# ZIRCONIUM SOLVENT EXTRACTION USING ORGANOPHOSPHORUS COMPOUNDS

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A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements for the degree of Master of Engineering

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## TO MY LOVELY DAUGHTER

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## NATCHAYA SURIYACHAT

## ABSTRACT

This study compares zirconium extraction from hydrochloric acid solutions using either Cyanex 923 or Cyanex 925 in kerosene. While both are mixtures of trialkyl phosphine oxides, the trialkyl groups in the former have straight chains, while those in the latter have branched chains.

The major variables studied were hydrochloric acid, extractant and zirconium concentrations, and phase ratio. With both reagents, zirconium is extracted rapidly. Extraction increases with increasing hydrochloric acid concentration, and zirconium is loaded as its neutral tetrachloride complex by a solvation reaction. The loaded zirconium forms a di-solvate, except at high excess extractant concentrations, where solvation numbers greater than 2 are found. At a constant total chloride concentration, the zirconium extraction level is maintained if hydrochloric acid is partially replaced by lithium chloride, provided sufficient hydrochloric acid is retained to prevent zirconium hydrolysis. Distribution coefficients decrease with increasing zirconium concentration, suggesting that polymerization occurs in the aqueous phase.

For given conditions, zirconium extraction into Cyanex 923 is higher than for Cyanex 925. However, loading selectivity for zirconium over other metals has not been studied. A few preliminary experiments have shown that aqueous solutions of ammonium carbonate are potential stripping agents.

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#### RESUME

Deux extractants organiques Cyanex 923 ou Cyanex 925 furent utilisées pour réaliser l'étude comparative de l'extractant du zirconium en milieu HCI. Bien que ces extractants soient des mélanges de trialkyl phosphine oxides, le groupement trialkyl du Cyanex 923 possède des chaînes linéaires et ceux du second des chaînes branchées.

Les principaux paramètres étudiés furent: la concentration de HCI, la concentration d'extractant et de zirconium. Ce dernier fut extrait rapidement par les deux extractants.

L'extraction augmente parallelement avec la concentration d'acide. Le zirconium est extrait sous forme d'un chloro-complexe, par solvation. Habituellement le complexe extrait contient deux molécules d'extractants par molécule de metal. Cependant lorsque la concentration d'extractant augmente, des stoichiometries differentes furent observées. L'effet combiné de HCl et LiCl sur l'extractant du zirconium fut aussi étudié. Les coefficients de distribution diminuent lorsque la concentration du zirconium augmente suggèrant une polymérisation du métal en phase aqueuse.

Dans des conditions similaires Cyanex 923 extrait plus de zirconium que Cyanex 925. Cependant, la séléctivité d'extraction de ces extractants n'a pas été étudiée. Quelques expériences préliminaires ont démontrées qu'une solution aqueuse de carbonate d'ammonium pourrait être un agent ré-extractant potentiel.

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## **CHAPTER 1**

## INTRODUCTION

#### 1.1 Background

Prior to the advent of the nuclear age, zirconium was considered as a rare element. It has been produced commercially in significant quantities since about 1950. Owing to its low thermal neutron absorption cross section, excellent corrosion resistance and low radioactivity after radiation exposure, hafnium-free zirconium is used as cladding for nuclear fuel, and as a structural material for nuclear reactors employing pressurized water heat exchangers.

Zirconium metal production is based almost exclusively on the treatment of two minerals. Zircon,  $ZrSiO_4$ , which generally contains nearly 49% zirconium and between 0.4 and 1.5% hafnium is the principal industrial mineral, while baddeleyite, an impure zirconium oxide,  $ZrO_2$ , is a commercially important but less abundant mineral containing as much as 73% zirconium and 0.4 to 1.7% hafnium.

The hafnium content of these minerals substitutes for zirconium in the mineral lattices. By reason of the chemical similarity of zirconium and hafnium, special and costly techniques are followed to remove the hafnium impurity. This is necessary for all zirconium used in nuclear reactors. Solvent extraction processes are universally used today to separate hafnium from zirconium. Such a separation and purification yields nuclear grade zirconium.

Zirconium was first prepared in elemental form in 1824, produced in relatively pure form in 1914, and made into high-purity grade in 1925 by the de Boer-van Arkel procedure. This procedure was later used for the first commercial zirconium production in the United States. High-purity zirconium was first produced on a commercial scale in 1944 under the direction of Dr. W.J. Kroll. The method used produced high-purity zirconium by magnesium reduction of zirconium tetrachloride in an inert atmosphere. Private industry adopted this process in 1953, and soon afterwards the zirconium industry expanded and was able to produce large quantities of zirconium in high-purity and commercial grades (Adams, 1985).

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Zirconium is a hard, shiny, ductile metal, similar to stainless steel in appearance and resistant to corrosion by water and steam, mineral acids, strong alkalies, organic acids, salt solutions and molten salts. Some important properties are given in Table 1.1.

Property	Zirconium
Atomic number	40
Atomic weight	91.22
Atomic radius	1.452 A°
Ionic radius(Zr <sup>4+</sup> )	0.74 A°
Density, g/cm <sup>3</sup>	6.49
Melting point, °C	1852
Boiling point, °C	3580
Vapour pressure, K	1949-2054
Thermal neutron cross-section	0.18 barns

Table 1.1 Physical properties of zirconium.

(\* Elinson and Petrov, 1969 and Mukherji, 1970)

#### 1.2 Occurrence and Mining Technology

Zirconium occurs naturally as a silicate in zircon, as an oxide in baddeleyite, and in other oxide compounds. Zircon is widely distributed in the earth's crust as a component of igneous, metamorphic, and sedimentary rocks. Due to zircon's resistance to weathering and attrition, it is found in the heavy residues of various rocks and beach sands. In beach sands, zircon is associated with ilmenite, rutile and monazite. All commercial sources of zircon are derived from the mining of unconsolidated beach deposits or recovered as coproducts and byproducts in the processing of heavy-mineral-bearing sands such as the titanium minerals.

Sand deposits are usually mined by floating suction or bucket-line dredges. The sand is treated by wet gravity methods to produce a bulk, mixed, heavymineral concentrate containing zircon, the two titanum minerals, rutile and ilmenite, and other marketable minerals. The specific gravity of zircon (4.7) enables it to be concentrated with other heavy minerals by gravity methods. Clean zircon is produced from heavy-mineral concentrates by a combination of drying, screening, electrostatic, electromagnetic and gravity processes. The enriched product is then usually heated at 650 °C to remove the remaining residual minerals. A 99% zircon product is usually obtained by these methods. The composition of a typical zircon beach sand is shown in Table 1.2.

Compound	wt %
2:02	62.8
Combined SiO <sub>2</sub>	30.9
HfO₂	1.2
Free SiO <sub>2</sub>	0.8
FeO	0.3
TiO <sub>2</sub>	0.25
Al <sub>2</sub> O <sub>3</sub>	0.2
Cr <sub>2</sub> O <sub>3</sub>	0.12
All others	< 0.1

Table 1.2 Composition of typical (Australian) zircon beach sand.

(\* MacDonald et al., 1982)

#### **1.3 Production of Pure Zirconium Metal**

Present commercial plants for producing zirconium metal are based on the Kroll process in which zirconium tetrachloride vapour is reduced with molten magnesium in an inert atmosphere. The conversion of the zirconium content of zircon to zirconium metal sponge is accomplished in the following steps.

#### Step I: Decomposition of zircon

Zircon is a highly refractory mineral on account of its geological stability. The ore is cracked only with strong reagents and high temperatures. Methods include carbothermic reduction, caustic fusion, fluorosilicate fusion, thermal dissociation and chlorination. In recent years, zircon sand has been chlorinated directly in a fluidized bed containing carbon. This reaction is endothermic and requires temperatures of 1,150 °C or higher to obtain reasonable production rates.

The product from this step is  $ZrCl_4$  (HfCl<sub>4</sub>) that condenses as a loose fluffy powder which contains small amounts of impurities such as iron, chromium and silicon.

#### Step II: Separation of hafnium

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Zirconium and hafnium always occur together in natural minerals and, therefore, all zirconium compounds derived therefrom contain hafnium, usually at about 2 wt% Hf/(Hf+Zr). However, the major applications of zirconium for cladding and as a structural material in nuclear reactor cores requires the hafnium content to be reduced to below 100 ppm. Separation processes that have been suggested include solvent extraction, ion exchange, distillation, selective partial reduction, vapour phase dechlorination, separation of tetrachloride vapours (Flengas and Dutrizac, 1977), fractional precipitation, and caustic leaching. Of these, the solvent extraction method has been adopted to the greatest extent using multistage counter-current liquid-liquid extraction. The details of zirconium solvent extraction are discussed in chapter 2. The purification step is very important, particularly as it provides a means of removing other major impurities, especially iron, that are otherwise left in the finished metal. In practice, purified zirconium tetrachloride containing about 0.1% iron can be produced.

#### Step III: Reduction

The Kroll process is the most common method of reduction, in which zirconium tetrachloride vapour is reduced by molten magnesium in a protective argon atmosphere. The main reaction that converts zircon to zirconium metal sponge is illustrated by the following simple equation:

#### Step IV: Refining

Zirconium sponge produced by the Kroll process has adequate purity and ductility for most uses. For applications requiring extremely soft metal, and for research studies on the properties of the pure metal, it can be further purified by the van Arkel-de Boer (iodide-bar process), by electrorefining, or by electron beam melting.

To better understand the basic process as originally developed, its flowsheet is shown as Figure 1.1. Various changes to this process have since been made to comply with environmental pollution regulations and pressures rather than to improve the process itself. In particular, MIBK has relatively high aqueous solubility and low flash point. Thus an alternative extractant that does not suffer from these defects would be advantageous.



Figure 1.1 Zirconium sponge production flowsheet (Conventional method).

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#### **1.4 Range of Applications**

In addition to its use in nuclear reactors, zirconium is consumed as the silicate mineral, zircon, and the oxide, zirconia, while lesser quantities are used in various corrosion resistant alloys, and in inorganic and organic chemicals.

Zircon is used for sand molds and cores, mold washes, and mold facings. Zircon and zirconia are also used in refractory applications, principally for brick for lining steel ladles, and for applications such as fused, cast, and bonded bricks and shapes. Glass and ceramic applications for zirconia and zircon are as crucibles, substrates for electronic equipment, and opacifiers for sanitary ware and in electronic and piezoelectronic equipment.

