene
Ethyl methyl butanoic acid (EMBA)	Synthetic Chemicals Ltd.	Liquid	50% in kerosene
Naphthenic acid	Fluka Chemie AG[a]	Liquid	40% in kerosene

Oleic acid	BDH	Liquid	100%
Versatic 10	Shell Chemicals Ltd.[a]	Liquid	40% in kerosene

[a] Industrial supplier also.

[b] Also known as Cyanex 921, produced commercially by Cyanamid international.

Table 3.1 Extractants Investigated

Extractants in solid form must be dissolved in a suitable solvent before use. Kerosene was used in many cases, but in some instances other diluents, such as chloroform were found to be more suitable. Amine concentrations are $\leq$10%, to prevent emulsification problems. The amine extractants have generally been used at PR5 and at 10% $^v/_v$ concentrations, which provides an equivalent amount of active species as PR1 at 50% $^v/_v$ concentration. Good solubility of the solid amines and chelating extractants was observed at 5–10% $^w/_v$ concentrations. The liquid solvating agents MIBK, ethanol, ethyl acetate and tributyl phosphate were of sufficiently low viscosity to allow their use without dilution. The solid solvating agents TOPO and TPP, were used in 10% concentration in kerosene, the TPP–kerosene requiring heating to alleviate low solubility problems.

TBP was used without dilution, alone with aqueous raffinates and with the preadditon of calcon/alloxan, and sodium thiocyanate to the aqueous phase. Liquid acid extractants were diluted in kerosene to 40–50% $^v/_v$, to give solutions of sufficiently low viscosities. The exception, oleic acid, was suitable for use without dilution. OPAP is a solid at 20°C, and for dissolution in kerosene requires heating. Above 30% $^w/_v$ concentration, OPAP solutions recrystallized upon cooling to ambient temperatures. Therefore, >30% OPAP solutions may only be used at elevated temperatures.

3.2.2. Survey of Extractants at 20°C

The results of the extraction of metals from Cr, Mg raffinates at 20°C are outlined in Tables 3.2–3.5.

a) Chelating Agents

Table 3.2 shows the extraction of residue metals by chelating agents at 20°C. These studies allow an evaluation of a range of properties of the extractants. At pH_f values >3, Cr was not extracted, although iron and aluminium were removed. (Extraction values for Fe and Al are not quoted where their concentrations are so low as not to significantly affect the loading capacity of the solvent.) The observed separation characteristics of salicylaldehyde hydrazone, N,N'bis salicylidene ethylene diamine, salicylaldoxime, acetaldoxime and acetyl acetone were excellent. Separation characteristics were taken as the loss of solvent to the aqueous phase or vice versa, formation of solids or a third layer, and of phase separation (including formation of any emulsions). The system involving sodium diethyl dithiocarbamate gave a one phase, grey coloured emulsion. Centrifugation of the mixture led to a three phase system consisting of an aqueous phase of reduced volume, a grey solid, and a dark brown organic phase, thus indicating its unsuitability for use at 20°C. The 8–hydroxyquinoline systems in both kerosene and chloroform, at 20°C, gave a thin third layer, which is probably due to the poor solubility of the extractable iron and aluminium complexes formed.

b) Amines

In Table 3.3, the results from the study of metal extraction from a Cr, Mg raffinate, at 20°C, by amines are outlined. The solid Armeens and dioctadecylamine dissolved upon heating but recrystallized from solution at 20°C, preventing their use at this temperature. The amines Primene JMT, cupferron and TOA all gave excellent phase separation. Cupferron did not extract Cr, but Primene JMT and TOA (both in the acid salt form) did exhibit Cr extraction. An aqueous raffinate containing Al (2350 ppm) was also studied with Primene JMT and TOA, with zero Al extraction and similar Cr extraction.

Chelating Agents	pHi/ pHf	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	Separation characteristics	% Cr(III) extraction
8-hydroxyquinoline	3.3/ 3.2[a] 4.2/ 3.7[b]	1900 8800	70 110	900 3800	14 5100	A thin third layer was observed in both cases	0 0
Sodium diethyl dithiocarbamate	3.3/ 3.3	1900	70	900	14	Unsatisfactory phase dispersion and coalescence	-
Salicylaldehyde hydrazone	3.3/ 3.2	1900	70	900	14	Excellent	0
N,N'bis salicylidene ethylene diamine	3.3/ 3.2	1900	70	900	14	Excellent	0
Salicylaldoxime	3.3/ 3.2	1900	70	900	14	Excellent	0
Acetaldoxime	3.3/ 3.2	1900	70	900	14	Excellent	0
Acetyl acetone	3.6/ 3.0 3.6/ 2.0 3.9/ 2.7	7250 9000 23500	5 160 20	4600 4500 3100	500 4600 500	Excellent Excellent Excellent	0 0 0

[a] 10% in chloroform

[b] PR = 2, Amines were pretreated with sulphuric acid [1.5 M, PR = 2.5]

Temperature = 20°C, PR = 1, Contact time = 30 minutes

Table 3.2 Extraction of Metals by Chelating Agents from Residue Solutions Containing High Concentrations of Cr(III) and Mg

Amine	pHi/ pHf	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	Separation characteristics	% Cr(III) extraction
N-benzoyl, N-phenyl hydroxylamine (Cupferron)	3.3/ 3.2	1900	70	900	14	Excellent	0
Primene JMT (PJMT)	4.4/ 1.7[a]	17500	20	2900	250	Excellent	5.7
	1.3/ 1.1[a]	20000	150	3400	2350	Excellent	5.0
Tri-n-octyl amine TOA	4.4/ 2.9[a]	17500	20	2900	250	Excellent	2.9
	1.3/ 1.1	20000	150	3400	2350	Excellent	5.0
Armeen 2C Armeen 12 D Armeen 16D Di-octa-decylamine						Upon cooling the amine solutions to 20°C, recrystallization occurred.	

[a] PR = 2, Amines were pretreated with sulphuric acid [1.5 M, PR = 2.5]

Temperature = 20°C, PR = 1, Contact time = 30 minutes

Table 3.3 Extraction of Metals by Amines from Residue Solutions Containing High Concentrations of Cr(III) and Mg

Solvating Agents	pHi/ pHf	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	Separation characteristics	% Cr(III) extraction
Methyl-iso-butyl ketone (MIBK)	3.3/ 3.3	1900	70	900	14	A third layer (stable to centrifugation) was formed	0
Ethanol	3.3/ 3.3	1900	70	900	14	Excellent	0
Ethyl acetate							
Tri-butyl-phosphate (TBP)	3.6/ 3.6	21500	90	3450	400	Excellent	0
	4.2/ 4.2	1900	70	990	10	Excellent	2.6
	2.0/ 1.9	10400	-	-	-	Excellent	0
Tri-n-octyl phosphine oxide (TOPO)	3.3/ 3.3	1900	70	900	14	Excellent	0
Tri-phenyl phosphate (TPP)						Not investigated at 20°C	
Solvating agents with complexing agents						Separation char., Concentration of complexing agent (SCN)gl^{-1}, (Calc.All.)$g20ml^{-1}$	
TBP-thiocyanate	4.2/ 4.5	1900	70	990	10	Excellent 9.1	2.6
	3.8/ 3.2	10400	-	-	-	Excellent 20.0	3.9
	3.5/ 2.9[a]	10400	-	-	-	Excellent 70.6	7.7
	1.9/ 3.3	10400	-	-	-	Excellent 91.6	11.5

TBP (20% in chloroform)-Calcon/Alloxan	3.0/ 3.3	15700	500	2100	2300	Excellent 0.5/0.5	0.3
	3.0/ 3.6	15700	500	2100	2300	Excellent 0.5/0.0	0.6
	3.1/ 3.1	15700	500	2100	2300	Excellent 0.0/0.5	0.1
	0.5/ 0.5	15700	500	2100	2300	Excellent 2.0/0.0	0.6
	0.5/ 0.5	15700	500	2100	2300	Excellent 0.0/2.0	0.0

[a]Artificially prepared solution.

Temperature = 20°C, PR = 1, Contact time = 30 minutes

Table 3.4 Extraction of Metals by Solvating Agents from Residue Solutions Containing High Concentrations of Cr(III) and Mg

c) Solvating Agents

The solvating extractants studied at 20°C (see Table 3.4) showed no extraction of Cr(III). Separation characteristics were excellent with the exception of MIBK with which a third layer was formed. Although zero Cr(III) extraction was observed with TBP, with addition of the complexing agents calcon and alloxan, slight Cr extraction was observed (0.6%). TBP, with the addition of sodium thiocyanate gave significantly higher Cr extraction. Variation of thiocyanate concentration in artificially prepared Cr(III) solutions showed an increase in Cr extraction with increased thiocyanate concentration.

d) Acid Extractants

The acid extractants at 20°C gave far more promising results (see Table 3.5a) than the other classes of extractants. Cr(III) extraction was observed with DEHPA, DBBP, DBPPA and Versatic 10. All of these, with the exception of DBPPA, gave excellent separation characteristics. With DBPPA, 15% entrainment of the aqueous phase into the organic phase was the main problem. DMPA, EMBA, naphthenic acid and oleic acid showed no extraction of Cr(III) at 20°C.

Acidic Extractants	pHi/ pHf	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	Separation characteristics	% Cr(III) extraction
Di-2-ethylhexyl phosphoric acid (DEHPA)	4.3/ 2.4 1.3/ 1.0[a]	25000 29000	100 165	3900 4150	400 2425	Excellent Excellent	0 6.9
Di-butylbutyl phosphonate (DBBP)	3.7/ 3.3 1.4/ 1.4	15500 19000	20 145	2400 3200	180 2150	Excellent	3.2 2.6
Dibutyl-pyrophosphoric acid (DBPPA)	3.7/ 0.3 3.7/ 0.5[b] 1.4/ 0.6	15500 15000 19000	20 20 145	2400 2400 3200	180 235 2150	15% of aqueous phase entrained in the organic phase. Mg also extracted (56.8, 50.0, 46.9% respectively).	65.8 60.7 28.9
Octyl phenyl acid phosphate (OPAP)						Cooling of OPAP solutions in kerosene to 20°C resulted in recrystallization.	
Cyanex 272						Not investigated at 20°C	
Dimethylpentanoic acid (DMPA)	3.8/ 3.7 1.0/ 1.0	24000 21500	550 560	2200 2200	3700 3800	Excellent Excellent	0 0
Ethyl methyl butanoic acid (EMBA)	3.8/ 3.7 1.4/ 1.4	24000 21500	550 560	2200 2200	3700 3800	Excellent Excellent	0 0

Naphthenic acid	3.5/ 3.5	10200	60	2000	1900	Excellent	0
	1.4/ 1.4	9200	140	2000	2100	Excellent	0
Oleic acid	3.3/ 3.2	1900	70	900	14	Excellent	0
Versatic 10	3.5/ 3.5	10200	60	2000	1900	Excellent	2.0
	1.4/ 1.4	9200	140	2000	2100	Excellent	2.2

[a] PR = 2

[b] In chloroform

Temperature = 20°C, PR = 1, Contact time = 30 minutes

Table 3.5a <u>Extraction of Metals by Acidic Extractants from Residue Solutions Containing High Concentrations of Cr(III) and Mg</u>

Acid extractants may be used in the acidic protonated form, or in the form of a metal salt, i.e. the proton may be exchanged for a metal such as sodium. The extraction of a metal from the aqueous phase is then a metal–metal substitution process. DEHPA (di–2–ethyl hexyl phosphoric acid) may be mixed with sodium hydroxide to form NaDEHP (the sodium salt of di–2–ethyl hexyl phosphate), before mixing with the aqueous feed solution.

$$\text{DEHPA} + \text{NaOH} \rightleftharpoons H_2O + \text{NaDEHP}$$

$$K = \frac{[H_2O] \, . \, [\text{NaDEHP}]}{[\text{DEHPA}] \, . \, [\text{NaOH}]}$$

K is high at high initial aqueous pH, and very small at pH >7. At high pH the alkali and DEHPA form a one phase mixture, but at low pH two distinct phases are observed. At pH <7, when residue solution is mixed with DEHPA the mixture rapidly separates into two distinct phases. If the pH of the initial aqueous phase is >10, a significant proportion of DEHPA exists as the sodium salt, the mixture existing as a one phase emulsion. When the solutions are mixed with residue solution a one phase emulsion is formed, which slowly separates into two phases. The results of the experiments outlined in Table 3.5b show very high metal extraction, at 20°C, by NaDEHP. Investigations were undertaken to assess the effect of sodium hydroxide concentration, in the formation of NaDEHP, on efficiency of metal extraction. Bulk metal extraction was found to be proportional to sodium hydroxide concentration, with >98% extraction of all metals at 1.5M NaOH, and with less than 16% extraction of Cr, Fe and Mg and 70.7% extraction of aluminium at pH_i/pH_f 3.2/2.2. The high metal extraction with NaDEHP compared to DEHPA is thought to be due to (i) the equilibrium of sodium–residue metal exchange tending more towards the right than the equilibrium for proton–residue metal exchange, and (ii) the metals being in sustained, intimate contact with DEHP molecules when in the emulsion (as a result of the low interfacial tension between residue solution and NaDEHP) thus improving the probability of residue metal–phosphate contact, compared to the limited surface interactions between an ionic moiety of the organic components and the metals of the aqueous phase in normal solvent extraction systems.

$$3\mathrm{NaDEHPA} + \mathrm{M}^{3+} \rightleftharpoons 3\mathrm{Na}^{+} + \mathrm{M(DEHP)}_3$$

$$2\mathrm{NaDEHPA} + \mathrm{Mg}^{2+} \rightleftharpoons 2\mathrm{Na}^{+} + \mathrm{Mg(DEHP)}_2$$

3.2.3. Survey of Extractions at Elevated Temperatures

Further studies were carried out at elevated temperatures, with 100°C being chosen as an estimate of the likely temperature of the feed solution.

Acidic Extractants (contd)	pHi/ pHf	NaOH added gl^{-1} of organic phase	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	Separation characteristics	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
Sodium di-2-ethylhexyl phosphate (NaDEHP)	3.8/ 6.0	60.5	18000	8000	2000	4000	Very poor	99.1	100	96.2	100
	3.4/ 12.0	60.0	18000	8000	2000	4000	Very poor	90.9	92.4	45.4	97.4
	3.4/ 3.4	10.0	18000	8000	2000	4000	Very poor	50.5	50.7	38.0	85.9
	3.3/ 2.2	4.6	18000	8000	2000	4000	Very good	11.3	13.7	15.6	76.7

Temperature = 20°C, PR = 2, Contact time = 30 minutes

Table 3.5b <u>Extraction of Metals from Residue Solutions by the Sodium Salt of DEHPA</u>

a) Chelating Agents

In Table 3.6, results from the treatment of Cr, Mg raffinates at 100°C are shown. Negligible Cr(III) extraction was observed in the cases of salicylaldoxime, N,N'bis salicylidene ethylene diamine, and salicylaldehyde hydrazone. With sodium diethyl dithiocarbamate bulk third layer formation was observed in kerosene, toluene, quinoline and chloroform. Acetyl acetone and 8–hydroxyquinoline, however, showed good to excellent Cr(III) extraction capabilities. Acetyl acetone will extract Cr over Mg, with efficiencies of 76.7% at pH_f 2.4 at low Cr(III) concentration, and 26.9% at pH_f 0.2, at high Cr(III) concentration.

Efficient Cr extraction was achieved by 8–hydroxyquinoline, the maximum observed value being 99.8% of 2200 ppm Cr, at pH_f 4.2. Further studies used residue raffinates containing significant quantities of aluminium. Extractions in quinoline and toluene showed poor separation characteristics, which improved when kerosene was used as the diluent. 5% solutions of 8–hydroxyquinoline showed excellent separation characteristics with typical Cr loading of 2000 ppm. 10% solutions of 8–hydroxyquinoline in kerosene gave higher metal extraction values than 5% solutions (46.5% compared to 18.2% Cr extraction respectively), but when high loading occurred (46.5% Cr [8600 ppm] extraction with 66.7% Al [5400 ppm] extraction;– total metal loading = 7600 ppm) a third layer was observed. The low solubility of the 8–hydroxyquinoline–metal complexes in the organic solvent, causes the readily formed complex to be observed as a third phase. Use of 8–hydroxyquinoline would therefore be limited to $\leq$5% concentration.

Chelating Agents	pHf	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	Separation characteristics	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
8-hydroxyquinoline	4.2	2200	67	1000	11	10% in kerosene - ok	99.8	98.7	0	100
	4.2	9500	2100	595	2400	10% in toluene - very poor	-	-	-	-
	1.1	12800	110	4600	7000	5% in toluene - poor	15.6	28.2	0	0.0
	4.5	8800	100	3600	4700	5% in quinoline - poor	35.7	76.0	0	32.7
	4.0	8800	100	3800	5100	5% in kerosene - Excellent	18.2	66.0	0	38.9
	1.0	10600	110	4600	7400	5% in kerosene - Excellent	16.2	10.0	0	0.0
	4.0	8600	100	3800	5400	10% in kerosene - 3rd layer	46.5	91.0	0	66.7
Sodium diethyl dithiocarbamate	9.6	2200	67	1000	11	Bulk third layer formation in kerosene, toluene, quinoline, and chloroform	-	-	-	-
	4.3	2200	67	1000	11					
	0.4	2200	67	1000	11					

Salicylaldehyde	5.4	2200	67	1000	11	CHCl$_3$ (62°C) Small 3rd	0.0	65.2	0.0	0.0
hydrazone	4.8	8800	100	3700	5200	layer	0.8	22.2	0.0	0.0
	-	2200	67	1000	11	Quinoline (PR2) - Poor				
						Kerosene - Yellow sludge				
N,N'bis salicylidene	5.2	2200	67	1000	11	Kerosene - 3rd layer	-	-	-	-
ethylene diamine	6.2	8800	100	3700	5200	formation	0.8	22.2	0.0	0.0
						Quinoline (PR2) - Excellent				
Salicylaldoxime	3.8	2200	67	1000	11	Kerosene - 3rd layer	-	-	-	-
	4.8	8800	100	3700	5200	formation	2.4	30	0.0	0.0
						Quinoline (PR2) - good				
Acetaldoxime	4.1	2200	67	1000	11	Kerosene - good	0.0	0.0	0.0	0.0
Acetyl acetone	0.25/ 0.2	19000	20	2700	270	Excellent - CHCl$_3$	26.9	-	0.0	-
	3.5/ 1.1	15000	20	2000	400	Excellent - CHCl$_3$	7.2	-	0.0	-
	5.8/ 2.4	2100	33	1400	10	Excellent - CHCl$_3$	76.7	-	0.0	-

Temperature = 100°C, PR = 1, Contact time = 30 minutes

Table 3.6 Extraction of Metals by Chelating Agents from Residue Solutions Containing High Concentrations of Cr(III) and Mg at 100°C

b) Amines

When amine salts are used the final pH of the solution is usually less than the initial pH. This is due to the liberation of the counter ion on the amine during extraction; probably HSO_4^-. The poor separation of some of the amine salts is due to emulsification caused by mixing the residue solutions with the amine acid salts. This problem arises because of the low interfacial tension between residue solution and the amine salts. The separation characteristics of these systems may be improved by using the free amines, and therefore studies were focussed on free amine systems (see Table 3.7b).

Studies of the acid salts of the amines Primene JMT, and TOA were conducted at 100°C, and studies of the Armeens and dioctadecylamine at 60°C (see Table 3.7a). Primene JMT extracted Cr(III) very well (51.4% at pH_f 1.7), with ideal separation of the phases. TOA extracted a negligible (2.5%) amount of Cr in one instance and 0.0% at a higher pH. Excellent phase separation was also observed for TOA. Of the amines studied at 60°C, only Armeen 16D showed significant Cr(III) extraction (25.7%). The other Armeens and dioctadecylamine exhibited only slight Cr(III) extraction ($\leq$5.7%). Armeen 16D, however, exhibited poor phase separation, together with Armeen 12D and dioctadecylamine. Only with Armeen 2C was excellent phase separation observed.

Using free amine systems, initial studies with Primene JMT were very promising, with high Cr extraction values at low pH_i and pH_f, and excellent phase separation again observed. Cupferron showed zero extraction of Cr, whilst TOA extracted Cr only by 4.5% at pH_f 4.4.

For the Armeens and dioctadecylamine a comparison of kerosene and chloroform was made in an attempt to improve phase separation characteristics. Armeen 2C and dioctadecylamine showed excellent separation characteristics in both kerosene and chloroform, which was also observed with Armeen 12D in kerosene. Centrifugation of the Armeen 12D/chloroform system was required.

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Amine (Acid salts)	pHi/ pHf	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	Separation Characteristics	Phase Ratio	Temperature °C	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
Primene JMT (PJMT)	1.3/ 1.3	20000	145	3400	2350	Excellent	2	100°C	20.0	-	0.0	4.3
	3.9/ 1.7	17500	20	2900	250	Excellent	2	100°C	51.4	-	0.0	56.0
Tri-n-octyl amine	1.3/ 1.0	20000	145	3400	2350	Excellent	2	100°C	2.5	-	0.0	0.0
	3.9/ 1.9	17500	20	2900	250	Excellent	2	100°C	0.0	-	0.0	2.0
Armeen 2C	3.9/ 3.7	17500	20	2900	250	Good	4	60°C	2.9	-	0.0	3.2
Armeen 12 D	3.9/ 3.7	17500	20	2900	250	Complete emulsification	4	60°C	4.0	-	1.7	41.9
Armeen 16D	3.9/ 3.7	17500	20	2900	250	Poor separation	4	60°C	25.7	-	13.8	43.5
Di-octa-decyl amine	3.9/ 3.7	17500	20	2900	250	Very slow and poor separation	4	60°C	5.7	-	10.3	43.5

Contact time = 30 minutes

Table 3.7a Extraction of Metals by Amines from Residue Solutions Containing High Concentrations of Cr(III) and Mg

Amine	pHi/ pHf	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	Separation Characteristics	Phase Ratio	Temperature °C	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
N-benzoyl, N-phenyl hydroxylamine (Cupferron)	4.1/ 3.6	2200	67	1000	11	Kerosene - Poor	1	100°C	0	42.9	0	-
Primene JMT (PJMT)	1.5/ 2.5	4400	0	2000	0	Excellent - Kerosene	5	100°C	100	-	0.0	-
	0.5/ 1.1	15600	0	9760	0	Excellent - Kerosene	5	100°C	96.5	-	0.0	-
Tri-n-octyl amine	3.8/ 4.4	22000	10	3360	600	Excellent - $CHCl_3$ - 10%	4	100°C	4.5	-	0.0	-

Armeen 2C (5% w/v)	0.4/ 0.8	15600	90	7600	10500	Excellent - Kerosene	5	100ºC	60.0	-	0	0
	0.0/ 0.6	12800	60	7600	10600	Excellent - Kerosene	5	100ºC	9.7	-	0	6.6
	0.25/ 0.3	26500	40	2750	280	Excellent - Kerosene	4	150ºC	56.6	-	0	-
	0.25/ 0.7	26500	40	2750	280	Excellent - Kerosene	4	100ºC	37.7	-	0	-
	0.25/ 0.8	26500	40	2750	280	Excellent - Kerosene	4	60ºC	11.3	-	0	-
	4.0/ 5.6	21500	10	3390	600	Excellent - $CHCl_3$	4	100ºC	32.6	-	15.6	-
	2.2/ 4.2	23000	10	3400	600	Excellent - $CHCl_3$	4	100ºC	45.7	-	14.7	-
	1.3/ 2.1	28000	20	3450	500	Excellent - $CHCl_3$	4	100ºC	27.9	-	0	-
	0.25/ 1.0	26000	50	2640	265	Excellent - $CHCl_3$	4	100ºC	6.9	-	21.5	-
Armeen 12 D	4.0/ 7.6	22000	10	3360	600	Centrifuge - $CHCl_3$, 5%	4	60ºC	98.6	-	52.8	98.3
	2.2/ 5.8	23000	10	3400	600	Centrifuge - $CHCl_3$, 5%	4	60ºC	81.1	-	28.5	86.3
	1.3/ 2.7	28000	20	3450	500	Centrifuge - $CHCl_3$, 5%	4	60ºC	84.3	-	49.3	87.5
	0.25/ 1.1	29000	50	3000	265	Centrifuge-$CHCl_3$,2.5%	4	60ºC	22.4	-	11.1	-
	0.25/ 0.6	26500	40	2750	280	Excellent - Ker., 2.5%	4	100ºC	11.3	-	0.0	-

Armeen 16D	4.0/ 7.6	22000	10	3400	600	Centrifuge - $CHCl_3$, 5%	4	60°C	98.6	-	75.0	97.8
	2.2/ 5.8	23000	10	3400	600	Centrifuge - $CHCl_3$, 5%	4	60°C	92.6	-	47.4	95.8
	1.3/ 2.7	28000	20	3450	500	Centrifuge - $CHCl_3$, 5%	4	60°C	50.0	-	23.2	-
	0.25/ 0.5	29000	50	3000	265	Centrifuge-$CHCl_3$,2.5%	4	60°C	13.8	-	6.5	-
	0.25/ 0.5	26500	40	2750	280	Centrifuge - Ker., 2.5%	4	100°C	22.6	-	13.5	-
Di-octa-decyl amine	4.0/ 5.0	21500	10	3390	600	Excellent - $CHCl_3$	4	60°C	39.5	-	28.9	-
(5% w/v)	2.2/ 4.3	23000	10	3400	600	Excellent - $CHCl_3$	4	60°C	46.3	-	36.5	-
	1.3/ 1.7	28000	20	3450	500	Excellent - $CHCl_3$	4	60°C	12.5	-	0.0	-
	0.25/ 0.7	29000	50	3000	295	Excellent - $CHCl_3$	4	60°C	10.3	-	12.5	-
	0.25/ 0.5	26500	40	2750	280	Excellent - Kerosene	4	100°C	11.3	-	0.0	-

Contact time = 30 minutes

Table 3.7b Extraction of Metals from Residue Solutions Containing High Concentrations of Cr(III) and Mg - By free amines

Armeen 2C exhibited good Cr extraction with good selectivity over Mg and Al at low pH. At pH_f 0.7, 37.7% of Cr was selectivity extracted from a Cr, Mg raffinate, and at pH_f 0.8, 60.0% selective Cr extraction was obtained from a residue solution containing 10500 ppm of Al. Armeen 12D extracted Cr slightly less efficiently than Armeen 2C, but coextraction of Mg and Al was also observed. 5% $^w/_v$ dioctadecylamine extracted Cr to the same extent (11.3%) as 2.5% $^w/_v$ Armeen 12D, at pH_i 0.25, at 100°C, which was the extraction achieved by 5% Armeen 2C at the same pH_i, at only 60°C. At higher pH, coextraction of Mg and Cr was observed. Armeen 16D systems exhibited poor separation in both solvents, and in both cases centrifugation was required. Cr(III), Mg and Al(III) were extracted with high efficiency by Armeen 16D.

c) Solvating Agents

There was a lack of metal extraction by the use of solvating agents alone, which indicated that under these experimental conditions, the sulphate and hydroxy metal species in solution are non–extractable by these solvating extractants (see Table 3.8). The separations of the solvents MIBK, ethanol and TBP were excellent, but solvent loss was observed with TPP and ethyl acetate. The 'extractions' observed with TBP alone are most probably due to aqueous entrainment of the aqueous phase in the solvent.

However, in the presence of complexing agents, TBP was observed to extract all of Cr, Fe, Mg and Al from solution at 100°C. Thiocyanate, and calcon/alloxan complexes of these metals were solvated and extracted by TBP. The extraction of Cr thiocyanate complexes was studied with respect to Cr and thiocyanate concentrations. At 2.0 gl^{-1} Cr, concentrations were varied from 1.9 ppm to 2800 ppm. Up to 156 ppm the extraction appeared to be fairly constant (21–28%) indicating a lack of dependence on Cr concentration (the variation was probably due to the slight difference in pH). At a Cr concentration of 2200 ppm, extraction decreased to 12%, and at 2800 ppm zero Cr extraction was observed. Even at pH 12.9 Cr was not extracted. This is probably due to the formation of polymeric aqueous Cr(III) complexes at the higher metal concentrations.[75]

Thiocyanate concentration was varied, with pH_i of the aqueous phase constant at 4.0, prior to SCN^- addition. The metal concentrations were Cr 7200 ppm, Fe 63 ppm, Mg 4600 ppm and Al 4600 ppm. Cr was not extracted at zero SCN^- concentrations, Al and Mg extraction being negligible over the full range of SCN^- concentrations. The extraction of Cr increased proportionally with SCN concentration, with a maximum of 35% Cr extraction at 50.0 gl^{-1} SCN^-. The formation of Al, Fe and Mg thiocyanate complexes are dependent upon the β_n values of each of the metal complexes, as outlined in Chapter 1. The stabilities of these complexes will determine the position of the equilibria involving ligand exchange between the metals. The high extraction values of Fe which are observed to increase with SCN^- concentration indicate that these complexes are fairly stable under the conditions employed. The relatively low extraction of Mg and Al, indicate that the β_n values of the extractable thiocyanate species are significantly lower than the β_n values for Cr.

In the case of calcon and alloxan (0.5g of each of the complexing agents in 20ml of aqueous solution) all four of the metals present in solution were extracted to a small extent (<6%).

(d) Acid Extractants

DEHPA was observed to extract Cr(III) from Cr, Mg raffinates very well between pH_f 2.2 and 0.6 (at a maximum of 37.7%) (see Table 3.9). Mg coextraction was also observed. In every case, excellent phase separation characteristics were observed.

DBBP exhibits excellent separability with no solvent losses only if the pH_i is <3. Cr extraction did not exceed 11%, even at pH_i/pH_f 3.7/3.7. It appears that use of DBBP at higher pH's is not possible without the addition of further components to the system. An increase in contact time did not improve Cr extraction.

Solvating Agents	pHi/ pHf	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	Separation characteristics	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
Methyl-iso-butyl ketone (MIBK)	4.1/ 3.8	2200	67	1000	11	Excellent	0.0	0.0	0.0	0.0
Ethanol	4.1/ 4.1	2200	67	1000	11	Excellent	0.0	0.0	0.0	0.0
Ethyl acetate	4.1/ 3.8	2200	67	1000	11	Solvent loss observed, (72°C)	0.0	0.0	0.0	0.0
Tri-butyl-phosphate (TBP)	4.0	7200	63	1000	11	Excellent	0.0	-	0.0	0.0
Tri-n-octyl phosphine oxide (TOPO)	4.1/ 3.7	2200	67	1000	11	Excellent	0.0	0.0	0.0	0.0
Tri-phenyl phosphate (TPP)	0.0/ 0.0	16400	31200	8720	11300	Poor	0.0	0.0	0.0	0.0

Solvating agents with complexing agents						Concentration of complexing agents gl^{-1} / Separation Characteristics				
TBP-thiocyanate	3.8/ 4.0	1.9	-	-	-	2 / Excellent	23	-	-	-
	2.0/ 2.2	2.2	-	-	-	2 / Excellent	21	-	-	-
	2.5/ 2.9	28.5	-	-	-	2 / Excellent	22	-	-	-
	13.0/ 13.0	156	-	-	-	2 / Excellent	21	-	-	-
	3.0/ 3.1	2200	-	-	-	2 / Excellent	12	-	-	-
	3.0/ 3.1	2200	-	-	-	15 / Excellent	15	-	-	-
	1.7/ 1.7	2800	-	-	-	2 / Excellent	0	-	-	-
	12.9/ 12.9	2800	-	-	-	2 / Excellent	0	-	-	-
	4.0	7200	63	3200	4600	0.0 / Excellent	0	0	0.0	0
	4.0	7200	63	3200	4600	2.0 / Excellent	5	15	0.2	1
	4.0	7200	63	3200	4600	10.0 / Excellent	4	45	0.2	2
	4.0	7200	63	3200	4600	30.0 / Excellent	11	70	0.3	2
	4.0	7200	63	3200	4600	50.0 / Excellent	35	75	0.7	2

TBP (50% in chloroform) [20ml] - Calcon (0.5g) / Alloxan (0.5g)	3.1/ 2.6	14400	500	1700	1800	PR2 / Excellent	1.6	5.7	1.0	4.0
	5.6/ 4.4	14400	500	1700	1800	PR2 / Excellent	0.9	5.0	0.1	0.0
	8.7/ 8.8	14400	500	1700	1800	PR1 / Excellent	0.2	2.5	0.3	2.2

Temperature = 100°C, PR = 1, Contact time = 30 minutes

Table 3.8 Extraction of Metals by Solvating Agents from Residue Solutions Containing High Concentrations of Cr(III) and Mg

DBPPA showed excellent phase separation in conjunction with very efficient extraction of all four residue metals. The extraction of >90% of Cr (1900 ppm), Fe (140 ppm), and Al (2500) ppm and 30% extraction of Mg (3300 ppm) in a one step reaction at pH_f 0.5 exemplifies the high loading capacity of DBPPA at such a low pH.

OPAP extracted 50% Cr at pH 0.8 with excellent phase separation characteristics. Mg was coextracted with the Cr.

Cyanex 272 exhibited poor phase separation, with zero Cr extraction. Mg extraction was observed, but the efficiency of Mg extraction was poor (5% at pH_f 2.5). The carboxylic acids all exhibited excellent phase separation under the conditions studied, but Cr extraction was poor in every case, even at pH_i >3.5.

3.3 Conclusions

a) Chelating Agent

Of the chelating agents investigated, only 8–hydroxyquinoline and acetyl acetone exhibited any potential for non ferric residue metal extraction. Sodium diethyl dithiocarbamate may be discounted on the grounds of its unsuitable phase separation characteristics even before metal extraction is addressed. Salicylaldoxime, N,N'bis salicylidene ethylene diamine, and salicylaldehyde hydrazone did not extract Cr at either 20°C or 100°C. Acetyl acetone extracted Cr(III) at 100°C and not 20°C, and was selected for further study (see Chapters 4 and 5). The difficulties encountered in the low solubility of the 8–hydroxyquinoline–metal complexes could be overcome on a laboratory scale by using sufficiently dilute 8–hydroxyquinoline with large phase ratios, but on an industrial scale this may prove less practical. The addition of a modifier would, however, be expected to improve the solubilities of the complexes. 8–hydroxyquinoline is not available commercially, unlike its alkyl derivative, Kelex 100. The larger organic component in Kelex 100 may improve complex solubility in the solvent, but unfortunately Kelex 100 was not available for these investigations.

Acidic Extractants	pHi/ pHf	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	Separation characteristics	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
Di-2-ethylhexyl phosphoric acid (DEHPA) (acid form)	3.3/ 1.3	30500	30	3770	265	Excellent - PR1	27.9	-	29.7	-
	3.9/ 2.2	30500	6	3600	500	Excellent - PR2	37.7	-	53.9	-
	2.0/ 1.5	8500	20	1065	30	Excellent - PR2	11.8	-	46.0	-
	0.6/ 0.6	6400	10	9120	100	Excellent - PR1	0.0	-	0.0	-
Di-butylbutyl phosphonate (DBBP)	3.7/ 3.7	15000	19	2400	235	Centrifuged	0.0	0.0	0.0	14.9
	1.2/ 0.8	19000	140	3300	2500	Excellent	10.5	10.7	3.0	8.0
	1.3/ 1.3	19000	130	3500	2300	Excellent	10.5	0.0	0.0	0.0
	1.3/ 1.1	19000	130	3500	2300	Excellent, 2 hours	5.0	30.8	0.0	0.0
	3.0/ 2.75	21000	70	2200	300	Small aq. in org., PR2	0.5	4.3	0.0	0.0
Dibutyl-pyrophosphoric acid (DBPPA)	1.2/ 0.5	19000	140	3300	2500	Excellent	92.4	95.8	30.33	96.0
	3.7/ 0.8	15000	19	2400	235	Excellent	87.0	39.5	49.0	89.4

Octyl phenyl acid phosphate (OPAP) (29% w/v)	1.0/ 0.8	20000	30	7000	200	Excellent	50.0	-	42.9	-
	0.25/ 0.1	19200	60	6600	200	Excellent	14.6	-	10.4	-
	0.0/ 0.0	21000	50	6800	200	Excellent	11.5	-	4.7	-
Cyanex 272	0.5/ 0.5	16000	10	9000	500	Poor PR2	0	-	0.0	-
	3.0/ 2.5	15200	10	9320	500	Poor PR2	0	-	5.4	-
	6.7/ -	17000	10	10000	500	Very poor PR2	0	-	21.8	-
Dimethylpentanoic acid (DMPA)	1.0/ 1.0	21500	560	2200	3800	Excellent	0.0	0.0	0.0	0.0
	3.9/ 2.8	24000	550	2190	3700	Excellent	3.0	92.3	0.0	43.2
	3.7/ 3.1	30500	10	3400	500	Excellent PR2	4.0	-	0.4	-
Ethyl methyl butanoic acid (EMBA)	1.4/ 1.4	22500	580	2195	3800	Excellent	0.0	0.0	0.0	0.0
	3.8/ 3.0	19500	540	2125	3500	Excellent	0.0	81.0	0.0	60.5
	3.7/ 3.1	30500	10	3400	500	Excellent PR2	3.6	-	0.4	-
Naphthenic acid	1.4/ 1.4	11400	60	2100	1580	Excellent	0.0	3.3	0.0	0.0
	3.5/ 2.9	9800	60	1750	1540	Excellent	3.5	80.0	0.0	5.0
Oleic acid	4.1/ 3.5	2200	67	1000	11	Excellent	0.0	92.2	0.0	0.0
Versatic 10	1.4/ 1.3	11400	60	2100	1580	Excellent	3.5	0.0	0.0	5.1
	3.5/ 3.2	9800	60	1750	1540	Excellent	3.0	80.0	0.0	10.0

Temperature = 100°C, PR = 1, Contact time = 30 minutes

Table 3.9 Extraction of Metals by Acidic Extractants from Residue Solutions Containing High Concentrations of Cr(III) and Mg

b) Amines

Primene JMT is a relatively cheap material, which showed good Cr extraction characteristics, and excellent separation characteristics. The loading capacity was low at 20°C, but considerably improved at 100°C. It is already used in commercial solvent extraction and therefore offers considerable potential for use with residue solution. The selective extraction of Cr by Armeen 2C, combined with its excellent separation characteristics suggests its potential applicability to the problem in hand. Armeen 2C, Armeen 12D, and dioctadecylamine solutions in kerosene all exhibited excellent phase separation characteristics in conjunction with significant Cr extraction and need to be considered further. Despite the good metal extractions observed, the very poor separation characteristics of Armeen 16D systems, are likely to preclude their use in any Cr extraction process.

c) Solvating Agents

The solvating extractants are not applicable to Cr, Fe, Mg or Al extraction from acidic sulphate solutions unless a complexing agent has been added to the aqueous feed, prior to phase mixing. Extraction of Cr thiocyanate depended upon the thiocyanate concentration, Cr concentration and temperature. The extracted species[75] are described as being $Cr(SCN)_3.nTBP$. Thiocyanate concentrations must be fairly high to enable high Cr extractions, and the extra cost of the thiocyanate would add significant cost to a process. The metal extraction efficiency was also not as high as for other systems. Recovery of thiocyanate would be essential; however, it would be difficult to strip the organic phase in such as way as to recycle the thiocyanate. Thus, this system does not appear to be suited for use in a residue extraction process.

Calcon and alloxan are known to form metal complexes which are extractable, on a spectrophotometric scale. The applicability to spectrophotometric analysis was confirmed by the extraction with TBP of these complexes, as small amounts of the four metals were extracted (with excellent phase separation characteristics), but also confirming their non–applicability to the bulk scale extraction of metals.

d) Acid Extractants

DEHPA showed good Cr extraction values, in conjunction with excellent phase separation characteristics which make it an ideal candidate for further study. The sodium salt of di–2–ethyl hexyl phosphate was found to have poor separation characteristics, when an excess of NaOH was used to form the extractant salt. At lower NaOH concentrations, i.e. when the pH_f of residue is <7, phase separation was adequate. Although very efficient metal extraction can be achieved using NaDEHP, the selectivity appears to be totally lost. Exchange of Na^+ for a metal from residue solution occurs so readily that it appears to be impossible to achieve selective metal extraction. The use of NaDEHP may have some application in removing the remaining metals in a non–selective manner from an aqueous raffinate, but not in the general scheme for metal separation. Therefore, DEHPA will be the subject of further investigation, but the study of NaDEHP is suspended.

DBBP exhibted low Cr extraction at 100°C, with a tendency towards entrainment at pH >~2.5 and therefore DBBP does not appear to be a viable candidate for further study.

DBPPA is a rather viscous liquid which does not dissolve well in kerosene. It extracts all four metals well at 20°C, even at low pH. However, at 20°C, the problem of 15% aqueous entrainment was incurred, although at 100°C phase separation was excellent. The extraction of all four metals at 100°C was accompanied by a lack of selectivity again. For this reason and also its poor mixing with kerosene, further investigations of this extractant were suspended.

OPAP was selected for further study as it displayed excellent separation characteristics together with high Cr extraction at low pH.

Selective Mg extraction from the Cr, Mg raffinate but with poor efficiency. Poor separation characteristics and zero extraction of Cr, established Cyanex 272 as being unsuitable for further study Cyanex 272 exhibited.

The renowned problems of solvent loss, and limited extraction power with respect to pH make carboxylic acids appear unattractive for process application. C_8 carboxylic acids are known to extract Cr(III) in application for analytical determinations. Shell are the major producers of carboxylic acids in the UK. They were not able to provide samples of C_8 acids but only the two C_7 acids, EMBA and DMPA. However, the limited extraction efficiency of Fe and Al and the poor extraction of Cr and Mg led to their study being discontinued. The low Cr extraction values for naphthenic acid, oleic acid, and Versatic 10 has also led to their exclusion from further study.

Particularly notable features of the extraction agents were the greater extraction values at elevated temperatures, and the strong dependence of separation characteristics on diluent choice. Also, the poor organic solubility of many complexes was observed upon extraction of macro quantities of metal. These systems may behave perfectly well on an analytical scale, but are not suitable for bulk metal extraction purposes.

Extractants which did not extract Cr(III) under the conditions employed, were considered to offer limited potential in a process flowsheet for residue. The prices, in £ per tonne, of the Cr(III) extractants are outlined in Table 3.10. Those extractants selected for further study from these feasibility studies include Primene JMT, DEHPA, OPAP, acetyl acetone, Armeen 2C, Armeen 12D and dioctadecylamine. NaDEHP and DBPPA are regarded as reserve candidates, primarily due to likely problems regarding phase separation.

Extractant	£ per tonne$^{a/b}$	Industrial Supplier
Acetyl acetone	3850	Courtaulds
Armeen 12D	1875/ 1900	Akzo Chemie
Armeen 16D	1750	Akzo Chemie
Armeen 2C	1800/ 1700	Akzo Chemie
8-hydroxyquinoline	-	Unknown
TBP, (thiocyanate)	2260, (-)/ 2760, (-)	Albright & Wilson, (Unknown)
TBP, (calcon & alloxan)	2260, (-)/ 2760, (-)	Albright & Wilson, (Unknown)
DEHPA	4060/ 4060	Albright & Wilson
DBBP	5240	Albright & Wilson
DBPPA	2330	Albright & Wilson
OPAP	3230/ 3230	Albright & Wilson
Primene JMT	2655/4995	Rohm & Haas

[a] Prices as at January 1989.