Advanced technology applications of zirconium include stabilized and partially stabilized zirconia (PSZ) used in extrusion dies, industrial cutting blades, ceramic engine parts, liners for engine exhaust chambers, thermal barrier coating for jet engine compressor blades, and in rocket nozzles. Zirconium fluoride glasses are used in fibre optics. Stabilized zirconium oxide refractories have high light reflectivity, good thermal stability, and resist penetration by metal.

In recent years, a transformation-toughened zirconia ceramic (Lewis, 1989) known as partially stabilized zirconia has been developed. This is achieved by the addition of calcium oxide, magnesium oxide, or yttrium oxide in lesser amounts than necessary to achieve full stabilization. This material shows significant increases in strength and fracture toughness and virtually eliminates the brittleness normally associated with ceramics. **PSZ** properties important to its application include high thermal shock resistance, low thermal conductivity, low coefficient of friction against steel, and a modulus of elasticity similar to that of steel. Yttria-

stabilized zirconia ceramics are also used in oxygen sensors in automobile exhaust systems to supply microprocessor data for automatically adjusting the air-fuel ratio to improve fuel efficiency and reduce pollution emissions.

#### 1.5 Present Work

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This thesis compares Cyanex 923 and 925 as extractants for zirconium present as chloride in hydrochloric acid solution. In all experiments, the extractant was dissolved in kerosene, while zirconium was the only metal in the aqueous feed.

#### **1.6 Research Objectives**

The following are the objectives of the present research:

1) To determine a reliable analytical method for the determination of zirconium in aqueous acidic chloride solution.

2) To compare quantitatively the extraction of zirconium by the two extractants;Cyanex 923 & Cyanex 925 from hydrochloric acid solutions.

3) To deduce the extraction mechanism.

### CHAPTER 2

### **ZIRCONIUM CHEMISTRY**

The chemistry of zirconium has been the subject of numerous investigations since its discovery in 1789, but there is still a lack of information about the exact species existing in aqueous solutions of its salts. In the present literature review, many papers involving solution chemistry were found covering the period 1950-1971, but over the past 20 years, there have been relatively few publications in this field. Recently, one of the most important research areas has been directed towards the separation of hafnium from zirconium, and several liquid-liquid separation processes have been developed for this purpose.

The aim of this literature review was to study the complexing of zirconium species existing in acidic aqueous solution, especially in hydrochloric, hydrofluoric, sulfuric and nitric acid, these systems being pertinent to solvent extraction of zirconium. The hydrolysis and polymerization of dissolved zirconium and methods of separating Hf from Zr have also been reviewed.

#### 2.1 Solution Chemistry of Zirconium

Zirconium, which has an atomic number 40, is a transition metal of the IVA group in the periodic table. The most common oxidation state of zirconium is +4, and all important complexes form with ions of this valence, although the +2 and

+3 oxidation states exist for zirconium in some crystalline compounds. Zirconium is a so-called Pearson hard acid (Pearson, 1963), showing a strong affinity for 'hard' ligands such as F,  $SO_4^{-}$ , OH,  $NO_3^{-}$  and intermediate ligands such as Cl.

Zirconium and all the elements of group IVA, have two electrons in their outermost (n) shells and two electrons in the (n-1)d shells. The +4 oxidation state, strongly characteristic of this group, is attained by the loss of these four electrons. Because of its high charge, the  $Zr^{4+}$  aqueous ion shows a relatively strong tendency to hydrolyse. This so-called "hard" ion forms more stable complexes with "hard" ligands such as F<sup>-</sup> than with "soft" ones such as the heavier halides (such as Cl<sup>-</sup>). Of the many experimental papers and literature reviews during the period 1960-75, most concerned the fluoro-complexes of zirconium. There has not been much information available on the chloride system.

Knowledge of the state of ions in aqueous solutions is essential in predicting the relative importance of different complexes of zirconium. The traditional belief was that the  $Zr^{4+}$  ion does not exist in solution, but rather, zirconium exists as the zirconyl ion ( $ZrO^{2+}$ ). In the latter half of this century, several studies (Elinson and Petrov, 1969 and Mukherji, 1970) of zirconium aqueous chemistry have resulted in the current belief that zirconium does exist in solution as the tetravalent ion, at least in extremely acidic solutions. In spite of this, infrared adsorption spectra of many solid zirconium compounds have clearly shown the existence of the Zr = 0 double bond (Kharitonov and Rozanov, 1962) and no study has yet demonstrated unequivocally that the zirconyl ion does not exist in any aqueous environment. It is therefore necessary to consider, at least qualitatively, the effect of the zirconyl ion on zirconium aqueous chemistry.

The zirconyl ion differs from the tetravalent zirconium in that the former is larger, it has a lower charge and it is highly polarized. These characteristics suggest that the zirconyl ion would be 'softer' in the **Pearson sense** than the tetravalent zirconium ion. The zirconyl ion should, therefore, have greater affinity for intermediate ligands such as Cl<sup>-</sup>, diminished affinity for hard ligands, and lesser tendency towards hydrolysis.

The size and the charge of zirconyl ion also have implications when calculating activity coefficients. The activity coefficient of an ion in solution is directly proportional to its charge and inversely related to an ion size parameter. Therefore the larger ion size and lower charge of zirconyl ion should both contribute to a lower activity than that of  $Zr^{4+}$  for solutions of identical ionic strength.

Covalent bonds such as the Zr = O double bond are categorized as polar if the electronegativities of the bonding atoms differ by greater than 0.5 (Douglas et al., 1983). Since the electronegativity (Pauling's scale) of zirconium is 1.33, while the value for oxygen is 3.44, this indicates that zirconyl ion is highly polarized. It is difficult to determine if there is any effect on the aqueous chemistry of zirconium that can be attributed to this polarity. It is most likely that the oxygen would be equivalent to a bidentate ligand in establishing the coordination number of the zirconyl complex.

#### 2.2 Zirconium Complexes in Aqueous Solution

Investigation of complexation equilibria and the determination of stability constants of complexes are necessary to predict complex-formation reactions in

aqueous media so that an appropriate choice of extractant can be made when solvent extraction is used. Poor agreement between studies arises from the fact that the complexation reactions are intrinsically more complicated than as presented below for individual ligands. Molecules of the solvent and competitive species of other kinds of ligands present in solution may also take part in formation of complex species such as hydroxo-complexes of the metal ion, as well as other mixed complexes.

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780 - 2 In studies of complex-formation involving dissolved zirconium various experimental techniques have been used. They are discussed in several literature reviews (Ahrland et al. (1963), Nazarenko & Mandzhgaladze (1969), Peshkova et al. (1961) and Vasil'ev & Vasil'eva (1977)) where references to original papers on the determination of stability constants of Zirconium complexes with common anion ligands can be found. Many published results appear to be contradictory, so that it is difficult to select reliable values of stability constants, such data being necessary since the solution chemistry of zirconium is important in solvent extraction. Apparent discrepancies arise due to factors such as differences in ionic strength or in the nature of 'supporting electrolytes.'

Studies of the relationship between hydrolysis and complex formation involving zirconium in acidic solutions are of considerable interest.

Belyavskaya and Mu ping-wen (1959) studied trace amounts of zirconium in acidic solutions using ion exchange and electrophoresis. They showed that it is reasonable to assume the presence of monovalent ions  $Zr(OH)_3^+$  in 0.1 N HCl, of divalent ions  $Zr(OH)_2^{2+}$  in 0.5-1.5 N HCl, and of trivalent ions  $Zr(OH)^{3+}$  in 2 N HCl. Apparently, this shows that in the range of 0.1-1 N HCl, about 90% of the total

zirconium is present in the form of ions with a positive charge. At higher acidity (from 1 to 5 N HCI - very acidic solutions) only negatively charged ions and neutral species can be present. Positively charged zirconium ions and neutral species predominate in 0.3-2 N HNO<sub>3</sub>. For  $H_2SO_4$ , it was noted that 0-4 N  $H_2SO_4$  solutions contain only negatively charged ions and neutral species.

Similar results were obtained by Paramonova and Voevodskii (1952) in their studies on the behavior of the radioactive isotope <sup>95</sup>Zr in solutions of sulphates and nitrates. They concluded that, at least two processes occur simultaneously in sulphate solutions, the formation of sulphate complexes and hydrolysis. Complex formation is related to the presence in solution of hydrolysed zirconium species with a positive or a zero charge and the absence of negatively charged species. According to these latter investigators, there is an absence of hydrolysis at an acidity of 0.5-1 N H<sub>2</sub>SO<sub>4</sub>. However, complex formation in a nitric acid medium is considerably weaker than in sulphuric acid.

Thus, it may be concluded that in hydrochloric, nitric, and sulphuric acids at  $[H^+] < 0.5$  M, zirconium is present predominantly in the cationic forms, while the amount of neutral species increases with increase in the concentration of  $[H^+]$ . It has also been noted that the relative stability of neutral and anionic zirconium complexes increases along the series  $CIO_4^- < CI^- < NO_3$  (Nabivanets, 1961). These data on the state of zirconium in HCl,  $H_2SO_4$ , HNO<sub>3</sub> and HClO<sub>4</sub><sup>-</sup> solutions demonstrate the complexity of the behaviour of zirconium ions, and its dependence on the acidity, zirconium concentration and nature of the anion.

Due to its high charge, small radius, and comparatively low ionization potential, it is possible to classify  $Zr^{4+}$  as a typical complex former. Many

complexes of zirconium have been studied and stability constants have been determined for many of the most significant ones. The most important inorganic ligands have been listed in order of decreasing stability by Elinson and Petrov (1969) as follows:

 $OH' > F' > PO_4^{3-} > SO_4^{2-} > NO_3^{-} > CI' > CIO_4^{-}$ 

Among all acceptors, zirconium (IV) forms the strongest fluoride complexes known so far. The strong affinity to  $F^{-}$  and  $O^{-}$  as donor atoms is typical of acceptors of high charge and small radius, and as  $Zr^{4+}$  possesses these two qualities to an unusual degree, strong complex formation is certainly expected.

The following description of the important complexes of zirconium with inorganic ligands in common acidic aqueous solutions is based on extrapolation of the known thermodynamic data obtained at room temperature using the correspondence principle (Criss and Cobble, 1964a,b). There are limitations to this technique which must be discussed. First of all, the correspondence principle applies to simple ionic species and furthermore, not all ionic species can be confidently dealt with using this method. Simple cations and anions, OH, oxy-anions of the form  $MO_n$ <sup>m</sup> and acid oxy-anions of the form  $MO_n(OH)$ <sup>m</sup> have been modelled. Other simple anions involved in aqueous solution chemistry of zirconium in acidic solution such as F, OH,  $SO_4^2$ ,  $NO_3^2$ , and especially CI, the main anion pertinent to this thesis, will be described in some detail here. However, when compared with the other common anions, chloride is an intermediate ligand and has lower affinity to form complexes with zirconium. Because the conventional production of zirconium metal is based on the treatment of zircon by chlorination, subsequent dissolution into a chloride medium is appropriate if purification by

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**د**ت دت solvent extraction is proposed to avoid interferences with other anion species that would otherwise be present.

#### Fiuoride Complexes

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Of all important ligands which form complexes with zirconium, none has been more thoroughly studied than the fluoride ion. A comparative study of fluoride complexes of several transition metals (including actinides and rare-earth elements) indicated that zirconium forms the most stable fluoride complexes of those studied, while hafnium is the second most stable (Babko, 1959). Complexation reactions involving fluoride are invariably modelled according to the following equation:

$$Zr^{+4} + nHF = ZrF_{n}^{4-n} + nH^{+}$$
 (2.1)

Equilibrium constants from several sources are presented in Table 2.1 for this reaction with zirconium. The equilibrium constants of the Zr-F complexes are plotted as a function of ionic strength in Figure 2.1.

#### Hydroxide Complexes

Zirconium has a great affinity for OH ions in solution. The ligation number, as is expected for hydroxyl ions, increases with increasing pH. The pH range for these complexes is still very acidic.

Table 2.2 presents published data on equilibrium constants for Zr hydroxide, and Figure 2.2 compares stepwise equilibrium constants for the reactions:

$$Zr^{+4} + nOH = Zr(OH)_n^{4\cdot n}$$
 (2.2)

Source	Log K1	Log K2	Log K3	Log K4	Log K5	Log K6
Busiaev, 1962 T=298 K, I=0.5			2.69	1.83	1.51	0.86
Connick & Mcvey, 1949 T=298 K, I=2.0	5.8	4.32	2.83			
Rydberg & Sullivan, 1959 T=298 K, I=2.0	5.8	4.29	2.88			
Ahrland et al., 1963 T=293 K, I=4.0	5.96	4.54				
Noren, 1967 T=293 K, I=4.0		4.41	3	2.3	1.53	0.3
Noren, 1969 T=293 K, I=4.0	5.88	4.36	3	2.26	1.85	
Hammer, 1979 T = 298 K, I = 0.96	5.79	4.54	2.96	2.44	1.4	1.23
T=298 K, I=2.88	5.83	4.51	3.1	2.36	1.56	1.01
T=308 K, I=0.96	5.73	4.4	2.97	2.48	1.56	0.96
T=308 K, I=2.88	5.71	4.3	3.09	2.36	1.65	0.94
T=318 K, I=0.96	5.78	4.41	2.9	2.43	1.47	1.07
T=318 K, I=2.88	5.78	4.22	3.07	2.19	1.65	1
T=333 K, I=0.96	5.77	4.21	3.09	2.28	1.54	0.7
T=333 K, I=2.88	5.88	4.06	3.11	2.16	1.35	1.29

 Table 2.1 Equilibrium data for stepwise Zr-F complexation reactions.

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Figure 2.1 Effect of ionic strength on equilibrium constants for the Zr-F complexes at 298 K.

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 Table 2.2 Equilibrium constant for Zr-OH complexes at 298 K.

Reaction :  $Zr^{4+}$  + nOH<sup>-</sup>  $\rightarrow$   $Zr(OH)_n^{4-n}$ 

Source	Log K1	Log K2	Log K3	Log K4
Nazarenko & Mandzhgaladze, 1969 I=0.1	14.08	27.83	41.4	54.6
I=0.3	14.12	27.9	41.5	54.75
I=0.5	14.15	27.96	41.57	54.85
I=1.0	14.3	28.23	41.91	55.25
Solovkin & Ivantsov, 1966 I = 1.0	14.56	28.76	42.69	56.52
Peshkova et al., 1961 I = 1.0	14.3	28.3	41.9	55.2

Reaction :	Zr <sup>4+</sup> +	H₂0		⇒ Zr(C	)H) <sup>3+</sup> +	H+	
	Zr(OH) <sup>3+</sup>	+	H <sub>2</sub> O		$Zr(OH)_{2}^{2+}$	4	_ <b>H</b> +
	Zr(OH) <sub>2</sub> <sup>2+</sup>	+	H <sub>2</sub> O		$Zr(OH)_{3}^{+}$	+	H+
	$Zr(OH)_3^+$	+	H <sub>2</sub> O		Zr(OH)₄	+	<b>H</b> *

Source	Log K1	Log K2	Log K3	Log K4
Peshkova et al., 1961 I=1.0	0.32	-0.06	-0.35	-0.64
Solovkin, 1958 I=2.0	-0.22	-0.62	-1.05	-1.17
Noren, 1973 I=4.0	0.3			
Noren, 1973 I=4.0 (Potentiometry)	-0.55			

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Figure 2.2 Effect of ionic strength on equilibrium constants for the Zr-OH complexes at 298 K.

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#### Sulphate complexes

Of all accepters, zirconium forms sulphate complexes that are among the strongest found. Thus, a number of studies have been reported on sulphate complexes with zirconium, and several have been identified. Table 2.3 presents several sources of data for Zr sulphate complexes. It is immediately obvious that considerable variation exists in equilibrium constants, this being due to disagreement as to the nature of Zr sulphate species in solution. The data in Table 2.3 are based on the complexation reaction:

$$Zr^{+4} + nHSO_4^- = Zr(SO_4)_n^{4-2n} + nH^+$$
 (2.3)

Tribalat and Schriver (1976) determined equilibrium constants for the reaction:

 $ZrOH^{+3} + nHSO_4^{-} = Zr(SO_4)_n^{4\cdot 2n} + H_2O + nH^+$  (2.4) Relevant data are included in Table 2.3.

#### Nitrate Complexes

Zirconium nitrate solutions are qualitatively similar to the chloride system. The nitrate ion forms somewhat stronger complexes with Zr (IV) when compared with perchlorate which is quite a weak complexing agent. Electromigration studies of the three inorganic ligands,  $NO_3^-$ , Cl<sup>-</sup>, and ClO<sub>4</sub><sup>-</sup> reveal relative stability constants in the following order:

 $NO_3 > CI > CIO_4$  (Nabivanets, 1961a, 1961b)

#### **Chloride Complexes**

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Several studies have been made of chloride complexation based on the equation:

$$Zr^{4+} + nCl^{*} = ZrCl_{n}^{4n}$$
(2.5)

and the results are presented in Table 2.4.

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As in the case of the sulphate system, agreement between the various studies is poor, due probably to the different experimental techniques used.

Source	Log K1	Log K2	Log K3
Connick & McVey, 1949 T=298 K, I=2.0	2.66	1.72	0
Rydberg & Sullivan, 1959 T=298 K, I=2.0	2.63	1.73	-0.08
Ryabchikov et al., 1964 T=298 K, I=2.33	2.56	0.78	2.27
Ahrland et al., 1963 T=293 K, I=4.0	2.85	1.85	
Noren, 1969 T=293 K, I=4.0	2.78	1.95	0.3
Tribalat & Schriver, 1976 T=298 K, I=4.0	1.6	1.12	

 Table 2.3 Equilibrium data for stepwise Zr-sulphate complexes.

Table 2.4 Equilibrium constants for Zr chloride complex reactions.

Source	Log K1	Log K2	Log K3	Log K4
Connick & Mcvey, 1949 T=298 K, I=2.0	0.30			
Marov & Ryabchikov, 1962 T=298 K, I=2.0	-0.02	-0.92	-1.15	-1 10
Solovkin, 1957 T=298 K, I=2.0	0.92	1.32	1.51	1.18
Ryachikov et al., 1964 T=298 K, I=4.0	0.04	-0.74	-1.10	

Reaction :  $Zr^{4+} + nCl^{-} = ZrCl_n^{4-n}$ 

#### 2.3 Hydrolysis and Polymerization of Zirconium

Elinson & Petrov (1969) have concluded that zirconium compounds in aqueous solution are characterized by their high degree of hydrolysis as well as their tendency to form various complex ions and polymer compounds. A major feature of the solution chemistry of tetravalent ions such as Zr<sup>4+</sup> is the strong tendency toward hydrolysis which is the characteristic of ions of high positive charge. Moreover this hydrolysis involves complicated polynuclear equilibria. In order to avoid difficulties arising from hydrolysis, experiments are often performed in strongly acid solutions and at low concentration of metal ion.

Because of extensive hydrolysis and polymer formation even in solutions of high acidity, the aqueous chemistry of zirconium (IV) is extremely complex. A variety of physicochemical methods have been employed in attempts to identify the various zirconium species in solution. The result of all these investigations is an array of postulated monomeric and polymeric hydrolysis products. The general case of combined hydrolysis and polymerization of zirconium is represented by the reaction(s):

$$nZr^{4+} + mH_2O = Zr_n(OH)_m^{4nm} + mH^+$$
 (2.6)

Consideration of hydrolysis and polymerization of zirconium is necessary because these phenomena directly affect the extraction of zirconium, and are also the main reasons for the lack of precision and accuracy in analytical methods for zirconium.

From the measurements of Zielen and Connick (1956), it is evident that at an acidity as high as 2 M, polynuclear hydrolysis exists in solutions of Zr (IV) more concentrated than  $10^{-4}$  M. Being polynuclear, the hydrolysis increases rapidly with the concentration of Zr(IV). On the other hand mononuclear hydrolytic complexes seem not to exist to a measurable degree, so that once polynuclear complex formation has been suppressed, then Zr<sup>4+</sup> ought to be the only mononuclear species present.