[b] Prices as at September 1990.

Table 3.10 Prices of Cr(III) Extractants

CHAPTER FOUR

SELECTIVE METAL EXTRACTION

4.1 Introduction

In Chapter 3, a brief survey of thirty two extractants was carried out with particular regard for their ability to extract Cr(III) from residue raffinate solutions; attention was also given to the phase separation characteristics of these systems. Of these, PJMT, OPAP, DEHPA, acetyl acetone, Armeen 2C Armeen 12D, and dioctadeylamine offered the greatest potential for process application to residue solutions.

In this chapter, initially the selectivities and loading capacities of the extractants are compared for Fe(III) removal; those extractants exhibiting favourable characteristics being studied in greater depth in the remainder of the chapter. These extractants are each discussed in turn; assuming a process flowsheet using one extractant only, the extraction characteristics at each metal extraction stage are discussed.

Within these more detailed investigations, % extractions, selectivities, extraction rates, loading capacities and phase separation characteristics are the main areas of study. Studies of single metal synthetic solutions have been made in a few cases.

The order of metal extraction may vary according to the extractant used. e.g. one extractant may extract Fe followed by Al to produce solutions of "high Cr and Mg concentration", whereas another extractant may extract Fe and Cr to produce solutions of high Al and Mg concentration. The range of solution types are also studied by each of the extractants, to provide information regarding the potential use of multi–extractant systems.

Where application of an extractant to residue solution processing appeared favourable, brief studies with ore solutions were also undertake. A lengthy study into the precise optimum conditions for selective metal extraction from *ore solutions* was not possible. Rather, the effects upon extraction, of changes in the composition of the aqueous feed solutions were analysed. The aim of the ore experiments was to give a general indication of the type of conditions that would need to be employed for selective metal extraction from ore solutions. Effectively, these studies show the effect upon extraction system characteristics of differences in the relative and absolute values in metal concentrations. Further to this, Cr(VI) may be present in residue/ore solutions, arising from CrO_3 addition in the digestion state (although this is not an essential requirement for effective residue digestion); the extraction characteristics of Cr(VI) from residue/ore solutions are discussed in Section 4.3.5.

It is highly likely that optimisation of all the factors influencing the suitability of an extractant for a particular metal, could lead to the conclusion that a different extractant is required for each metal. This has to be balanced against the economic and technical advantages of optimising the overall process for one or two extractants. Such advantages would include reduced material transport and storage costs. A likely potential problem in a multi–extractant system could be undesirable extractant mixing, arising from entrainment in a previous stage.

The availability, characteristics and properties of those solvents selected for further investigations are outlined below.

4.2 Further Solvent Selection

4.2.1. Solvent Component Properties

a) OPAP[114,115]

OPAP, manufactured by Albright & Wilson in the U.S.A., is a semisolid material which comprises a mixture of mono– and di–hydrogen phosphate esters. OPAP is octylphenyl dihydrogen phosphate (26%), and dioctylphenyl hydrogen phosphate (73%), both of which are strong acids which form salts with alkalis and amines. The structure of the mono–hydrogen ester is represented in Section 1.5.3. where two of the substituents (X, Y and Z) are H, and one is an octyl group.

OPAP has a specific gravity of 1.08 (determined at 15°C and 65°C), and 0.0 mm Hg vapour pressure at 20°C. Melting and boiling points at atmospheric pressure have been established, due to unstable products being formed before the required temperatures are reached. It is soluble in kerosene type diluents, and has negligible solubility in water. Its flash point, determined by the Cleveland Open Cup method, is quoted as 158°C. OPAP is incompatible with strong oxidizers, the decomposition products of which are toxic phosphorus oxides and carbon monoxide. OPAP is an acute skin and eye irritant, and is readily absorbed by the skin.

b) DEHPA[114,116]

This mobile, colourless liquid, manufactured by Albright & Wilson in the U.K. is soluble in kerosene type organic type diluents. Its structure is $(RO)_2POOH$, (where $R = CH_3(CH_2)_3\ C(C_2H_5)_2C-$). It has a specific gravity of 0.972 at 20°C, and a melting point of −60°C. Unstable decomposition products are formed before its boiling point is reached. The flash point, determined by the Pensky–Martens Closed Cup method, is 93°C. DEHPA is incompatible with strong bases and oxidizing agents. Hazardous combustion or decomposition products are CO and CO_2, with thermal decomposition producing toxic fumes of phosphorus oxides, and/or phosphine. It is harmful if inhaled, swallowed, or absorbed through the skin.

c) Primene JMT[117,118]

PJMT, a brown liquid, is a mixture of C_{16-22} tertiary alkyl primary amines, with the principal formula;

$$t{-}C_xH_y{-}C(CH_3)_2{-}NH_2 \qquad x = 15{-}19,\ y = 31{-}39$$

Its neutral equivalent molecular weight is 336. The product provided by Rohm & Haas contains 0.10% water, although it is quoted as having negligible solubility in water. It is soluble in common organic solvents, with excellent solubility in petroleum hydrocarbons. It has a specific gravity of 0.840 at 25°C, and a flash point of 129°C (determined by the Tag Open Cup method). At 25°C, PJMT has a pK_b of 9.76. PJMT is incompatible with strong oxidizers, and is known to cause severe eye and skin irritation.

d) Acetyl Acetone[116]

This colourless liquid, available from Courtaulds has a specific gravity of 0.975 at 25°C, a melting point of −23°C, a boiling point of 140.4°C, and a vapour density of 6 mm Hg at 20°C. The flashpoint temperature is very low at 34.4°C. Acetyl acetone auto–ignites at 350°C. The explosion level limits are 1.7% – 11.4%. The tendency of acetyl acetone vapour to travel a considerable distance to the source of ignition and to flash back, is particularly hazardous. Chemically, it is incompatible with oxidizing agents, halogens, strong reducing agents and strong bases. Toxic fumes of CO and CO_2 are produced upon combustion or decomposition. Acetyl acetone is harmful if inhaled, swallowed or absorbed through the skin.

e) Armeen 12D[119]

Armeen 12D, manufactured by Akzo Chemie, is the distilled n–dodecylamine amine fraction, with composition >98.0% primary amine and <2.0% secondary and tertiary amine. The only solvent extraction application of the Akzo amines is in the phase transfer of pharmaceuticals, e.g. penicillin and tetracyclins. The typical chain length distribution of Armeen 12D is 1% C_{10}, 98.0% C_{12} and 1% C_{14}, with a typical equivalent molecular weight of 185. The commercial product contains <0.5% water. Its melting point range is 24°–29°C, and it has specific gravity of 0.78 at 60°C, and 0.80 at 25°C. Its flash point is 112°C, as determined by the Cleveland Open Cup method.

f) Armeen 2C[119]

Armeen 2C, also known as dicocoamine and manufactured by Akzo Chemie, is composed of <5% primary amine, >90% secondary amine, and <5% tertiary amine. The typical alkyl chain length distribution is C_{10} 3%, C_{12} 58%, C_{14} 22%, C_{16} 10% and C_{18} 7%. Moisture represents <1.0% of the commercial product. It has a typical equivalent molecular weight of 383. Armeen 2C has a specific gravity of 0.79 at 60°C, a melting range of 40°–47°C, and a flash point (determined by the Cleveland Open Cup method) of 172°C.

g) Dioctadecylamine[119]

Dioctadecylamine, also known as distearylamine, is not produced commercially, but Armeen 2HT (an amine mixture containing 64% C_{18}, 31% C_{16}, 4% C_{14} and 1% C_{10} secondary amines) is produced commercially by Akzo

Chemie. Armeen 2HT has a specific gravity of 0.80 at 60°C, a melting point range of 60°–64°C, and a flash point (determined by the Cleveland Open Cup method) of 224°C.

h) TBP

Tri–butyl phosphate, $[CH_3(CH_2)_3O]_3PO$, is manufactured by Albright & Wilson, and is a colourless liquid with a melting point of –79°C, a boiling range of 180°–183°C, and a density of 0.979. Its flash point is 193°C. It is soluble in kerosene type diluents and has negligible solubility in water. TBP is harmful if in contact with eyes or skin. Toxic phosphorus oxides and carbons monoxide are produced upon decomposition.

i) Kerosene

The most commonly used diluent in these studies, kerosene, (purum quality) was obtained from Fluka Chemie AG, and is industrially widely available. The material used has a boiling range of 200°–250°C, and a specific gravity of 0.80 at 20°C. The solubilities of PJMT, DEHPA and acetyl acetone in kerosene were excellent. The solids OPAP, Armeen 12D, Armeen 2C and dioctadecylamine required warming for efficient dissolution, and could only be used at elevated temperatures.

Under the full range of experimental conditions in this chapter, all of the solvents exhibited acceptable flow characteristics (i.e. were of sufficiently low viscosity), with good mixing and settling characteristics (i.e. exhibiting acceptable difference in phase densities, and low interfacial tensions). The solvents showed no sign of decomposition with residue solution, over the range of conditions used. Highly loaded solvents were left at ambient temperature for >6 months, with no signs of discolouration, decomposition, or third layer formation, with the sole exception of TBP–Cr(VI) solutions. TBP in TBP–Cr(VI) solutions underwent oxidative decomposition after 6 months.

4.2.2. Residue Solution Nomenclature

The variation of the composition of residue solutions arising from the digestion stage is discussed briefly in Section 2.5. The exact composition of the residue raffinates is entirely dependent upon the extraction in the previous metal extraction stage. It is impossible to cover the full range of all absolute and relative metal concentrations, but rather, anticipated ranges of metal concentrations emanating from digestion/extraction cycles are investigated. These solutions are divided into the following categories;

a) "Fe rich residue solutions", (Fe concentration approx. = 20,000–35,000 ppm). These are residue solutions that arise directly from the digestion stage, having been subjected to dilution.

b) "Fe medium residue solutions". These are those solutions from (a) that have been subjected to one extraction stage, where Fe has been removed to medium concentrations (e.g. approx. 2000–5000 ppm).

c) "Al, Cr, Mg high residue solutions". These are raffinates from (a) and (b) that have been subject to virtually complete Fe extraction without substantial extraction of other metals (e.g. Fe < 1000 ppm, Al ≈ 10,000 ppm, Cr ≈ 12,000–25,000 ppm, Mg ≈ 7000–12,000 ppm).

d) "Al medium, Cr high residue solutions". These are solutions from (c), where Al levels have been reduced to approx. 500–7000 ppm.

e) "Cr medium, Al high residue solutions". These are solutions from (c), where Cr levels have been reduced to approx. 8000–10,000 ppm.

f) "Al, Mg only residue solutions". These are solutions from (c) or (e) that have been subject to almost complete, or complete Cr extraction, without substantial extraction of the remaining Al and Mg, (e.g. Al ≈ 10,000 ppm, Mg ≈ 7000 ppm).

g) "Cr, Mg only residue solutions". These are solutions from (c) or (d) that have been subject to almost complete, or complete Al extraction, without substantial extraction of the remaining Cr and Mg, (e.g. Cr ≈ 10,000–20,000 ppm, Mg ≈ 5000–7000 ppm).

4.2.3. Evaluation of Extractants for Fe(III) Removal

Since Fe(III) is the most readily removed of the component metals, it will be necessary for the extractant to achieve optimum selectivity at this stage. Therefore, each extractant was evaluated for its ability to remove Fe(III) from the residue mixture, as an additional extractant screening stage.

A range of experiments (using an iron rich residue solution) were conducted, and the relative extractabilities of Fe were assessed for each solvent. The results are outlined in Table 4.1.

Amine	pH_i/ pH_f	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	Characteristics	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
Armeen 2C	0.0/ 0.3	14000 14000	30000 30000	8000 8000	12000 12000	PR5 T=10 T=30	16.1 24.3	38.5 40.8	0.0 0.0	0.0 0.0
Armeen 12D	0.0/ 0.4	14000	30000	8000	12000	PR5	38.2	24.3	13.3	13.6
Di-octa-decyl-amine	0.0/0.25	14000	30000	8000	12000	PR5	0.0	24.0	0.0	0.0
Acetyl acetone	0.0/ 0.0	14000 14000	30000 30000	8000 8000	12000 12000	PR2 T=10 T=30	2.4 14.6	40.9 39.7	0.0 0.0	0.0 0.0
OPAP 29%w/v	0.0/ 0.0	14000	30000	8000	12000	PR2	0.0	75.0	0.0	6.0
DEHPA	0.0/ -0.3	14000	30000	8000	12000	PR2	0.0	84.3	0.0	6.0
PJMT	0.0/ 0.4	14000	30000	8000	12000	PR5	47.2	82.4	0.0	0.0

Table 4.1 Fe Rich Residue Solutions – A Comparison; Extractants at 100°C

Solvent = Kerosene, Contact time = 30 minutes

OPAP and DEHPA exhibited good selectivity with high Fe extraction (<75%). Acetyl acetone extracted 40.9% Fe, with 2.4% Cr coextraction after 10 minutes, but after 30 minutes Fe extraction was 39.7%, with 14.6% Cr co-extraction. Although Fe extraction efficiency with acetyl acetone was not as high as that for OPAP or DEHPA, a reasonable degree of selectivity was observed.

In the Armeen 2C system, iron extraction was ~40% after 10 and 30 minutes but with significant Cr extraction (≥16%) in both cases. Armeen 12D exhibited a complete lack of metal selectivity, with Fe extraction at only 24.3%. Dioctadecylamine, although completely selective for Fe under these conditions, achieved only 24.0% Fe extraction. PJMT achieved 82.4% Fe extraction, although significant Cr extraction was observed. Normally the loading capacity of amines is regarded as a limiting factor, but this was not apparent with PJMT. Armeen 12D and dioctadecylamine, however, showed a relatively limited loading capacity, and are therefore less likely to be of potential use for the extraction of large quantities of metal. Fe extraction by Armeen 2C is also not as high as other solvents, low loading efficiencies and coextraction suggested that the amines Armeen 2C, Armeen 12D and dioctadecylamine would not be appropriate.

Thus, DEHPA, OPAP, PJMT and acetyl acetone were selected for further study. In the following sections, each of these extractants is evaluated: the experimental conditions of the residue–solvent systems were varied, with the prime aim of optimizing metal separation conditions, i.e. maximizing extraction efficiency whilst maintaining acceptable selectivities. The extraction behaviour of the solvents with ore solutions has also been briefly investigated.

4.3 Evaluation of Extractants for Solutions of Differing Metal Concentration

The experiments discussed in this section were carried out at 100°C unless otherwise specified.

4.3.1. Acetyl Acetone

The low boiling point and high flash point of acetyl acetone indicate that use of this solvent at 100°C would require special containment. Therefore, investigations of the extraction behaviour of this extractant have been investigated at lower temperatures, from 20°–100°C.

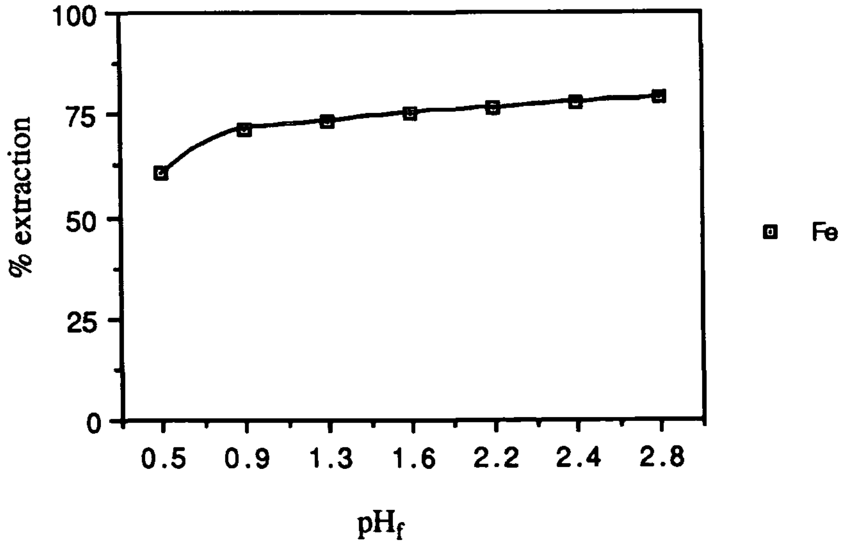
a) Single Metal Solutions

The extraction of Cr, Fe and Al from single metal solutions at 20°C was studied. The effect of pH upon Fe extraction is shown in Table 4.2, and Graph 4.1.

Conditions	pH_i/ pH_f	[Fe] ppm	% Fe(III) extraction
PR 1	0.5/ 0.5	2150	60.5
	0.9/ 0.9	2275	71.4
	1.3/ 1.3	2150	73.4
	1.6/ 1.6	2125	75.3
	2.3/ 2.2	2075	76.5
	2.6/ 2.4	2100	77.9
	3.6/ 2.8	1975	79.0

Table 4.2 Acetyl Acetone – Single Metal System – Fe 20°C

Solvent = Chloroform, Contact time = 30 minutes



Graph 4.1 Acetyl Acetone – Single Metal System – Fe 20°C

Extraction increases from 60.5% at $pH_{i/f}$ 0.5/0.5, to 73.4% at $pH_{i/f}$ 1.3/1.3, with only a slight increase in extraction (to 79.0%) up to $pH_{i/f}$ 3.6/2.8.

Extraction of Cr from single metal solutions, at 40°C, and $pH_{i/f}$ 2.8/2.5, was very low at 1.9% (see Table 4.3).

Conditions	pH_i/ pH_f	Temperature (°C)	[Cr] ppm	% Cr(III) extraction
PR 1	2.8/ 2.5	40	1500	1.9
	2.8/ 2.2	60	1500	5.1
	3.0/ 2.2	60	1500	23.5
	3.2/ 1.4	95	1500	90.9

Table 4.3 Acetyl Acetone – Single Metal (Cr) System – Cr

Solvent = Chloroform, Contact time = 30 minutes

At 60°C, and $pH_{i/f}$ 2.8/2.2, extraction slightly increased to 5.1%. An increase in pH_i to 3.0, at 60°C, led to an equivalent pH_f of 2.2, but an increase in Cr extraction to 23.5% was observed. A high Cr extraction efficiency (90.9%) was obtained at pH_i 3.2 and 95°C. The dramatic increase in Cr extraction for a relatively small increase in pH at 60°C, suggests that the pH plays a dominant role here.

At 20°C, Al extraction was studied with variation in pH (see Table 4.4, Graph 4.2). At $pH_{i/f}$ $\leq$3.2/3.2, zero Al extraction was observed. 26.2% Al was extracted at $pH_{i/f}$ 3.9/3.8, and at $pH_{i/f}$ 4.6/4.0 this value increased to 81.3%. High pH_i's (>90%) were required for >90% Al extraction, where pH_f values were >3.8. The three pH_f points at 3.8, with different extraction values show that pH_i has an important bearing upon extraction, and not just pH_f. At higher Al concentrations (~200 ppm), comparable Al extraction was observed at lower pH's than at Al concentrations of ~50 ppm.

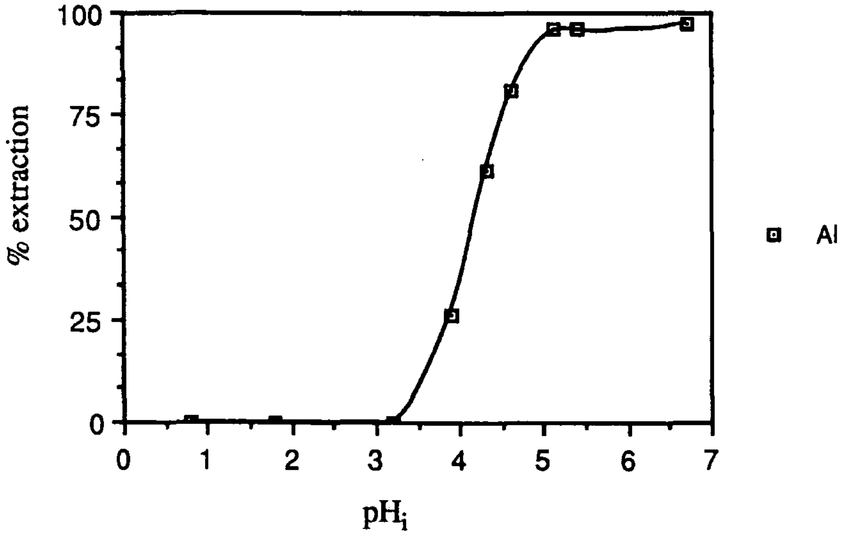
Conditions	pH_i/ pH_f	Temperature (°C)	[Al] ppm	% Al(III) extraction
PR 1	0.8/ 0.8	20	52	0.0
	1.8/ 1.8	20	55	0.0
	3.2/ 3.2	20	44	0.0
	3.9/ 3.8	20	42	26.2
	4.3/ 3.8	20	50	61.2
	4.6/ 3.8	20	47	81.3
	5.1/ 3.8	20	56	96.2
	5.4/ 3.9	20	64	94.1
	6.7/ 4.3	20	42	88.6
PR 1	2.2/ 2.1	20	200	10.2
	2.8/ 2.7	20	200	34.3
	4.0/ 3.6	20	200	44.9
	5.4/ 3.7	20	200	53.8
PR 1	3.2/ 1.9	20	4800	13.5
	3.2/ 1.6	50	4800	20.7
	3.5/ 1.9	20	4800	13.8
	3.5/ 1.6	50	4800	23.6
	3.6/ 2.0	20	4800	14.6
	3.6/ 1.6	50	4800	29.2
PR 2	3.6/ 2.0	20	4800	18.8
	3.6/ 4.6[a]	20	4800	60.0
	3.6/ 1.7	50	4800	39.6
	3.6/ 4.3[a]	50	4800	74.8

[a] OH^- added to artificially increase pH_f.

Table 4.4 Acetyl Acetone – Single Metal Systems – Al

Solvent = chloroform, Contact time = 30 minutes

From pH_i 3.2 to 3.6, the effect of temperature upon extraction was investigated. At 50°C, Al extraction was significantly greater than extraction at 20°C. Although an increase in PR resulted in an increase in absolute metal extraction, the efficiency of use of the solvent is decreased. It is also apparent that changes in Al concentration significantly affected metal extraction in the single metal system.



Graph 4.2 Acetyl Acetone – Single Metal Systems – Al[50 ppm], 20°C

The effect of changing from a single metal aqueous solution to a residue solution containing high concentrations of Cr, Fe, Mg, Al, Na and sulphate, causes a significant change in the complex equilibria influencing extraction. Therefore, the information provided from the single metal systems is limited to general trends in the variation of pH, PR, temperature, and metal concentration. Metal extraction values from single metal systems cannot be transposed to residue solutions.

b) Residue Solutions

i) Fe rich solutions

The extraction behaviour of acetyl acetone with iron rich residue solutions was studied at 20°C (see Table 4.5, Graph 4.3). Complete selective iron extraction was only observed at pH_i/pH_f 0.3/0.3 (43.1 %). An increase in pH_i/pH_f to 2.1/2.1 is accompanied by increases in Fe and Al extraction. Subsequent increases in pH led to decreases in Fe extraction and increases in Al extraction. This is likely to be due to ligand exchange as shown in the following equation.

$$Fe(acac)_a{}^{3-a+} + Al(acac)_b{}^{3-b+} \rightleftharpoons Fe(acac)_{a+1}{}^{2-a+} + Al(acac)_{b-1}{}^{4-b+}$$

a = 0, 1, 2,

b = 1, 2, 3

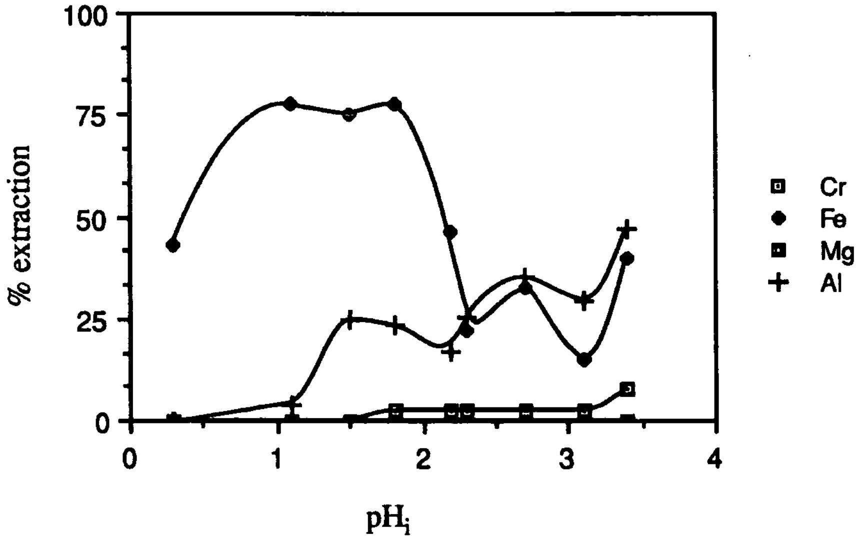
Conditions	pH_i/ pH_f	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 1	0.3/ 0.3	12000	20400	6200	9400	0.0	43.1	0.0	0.0
	1.3/ 1.1	8000	14200	4700	5000	0.0	77.5	0.0	4.0
	1.8/ 1.5	7200	12800	4000	5200	0.0	75.0	0.0	25.0
	2.1/ 1.8	7200	12800	4000	3800	2.7	78.1	0.0	23.7
	2.6/ 2.2	7200	13000	4100	3600	2.8	46.2	0.0	16.7
	2.7/ 2.3	7800	13600	4200	4700	2.6	22.1	0.0	25.5
	3.2/ 2.7	7800	13600	4200	4800	2.6	32.4	0.0	35.4
	3.7/ 3.1	7600	13200	4200	4100	2.6	15.2	0.0	29.3
	4.1/ 3.4	7600	13600	4200	5500	7.9	39.7	0.0	47.3
	2.9/ 2.4	7400	13200	4200	2700	2.7	66.7	0.0	7.4
PR 1	0.0/ 0.0[a]	18000	28400	7400	10000	0.0	22.0	0.0	0.0
	0.0/ 0.0[b]	18000	28400	7400	10000	0.0	20.4	0.0	0.0

[a] Contact time = 10 minutes

[b] Contact time = 120 minutes

Table 4.5 Acetyl Acetone – Fe Rich Residue Solutions, 20°C

Solvent = Chloroform, Contact time = 30 minutes



Graph 4.3 Acetyl Acetone – Fe Rich Residue Solutions, 20°C

The relative stability constants of the species is the determining factor in the position of equilibrium. At low pH, the equilibrium is fully to the left, and at higher pH, significant ligand exchange occurs to supress Fe extraction; i.e. at high pH_f (pH_f >2.0) the presence of Al causes a significant decrease in Fe extraction. A residue solution with Al at 2700 ppm was studied, with Fe extraction significantly higher at 66.7%, and Al coextraction substantially less at 7.4%, than for an Al concentration of 4700 ppm. The equilibrium outlined in Equation 4.1 is therefore not only very dependent upon pH, but also upon the absolute and relative metal concentrations. Slight Cr extraction is also observed at pH_i/pH_f >2.1/1.8 , which will add to the complexity of the ligand exchange equilibria.

Fe extractable complexes form at lower pH's than the Al complexes. Thus, with low pH aqueous solutions, Fe extraction is observed. As pH increases, the stability of the extractable Al complexes increases, and the extractable Al complexes become more stable than the extractable Fe complexes. Thus ligand exchange from Fe species to Al species probably occurs.

At 100°C, (see Table 4.6), iron was extracted at pH 0.0, (40.9%) with 2.4% Cr coextraction, after 10 minutes. An increase in contact time led to a sharp increase in Cr extraction, which caused a small reduction in Fe extraction.

Conditions	pH_i/ pH_f	Time (mins)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 2	0.0/	10	14000	30000	8000	12000	2.4	40.9	0.0	0.0
	0.0/	30	14000	30000	8000	12000	14.6	39.7	0.0	0.0
	0.0/ -0.1	120	1400	30000	8000	12000	54.3	37.3	0.0	0.0

Table 4.6 Acetyl Acetone – Fe Rich Residue Solutions, 100°C
Solvent = Kerosene

The formation rate of the extracted Cr–acetylacetonate complex is slow, due to the high hydration energy of $Cr(H_2O)_6^{3+}$. At 20°C, insufficient energy is available to overcome the activation barrier of acetylacetonate substitution of H_2O. At, 100°C, however, Cr–acetylacetonate is slowly formed, and Cr extraction is observed. Due to the relatively high stability of Cr–acetylacetonate the equilibrium involving ligand exchange between Fe and Cr is heavily weighted towards Cr (i.e. towards the right of Equation 2).

$$Cr(acac)_a{}^{3-a\,+} + Fe(acac)_b{}^{3-b\,+} \rightleftharpoons Cr(acac)_{a+1}{}^{2-a\,+} + Fe(acac)_{b-1}{}^{4-b}$$

$a = 0, 1, 2,$

$b = 1, 2, 3$

Aqueous phase metal concentrations are fairly 'high' in residue solutions, and therefore when significant metal extraction is observed, the system is operating in the region of full solvent loading capacity. Thus, if the solvent is fully loaded with Fe, subsequent Cr extraction reduces Fe extraction.

ii) Al, Cr, Mg high solutions

From solutions where Fe has been effectively removed (see Table 4.7), the coextraction of Cr and Al, at 100°C, and pH_i 0.0 and 0.4 was observed. At 20°C, neither Cr or Al were extracted at these pH.

Conditions	pH_i/ pH_f	Temp. (°C)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR1	0.4/ 0.4	20	15600	90	7600	10500	0.0	-	0.0	0.0
	0.4/ 0.4	20	15600	90	7600	10500	0.0	-	0.0	0.0
PR1	0.0/ 0.0	100	12800	60	7600	10600	6.5	-	0.0	7.5
	0.4/ 0.4	100	15600	90	7600	10500	20.0	-	0.0	55.5
	0.4/ 0.4	100	15600	90	7600	10500	22.5	-	0.0	55.5

Table 4.7 <u>Acetyl Acetone – Cr, Al, Mg High Residue Solutions</u>

Solvent = Chloroform, Contact time = 30 minutes

iii) Cr, Mg only solutions

Cr, Mg only residue solutions were briefly studied at 100°C (see Table 4.8). Selective Cr extraction (up to 76.7%) was observed over the $pH_{i/f}$ range up to

5.8/2.4. Although, $Mg(acac)_2$ is formed at higher pH's, this species is non–extractable.

Conditions	pH_i/ pH_f	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 1	0.25/ 0.2	19000	20	2700	80	26.9	-	0.0	-
	3.5/ 1.1	15000	20	2000	90	28.1	-	0.0	-
	5.8/ 2.4	2100	33	1400	10	76.7	-	0.0	-

Table 4.8 Acetyl Acetone – Cr, Mg only Residue Solutions, 100°C

Solvent = Kerosene, Contact time = 30 minutes

Table 4.9 outlines an extraction cycle, illustrating the consecutive extraction of Fe, Al and Cr. Two stages effected 99.0% Fe extraction, with only 3.1% Al extraction, pH adjustment allowed Al extraction at 20°C to be completed, before the temperature was raised for Cr extraction.

Conditions	pH_i/ pH_f	Temp. (°C)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 1	1.5/ 1.3	20	9000	15750	4500	4750	0.0	86.7	0.0	3.1
	1.5/ 1.4	20	9000	2100	4500	4600	0.0	92.3	0.0	0.0
	3.6/ 2.0	20	9000	162	4500	4600	0.0	97.5	0.0	86.7
	1.2/ 1.2	20	9000	16	4500	612	0.0	-	0.0	84.0
	1.5/ 1.3	70	9000	0	4500	98	46.5	-	0.0	-

Table 4.9 Acetyl Acetone – Extraction Cycles of Residue Solutions

Solvent = Chloroform, Contact time = 30 minutes

4.3.2. DEHPA

a) Residue Solutions

i) Fe rich residue solutions

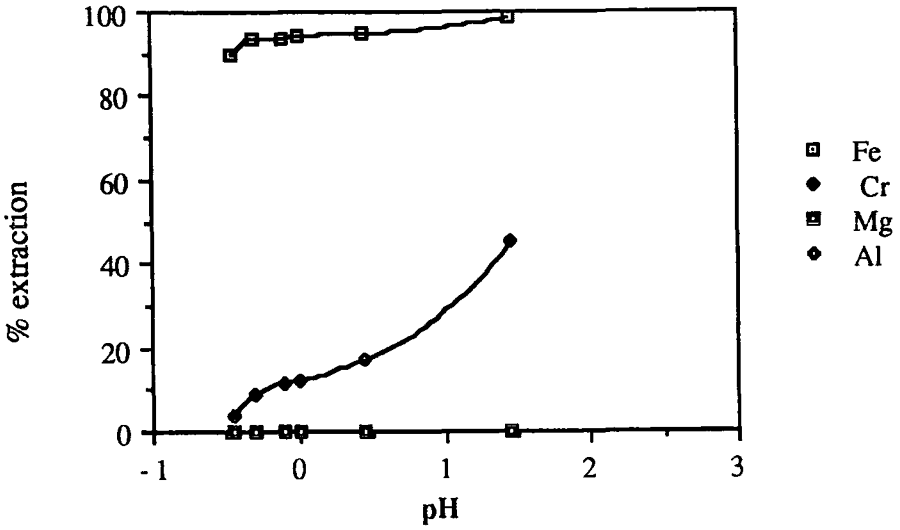
The extraction behaviour of DEHPA with iron rich residue solutions was studied at 100°C, at PR's of 1, 2 and 4 (see Table 4.10).

Conditions	pH_i/ pH_f	Time (mins)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 1	0.0/ -0.2	30	16400	34400	9600	11700	0.0	44.4	0.0	0.0
	0.5/ 0.05	30	14800	30800	8120	10800	0.0	59.7	0.0	0.9
PR 2	-0.3/-0.4	30	18400	36800	10440	14000	0.0	65.2	0.0	0.0
	-0.1/-0.3	30	22400	32400	9840	11500	0.0	81.5	0.0	4.3
	0.0/ -0.3	30	22400	33200	9880	11600	0.0	84.3	0.0	6.0
	0.2/ -0.1	30	25200	31200	9400	11100	0.0	87.2	0.0	6.3
	0.4/ 0.0	30	23200	33600	9200	11200	0.0	90.5	0.0	12.5
	0.6/ 0.1	30	17600	28800	8000	11300	0.0	91.7	0.0	15.0
	1.5/0.4	30	14000	30000	7680	10600	0.0	89.9	0.0	21.0
	2.6/ 0.6	30	17200	26000	7320	10400	0.0	98.4	0.0	47.1
	0.0/ -0.3	40	14000	30000	8000	12000	0.0	87.8	0.0	5.3
PR4	-0.8/-0.8	30	14000	34400	7600	12800	0.0	80.2	0.0	1.6
	-0.5/-0.5	30	15200	35600	8400	13400	0.0	89.9	0.0	3.0
	-0.5/-0.4	30	15200	34800	9280	12300	0.0	89.7	0.0	4.1
	-0.3/-0.4	30	17600	31200	8840	11100	0.0	93.6	0.0	9.0
	-0.1/-0.3	30	16000	30800	9000	11000	0.0	93.5	0.0	11.7
	0.0/ -0.3	30	16400	34400	9600	11700	0.0	94.4	0.0	12.0
	0.5/ 0.0	30	14800	30800	8120	10800	0.0	94.9	0.0	17.0
	1.5/ 0.1	30	13600	30000	7680	10600	0.0	98.9	0.0	45.1

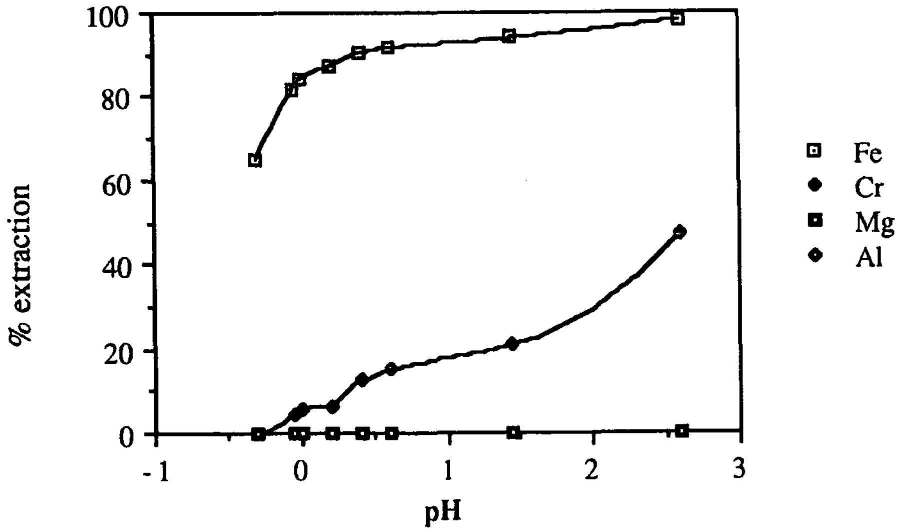
Table 4.10 DEHPA – Fe Rich Residue Solutions, 100°C

The primary object of the study was to achieve high Fe extraction, with low or zero Al co–extraction, by variation of pH and PR. At PR1, less than 1% Al extraction was observed at and below $pH_{i/f}$ 0.5/0.5. At PR2, at and below $pH_{i/f}$ –0.1/0.3 less than 5% Al extraction was observed. At PR4, and $pH_{i/f}$ –0.5/–0.4

only 4.1% Al was extracted. The respective Fe extraction efficiencies were 59.7%, 81.5%, and 89.7%. Thus, it appears that selective and efficient Fe extraction may be improved by increasing the PR and acidity. However, if a high PR is used, the pH must be very low to prevent significant Al coextraction (see Graphs 4.4 and 4.5).



Graph 4.4 DEHPA – Fe Rich Residue Solutions, 100°C, PR4



Graph 4.5 DEHPA – Fe Rich Residue Solutions, 100°C, PR2

ii) Fe medium residue solutions

Fe extraction by DEHPA is likely to be ~85–90% efficient, yielding raffinates of the concentrations studied in Table 4.11. Extraction of Fe was repeated at $pH_i/_f$ 0.4/0.4 to gauge the accuracy of the result. An increase in pH to $pH_i/_f$ 0.7/0.3, substantially decreased iron extraction to 47.8%. This is due to significant Al extraction (45.2%), the equilibria involving ligand exchange between Fe and Al favouring Al complexation and extraction, i.e. Al extracted complexes probably have higher stability constants than the Fe extracted complexes.

Conditions	pH_i/ pH_f	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 1	-0.4/-0.4	15200	3600	9200	11700	0.0	90.2	0.0	0.0
	-0.4/-0.4	15200	3600	9200	11700	0.0	89.9	0.0	0.0
	-0.4/-0.4	15200	3600	9200	11700	0.0	90.8	0.0	0.0
	0.7/ 0.3	17600	2300	13800	11000	0.0	47.8	0.0	45.2
	2.2/ 0.5	14400	2900	12000	11000	0.0	48.3	0.0	50.7
PR 2	-0.4/-0.4	15200	3600	9200	11700	0.0	92.8	0.0	0.0

Table 4.11 DEHPA – Fe Medium Residue Solutions, 100^{o}C

Contact time = 30 minutes

An increase in the PR to 2 increased Fe extraction slightly to 92.8%, (at $pH_i/_f$ 0.4/0.4), whilst maintaining zero Al coextraction.

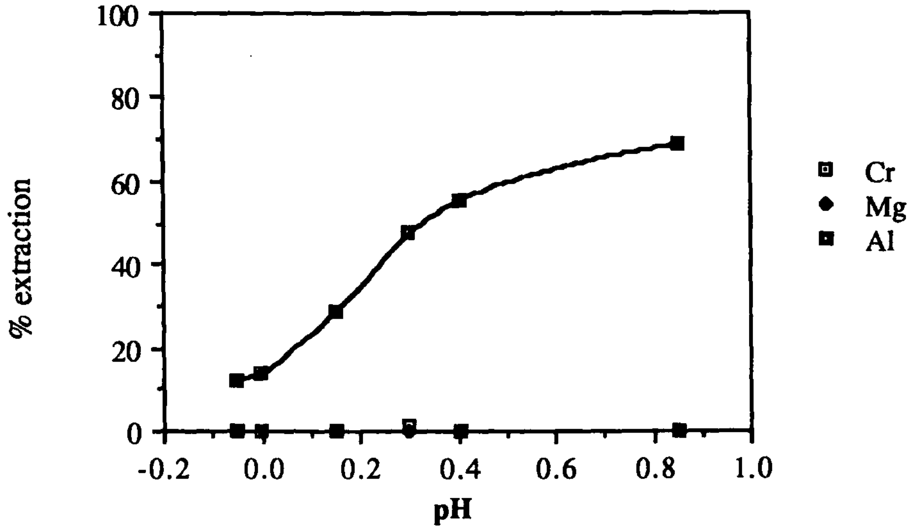
iii) Al, Cr, Mg high residue solutions

Over 90% selective Fe extraction from solutions of medium Fe concentration would yield solutions with concentrations as those in Table 4.12; i.e. solutions of high Al, Cr and Mg concentrations. Over the full range of conditions studied, Mg was not extracted at all, and negligible to zero Cr extraction was observed in each case. The effect upon extraction of variation of pH, at PR1, is shown in Graph 4.6 and at PR4 in Graph 4.7.

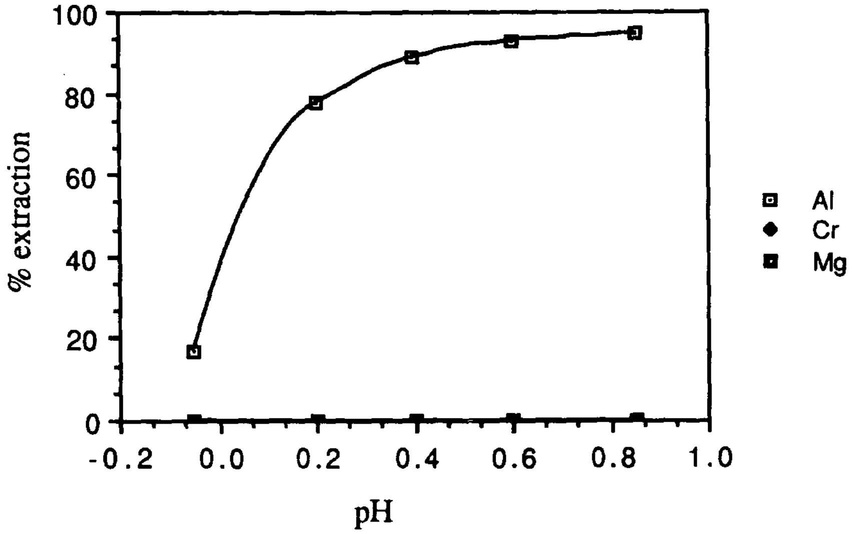
Conditions	pH$_i$/ pH$_f$	Time (mins)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 1	-0.1/-0.1	30	19200	260	9320	11400	0.0	88.9	0.0	12.2
	0.0/ 0.0	30	12800	60	7600	10600	0.0	-	0.0	13.8
	0.2/ 0.2	30	18400	10	9080	9200	0.0	-	0.0	28.6
	0.3/ 0.3	30	16400	40	8000	10500	1.2	-	0.0	47.6
	0.4/ 0.3	30	16000	60	7640	11000	0.0	-	0.0	55.5
	0.4/ 0.3	60	16000	60	7640	11000	2.5	-	0.0	55.5
	0.6/ 0.4	30	20800	360	10560	14500	0.0	89.2	0.0	36.4
	0.8/ 0.7	30	22400	380	11440	15750	0.0	77.1	0.0	44.2
	0.9/ 0.8	30	18000	10	9080	9200	0.0	-	0.0	68.8
PR 2	0.4/ 0.1	30	16000	30	7760	11000	0.0	-	0.0	74.2
PR 4	-0.1/-0.1	30	19200	260	9320	11400	0.0	96.2	0.0	16.7
	0.2/ 0.0	30	17000	10	8500	11000	0.0	-	0.0	77.6
	0.4/ 0.1	30	16000	20	7760	11000	0.0	-	0.0	89.1
	0.6/ 0.2	30	18500	10	9200	11000	0.0	-	0.0	92.9
	0.9/ 0.9	30	18000	10	9080	9200	0.0	-	0.0	94.8
PR 8	0.4/ 0.1	30	16000	30	7760	11000	0.0	-	0.0	93.6

Table 4.12 <u>DEHPA - Al, Cr, Mg High Residue Solutions, 100°C</u>

Contact time = 30 minutes

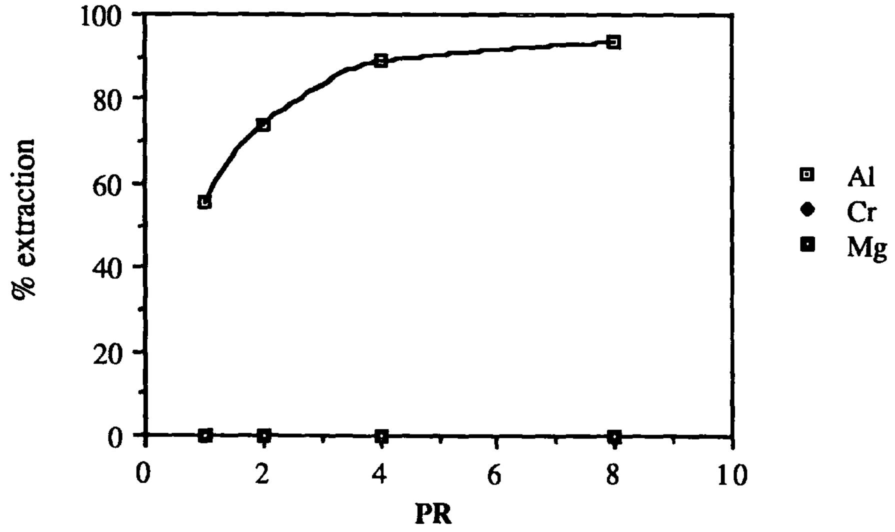


Graph 4.6 <u>DEHPA - Al, Cr, Mg High Residue Solutions, 100°C, PR1</u>



Graph 4.7 DEHPA – Al, Cr, Mg High Residue Solutions, 100°C, PR4

In both cases Al extraction appears to be completely selective up to the highest pHi (0.9) studied, where Al extraction at PR1 and PR4, was 68.8% and 94.8% respectively. Graph 4.6 shows that the rate of increase in % Al extraction decreases around pHi 0.4. Thus, a study of the effect upon extraction of variation in PR at pHi 0.4 was undertaken (see Graph 4.8). The optimum PR for Al extraction at pHi 0.4 appeared to be PR4 (89.1%).



Graph 4.8 DEHPA – Al, Cr, Mg High Residue Solutions, 100°C, pHi 0.4

iv) Al medium, Cr high residue solutions

Solutions of medium Al and high Cr concentration were studied at PR1 and 2 (see Table 4.13). Selective and virtually complete Al extraction is possible at PR1, $pH_{i}/_{f}$ 1.8/1.4, and at PR2, $pH_{i}/_{f}$ in 0.7. However, a one stage extraction of Al is likely to accomplish complete Al extraction from the Al, Cr, Mg high residue solutions.

v) Cr, Mg only residue solutions

Cr, Mg only residue solutions were examined over a wide range of pH, PR and contact times in an effort to obtain conditions which led to selective and efficient extraction of either of the two metals (see Table 4.14). At PR1, up to $pH_{i}/_{f}$ 0.6/0.6, Cr and Mg extraction were both zero. At PR2, the system was studied over the pH_i range 0.2 to 6.7. (See Graph 4.9) from pH_i 0.2 to 3.8, Cr extraction was effectively zero, with Mg extraction gradually increasing from zero to 37.1%. At $pH_{i}/_{f}$ 6.7/2.4, Cr extraction did occur (13.2%), with Mg extracted to 66.9%. The rate of extraction (i.e. rate of formation of the extracted metal complexes) was examined at pH_i 1.2, at PR2 and PR4. Cr extraction was only observed after $\geq$2 hours. The rate of Mg extraction did not increase significantly after 5 minutes, at either PR. An experiment with low concentrations of Cr and Mg obtained 75.4% selective Mg extraction at PR2, $pH_{i}/_{f}$ 4.0/2.2, after 30 minutes. The results from the experiments in Table 4.14 indicate that as long as the contact time remains between 5 and 30 minutes, and the pH_i does not exceed ~3.5 (depending upon PR), selective Mg extraction may be obtained. Continued selective Mg extraction yields a solution of chromic sulphate.

The sequence of metal extraction when using DEHPA alone is Fe, Al, Mg, Cr. However, other extractants may extract Cr before Al or Mg to give raffinates containing only Al and Mg. Therefore a study of the extraction behaviour of DEHPA with Al, Mg high residue raffinates was undertaken (see Table 4.16).

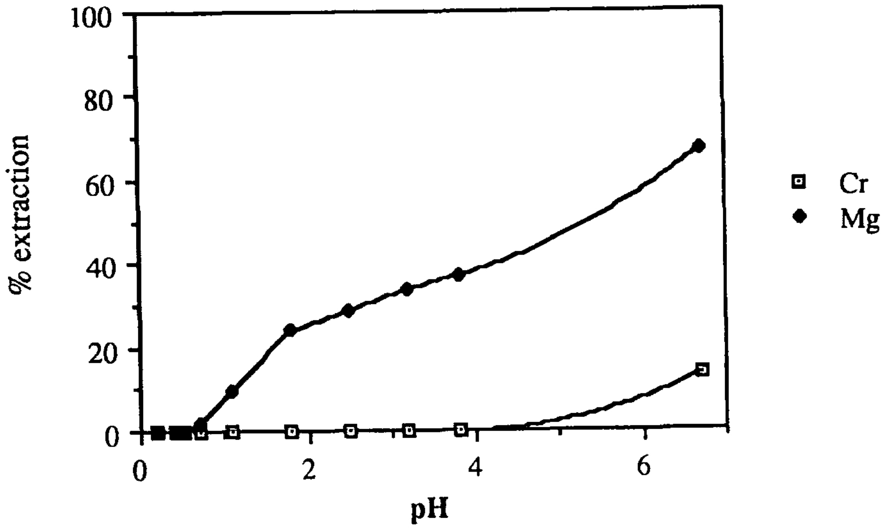
Conditions	pH_i/ pH_f	Time (mins)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 1	0.0/ 0.0	30	28000	20	10000	800	0.0	-	0.0	-
	0.3/ 0.3	30	20000	10	9500	400	0.0	-	0.0	-
	0.6/ 0.6	30	16400	10	9120	100	0.0	-	0.0	-
PR 2	0.2/ 0.2	30	16000	70	10200	200	0.0	-	0.0	-
	0.4/ 0.3	30	15000	50	10000	200	0.0	-	0.0	-
	0.4/ 0.4	30	22000	10	9800	100	3.6	-	2.0	-
	0.5/ 0.5	30	16000	10	9000	500	0.0	-	0.0	-
	0.7/ 0.6	30	16000	40	9400	200	1.6	-	2.1	-
	1.1/ 0.9	30	16000	60	8840	300	0.0	-	9.5	-
	1.8/ 1.3	30	16000	50	7840	300	0.0	-	24.0	-
	2.5/ 1.4	30	16000	50	10800	300	0.0	-	28.9	-
	3.2/ 1.3	30	15200	10	9320	500	0.0	-	33.9	-
	3.8/ 2.4	30	12000	40	7000	300	0.0	-	37.1	-
	6.7/ 2.4	30	17000	10	10300	500	13.2	-	66.9	-
	1.8/ 1.3	30	10800	0	1440	100	2.6	-	51.4	-
	1.2/	1	9200	30	4500	0	0.0	-	13.3	-
	1.2/	5	9200	30	4500	0	0.0	-	21.7	-
	1.2/	15	9200	30	4500	0	0.0	-	21.9	-
	1.2/	30	9200	30	4500	0	0.0	-	24.2	-
	1.2/ 0.9	120	9200	30	4500	0	4.0	-	24.8	-
	1.6/ 1.8	30	5600	20	300	0	0.0	-	35.5	-
	2.6/ 2.1	30	5600	20	300	0	0.0	-	46.8	-
	3.0/ 2.3	30	5600	20	300	0	0.0	-	64.5	-
	4.0/ 2.2	30	5600	20	300	0	0.0	-	75.4	-
	3.0/ 2.0	500	5600	20	300	0	42.3	-	67.7	-

Conditions	pH_i/ pH_f	Time (mins)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 1	0.3/ 0.1	30	16200	10	8000	2600	0.0	-	0.0	46.2
	0.4/ 0.4	30	14400	10	8400	1300	0.0	-	0.0	92.3
	0.5/ 0.5	90	17600	10	10000	3300	2.3	-	0.0	87.9
	0.6/ 0.5	30	16200	10	8000	5500	0.0	-	0.0	52.7
	1.8/ 1.4	30	10800	310	3680	4700	0.0	100	0.0	97.9
	3.9/ 1.8	30	10800	360	4400	5400	0.0	100	24.5	98.1
PR 2	0.7/ 0.5	30	16400	0	7840	3600	0.0	-	0.0	97.2
	0.8/ 0.7	30	18000	140	7920	6700	0.0	-	0.0	93.3

Table 4.13 DEHPA – Cr High, Al Medium Residue Solutions, 100°C

PR 4	1.2/	1	11600	30	5700	100	0.0	-	17	-
	1.2/	5	11600	30	5700	100	0.0	-	22	-
	1.2/	15	11600	30	5700	100	0.0	-	28	-
	1.2/	30	11600	30	5700	100	0.0	-	33	-
	1.2/	60	11600	30	5700	100	0.0	-	33	-
	1.2/	120	11600	30	5700	100	0.0	-	33	-
	1.2/ 0.8	1140	11600	30	5700	100	32.0	-	13	-
PR 8	1.8/ 0.6	30	12800	0	8600	0	3.1	-	43.9	-
	3.5/ 1.6	30	12800	0	4280	0	9.4	-	70.1	-
	2.1/ 1.4	30	12400	60	7200	300	0.0	-	46.6	-
	3.8/ 1.7	30	12400	0	7200	300	0.0	-	54.3	-
PR32	1.8/ 0.8	30	19200	50	7000	200	0.0	-	57.1	-
	3.4/ 1.1	30	12200	0	4540	100	8.2	-	72.2	-

Table 4.14 DEHPA – Cr, Mg only Residue Solutions, 100°C



Graph 4.9 DEHPA – Cr, Mg only Residue Solutions, 100°C

Conditions	pH_i/ pH_f	Time (mins)/ Temperature (°C)	[Cr] ppm	% Cr(III) extraction
PR 1	0.9/ 0.9	15/ 20	10000	0.0
Chromic	3.7/ 1.9	15/ 20	10000	13.2
Sulphate				
	0.7/ 0.7	15/ 20	1000	3.1
	3.0/ 1.6	15/ 20	1000	59.6
	5.1/ 1.9	15/ 20	1000	74.1
PR 1 Chromic Chloride	5.1/ 1.6	15/ 20	1000	74.1
PR 2	3.6/	15/ 128	10250	82.9
Chromic	3.6/	30/ 128	10250	88.5
Sulphate	3.6/ 1.2	60/ 128	10250	95.0

Table 4.15 DEHPA – Synthetic Cr Solutions

vi) Al, Mg only residue solutions

Cr extraction (1.5% –3.3%) was observed in every case with the extraction of Al. Over a $pH_i/_f$ range of –0.2/–0.2 to 1.8/1.1, zero Mg extraction was observed with Al extraction increasing from 10.3% to 99.5%.

Conditions	pH_i/ pH_f	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 2	-0.2/-0.2	600	20	4400	6800	3.3	-	0.0	10.3
	0.4/ 0.2	600	20	5200	6800	1.7	-	0.0	61.8
	0.9/ 0.6	610	20	6000	6900	1.6	-	0.0	87.0
	1.4/ 1.0	650	20	5440	7000	1.5	-	0.0	99.0
	1.8/ 1.1	690	20	5700	7800	2.9	-	0.0	99.5

Table 4.16 DEHPA – Al, Mg only Residue Solutions, 100°C

Contact time = 30 minutes

b) Single Metal Solutions

The results shown in Table 4.15 demonstrate that DEHPA can be used to extract Cr(III) from a single metal solution.

c) Ore Studies

As the extraction cycle of residue with DEHPA appeared to have potential for industrial application, a brief study of ore solutions with DEHPA was undertaken. Cr(VI) in the ore solutions (due to excess addition of CrO_3 in the digestion stage) was removed by TBP (see Section 4.8).

Iron was efficiently extracted from Fe rich ore solutions at 20°C and 100°C, (see Table 4.17) although Al coextraction was observed at pH_i ~1.0. 95% Fe extraction was observed at PR1, $pH_{i/f}$ 0.5/0.5, indicating the potential for selective and efficient Fe extraction, at 100°C.

Al, Cr, and Mg high ore solutions were studied at 100°C (See Table 4.18). The results at PR1 show >90% Al extraction where Al concentration is 3000 ppm, but depressed Al extraction (75.4%) at Al concentration 5700 ppm even at $pH_{i/f}$ 3.0/1.4. At PR2, Al extraction is –100%, as the solvent loading capacity is not limiting Al extraction.

Conditions	pH_i/ pH_f	Time (mins)/ Temp. °C	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 2	1.0/ 0.3	30/100	34000	18000	4000	5500	0.0	97.0	0.0	18.3
PR 1	0.5/ 0.5	30/ 20	22000	8500	2310	3900	0.0	95.8	0.0	0.0
	0.7/ 0.3	30/ 20	27000	7500	2080	3500	1.3	96.7	0.0	4.3
	1.6/ 1.0	30/ 20	31200	8500	1980	3600	1.3	99.2	4.0	11.1
	3.0/ 1.9	30/ 20	18000	8600	2100	3400	0.0	91.9	1.4	29.4
	3.8/ 2.8	30/ 20	16250	7300	1380	2900	2.7	77.6	32.7	85.9
PR 1	0.8/ 0.4	30/ 20	17600	1800	1630	2200	0.0	63.4	0.0	0.0
	1.3/ 1.3	30/ 20	18800	4650	1750	2300	0.0	62.4	0.0	14.8

Table 4.17 DEHPA – Fe Rich and Medium Ore Solutions

Conditions	pH_i/ pH_f	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 1	0.9/ 0.9	34000	550	2000	3600	0.6	98.0	0.0	91.7
	3.0/ 1.4	33500	280	3150	5700	0.0	96.4	0.0	75.4
	3.5/ 1.4	18500	210	1600	3000	7.8	97.6	16.0	100
PR 2	0.9/ 0.9	34500	540	2110	3900	13.0	98.1	0.0	100
	1.3/ 0.7	29000	165	4150	2425	29.3	63.6	4.8	100
	3.0/ 1.3	33500	280	3150	5700	0.0	96.4	0.0	98.2
	3.5/ 1.4	13000	450	1800	2700	14.3	97.8	35.7	100
	3.6/ 1.5	22500	430	1600	2900	8.9	97.6	16.6	100
PR 1	1.3/ 1.0[a]	29000	165	4150	2425	6.9	-	2.4	58.8
PR 2	3.5/ 1.4[b]	23500	430	1620	2900	33.0	-	31.9	100
	4.0/ 2.0[b]	23500	430	1620	2900	50.8	-	64.0	100
PR 4	3.6/ 1.2[c]	23500	430	1620	2900	90.2	-	41.4	100

[a] 20°C

[b] 140°C

[c] 140°C, 240 minutes

Table 4.18 DEHPA – Al, Cr, Mg High Ore Solutions, 100°C

However, the concentration of Al does affect Cr extraction, e.g. where Al concentration is 5700 ppm (approximately double the Al concentration of the other solutions), zero Cr co–extraction is observed, whereas significant Cr coextraction is observed in the other cases. This demonstrates the controlling effect over selectivity of metal concentration in mixed metal solutions. The high solvent loading of Al (5700 ppm) preventing Cr co–extraction.

The ore solution in Table 4.19 and the counterpart solutions in Table 4.14, both contain similar concentrations of Fe and Al, but in residue solutions the Cr:Mg ratio is ~16000:8000, (i.e. 2:1), whereas in ore solutions this ratio is in 30000:3000 (i.e. 10:1). At $pH_i \leq 3.0$ PR2, significant selective Mg extraction is observed from residue solutions, but significant coextraction of Cr and Mg is observed from ore solutions. In Table 4.19, at PR2, the ratios of %Cr/%Mg extraction is greater when there are higher Cr ratios in solutions, i.e. the relative concentrations of Cr and Mg in these solutions appears to exert a controlling influence over the metal extraction values. Artificial variation of Na^+ in ore solution (e.g. by addition of Na_2SO_4) over the range 170 ppm to 300 ppm, did not significantly alter the metal extraction values.

At 20°C, zero Cr and Mg extraction was observed at $pH_{i/f} \leq 5.7/1.9$, and at $pH_{i/f}$ 6.4/1.6 only 3.7% Mg extraction was observed. This clearly demonstrates the requirement of elevated temperatures for efficient Cr and Mg extraction, with these solutions.

The extraction equation involving DEHPA is represented in Equation 3. (HA = DEHPA).

$$H_2A_{2\,org} + M(OH)^{2+}_{aq} \rightleftharpoons M(OH)A_{2\,org} + 2H^+_{aq} \qquad (3)$$

Cr is extracted as Cr $(OH)^{2+}$ by DEHPA from sulphate media [4.7]. The DEHPA dimer exists in solution and must be cleared before metal complexation can occur.

Conditions	pH_i/ pH_f	Time (mins)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 1	3.3/ 1.3	30	30500	27	3770	265	27.9	-	29.7	-
	3.3/ 3.0[a]	30	30500	27	3770	265	57.4	-	69.5	-
PR 2	2.7/ 1.6	30	30500	6	3600	500	19.7	-	21.7	-
Cr	3.3/ 1.9	30	30500	6	3600	500	24.6	-	31.3	-
high	3.9/ 2.2	30	30500	6	3600	500	37.7	-	53.9	-
PR 2	1.7/ 1.6	60	16500	7	1426	20	9.1	-	40.0	-
Cr	1.7/ 1.6[b]	60	16500	7	1425	20	9.1	-	39.6	-
med.	1.7/ 1.6[c]	60	16500	7	1425	20	9.1	-	38.2	-
	1.7/ 1.6[d]	60	16500	7	1425	20	9.1	-	40.9	-
	3.4/ 1.8	30	15500	10	550	0	12.9	-	66.4	-
PR 2	1.6/ 1.5	30	9200	0	900	0	12.9	-	33.9	-
	2.0/ 1.5	30	8500	20	1065	30	11.8	-	46.0	-
	5.0/ 1.6	30	6500	10	475	0	23.1	-	58.9	-
PR 2.5	2.7/ 1.7	30[e]	11400	125	750	228	0.0	-	0.0	-
	3.5/ 1.8	30[e]	11400	125	750	228	0.0	-	0.0	-
	4.3/ 1.8	30[e]	11400	125	750	228	0.0	-	0.0	-
	5.7/ 1.9	30[e]	6750	125	550	130	0.0	-	0.0	-
	6.4/ 1.6	30[e]	8400	125	675	200	0.0	-	3.7	-

[a] OH^- added to artificially increase pH_f

[b] $[Na^+]_i$ = 170 ppm, $[Na^+]_f$ = 40 ppm.

[c] $[Na^+]_i$ = 200 ppm, $[Na^+]_f$ = 65 ppm.

[d] $[Na^+]_i$ = 300 ppm, $[Na^+]_f$ = 100 ppm

[e] 20°C

Table 4.19 DEHPA – Cr, Mg only Ore Solutions, 100°C

4.3.3. OPAP

a) Residue Solutions

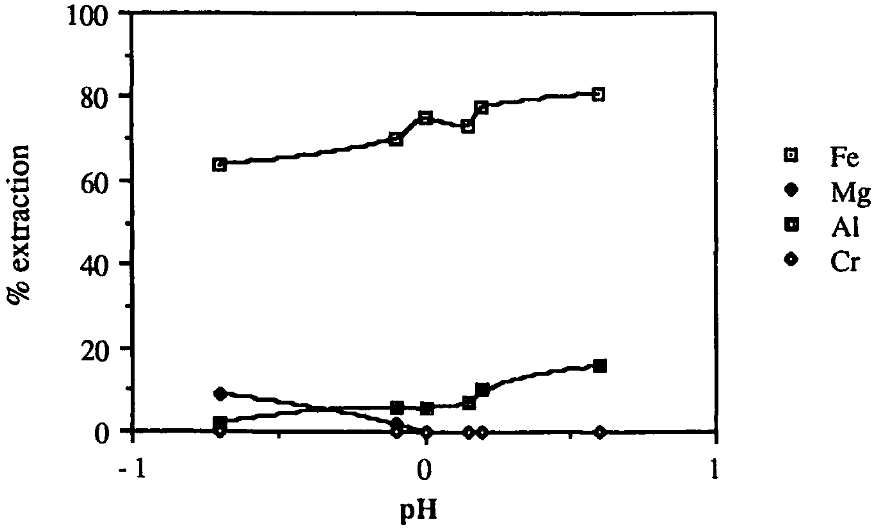
i) Fe rich solutions

The semi–solid, OPAP, was used at various concentrations in kerosene. With Fe rich residue solutions, the OPAP solvents generally extracted Fe efficiently at low pH, but with Al coextraction (see Table 4.20 and Graph 4.10).

Conditions	pH_i/ pH_f	Conc. %w/v	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 4	0.7/	22	12000	26400	4680	10100	3.3	89.4	19.7	49.5
PR 2	-0.7/-0.8	29	13000	27000	7500	11000	0	64	0	2
	-0.1/-0.2	29	13000	27000	7500	11000	0	70	0	6
	0.0/ 0.0	29	13000	27000	7500	11000	0	75	0	6
	0.15/ 0.0	29	13000	27000	7500	11000	0	73	0	7
	0.15/ 0.0	29	13000	27000	7500	11000	0	78	0	10
	0.6/ 0.2	29	13000	27000	7500	11000	0	81	0	16
PR 3	-0.7/-0.8	29	13000	27000	7500	11000	4	92	3	22
	-0.1/-0.3	29	13000	27000	7500	11000	0	91	4	26
PR 2	-1.2/-1.2	35	13000	27000	7500	11000	0	89	0	2
	-0.7/-0.8	35	13000	27000	7500	11000	0	88	0	12
	-0.5/-0.6	35	13000	27000	7500	11000	0	86	0	12
	-0.1/-0.3	35	13000	27000	7500	11000	0	87	0	15
	0.2/-0.1	35	13000	27000	7500	11000	0	88	0	23
PR 4	0.2/-0.2	35	13000	27000	7500	11000	0	99	0	89
PR 2	-0.9/-0.9	45	12000	26000	7000	10700	0	97	0	22
	-0.1/-0.6	45	12000	26000	7000	10700	0	97	0	40

Table 4.20 OPAP – Fe Rich, Residue Solutions, 100°C

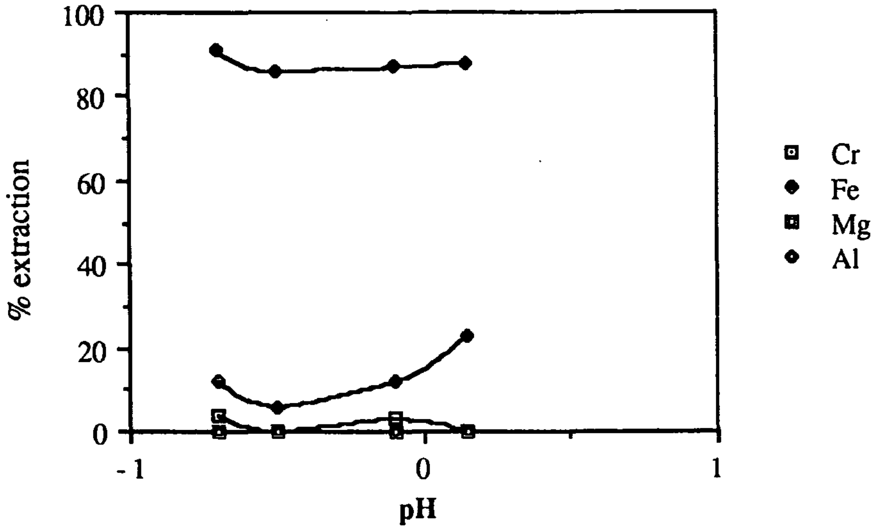
Contact time = 30 minutes



Graph 4.10 OPAP 29% $^{w}/_{v}$, Fe Rich Residue Solutions, 100°C

Variation of pH with 29% $^{w}/_{v}$ OPAP, at PR2, showed a gradual increase in Fe extraction with pH (from 64% to 81% over the $pH_{i/f}$ range –0.7/–0.8 to 0.6/0.2). Al coextraction was also observed, increasing from 2% to 16% over this pH range. At PR3, OPAP extracted 91% Fe at $pH_{i/f}$ –0.1/–0.3, but Al co–extraction was high, at 26%.

An increase in OPAP concentration to 35% $^{w}/_{v}$ showed improved Fe extraction (86–89%) over the $pH_{i/f}$ region –1.2/–1.2 to 0.2–0.1. Al coextraction gradually increased with pH, from 2% up to 23% (see Graph 4.11).



Graph 4.11 <u>OPAP 35% $^{w}/_{v}$, Fe Rich Residue Solutions, 100°C</u>

From PR2 to PR4, (with OPAP 35% $^{w}/_{v}$), metal extraction at pH_{i} 0.2 increased from 88% Fe and 23% Al extraction, to 99% Fe, and 89% Al extraction. It appears that OPAP 35% $^{w}/_{v}$ would be suitable for removing iron (90%) from residue solution without any requirements for base addition. The Al co–extraction (~10%) could be removed by scrubbing. OPAP 45% $^{w}/_{v}$ coextracted 22% Al with 97% Fe, at the highly acidic $pH_{i/f}$ of –0.9/–0.9. Thus, this strength of OPAP would appear too high as metal selectivity would be compromized.

ii) Fe medium solutions

If solutions of medium Fe concentration (2000–8000 ppm) were to be processed by OPAP, the only way to achieve selectivity for Fe would be to reduce the amount of available extractant, e.g. reduce PR to 0.5. At PR 0.5, OPAP 29% $^{w}/_{v}$ extracted 74% Fe (7600 ppm) at $pH_{i}/_{f}$ –0.5/–0.5, but at any higher pH or PR, Al co–extraction was observed (see Table 4.21).

Conditions	pH_i/ pH_f	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 0.5	-0.5/-0.5	25000	7600	8400	10300	0	74	0	0
	-0.5/-0.5	20400	2000	8640	10400	2	91	0	13
	0.4/ 0.1	20000	2400	6800	8600	2	91	0	31
PR 1	-0.5/-0.5	24000	7500	8500	10000	2	56	0	11
	0.4/ -0.1	16000	7200	8300	11000	6	71	0	70
	1.0/ 0.7	10400	2400	5300	7100	4	100	0	92
PR 4	0.2/ 0.0	13200	5000	5660	10200	8	100	7	74

Table 4.21 OPAP – Fe Medium Residue Solutions, 100°C

OPAP 29% $^{w}/_{v}$

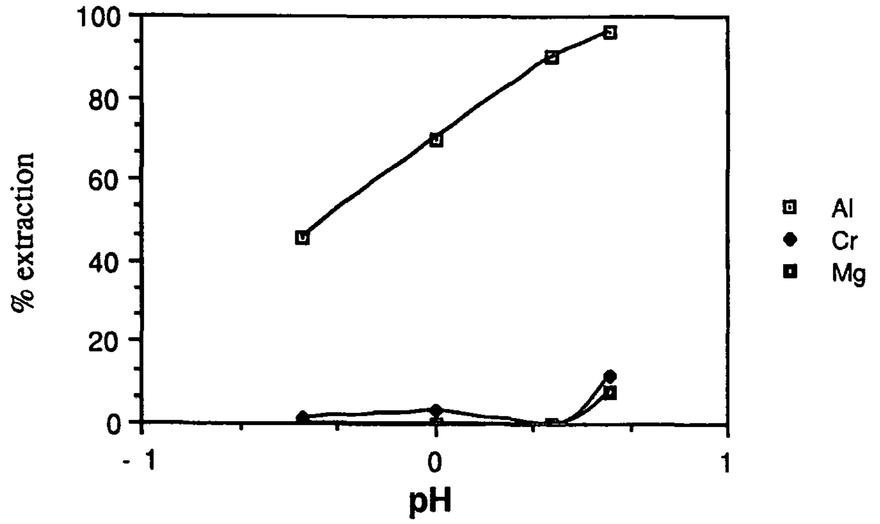
iii) Al, Cr, Mg high solutions

The extraction of Al from residue solutions of high Al and Cr concentrations were studied over a range of pH and PR (see Table 4.22 and Graphs 4.12 and 4.13). At PR1, Al extraction substantially increased from 46% to 96%, from $pH_{i}/_{f}$ –0.5/–0.5 to 0.8/0.5. However, at the two highest pH's studied, Cr and Mg coextraction were observed. Raising the PR to 2 and 4, at pH_i –0.5, increased Al extraction without incurring any Cr or Mg coextraction. Thus in this case using a PR of 2 or 4 at the low pH_i of ~–0.5, appears to give suitable extraction behaviour for efficient and selective metal (Al) extraction.

Conditions	pH_i/ pH_f	Time (mins)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 1	-0.5/-0.5	30	17000	200	8400	10000	1	-	0	46
	0.0/ -0.1	30	13000	60	7600	10600	0	-	0	57
	0.0/ -0.1	30	14000	200	7200	8300	3	-	0	70
	0.4/ 0.3	30	15600	90	7600	10500	0	-	0	58
	0.4/ 0.3	60	15600	90	7600	10500	0	-	0	56
	0.6/ 0.5	30	14000	200	7600	9100	12	-	8	96
PR 2	-0.5/-0.5	30	17000	200	8400	10000	0	-	0	75
PR 4	-0.5/-0.5	30	16200	420	9400	13700	0	-	0	92

Table 4.22 OPAP – Al, Cr, Mg High Residue Solutions, 100°C

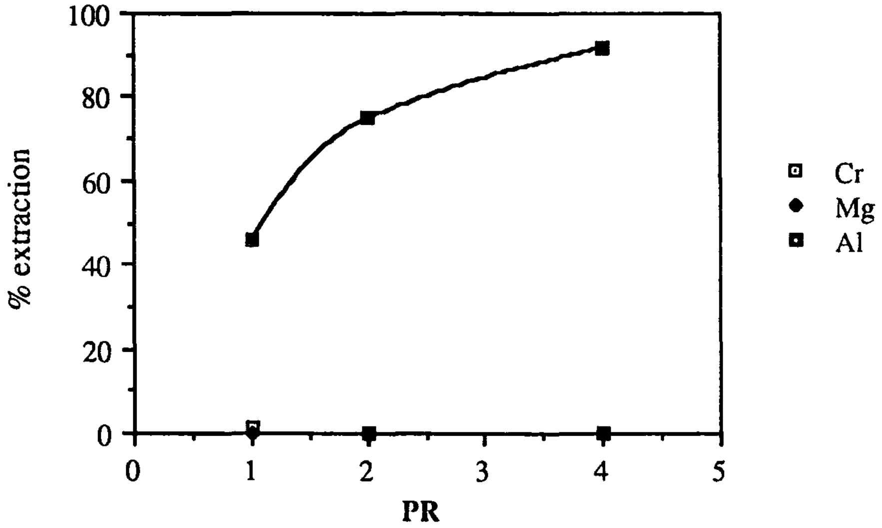
OPAP 29% $^{w}/_{v}$



Graph 4.12 OPAP 29% $^{w}/_{v}$, PR1 Al, Cr,Mg High, Residue Solutions, 100°C

iv) Medium Al; high Cr, Mg solutions

If solutions of medium Al and high Cr concentrations needed to be processed by OPAP, this could also be done efficiently and selectively (see Table 4.23 and Graph 4.14). At PR1, over the $PH_{i}/_{f}$ range –0.2/–0.2 to 0.4/0.2, Al was extracted 89% to 98%, with only very slight Mg coextraction at the higher pH's.



Graph 4.13 OPAP 29% $^w/_v$ $pH_i/_f$ –0.5/–0.5, Al, Cr, Mg High, Residue Solutions, 100°C

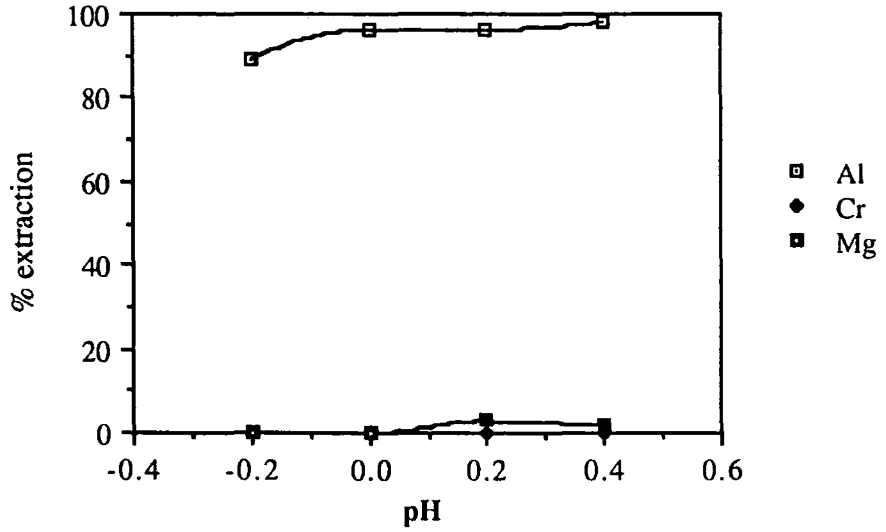
Conditions	pH_i/ pH_f	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 1	-0.2/-0.2	15200	550	7640	5500	0.0	-	0.0	89.1
	0.0/ 0.0	18000	570	7920	5400	0.0	-	0.0	96.3
	0.2/ 0.1	18400	550	8400	5400	0.0	-	2.9	96.3
	0.4/ 0.2	14800	540	7360	4900	0.0	-	1.6	98.0

Table 4.23 OPAP – Al Medium Residue Solutions, 100°C

OPAP 29% $^w/_v$

v) High Al, Mg solutions

Solutions of high Al and Mg concentrations (as might be produced by PJMT) were studied using OPAP 29% $^w/_v$, at PR2 (see Table 4.24). Over 90% Al extraction was observed over the $pH_i/_f$ range –0.2/–0.2 to 1.8/1.1, with 99.9% extraction at $pH_i/_f$'s 1.4/1.0 and 1.8/1.1. Mg was not coextracted at all, although very slight quantities (≤3%) of Cr were coextracted.



Graph 4.14 OPAP 29% $^w/_v$, PR1, Al Medium Residue Solutions, 100°C

Conditions	pH$_i$/ pH$_f$	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 2	-0.2/-0.2	600	20	4400	6800	3	-	0.0	92.6
	0.4/ 0.2	600	20	5200	6800	3	-	0.0	99.5
	0.9/ 0.6	610	20	6000	6900	3	-	0.0	99.7
	1.4/ 1.0	650	20	5440	7000	2	-	0.0	99.9
	1.8/ 1.1	690	20	5700	7800	1	-	0.0	99.9

Table 4.24 OPAP–Al, Mg only, Residue Solutions, 100°C

OPAP 29% $^w/_v$

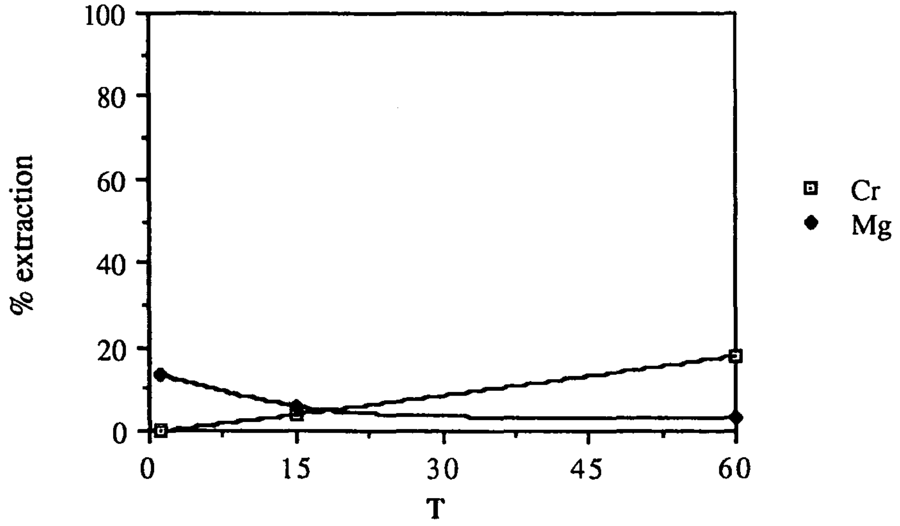
vi) Cr, Mg high solutions

Residue solutions of high Cr and Mg concentrations were studied with OPAP 29% $^w/_v$ at PR1, 4, 8 and 16 (see Table 4.25). At PR1, from pH$_{i/f}$ 0.0/0.0 to 1.0/0.8, Cr and Mg were coextracted with the extraction values for Cr being 6–7% larger than those for Mg in each case. The aim of each extraction stage is efficient and selective extraction which does not appear possible in this system when the contact time is 30 minutes. Thus, the extractions were assessed at particular pH's, whilst varying the contact time. At both pH$_{i/f}$ 0.25/0.2 and 0.3/0.2, maximum Mg extraction (13.5% and 15.4% respectively) was observed after 1 minute, accompanied by zero Cr extraction (see Graphs 4.15, 4.16).

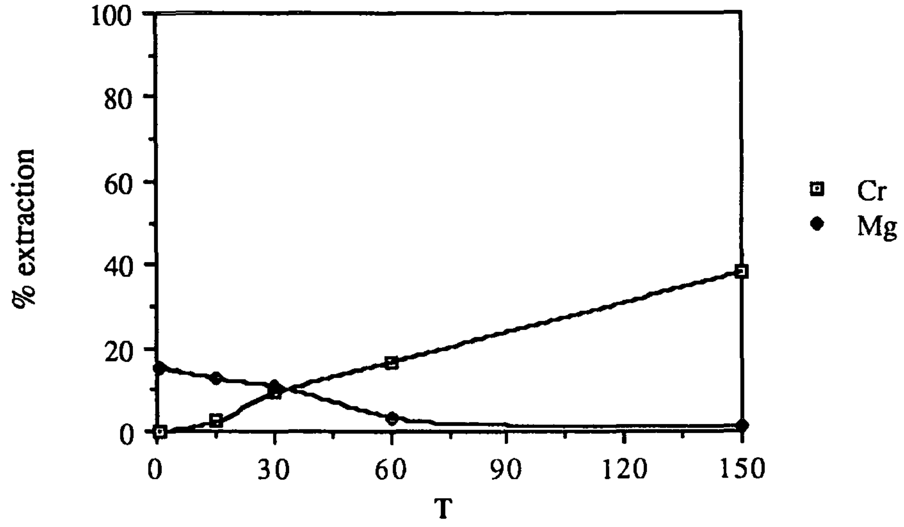
Table 4.25 OPAP – Cr, Mg only Residue Solutions, 100°C

OPAP 29% $^{w}/_{v}$

itions		(mins)	ppm	ppm	ppm	ppm	Cr(III) extraction	Fe(III) extraction	Mg(II) extraction	Al(III) extraction
PR 1	0.0/ 0.0	30	21000	50	6800	200	11.5	-	4.7	-
	0.3/ 0.1	30	19200	60	6600	200	14.6	-	10.4	-
	0.6/ 0.4	30	21000	30	6800	200	25.5	-	19.1	-
	1.0/ 0.8	30	20000	40	7000	200	50.0	-	42.9	-
	0.25/	1	20000	40	6800	300	0.0	-	13.5	-
	0.25/	15	20000	40	6800	300	4.0	-	5.9	-
	0.25/0.2	60	20000	40	6800	300	18.0	-	2.9	-
	0.3/	1	16800	50	7000	300	0.0	-	15.4	-
	0.3/	15	16800	50	7000	300	2.4	-	12.6	-
	0.3/	30	16800	50	7000	300	9.5	-	10.9	-
	0.3/	60	16800	50	7000	300	16.7	-	3.4	-
	0.3/ 0.2	150	16800	50	7000	300	38.1	-	1.1	-
PR 4	-0.1/-0.1	1	12000	70	5800	200	0.0	-	24.9	-
	-0.1/-0.1	15	12000	70	5800	200	6.7	-	24.3	-
	-0.1/-0.1	60	12000	70	5800	200	36.7	-	24.3	-
	-0.1/-0.1	150	12000	70	5800	200	66.7	-	20.8	-
	-0.1/-0.1	300	12000	70	5800	200	83.3	-	11.1	-
	0.3/	1	13200	30	6920	400	0.0	-	41.1	-
	0.3/	15	13200	30	6920	400	21.2	-	47.4	-
	0.3/	30	13200	30	6920	400	39.4	-	41.7	-
	0.3/	60	13200	30	6920	400	45.5	-	36.4	-
	0.3/	150	13200	30	6920	400	77.9	-	31.6	-
	0.3/ 0.2	1020	13200	30	6920	400	99.2	-	9.4	-
	1.0/	1	9350	50	4800	200	0.0	-	55.0	-
	1.0/	5	9350	50	4800	200	4.2	-	56.7	-
	1.0/	15	9350	50	4800	200	20.8	-	58.3	-
	1.0/ 0.8	30	9350	50	4800	200	37.5	-	54.2	-
	0.6/ 0.3	1	11250	2	1310	0	2.2	-	71.0	-
	1.3/ 1.1	1	10400	2	6500	400	1.8	-	42.5	-
PR 8	0.3/	1	13300	50	7300	300	0.0	-	52.6	-
	0.3/	5	13300	50	7300	300	5.6	-	56.3	-
	0.3/	15	13300	50	7300	300	15.6	-	57.2	-
	0.3/ 0.2	30	13300	50	7300	300	33.3	-	52.8	-
	0.5/0.0	1	12000	2	1720	3	6.7	-	71.0	-
PR16	0.3/	1	13600	60	7000	300	0.0	-	57.6	-
	0.3/ 0.1	5	13600	60	7000	300	2.6	-	58.1	-

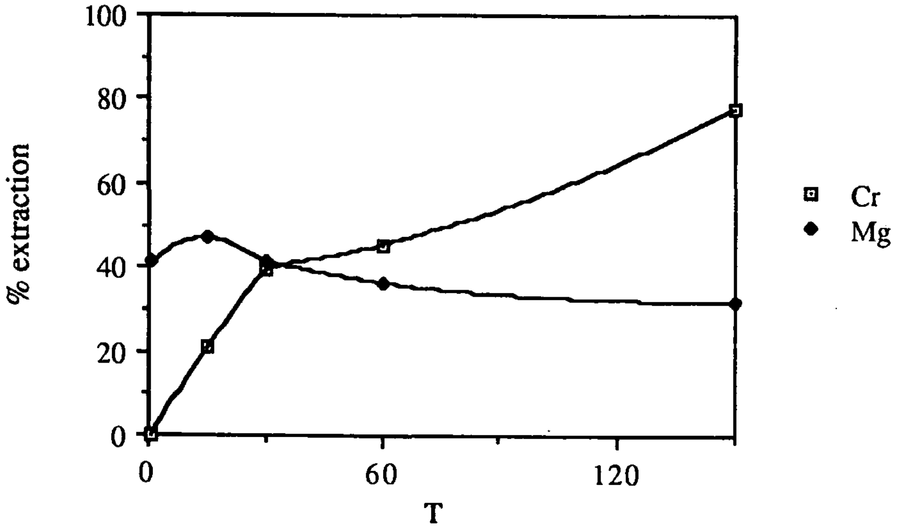


Graph 4.15 OPAP 29% $^{w}/_{v}$, pHi 0.25, PR1, Cr, Mg only, Residue Solutons, 100°C

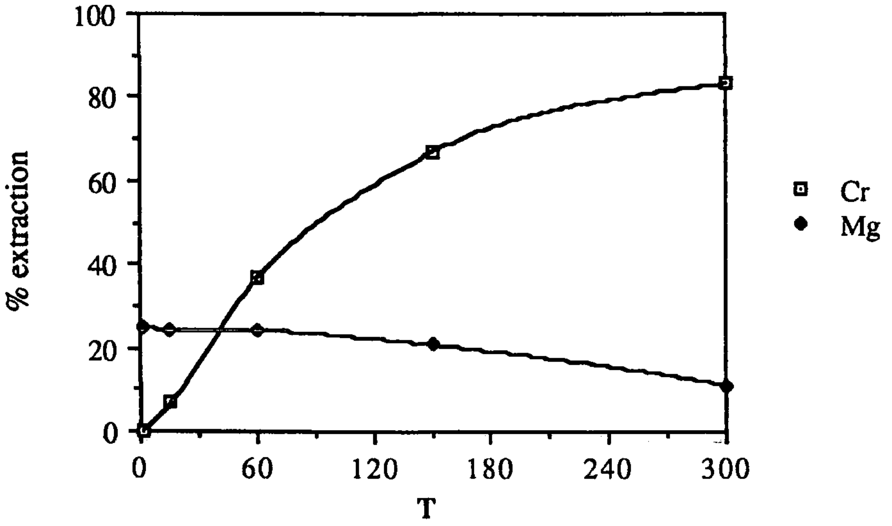


Graph 4.16 OPAP 29% $^{w}/_{v}$, pHi 0.3, PR1, Cr, Mg only, Residue Solutions, 100°C

As contact time increased, Cr extraction increased, and Mg extraction correspondingly decreased. Also at PR4, pH_i 0.3 and 1.0; and at PR8, pH_i 0.3; and at PR16 pH_i 0.3; the same trend of zero Cr extraction and near maximum. Mg extraction was observed (at a contact time of 1 minute). In every case Mg extraction decreased, and Cr extraction generally increased with an increase in contact time (see Graphs 4.17 – 4.20).