Thus, it can be concluded that zirconium is polymerized in solution, and that the degree of polymerization is a function of pH, ionic strength of solution and zirconium concentration. Connick and Reas (1951), working on zirconium solvent extraction from perchloric acid solutions, supported the above conclusions. They found that the distribution coefficient depends on degree of polymerization according to the equation:

$$xZr (IV) = Zr_x (IV)$$
(2.7)

Spectrophotometric studies later confirmed the existence of trimers and tetramers of Zr(IV) in aqueous solution (Johnson and Kraus, 1956). Schultz and Larsen (1950) studied zirconium polymerization and determined that it proceeded according to the following equation:
$$Zr_{n}(OH)_{nx}^{n(4-x)} = nZr(OH)_{x}^{(4-x)+}$$
 (2.8)

Their findings indicated that in 2M HCIO<sub>4</sub> solution, polymers formed at zirconium concentrations of approximately  $2\times10^{-3}$  M, but at a perchloric acid concentration of 1 M, polymerization occurred at zirconium concentrations as low as  $2\times10^{-4}$  M.

#### 2.4 Solvent Extraction Systems

Many procedures for the determination of the species' formulas in solution are not readily applicable in the case of zirconium because of the great tendency for hydrolysis to take place, except in the case of very acidic solutions.

Solvent extraction studies involve the measurement of an equilibrium in which zirconium (IV) is distributed between the aqueous phase and organic phase. The zirconium is inappreciably complexed by the extractant when in the aqueous phase, yet forms a complex which is soluble in the organic phase and which is in equilibrium with whatever species exist in the aqueous phase. Any complexing of species in the aqueous phase is quantitatively reflected in the amount of zirconium extracted into the organic phase.

The probable equation for the extraction of zirconium from chloride solution by a neutral organophosphorus compound is:

 $Zr^{4+}$  (aq) + 4Cl (aq) + n[(RO)<sub>3</sub>P=O](org) =  $ZrCl_4.n[(RO)_3P=O]$  (org) (2.9) where  $(RO)_3P=O$  can be an extractant such as Cyanex 923 and Cyanex 925. However, the zirconium in the aqueous phase may be hydrolysed and complexed by the anions present.

Assuming, the formation of  $ZrCl_4$  complex in the aqueous phase, the equilibrium constant for reaction (2.9) can be represented as:

$$k = \frac{a_{Z_{1}C_{1},n(RO)_{8}P=0}}{(a_{Z_{1}C_{1}}).(a_{(RO)_{8}P=0})^{n}}$$
(2.10)

Solvent or liquid-liquid extraction is based on the principle that a solute can distribute itself in a certain ratio between two immiscible solvents, one of which is usually water (aqueous phase) and the other an organic solvent. In certain cases the solute can be more or less completely transferred into the organic phase. This technique can be used for purposes of preparation, purification, enrichment, separation and analysis, on all scales of use, from microanalysis to production processes.

There are several mechanisms by which a metal-containing species may transfer from an aqueous to an organic phase and they have been classified in various ways. Perhaps the best classification system is based on the type of chemical reactions involved, which leads to 3 groups of extraction processes:

1) Compound Formation

2) Ion-pair Formation

3) Solvation

Table 2.5 shows some relevant details of the above 3 groups.

Solvent Extraction System	Stripping Againts	Some applications
A) Compound Formation 1) Acidic -Organophosphorus acids -Carboxylic acids 2) Chelating -Oximes -Derivatives of quinoline	Strong acids	For the extraction of cationic metal species -Co/Ni in sulphate -U(IV) in sulphate -Cu(II) in sulphate -Ga(III); Ge(IV)
<u>B) Ion-Pair formation</u> 1) Amines -primary -secondary -tertiary -quarternary	Water or alkaline reagents	For the extraction of anionic metal species: -UO <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> <sup>2.</sup> -CoCl <sub>4</sub> <sup>2.</sup> (Co/Ni separation)
<u>C) Solvation</u> 1) Organophosphorus Compounds -TBP ; TOPO 2) Ethers, Ketones -Dibutyl carbitol -MIBK	Water or alkaline reagents	For the extraction of neutral metal species: -UO <sup>2</sup> (NO <sub>3</sub> ) -Zr/Hf separation -HAuCl <sub>4</sub>

 Table 2.5 Classification of solvent extraction systems.

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When considering the extraction of zirconium by organophosphorus compounds, possible extraction systems may include compound formation or solvation, depending mainly on the zirconium complex species which are formed.

#### 2.5 Separation of Hafnium from Zirconium

The chemical properties of hafnium and zirconium are almost identical. This similarity is greater than for any other pair of elements, mainly because of similar ionic radii ( $Hf^{4+} = 0.78 A^{\circ}$ ,  $Zr^{4+} = 0.79 A^{\circ}$ ) and outer electronic structure. The

analytical chemistry of the two metals has recently been reviewed (Elinson & Petrov, 1969 and Mukherji, 1970). Their chemical similarity makes the separation of hafnium from zirconium a difficult but challenging analytical problem. Thus, it has been difficult to develop reliable methods for the separation of these two metals.

Many methods have been devised for hafnium/zirconium separation, including fractional crystallization, fractional precipitation, fractional dissolution, fractional distillation and sublimation, diffusion of volatile compounds, ionexchange, adsorption and also solvent-extraction. The latter is utilized for separations using the simple batch process or can be adapted to a continuous countercurrent process widely used for industrial-scale operations. Brookes and Townshend (1970) reviewed all available methods for the determination of hafnium and zirconium when mixed together, these techniques relying on one of the following types of differences between the two me:als:

i) differences in physical properties

- ii) quantitative differences in chemical properties
- iii) differences in electronic and nuclear properties

Flengas and Dutrizac (1977) developed a new process for separation of hafnium from zirconium. This process is based on the repeated reaction of the mixed tetrachloride vapours of zirconium and hafnium with alkaline metal chloride salts in a solid form. This technique was investigated experimentally, and the mechanism of the separation process was discussed in terms of thermodynamic considerations.

Thus various alternatives to solvent extraction have been tried for zirconium and hafnium separation. However, it seems that none of these methods are economically satisfactory when applied on a commercial industrial scale. Sovent extraction from chloride solution using MIBK is the most widely applied technique.

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# CHAPTER 3

# SOLVENT EXTRACTION OF ZIRCONIUM BY ORGANOPHOSPHORUS COMPOUNDS

## 3.1 Introduction

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The electronic structure of phosphorus (1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>6</sup>, 3s<sup>2</sup>, 3p<sup>3</sup>) and some important chemical properties are the following: first, phosphorus has a low electronegativity that gives rise to strong bonding of phosphorus to oxygen and halogens; second, phosphorus has a strongly reactive lone pair of electrons (large polarizability): and third, phosphorus has vacant d orbitals for chemical bonding. These last two features lead to a strong tendency for phosphorus to make pentavalent phosphorus compounds. Almost all pentavalent organophosphorus compounds contain four atoms attached to phosphorus by covalent bonds, which consist of three single bonds to phosphorus and one semipolar bond between phosphorus and oxygen. The following examples show the basic chemical structures most frequently involved in this thesis.

$R_3P = O$	Phosphine oxide	(R = alkyl group)
$R_2(OH)P=O$	Phosphinic acid	
R(OR)(OH)P = O	Phosphonic acid	
$(RO)_2(OH)P = O$	Phosphoric acid	

Interest in organophosphorus compounds and their derivatives can be traced to 1763 when phosphine was discovered by Gengembre (Partington, 1966). In 1955, the Cyanamid company began synthetic work with phosphine derivatives, concentrating on replacing one or more of the P-H bonds by P-C bonds. More recently, Rickelton & Boyle (1988) reported on basic research results focusing on creating, then introducing into commercial practice, new organophosphine extractants for various metals and organic solutes. They were concerned with the derivatives obtained by the reaction of phosphine with olefins and subsequent oxidation of the reaction products to oxides, sulfides and acids. For example, the following relactions show how phosphine can be converted to trioctyl phosphine oxide (TOPO), this being marketed as Cyanex 921.

Provide State

$PH_3$ / Initiator + Octene-1	$\rightarrow$	(CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> ) <sub>3</sub> P
(CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> ) <sub>3</sub> P	$\longrightarrow$	$(CH_3 (CH_2)_7)_3 P = O$
	H <sub>2</sub> O <sub>2</sub>	Cyanex 921 extractant (TOPO)

Major studies have also been concerned with the preparation of important organic extractants:- Cyanex 923 and Cyanex 925 (Rickelton and Boyle (1988)). For the former, a mixture of 60% octene-1 and 40% hexene-1 when reacted with phosphine will give a mixture of trialkylphosphines which are then oxidized to give the following mixture for the extractant " Cyanex 923 ".

> $R'R_2P=O(31\%)$   $R'_2RP=O(42\%)$  $R'_3P=O(14\%)$   $R_3P=O(8\%)$

In contrast, Cyanex 925, a recent organophosphine oxide extractant produced by Cyanamid Ltd., can be made by reacting 2,4,4-trimethylpentene-1

with an alpha olefin to give an intermediate which is then oxidized with peroxide giving a mixed trialkylphosphine oxide as the following reactions show:



Details of the properties and performance characteristics of these two extractants and their applications will be discussed later in section 3.2.

Generally, organophosphorus compounds have the ability to form complexes with various metals, but with two different types of mechanisms. While phosphinic and dithiophosphinic acids are compound formers which extract cations, phosphine oxides and sulfides are solvating agents. Important examples of solvating agents are the organophosphorus esters such as tri-n-butyl phc sphate (TBP),trialkyl-phosphine oxide, etc., which are strongly basic. The highly basic trialkylphosphine oxides resemble the strongly basic liquid anion exchangers. Phosphorus esters such as phosphate, phosphonate and phosphinate esters have also been extensively used as extractants in recent years.

Compounds with a more basic phosphoryl group, P=0, than that in TBP, are stronger extractants than TBP, meaning that extractability of a given metal decreases in the order:

phosphine oxide > phosphinate > phosphonate > phosphate ( De, A.K., 1970),

or

 $R_{3}P=0$  > phosphinic acid > phosphonic acid > phosphoric acid



3.2 Properties, Performance and Applications of Cyanex 921<sup>\*1</sup>, Cyanex 923<sup>\*1</sup> and Cyanex 925<sup>\*1</sup>

## Cyanex 921 Extractant

#### **Chemical Structure**

The chemical structure of Cyanex 921 extractant is as follows:

At room temperature it is a waxy solid which melts at 50 °C. Other properties are as follows:

Molecular weight = 386 , Specific gravity (25 °C) = 0.88 (93% Trioctylphosphine oxide) , Viscosity (55 °C) = 15 centipoise

1 \* products from American Cyanamid Company, U.S.A.

The most widely used phosphine oxide is tri-n-octylphosphine oxide (TOPO). Cyanex 921 is one example of this reagent, and was the first member of a family of extractants developed by Cyanamid. TOPO has been used for the extraction and determination of more than 30 elements in an aqueous phase, including uranium, titanium, thorium, iron and molybdenum etc. (Welcher, 1961). Generally, TOPO is known as one of the most stable members of the group of organophosphorus solvating reagents (Ritcey & Ashbrook, 1984).

This reagent has been used in two commercial processes that have existed for many years. The first recovers uranium from wet process phosphoric acid. This process, developed at the Oak Ridge National Laboratory (Hurst et al., 1969, 1972, 1973), is based on the extraction of uranium (VI) using a D2EHPA-TOPO mixture (synergic behaviour). The other industrial application is the recovery of acetic acid from effluent streams, and a number of informative papers have been published in recent years by Ricker et al., 1971, 1980 and Golob et al., 1981. The advantages of Cyanex 921 are based on low solubility losses, stability during distillation at elevated temperatures and also high extraction coefficients for acetic acid in comparison to other solvating reagents <sup>2</sup>.

# Cyanex 923 Extractant<sup>3</sup>

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## **Chemical Structure**

<sup>&</sup>lt;sup>2</sup>American Cyanamid Co., Cyanex 921 Extractant Sales Brochure <sup>3</sup>American Cyanamid Co., Cyanex 923 Extractant Sales Brochure

As indicated in section 3.1, Cyanex 923 is a mixture of four trialkylphosphine oxides as follows:

$$R'_{3}P(O)$$
  $RR'_{2}P(O)$   $R_{2}R'P(O)$   $R_{3}P(O)$ 

(1) (2) (3) (4)

where  $R = [CH_3(CH_2)_7]$  - normal octyl  $R' = [CH_3(CH_2)_5]$  - normal hexyl

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Average molecular weight = 348 (approximately)

The four major components are: trihexylphosphine oxide(1), dihexylmonooctylphosphine oxide(2), dioctylmonohexylphosphine oxide(3), and trioctylphosphine oxide(4). Important properties are as follows:

Specific gravity  $(25 \,^{\circ}C) = 0.88$ , Viscosity  $(55 \,^{\circ}C) = 40$  centipoise

Cyanex 923 is a liquid phosphine oxide while TOPO is a solid at room temperature. The former is a potential substitute for TOPO in the conventional process for recovering uranium from wet process phosphoric acid. Cyanex 923 also has potential applications in the recovery of both organic and inorganic solutes, described as follows. Several processes (e.g. petrochemical plants and others manufacturing common chemical products) generate aqueous effluents containing carboxylic acids (particularly acetic acid) or phenols. Here, recovery of these organic solutes by solvent extraction with TOPO has been operated successfully. Cyanex 923, being a liquid, can be used to advantage over TOPO in these applications because of ability to prepare a concentrated, low freezing point extractant. It is also completely miscible with all commonly used diluents even at low ambient temperature. This virtually eliminates the problem of plant

freeze-up during cold periods. For phenol recovery, the potential benefit is the ability to construct plants with minimum staging requirements. Since phenol is strongly extracted by phosphine oxides, the advantages of Cyanex 923 over TOPO are less marked than in the case of the more weakly extracted acetic acid (Eckert and Bauer, 1984). The major factor in choosing between the two in phenol systems will apparently depend on the concentration of phenol in the effluent. Another advantage of Cyanex 923 lies in its very low solubility in water (0.001 wt%) when compared with many other reagents (Cyanex 923 extractant brochure). This feature can minimize extra processing of raffinate that would be required by more soluble extractants. In particular, Cyanex 923 is also effective in separating ethanol from water, this finding application in treatment of continuous fermentation broths. and the second s

An example of the potential use of Cyanex 923 in treating inorganic solutes is its ability to remove impurities such as arsenic, antimony and bismuth from copper electrolytes by solvent extraction rather than by conventional processes (Rickelton and Brown, 1985). Arsenic, antimony and bismuth removal are important because the production of pure copper is promoted and the current efficiency of the process is increased.

Another potential application of Cyanex 923 in treating inorganic solutes is, again, related to its liquid state and higher organic solubility than shown by TOPO. Recent work by Hahn and Retelsdorf (1984) reported on the ability of using TOPO in niobium-tantalum separation to produce higher purity niobium oxide than MIBK, as conventionally used. However Cyanex 923 is likely to be preferable to TOPO.

#### Chemical Structure

Cyanex 925 is a mixture of two compounds which have the following structure:

R₃P(O)	R₂R′P(O)	
(I)	(11)	

where

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R =	СH <sub>3</sub> СH <sub>3</sub> -СH-СH-СH-СH- СH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>
R' =	сң(сң)

and (I) is bis(2,4,4-trimethylpentyl)octylphosphine oxide and (II) is tris(2,4,4-trimethyl-pentyl)phosphine oxide Component II predominates, representing approximately 85% of the mixture. The molecular weight of both components is 386. Specific gravity and viscosity are (at 21 °C) 0.88 and 117 centipoise respectively.

As indicated by its chemical structure, Cyanex 925 is a branched chain phosphine oxide when compared to analogous straight chain phosphine oxides; Cyanex 921(TOPO) and Cyanex 923. This structural difference may result in greater selectivity of extraction than when using the other phosphine oxides, this having been shown especially in the case of tin recovery from secondary sources (e.g in chloride media).

<sup>&</sup>lt;sup>4</sup>American Cyanamid Co., Cyanex 925 Extractant Sales Brochure.

Another potential application of Cyanex 925, which is one of the latest organic phosphine oxides developed by Cyanamid Co., is gallium recovery from aqueous solutions derived from zinc ore processing. This is an important commercial source of gallium that contains iron as the major impurity. Also indium recovery as a by-product from the processing of base metal sulphide ores can be achieved through solvent extraction using Cyanex 925.

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Cyanex 925, like Cyanex 923, is a liquid phosphine oxide which can also extract impurities such as arsenic from copper electrolytes, but the former is a weaker extractant than Cyanex 923 because of the chain branching structure. Figures 3.1 and 3.2 show results comparing the extraction power of Cyanex 923 & Cyanex 925 on arsenic and sulfuric acid respectively ( data from American Cyanamid Co.,Cyanex 925 Sales Brochure.).



Figure 3.1 Arsenic extraction isotherms (After Cyanamid Ltd.).

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Figure 3.2 Sulfuric acid extraction isotherms (After Cyanamid Ltd.).

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#### 3.3 Use of Organophosphorus Compounds in Zirconium Solvent Extraction

Solvent extraction is a potential method for separating zirconium (IV) from acidic zircon leach solutions. The extraction of zirconium (IV) from acidic aqueous solution by various organophosphorus compounds has been investigated. It has been shown that the nature of the extracted species depends greatly on experimental parameters such as the anionic nature of the acid solution (chloride, nitrate, etc.), metal and acid concentrations in these aqueous media and also the concentration of the extractant in the diluent.

Table 3.1, below, briefly summarizes some extraction data for zirconium using organophosphorus compounds.

Reagent	Extraction data	
dibutylphosphoric acid	From 2-4M HNO <sub>3</sub> , >99% extraction with	
(HDBP)	0.001M HDBP in toluene (Hardy et al., 1961)	
di-2-ethylhexylphosphoric	Quantitative extraction in 0.1-1M HCI-1.5M	
acid (DEHPA)	HDEHP (toluene) (Kimura, 1960,1961)	
tri-n-butyl phosphate (TBP)	HCI(8-10M)-TBP(1%)-toluene: Zr is separated	
	from Nb; radiometrically pure Zr is obtained	
	(Rolf, 1961). HCI(0.2M)-TBP(50%)-ethyl methyl	
	ketone or chloroform or kerosene: quantitative	

Table 3.1 Solvent extraction of zirconium(IV).

extraction; Zr is back-extracted with 2-2.5M HCI (Morachevskii et al., 1961).

 $HNO_3$ -TBP (100%): Zr is separated from Hf and Nb. The extracted species is  $Zr(NO_3)_4.2TBP$  (Alcock et al., 1957). Zr is isolated from fission products (Scadden et al., 1953) (Hure et al., 1961) (Brezhneva et al., 1964) (Wallace & Pollock, 1958) (Owens, 1964).

 $H_2SO_4(11M)$ -TBP(30%)-CCI<sub>4</sub> : only about 3% Zr is extracted; separation from Ti(IV), which is 85% extracted (Zharovskii & Vyazovskaya, 1966).

tri-n-butyl phosphine oxideExtracted species Zr(NO3)4.2TBPO (1.5-8M(TBPO)HNO3), Zr(NO3)4.HNO3.2TBPO from 12M HNO3,<br/>and a mixture of these complexes from 8-12M<br/>HNO3 (Nikitina & Pushlenkov, 1964). Extraction<br/>values increase steeply with increasing HNO3<br/>concentration (Umezawa & Hara, 1961).

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tri-n-octyl phosphine oxide Quantitative cxtraction of Zr(IV) (both in (TOPO) tracer, i.e., 20  $\mu$ g, and large, 10 mg, amounts) occurs from HCl(>5M), HCl(1M) + NaCl(4-5M),

HNO<sub>3</sub>(0.5-10M), HNO<sub>3</sub>(1M) + NaNO<sub>3</sub>(3-4M), or H<sub>2</sub>SO<sub>4</sub>(0.2-7M) (E  $\geq$  10<sup>2</sup>-10<sup>3</sup>); 0.02M TOPO (cyclohexane) is the extractant.

Zr(IV) is extracted to a lesser extent from  $HCIO_4$ , which is also not a satisfactory medium for analytical separations.

The Zr in the TOPO extract can be directly measured as the blue zirconium-Pyrocatechol violet complex at 660 nm ( $\varepsilon$  = 3.8x10<sup>4</sup>) in TOPO-cyclohexane-ethanol medium.

The species  $Zr(NO_3)_4$ .2TOPO and  $ZrCl_4$ .2TOPO are extracted in the nitrate and chloride systems respectively.