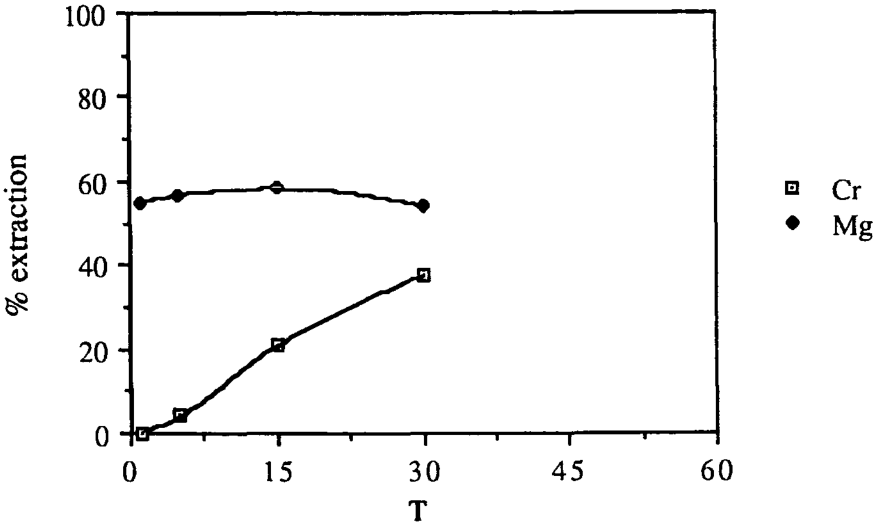


Graph 4.17 OPAP 29% $^w/_v$, pH$_i$ 0.3, PR4, Cr, Mg only, Residue Solutions 100°C

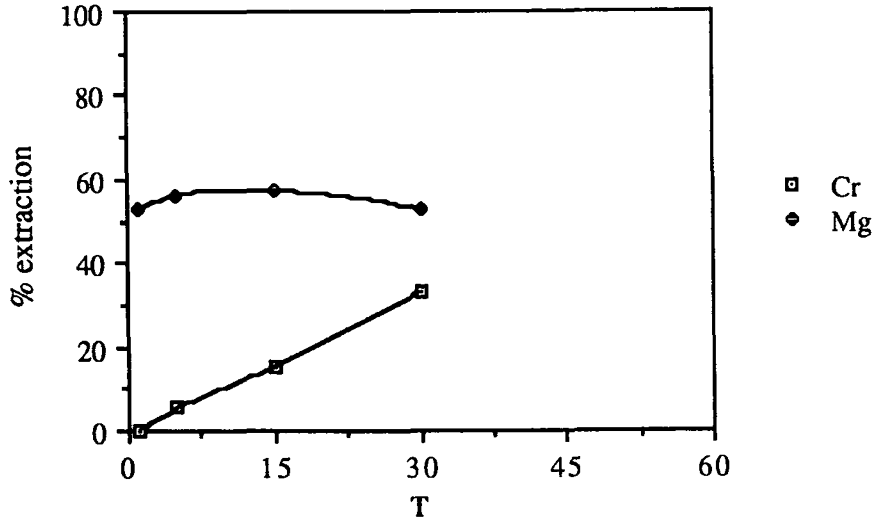


Graph 4.18 OPAP 20% $^w/_v$, pH$_i$ −0.05, PR4, Cr, Mg only, Residue Solutions, 100°C

This slow rate of Cr extraction indicates that the formation of the extracted Cr complex is a slow process. It is most likely due to the high hydration energy of $Cr(H_2O)_6^{3+}$, and the high energy barrier that must be overcome for ligand substitution on Cr. Also, the destruction of polymeric Cr in aqueous solutions is an energy intensive process, and therefore may be slow.



Graph 4.19 OPAP 29%, $^w/_v$, pH$_i$ 1.0, PR4, Cr, Mg only, Residue Solutions, 100°C



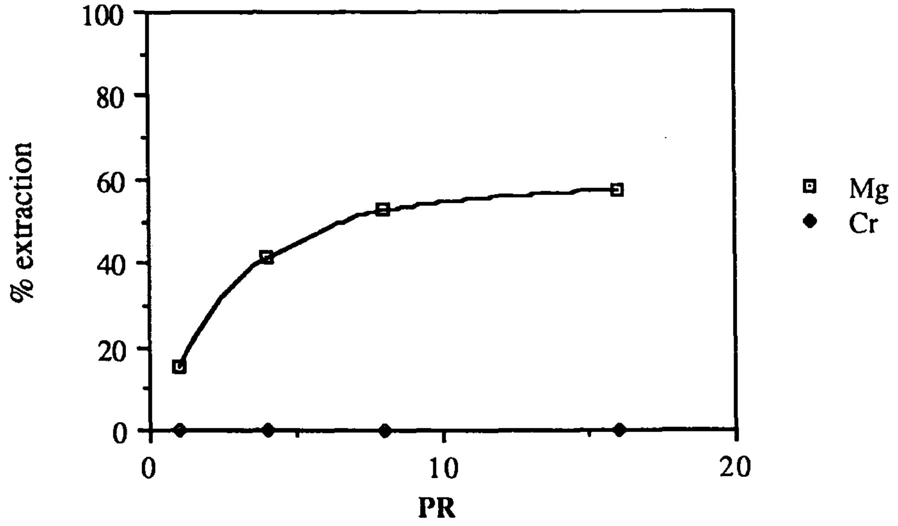
Graph 4.20 OPAP 29% $^w/_v$, ph$_i$ 0.3, PR8, Cr, Mg only, Residue Solutions 100°C

As contact time is increased more of the Cr–extracted complex forms, but as the systems are operating in the vicinity of the solvent loading capacity, the extraction of Cr depresses Mg extraction. Either (i) ligand substitution occurs between Mg extractable species and non–extractable Cr species, or (ii) the equilibrium between the Mg extracted species and Mg non–extracted species is altered due to the decreased availability of extractant. Both factors probably influence Mg extraction, but the former is the more likely to be able to decrease

Mg extraction values from 41.1% after one minute, to such low values as 9.4% after 17 hours (at PR4, pH_i 0.3).

Up to 99% Cr extraction was achieved by using long contact times (PR4, pH_i 0.3, 17 hours), but this method of achieving high Cr extraction is not possible in application, as such long contact times in a process would be too expensive. However, the potential of OPAP for Cr extraction from acidic Cr, Mg sulphate solutions may yet find application.

The selective and efficient extraction of Mg from these solutions offers greater direct applicability to an envisaged process. Under the conditions studied, the largest selective Mg extraction value was 57.6% (>5000 ppm Mg), at PR16, pH_i 0.3. Such a high PR, however, would lead to an excessive contactor size, and therefore PR4, pH_i 1.0 would be more appropriate (giving 55.0% selective Mg extraction after 1 minute). Graph 4.21 shows the effect of PR variation upon metal extraction from Cr, Mg residue solutions after one minute.



Graph 4.21 OPAP 29% $^w/_v$, pH_i 0.3, Cr, Mg only Residue Solutions

Contact time = 1 minute, 100°C

Table 4.26 shows the metal extraction values from residue solutions of high Cr and Mg concentrations, (at PR1, pH_i 0.25), by OPAP at concentration of 38% $^{w}/_{v}$ and 45% $^{w}/_{v}$. The result using OPAP 45% $^{w}/_{v}$ is directly comparable with that at 29% $^{w}/_{v}$, the higher OPAP concentration giving higher Cr and Mg extraction, as expected.

Conditions	pH_i/ pH_f	Time (mins)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 1 38% w/v	0.25/	1	15750	0	3825	0	0.8	-	40.4	-
	0.25/	15	15750	0	3825	0	3.2	-	30.1	-
	0.25/ 0.1	60	15750	0	3825	0	6.3	-	25.5	-
PR 1 45% w/v	0.25/ 0.1	30	20000	40	6800	300	14.0	-	12.4	-

Table 4.26 OPAP – Residue Solutions, 100°C

a) ORE Studies

i) Fe rich solutions

The use of OPAP for metal extraction from ore solutions is shown in Table 4.27. Brief studies show the general characteristics of the ore systems. Using OPAP with an Fe rich solution, 22% $^{w}/_{v}$, Fe is efficiently (92%) (but not selectively) extraction at $pH_i/_f$ 1.6/1.2, but an increase in pH decreases Fe extraction to 60% due to high Al co-extraction (78%) and the consequent ligand exchange.

ii) Al, Cr, Mg high Solutions

High Al extraction efficiency (Table 4.27, Graph 4.22) (91.7% at $pH_i/_f$ 0.9/0.5) with good selectivity is observed in the OPAP 22% $^{w}/_{v}$ high Al, Cr, Mg system at PR1.

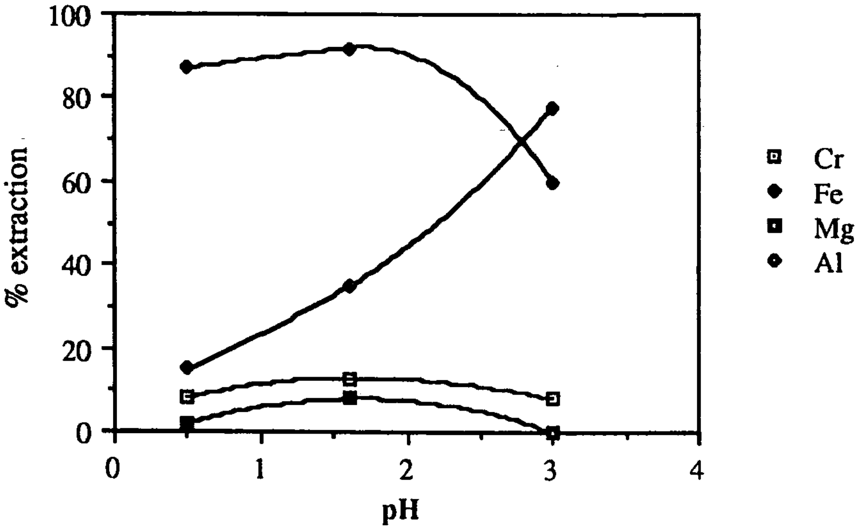
Conditions	pH_i/ pH_f	Concentration, % w/v	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 1	0.5/ 0.5	22	19500	10000	2100	3400	8.0	87.4	2.6	15.5
	1.6/ 1.2	22	19500	10000	2100	3400	8.0	92.7	8.4	35.4
	3.0/ 2.9	22	19500	10000	2100	3400	8.0	60.3	0.9	78.4
PR 1	0.9/ 0.5	22	20000	550	2000	3600	0.6	-	0.2	91.7
	3.5/ 1.3	22	18500	410	1600	3000	14.1	-	2.4	84.1
PR 1	1.2/ 0.5	32	19000	140	3300	2500	46.1	-	3.0	99.8
PR 1	3.7/ 1.1	32	15000	19	2400	235	65.0	-	18.8	-
	3.7/ 1.3	65	15000	19	2400	235	70.0	-	18.8	-
PR 1	0.3/ 0.2[a]	38	26000	50	2640	265	0.0	-	19.2	-
	0.3/ 0.2[b]	38	26000	50	2640	265	2.4	-	16.3	-
	0.3/ 0.2[c]	38	26000	50	2640	265	25.0	-	13.9	-

[a] Contact time = 1 minute

[b] Contact time = 15 minutes

[c] Contact time = 30 minutes

Table 4.27 OPAP – Ore Solutions, 100°C



Graph 4.22 OPAP – Fe Rich Ore Solutions 22% w/v

An increase in pH (to pH 3.5/1.3) causes a decrease in Al extraction (84.1%), due to ligand exchange to Cr (Cr extraction is 14.1%). High Al extraction (99.8%) and significant Cr extraction (46.1%) is observed at $pH_{i}/_{f}$ 1.2/0.5, at PR1, with OPAP 32% $^{w}/_{v}$.

iii) Cr, Mg high solutions

Cr, Mg ore raffinates showed Cr, Mg coextraction under the studied when the contact time was 30 minutes, but after 1 minute selective Mg extraction was observed, as for the residue solutions.

4.3.4. Primene JMT

An outstanding feature of free amine systems, is the increase in pH from extraction, (as opposed to the decrease in pH associated with systems using acidic extractants). Thus, aqueous solutions of lower pH may be treated for metal extraction, than would otherwise be possible without base addition. PJMT is the only liquid amine at room temperature, that has been used in these further investigations. At 10% $^{v}/_{v}$ in kerosene, excellent separation characteristics have always been observed, even with high metal loading. The investigations in Chapter 3 produced PJMT as the only macro Cr extractant, at 20°C. The low concentration of PJMT in this solvent (10% $^{v}/_{v}$), and low relative cost, led to the decision to investigate PJMT, mainly at PR5.

a) Residue Solutions – 100°C

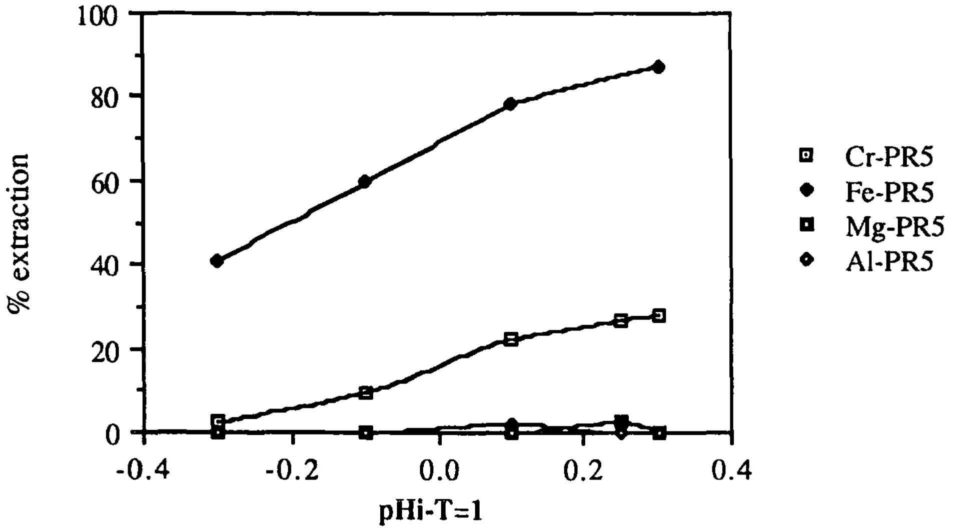
i) Fe rich solutions

The selective extraction of Fe from iron rich residue solutions was attempted at PR 2, 3, 4 and 5 (see Table 4.28). At PR5, its extraction behaviour was studied over the pH_i range –0.3 to 0.3, including the variation of contact time, in each case.

Cr co–extraction with the Fe was observed in every case, even at contact times of one minute. The general trend of increasing Cr and Fe extraction with pH is observed (see Graphs 4.23 to 4.25).

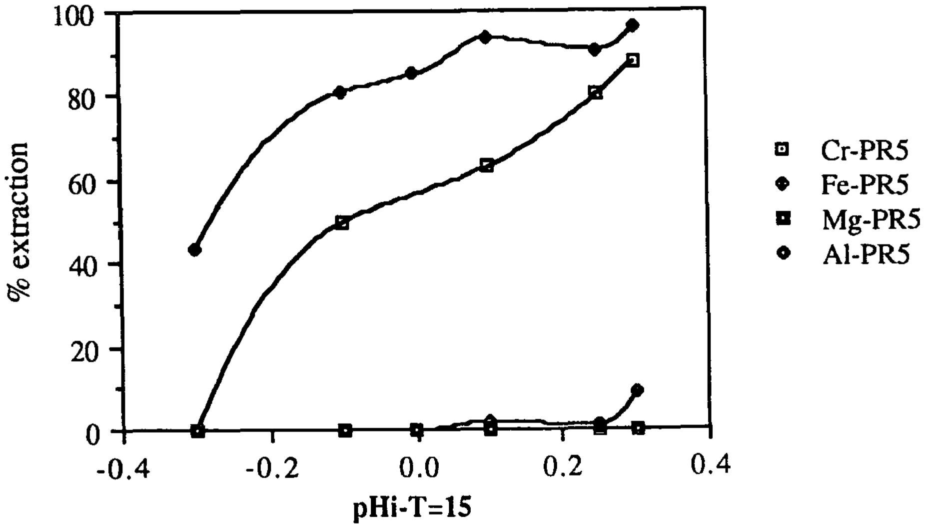
Conditions	pH_i/ pH_f	Time (mins)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR2	-0.1/	1	13000	20400	7000	10000	0.0	13.7	0.0	0.0
	-0.1/	15	13000	20400	7000	10000	11.6	20.5	0.0	0.0
	-0.1/ 0.2	30	13000	20400	7000	10000	15.6	20.5	0.0	0.0
PR3	0.1/ 0.2	1	10800	25600	7120	9600	7.4	45.3	0.0	2.0
PR4	0.1/ 0.3	1	10800	25600	7120	9600	15.8	55.6	0.0	5.3
	-0.1/ 0.5	1	12800	24800	7000	10000	0.0	51.0	0.0	0.0
PR5	-0.3/	1	16800	40400	11000	14800	2.4	40.6	0.0	0.0
	-0.3/	15	16800	40400	11000	14800	6.5	47.2	0.0	0.0
	-0.3/ 0.0	30	16800	40400	11000	14800	8.8	47.5	0.0	0.0
	-0.1/	1	16800	23200	7200	10100	9.7	59.7	0.0	0.0
	-0.1/	15	16800	23200	7200	10100	50.0	81.0	0.0	0.0
	-0.1/ 0.6	30	16800	23200	7200	10100	62.4	81.0	0.0	0.0
	0.0/	10	14000	30000	8000	12000	19.4	85.1	0.0	0.0
	0.0/	30	14000	30000	8000	12000	47.2	82.4	0.0	0.0
	0.0/	60	14000	30000	8000	12000	58.3	81.1	0.0	0.0
	0.0/ 0.7	120	14000	30000	8000	12000	61.1	79.7	0.0	0.0
	0.1/	1	10800	25600	7120	9600	26.0	79.2	0.0	6.8
	0.1/	5	10800	25600	7120	9600	44.5	89.1	0.0	8.3
	0.1/ 0.8	15	10800	25600	7120	9600	66.2	93.8	0.0	10.6
	0.25/	1	18000	21600	6800	8600	26.7	61.1	0.0	0.0
	0.25/	15	18000	21600	6800	8600	80.0	90.7	0.0	1.2
	0.25/1.1	30	18000	21600	6800	8600	88.9	90.7	0.0	1.2
	0.3/	1	10000	15600	8840	11600	32.0	87.9	0.0	5.6
	0.3/	5	10000	15600	8840	11600	66.9	96.2	0.0	11.2
	0.3/	15	10000	15600	8840	11600	89.5	96.7	0.0	19.9
	0.3/ 1.4	30	10000	15600	8840	11600	92.7	95.7	0.0	22.1

Table 4.28 <u>Primene JMT – Fe Rich Residue Solutions, 100°C</u>



Graph 4.23 PJMT, Fe Rich Residue Solutions

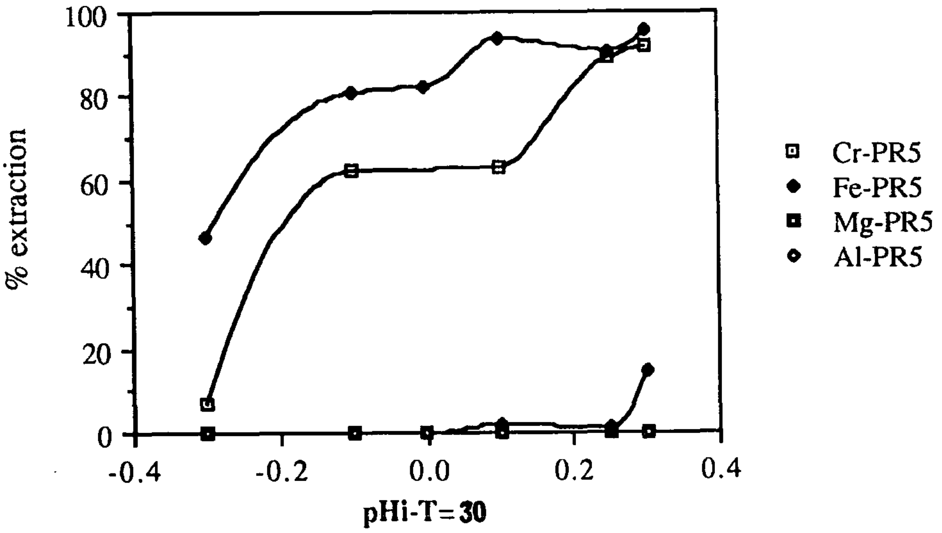
Contact time = 1 minute



Graph 4.24 PJMT, Fe Rich Residue Solutions

Contact time = 15 minutes

At PR5, if >85% Fe extraction is desired, the lowest observed Cr co-extraction is 19.4%, obtained after 10 minutes, at pH_i 0.0. This represents a large quantity of coextracted Cr and could present difficulties for subsequent purification steps (see Chapter 5).



Graph 4.25 PJMT, Fe Rich Residue Solutions

Contact time = 30 minutes

Thus, extraction behaviour was looked at, with PR at 2, 3 and 4. The 'best' result obtained at these PR's was the completely selective extraction of Fe (51.0%) at PR4, pH_i 0.1/0.5. Otherwise, no improvement was made upon the results at PR5. The decision as to the optimum conditions for iron extraction must depend upon further purification stages as discussed in Chapter 5. The choices of optimum conditions for process application are discussed in Chapter 6.

ii) Fe medium residue solutions

Incomplete iron extraction would lead to solutions of medium Fe concentration, as examined in Table 4.29. At PR1 and 3 the highest completely selective Fe extraction value was 29.4%, obtained at $pH_{i/f}$ –0.4/–0.3, after 30 minutes. It appears that the conds. of pH_i –0.4, a contact time of 1 minute, at PR3 would give the 'best' separation of Fe and Cr, out of the conditions studied (Fe extraction 59.6% and 6.7% Cr co–extraction).

The results of a further study with fresh amine, acid stripped amine, NaOH regenerated stripped amine, and acid stripped amine with NaOH added to the aqueous phase, is shown in Table 4.29.

Conditions	pH$_i$/ pH$_f$	Time (mins)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR1	-0.4/	1	14000	6800	9400	10900	0.0	0.0	0.0	0.0
	-0.4/	15	14000	6800	9400	10900	0.0	17.6	0.0	0.0
	-0.4/-0.3	30	14000	6800	9400	10900	0.0	29.4	0.0	0.0
	0.5/	1	18800	6800	15600	23600	14.9	42.6	0.0	0.0
	0.5/	15	18800	6800	15600	23600	22.7	47.9	0.0	1.7
	0.5/ 0.65	30	18800	6800	15600	23600	22.9	45.4	0.0	3.4
PR3	-0.4/	1	15200	7600	9200	10000	6.7	59.6	0.0	0.0
	-0.4/	15	15200	7600	9200	10000	10.4	56.4	0.0	0.0
	-0.4/-0.3	30	15200	7600	9200	10000	9.2	59.6	0.0	0.0
	0.0/	1	20800	7600	13600	18400	14.6	65.2	0.0	0.0
	0.0/	15	20800	7600	13600	18400	47.3	75.1	0.0	0.0
	0.0/ 0.1	30	20800	7600	13600	18400	51.4	79.5	0.0	0.0
PR3										
a	-0.3/-0.2	30	13400	6200	6420	11100	21	80	0	0
b	-0.3/-0.2	30	13400	6200	6420	11100	7	65	0	0
c	-0.3/-0.2	30	13400	6200	6420	11100	20	80	0	0
d	-0.2/-0.1	30	13400	6200	6420	11100	28	83	0	0

[a] Fresh

[b] H_2SO_4 stripped amine

[c] NaOH regenerated stripped amine

[d] H_2SO_4 stripped amine + NaOH to aqueous phase

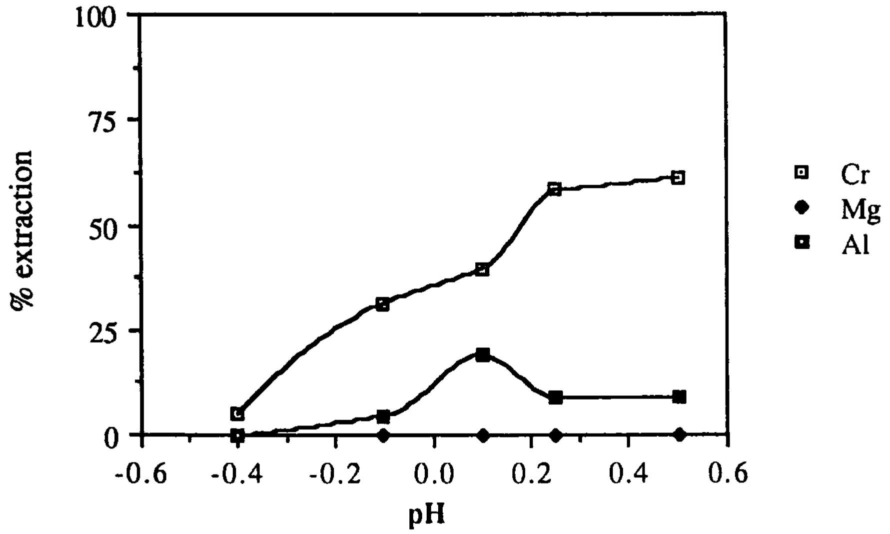
Table 4.29 Primene JMT – Fe Medium Residue Solutions, 100°C

Regenerated amine shows the same extraction characteristics as fresh amine. Acid stripped amine exhibits depressed metal extraction (as would be expected due to acidity differences). Where an equivalent molarity of NaOH (to that used for regeneration) was added to the aqueous phase, extraction was slightly higher than for the other cases. Thus, it appears that extraction is slightly more efficient if PJMT is used in its acid salt form with the base being used completely for pH alteration. Once equilibrium is reached (after contacting the 2 phases), the extraction of systems c and d might be expected to be identical, but apparently the pH effect in d does improve extraction. The alternative is to postulate that c and d are not at equilibrium as demonstrated by the difference in pH_f.

iii) Cr, Al, Mg high solutions

Table 4.30 shows the results from PJMT extraction studies with solutions of high Cr, Al and Mg concentrations. At PR2.5, pH_i 0.5, significant Cr extraction was observed (26%–42% from Cr 1–30 minutes), with slight Al co–extraction (2%–5%). At this pH_i (0.5) at PR10, Cr extraction was much higher (72%–96% from contact times 1–30 minutes respectively), but Al extraction was also substantially increased (30%–46%).

A study at PR5 over the pH_i range –0.4 to 0.5, with varying contact times, showed that efficient and selective Cr extraction from Cr, Al high solutions is very difficult (see Graphs 4.26 – 4.28).



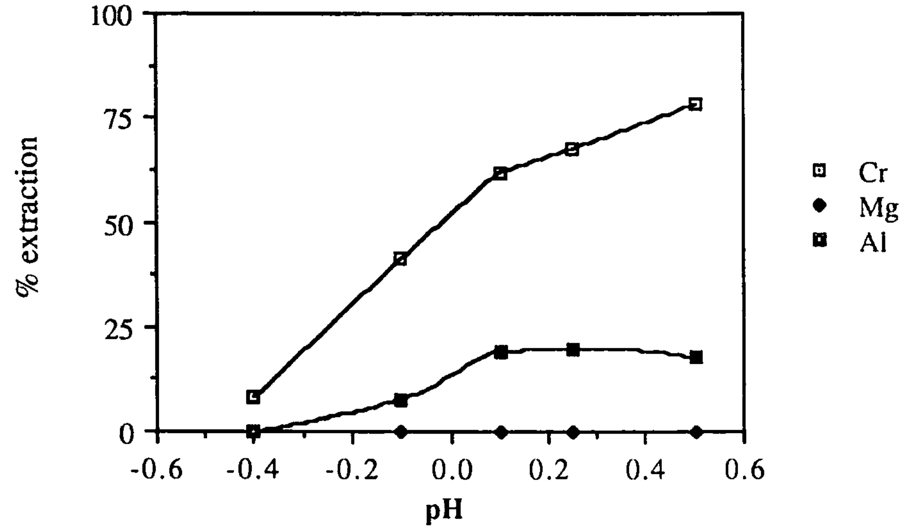
Graph 4.26 PJMT, Al, Cr, Mg High Residue Solutions

Contact time = 1 minute

Conditions	pH_i/ pH_f	Time (mins)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 2.5	0.5/	1	16800	230	8680	8800	26.2	-	0.0	2.3
	0.5/	15	16800	230	8680	8800	38.0	-	0.0	4.7
	0.5/ 0.6	30	16800	230	8680	8800	42.3	-	0.0	5.3
PR5	-0.4/	1	15200	210	10000	9700	5.4	-	0.0	0.0
	-0.4/	20	15200	210	10000	9700	8.1	-	0.0	0.0
	-0.4/-0.2	30	15200	210	10000	9700	4.9	-	0.0	2.6
	-0.1/	1	14800	150	8000	7600	31.5	-	0.0	4.7
	-0.1/	15	14800	150	8000	7600	41.4	-	0.0	7.9
	-0.1/0.15	30	14800	150	8000	7600	45.2	-	0.0	7.8
	0.1/	1	16000	240	9960	9200	39.7	-	0.0	19.2
	0.1/	15	16000	240	9960	9200	62.0	-	0.0	19.2
	0.1/ 0.7	30	16000	240	9960	9200	60.9	-	0.0	19.3
	0.25/	1	16000	240	10800	9700	58.3	-	0.0	8.9
	0.25/	15	16000	240	10800	9700	67.7	-	0.0	19.0
	0.25/ 0.9	30	16000	240	10800	9700	68.1	-	0.0	17.0
	0.5/	1	12800	260	8480	8400	61.2	-	0.0	9.1
	0.5/	15	12800	260	8480	8400	78.4	-	0.0	17.6
	0.5/ 1.1	30	12800	260	8480	8400	79.7	-	0.0	18.1
PR10	0.5/	1	12800	260	8480	8400	71.7	-	0.0	29.9
	0.5/	15	12800	260	8480	8400	94.9	-	0.0	45.4
	0.5/ 1.3	30	12800	260	8480	8400	95.9	-	0.0	45.5

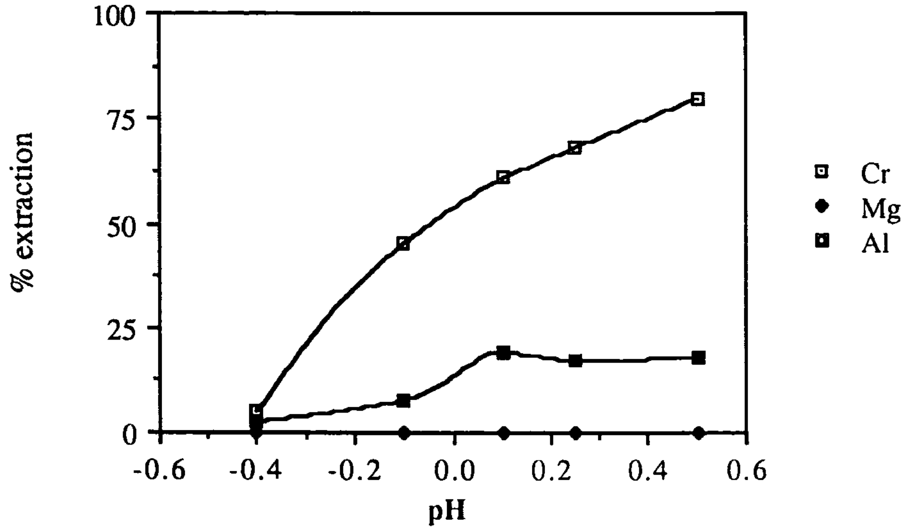
Table 4.30 Primene JMT – Cr, Al, Mg High Residue Solutions, 100°C

The highest observed completely selective Cr extraction was 8.1%, at pH_i –0.4 after 20 minutes. Thus, it appears that Al coextraction must be tolerated to achieve high Cr extraction. The difficulty is in deciding the upper allowable limit of Al coextraction, a decision which cannot be properly made until all the scrubbing and stripping information has also been assessed.



Graph 4. 27 PJMT, Al, Cr, Mg High Residue Solutions

Contact time = 15 minutes



Graph 4.28 PJMT, Al, Cr, Mg High Residue Solutions

Contact time = 30 mintues

A solution containing a smaller Cr:Al ratio was studied at pH 0.0, giving high Cr extraction (84.4%) with fairly low Al extraction (6.7%). In the residue solutions of larger Cr:Al ratio, when Al extraction was 7–9%, Cr extraction did not exceed 61.2%. This is a good example of the effect of a change in aqueous feed composition.

A comparison of two experiments at PR5, pH_i 0.5 was made; high Cr and Al concentrations (Cr 12800 ppm, Al 8400 ppm) (Table 4.30) with medium Cr and high Al concentrations (Cr 9100 ppm, Al 9500 ppm) (Table 4.31). In both cases Al extraction was 18–19%, with Cr extraction values of 79.7% and 93.5%

respectively. Although the proportion of extracted Cr was greater from the solutions of lower Cr concentrations, a larger absolute quantity of Cr was extracted from the solution of higher Cr concentration.

Conditions	pH_i/ pH_f	Time (mins)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 3	-0.1/ 0.3	30	8800	390	10400	9400	25.9	-	0.0	1.0
	0.15/ 0.5	30	9000	120	10400	9000	51.6	-	0.0	4.4
PR 5	0.5/ 1.7	30	9100	440	5400	9500	93.5	-	0.0	18.8
	0.5/ 1.0[a]	30	9100	440	5400	9500	86.2	-	0.0	14.7
PR 6	0.15/ 0.9	30	9000	120	10500	9000	85.9	-	0.0	22.1

[a] Regenerated with 100% stoichiometric quantity of NaOH.

Table 4.31 Primene JMT – Al High, Cr Medium Residue Solutions 100°C

iv) Al medium, Cr, Mg high solutions

Table 4.32 shows the results from studies on solutions containing different absolute and relative concentrations of Cr and Al.

v) Al, Mg only solutions

Solutions containing only Al and Mg can be produced by Cr extraction using a PJMT solvent, the results of which are outlined in Table 4.33, Graph 4.29. It is demonstrated here that selective and virtually complete Al extraction is feasible. A high PR was used in these experiments, although it would also be feasible to use a lower PR and higher pH.

vi) Cr, Mg only solutions

Similarly, Cr can be selectively and completely extracted from solutions containing only Cr and Mg. See Table 4.34.

b) Residue Solutions – 20°C

Extraction studies of PJMT with residue solutions at 20°C are shown in Table 4.35. Cr, Al and Fe are all extracted at 20°C, but with lower efficiencies than at 100°C.

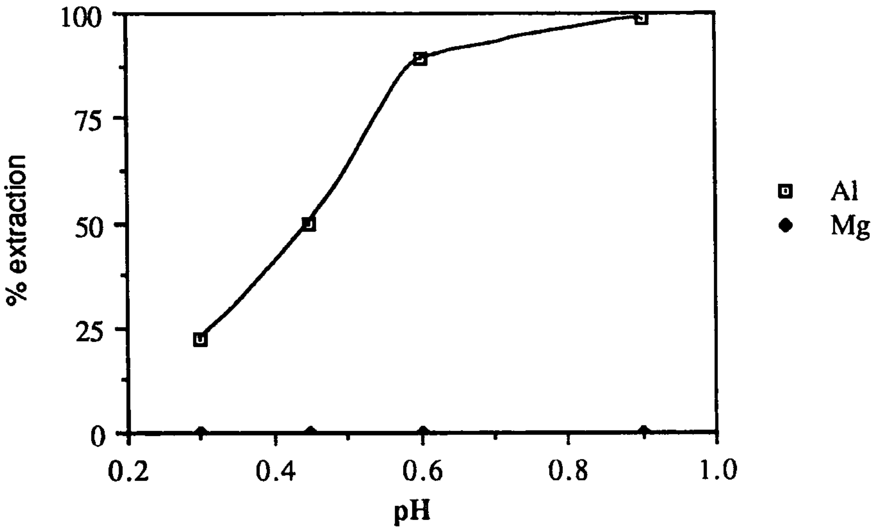
Conditions	pH_i/ pH_f	Time (mins)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 1	0.8/ 0.9	30	23250	390	4625	5800	16.1	72	0.0	19.0
	0.8/ 0.9[a]	30	23250	390	4625	5800	16.1	72	0.0	19.0
	3.4/ 4.3	30	17500	330	3875	5500	32.9	46	0.0	20.0
	3.4/ 4.2[a]	30	17500	330	3875	5500	32.9	52	0.0	20.0
PR 5	0.1/	1	12000	120	6560	6200	72.4	-	0.0	13.8
	0.1/	15	12000	120	6560	6200	78.5	-	0.0	18.0
	0.1/ 0.6	30	12000	120	6560	6200	84.6	-	0.0	19.8
	0.3/	1	6400	110	4400	4500	77.1	-	0.0	36.9
	0.3/	15	6400	110	4400	4500	95.6	-	0.0	49.2
	0.3/ 1.5	30	6400	110	4400	4500	96.0	-	0.0	49.1
	0.4/	30	15600	90	7600	1000	70.0	-	0.0	65.5
	0.4/ 0.9	60	15600	90	7600	1000	75.0	-	0.0	65.5
	1.4/ 3.8	30	12200	10	5000	2300	97.4	-	0.0	87.0

[a] Regenerated with 100% stoichiometric quantity of NaOH

Table 4.32 Primene JMT – Cr, Al Medium, Mg High Residue Solutions, 100°C

Conditions	pH_i/ pH_f	Time (mins)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 8	0.3/ 1.0	30	0	0	6650	9300	-	-	0.0	2.2
	0.4/ 1.3	30	0	0	6800	9500	-	-	0.0	49.9
	0.5/ 1.5	30	0	0	6900	9700	-	-	0.0	73.6
	0.6/ 1.7	30	0	0	7000	9800	-	-	0.0	89.3
	0.9/ 4.0	30	0	0	7000	9900	-	-	0.0	99.0

Table 4.33 Primene JMT – Al, Mg only Residue Solutions, 100°C



Graph 4.29 PJMT, Al, Mg High Residue Solutions 100°C, PR8

Conditions	pH_i/ pH_f	Time (mins)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 5	0.5/ 1.3	15	4400	0	1800	0	97.3	-	0.0	-
	0.7/ 1.6	15	17600	0	6600	100	80.5	-	0.0	-
	1.5/ 2.5	15	4400	0	2000	0	100	-	0.0	-
PR 5	0.1/0.7	30	14000	0	8640	0	89.3	-	0.0	-
	0.5/1.1	30	15600	0	9760	0	96.5	-	0.0	-
	1.0/ 2.9	30	13600	0	8080	0	98.7	-	0.0	-

Table 4.34 Primene JMT – Cr, Mg only Residue Solutions, 100°C

c) ORE Solutions

Ore solutions were briefly studied with PJMT. The metal extraction values are different from residue, in line with the different absolute and relative metal values (Table 4.36).