Zr(IV) is not extracted from HF solution, which can, therefore, be used as stripping agent (White & Ross, 1958).

(Data for Table 3.1 have been taken from De,A.K., et al., 1970)

The following papers are especially important with regard to zirconium extraction from chloride solutions.

Levitt and Freund (1956) studied the effect of certain variables on the extraction of zirconium from hydrochloric acid solutions by tributyl phosphate (TBP). Investigations of the variation of the distribution coefficient (D) with aqueous chloride concentration (at constant acidity and constant ionic strength) and with TBP concentration in TBP-benzene solutions were made. They also

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studied the CI:Zr ratio in the organic phase. The results of these studies offer evidence of  $ZrCl_{4}(TBP)_{2}$  as the species present in the organic phase.

Sato and Watanabe (1970) investigated the extraction of zirconium(IV) from hydrochloric acid solutions by high-molecular-weight quaternary ammonium halides (tricaprylmonomethylammonium chloride) in various organic solvents as diluents. Usually, quaternary ammonium compounds are better extractants for a given metal than secondary or tertiary amines. Furthermore, they examined the effect of organic diluent on the extraction under different conditions and also the mechanism of zirconium extraction. The following conclusions can be made:

1) Results for the extraction of HCI without zirconium by this type of quaternary compound show that most or all of HCI dissolves in the organic phase in the form of a 1:1 compound, HCI.R<sub>3</sub>R'NCI (the slopes of the plots between [H<sup>+</sup>] or [CI] in organic phase and initial aqueous [HCI] are close to unity).

2) The effect on extraction of the presence of LiCl shows that when HCl in the aqueous phase was partly replaced by LiCl, the partition coefficient was similar to that in the presence of HCl alone at the same chloride concentration. This means that total chloride ion concentration is the controlling factor in this system.

3) The effects of concentration of zirconium and temperature on zirconium extraction were also examined, and it was found that the zirconium complex formed in the organic phase does not contain water molecules and the partition coefficient increases with increasing temperature.

4) The extraction efficiency of quaternary compounds is strongly influenced by the diluent, but no relationship between extraction efficiency and a physical parameter of the diluent was found. In addition, the mechanism of zirconium

extraction was studied, and it may be concluded that the quaternary salts undoubtedly behave as liquid anion exchangers. Infrared and high-resolution nuclear magnetic resonance spectroscopy were used to examine the composition of the extracted complexes.

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Sato (1970) also studied the extraction of zirconium(IV) from hydrochloric acid solutions by tri-n-butyl phosphate (TBP) and di-(2-ethylhexyl)-phosphoric acid (DEHPA) in kerosene under different conditions. In both cases, the mechanism of extraction was discussed on the basis of the experimental /esults obtained as follows:

1) For the TBP extraction system, the extraction of zirconium increases steeply with initial acidity of the aqueous phase above about 6 M HCI. In the presence of LiCI, it was found that when HCI in the aqueous phase was partly replaced by LiCI, the partition coefficient was lower than in the presence of HCI alone at the same total chloride concentration. This implied that the controlling factor is the total chloride ion concentration.

According to log-log plots of the partition coefficient vs the TBP concentration, straight lines with a slope of nearly 2 were obtained, indicating the occurrence of a solvating reaction with TBP, which is in good agreement with the results of Levitt & Freund (1956). Thus, it can assumed that the species ZrCl<sub>4</sub>.2TBP is formed in the Zr-HCl-TBP extraction system.

2) For the DEHPA extraction system, the experimental results show that at low aqueous acidity, zirconium is extracted by a cation exchange reaction in which hydrogen ion is liberated, and at high aqueous acidity by a solvating reaction similar to that with a non-ionic reagent such as TBP. When comparing the effects

on the extraction of zirconium of presence of LiCl, the results show that at acidities below 2 M, the partition coefficient is only slightly influenced by the chloride ion concentration, but decreases with increasing hydrogen ion concentration. At acidities above 2 M, the partition coefficient in the mixture of HCI-LiCl increases continuously with the total concentration of chloride ion, in analogous manner to that in the presence of hydrochloric acid only.

In addition, using high resolution N.M.R spectroscopy, the spectra of the organic phase (both TBP & DEHPA) produced by extraction from aqueous solutions containing zirconium chloride in 1-8M HCl were also examined. These spectra confirmed that a cation exchange reaction operates at low acidity, while extraction via solvation applies at high acidity.

Sella and Bauer (1986) compared zirconium extraction from sulphuric acid media by three commercial extractants; di-2-ethylhexylphosphoric acid (DEHPA), 2-ethylhexylphosphonic and mono-2-ethyl-hexyl ester (PC 88A) and di(2,4,4trimethylpentyl) phosphinic acid (Cyanex 272) in kerosene. Both thermodynamic and kinetic aspects were studied. The experimental results showed differences in the degree of extraction, rates of extraction and the nature of extracted organic complexes, all of which were shown to depend on variations in the activities of the species H<sup>+</sup>, HSO<sub>4</sub><sup>-</sup>, H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O in the sulphuric acid solutions investigated.

From the many papers investigating zirconium (IV) extraction from acid media using phosphine oxides, it may be concluded that:

1) Generally, the extraction mechanism of zirconium(IV) involves ion association to produce neutral species by charge-neutralization, followed by solvation depending on many factors as described above.

2) All or most of the major species present in the organic phase may be generally represented as

$$(ZrX_{n}^{4-x})(R_{3}P=0)_{2}$$

where x = charge on anions such as Cl<sup>-</sup>, SO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>

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n = number of anions associated with Zr

 $R_3P=0$  is organophosphorus compound such as TBP or TOPO.

Thus the extraction reaction may be represented as:

 $ZrX_{n}^{4-x} + 2R_{3}P = 0$   $(ZrX_{n}^{4-x})(R_{3}PO)_{2}$ 

Many data support the conclusion that the molar ratio of TBP or TOPO to zirconium

= 2:1 in instances where either of these is the extractant.

# **CHAPTER 4**

# EXPERIMENTAL AND ANALYTICAL METHODS

## 4.1 Materials

All chemical reagents and solutions used were of reagent grade, and glassware was rinsed thoroughly with distilled water and dried before use.

#### Zirconyl Chloride Octahydrate (ZrOCl<sub>2</sub>,8H<sub>2</sub>O), 98%

A stock solution of zirconium in hydrochloric acid was prepared by dissolving zirconyl chloride octahydrate ( $ZrOCl_2.8H_2O$ ) powder in distilled water, with addition of HCl at the required concentration.

For some tests investigating atomic absorption analysis, acidic zirconium solutions were prepared by dissolving zirconium sheet of 99.99% purity in hydrofluoric acid or a mixture of concentrated hydrochloric with nitric acid or sulphuric acid.

#### Hydrochloric acid

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Solutions were prepared by cautiously adding required amount of concentrated acid, with mixing, to a designated volume of the distilled water.

#### Sodium Hydroxide

Predetermined amounts of NaOH crystals were dissolved in distilled water to form 1 litre solutions which were stored in polyethylene bottles with polyethylene screw caps.

# Bismuth (III) Nitrate pentahydrate, (99,999%)

This reagent was required for an analytical procedure and was prepared by dissolving 0.9701 g Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O white crystal in 1L water. These crystals are only slightly dissolved by cold water, thus boiling water is necessary.

### Ethylenediaminetetraacetic acid, disodium salt (EDTA)

A volumetric standard of 0.0499 M in water was supplied by Aldrich Chemical Company, and used in the titrimetric method for zirconium determination.

#### Silver Nitrate

A 1.050 M volumetric standard solution was supplied by Aldrich Chemical Company, and used in the argentometric titration method for chloride determination.

#### Indicator Solutions:

#### -Methyl orange indicator solution; (pH range 3.2-4.4)

Here, 500 mg methyl orange powder were dissolved in distilled water and diluted to 1L. This reagent was used for standardizing hydrochloric acid solutions.

#### -Xylenol orange indicator solution

Xylenol orange powder (0.10 g) was dissolved in distilled water and diluted to 100 ml. This reagent was used in the back titration procedure for zirconium using bismuth (III) nitrate pentahydrate.

#### -Pyrocatechol violet

Here, 0.1 g pyrocatechol violet powder was dissolved in distilled water and diluted to 100 ml. This reagent was used in the procedure for standardizing the bismuth (III) nitrate pentahydrate solution through titration with 0.01M EDTA standard solution.

#### -Potassium dichomate (98%)

Here, 50 g K<sub>2</sub>CrO<sub>4</sub> were dissolved in a little distilled water. A few drops of AgNO<sub>3</sub> solution were added until a definite red precipitate formed. This ensures that traces of chloride have been removed from the potassium chromate. After standing for 12 hr, the solution was filtered and diluted to 1L with distilled water. This indicator was used in the argentometric method for chloride determination.

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#### Organic reagents

-Cyanex 923 and Cyanex 925 were used as received from American Cyanamid Co. -Kerosene, containing less than 1% aromatics, was used as received from Fisher Scientific Co.

#### 4.2 Solvent Extraction Procedure (Method of Equilibration)

Equal volumes (20 ml) of a Cyanex solution in kerosene and the aqueous phase prepared from zirconium stock solution in hydrochloric acid of the required concentration, were placed in a 125 ml stoppered Erlenmeyer flask and mechanically shaken with a wrist-action shaker for 30 min at room temperature. Equilibration was assured, since a shaking time of about 20 min was sufficient for both Cyanex extractants (923 & 925) to reach equilibrium. This is discussed more fully in chapter 5. After equilibration, the two phases were separated using a separatory funnel. About 15-20 minutes was required for phase disengagement. Then the aqueous phase was slowly withdrawn for subsequent analysis. The flow was stopped when the interface was a little above the stopcock. Zirconium in the organic phase was stripped with aqueous ammonium carbonate solution  $[(NH_4)_2CO_3]$  when required. The raffinate was analyzed as described below. The distribution coefficient was obtained as the ratio of the equilibrium concentration of zirconium in the organic phase to that in the acueous phase.

## 4.3 Analytical Methods

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A variety of techniques for zirconium determination were examined. These included atomic absorption spectrophotometry as well as direct and indirect complexometric titrations using EDTA.

#### **4.3.1 Determination of Zirconium by Atomic Absorption Spectrophotometry**

The determination of elements by atomic absorption spectrophotometry (AAS) involves valence electron transitions yielding radiation with wavelengths in the ultraviolet-visible region of the spectrum. In order to have atomic absorption,

it is necessary to produce free ground-state atoms of the element of interest. Spectral interferences are expected to be absent. However, the presence of species which alter the concentration of the ground-state metal atoms of the analyte in the flame will give rise to differences in the atomic absorption signal. These changes in the absorption are generally termed chemical interferences. They occur when the analyte is contained in a chemical compound that is not broken down by the flame or furnace. This results in a lower concentration of 'free' analyte atoms than would occur in the absence of the interference. Chemical interferences can be minimized either by using a high-temperature flame and/or through addition of a releasing agent.

In the determination of zirconium by AAS, a few studies in the literature have shown the development of using a high-temperature (nitrous oxide-acetylene) flame to overcome or depress chemical interference effects on zirconium absorbance. Bond (1970) investigated the addition of some electrolytes to improve the sensitivity of zirconium absorbance. Problem are caused by a number of phenomena. Many elements, such as Zr, Ti, Nd & U that have been determined by flame atomic absorption, form refractory compounds (stable oxide) which are difficult to vaporize or dissociate even in the high temperature nitrous oxideacetylene flame (2955 °C). It is difficult to generate free atoms of these elements. Consequently low concentrations of Zr ion in the vapour phase appear, and cause erroneous results (analytical results significantly lower than actual values). In addition to the formation of stable oxides in the flame, stable carbides can form in certain circumstances and cause relatively low sensitivity in the AA signal. Generally, high sensitivity is required in the case of determination of zirconium with

AAS. This may be improved by paying attention to some important experimental factors. These include obtaining a linear calibration curve and as much freedom from interferences as possible. Special care must be taken with operating parameters such as fuel-to-oxidant ratio, observation height, aspiration rate and acetylene purity.

In the present work atomic absorption measurements were carried out with a GBC 902 Double Beam atomic absorption spectrophotometer. The standard nebulizer and spray chamber system was employed, along with the grooved head burner for supporting the nitrous oxide-acetylene flame. The hollow-cathode lamp was supplied by Fisher Scientific Co. Gas flow rates were adjusted for maximum absorption signal for zirconium. Height of the flame was assessed relative to the point where the burner head started. Normally, a fairly fuel-rich flame was used, the interconal zone (red cone)being about 10-15 mm high. The experimental parameters for zirconium determination are summarized in Table 4.1.

Wavelength (nm)	360.10
Lamp Current (mA)	0.2
Slit Width (nm)	18
Burner Head	N₂O
Flame	N <sub>2</sub> O-C <sub>2</sub> H <sub>2</sub>
Sensitivity ( µg/ml)	9

 Table 4.1 Operating parameters for Zr analysis by AAS.

The reagents used for AA analysis were supplied by Aldrich Chemical Company. These consisted of two zirconium AA standard solutions containing

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1010  $\mu$ g/ml of Zr in 5 wt.% HCl, or 1030  $\mu$ g/ml of Zr in 2 % HF, ammonium fluoride, (97% NH<sub>4</sub>F, ACS reagent) and hydrofluoric acid (48% HF, ACS reagent).

Since it is difficult to generate free atoms of zirconium in the direct determination by AAS even in high temperature  $N_2O-C_2H_2$  flame, and AA sensitivity is relatively low, an electrolyte (ammonium fluoride) is added to the samples. Enhancement effects from both the ammonium and fluoride ions improve the sensitivity of zirconium determination by AA (Amos and Willis, 1966; Bond and O'Donnell, 1968; Sastri et al, 1968; Sastri et al, 1968; Bond, 1970). An addition of 0.1 M ammonium fluoride to the zirconium solution showed a significant sensitivity improvement as compared to other zirconium solutions with different species of electrolytes (sodium fluoride or ammonium chloride) or a zirconium solution with no electrolyte addition (Figure 4.1, Bond (1970)). Bond further showed that the optimum concentration of ammonium fluoride added in this process is 0.1 M (Figure 4.2), at least when the solution contains 0.01 M Zr. Though this modification shows an improvement in absorbance, the percentage of measurement error is still high (approximately 5-10%). In the present work, AAS was extensively studied. Although 0.1 M ammonium fluoride addition improved absorbance, sensitivity was still too low for satisfactory determinations. Therefore, it was necessary to search for another reliable analytical method.

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Figure 4.1 Influence of various species on absorbance of zirconium (After Bond A. M., 1970).



Figure 4.2 Absorbance of zirconium as a function of concentration of added species [Zr] = 0.01 M (After Bond A. M., 1970).

**4.3.2 Determination of Zirconium by Complexometric Reaction (Direct and Indirect** titration)

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Titrimetric procedures are available for zirconium. These are considered to be both rapid and precise, and will yield satisfactorily exact results in the presence of various cationic and anionic species. In general, titrimetric methods can be classified in several broad groups according to the type of reaction involved (e.g. neutralization, precipitation, oxidation or reduction and complexometric) (Mukherji, 1970). Complexometric titrations are the most suitable type for zirconium.

Direct titration methods for the determination of zirconium were first attempted following the introduction of EDTA as a titrant. Difficulties attributed to hydrolysis and polymerization arose when direct titration was attempted. It became evident that direct titration does not offer a sharp end point, thus accuracy is poor. In addition, results were always lower than theoretical to an extent which depended particularly on the zirconium concentration, temperature and pH.

Several paper (Fritz (1954), Fritz & Johnson (1955), Sato (1970), Sato & Watanabe (1970) and Sella & Bauer (1986)) have confirmed and supported these conclusions. Many investigators showed that problems with Zr-EDTA titrations are directly attributed to the formation of polynuclear zirconium species (polymerization), and depolymerization is an essential pre-requisite to direct titration. Polymerization in zirconium solutions is a well known effect (Nabivanets, 1961a; Kolikov, 1961; Zaitsev & Bochkarev, 1962; Kuznetsov & Fang., 1962; Babko & Gridchina, 1962; Solovkin & Tsvetkova, 1962 and Ahrland, 1963)), and

always results from hydrolysis of zirconium ions in aqueous solution. This has been discussed above in section 2.3

A major result of significant polymerization is that the mole ratio between the polymeric species and EDTA will be different from the assumed 1:1 stoichiometry. As a result of this phenomenon, the error from change of stoichiometry will be directly proportional to the total concentration of polymeric zirconium species present in the aqueous zirconium solution. Zirconium polymerization, and depolymerization by boiling and ageing in various concentrations of nitric, hydrochloric and sulphuric acid have been summarized in studies by Sinha and Das Gupta, 1967. It can be concluded that ease of depolymerization depends on the nature of the acid, its strength, and the time of boiling. Extent of depolymerization increases with increase in acid strength and time of boiling. Although hydrochloric and sulphuric acids were found to be unsuitable media for depolymerization by ageing alone, complete depolymerization could be achieved by ageing for nitric acid solutions of zirconium.

Due to the restrictions described above, direct titration is particularly unsuitable for the determination of zirconium. Indirect titration by back-titration with a known volume of excess standard EDTA solution is the preferred method. For all back-titration procedures, it is important that depolymerization be carried out first by hot digestion with acid solution. Here, the acidity should be adjusted, particularly for zirconium concentrations higher than 0.01 M, before addition of EDTA, to prevent polymerization and the possibility of precipitation. Subsequently, the pH should be maintained at a value between 1.6-2 for titration of excess EDTA.

Zirconium (IV) has been determined by a back-titration method involving EDTA with xylenol orange as indicator (Sato and Watanabe, 1970). The sample solution, with an excess of EDTA, was boiled for about 10-15 min, cooled, adjusted to pH 1.6-2 with amrnonia solution or hydrochloric acid and then backtitrated with bismuth nitrate solution. This indirect titration procedure has been found particularly suitable for the determination of zirconium in hydrochloric acid solution, and is used in routine laboratory studies.

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In the present work, titrations were performed using a 50 ml buret which could be read easily to within 0.05 ml. Magnetic stirring was employed. An Accumet pH Meter 910 (Fisher Scientific Co.) equipped with standard glass and calomel electrodes was used for all pH measurements. The procedure used is as follows. Take a 10 ml aliguot of the sample solution containing zirconium 13-36 mg Zr and adjust the volume to about 20 ml. Add about 3 ml of 0.0499 M EDTA (the exact amount of EDTA addition is known, and is in excess of that required to complex zirconium in the aqueous feeds and hence in the raffinates). Boil the solution for about 5-10 min after the EDTA has been added, then cool and adjust the pH in the range 1.6-2, with ammonia solution or hydrochloric acid. The excess EDTA is then titrated with bismuth nitrate solution using xylenol orange as indicator. For the present study, back-titration with EDTA is considered more suitable than AAS. Some experiments with the latter showed that it was not possible to determine zirconium reliably in macro amount ( 6 g/l) with an error of less than 10%. Also sensitivity was poor, even with electrolyte (NH<sub>4</sub>F) addition to enhance the absorption signal. Some advantages of the back-titration method adopted are as follow:

1. This technique is rapid, simple and operates at room temperature.

2. Zirconium and bismuth form stronger complexes with EDTA than most other metal ions, thereby promoting selectivity. Moderate amounts of titanium and iron can be tolerated, these being commonly found in zircon leach solutions.

3. An important advantage is that zirconium can be determined in the presence of most anions such as phosphate, sulphate, thiocyanate and small amounts of fluoride.

4. It gives good sensitivity and high precision.

5. It is very easy to control.

#### 4.3.3 The Role of EDTA and Xylenol Orange

Ethylenediaminetetraacetic acid (EDTA) is by far the most widely used reagent in analytical chemistry because strong 1:1 complexes are formed with most metal ions in the periodic table by direct titration or through an indirect titration. EDTA is a hexaprotic system;  $H_eY^{2+}$ . Its acid-base properties are summarized by the following pK<sub>e</sub> values:



Here, the first four pK values apply to carboxyl protons, while the last two are for the ammonium protons.