Conditions	pH_i/ pH_f	Time (mins)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 1	0.2/ 0.6	30	17600	29600	5440	9500	0.0	6.8	0.0	0.0
	0.6/ 0.9	30	15600	25600	4120	8800	2.6	12.5	0.0	0.0
	0.6/ 0.9[a]	30	15600	25600	4120	8800	2.6	12.5	0.0	0.0
	0.6/ 0.9[a]	30	15600	25600	4120	8800	2.6	10.9	0.0	0.0
	0.7/ 1.0	30	13200	30400	8000	12200	3.0	18.4	0.0	2.0
PR 5	0.0/	10	14000	30000	8000	12000	0.0	62.7	0.0	0.0
	0.0/	30	14000	30000	8000	12000	0.0	68.0	0.0	0.0
	0.0/ 0.5	120	14000	30000	8000	12000	0.0	70.7	0.0	0.0
	0.2/ 1.1	30	15200	30400	8000	11800	0.0	64.5	0.0	0.0
	0.6/ 3.6	30	14400	7600	8000	11800	86.1	97.4	0.0	26.3
PR 5	0.9/	30	15600	90	7600	1000	56.4	-	0.0	11.0
	0.9/ 2.6	60	15600	90	7600	1000	66.7	-	0.0	11.0

[a] Regenerated with NaOH

Table 4.35 Primene JMT – Residue Solutions, 20°C

As described in Chapter 1, PJMT (as an amine) extracts metals in the form of ion association complexes. It appears likely that the trivalent metals are extracted as adducts, such as $(RNH_3^+)_2\ SO_4^{2-}.n\ [Fe_2(SO_4)_3]$, as described in Equation 1.45.

To briefly summarize, PJMT appears to exhibit good potential for Fe, Cr and Al extraction from residue solutions. PJMT was not observed to form extracted Mg species, under the range of conditions used.

4.3.5. Cr(VI) Extraction from Residue/Ore Solutions

The industrial application of using TBP for the removal of Cr(VI) from acidic sulphate liquors is well known (see Section 1.5). TBP is a solvating rather than an acidic or basic extractant, and therefore aqueous pH does not change upon contacting the solvent. This was experimentally verified in each case (i.e. $pH_i = pH_f$).

Conditions	pH_i/ pH_f	Temperature (^{o}C)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR 1	0.5/ 1.1	20	22000	8500	2300	3900	1.0	29.4	0.0	0.0
	0.7/ 1.0	20	22000	9500	2300	3600	2.9	52.1	0.0	3.0
	1.6/ 2.7	20	31200	9000	2000	3600	7.7	64.7	0.0	0.0
	3.0/ 4.0	20	18000	8600	2100	3400	30.6	47.7	0.0	32.4
PR 1	0.85/ 1.1	100	34000	550	2000	3600	18.1	-	0.0	12.5
	3.5/ 3.9	100	18500	410	1600	3000	40.0	-	0.0	27.0
PR 5	0.25/ 0.4	100	29000	50	3000	265	23.4	-	0.0	-
	1.0/ 2.2	100	27000	40	2750	260	64.1	-	0.0	-

Table 4.36 Primene JMT – Ore Solutions, 20^{o}C

Contact time = 30 minutes

Experiments with DEHPA, OPAP, PJMT and acetyl acetone were conducted with residue solutions, and ore solutions containing Cr(VI) (from CrO_3 addition during digestion). Conditions were used in an attempt to obtain selective Fe extraction from Cr(VI) solutions. In every case Cr(VI) coextraction with Fe was observed, illustrating the requirement for prior Cr(VI) removal.

Ore digestions which involved the addition of excess stoichiometric quantities of CrO_3 (added for Fe(II) oxidation) required Cr(VI) removal prior to further metal separation. Three examples of TBP–Cr(VI) extraction are shown in Table 4.37. In the first case, at PR1, and 20^{o}C, almost all of the Cr(VI) was extracted in the first stage, at pH –0.1. (25.5% of the Cr in the solution from digestion was Cr(VI)). A different ore solution was treated with TBP at pH 0.0, PR$^{1}/_{4}$, and at 20^{o} and 100^{o}C. In both cases, two stages were required for bulk Cr(VI) removal (12.5% of the Cr in the original solution was Cr(VI)).

Conditions	pH_i=pH_f	Contact time	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
PR1, 20°C	-1.0	30	21.8	0.0	0.0	0.0	22000	39600	10400	13200
	-1.0	165	4.7	0.0	0.0	0.0	17200	39600	10400	13200
	0.0	120	0.0	0.0	0.0	0.0	16400	39600	10400	13200
PR1/4, 20°C	0.0	30	8.5	0.0	0.0	0.0	15200	29200	7720	11400
	0.0	30	7.3	0.0	0.0	0.0	14360	29200	7720	11400
	0.0	30	0.1	0.0	0.0	0.0	13310	29200	7720	11400
	0.0	30	0.0	0.0	0.0	0.0	13300	29200	7720	11400
PR1/4, 100°C	0.0	30	10.5	0.0	0.0	0.0	15200	29200	7720	11400
	0.0	30	4.4	0.0	0.0	0.0	13600	29200	7720	11400
	0.0	30	0.0	0.0	0.0	0.0	13300	29200	7720	11400

Table 4.37 TBP–Cr(VI) Extraction from Ore Solutions

Solvent = Kerosene

4.4 Summary

Fe(III) was extracted relatively easily, and with a certain degree of selectivity for all of the extractants under consideration, in each case being the first metal to be removed. The remaining metals for extraction may be removed in a variety of orders according to the extractant used.

The extraction data at 100°C of each of DEHPA, OPAP, and PJMT look very promising for the successful separation of one or more of the metals in chrome residue solutions. Their physical properties, toxicities, etc., and phase separation characteristics all appear to be acceptable for their use in an envisaged solvent extraction process.

Acetyl acetone, however, exhibits certain features which place doubt over its potential successful application. The low boiling point and flash point of acetyl acetone indicate that use of this extractant at high temperatures (~100°C) would be hazardous. The explosion level limits of 1.7%–11.4%, and tendency towards flash back over considerable distances are also causes for concern. From the solvent extraction side, the solubility of acetyl acetone in acidic aqueous solution is a matter of concern as significant solvent losses could arise, unless additional costly stages of aqueous raffinate washing were employed. However, the extraction data regarding residue metal extraction by acetyl acetone indicates that this extractant is very effective in metals separation, and therefore limited study of the stripping and scrubbing characteristics of acetyl acetone was undertaken.

The scrubbing and stripping characteristics of loaded solvents (DEHPA, OPAP, PJMT and acetyl acetone produced in the experiments outlined in this chapter) will be examined in Chapter 5. Also, the nature of the species in residue raffinates containing significant quantities of entrained acetyl acetone are investigated.

The characteristics of metal extraction over the range of residue solution types have been discussed in this chapter for each of the main extractants. The permutations of extractants offering favourable potential for process applications will be discussed fully in Chapter 6.

CHAPTER FIVE

METAL RECOVERY FROM ORGANIC SOLUTION

5.1 Introduction

This chapter is concerned with the recovery of the extracted metals and the regeneration of the solvents from loaded organic solutions. Metals are commonly acid stripped from the loaded solvents, as previously mentioned in Section 1.4.1. Product recovery from the strip liquors is commonly achieved by one of electrowinning, crystallisation, cementation, precipitation, or pressure reduction procedures [123]. Literature stripping studies, particularly regarding Fe, have been discussed in Section 1.4.7 and in some instances are of direct relevance to the loaded solvents produced in the studies outlined in Chapter 4. In this chapter acid scrubbing and stripping agents are investigated with a view to determining their viability in potential residue/ore extraction processes. The regeneration of the solvents, and their re–use is assessed. Studies into the effect and correction of entrainment in acetyl acetone systems has also been undertaken. All loaded organic solutions were produced from contacting residue solutions unless otherwise specified.

5.2 Scrubbing of Impurities from Loaded Organic Residue Solutions

Studies into the extraction of metals from residue solutions, as discussed in Chapter 4, have focused upon achieving the highest extraction efficiencies whilst maintaining acceptable selectivity. In many cases high extraction efficiencies of the metal of interest were accompanied by co–extraction of other metals, regarded as impurities. Brief scrubbing investigations were undertaken in an attempt to identify which metal impurities could be efficiently removed from particular loaded solvents, to improve the purity of the strip solutions.

5.2.1. Primene JMT

In the efficient extraction of Fe(III) from untreated residue solutions, Primene JMT has been observed to coextract Cr in significant quantities (see

Table 4.28). Typical PJMT solutions produced from these extractions may contain Cr 1460 ppm and Fe 3255 ppm, or Cr 1850 ppm and Fe 3380 ppm, or Cr 243 ppm and Fe 2505 ppm. The scrubbing of PJMT solutions, containing Cr and Fe at these concentrations, (as outlined in Table 5.1), was undertaken using sulphuric acid solutions, varying the contact time in each case.

Phase ratio $\frac{org}{aq.}$	pH of scrub solution	Time (mins)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
5	0.0	1	1460	3255	0	0	6.8	10.4	-	-
		5	1460	3255	0	0	23.3	8.9	-	-
		15	1460	3255	0	0	37.0	8.0	-	-
5	-0.45	1	1850	3380	0	0	42.9	23.7	-	-
		5	1850	3380	0	0	73.6	26.0	-	-
		15	1850	3380	0	0	84.6	26.6	-	-
		30	1850	3380	0	0	97.8	23.7	-	-
		85	1850	3380	0	0	87.2	25.9	-	-
5	0.0	1	243	2505	0	0	57.6	7.6	-	-
		5	243	2505	0	0	65.8	8.0	-	-
		15	243	2505	0	0	74.1	7.6	-	-
5	0.5	1	2500	0	0	350	5.4	-	-	62.9
		5	2500	0	0	350	5.1	-	-	57.1
		15	2500	0	0	350	5.1	-	-	57.1
5	0.0	1	2500	0	0	350	16.0	-	-	82.9
		5	2500	0	0	350	16.0	-	-	82.9
		15	2500	0	0	350	16.0	-	-	82.9

H_2SO_4 scrub solution, 100°C

Table 5.1 Primene JMT – Scrubbing of Loaded Organic Residue Solutions

The efficiency of Cr removed from the organic phase appears to be dependent upon the metal concentrations; e.g. after 15 minutes, 37.0% Cr was scrubbed from the PJMT solutions containing 1460 ppm Cr and 3255 ppm Fe (8.0%

co–scrubbing of Fe), and 74.1% Cr was removed from a PJMT solution with the lower Cr concentration of 243 ppm (7.6% co–scrubbing of Fe). The difference in efficiencies is probably a function of the loading capacity of the scrub solution under the particular experimental conditions. Very low quantities of scrub solution were used in each case (org./aq. phase ratio = 5), in an attempt to reduce scrubbing of the metal which is required to be left in the organic phase, for subsequent stripping. An experiment using a more acidic scrub solution achieved 97.8% scrubbing of Cr from the loaded solvent (Cr 1850 ppm, Fe 3380 ppm), although 23.7% Fe was co–scrubbed. It is envisaged that acid scrub solutions would be recycled into either (i) the acid dissolution process, or (ii) a residue raffinate solution.

In the extraction of Cr from PJMT solutions containing high concentrations of Cr, Mg and Al only, some Al coextraction may be observed. A loaded organic solution containing Cr 2500 ppm, and Al 350 ppm, was scrubbed with sulphuric acid (at pH's 0.0 and 0.5). Scrubbing efficiencies were greater for both Cr and Al using the more acidic scrub solution. Using a pH 0.0 scrub solution, 82.9% Al scrubbing was effected after 1, 10 and 15 minutes, with 16.0% co–scrubbing of Cr. The amount of Cr scrubbed is reduced to 5.1%, with a pH 0.5 scrub solution, but Al removal is also severely reduced.

It is outside the scope of these studies to declare the optimum conditions for scrubbing. This will depend upon the precise nature of the loaded solvent, and (most of all) the desired purity levels of the product (dependent upon the application for which the product is to be used). It seems likely that for a PJMT solution described as above, a pH 0.0 scrub solution would prove applicable for Al removal. This would convert a Cr 2500 ppm, Al 350 ppm PJMT solution to one containing Cr 2100 ppm, Al 60 ppm, of which Al is equivalent to 2.2% total metal content. Further scrubbing of this solution would improve Cr purity, but the extra contacting stage may prove economically disadvantageous.

5.2.2. DEHPA

Similarly to PJMT, loaded DEHPA solutions may contain metals surplus to the metal of interest. Loaded DEHPA Fe solutions containing significant Al impurities were subject to scrubbing studies (see Table 5.2).

Phase ratio org/aq.	pH of scrub solution	Time (mins)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
4	-0.75	1	5	7650	1	170	-	-	-	8.8
		8	5	7650	1	170	-	10.5	-	88.8
		15	5	7650	1	170	-	15.0	-	100
4	-0.45	2	5	7650	1	170	-	0.5	-	18.2
		5	5	7650	1	170	-	2.0	-	32.9
		15	5	7650	1	170	-	3.8	-	99.4
4	0.0	1	5	7650	1	170	-	0.0	-	7.6
		5	5	7650	1	170	-	0.1	-	11.2
		15	5	7650	1	170	-	0.2	-	22.4
4	0.0	15	4	2	367	1605	-	-	99.5	31.2

H_2SO_4 scrub solution, 100°C

Table 5.2 DEHPA – Scrubbing of Loaded Organic Residue Solutions

The acidity of the scrub solutions was varied between 5.6M, 2.8M and 1M, (or alternatively represented as pH –0.75, –0.45 and 0.0). Although, it would be more correct to describe the acidity of scrub solution in molarities, they have been represented as – $\log_{10}[H^+]$ for a comparison to aqueous feed liquors. The conditions producing the most favourable results (high Al removal with low Fe removal) were with a pH –0.45 solution, after 15 minutes, (giving 99.4% Al removal and only 3.8 Fe removal). This would produce a DEHPA solution containing Cr 7360 ppm, and Al 1 ppm.

In the extraction of Al by DEHPA, significant quantities of Mg may be coextracted. A single experiment using a pH 0.0 scrub solution, (with a DEHPA solution containing Mg 367 ppm, Al 1605 ppm), gave almost complete Mg removal with 31.2% Al removal.

5.2.3. OPAP

In studies examining the scrubbing characteristics of loaded OPAP solutions with sulphuric acid, very small quantities of Cr, Fe and Al were removed, although Mg was removed in significant proportions (see Table 5.3). This is in agreement with the stripping studies of OPAP, when using 2 molar sulphuric acid. Thus, it appears that only Mg may be scrubbed from loaded OPAP solutions, without using high strength acids (see Table 5.3).

Phase ratio org aq.	pH of scrub solution	Time (mins)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
4	0.0	1	250	100	0	3100	0.0	0.6	-	0.2
		5	250	100	0	3100	0.0	1.3	-	0.2
		15	250	100	0	3100	0.0	1.3	-	0.3
4	0.0	15	35	71	495	900	0.0	1.4	88.0	0.4

H_2SO_4 scrub solution, 100°C

Table 5.3 OPAP – Scrubbing of Loaded Organic Residue Solutions

5.3 Bulk Stripping of Metals from Loaded Organic Solutions

The objectives of these studies were to (i) produce regenerated solvents for recycling to the metal extraction stages of the process, (ii) purify mixed metal loaded organic solutions by selective stripping, and (iii) produce strip solutions containing metal(s) of interest with as high stripping efficiencies as possible.

Initially, stripping studies were undertaken using single metal organic solutions, prepared by the solvent extraction of the particular metal from single–metal sulphate solutions, (rather than from processed chrome residue).

5.3.1. Stripping Studies on Single Metal Organic Solutions

Stripping studies at 100°C were undertaken using 2, 6 and 10 molar concentrations of sulphuric and hydrochloric acids. Contact times of 30 minutes were used for each metal–solvent experiment, and in addition contact times of 120 minutes were used in the Cr studies.

a) Primene JMT

The results from these studies are tabulated in Tables 5.4, 5.5 and 5.6 for Fe, Al and Cr respectively. The results are represented graphically in Graphs 5.1, 5.2 and 5.3.

Acid Type	Acid concentration (M)	[Fe] ppm	% Fe stripped
HCl	2	2400	100
	6	2400	67.7[a]
	10	2400	33.8
H_2SO_4	2	2400	75.0
	6	2400	87.5
	10	2400	70.8

[a] At 20°C, under identical conditions stripping was 78.9%.

Table 5.4 Single Metal Stripping of Fe from Fe–PJMT Solutions

100°C, Contact time = 30 minutes, PR = 1

Acid Type	Acid concentration (M)	Time (minutes)	[Cr] ppm	% Cr stripped
HCl	2	30	3850	74.8
	6	30	3850	100
	10	30	3850	93.5
H_2SO_4	2	30	3850	12.5
	6	30	3850	85.2
	10	30	3850	86.2
HCl	2	120	3850	80.0
	6	120	3850	93.5
	10	120	3850	94.8
H_2SO_4	2	120	3850	14.3
	6	120	3850	88.3
	10	120	3850	88.3
H_2SO_4	2	1	3800	15.6
		5	3800	16.4
		15	3800	16.4
		30	3800	16.6

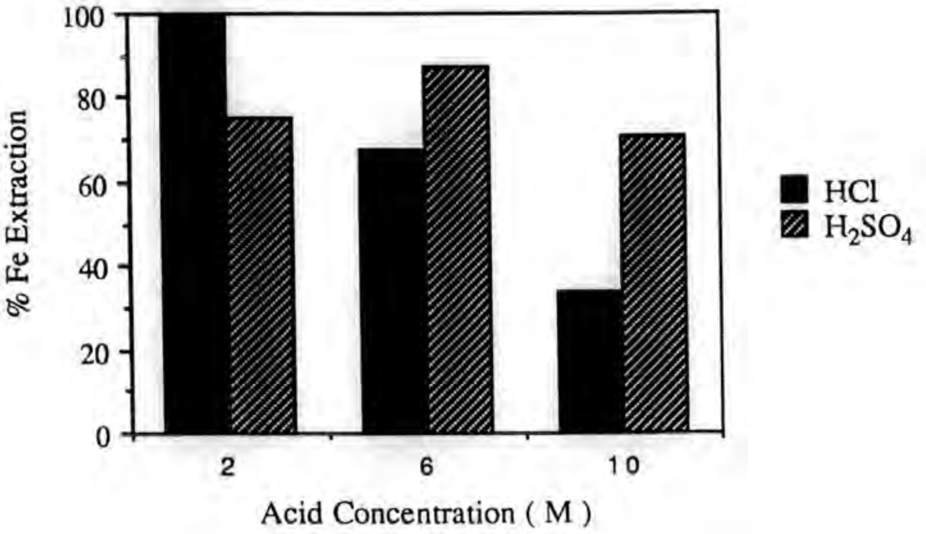
Table 5.6 Single Metal Stripping of Cr from Cr–PJMT Solutions

100°C, PR = 1

Acid Type	Acid concentration (M)	[Al] ppm	% Al stripped
HCl	2	2750	91.8
	6	2750	94.5
	10	2750	94.5
H_2SO_4	2	2750	99.6
	6	2750	92.4
	10	2750	92.4

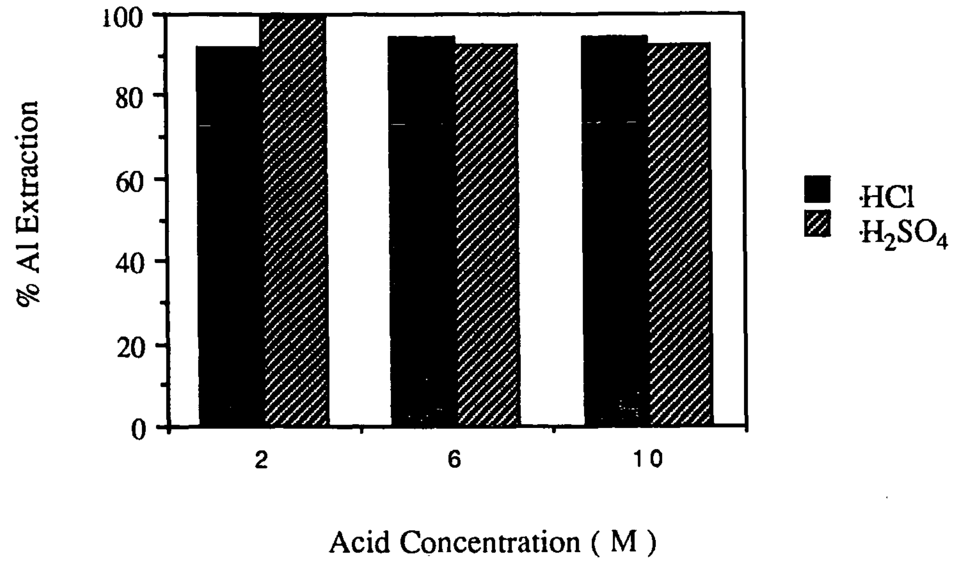
Table 5.5 Single Metal Stripping of Al from Al–PJMT Solutions

100°C, Contact time = 30 minutes, PR = 1

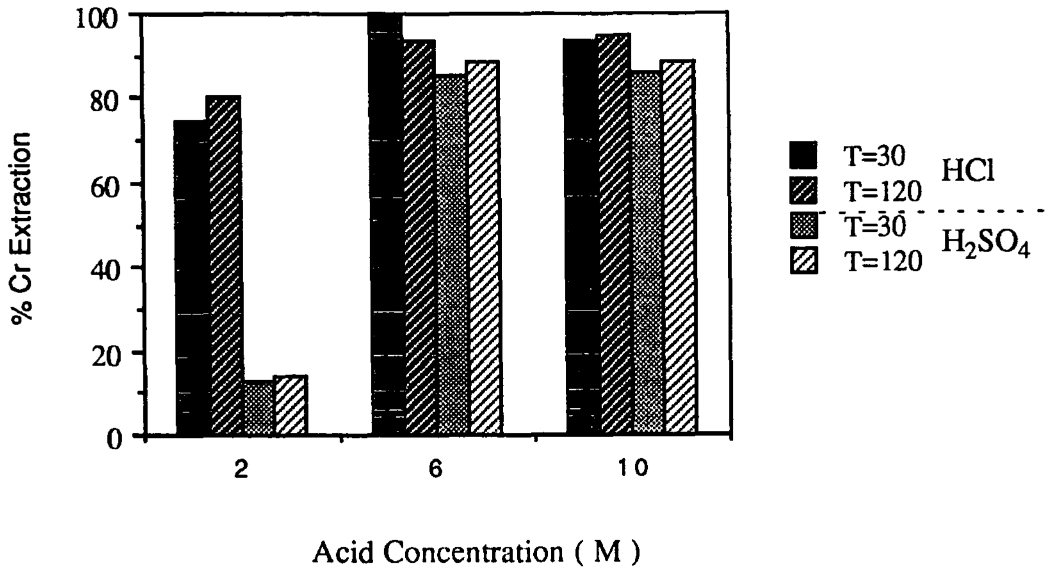


Graph 5.1 Single Metal Stripping of Fe from Fe – PJMT Solutions

Fe is preferentially stripped by sulphuric acid with 6 and 10 molar acid concentrations, but at 2 molar concentration hydrochloric acid effects a higher stripping efficiency. Al is efficiently stripped over the whole acid concentration range, with both sulphuric and hydrochloric acids (>90% in every case). Cr was fairly efficiently stripped over the range of conditions, with the exception of 2 molar sulphuric acid (>15%).



Graph 5.2 Single Metal Stripping of Al from Al – PJMT Solution



Graph 5.3 Single Metal Stripping of Cr from Cr – PJMT Solutions

b) OPAP

The results from the OPAP single metal stripping studies are outlined in Tables 5.7, 5.8, 5.9 and 5.10. Graphical representations of the data are shown in Graphs 5.4, 5.5, 5.6 and 5.7. The trends in the stripping of the metals is clear by analysis of these graphs. Fe may only be efficiently stripped by 10M hydrochloric acid (100%). Mg is efficiently stripped by the whole range of acids studied (80.3% – 97.4%). Cr stripping is negligible with 2 molar acids. 'Efficient' Cr removal with sulphuric acid was only observed with 10 molar acid after 120 minutes (41.9%). 'Efficient' stripping of Cr with hydrochloric acid was achieved using 6 molar acid for 120 minutes, and 10 molar acid for 30 and 120 minutes (62%–100%). Al stripping (~45%–60%) was achieved by the 6 and 10 molar acids.

Acid Type	Acid concentration (M)	[Fe] ppm	% Fe stripped
HCl	2	2075	0.3
	6	2075	1.7
	10	2075	100
H_2SO_4	2	2075	0.3
	6	2075	1.6
	10	2075	8.7

Table 5.7 Single Metal Stripping of Fe from Fe–OPAP Solutions

100°C, Contact time = 30 minutes, PR = 1

Acid Type	Acid concentration (M)	[Mg] ppm	% Mg stripped
HCl	2	2340	97.4
	6	2340	94.0
	10	2340	80.3
H_2SO_4	2	2340	85.5
	6	2340	92.3
	10	2340	87.2

Table 5.8 Single Metal Stripping of Mg from Mg–OPAP Solutions

100°C, Contact time = 30 minutes, PR = 1

Acid Type	Acid concentration (M)	Time (minutes)	[Cr] ppm	% Cr stripped
HCl	2	30	1720	1.7
	6	30	1720	16.9
	10	30	1720	100
H_2SO_4	2	30	1720	2.3
	6	30	1720	2.3
	10	30	1720	11.0
HCl	2	120	1720	1.9
	6	120	1720	62.8
	10	120	1720	95.3
H_2SO_4	2	120	1720	2.4
	6	120	1720	7.1
	10	120	1720	41.9

Table 5.9 Single Metal Stripping of Cr from Cr–OPAP Solutions

100°C, PR = 1

Acid Type	Acid concentration (M)	[Al] ppm	% Al stripped
HCl	2	2200	9.1
	6	2200	49.1
	10	2200	45.5
H_2SO_4	2	2200	11.8
	6	2200	61.8
	10	2200	57.3

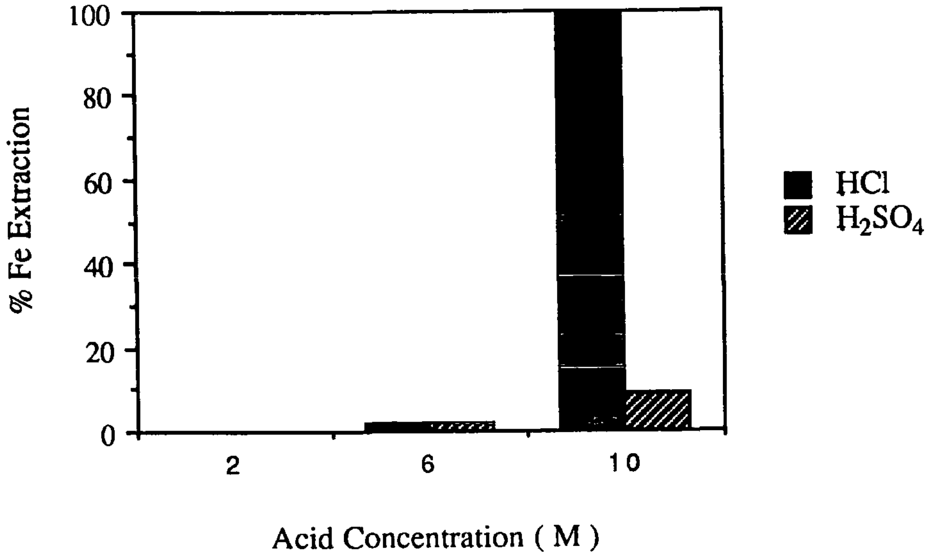
Table 5.10 Single Metal Stripping of Al from Al–OPAP Solutions

100°C, Contact time = 30 minutes, PR = 1

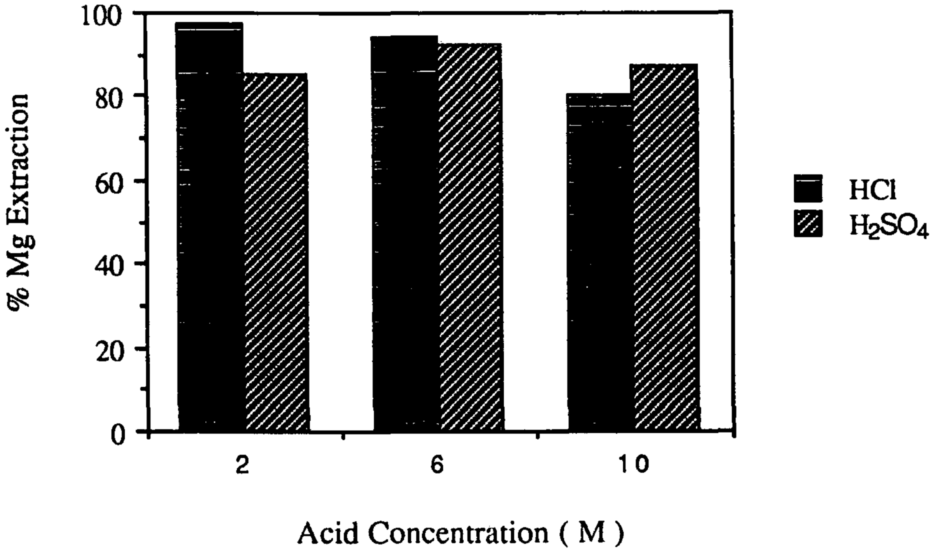
c) DEHPA

Al and Mg were efficiently stripped from DEHPA over all of the concentrations of both sulphuric and hydrochloric acids (>79%) (see Tables 5.11, 5.12, 5.13, and 5.14), and Graphs 5.8, 5.9, 5.10 and 5.11. Iron stripping was a maximum for the acids at 6 molar concentrations (48.0% with HCl, and 58.7%

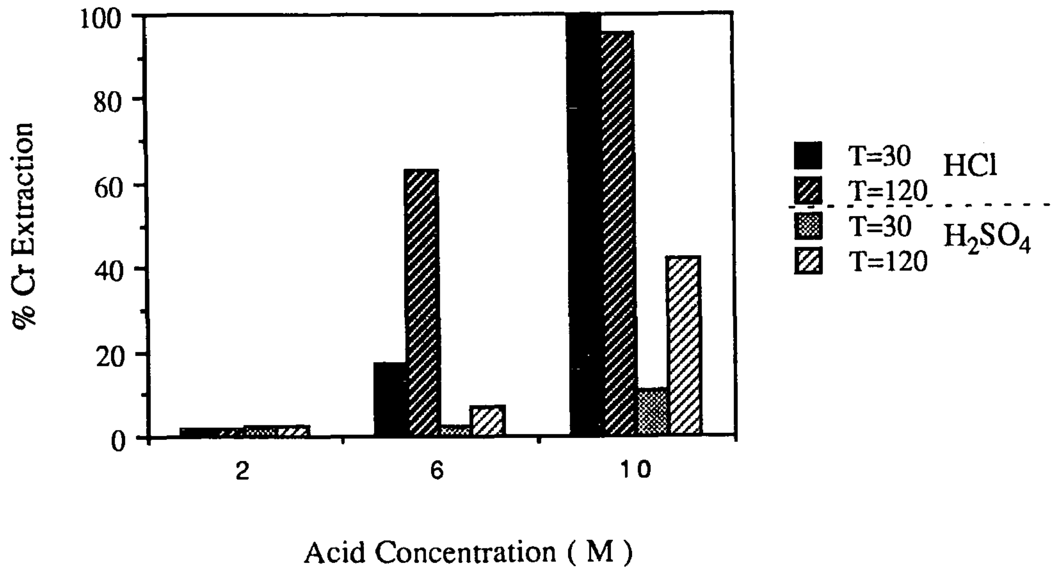
with H_2SO_4). Negligible to low stripping of Cr was observed for all concentrations of sulphuric acid strip solutions. 6 and 10 molar hydrochloric acid gave high Cr stripping values (>73%).



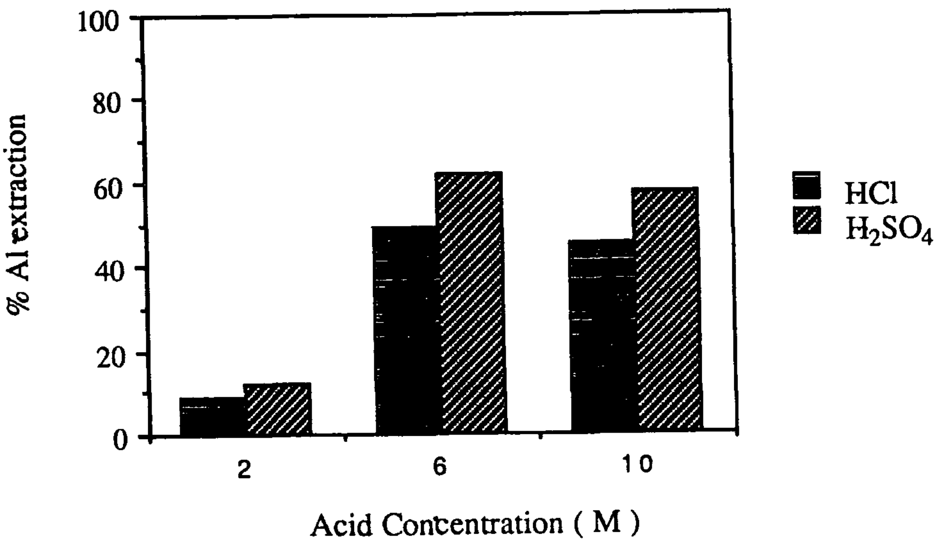
Graph 5.4 Single Metal Stripping of Fe from Fe – OPAP Solutions



Graph 5.5 Single Metal Stripping of Mg from Mg – OPAP Solutions



Graph 5.6 Single Metal Stripping of Cr from Cr – OPAP Solutions



Graph 5.7 Single Metal Stripping of Al from Al – OPAP Solutions

Acid Type	Acid concentration (M)	[Fe] ppm	% Fe stripped
HCl	2	1875	26.7
	6	1875	48.0[a]
	10	1875	16.0
H_2SO_4	2	1875	9.6
	6	1875	58.7[b]
	10	1875	12.3

[a] At 20°C, under identical conditions, stripping was 65.4%.

[b] At 20°C, under identical conditions, stripping was 3.8%.

Table 5.11 <u>Single Metal Stripping of Fe from Fe–DEHPA Solutions</u>

100°C, Contact time = 30 minutes, PR = 1

Acid Type	Acid concentration (M)	[Al] ppm	% Al stripped
HCl	2	2600	82.3
	6	2600	86.9
	10	2600	98.5
H_2SO_4	2	2600	90.8
	6	2600	86.9
	10	2600	83.8

Table 5.12 <u>Single Metal Stripping of Al from Al–DEHPA Solutions</u>

100°C, Contact time = 30 minutes, PR = 1

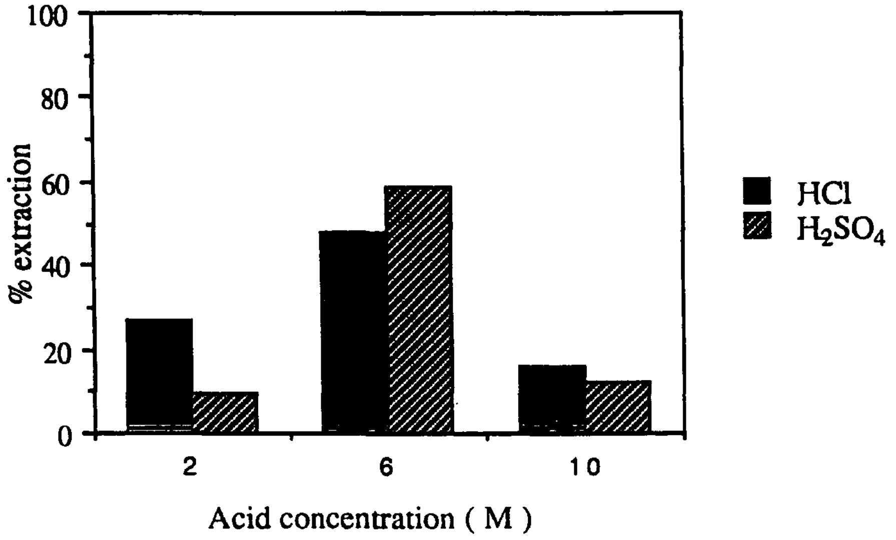
Acid Type	Acid concentration (M)	Time (minutes)	[Cr] ppm	% Cr stripped
HCl	2	30	1300	1.5
	6	30	1300	73.8
	10	30	1300	98.5
H2SO4	2	30	1300	0.0
	6	30	1300	3.1
	10	30	1300	10.0
HCl	2	120	1300	2.2
	6	120	1300	100
	10	120	1300	98.5
H_2SO_4	2	120	1300	0.5
	6	120	1300	8.5
	10	120	1300	8.9

Table 5.13 Single Metal Stripping of Cr from Cr – DEHPA Solutions 100°C, PR = 1

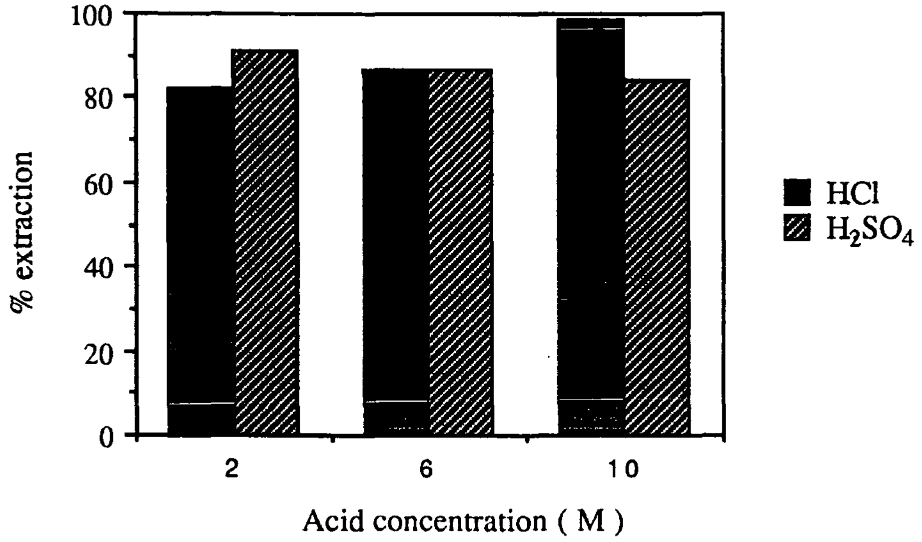
Acid Type	Acid concentration (M)	[Mg] ppm	% Mg stripped
HCl	2	2630	97.3
	6	2630	91.3
	10	2630	91.3
H_2SO_4	2	2630	79.1
	6	2630	85.2
	10	2630	92.8

Table 5.14 Single Metal Stripping of Mg from Mg–DEHPA Solutions

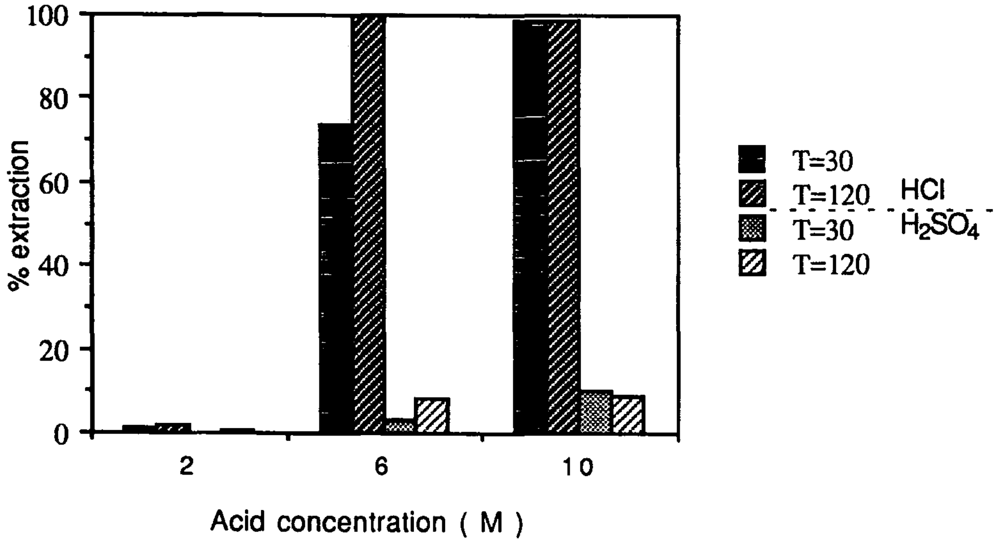
Contact time = 30 minutes, PR = 1



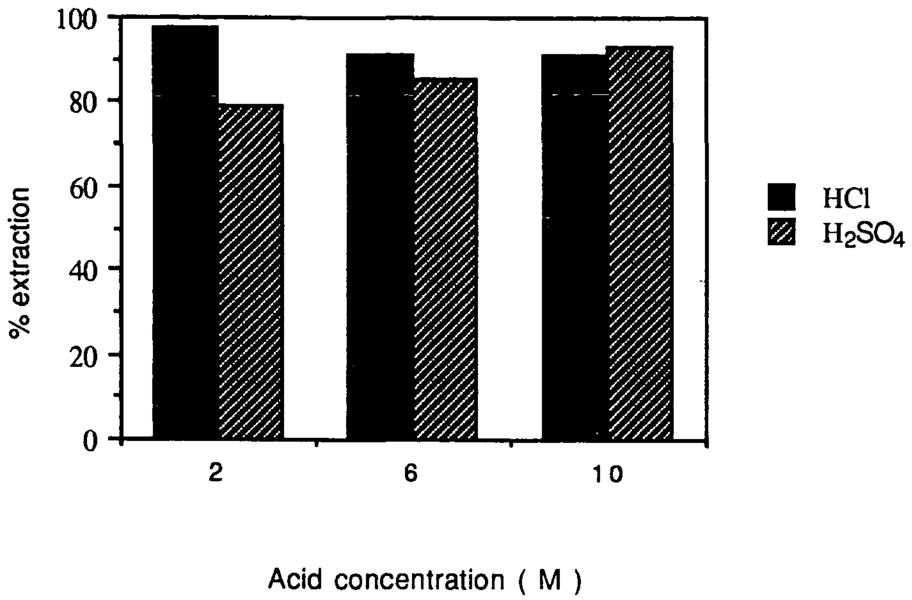
Graph 5.8 Single Metal Stripping of Fe from – Fe DEHPA Solutions



Graph 5.9 Single Metal Stripping of Al from Al – DEHPA Solutions



Graph 5.10 Single Metal Stripping of Cr from Cr – DEHPA Solutions



Graph 5.11 Single Metal Stripping of Mg from Mg – DEHPA Solutions

d) Acetyl Acetone

The stripping experiments involving acetyl acetone yielded high stripping efficiencies for each of Fe, Al and Cr over the whole range of conditions studied (see Tables 5.15, 5.16 and 5.17, and Graphs 5.12, 5.13 and 5.14). High entrainment of the acids into the organic phase led to further investigations, (see Section 5.5).

Acid Type	Acid concentration (M)	[Fe] ppm	% Fe stripped
HCl	2	590	78.0
	6	590	78.0[a]
	10	590	74.6
H_2SO_4	2	590	93.2
	6	590	91.5
	10	590	89.8

[a] At 20°C, under identical conditions stripping was 87.4%

Table 5.15 Single Metal Stripping of Fe from Fe–Acetyl Acetone Solutions

100°C, Contact time = 30 minutes, PR = 1

Acid Type	Acid concentration (M)	[Al] ppm	% Al stripped
HCl	2	770	94.8
	6	770	94.8
	10	770	94.8
H_2SO_4	2	1380	89.9
	6	1380	89.1
	10	1380	99.3

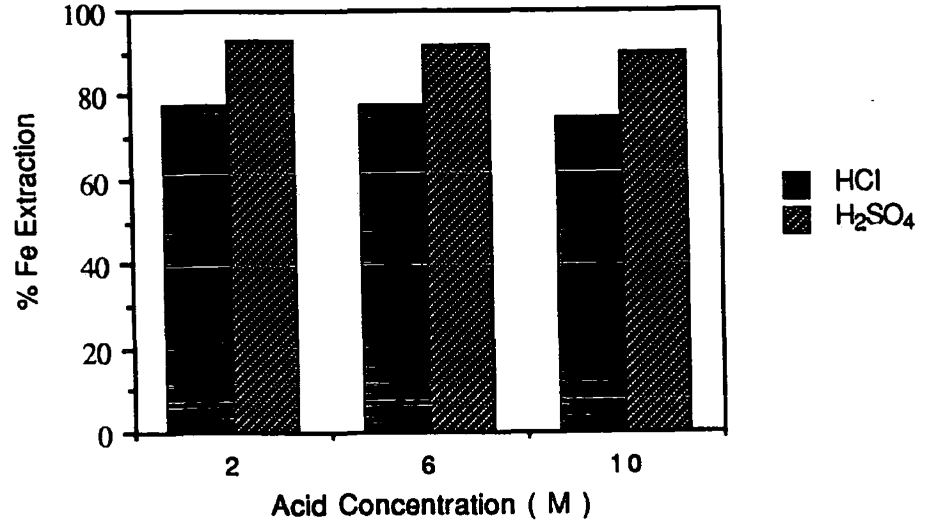
Table 5.16 Single Metal Stripping of Al from Al–Acetyl Acetone Solutions
100°C, Contact time = 30 minutes, PR = 1

Acid Type	Acid concentration (M)	Time (minutes)	[Cr] ppm	% Cr stripped
HCl	2	30	1060	87.7
	6	30	1060	94.3
	10	30	1060	99.1
H_2SO_4	2	30	1060	90.6
	6	30	1060	100
	10	30	1060	94.3
HCl	2	120	1060	87.7
	6	120	1060	99.1
	10	120	1060	100
H_2SO_4	2	120	1060	95.3
	6	120	1060	99.1
	10	120	1060	94.3

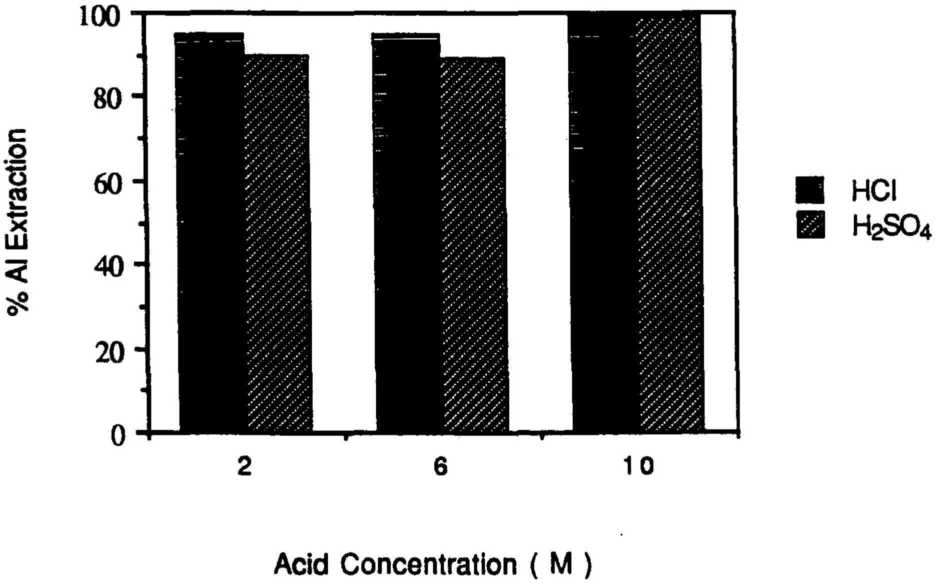
Table 5.17 Single Metal Stripping of Cr from Cr–Acetyl Acetone Solutions
100°C, PR = 1

e) Summary

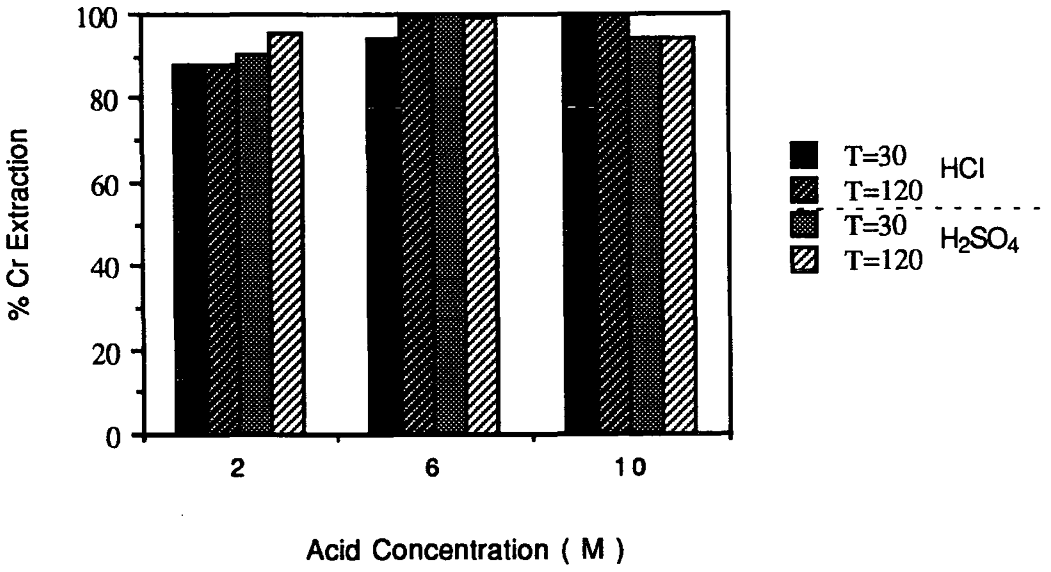
In many of the acid stripping experiments, the stripping values were either quite high (~>80%) or quite low (~<10%). For the acid extractants, the metal oxygen bonds must be broken for stripping to occur; i.e. an activation barrier must be overcome for bond cleavage. This is dependent upon acid type and concentrations, and also temperature. The stripping of Fe by 6M sulphuric acid from DEHPA solution was 3.8% at 20°C, and 58.7% at 100°C (see Table 5.11). This result indicates the requirement of heat to overcome the activation barrier.



Graph 5.12 Single Metal Stripping of Fe from Fe–Acetyl Acetone Solutions



Graph 5.13 Single Metal Stripping of Al from Al–Acetyl Acetone Solutions



Graph 5.14 Single Metal Stripping of Cr from Cr–Acetyl Acetone Solutions

However, in other cases, the use of higher stripping temperatures reduces metal stripping values. This is observed in the system 6M HCl, Fe – acetyl acetone (Table 5.5), 6M HCl, Fe – DEHPA (Table 5.11), 6M HCl, Fe – PJMT (Table 5.4), the stripping values at 20°C being 9.4%, 17.4% and 11.2% higher respectively than those at 100°C. This effect is probably due to the effect of temperature upon the stripping equilibrium as shown in the following equation (the reverse of the extraction equation).

$$MAn_{org} + nH^{+}_{aq} \rightleftharpoons nHA_{org} + M^{n+}_{aq}$$

As an increase in temperature will shift the extraction equilibrium to the right, it will similarly shift the stripping equilibrium to the left.

Often, upon increasing the concentration of the stripping acid, the metal stripping values correspondingly decrease whereas an increase might be expected; (e.g. in the Fe – PJMT, hydrochloric acid system). This phenomenon might be attributable to the change in aqueous metal species composition as acidity increases. An example is the formation of $[FeCl_4]^-$ in high hydrochloric acid concentrations. Depending on the organic component, $[H_2R]^+$ may form under conditions of high acidity, which can then form an ion–association type complex of the form, $[H_2R]^+.[FeCl_4]^-$ which are organically soluble. As this ion–association complex formation increases, the concentration of metal in the aqueous phase decreases.

The information derived from the stripping of 'synthetic' single metal loaded organic solutions was used in the subsequent investigations with loaded organic solutions produced from contact with residue solutions; i.e. (i) the sulphuric acid concentrations that gave the highest stripping values for each metal–solvent system were used in the subsequent investigations, (ii) sulphuric acid of specific concentrations were used on mixed metal loaded organic solutions in attempts to effect selective stripping procedures.

Hydrochloric acid was not used in the stripping studies of residue treated organic loaded solutions, as it was deemed inappropriate for use in high temperature stripping procedures.

5.3.2 Stripping Studies on Organic Residue Solutions

a) Primene JMT

Iron was stripped from Fe – PJMT solutions very efficiently with 2 and 6M sulphuric acid (see Table 5.18).

Acid concentration (M)	Time (minutes)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr stripped	% Fe stripped
2	1	60	4350	14	46	-	89.7
	15	60	4350	14	46	-	89.7
	30	60	4350	14	46	-	89.7
	85	60	4350	14	46	83.5	89.7
6	30	70	4064	5	12	98.6	96.0
	30	0	164	0	0	-	97.6
	30	0	4	0	0	-	100

H_2SO_4, 100°C, PR1

Table 5.18 Stripping of Fe–PJMT Residue Solutions

The small quantities of metal impurities were almost fully stripped also. Thus, using such conditions, the purity of the iron product would be completely dependent upon the composition of the loaded organic solution. For a PJMT solution containing ~4000 ppm Fe, only two stripping stages are required for 99.9% Fe removal.

Chromium is also efficiently stripped using 6M sulphuric acid, the stripping values increasing with contact time up to 30 minutes (see Table 5.19). Two stripping stages were required to strip 99.2% of 6200 ppm Cr, with 6M sulphuric acid.

Acid concentration (M)	Time (minutes)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr stripped
6	1	6200	0	0	0	80.5
	2	6200	0	0	0	82.1
	5	6200	0	0	0	88.6
	15	6200	0	0	0	91.8
	30	6200	0	0	0	91.8
6	15	6200	0	0	0	96.6
	15	500	0	0	0	90.3

Table 5.19 Stripping of Cr–PJMT Residue Solutions H_2SO_4, 100°C, PR1

Aluminium stripping from PJMT with 2 and 6M sulphuric acid was observed to be $\geq$98.9% in every case (see Table 5.20).

Acid concentration (M)	Time (minutes)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Al stripped
2	1	0	0	0	990	98.9
	5	0	0	0	990	98.9
	15	0	0	0	990	100
	30	0	0	0	990	100
2	5	0	0	0	990	98.0
	5	0	0	0	20	100
6	30	0	0	0	1308	99.4

Table 5.20 Stripping of Al–PJMT Residue Solutions H_2SO_4, 100°C, PR1

The stripping data from single metal PJMT solutions (see Section 5.3.1.) indicated that Fe and Al would be efficiently stripped with 2M sulphuric acid, but that Cr stripping with the same would be ~10%. However, in the stripping experiments with mixed metal PJMT solutions with 2M sulphuric acid, high Cr stripping values were observed (see Table 5.21). This indicates that the state of Cr in the single metal organic solution is different from that in residue treated solutions. A plausible explanation is the possibility of Cr having been extracted in a mixed metal complex from residue solution, and as the non–chromic metal – extractant bonds are acid cleaved, Cr species are also liberated. Thus, Cr, Fe and Al were all efficiently stripped from mixed metal PJMT solutions.

Time (minutes)	[Cr] ppm	[Fe] ppm	[Al] ppm	% Cr stripped	% Fe stripped	% Al stripped
1	1600	1222	850	82.5	86.7	85.8
5	1600	1222	850	96.3	94.9	98.8
1	1460	3255	0	70.2	83.7	-
5	1460	3255	0	92.5	90.6	-
1	1360	40	88	92	-	74
5	1360	40	88	96	-	80
15	1360	40	88	97	-	91
30	1360	40	88	97	-	91

2 M H_2SO_4, 100°C, PR 1

Table 5.21 Selective Stripping of PJMT Residue Solutions

b) OPAP

Fe stripping studies with residue treated OPAP solutions using 2, 6 and 10M sulphuric acid, gave very low stripping values (<10%), showing that sulphuric acid is not suitable for this particular metal stripping stage.

Aluminium stripping was 50–60% (after 15 minutes contact time), and 60–70% (after 30 minutes) (see Table 5.22). Using a contact time of 30 minutes, two strip stages achieved 87.5% Al removal.

Acid concentration (M)	Time (minutes)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Al stripped
6	15	0	0	0	3100	60.5
	15	0	0	0	1225	52.2
	15	0	0	0	585	54.7
6	30	0	0	0	3200	62.5
	30	0	0	0	1200	66.7

H_2SO_4, 100°C, PR 1

Table 5.22 Stripping of Al–OPAP Residue Solutions

Magnesium stripping with 6M sulphuric acid was very efficient ($\geq$98.9% with contact times $\geq$15 minutes) (see Table 5.23).

Acid concentration (M)	Time (minutes)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Mg stripped
6	1	1	0	710	25	96.4
	5	1	0	710	25	97.5
	15	1	0	710	25	98.9
	30	1	0	710	25	100
6	30	0	0	521	0	99.8

H_2SO_4, 100°C, PR1

Table 5.23 Stripping of Mg–OPAP Residue Solutions

The stripping characteristics of a mixed metal loaded OPAP solution were studied using 6M sulphuric acid, at various contact times (see Table 5.24).

Time (minutes)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr stripped	% Fe stripped	% Al stripped
1	1165	136	250	1425	0.6	-	15.8
15	1165	136	250	1425	2.6	-	71.9
30	1165	136	250	1425	8.4	-	73.7
80	1165	136	250	1425	14.9	-	73.7

6 M H_2SO_4, 100°C, PR1

Table 5.24 Selective Stripping of OPAP Residue Solutions

Chromium stripping values increased with time (0.6% to 14.9%, after 1 minute and 80 minutes respectively). Aluminium was removed >70% after ≥15 minutes. A strip of Al, Cr – OPAP with 6M sulphuric acid led to 71.9% Al removal and 2.6% Cr removal, successfully accomplishing selective stripping.

c) DEHPA

The stripping of iron from DEHPA was studied at phase ratios of 1 and 4 (see Table 5.25). A stagewise study of Fe stripping at PR1, 5 minutes, exhibited 50.0% Fe removal in the first stage, with subsequent decreasing Fe stripping efficiency.

Studies regarding the stripping of Al (Table 5.26) indicated that using 6M sulphuric acid for 15–30 minutes gave excellent Al removal.

Mg stripping from DEHPA required 10M sulphuric acid over 15–30 minutes for >80% Mg removal (see Table 5.27). Stagewise Mg stripping showed poor Mg removal at very low concentrations.

Phase Ratio	Time (minutes)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Fe stripped
1	2	8	3250	5	300	55.4
1	15	8	3250	5	300	55.4
1	30	8	3250	5	300	56.9
1	80	8	3250	5	300	56.9
1	5	8	3250	5	300	50.0
1	5	-	1625	-	-	35.0
1	5	-	1055	-	-	18.7
1	20	0	6900	0	0	46.4
4	30	-	857	-	-	88.7

6 M H_2SO_4, 100°C

Table 5.25 Stripping of Fe–DEHPA Residue Solutions

Selective stripping studies were undertaken to separate Al from Fe and Mg from Cr (see Table 5.28). Using 6M sulphuric acid, separation of Al from Fe was met with limited success. 25% selective stripping of Al was accompanied by 5% Fe removal, and 98% Al was accompanied by 24% Fe removal. 2M sulphuric acid was completely successful in efficiently and selectively stripping Mg from Cr, Mg – DEHPA solutions.

5.4 Solvent Regeneration

Removal of metals from loaded organic solutions by acid stripping, produces the extractant in acid form. In many cases, the solvent is immediately ready for reuse in a metal extraction stage. However, the acid anion must, in some cases, be washed from the stripped solvent. This is especially required where hydrochloric acid has been used as the stripping agent, and the solvent is for reuse with a sulphate system. Unwashed solutions of DEHPA (e.g. Fe stripped using 6M hydrochloric acid) exhibited depressed metal extraction values compared to the water washed solvents or fresh solvents. It is suspected that entrained chloride exerts an additional chemical effect upon DEHPA metal extraction from sulphate solutions.

Acid concentration (M)	Time (minutes)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Al stripped
6	1	0	0	0	2280	26.3
	7	0	0	0	2280	70.2
	17	0	0	0	2280	95.4
	30	0	0	0	2280	99.8
6	30	0	0	0	3000	99.8
	30	0	0	0	1105	99.5
2	15	0	0	0	2280	71.3
	15	0	0	0	655	72.5
	15	0	0	0	180	22.2
6	15	0	0	0	2280	98.3

H_2SO_4, 100°C, PR1

Table 5.26 Stripping of Al–DEHPA Residue Solutions

Sulphuric acid stripped acidic solvents exhibited comparable metal extraction values to fresh solvents, as shown in the extraction tables in Chapter 4. These include DEHPA, OPAP and acetyl acetone. Primene JMT, however, is a primary amine, and upon acid treatment forms the acid salt, $RNH_3^+X^-$, (where X = HSO_4^-, Cl^-). HX must be removed from PJMT, in a regeneration process, for the recycled solvent to exhibit the same metal extraction characteristics as the fresh amine solvents.

Treatment with sodium hydroxide, followed by washing with water yielded fully regenerated PJMT which gave comparable metal extraction values, and pH effects comparable to the fresh solvent.

Acid concentration (M)	Time (minutes)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Mg stripped
10	2	10	0	415	0	52.0
	5	10	0	415	0	75.2
	15	10	0	415	0	82.9
	30	10	0	415	0	81.9
10	15	0	0	415	0	89.2
	15	0	0	45	0	12.2
6	15	0	0	415	0	51.8
	15	0	0	200	0	40.0

H_2SO_4, 100^{o}C, PR1

Table 5.27 <u>Stripping of Mg–DEHPA Residue Solutions</u>

Time (minutes) /Acid concentration	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr stripped	% Fe stripped	% Mg stripped	% Al stripped
1 / 6M	0	5000	80	910	-	5	-	25
5	0	5000	80	910	-	12	-	52
15	0	5000	80	910	-	24	-	98
30	0	5000	80	910	-	24	-	97
1 / 2M	2140	0	85	0	0.0	-	78.8	-
5	2140	0	85	0	0.0	-	98.8	-
15	2140	0	85	0	0.0	-	98.8	-
30	2140	0	85	0	0.4	-	98.8	-
15 / 2M	140	0	350	0	0.1	-	99.7	-
15 / 2M	43	0	860	0	0.2	-	99.8	-

H_2SO_4, 100^{o}C, PR1

Table 5.28. <u>Selective Stripping of DEHPA Residue Solutions</u>

5.5 Acetyl Acetone Regeneration and Subsequent Metal Recovery

Acetyl acetone, (unlike the other extractants, studied in this chapter), has a sufficiently low boiling point to enable the evaporation of the extractant for a regenerative purpose. When the diluent is also low boiling (e.g. chloroform), solid acetyl acetonate complexes may be obtained. Three methods become available for the recovery of metals and solvent from loaded acetyl acetone solutions.

5.5.1. Evaporation of Solvent and Thermal Decomposition of Complexes

Acetyl acetone and chloroform may be recovered by evaporation from loaded solutions by recovery of the distillates, at temperatures less than 140°C. The remaining metal(s) may be recovered as the acetyl acetonate complex(es), or as the oxide(s) from thermal decomposition. Required temperatures were found to be in excess of 300°C.

5.5.2. Evaporation of Solvent and Acid Treatment of Metal Residues

The solid metal acetyl acetonates produced by solvent evaporation may alternatively be treated with acid to effect metal decomplexation. The main advantage of this method, (over the acid treatment of loaded acetyl acetone solutions), is the lack of a phase separation stage.

5.5.3. Acid Stripping of Loaded Acetyl Acetone Solutions

The conventional route of acid stripping is accompanied by significant entrainment (solubilization) losses of acetyl acetone in the aqueous strip solutions.

Experiments were conducted with strip solutions of various acidities, with 'synthetic' loaded organic solutions. The solubility of acetyl acetone in the strip solutions, increased with the acidity of the strip solutions (see Tables 5.29–5.33). The chemical states of the metals in the strip solutions were studied by ultra violet spectroscopic techniques. The ratios of complexed to decomplexed metal acetyl acetonates were obtained for strip solutions and for chloroform washed solutions.

Physical state	H_2SO_4 concentration, M	% Fe extraction	% acetyl acetone in aqueous phase	% decomplexation	% decomplexation after washing with $CHCl_3$
Solution	2	92.5	40	55	99
Solution	4	92.5	40	64	99
Solution	6	94.1	70	69	99
Solid	2	100	-	73	99

Table 5.29 Acid Stripping of $Fe(acac)_3$

Temperature = 20°C, $[Fe]_i$ = 6400 ppm, PR = 1, Contact time = 15 mintues

Physical state	Acid	Acid concentration, (M)	% Cr extraction	% acetyl acetone in aqueous phase
Solution	H_2SO_4	1×10^{-4}	5.4	Negligible
		1×10^{-1}	4.6	Negligible
		2	3.4	Negligible
		4	7.0	20
		6	28.1	25
		10	100	100
Solution	HCl	4	14.7	15
		6	41.0	35
		10	100	80

Table 5.30 Acid Stripping of $Cr(acac)_3$ Solution

Temperature = 20°C, $[Cr]_i$ = 4090 ppm, PR = 1, Contact time = 15 mintues

Physical state	Acid	Acid concentration, (M)	% dissolution	% decomplexation	% decomplexation after washing with $CHCl_3$
Solid	H_2SO_4	6[a]	2.5	-	-
		6[b]	90.1	64.0	71.0
		6[c]	99.0	97.3	97.6
Solid	HCl	6[a]	2.6	-	-
		6[b]	97.7	61.2	64.3

[a] Temperature = 20°C

[b] Temperature = 100°C

[c] Temperature = 150°C

Table 5.31 Acid Stripping of Solid $Cr(acac)_3$

PR = 1, Contact time = 15 minutes, $Cr(acac)_3$ solid [2 g in 20 ml strip solution]

Acid	Acid concentration (M)	% Al extraction
H_2SO_4	1×10^{-4}	0.2
	1×10^{-3}	15.2
	1×10^{-1}	65.9
	4	96.3
	6	95.1
	10	70.7
HCl	2	81.7
	6	91.5
	10	96.3

Table 5.32 Acid Stripping of $Al(acac)_3$ Solution

Temperature = 2O°C, $[Al]_i$ = 4100 ppm, PR = 1, Contact time = 15 minutes

Acid	Acid concentration, (M)	% dissolution	% decomplexation	% decomplexation after washing with $CHCl_3$
H_2SO_4	2	73	44	82.5
	4	100	67	91.8
	6	100	100	100

Table 5.33 Acid Stripping of Solid $Al(acac)_3$

PR = 1, Contact time = 15 mintues, $Al(acac)_3$ solid [2 g in 20 ml strip solution]

The general observed trend was for a significant proportion of the metals in the strip solution to exist in the complexed acetyl acetonate form, where significant amounts of acetyl acetone existed. Removal of the entrained acetyl acetone, by washing with chloroform led to the decomplexation of almost 100% of the metals, (with no observed extraction of the metals from the aqueous strip solution).

5.6 Summary

studies

The Studies into the scrubbing of metal impurities from loaded organic residue solutions gave an indication of viable scrubbing systems; e.g. Cr scrubbing from Cr–Fe PJMT solutions was efficient, although Fe was also partially scrubbed. The acidity of the scrub solutions and metal concentrations and extractant type of the loaded organic solutions were observed to have a marked affect upon stripping characteristics.

The bulk stripping studies of metals from single metal organic solutions found stripping to be dependent upon acid type and concentration, and temperature. Stripping behaviour with organic residue solutions was in some cases different from single metal solutions. This is obviously due to the differences between the organic solutions; probably metal concentrations and the existence of mixed metal complexes in organic residue solutions. The differences in behaviour observed between 'synthetic' and 'process' solutions illustrates the necessity to study actual process liquors.

Statewise stripping studies of organic residue solutions showed the number of contact stages required (and their variation in efficiency) for the partial and complete removal of metals from organic solutions.

Solvent regeneration resulting from stripping has been demonstrated, with (e.g. PJMT) and without (e.g. DEHPA) further processing. Regenerated solvents have shown identical behaviour (within accuracy of measurement) to fresh solvents.

The scrubbing and stripping characteristics of PJMT and DEHPA are favourable to process application, where sulphuric acid alone is the scrubbing/stripping agent. OPAP requires the use of hydrochloric acid for the efficient stripping of some metals. In the case of acetyl acetone, high entrainment values were observed in the stripping study of single metal acetyl acetone solutions. The additional required stage of solvent washing from the scrub/strip solution has led to the conclusion that acetyl acetone is unlikely to be the most favourable extractant for process applications, unless an alternative metal recovery state (as outlined in Sections 5.5.1 and 5.5.2) is employed. As a result, a study of the stripping characteristics of acetyl acetone residue solutions was not undertaken.

CHAPTER SIX

PROCESS APPLICATIONS

6.1 Introduction

This chapter is concerned with an assessment of the information outlined in Chapters 1 to 5, for potential commercial application. Various routes for the extraction of metals from ores and secondary sources are outlined in Chapter 1, involving techniques which could be adapted for the processing of chromite residue and ore. The route starting with acid digestion of residue and ore was examined in Chapter 2, with notable success. The process of extractant screening, (as outlined in Chapters 3 and 4) led to the selection of 4 extractant based solvents for detailed study (i.e. OPAP, PJMT, DEHPA and acetyl acetone). The behaviour of these extractant based systems with residue solutions were investigated in sufficient depth to enable an assessment of processing options. The potential options for residue processing, the wider possibilities for chromite residue/ore and, as far as it is possible (within the scope of this thesis), the economic implications are discussed in this chapter.

6.2 Residue Processing Options

6.2.1. Digestion of Chromite Residue/Ore

The dissolution of chrome residue and ore has been shown to be a non–trivial process. It must be stressed that chromite ores differ in their composition, and that the studies outlined in Chapter 2 were only for the ore imported by B.C.C. from the Bushveld province in South Africa, and the subsequently produced residue from the B.C.C. Cr extraction process. However, the principles applied to the problem of residue/ore digestion might be expected to be relevant in the digestion of many chromite ores/residues.

It is tempting to proclaim that the conditions producing the highest digestion efficiencies would form the basis of the 'best' process. However, this is not necessarily the case: various factors must be assessed in the determination of the optimum set of parameters for digestion of residue/ore. These include;

(i) Efficiency of use of sulphuric acid, relating acid concentration to digestion efficiency. (Dissolved residue or ore : acid ratio.)

(ii) Cost of additives

(iii) Heating costs

(iv) Design of equipment, including incorporation of appropriate safety measures.

(v) Duration of digestion

The data in Chapter 2 shows that virtually complete residue/ore digestion is possible at 140–148°C and 150–200°C, respectively (depending on the solid: acid ratio). Optimum conditions to maximize the cost effectiveness of such a process may necessitate use of conditions which obtain lower digestion values, but for which the safety constraints are significantly reduced. The addition of CrO_3 has been shown to be beneficial to digestion values, for residue, and more significantly, for ore.

However, it is essential to the further investigations regarding hydrometallurgical extraction of the component metals in residue/ore, that digestion of the solid material has been shown to be technically viable.

6.2.2. Metal Extraction from Residue Solutions

a) Introduction

As outlined in Chapters 3 and 4, extractants were assessed for their behaviour regarding Cr(III) extraction from residue solutions. It was anticipated that a solvent extraction circuit involving only one extractant might prove to offer the most cost effective flowsheet. The extractants that offered the greatest potential were PJMT, DEHPA, OPAP, and acetyl acetone and thus these extractants were studied in further depth for their applicability to selective and efficient metal extraction from residue solutions. However, the applicability of acetyl acetone will not be discussed in this chapter, as its stripping characteristics were found to be unfavourable. The results were discussed in Chapter 4 with respect to how efficiencies and selectivities of the extractions varied with the experimental conditions. In this chapter, these same results will be reviewed, in an attempt to identify the most suitable conditions for viable process flowsheets, using these extractants. The likely stripping characteristics of the loaded solvents, as examined in Chapter 5, are also discussed.

The hot residue solution coming from the filtration state of digestion, may require removal of Cr(VI).

TBP has been shown to be an effective (and completely selective) extractant for Cr(VI) from residue and ore solutions. 2 or 3 contact stages with 50% TBP in kerosene may typically be required. The chemistry of this technique is well documented, as illustrated in Chapter 1. An alternative method to Cr(VI) removal by TBP, is the reduction of Cr(VI) to Cr(III) by means of a suitable reducing agent, such as hydrogen peroxide under acid conditions.[124] Hydrogen peroxide is particularly suited for this purpose, as the reaction products are only oxygen and protons.

$$H_2O_2 \rightleftharpoons 2H^+ + O_2 + 2e^-$$

The next stage is removal of iron from the solutions. Selective extraction of Cr(III), Al or Mg over Fe(III) from the sulphate solutions was not observed under any set of conditions examined. Various procedures are known for the removal of Fe(III) from solvent extraction feed solutions.[109] (i) Prior reduction of Fe(III) to Fe(II), (ii) aqueous phase complexation with a specific masking agent, (iii) coextraction of Fe with other metals followed by selective Fe(III) scrubbing or stripping, (iv) selective Fe(III) precipitation, and (v) preferential Fe(III) solvent extraction are useful techniques for iron control. In application to residue solutions, the techniques (iii) and (v) have been selected as offering the most promising routes for iron removal.

There is a range of permutations for a solvent extraction flowsheet for the separation of the component metals in a residue feed solution. The metals may be consecutively extracted by one or more reagents, or two or more metals may be extracted together with the selective extraction of only two, one or none of the metals. With reference to scrubbing and stripping data, these various routes will be identified, and the most attractive circuits discussed in further detail.

DEHPA has been demonstrated to extract the metal components from residue solutions in the order; Fe, Al, Mg, Cr. The same order of extraction is possible using OPAP, but it is also possible to reverse the order of the Mg/Cr extraction. PJMT has been shown to extract the metals in the order Fe, Cr, Al with no significant Mg extraction.

Any route leaving a solution consisting essentially of Cr(III) could be subjected to Cr(III) extraction. The extraction and stripping of Cr would be readily accomplished using Primene JMT.

For each case, potential routes will be postulated. However, various other potential routes achieving different efficiencies and selectivities of metal extraction, may be viable but the concentrations of metals in raffinates will vary from those described.

For process application it is important to gain a balance between high extraction of the metal of interest and low coextraction of impurities. However, though the metal extraction stage from aqueous solutions might ideally be completely selective, product purity may be improved by scrubbing or selective stripping (see Chapter 5). These studies have been designed to enable the best choice of conditions for high extraction efficiency and selectivity.

Low solubility of metal complexes, under conditions of high loading (especially when cooled in the laboratory) with higher concentrations of OPAP, led to the decision that an OPAP concentration of 29% $^{w}/_{v}$ would probably provide the most suitable physical S.E. characteristics whilst maintaining a high loading capacity.

It is interesting to compare the pH's of Fe and Al extraction for the 2 phosphate extractants, DEHPA 50% $^w/_v$ and OPAP 45% $^w/_v$. At PR2 for DEHPA 50% $^w/_v$ to obtain 90% Fe extraction and 21% Al extraction, the aqueous $pH_i/_f$ is 1.5/0.4, whereas for OPAP 45% $^w/_v$ to obtain 97% Fe extraction and 22% Al extraction the aqueous $pH_i/_f$ was –0.9/–0.9. The difference in pH between DEHPA and OPAP for equivalent metals extraction is observed over all conditions studied. Thus, it is evident that OPAP is a much more acidic extractant than DEHPA, i.e. much greater metal extraction values are observed with OPAP than with DEHPA, for the same aqueous solutions. This higher metal extraction efficiency for OPAP is not always necessarily better as selectivity may be lost.

b) Sequential Extraction of Metals Using One Extractant

i) DEHPA

The sequential extraction of Fe, Al and Mg from residue solution is shown in Table 6.1. Within this exercise it is difficult to equate the relative importance of, for example, pH alteration and PR to cost. In the extraction of Fe from DEHPA solutions the highest Fe extraction values are accompanied by significant Al co–extraction. As metal purity may be improved by scrubbing and/or selective stripping, a small quantity of co–extracted Al is permissible in the initial extraction stage. Extremes of certain parameters have been avoided. In Table 6.1, two stages of Fe removal yielded 99.0% Fe removal. The DEHPA solutions contain '7800 ppm Fe, 500 ppm Al' and '3240 ppm Fe' respectively, as calculated using Equation 2.

$$\text{Metal concentration in organic solution} = \frac{\text{(initial aqueous metal concentration)} \times \text{\% extraction}}{\text{PR}}$$

PR	pH_i/ pH_f	Time (mins)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
4	-0.5/-0.4	30	15200	34800	9280	12300	0	89.7	0	4.1
1	-0.4/-0.4	30	15200	3600	9200	11700	0	89.9	0	0.0
4	0.4/ 0.1	30	15200	360	9200	11700	0	100	0	89.1
1	0.4/ 0.4	30	15200	0	8400	1300	0	-	0	92.3
2	3.2/ 1.3	30	15200	0	8400	100	0	-	33.9	-

Table 6.1 DEHPA Sequential Extraction of Fe, Al, Mg

The scrubbing and stripping of iron from residue solution treated DEHPA, is shown in Tables 5.2 and 5.25. If increased iron purity is desired (depending on the fate of the iron product), aluminium may be effectively scrubbed from the DEHPA solution, e.g. using conditions PR4, pH_{iscrub} –0.45, over 15 minutes (99.4% Al and 3.8% Fe removal). The 6 M sulphuric acid stripping of iron from the DEHPA will initially be in the region of 46–56% efficiency, with further stripping stages yielding 35–80% Fe removal, depending upon PR and contact time.

Aluminium extraction from the residue solution is also a two stage process, giving DEHPA solutions containing 2600 ppm Al and 1200 ppm Al respectively. 6 M sulphuric acid stripping of the DEHPA is up to 99.8% efficient. Magnesium extraction from Cr, Mg only residue solutions would require several stages (at ~33% Mg extraction per stage), unless large alkali additions are made to reach pH_i ~6 (which is likely to be uneconomical). Extracted Mg is efficiently (≥80%) scrubbed by sulphuric acid (≥2M).

Were this route to be followed (with complete Mg removal), an aqueous chromium sulphate solution would remain. The extraction of Cr by DEHPA would be undesirable, as Cr stripping by sulphuric acid is very inefficient (see Tables 5.13 and Graph 5.10).

(An alternative could involve the co–extraction of Cr and Mg from residue solution by DEHPA. Mg could be selectively stripped by sulphuric acid. The major difficulty is the stripping of Cr from DEHPA, although the relatively expensive hydrochloric acid stripping route is technically viable. However, this also adds chloride into the solvent, which would necessitate a further solvent washing stage).

ii) OPAP

Sulphuric acid stripping of metals from OPAP is only viable for magnesium and aluminium. A flowsheet involving the use of hydrochloric acid (as required for effective acid stripping of iron) could be postulated from the data in Chapters 4 and 5. But, as the use of hydrochloric acid requires significantly higher capital costs, the sequential metal extraction flowsheet for OPAP will not be examined further.

iii) PJMT

Two initial approaches to the extraction of the metals by PJMT are immediately apparent. The first begins with the selective extraction of iron but with a relatively poor extraction efficiency, and the second involves the co–extraction of Cr with Fe, as outlined in Table 6.2, allowing improved Fe extraction efficiency.

PR	pH_i/ pH_f	Time (mins)	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
5	0.0/ 0.4	10	14000	30000	8000	12000	19.4	85.1	0.0	0.0
3	-0.3/-0.2	30	11280	4470	8000	12000	21.1	80.0	0.0	0.0
10	0.5/ 1.3	30	8900	890	8000	12000	95.9	-	0.0	45.5
8	0.9/ 4.0	30	365	50	8000	6540	-	-	0.0	99.0

Table 6.2 <u>PJMT Sequential Extraction of Fe, Cr, Al</u>

In the first case, the selective iron extraction efficiency is 51.0%, yielding a PJMT solution containing Fe 3160 ppm. Acidification of the raffinate is required to obtain an aqueous solution that will be suitable for 59.6% Fe extraction. (Fe 2400 ppm, Cr 390 ppm, in PJMT) with 9.2% Cr coextraction. Further extractions are required to remove significant quantities of residual Fe (approximately 5 stages to reduce Fe concentrations to <1000 ppm), and in these further stages Cr co-extraction is unavoidable. Therefore, it appears that the route involving high Fe extraction with significant Cr extraction would prove more suitable.

Iron may be reduced to <1000 ppm by two stages of extraction with PJMT, producing organic solutions with, 'Fe 5100 ppm, Cr 540 ppm', and 'Fe 1190 ppm, Cr 790 ppm' respectively. Although stripping studies of synthetic single metal PJMT, Cr and Fe solutions indicated the possible selective stripping of Fe from Fe, Cr–PJMT solutions, stripping studies of residue treated Cr, Fe–PJMT solutions showed that such selective stripping is not possible. Scrubbing studies of these solutions indicated that removal of substantial proportions of Cr (e.g. 97.8%) are possible with the co-removal of smaller proportions of Fe (23.7%, at PR5, pH_{iscrub} –0.45, over 30 minutes, see Table 5.1).

When the aqueous solutions, resulting from substantial Fe extraction, are treated with PJMT, Cr is preferentially extracted to Mg or Al. However, substantial Cr extraction is always accompanied by Al coextraction (see Table 4.30). Al may be scrubbed (63%) in preference to Cr, by sulphuric acid, although a small proportion of Cr (5%) is co-scrubbed. Cr may be efficiently (>90%) stripped with 6M H_2SO_4.

Aluminium may be 99.0% extracted by PJMT, without Mg co-extraction, from Al, Mg only residue solutions. Stripping of Al from PJMT – Al solutions may be effected to >99% with 2M H_2SO_4, after 1 minute (see Table 5.5).

According to the number of stages of scrubbing and stripping that are deemed to be cost effective, the purity of the metals in the strip solutions can vary considerably. It is technically viable, for metal impurities in final strip liquors to represent <1% total metal concentration. Re–extraction, scrubbing and stripping may be used to increase metal purity and concentration levels in the strip solutions. Efforts to increase purity will purely be functional upon the cost effectiveness of the procedure with respect to the suitable price for its end use.

Within each of the three routes with DEHPA, OPAP and PJMT, for sequential metal extraction, drawbacks might be expected to severely hinder the successful economic implementation of any of these routes. None of DEHPA, OPAP or PJMT alone provide completely selective and efficient separations of Cr, Fe, Mg and Al. But, it is possible that the use of these extractants in combination with each other could provide more cost effective routes (despite the associated drawbacks outlined in Section 4.1). Therefore, the various permutations of the use of these extractants in conjunction with each other will now be considered.

c) Extraction of Metals using Permutations of Extractants

The permutations involving OPAP extraction of Fe or Cr have been ruled out initially as their extraction by OPAP necessarily requires the unfavourable hydrochloric acid stripping route. Several permutations are discussed in order to demonstrate the wide variety of technically feasible choices.

i) DEHPA–Fe, PJMT–Cr, DEHPA–Al

DEHPA may be used to extract Fe in two stages, as in Table 6.1, removing 99.0% Fe and 4.1% Al. As outlined in 6.2.2.(a), Al may be removed from the loaded scrub solution by scrubbing (99.4% Al and 3.8% Fe removal). However, the relatively low (~50%) efficiency of sulphuric acid stripping of iron necessitates a multi stage stripping operation for Fe recovery.

PJMT could then be used to selectively extract Cr from the Cr, Al, Mg high residue solution. Efficient Cr extraction is always observed to be accompanied by Al co–extraction (a favourable extraction system achieves 96% Cr extraction and 45.5% Al co–extraction). Al scrubbing (63% efficiency with 5% Cr coscrubbed) can be used to increase Cr purity – ~2 scrub stages to reduce Al to ~50 ppm and Cr from ~12000 ppm to ~11000 ppm.

Obviously, further scrubs would further increase Cr purity, before Cr stripping with 6 M H_2SO_4 (>90% per stage).

DEHPA may then be used again to extract Al from the Al, Mg only solution (see Table 4.16). 99.5% Al extraction of the Al has been observed (PR2, $pH_{i/f}$ 1.8/1.1) with zero Mg coextraction. The 2.9% coextraction of Cr in the solution in Table 4.16 represents a total metal impurity of 0.3% in the DEHPA solution. In such a process, the Cr impurity would be dependent upon the residual Cr concentration after bulk Cr extraction had been effected. Stripping of Al by sulphuric acid from DEHPA has been observed at up to 99.8%.

ii) DEHPA–Fe, PJMT–Cr, PJMT–Al

This procedure follows the same route as 6.2.2.(c)(i) for Fe and Cr removal. For Al removal from Al, Mg only solutions, PJMT may alternatively be used. This is highly efficient and selective, as shown in 6.2.2.(b)(iii) and Table 6.2.

iii) DEHPA–Fe, PJMT–Cr, OPAP–Al

Again, the Fe and Cr removal techniques are the same as in 6.2.2.(c)i) but instead, OPAP may be used for efficient and selective removal. >99.5% Al extraction, completely selective over Mg, is easily achieved using OPAP. Residual Cr impurity levels are comparable to those obtained from a DEHPA system. Sulphuric acid stripping of Al from OPAP has been observed in the region 52 – 67%, less efficient than in the corresponding DEHPA system.

iv) DEHPA–Fe, DEHPA–Al, PJMT–Cr

The sequential extraction of Fe and Al may be achieved by DEHPA, as outlined in 6.2.2.(c)(i) and Table 6.1. As opposed to the poor extraction of Mg from Cr, Mg only solutions by DEHPA (in 6.2.2.(b)(i), a change of solvent to PJMT allows the highly efficient and completely selective (over Mg) extraction of Cr. The only outstanding detraction from this process permutation is the persistent problem of multi–stage Fe stripping from DEHPA, by sulphuric acid.

v) DEHPA–Fe, DEHPA–Al, OPAP–Mg

As in 6.2.2.(c)(iv), DEHPA can be used to extract Fe and Al. If OPAP is used as the extractant with a Cr, Mg only solution, a choice may be made (according to process conditions) whether Cr or Mg is next extracted. Cr extraction by OPAP requires long contact times and lengthy stripping with strong hydrochloric acid. The more attractive method for this metal separation is Mg extraction which using H_2SO_4 at contact times of only 1 minute, is fairly efficient and selective (e.g. 55.0% selective Mg extraction by OPAP in 1 minutes from a residue solution at pH 1.0, PR4).

vi) DEHPA–Fe, OPAP–Al, DEHPA–Mg

This route is similar to that in 6.2.2.(a)(i), but OPAP is used to extract aluminium rather than DEHPA. OPAP can achieve selective Al extraction at the efficiencies of 92% (PR4, $pH_i/_f$ −0.5/−0.5), 75% (PR2, $pH_i/_f$ −0.5/−0.5), and 58% (PR1, $pH_i/_f$ 0.4/0.3), with Al, Cr, Mg high residue solutions. Subsequent Al stripping with 6 M H_2SO_4 for 30 minutes has been observed at 63 – 67% (Table 5.22).

vii) DEHPA–Fe, OPAP–Al, OPAP–Mg

DEHPA extraction of iron, and OPAP extraction of aluminium may be used (as above in 6.2.2.(b)(vi), followed by OPAP extraction of Mg instead of DEHPA. OPAP–Mg extraction from such solutions is discussed in 6.2.2.(b)(v).

viii) DEHPA–Fe, OPAP–Al, PJMT–Cr

In most of the stages of this particular route, metals extraction and stripping are efficient and selective. DEHPA–Fe extraction is excellent, and although stripping values by sulphuric acid are not very high (~50%, see Table 5.25), DEHPA appears to be a more suitable iron extractant than PJMT. OPAP extraction and stripping of aluminium is very good (see 6.2.2.(b)(vi), although not quite as good as for DEHPA. PJMT extraction and stripping Cr from Cr, Mg only solutions, as shown in 6.2.3.(b)(iv), is highly efficient and completely selective.

ix) PJMT–Fe, PJMT–Cr, DEHPA–Al

PJMT may be used to extract iron and chromium as outlined in 6.2.2.(b)(iii). DEHPA may be used to extract Al from Al, Mg only residue solutions, as shown in Table 4.16. 99.0% Al extraction may be achieved at $pH_i/_f$ 1.4/1.0, PR2. (Cr contamination is dependent upon residual Cr concentration.)

x) PJMT–Fe, DEHPA–Al, PJMT–Cr

Alternatively, the order of Al and Cr extraction may be exchanged, still using the same extractants for these metals. Again, efficient and selective extractions of Al (92%, at $pH_i/_f$ 0.4/0.4, PR1) and Cr (99%, at $pH_i/_f$ 1.0/2.9, PR5) are possible, followed by efficient stripping.

xi) PJMT–Fe, DEHPA–Al, DEHPA–Mg

This route may be considered to compare unfavourably to other routes; e.g. to a DEHPA only route, PJMT extracts Fe from Fe high residue solutions less favourably than DEHPA. Also, DEHPA extraction of Mg cannot be efficiently achieved without an excessively high phase ratio, whereas an efficient alternative (e.g. PJMT extraction of Cr) may be easily achieved.

xii) PJMT–Fe, OPAP–Al, PJMT–Cr

In a similar route to that in 6.2.2.(c)(viii), iron may be extracted by PJMT, followed by OPAP–Al extraction and PJMT–Cr extraction. This route appears to provide a favourable series of metals extraction, however, the extraction of iron by PJMT is likely to be less favourable than by DEHPA (as in 6.2.2.(c)(viii)).

xiii) PJMT–Fe, PJMT–Cr, OPAP–Al

This route, similar to 6.2.2.(c)(iii), uses OPAP to extract Al rather than PJMT. OPAP is more suitable for Al extraction from solutions of lower pH (e.g. at pH_i 0.4, PJMT extracted 50% Al (PR8), whereas OPAP extracted 99.5% Al (PR2)). However, PJMT would be likely to be preferred as stripping of Al from PJMT is typically >95% whereas from OPAP it is <70%.

xiv) PJMT–Fe, OPAP–Al, OPAP–Mg

This route demonstrates the possibility of a technically feasible route, which would involve several metal extraction stages (i.e. for PJMT–Fe and OPAP–Mg) and several stripping stages for each metal. The overall scheme therefore compares unfavourably with other routes.

xv) PJMT–Fe, DEHPA–Al, OPAP–Mg

The parts of this extraction scheme have been discussed in other sections above. This route would be feasibly operated, but the selective stripping required for Cr/Fe separation from PJMT, and poor OPAP–Mg extraction characteristics mean that it is unlikely to prove the most cost effective choice.

xvi) PJMT–Fe, OPAP–Al, DEHPA–Mg

For similar reasons to 6.2.2.(c)(xi), this route is unlikely to prove the most cost effective choice.

6.2.3. Selection of Extraction Routes Offering Greatest Potential

Of the above routes 6.2.2.(b) and 6.2.2.(c), all are technically feasible, although various aspects of the individual metals extracted by each extractant mean that there are extractants which are more suited to the efficient and selective extraction and stripping of each metal (depending on the solution composition). In the choice of a route, considerations should include:

(i) the number of extraction and stripping stages,

(ii) metal product purity (depending upon future application)

(iii) order of metals extraction,

(iv) number of different solvents involved.

For the order of extraction, Fe, Al, Cr; the route DEHPA–Fe, DEHPA–Al, PJMT–Cr (6.2.2.(c)(iv)) would appear to best meet the above criteria. As Mg extraction has been shown to require high pH and PR for efficient operation, it appears that extraction of Mg before Cr is unlikely to prove worthwhile. It remains a possibility however, as outlined in 6.2.2.(c)(v) and 6.2.2.(c)(vii);

(DEHPA–Fe, DEHPA–Al, OPAP–Mg and DEHPA–Fe, OPAP–Al, OPAP–Mg.) OPAP removal of Mg appears to be more suitable than using DEHPA.

Conditions	pH_i/ pH_f	Extractant	[Cr] ppm	[Fe] ppm	[Mg] ppm	[Al] ppm	% Cr(III) extraction	% Fe(III) extraction	% Mg(II) extraction	% Al(III) extraction
4	-0.5/-0.4	DEHPA	15200	34800	9280	12300	0.0	89.7	0.0	4.1
1	-0.4/-0.4	DEHPA	15200	3600	9200	11700	0.0	89.9	0.0	0.0
4	0.4/ 0.1	DEHPA	15200	360	9200	11700	0.0	100	0.0	89.1
1	0.4/ 0.4	DEHPA	15200	0	8400	1300	0.0	-	0.0	92.3
5	0.5/ 1.1	PJMT	15200	0	8400	100	96.5	-	0.0	-

Table 6.3 DEHPA Extraction of Fe and Al Followed by PJMT Extraction of Cr

Time = 30 minutes

The order of Fe, Cr, Al may be suitably achieved by using DEHPA–Fe, PJMT–Cr, and either PJMT or DEHPA for Al.

Thus a wide range of options for the separation of the component metals of chrome residue solution are available.

6.3 Discussion of Other Potential Routes for the Separation of the Component Metals from Chrome Residue/Ore

The present routes for the production of chromium compounds for industry, from chromite ore, are outlined in Figure 6.1.

6.3.1. Solvent Extraction Route from Sulphuric Acid Digest Solutions

It is possible for the solvent extraction systems to operate in a counter current manner. In such cases loaded solvents would be used to extract the smaller concentrations of metals remaining in residue solutions. Similarly, loaded scrub and strip solutions would be used to remove small quantities of metals from loaded organic solvents. These studies are beyond the scope of this thesis, however, the results contained in the thesis would provide vital information were a study of a counter current operation pursued.

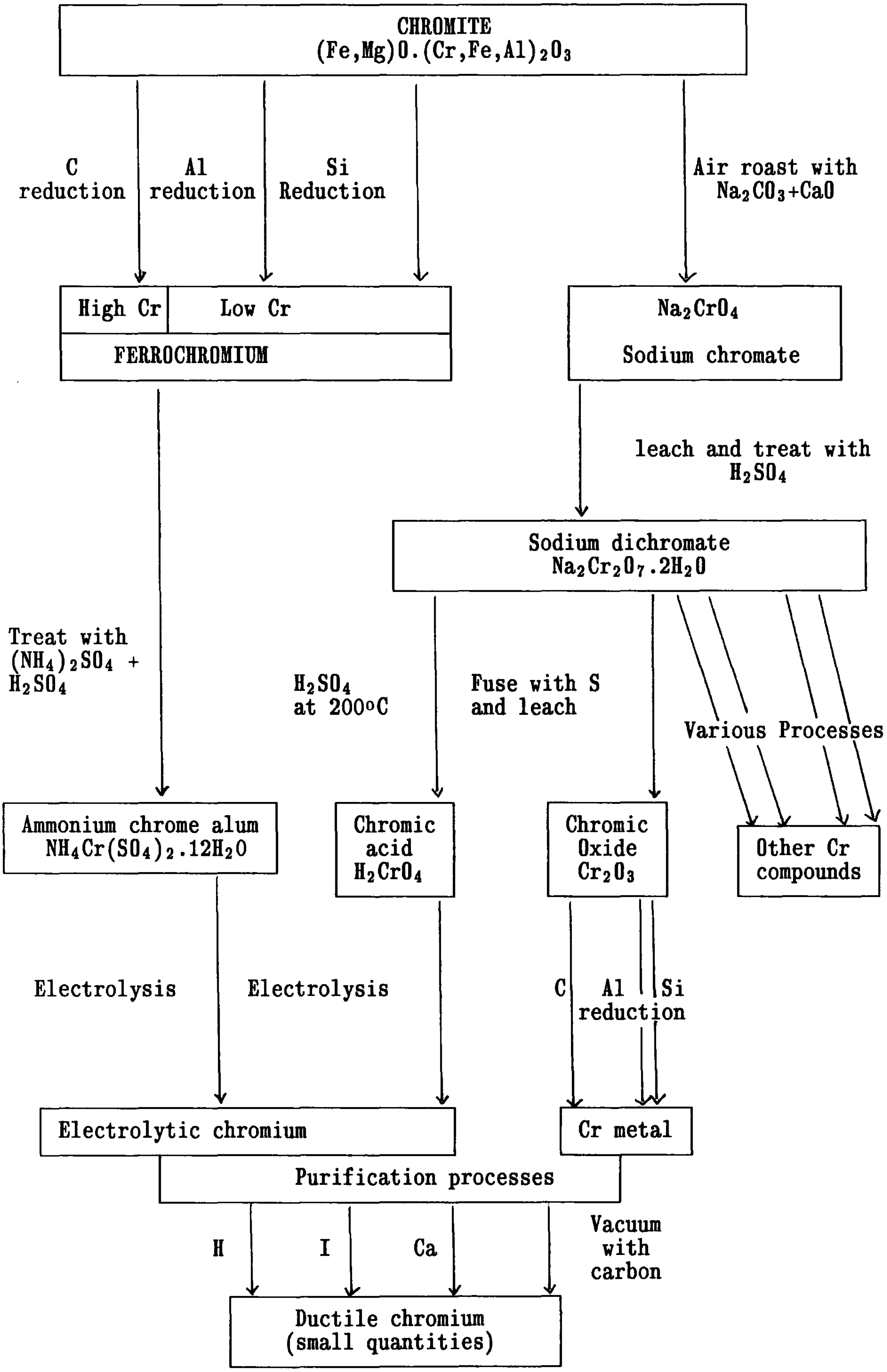


Figure 6.1 Chromium Processing from Chromite Ore

An alternative to the purification of loaded organic solutions (containing metals with little or no market value) is to strip all these metals from the organic solution into sulphuric acid. The loaded sulphuric acid would be used as part of the acid used for residue digestion, (although difficulties could then arise in the solvent extraction circuit, as recycling could cause metal build up followed by significant changes in metal concentrations in aqueous feed solutions).

The series of metal extractions could be stopped at any stage, once the metal(s) of interest has been removed, e.g. if Cr is the metal of interest, a process involving DEHPA extraction of Fe, and PJMT extraction of Cr might prove acceptable. The Al, Mg raffinate could be disposed of, rather than perhaps unnecessary further metal extraction.

Where two metals may be coextracted, their separation by scrubbing or selective stripping could prove to be economically untenable. An alternative, e.g. in the case of iron and aluminium, could be costripping with dilute acid followed by alkaline pH adjustment to produce an aluminate solution and iron precipitate.

Within the discussions on the selection of suitable systems for metal separations, attention has focussed upon sulphate systems (for digestion and in stripping/scrubbing). Chloride systems were briefly investigated for their characteristics in stripping, but although efficiencies were promising their use was not thought to be desirable. Chloride metallurgy has made considerable progress in the laboratory and pilot plant in recent years, and a few commercial plants are using some aspect of chloride technology. Corrosion is still a problem, but not to the same extent as formerly with the development of synthetic materials. Low temperature processes are presently more viable compared to high temperature chlorination processes mainly because many engineering problems remain unsolved at the higher temperatures. Were these problems to be overcome, hydrochloric acid processes at high temperature could become more cost competitive with respect to sulphate processes. In such a scenario, the data for hydrochloric acid stripping of the loaded solvents (see Chapter 5) would be of practical relevance. Advantages would immediately become apparent, i.e. (i) improved stripping efficiencies (ii) some metal extractions would become available for application e.g. Cr or Fe with OPAP.

6.3.2. Hydrometallurgical Alternatives to Removal of Cr as Cr(III)

This thesis is concerned with obtaining Cr in the +3 oxidation state. Presently, Cr(III) compounds are produced by the reduction of sodium dichromate (from the Na_2CO_3 pyrometallurgical extraction of chromium from chromite ore). The dichromate is fused with sulphur and the chromic oxide leached out (see Figure 6.1). Depending on the various economic aspects of the solvent extraction route to Cr(III) (as outlined in Section 6.4), the scheme developed in this thesis could supersede the sulphur fusion route to Cr(III) compounds.

Were the production of Cr in the +6 state to be considered, hydrometallurgy could offer viable routes. These include the digestion of ore/residue in chromic acid[12], sulphuric acid, and perhaps Caro's acid. The chromic acid digestion of chromite ore is patented; 76% of oxidized ore being dissolved in a 24 hour leach [chromic acid 50% $^w/_w$, 110°C]. The patent describes the oxidation of Cr(III) to Cr(VI), by the addition of an oxidizing agent (e.g. a persulphate salt or Caro's acid), or electrochemically. Removal of the dichromates of Fe, Mg and Al is by a strongly acidic cation exchange resin (e.g. Amberlite 200), or by acidic extractant liquids (e.g. DEHPA, DNNSA (dinonyl naphthalene sulphonic acid).

An interesting alternative possibility is the digestion of chrome ore/residue in the oxidizing agent, Caro's acid. Caro's acid is an equilibrium mixture of H_2SO_5, H_2SO_4 and H_2O_2. The digestion of ore/residue in strong Caro's acid would be expected to be relatively efficient. The advantage of Caro's acid over the electrolytic oxidation or addition of an oxidant (e.g. CrO_3) to sulphuric acid is the ease and efficiency (and therefore cost) of oxidation of the spinel components. The only envisaged possible difficulty would be whether Caro's acid had sufficient stability at the temperatures required for efficient digestion. In addition to oxidation of the ferrous spinel, Caro's acid would effect complete oxidation of Cr(III) to Cr(VI). Caro's acid is a readily available material, with on site generation of hot Caro's acid a possibility. Alternatively, after digestion of ore/residue in sulphuric acid, the addition of Caro's acid to the digest solution could be used to effect Cr(III) to Cr(VI) oxidation. Either way, Cr(VI) solutions with Fe, Mg and Al are produced. Metal extraction could be accomplished using an acidic resin or liquid extractant.[12] Cr(VI) could be removed by TBP, as outlined in Chapter 1, as previously demonstrated industrially by Ugine Kuhlmann. Detoxification of Cr(VI) in effluent waters could be achieved by reduction with hydrogen peroxide. An increase in pH of a Fe, Mg, Al sulphate solution to alkaline conditions would remove Fe and Mg as solid precipitates, leaving aluminium in solution as aluminate, $[Al(OH)_4]^-$. Alternatively, a solvent extraction route could be employed if desired, for the separation of Fe, Al and Mg.

The chemical method involving the fusion of sodium hydroxide with chromite ore[5], as outlined in 1.2.1 could be applied to residue. This method has advantages over the traditional pyrometallurgical chromium extraction route with sodium carbonate, in that high silica ores can be used and the temperature is greatly reduced (~1100°C to 550°–660°C). Methanol (for NaOH) and water (for sodium chromate) leaching of the fused product achieves excellent separation of sodium hydroxide and sodium chromate. Again, the Cr produced is in the +6 state. Experiments involving the fusions of NaOH with chrome residue and ore at 500°C were attempted, but laboratory facilities proved inappropriate.

6.4 Economic Analysis of a Solvent Extraction Route

6.4.1. Introduction

In the economic analysis of a metals separation process, involving leaching followed by solvent extraction, there are several factors that must be assessed. The capital and operating costs are central to any process, but process viability is also subject to fluctuations in the value of the end products. In the construction of a plant the potential for process adaptability must be accounted for. Market forces may require changes in product purity, or feed composition, either of which could require a change in process conditions; e.g. at a point in time it could be profitable to produce Cr(III), Fe and Al compounds from residue, in high purity, and at a later data solely Cr(III) production could be required. The discussions of the various permutations in metal extraction order and solvent choice have borne in mind these potential fluctuations in process requirements.

As the metals industry approaches a new millennium, there are four key issues to be faced. These are the increased environmental expectations (coupled with legislation), international competition within existing markets, the development of new products and markets and the increased usage of secondary metal processing and waste recycling. The metals industry will be required to reckon with living in a world without tarriffs, without non–tarriff barriers, without trade distorting subsidies and yet still be profitable. Specialization into areas will need to be accompanied by adaptability to change. It is essential for the industry to recognize the importance of developing new technology for improved cost effectiveness of existing and new processes for metal recovery. The process of extraction of the metals from chrome residue (regarded as an environmental hazard) is a prime example of the development of technology in the meeting of new requirements.

With the undoubted success of hydrometallurgical processing in the primary sector, it is only natural that application in the secondary sector (of metal wastes) should be considered. It is expected that solvent extraction will be widely successful because of its flexibility, capital cost savings and scale advantages over traditional forms of metal processing, and that small plants can be built and operated economically.[22]

6.4.2. Capital and Operating Costs

In general, the capital costs of a solvent extraction plant can be influenced by;

(i) Flow rates and flow ratios (were a countercurrent system employed)
(ii) The kinetics of extraction (and thus the size of the mixing vessel)
(iii) The phase ratios (and thus the size of the mixing vessel)
(iv) Coalescence (the settling requirements dictate equipment costs)
(v) Entrainment (thus the cost of solvent recovery equipment)
(vi) The number of stages (thus the number of mixer settlers or columns necessary)
(vii) Building requirements.

Ongoing operating costs generally involve the following factors;

(i) Sulphuric acid for dissolution (or acid reprocessing costs from spent residue solutions)
(ii) Preequilibration of the solvent may be required
(iii) General process running costs, e.g. solvent loss, stripping acid, etc.
(iv) Energy costs.

In the digestion of chrome residue and sulphuric acid, the main source of reagent cost is that of the sulphuric acid ($68 per tonne, November 1990). It is envisaged that the site of a plant would be in close proximity to a large chrome residue stockpile, thus minimizing transport costs. The other major operating costs would be in heating, maintenance, and labour. The addition of water to highly concentrated sulphuric acid may be used to obtain high initial solution temperatures. 'Water', for acid dilution, may be recycled from other parts of the flowsheet, and may contain residual small quantities of the metals of interest.

However, capital costs for the digestion procedure, as described in Chapter 2, might be expected to be considerable in relation to operating costs. In particular the safety considerations in the exothermic dissolution of residue would require stringent safeguards. The digestion, filtration and dilution must be a continuous high temperature process to alleviate cooling of the mixture, which would result in solidification. The efficiency of the dissolution stage is essential for the smooth running of the filtration stage. Filtration becomes a more difficult and lengthy task as the percentage solids in the slurry are increased.

The degree of filtrate dilution has significant effects upon operating costs. In the processing of feed solutions it is generally accepted that the economic efficiency of extraction increases with aqueous metal concentration. A cut off point will be reached at a particular metals concentration, above which processing costs will not significantly deviate. However, precise metal extraction data will deviate according to feed solution concentrations, due to limitations in solvent loading capacities and available volumes. Precautions for problematic eventualities must be built in to the system.

A significant part of the capital cost of a solvent extraction process is the reagent cost. In the assessment of different solvent extractants, extraction cost will be rated fairly high in the list of considerations. However, given that the extractants exhibit comparable metal extraction values, the extractants with the lowest price may not be the best choice for the system. This is exemplified in an operating cost comparison of DEHPA, naphthenic acid, and Versatic 911 for Co/Ni extraction. These extractants are compared because of their similar extractive properties. The prices quoted in Table 6.4 are from 1973, but the principle of the sources of total cost of using each extractant is clear. Solvent losses, the primary sources of difference in operating costs, are based on 30 ppm DEHPA at $1.25 per lb, 900 ppm naphthenic acid at $0.17 per lb, and 900 ppm Versatic 911 at $0.30 per lb.

Although treatment of effluent streams for solvent recovery could be expensive, it may be necessary for compliance with environmental specifications. Water reuse is nowadays more popular within industry; the water from spent residue solutions could be diverted to the acid dissolution stage (which could reduce the throughout of a solvent recovery plant). In addition to effluents containing solvent, environmental legislation may force hydrometallurgical industries to discontinue producing certain metal containing effluents. To handle this situation, some industries use solvent extraction "kidney" units to avoid the build up of undesirable metal contaminations.

	cent per pound (lb) of metal produced		
Process Stage	Naphthenic acid (1 M)	Versatic 911 (1 M)	DEHPA (0.6 M)
Solvent Loss	1.53	2.70	0.38
Alkali Requirements (pH control)	3.00	3.00	3.00
Scrubbing (recycle strip liquor)	0.20	0.20	0.20
Stripping (10% H_2SO_4)	1.80	1.80	1.80
Maintenance and Labour	1.30	1.30	1.30
Depreciation (equipment and instrumentation)	0.41	0.41	0.33
Total Estimated Cost	8.2	9.4	7.0

Table 6.4 Estimated Processing Costs for the Extraction of Cobalt or Nickel Using Napthenic acid, Versatic 911, and DEHPA

This data indicates that it is more favourable to use DEHPA than carboxylic acids in commercial solvent extraction processes. DEHPA exhibits superior solvent losses, loading capabilities, and extraction rate. These aspects of extraction have an appreciable effect on the size and type of equipment.

The extractant systems recommended for use with residue solutions are Primene JMT (10% $^v/_v$ in kerosene), DEHPA (50% $^v/_v$ in Kerosene), and OPAP (29% $^w/_v$ in kerosene). The equipment depreciation, alkali requirements, and stripping and scrubbing requirements would be expected to be different for each of these solvents. Solvent losses of these solvents have been observed to be negligible under the employed experimental conditions. Many of the solvent extraction characteristics of the 3 different solvents, as outlined in Section 3.2., have all been observed to be favourable and fairly comparable; i.e. extractant availability, extraction rate, solvent stability, solubility in hydrocarbon media, solvent density, interfacial tension, solubility in aqueous media, toxicity and corrosiveness. However, the required pH_i of the aqueous feed solutions is markedly different; OPAP being the most acidic of these extractants requires the feed solutions to be at lower pH_i than DEHPA, for comparable extraction. Thus, alkali addition, to aqueous solutions for OPAP treatment, is minimized. The prices of alkali and acid (November 1990) are H_2SO_4 98% \$68 per tonne, and NaOH 50% $^{v}/_{v}$ \$263 per tonne, quoted from the publication "Chemical Marketing Reporter". However, the acid requirements for OPAP stripping are higher than for PJMT, for example. Primene JMT will require low alkali additions for aqueous pH_i control, but will instead require alkali for solvent regeneration. (The alternative is high alkali addition to the aqueous solution, with initial addition of sulphuric acid required to convert PJMT to its acid salt.)

Acid requirements for stripping and scrubbing are markedly different. Generally, the metals are efficiently stripped from PJMT by relatively dilute (2M) sulphuric acid. DEHPA requires 2M sulphuric acid for Al and Mg stripping, several stages for stripping of Fe with 6M H_2SO_4, and even hydrochloric acid for efficient Cr stripping. Capital costs for equipment for stripping with hydrochloric acid are substantially greater than with sulphuric acid. This is the main reason for the discounting of OPAP as a primary candidate for use in a residue solution.

The prices of the extractants are, as described in Chapter 3, subject to fluctuation. Over the period January 1989 to September 1990, the prices of DEHPA and OPAP remained at £4060 and £3230 per tonne, respectively. Both are produced by Albright and Wilson. In the same period, the price of PJMT (produced by Rohm and Haas) rocketed from £2655 to £4995 per tonne, a 88%

rise. In a tonne of the respective solvents, the price of the extractants are (according to % content);

50% DEHPA	£2030	
29% OPAP	£937	
10% PJMT	£500	(September 1990 prices).

These prices do not include the price of kerosene, which would be expected to be small, relative to the extractants. Still, these prices are not directly comparable as regards metal extraction, as different phase ratios are typically used. Primene JMT is typically used at phase ratios of 3, 5 and 6 and DEHPA and OPAP typically at PR's of 1, 2 and 4. The relative price of PJMT 10% would therefore roughly double, to ~£1000. Thus, the relative prices of the solvents do not appear to differ by more than a factor of 2. The price of a solvent is merely one part of the capital cost of a process. It is likely that for a solvent extraction process for residue, the number of size of contactors and settlers, (dependent upon extraction efficiencies, selectivities, and phase ratios) would carry a greater weight in capital cost calculations than solvent price. These considerations will also be influential in the choice of reaction conditions. In the analysis of required conditions for efficient and selective metals extraction, a pattern emerges of a balance between PR and pH_i, i.e. similar metals extraction behaviour may be observed in a system as the PR is increased and pH_i decreased, or vice versa. In many cases, it is likely that lower PR's will be favoured over low pH (within certain ranges) as the cost of larger equipment is likely to be much greater than the increased cost of alkali. (However, cut off points in terms of chemical behaviour and cost means that these ranges are likely to be fairly narrow.) The ranges in choice of conditions, and the choice of solvent system (with the respective scrubbing and stripping characteristics) enables considerable flexibility in the design of a solvent extraction plant.

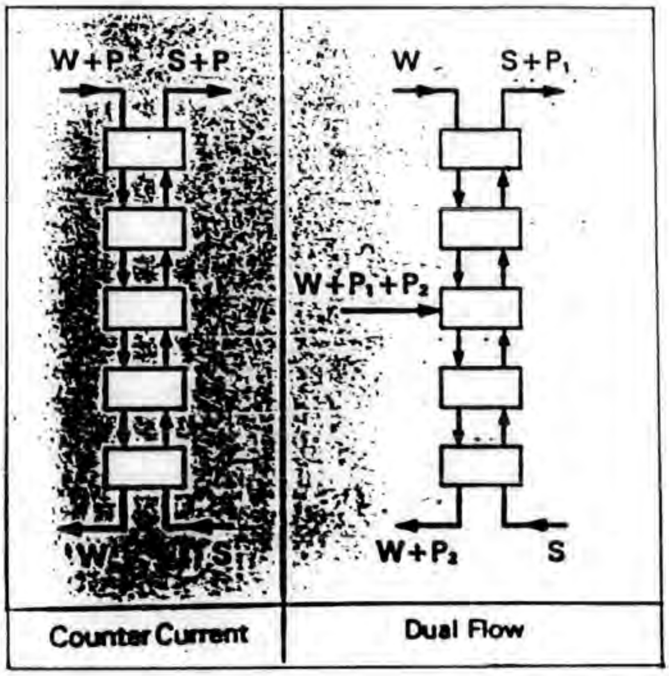
6.4.3. Equipment Design

There are several companies which supply industrial solvent extraction equipment; e.g. Metallextraktion AB, Sweden[121] MSU mixer settler units, suited to pilot plant and small scale production have mixer active volumes up to 360 litres and settler active volumes up to 655 litres. Materials of construction are polypropylene or polyvinylchloride. Kuhni[122], based in Switzerland, produce industrial scale mixer settlers in tanks and in columns. Mixer settler tanks comprise the mixer for intensive phase mixing followed by the settler (for phase separation). Phase transport between a series a mixer settlers is achieved by pumps or pump mix agitators. The mixer settler column combines the stagewise operation of the mixer settler with the compact design of the column. The mixer settler units arranged on top of the other are driven by turbines mounted on a common central shaft. The mixer settler column is an alternative to conventional mixer settler tanks and has remarkable technical and economic advantages. In particular, mixer setter columns are suited to processes involving extreme phase ratios (as occasionally quoted in Chapter 4), slow mass transfer (e.g. metal ion extraction which require long contact times), and stagewise control of pH or concentration. It also can be operated on a cross flow configuration, i.e. the same flow design as the experiments discussed within this thesis. These aspects of mixer settler columns indicate their suitability for use with the envisaged residue metal extraction processes.

The criteria for equipment selection are outlined below, with + and – indicating positive and negative respective characteristics of the type of equipment.

For correct design of extraction equipment, a good knowledge of hydrodynamics and mass transfer processes is required; e.g. droplet size influences turbine geometry, and the rate of agitation, requirements for axial mixing influences stage geometry, rate of rotation and throughput, and the process scale up characteristics influences mixer setter column diameter. Pilot tests are essential for scale up, in addition to a good basic knowledge.

TYPICAL FLOW CONFIGURATIONS



Counter Current

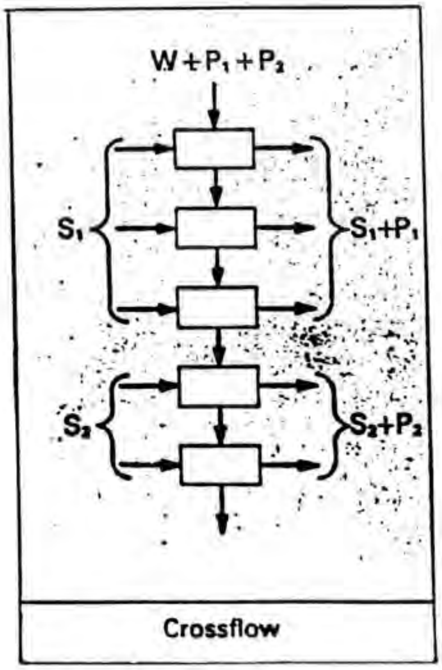
Dual Flow

counter current:
standard configuration for separation of one component (P)

dual flow:
Suitable for the selective separation of two components (P_1, P_2)

crossflow:
possibility for the isolation of several components

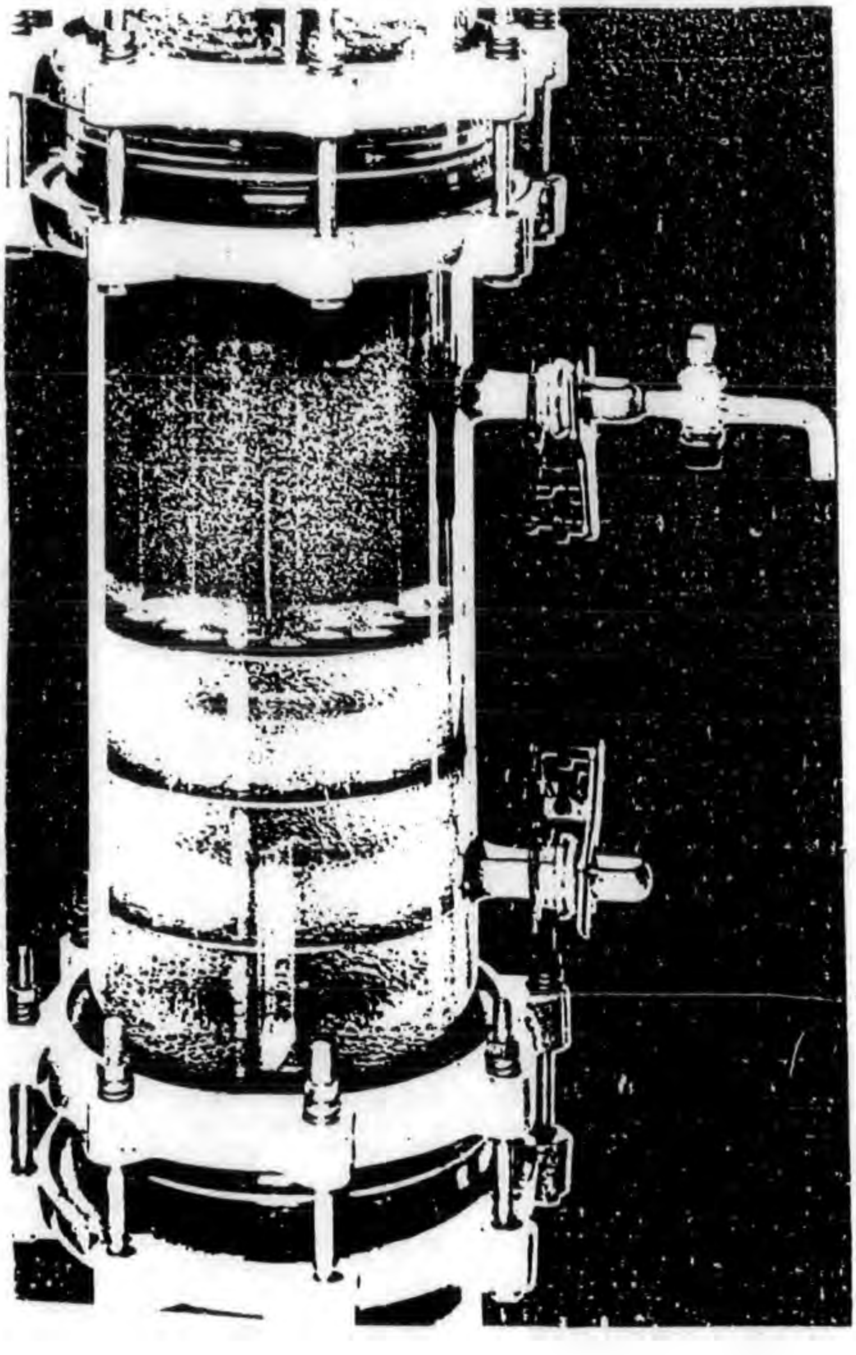
W = raffinate
S = solvent
P = product

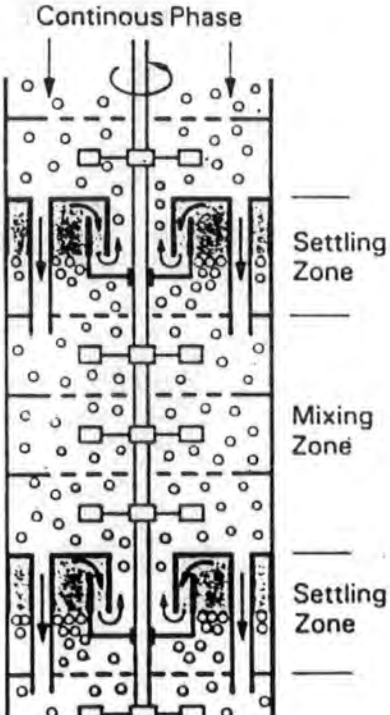


Crossflow

Figure 6.2.

PILOT MS–COLUMN IN OPERATION





PRINCIPAL OF CONSTRUCTION OF THE MS–COLUMN

Figure 6.3.

Criteria for Equipment Selection	Mixer-Settler Tank	Mixer-Settler Column
High number of transfer units (>5)	-	+
Low number of transfer units	+	+
Compact design, low hold up	-	+
Solid particles	-	-
Tendency to emulsification	-	+
Extreme phase ratios	-	++
Slow reaction kinetics	++	++
Stagewise control of conditions	++	++
Cross flow	++	+

Table 6.5 Criteria for Equipment Selection

6.4.4. Conclusions

The successful separation of the metal components from chrome residue has been demonstrated. This may be accomplished by digestion in acid, followed by any of a number of solvent extraction routes. The results described in Chapters 2–5 and the possible process configurations outlined in this chapter have clearly demonstrated that a number of viable options exist for the separation of the component metals of chrome ore and residue using solvent extractants.

REFERENCES

1. Papp J.F., "Chromium", U.S. Bureau of Mines, Mineral Facts and Problems, 1985, *Bulletin* 675, 139.
2. Anger G., Halstenberg J., Hochgeschwender K., Ueker G., Korallus U., Knopf H., Schmidt P., Ohlinger M., "Chromium compounds", *Ullmann's Encyclopedia of Industrial Chemistry*, 1986, A7, 67.
3. Mikami H.M., "Chromite", *Ceramic Bulletin*, 1986, 65, (5), 731.
4. Pinto C.R.O., Boas R.C.V., *Proceedings from the 11th International Mineral Process Congress*, 1975, 849.
5. Hundley G.L., Olsen R.S., "A chemical method for removing chromium from domestic chromite", U.S. Bureau of Mines Assessment and Research, 1986, IC, (9087), 63.
6. Malouf E.E., "Leaching as a mining tool", *International Symposium of Hydrometallurgy*, Ed. Evans D.J.I., Shoemaker R.S., 1973, Chapter 23, 615.
7. Hussein M.K., "Chlorination behaviour of the main oxide components of chromite ores", Winterhager H., Kammel R., El–Barawi K., *Trans. Inst. Min. Metall.*, 1977, 83, (C), 154.
8. Maude C.R., Sale F.R., "Hydrochlorination of chromite with in–situ generation of HCl", *Trans. Inst. Metall.*, 1977, 86, (C), 82.
9. Thornhill P.G., Wigstol E., Van Weert G., "The Falconbridge matte leach process", *Journal of Metals*, 1971, 13.
10. De Andrade J., Costa A.C., "The use of phosphoric acid in chromite ores dissolution", *Quimica Nova*, 1984, 7, (2), 117.
11. Wylie A.W., "Studies in the production of chromic anhydride from chromite ore by an acid process", *Australian Journal of Applied Science*, 1950, 1, 376.
12. Bruen C.P., Wamser C.A., "Process for recovering chromium values from chrome ore", U.S. Patent 3,787,555, 22nd. January 1974.
13. Rosenbaum J.B., Dannenberg R.O., George D.R., "Considerations in solvent extraction processing of U.S. beryllium ores", *Proceedings UKAEA*, 1965, 315.

14. Marshall M., B.C.C., Private communication, 27/10/87.

15. Nestler N., Patent DD 210,613, 20th June 1984.

16. Fraser T.M., U.S. Patent 4,544,643, 1st October 1985.

17. Chapman M.S., "The recovery of 'no–lime' residue for use as flocculants in the treatment of sewage", Albright & Wilson Ltd., Associated Chemical Companies Division, Report No. TSDD/R/135, February 1972.

18. Deighton G.M., "The recovery of the components of 'no–lime' residue", Associated Chemical Co. Ltd., Report No TSSL/R/75, March 1965.

19. Farquhar J.T., "Recovery of chromium from 'no–lime' residue", Associated Chemical Co. Ltd., Report No. 610, May 1962.

20. Marshall M.A., B.C.C., "Solution of chrome residue in hot sulphuric acid", 1980, unpublished data.

21. Marshall M.A., B.C.C. Report CCD/V/1378 April 1980.

22. Ritcey G.M., Slater M.J., "Solvent extraction technology", Workshop 107/78, Australian Mineral Foundation, Adelaide 20th–24th November 1978,
    (a) "Phase separation", 128.
    (b) "Comparison of ion exchange and solvent extraction", 185.

23. Bailes P.J., "The recovery of metals by solvent extraction", *4th International Congress in Scandinavia on Chemical Engineering*, 1977, 145.

24. Flett D.S., Moit D.N., "Current trends and problems in mineral processing and solvent extraction", *J. Sep. Process Technol.*, 1981, $\underline{2}$, (1), 16.

25. Flett D.S., "The role of hydrometallurgy in extractive metallurgy", *Chemistry and Industry* 1981, 427.

26. Ritcey G.M., Ashbrook A.W., "Solvent extraction – principles and applications to process metallurgy", Elsevier, Oxford, 1979.

27. Hughes M.A., "The recovery of metals from secondary sources: Solvent extraction routes", *Chemistry and Industry*, 1975, 1042.

28. (a) Hanson C., "The technology of solvent extraction in metallurgical processes", *Het ingenieursblad*, 41e Jaargang 1972, nr. 15–16, 408.

(b) Spitzer E.L.T.M., "The use of organic chemicals for the selective liquid/liquid extraction of metals", *Het ingenieursblad*, 41e Jaargang 1972, nr. 15–16, 418.

(c) Flett D.S., "A survey of reagents used for solvent extraction in extractive metallurgy", *Het ingenieursblad*, 41e Jaargang 1972, nr, 15–16, 424.

29. Reinhardt H., "Solvent extraction for the recovery of metal wastes", *Chemistry and Industry*, 1975, 210.

30. Jackson E., "Hydrometallurgical extraction and reclamation", Ellis Horwood, Chichester, 1986.

31. (a) Irving H., Williams J.P., "Order of stability of metal complexes", *Nature*, 1948, 162, 746.

(b) Ed. Alegret S., "Developments in solvent extraction", Ellis Horwood 1988.

32. Johnston B.E., "Commercial applications of phosphorous–based solvent extractants", Albright & Wilson Ltd. Internal Report.

33. Barnes J.E., Setchfield J.H., Williams G.O.R., "Solvent extraction with DEHPA; A correlation between selectivity and the structure of the complex", *J. Inorg., Nucl. Chem.*, 1976, 38, 1065.

34. (a) "Ionquest 801 metal extractant", Albright & Wilson Americas, Technical Bulletin.

(b) Sun S., Gao Z., Xi Z., Jia Z., Chen B., Shen J., "Extraction of chromium(III) from sulfate solution with Mono (2–ethylhexyl) 2–ethylhexylphosphonate"; Wuji Huaxue, 1987, 3, (1) 7,

35. Yamada H., Tanaka M., "Solvent extraction of metal carboxylates", *Advances in Inorganic Chemistry and Radiochemistry*, 1985, 29, 143.

36. Flett D.S., Jaycock M.J., "Extraction of metals by carboxylic acids", *Ion Exchange and Solvent Extraction* 1973, 3, Chapter 1, 1.

37. Preston J.S., "Solvent extraction of metals by carboxylic acids", *Hydrometallurgy*, 1985, 14, 171.

38. Ashbrook A.W., "A review of the use of carboxylic acids in extractants for the separation of metals in commercial liquid–liquid extraction operations", *Mineral Sci. Eng.*, 173, 5, (3), 169.

39. "Armak Chemicals Product Bulletin", Akzo Chemie, U.K.

40. Monhemius A.J., Thorsen G., "The application of hydrolytic stripping to the iron problem in hydrometallurgy", *Proc. ISEC*, 1980, 3, 80.

41. Doyle F.M., "The physical chemistry of precipitation stripping for removing iron(III) from carboxylate solutions with dilute sulphuric acid", *Hydrometallurgy*, 1988, 20, 65.

42. Watanabe M., Nishimura S., "Process of the production of high purity iron oxide", European Patent No. 0046973, 25th August 1981.

43. Ritcey G.M., Lucas B.H., "Diluents and modifiers – their effect on mass transfer and separation", *Proc. ISEC*, 1974, 3, 2437.

44. Mc Kay H.A.C., "Solvent extraction chemistry of metals", Macmillan London, 1965, 377.

45. Hughes M.A., "The influence of kinetic effects on extractive distribution processes – solvent extraction", *Proc., 5th Int. Symp., on High Purity Mater. Sci. Technol.*, 1980, 1, 187.

46. Hanson C., "Recent advances in liquid–liquid extraction", Pergamon Press, 1971.

47. Ritcey G.M., Ashbrook A.W., Lucas B.H., "Treatment of solvent extraction raffinates for the removal of organic reagents", *Proc. ISEC*, 1974, 1, 943.

48. Irving H.M.N.H., "Synergism in the solvent extraction of metal chelates", North Holland Amsterdam 1967.

49. Ugine Kuhlmann, "Treatment of residual solutions containing hexavalent chromium compounds", France Patent 1395286 Appl, No. 14880/73. 28th March 1973. Complete Specification 21st May 1975.

50. Cuer J.P., Stuckens W., Texier N., "The techniques of solvent extraction applied to the treatment of industrial effluents", *Proc. ISEC*, 1974, 1185.

51. Bolt A., Kamphius B.A., Van Gemert W.J.T., Tels M., "Method for the separate recovery of metals from waste in particular chemical waste", European Patent 0,122,658 A1, 1984.

52. Bailes P.J., Hanson C., Hughes M.A., "Liquid–liquid extraction: Metals", *Chemical Engineering*, 1976, 86.

53. Flett D.S., "Solvent extraction in hydrometallurgy", *Chemistry and Industry*, 1977, 706.

54. Demopoulos G.P., Pouskouleli G., "Solvent extraction of iron(III) from acid sulphate solutions by mono(2–ethyl hexyl) phosphoric acid", *Canadian Metallurgical Quarterly*, 1989, 28, (1), 13.

55. Jain S.K., Puri B.K., Singla A.L., Rao A.L.J., "Spectrophotometric determination of chromium(III) in steel and alloys after extraction of its N–methylpiperaryine–4–carbodithiote into molten naphthalene", *Microchemical Journal*, 1988, 37, 167.

56. Puri B.K., Gautam M., "Spectrophotometric determination of chromium(III) and rhodium(III) after extraction with oxime into molten naphthalene", *Talanta*, 1978, 25, 484.

57. Wasey A., Bansal R.K. Satake M., Puri B.K., "Extractive spectrophotometric determination of chromium(III) with phenanthrenequinone monoxime into molten naphthalene", *Microchemical Journal*, 1986, 33, 352.

58. Anjaneyulu Y, Reddy M.R.P., Kavipuvapu C.S., "Extractive spectrophotometric determination of chromium(III) in steels using 4–(2–pyridylazo) resorcinol and xylometazoline hydrochloride", *Analyst*, 1986, III, 1167.

59. Rathaiah G.V., Eshwar M.C., "Rapid spectrophotometric determination of chromium(III) with 1–(2–Thiazolylazo)–2–naphthol in presence of surfactant", *Bull. Chem. Soc. Japan*, 1985, 58, 2447.

60. Fu–Sheng S., "The reaction of phenylarsenazo with chromium(III)", *Talanta*, 1983, 30, (6), 446.

61. Fang G., Miao C., "2–(5–bromo–2–pyridylazo)–5–diethylaminophenol as a photometric reagent for the spectrophotometric determination of chromium(III) and/or chromium(VI) and its application to the sequential determination of chromium(III) and chromium(VI) in mixtures", *Analyst*, 1985, 110, 65.

62. Noriki S., Nishimura M., "Effects of quaternary ammonium bases on valence saturated but coordination – unsaturated chelates – Part II. Extraction of magnesium 8–hydroxyquinolinate", *Analytica Chimica Acta.*, 1974, 72, 339.

63. (a) Bel Tyukova, Drobyazko V.N., Kononenko L.I., Poluektov N.S., "Extraction of magnesium and calcium in the form of ionic associated with 5,7–dinitro–8–hydroxyquinoline and Rhodamine B", *Ukr. Khim. Zh*, 1976, 42, (1), S83.

    (b) Kusakabe S., Maseki Y., Sekine T., "Solvent extraction of magnesium(II) and calcium(II) with benzoyltrifluoroacetone in carbon tetrachloride in the absence and presence of tetra alkyl ammonium", *Bunseki Kagaku*, 1982, 31, E 327.

64. Shevchenko F.D., Kuzina L.A., "Magnesium extraction by phenylsulfonyl–amidophosphoric acid dioctyl ester", *Ukrainskii Khimicheskii Zhurnal*, 1970, 36, (1), 94.

65. Steinbach J.F., "Acetylacetone as an analytical extraction agent", Ph.D. Thesis 1953 University Pittsburgh.

66. Sarghie S.F., "Cinetica extractiei de schimb a fierului cu acetilacetonat de aluminiu", *Buletinul Institutului Politehnic diu Iasi*, 1975, XX1, (XXV), 7.

67. Nyman B.G., Hultholm S.E., "Process for selective extraction of ferric iron from trivalent chromium by alkyl–phosphorous compounds", U.S. Patent 3,875,285 1975.

68. Grunig J.K., Anderson R.J., "Solvent extraction of aluminium", U.S. Patent 3,966,909 1976.

69. Matsui S., Era A., "Solvent extraction of aluminium from hydrochloric, nitric, and sulphuric acid solutions with 2–ethylhexylphosphoric acid mono–2–ethylhexyl ester", *Transactions of the Japan Institute of Metals*, 1983, 24, (11), 759.

70. Kamitani M., Shibata J., Sano M., Nishimura S., "Extraction of metal ions with D2EHPA from mixed aqueous–organic media", *Solvent Extraction and Ion Exchange* 1988, 6, (4), 605.

71. Kimura K., *Bull. Chem. Soc. Japan*, 1960, 33, 1038.

72. Xiu L., Tang Z.S., "Studies of extraction of Co(II) and Mg with DEHPA in sulfate systems", *Hua Hsueh Tung Pao*, 1981, 5, 10.

73. Preston J.S., Du Preez A.C., "The solvent extraction of zinc, iron and indium from chloride solutions by neutral organophosphorous compounds", *Council for Mineral Technology, Randburg*, MINTEK Report No. M228, 1985, ISSN 0 86999 7289.

74. Du Preez R., Preston J.S., "Solvent Extraction of metals by neutral organophosphorus compounds. Part 1. Extraction of zinc(II), iron(III) and indium(III) from chloride solutions", *South Africa Journal of Chemistry*, 1986, 39, (2), 89.

75. Sukhanovskaya A.I., Solov'ev E.A., Tikhoner G.P., Golubev V.Y., Bezhevol'nov E.A., "Extraction of the thiocyanate complexes of chromium(III)", *J. Anal. Chem. USSR.* 1970, 25, 1348.

76. Sammour H.M., Abdel–Gawad F.M., Aly F.A., "Extraction behaviour of iron thiocyanate with cyclohexanol and tri–n–butyl phosphate solvents", *Egypt J. Chem.*, 1975, 18, (6), 1031.

77. Kichkina E.D., Gorbenko F.P., Litvinova G.V., "Extraction of magnesium as its thiocyanate by tributyl phosphate", *J. Anal. Chem. USSR.*, 1973, 28, 528.

78. Agett J., Udy D.J., *J. Inorg. Nucl. Chem.*, 1970, 32, 2802.

79. Gavrilova I.M., Klyuchnikov V.M., Zaitser L.M., Apraksin I.A., "Extraction of hydrolysed aluminium perchlorate with tributyl phosphate", *Russian Journal of Inorganic Chemistry*, 1973, 18, (6), 865.

80. Rai S., Narayanaswamy M.S., Rupainwar D.C., "Removal of chromium(III) from aqueous solutions and polluted waters by its extracton into tri–iso–amyl phosphate (TAP)", *Poll. Res. Vol.*, 1984, 3, 45.

81. Pandey B.D., Rupainwar D.C., "Use of tri–isoamyl phosphate as a solvent for extraction of iron(III) from its thiocyanate solutions", *Indian Journal Technology,* 1978, 17, 117.

82. Tuck D.G., Walters R.M., "The extraction of chromium(VI) from aqueous solutions by Tri–n–butyl phosphate", *Journal Chemical Society,* 1963, 1111.

83. White S.C., Ross W.J., "Extraction of chromium with TOPO", U.S. Atomic Energy Commision Report No. ORNL–2326, 1955.

84. Seeley F.G., Crouse D.J., "Extraction of metals from nitrate and sulfate solutions", *Journal of Chemicals and Engineering Data,* 1971, 16, (4), 393.

85. Flett D.S., West D.W., "Solvent extraction of chromium(III) from sulfate solutions by a primary amine", *AIME transactions,* 1970, 288.

86. Singh J.M., Singh O.V., Tandon S.N., "Extraction of Cr(III) oxalate complex by high molecular weight amines and quaternary ammonium salt", *Journal of Inorganic and Nuclear Chemistry,* 1980, (42), 1662.

87. Sato T., Takeuchi Y., Nakamura T., "Extraction of chromium(VI) from alkaline solutions by high–molecular weight quaternary ammonium salt", *Proc. Symp. Solvent Extraction,* 1983, V, 13.

88. (a) Lucas B.H., Ritcey G.M., "Solvent extraction of chromium and vanadium", Canadian Patent 1,124,083.

    (b) Leaver T.M., "Solvent extraction of anions from chromium bearing leach liquors", Ph.D. Thesis 1974, Bradford.

89. Deptula C., "Extraction of chromium(VI) from sulphuric acid solutions by means of tri–n–octylamine", *J. Inorg. Nucl. Chem.*, 1968, 30, 1309.

90. Verhaege M., Sinnesael J., Van Petegham A., "Liquid–liquid extraction of chromium(VI) from diluted chromic acid containing solutions" *Bull. Soc. Chim. Belg.*, 1984, 93, (12), 1107.

91. Meack W.J., Booman G.L., Kussy M.E., Reis J.E., "Extraction of the elements as quaternary (propyl, butyl and hexyl) amine complexes", *Anal. Chem.*, 1961, 33, (12), 1775.

92. Good M.L., Bryan S.E., Juge F., "Extraction of group VIII metals by long chain alkyl amines. IV. Studies on the extraction of iron(II), iron(II), colbalt(II) and nickel(II) from aqueous sulfate media", *Inorganic chemistry*, 1963, 2, (5), 963.

93. Seeley F.G., McDowell W.J., Felker L.K., Kelmess A.D., Egan B.Z., "Determination of extraction equilibria for several metals in the development of a process design to recover aluminium and other metals from coal combustion ash", *Hydrometallurgy*, 1981, 6, 277.

94. Schmidt V.S., "Amine Extraction", Jerusalem, 1971, 136.

95. Meng X., Yu S., Chen J., "New synergistic extraction system for removal of Fe(III) in sulfate solutions", *Proc. ISEC*, 1986, II, (5), 565.

96. Gindin L.M., Fedyashina A.F., Yudelevich I.G., Artyukhin P.I., "Extraction of certain elements by aliphatic monocarboxylic acids", *Izv. Sib. Otdel. Akad. Nauk. SSR*, *Ser. Khim. Nauk.*, 1967, 3, 95.

97. Spitzer E.L.T.M., Radder J., Muys H.M., "Extraction tests on aqueous metal sulphate solutions using Versatic 9", *Trans. Inst. Min. Met.*, 1966, C75, (2), 265.

98. Doyle F.M., Pouillon D., "Solvent extraction of metals with carboxylic acids – coextraction of base metals with Fe(III) and characterisation of selected carboxylate complexes", *Hydrometallurgy*, 1988, 19, 289.

99. Ng S.W., Zuckerman J.J., "Solvent extraction of metal carboxylates", *Advances in Inorganic Chemistry and Radiochemistry*, 1984, 29, 143.

100. Stefanakis M.I., Monhemius A.J., "Determination of organic phase complexes formed on extraction of iron(III) from aluminium nitrate solutions with Versatic 10", *Hydrometallurgy*, 1985, 15, 113.

101. Bold A., Fisel S., "Mechanism of the extraction of iron(III) with higher fatty acids" *An. Stiint.*, 1971, 17, 19.

102. Treybal R.E., "Liquid–liquid extraction", McGraw–Hill, 1963, 2nd Edition,
    (a) Bench scale extraction, 359.
    (b) Metal separations, 577.

103. (a) Stefanakis M.I., Ph.D. Thesis 1982, Imperial College, London.

(b) Bates R.G., "Determination of pH–theory and practice", 1964, J. Wiley, London.

104. Rickelton W.A., Boyle R.J., "Solvent extraction with organophosphines – commercial and potential applications", *Separation Science and Technology*, 1988, 23, 1227.

105. Litvinova G.V., Kuchkina E.D., Gorbenko F.P., "Extraction of magnesium as the iodide by tributyl phosphate", *J. Anal. Chem. USSR.*, 1987, 42, (3), 366.

106. Schuly W.W., Navratil J.D., Bass T., "Science and technology of tributyl phosphate", Volume II, Part A. CRC Press inc., Boca Raton, Florida (a) p.79 and (b) p.83.

107. Sekine T., Inaba K., Morimoto T., Aikawa H., "Rate of solvent extraction of chromium(III) with acetylacetone into carbon tetrachloride", *Bull. Chem. Soc. Japan*, 1988, 61, 1131.

108. Hullwege H.E., Schweitzer G.K., "Kinetics of the extraction of chromium(III) into chloroform containing acetyl acetone", *Analytica Chimica Acta*, 1963, 29, 46.

109. Dutrizac J.E., Monhemius A.J., "Iron control in hydrometallurgy", Ellis Horwood Chichester, 1986.

110. Poppe W., Muller H., Krajewski W., Schugerl K., "Verfahren zur entfernung von eissen (III) aus sauren zinksalzlösungun durch solvent extraktion", Deutsches patentamt DE 3801,430 A1 1989.

111. Ishimori T., Akatsu E., Chung W., Tsukuechi K., Osakabe T., "Data of inorganic solvent extraction (2)", *Japanese Atomic Energy Research Institute* 1964, 1062.

112. Udy M.J., "Chromium", Volume 1., P.135.

113. Szepvolgyi J., Bertoti I., Szekely T., *Hungarian Journal of Industrial Chemistry Veszprem*; 1988, 16, 109.

114. Mobil Organic Chemicals, Data sheet for phoshates.

115. Albright & Wilson Americas Inc., Material safety data sheet 929, "Albrite Octylphenyl acid phosphate".

116. Sigma–Aldrich chemicals computer database.

117. Rohm & Haas material safety data sheet (23/5/85) No. 65785.

118. T–Alkyl primary amines, Rohm & Haas Company, 1978.

119. Akzo brochure, "Armak chemicals, product bulletin".

120. Kimura K., *Bull. Chem. Soc. Japan.*, 1960, 33, 1038.

121. Metallextraktion AB, Box 83, S–42121, Vastra Frolunda, Sweden "MSU Technical Brochure".

122. Kuhni Limited, Chemical Engineering and Manufacturing, Mühlebachweg 9 15, CH–4123 Allschwil, Switzerland, "Solvent Extraction – Agitated columns Mixer Settler – Technical Brochure".

123. Ritcey G.M. "Hydrometallurgy – Its development and Future", *Chem. Sep. Set. Pap. Int. Conf. Sep. Sci. Technol. 1st.*, 1986, 257.

124. Morico J.L., "Process for Reduction of Hexavalent Chromium", European Patent WO90/15026, 13th December 1990.

Appendix 1

Experimental Results from B.C.C. Studies into Sulphuric Acid Digestion of Residue

1a[19]

Mass residue = 99.2g; Temperature = 120°–145°C

H_2SO_4 used. (% of stoichiometric amount)	Initial H_2SO_4 concentration.	Digestion time (hours)	% Cr dissolution	% residue dissolution
100	88	1.25	57	63
150	91	1.0	69	78
100	72	1.0	50	64
200	90	1.5	85	91.5
75	75	1.75	58	68
75	67	3.5	62	72.5

After digestion, the mixtures were cooled, diluted by 2 with water, boiled until no further material dissolved, and filtered.

1b[20]

65% H_2SO_4 concentration, 50% excess acid, 2 hours

Method.	Boiling point of acid. °C	Final boiling point of mixture.	% residue dissolution.	Volume of distillate (ml)
Reflux	153.5	134	79.4	-
Distillation	153.5	150.5	86.1	100

Appendix 2

In dilute metal solutions, where the metal concentration [M] is ≤ 0.1 molar, the equilibrium constant, K_D, is represented as;

$$K_D = \frac{[MA_{n\,org}]\,[H^+{}_{aq}]^n}{[M^{n+}{}_{aq}]\,[HA_{org}]^n} \qquad (1)$$

Since,

$$D = \frac{[MA_{n\,org}]}{[M^{n+}{}_{aq}]} \qquad (2)$$

$$\therefore \quad D = K_D \frac{[HA_{org}]^n}{[H^+]^n_{aq}} \qquad (3)$$

Now,

$$\text{Log } D = \log K_D + n\log\,[HA_{org}] - n\log\,[H^+{}_{aq}] \qquad (4)$$

$$\text{Log } D = \log K_D + n\log\,[HA_{org}] + npH \qquad (5)$$

The percentage extraction of a metal (P) may be expressed in terms of the distribution coefficient as in Equation 6.

$$P = \%\text{ extraction} = \frac{100D}{D + {}^{vaq}/{}_{vorg}} \qquad (6)$$

$$D.P = 100D - P\;{}^{vaq}/{}_{vorg} \qquad (7)$$

The distribution coefficient may be represented in terms of percentage extraction or the equilibrium constant, as in Equation 8.

$$D = \frac{P}{100-P} \, {}^{v_{aq}}/_{v_{orq}} = K_D \frac{[HA_{org}]^n}{[H^+_{aq}]^n} \qquad (8)$$

A plot of log D against pH (Equation 5) gives a slope n (where n is equal to the number of extractant molecules in the complex and y axis is the intercept log K_D + nlog[HA_{org}]). From the experiment data of extractant concentration, the equilibrium constant K_D may then be calculated. For concentrated solutions (i.e. solutions of ionic strength >0.1 molar), the lack of equivalence between activity and ionic strength, means that these mathematical expressions become only qualitative.

It is the activities of these reacting species in solution that the above equations are describing. In dilute solutions, activity and concentration may be regarded as being the same, but in practical applications, salt concentrations are high (>0.1 molar) and there will be significant differences between activity and concentration. Thus, data determined from studies employing extractant with dilute metal solutions should not be used to predict their use for practical situations (e.g. with residue solution). The bulk of reported extractant behaviour is with dilute solutions and is therefore not directly applicable to concentrated leach liquors.

Equation 9 in Chapter 1 represents a rather simplistic view of metal extraction. The following equations attempt to give a more realistic impression of the equilibria which are involved in metal extraction systems.

The phase distribution of the extractant (HA) is shown in Equation 9, below.

$$HA_{aq} \rightleftharpoons HA_{orq} \quad K_{ex} = \frac{[HA_{org}]}{[HA_{aq}]} \qquad (9)$$

K_{ex} depends essentially on the solubility of the extractant in the aqueous phase, but varies considerably with salt concentration, temperature, and the pH of the aqueous phase.

Ionization of the extractant occurs at the aqueous–organic interface (Equation 10).

$$HA_{aq} \rightleftharpoons H^{+}_{aq} + A^{-}_{aq} \quad K_i = \frac{[H^{+}_{aq}][A^{-}_{aq}]}{[HA_{aq}]} \qquad (10)$$

The metal in the aqueous phase forms complexes with a range of aqueous species including acid hydrolysis as shown in Equations 11–14.

$$M(H_2O)_m{}^{n+} \rightleftharpoons M(H_2O)_{m-1}(OH)^{n-1\,+} + H^{+} \qquad (11)$$

$$M(H_2O)_{m-1}(OH)^{n-1\,+} \rightleftharpoons M(H_2O)_{m-2}(OH)_2{}^{n-2\,+} + H^{+} \qquad (12)$$

$$M(H_2O)_{m-2}(OH)_2{}^{n-2\,+} \rightleftharpoons M(H_2O)_{m-3}(OH)_3{}^{n-3\,+} + H^{+} \qquad (13)$$

Typically, $n=3$ and $m=6$

$$M(H_2O_6)^{3+} \rightleftharpoons M(H_2O)_3(OH)_3 + 3H^{+} \qquad (14)$$

This leads to a condensation reaction at higher pH, as shown in Equation 15;

$$2MOH \rightleftharpoons M{-}O{-}M\ ppt + H_2O \qquad (15)$$

Outer sphere complexation of the metal aquo complex may produce quite stable species (Equations 16–18), which may inhibit substitution with an extractant molecule.

$$M(H_2O)_m{}^{n+} + yX^- \overset{\beta_{MX}}{\rightleftharpoons} M(H_2O)_{m-y}(X)_y{}^{n-y+} + yH_2O \qquad (16)$$

e.g.
$M = Fe$
$X = Cl^-$
$y = 3$
$n = 3$
$m = 6$

$$\text{e.g.} \quad M(H_2O)_6{}^{2+} + SO_4{}^{2-} \rightleftharpoons \{M(H_2O)_6{}^{2+}.SO_4{}^{2-}\} \qquad (17)$$

e.g. where $M = Co$

$$Co(H_2O)_6{}^{2+}\ SO_4{}^{2-} + 6NH_3 \rightleftharpoons Co(NH_3)_6{}^{2+}.SO_4{}^{2-} + 6H_2O \qquad (18)$$

A metal may complex with a strongly coordinating ligand (e.g. cyanide) which prevents formation of the extracted metal complex. The masking of the metal is an aqueous phase process and is shown in Equation 19.

$$M^{n+} + Y^{m-} \rightleftharpoons MY^{n-m+} \quad \beta_{MY} = \frac{[MY]}{[M^{n+}][Y]} \qquad (19)$$

If the aqueous metal complexation reactions produce more stable complexes than the metal–extractant complex, then the metal will not be extracted. The extent of formation of these complexes will be dependent upon the concentration of the ligands, i.e. solute concentrations and pH. Solute concentrations in synthetic leach liquors may be significantly different from those obtained using actual leach liquors, which may significantly affect extraction data. Standard mathematical treatment of extraction data assumes that outer–sphere complexation and hydrolysis do not occur. Deviations occur for commercial systems with high salt concentrations, because of aqueous phase complexation, adduct formation, and organic phase polymerization. The nature of the inorganic ion affects the stability constants of the aqueous phase metal complexes, which controls extraction rates.

Salt effects are important in the position of the extraction equilibrium. An increase in the concentration of the aqueous salt (e.g. sulphate concentration is increased by the addition of sodium sulphate) will force the equilibria to the right, in Equation 20, which then causes a shift to the right in the equilibrium in Equations 21–25.

$$M^{n+}{}_{aq} + nSO_4{}^{2-}{}_{aq} \rightleftharpoons M_2(SO_4)_{naq} \qquad (20)$$

$$M_2(SO_4)_{naq} + 2nHA_{org} \rightleftharpoons 2MA_{norg} + nH_2SO_{4aq} \qquad (21)$$

The formation of the extracted species is an aqueous phase process, as shown in Equations 22–25.

$$M^{n+} + A^- \overset{k_1}{\rightleftharpoons} MA^{n-1\,+} \quad k_1 = \frac{[MA^{n-1\,+}]}{[M^{n+}][A^-]} \qquad (22)$$

$$MA^{n-1} + A^- \overset{k_2}{\rightleftharpoons} MA_2{}^{n-2\,+} \quad k_2 = \frac{[MA_2{}^{n-2\,+}]}{[MA^{n-1\,+}][A^-]} \qquad (23)$$

$$MA_{n-1\,+} + A^- \overset{k_n}{\rightleftharpoons} MA_n \quad k_n = \frac{[MA_n]}{[MA_{n-1}][A^-]} \qquad (24)$$

$$\text{Overall; } M^{n+} + nA^- \overset{\beta_n}{\rightleftharpoons} MA_n \quad \beta_n = \frac{[MA_n]}{[Mn^+][A^-]^n} \qquad (25)$$

If the extractant concentration is much greater than the metal ion concentration, it is reasonable to assume that concentrations of the intermediate metal complex species are negligible. An exception to this rule is in the case of ammine formation, where differences between concurrent formation constants are small.

Ligand exchange between metals is common in the aqueous phase, Equation 26.

$$M'^{n+} + M''A_n \rightleftharpoons M'A_n + M''^{n+} \qquad (26)$$

In multi–metal component solutions ligand exchange will occur between metals according to their relative metal complex stability constant. The removal of the extracted species will cause a shift in these equilibria. For a specific metal ion concentration this will depend upon the extents of metal hydrolysis and outer sphere complexation, which again are dependent upon solute concentration.

The distribution of the extracted species (the chelate) between the phases is shown in Equation 27.

$$MA_{n\,aq} \rightleftharpoons MA_{n\,org} \qquad K_{MAn} = \frac{[MA_{n\,org}]}{[MA_{n\,aq}]} \qquad (27)$$

For a viable solvent extraction system, the value of K_{MAn} must be very high, i.e. the extractable metal complex MA_n must have negligible solubility in the aqueous phase. It is also assumed that the intermediate metal–extractant species have negligible organic phase solubility and are therefore not extracted.

Mixed ligand chelate formation may occur in the organic phase, Equation 28 shows a molecule B with donor properties coordinating to the extracted species.

$$MA_n + bB \rightleftharpoons MA_n.bB$$

$$K_{MAn \cdot bB} = \frac{[MA_n \,.\, bB]}{[MA_n]\,[B]^b} \qquad (28)$$

The formation of an extracted species–extractant adduct may occur in the organic phase, Equation 29.

$$MA_n + aHA \rightleftharpoons MA_n.aHA \quad K_{adduct} = \frac{[MA_n \,.\, aHA]}{[MA_n]\,[HA]^n} \qquad (29)$$

Metal extraction is dependent upon the effects of all these equilibria, especially those involving pH and availability of the amount of free extractant. The order of stability of extractable metal species determines the order of extraction[31a]. In Equation 30, the formation of the metal extracted species is

$$M^{n+} + nHR \rightleftharpoons MR_n + nH_+ \qquad (30)$$

essentially a competition between hydrated protons and metal cations for the extractant anion. The greater the stability of the metal complex, the higher the acidity (and the lower the pH) at which the complex will persist. The ligand displaces an equivalent number of water molecules from the hydrated cation.

Factors affecting chelate stability can be summarized as follows[31b];

Chelate characteristics

1. Resonance effects
2. Steric factors

Reagent characteristics

1. Ring size
2. Reagent basicity (i.e. ability for electron pair donation)
3. Electronegativity of donor atoms (i.e. hard and soft)
4. Chelate effect (i.e. number of rings formed)

Metal Characteristics

1. Electrostatic bonding (acidity is related to charge^2/radius)
2. Covalent bonding (acidity related to (i) electronegativity (ii) positioning of available orbitals)
3. Ligand field effects.

Much work has resulted in well defined principles (as above) that describe the effect of ligand structural changes and of the nature of the metal ion on β_n values.

Appendix 3

Chlorination of Residue and Single Metal Oxides

Solid	Mass (g)	Initial temperature °C	Final temperature °C	Time (mins)	Mass residual solid (g)	Mass product (g)	Observed product	Product
Residue	30.0	405	405	60			Red liquid Red solid	CrO_2Cl_2 [a] $FeCl_3$ [b]
Residue	30.0	420	398	375	29.5	0.52 1.01	Red liquid Red solid	CrO_2Cl_2 [a] $FeCl_3$ [b]
Residue	10.0	452	498	60	9.6	0.71	Red liquid red solid	CrO_2Cl_2 [a] $FeCl_3$ [b]
Residual solid from above	9.6	447	540	45	9.6	0	-	-
Cr_2O_3	10.0	460	480	120	10.0	0	-	-
Cr_2O_3	10.0	470	492	60	10.0	0	-	-
Cr_2O_3 + H_2O [c]	10.2	520	520	20	10.0	0.2	Yellow liquid Water	$H_2Cr_2O_7$ [a] H_2O
$Na_2CrO_4.xH_2O$	5.0	444	520	20			Colourless condensate	H_2O
$Cr(OH)_3.3H_2O$	1.0	440	460	20			Red Liquid	CrO_2Cl_2 [a]

[a] Cr = 33.9% for chromyl chloride. Infra red confirms chromyl chloride.

[b] $FeCl_3$ confirmed by atomic analysis – Molar ratio Fe:Cr :: 1:3.

[c] Water was added to Cr_2O_3, and the slurry was placed in an oven overnight at 120°C.

Appendix 4

Experimental

A. Acid Digestion

B. Chlorination

C. Metal Extraction/Scrubbing/Stripping

D. pH Measurements

A. Acid Digestion Experiments

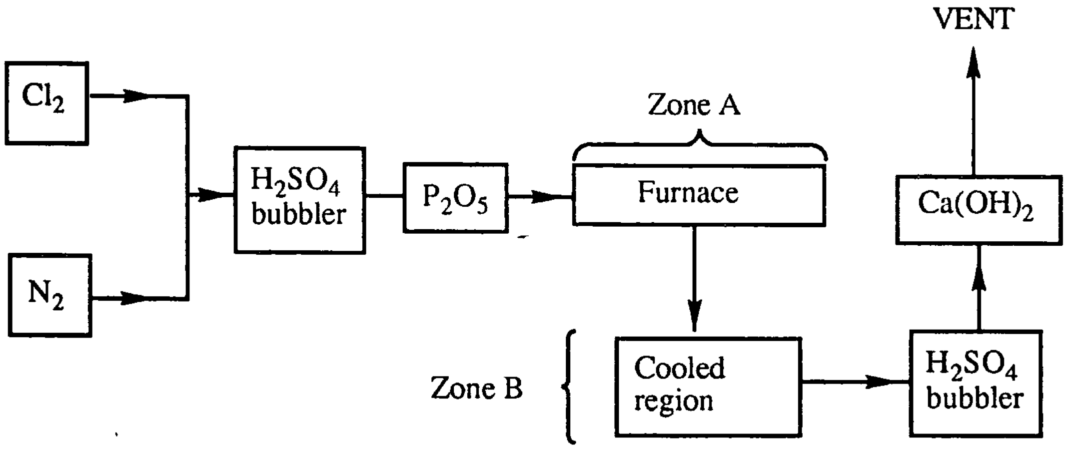
Chrome ore is provided in a dry, ground powdery form (mesh size ***), by B.C.C., who obtain it from the Bushveld complex in South Africa. Chrome residue is the waste product from the B.C.C. chromate extraction process using the above ore. Residue[a] has been roasted in a kiln at 1100°C for 3 hours, the residue quoted in Chapter 2 obtained from the B.C.C. kilns on 8/10/87.

Experiments were conducted using a three necked, 1 litre round bottom flask, with an isomantle as the heat source. A mechanical stirrer with a teflon paddle was used for agitation, and a Liebig condenser for refluxing and distillation. Acid was added to water in the flask, allowed to cool to <130°C, and ore/residue was added. All ore/residue masses quoted are for predried material (>120°C for >7 days). Constant boiling rates were maintained by adjustment of the heat setting on the isomantle. In distillation experiments the heating was adjusted to obtain fast or slow boiling rates as desired. When the mixtures rose in the flask, the heating was adjusted to prevent boiling over. After 2 hours of boiling, the mixtures were allowed to cool to 120°C, and hot water was slowly added. The mixtures were stirred for a further 15 minutes at 120°C. Filtration apparatus (Buchner flask and glass sinter) was preheated in an oven at 120°C, and was wrapped in aluminium foil. Frequent dilution of the mixture with hot water (distillate was used for the distillation processes) maintained high temperatures during filtration. Insoluble solid was washed with water, dried at 120°C overnight, and weighted. The filtrate was analysed by atomic absorption analysis. Solid materials (ore, residue and insoluble solids) were analysed by the sodium peroxide fusion method, followed by dilution and atomic absorption analysis.

[a] Chrome residue has been analysed to be of the following particle size distribution

Mesh size	%
<170	0.4
170–220	1.3
200–350	16.8
>350	81.5

B. Chlorination Experiments



Glass and plastic tubing was used throughout the system with P_2O_5 used to dry all the gases. Nitrogen was used to purge the system, before the furnace reached the reaction temperature. Chlorine was passed through the circuit for the whole of the reaction period. The solid reactants were placed in the centre of the furnace (Zone A), the temperature of which was measured using a thermocouple. Glass wool was packed at the entrance and exit of the furnace around the tubing. The gaseous flow rate was monitored using the acid bubbler.

Sublimation and condensation products in Zone B were collected by cooling the region using ice, cardice and a carbon tetrachloride slush bath. The products were analysed by infra red spectroscopy, the metals by atomic absorption analysis, and chlorine by titremetric analysis.

$Cr(OH)_3.3H_2O$ solid was obtained by dissolving chromic sulphate in water followed by precipitation with base, and filtration.

C. Metal Extraction/Scrubbing/Stripping

For each solvent extraction/stripping/scrubbing experiment, aliquots of aqueous and organic solutions were taken and placed in a round bottom flask, which was in an oil bath at the designated temperature. The flask was equipped with a reflux condenser and a mechanical stirrer, with a teflon paddle. Time for temperature equilibration of the mixture and oil bath was allowed before mixing the designated contact time. The mixture was then separated as soon as phase separation had occurred in a separating funnel (preheated if required). Centrifugation of the mixtures was used where appropriate using a MSE Centaur 2 centrifuge. The volumes of the cooled phases were measured, and subsequent aqueous metal analysis by atomic absorption spectrophotometry was undertaken, using a Perkin Elmer 5000 Atomic Absorption Spectrophotometer.

The ranges of concentrations of the extractants and type of diluent in the solvents are given in Table 3.1 Liquid Amines are used as 10% $^{v}/_{v}$ in kerosene, as solid amines as 10% $^{w}/_{v}$ in kerosene unless otherwise stated. OPAP is used as 29% $^{w}/_{v}$, and the remaining extractants used as 50% $^{v}/_{v}$ (for liquid extractants) and 50% $^{w}/_{v}$ for solid extractants in all experiments, unless otherwise stated.

Errors Analysis

There are several sources of error associated with the calculation of extraction data. Viscous residue solutions from the digestion stage required precise dilution for metal analysis. Concentrated solutions required dilution up to 4000 x their original strength for atomic absorption analysis. The accuracy of the measurement of the metal values, assuming perfectly accurate dilution, is as outlined in Table 1.

Table 1

	Cr	Fe	Mg	Al
Accuracy of instrument (±) ppm	0.1	0.1	0.05	2
Linear Range	7.5	10.0	5.00	100
% error (±)	1.3	1.0	1.0	2

The standards used for atomic absorption analysis were matrix matched to the residue solutions as far as possible. For Fe rich residue solutions mixed standards containing Cr 7.5 ppm, Fe 10.0 ppm, Mg 5.0 ppm, Al 5.0 ppm were used in the analysis of Cr, Fe and Mg, and standards containing Cr 150 ppm, Fe 200 ppm, Mg 100 ppm, Al 100 ppm were used for Al analysis. The relative concentrations of the residue solutions was approximately matched by those in the standards. Residue raffinates which had been treated with kerosene based solvents were compared to standards which had been 'washed' with kerosene, and so on, in order to achieve as close as possible matrix matching of the standards to the residue solutions. If entrainment of the organic phase into the aqueous phase had been observed in the extraction process, a portion of the residue raffinates were washed of the organic impurity, and both unwashed and washed residue raffinates were analysed for Al concentration, to examine the effect of the impurity upon analysis.

Highly acid solutions for metal analysis were tested with highly acid and low acid standards to compare the effects. (E.g. in stripping experiments.)

Where doubt over the accuracy of the aqueous raffinate analysis occurred, metal analysis of the organic phase was conducted. This involved taking an aliquot of the loaded organic phase, boiling off the organic components using a boiling flask and bunsen burner, and digestion of the residual components with hydrochlorine, nitric and perchloric acids. These solutions were diluted and tested with standards containing appropriate quantities of the acids. Controls with unloaded solvents, following the boiling and digestion process, gave identical results to demineralized water. In the identification of species (as outlined in Chapter 5), a Philips ultra violet/visible PU 8720 spectrophotometer was used.

D. pH Measurements

The quoted pH's of the residue solutions which have been in contact with organic solvents, are only "apparent pH". The presence of organic solvent in the aqueous phase (even at very low concentrations) means that the aqueous pH measurement may only be described as "apparent pH".

pH measurements were undertaken using a Jenway 3070 pH meter with combined electrodes, and also a special double junction reference electrode, and a PTI–15 pH meter with combined electrodes. A potential source of error in pH measurement arises from the clogging of the membrane in the pH electrode.

Penetration of anions through the pH sensitive surface layer of the glass lead to erroneous values does occur with highly acidic concentrated solutions after prolonged electrode use. This problem was overcome by (i) frequent replacement of electrodes; or (ii) use of a Jenway special renewable double junction reference electrode. The electrode is dismantleable and the electrolytes can be renewed. pH's were often measured using 2 types of pH meter and electrodes to guarantee reproducibility of pH values.

The feed solution used was often at pH <0.0. The measurement of H^+ in this region does not give a good indication of activity due to the high proton concentration.

However, extrapolation of the linear relationship between pH and mV, beyond pH 0.0, is theoretically accepted.[103] This method was used for evaluation of the relative acidities.

Potentiometric base titrations of H^+, to verify these pH values were unsuccessful due to metal hydrolysis. The change in pH observed in the titrations did not equal the amount of base added.

Theoretically, pH measurement as the activity of hydrogen ions is only valid for fairly dilute aqueous solutions of simple solutes, where hydrogen activity is synonymous with concentration. In concentrated solutions however, as stated before, activity is not equal to concentration.

$$a = \gamma m$$

$\gamma \neq 1$; concentrated solutions
$\gamma = 1$; dilute solutions
m = molality

It is impossible to give an accurate quantitative interpretation of pH in concentrated solutions (Ionic strength >0.2M). However, it is essential in the solvent extraction studies of typical aqueous feed solutions to give an indication of hydrogen ion concentration. Therefore, pH meters and electrodes were used in these studies, to gauge acidity but it is important to note that all the quoted pH values are only an indication of the H^+ concentration.

CONFERENCES AND LECTURES

Conferences

28th International Conference on Coordination Chemistry
Gera, German Democratic Republic
August 13th – 18th, 1990.

Graduate Symposium, Durham 1988, 1989.

Inorganic Graduate Symposium, Strathclyde, Scotland 1988.

Inorganic Chemistry Symposium, Sheffield 1988.

Inorganic Symposium, Imperial College, London 1988.

Colloquia, Lectures and Seminars at Durham

1st August 1987 to 31st July 1988

BIRCHALL, Prof. D. (I.C.I. Advanced Materials) Environmental Chemistry of Aluminium	25th April 1988
BORER, Dr. K. (University of Durham Industrial Research Labs.) The Brighton Bomb – A Forensic Science View	18th February 1988
BUTLER, Dr. A.R. (University of St. Andrews) Chinese Alchemy	5th November 1987
CAIRNS-SMITH, Dr. (Glasgow University) Clay Minerals and the Origin of Life	28th January 1988
GRADUATE CHEMISTS, (Northeast Polytechnics & Universities) R.S.C. Graduate Symposium	19th April 1988

GRAHAM, Prof. W.A.G. (University of Alberta, Canada) Rhodium and Iridium Complexes in the Activation of Carbon–Hydrogen Bonds	3rd March 1988
GRAY, Prof. G.W. (University of Hull) Liquid Crystals and their Applications	22nd October 1987
HARTSHORN, Prof. M.P. (University of Canterbury, New Zealand) Aspects of Ipso–Nitration	7th April 1988
LUDMAN, Dr. C.J. (Durham University) Explosives	10th December 1987
McDONALD, Dr. W.A. (I.C.I. Wilton) Liquid Crystal Polymers	11th May 1988
PALMER, Dr. F. (University of Nottingham) Luminescence (Demonstration Lecture)	21st January 1988
ROBINSON, Dr. J.A. (University of Southampton) Aspects of Antibiotic Biosynthesis	27th April 1988
ROSE van Mrs. S. (Geological Museum) Chemistry of Volcanoes	29th October 1987
UNDERHILL, Prof. A. (University of Bangor) Molecular Electronics	25th February 1988
WINTER, Dr. M.J. (University of Sheffield) Pyrotechnics (Demonstration Lecture)	15th October 1987

1st August 1988 to 31st July 1989

AVEYARD, Dr. R. (University of Hull) Surfactants at your Surface	15th March 1989
AYLETT, Prof. B.J. (Queen Mary College, London) Silicon–Based Chips:– The Chemist's Contribution	16th February 1989
BALDWIN, Prof. J.E. (Oxford University) Recent Advances in the Bioorganic Chemistry of Penicillin Biosynthesis	9th February 1989

BALDWIN & WALKER, Drs. R.R. & R.W. (Hull University) 24th November 1988

Combustion: Some Burning Problems

CADOGAN, Prof. J.I.G. (British Petroleum) 10th November 1988

From Pure Science to Profit

CASEY, Dr. M. (University of Salford) 20th April 1989

Sulphoxides in stereoselective Synthesis

HALL, Prof. L.D. (Addenbrooke's Hospital, Cambridge) 2nd February 1989

NMR – A Window to the Human Body

LUDMAN, Dr. C.J. (Durham University) 18th October 1988

The Energetics of Explosives

MARKO, Dr. I. (Sheffield University) 9th March 1989

Catalytic Asymmetric Osmylation of Olefins

NICHOLLS, Dr. D. (Durham Chemistry Teachers' Centre) 11th July 1989

Demo. "Liquid Air"

REES, Prof. C.W. (Imperial College London) 27th October 1988

Some Very Heterocyclic Compounds

SCHROCK, Prof. R.R. (M.I.T.) 13th February 1989

Recent Advances in Living Metathesis

SINGH, Dr. G. (Teesside Polytechnic) 9th November 1988

Towards Third Generation Anti–Leukaemics

SNAITH, Dr. R. (Cambridge University) 1st December 1988

Egyptian Mummies: What, Where, Why and How?

1st August 1989 to 31st July 1990

BLEASDALE, Dr. C. (Newcastle University) 21st February 1990

The Mode of Action of some Anti–tumour Agents

CROMBIE, Prof. L. (Nottingham University) 15th February 1990

The Chemistry of Cannabis and Khat

HOLLOWAY, Prof. J.H. (University of Leicester) 1st February 1990

Noble Gas Chemistry

HUGHES, Dr. M.N. (King's College, London) A Bug's Eye View of the Periodic Table	30th November 1989
IDDON, Dr. B. (University of Salford) Schools' Christmas Lecture – The Magic of Chemistry	15th December 1989
LANCASTER, Rev. R. (Kimbolton Fireworks) Fireworks – Principles and Practice	8th February 1990
PALMER, Dr. F. (Nottingham University) Thunder and Lightning	17th October 1989
PARKER, Dr. D. (Durham University) Macrocycles, Drugs and Rock 'n' roll	16th November 1989
PERUTZ, Dr. R.N. (York University) Plotting the Course of C–H Activations with Organometallics	24th January 1990

ACKNOWLEDGEMENTS

The author would like to express his thanks to all those (too numerous to mention) who have aided and encouraged him in both the execution of these investigations, and in the writing of this thesis. His special thanks, first of all, go to Dr. V.C. Gibson, for his continued interest, advice and encouragement. The group also encompassing Terry Kee, Dave Williams, Alan, Ezat, Jon, Oliver, Andy, Ed and not least Jens, have provided a stimulating environment. Indeed, all members of the Department of Chemistry have made it an enjoyable place in which to work. Special appreciation goes to Bob Coult, for his valued expertise and friendship.

He would like to thank those companies which supplied commercial samples and technical information, especially Albright and Wilson, Akzo Chemie and Rohm and Haas.

He is indebted to British Chrome and Chemicals Limited for their generous full sponsorship of these studies, and expresses his gratitude.

Finally, the following people must be mentioned for their contributions to this thesis; Jane (typing), Jules (translations) and Rob (the occasional beer!).

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