The common neutral acid is tetraprotic:  $H_4Y$ , and its'disodium salt  $Na_2H_2Y.2H_2O$ , is widely used in analytical chemistry (Harris, 1987). The formation constant,  $K_t$ , of a metal-EDTA complex is the equilibrium constant for the reaction:

$$K_{f} = \frac{[MY^{n-4}]}{[M^{n+1}][Y^{4-1}]}$$

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Table 4.2 shows the formation constants for most EDTA complexes with metal ions. The values are relatively large for highly charged metal ions. Thus, the equilibrium constant of Zr-EDTA complex is larger giving a more stable complex than that of for example, Bi-EDTA. In the back-titration procedure for zirconium determination, it is necessary that the metal ion  $(Bi^{3+})$  used in the back-titration of excess EDTA should not displace the analyte metal ion  $(Zr^{4+})$  from its EDTA complex. This method provides a strategy for the selective complex formation of one metal ion  $(Zr^{4+})$  first, in the presence of another ion  $(Bi^{3+})$ .
lon	Log K,	lon	Log K,	lon	Log K,
Li+	2.79	Mn <sup>3+</sup>	25.3 (25°C)	Ce <sup>3+</sup>	15.98
Na <sup>+</sup>	1.66	Fe <sup>3+</sup>	25.1	Pr <sup>3+</sup>	16.40
K+	0.8	Co <sup>3+</sup>	41.4 (25°C)	Nd <sup>3+</sup>	16.61
Be <sup>2+</sup>	9.2	Zr <sup>4+</sup>	29.5	Pm <sup>3+</sup>	17.0
Mg <sup>2+</sup>	8.79	Hf <sup>4+</sup>	$29.5 (\mu = 0.2)$	Sm <sup>3+</sup>	17.14
Ca <sup>2+</sup>	10.69	VO <sup>2+</sup>	18.8	Eu <sup>3+</sup>	17.35
Sr <sup>2+</sup>	8.73	vo,+	15.55	Gd <sup>3+</sup>	17.37
Ba <sup>2+</sup>	7.86	Ag <sup>+</sup>	7.32	Tb <sup>3+</sup>	17.93
Ra <sup>2+</sup>	7.1	TI+	6.54	Dy <sup>3+</sup>	18.3
Sc <sup>3+</sup>	23.1	Pd <sup>2+</sup>	18.5 (25°C, $\mu = 0.2$ )	Ho <sup>3+</sup>	18.62
Y <sup>3+</sup>	18.09	Zn <sup>2+</sup>	16.5	Er <sup>3+</sup>	18.85
La <sup>3+</sup>	15.50	Cd <sup>2+</sup>	16.46	Tm <sup>3+</sup>	19.32
V <sup>2+</sup>	12.7	Hg <sup>2+</sup>	21.7	Yb3+	19.51
Cr <sup>2+</sup>	13.6	Sn²+	18.3 ( <i>u</i> = 0)	Lu <sup>3+</sup>	19.83
Mn²+	13.87	Pb <sup>2+</sup>	18.04	Am <sup>3+</sup>	17.8 (25°C)
Fe <sup>2+</sup>	14.32	Al <sup>3+</sup>	16.3	Cm <sup>3+</sup>	18.1 (25°C)
Co <sup>2+</sup>	16.31	Ga <sup>3+</sup>	20.3	Bk <sup>3+</sup>	18.5 (25°C)
Ni <sup>2+</sup>	18.62	In <sup>3+</sup>	25.0	Cf <sup>3+</sup>	18.7 (25°C)
Cu <sup>2+</sup>	18.80	Tl3+	$37.8 (\mu = 1)$	Th <sup>4+</sup>	23.2
Ti <sup>3+</sup>	21.3 (25°C)	Bi <sup>3+</sup>	27.8	U <sup>4+</sup>	25.8
V <sup>3+</sup>	26.0			Np <sup>4+</sup>	24.6 (25°C, $\mu = 1$ )
Cr <sup>3+</sup>	23.4				

Table 4.2 Formation constants for metal-EDTA complexes

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Note: The stability constant is the equilibrium constant for the reaction M<sup>\*\*</sup> + Y<sup>\*</sup> = MY<sup>\*\*</sup> . Values in table apply at 20 °C, and ionic strength 0.1 M, unless otherwise noted. Source: Data from A.E. Martall and R.M. Smith, *Critical Stability Constants*, Vol.1 (New York: Plenum Press, 1974), pp. 204-211. Several methods can be used to detect end-points in EDTA titrations. Since the discovery of suitable indicators for direct titrations, the most common metal ion indicator now used is probably Xylenol Orange. Since the colour of free indicator is pH dependent, most indicators can be used only in a certain pH range. For example, xylenol orange changes from yellow to red when it binds to a metal ion at pH 1.6 to 2. This is an easy colour change to observe. In the present case, bismuth (as nitrate) is added to complex excess EDTA. At the end point, further addition causes the yellow to red transition associated with the bismuth/indicator complex. This is weaker than the bismuth/EDTA complex formed initially.

#### 4.4 Chloride Determination

Direct titration of chloride with  $AgNO_3$  was the procedure chosen for the determination of CI:Zr ratio in strip solutions. Thus an indication of the zirconium chloride complex extracted into the organic phase could be obtained. The argentometric method is suitable for use in relatively clear solutions when 0.15 to 10 mg Cl are present in the portion titrated. Potassium chromate can indicate the end-point of the silver nitrate titration of chloride in neutral or slightly alkaline solution. Silver chloride is precipitated quantitatively as white crystals before red silver chromate is formed. Thus the end point is marked by a distinctive yellow to pinkish-red transition. In the present work, the following procedure was adopted. Directly titrate samples in the pH range 7 to 10. Adjust sample pH to 7 to 10 with  $H_2SO_4$  or NaOH if pH is not in this range. Add 1.0 ml K<sub>2</sub>CrO<sub>4</sub> indicator solution. Titrate with standard AgNO<sub>3</sub> titrant to a pinkish red end point. It is necessary to establish a 'blank value' for this titration method. A blank of 0.2 to 0.3 ml is usual

(from Standard Methods for the Examination of Water and Waste Water, 1981). The relevant calculation is given as follows:

where:

A = ml titration for sample

B = ml titration for blank, and

 $N = normality of AgNO_3$ 

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# **CHAPTER 5**

## **RESULTS AND DISCUSSION**

## 5.1 Introduction

The increasing use of organophosphorus compounds, such as TOPO, trioctyl-phosphine oxide, in solvent extraction is due to their selectivity and efficiency in removing metal ions from aqueous solutions. Generally, TOPO dissolved in an inert hydrocarbon solvent is outstanding amongst the newer reagents. The present work compares quantitatively the extraction of zirconium by two commercial extractants which have TOPO as a major chemical component. The results have allowed the extraction mechanism to be deduced. Evidence from several papers has shown that TOPO can extract at least twenty-three different metal ions (Martin et al., 1960) with the conditions for extraction varying considerably. In general, most recovery is performed from acidic solutions, where the nature and strength of acid are critical factors in addition to the charge on the metal ion and also its complexes. Similar considerations also apply to the extraction of zirconium, which is one of the twenty-three metals extracted by Cyanex 923 and Cyanex 925.

Experiments were carried out to study the extraction of zirconium by Cyanex 923 and Cyanex 925 from acidic chloride media. Due to the difficulty in obtaining precise results by AAS when analyzing macro amounts of zirconium (6 g/l), all results presented in this chapter are based on the back-titration of excess

EDTA with bismuth nitrate, as discussed in chapter 4. The effects of important variables on zirconium extraction are presented and discussed. Parameter studied were hydrochloric acid level, chloride level, zirconium concentration and Cyanex concentration. Some stripping tests were carried out.

#### 5.2 Establishment of Equilibrium

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The present work is a study of reaction equilibrium rather than kinetics. In order to make valid interpretations of the effects of experimental parameters, and valid comparisons of the two reagents studied, it must be ensured that equilibrium is reached in all experiments. Thus it is necessary to determine the minimum time required to establish equilibrium using the experimental procedure adopted.

Zirconium extraction was investigated by shaking 20 ml of organic solvent (Cyanex 923 & 925 in kerosene) vigorously with 20 ml aqueous phase for various times. The period of equilibration was varied from 5 min to 120 min. Figures 5.1 & 5.2 compare zirconium extraction kinetics for two different sets of conditions. It should be emphasized at this point that in these initial tests, important parameters such as hydrochloric acid concentration had not been optimized, so that 'final' extractions were at lower levels than obtained subsequently. The minimum shaking time that was necessary to achieve apparent equilibrium was around 5-10 min for both extractants, and it was found that more prolonged shaking time had no effect on the extraction of the zirconium species.

In these preliminary tests, it was noted that there were no phase separation problems that would have required investigation of modifier addition. Phase

separation was rapid, and the separated phases were clear without the presence of a modifier.

Table 5.1 summarizes some information on shaking time, when given, for zirconium extraction into chloride, sulphate and nitrate media using various extractant systems. It can be seen that, for 'shake-out' tests, a contact time of 10 minutes is typically required for extraction from chloride media.



Figure 5.1 Kinetics of zirconium extraction from 0.05 M Zr / 2 M HCl into 5 % (v/v) Cyanex 923 and 925 in kerosene.



Figure 5.2 Kinetics of zirconium extraction from 0.02 M Zr / 2 M HCl into 1 % (v/v) Cyanex 923 and 925 in kerosene.

Aqueous medium	Extractant	Special features	References
Chloride and thiocyanate	Aliquat 336	-	Sato et al. 1976
Chloride	Aliquat 336	Shaking period, 10 min at 20 °C	Sato & Watanabe, 1970
	Methyldioctyl- amine	Shaking period, 5 min	Moore, 1957
	ΤΟΑ	Contact time, 10 min; strict temperature control (18 °C)	Cerrai & Testa, 1959
	ΤΟΑ	•	Floh et al., 1978
	Hxwg-chain amines	-	Sato & Watanabe, 1971
	Aliquat 336 TOA	Separation Of niobium, zirconium or tantalum achieved	Bagreev et al., 1975
	ΤΟΑ	Shaking period, 10 min. Many ions tolerated	Cerrai & Testa, 1962a
	Hyamine 1622	Shaking period, 10 min at 20 °C	El-Yamani et al., 1978
	Primary, secondary and tertiary amines	Shaking period, 10 min. Effect of temperature studied	Cerrai & Testa, 1959b
Sulphate	Alamine 336	Emulsification problem; 10 min extraction	El-Yamani, 1978
	Adogen 364	Modifier used to avoid emulsion; shaking period, 20 min	El-Yamani et al., 1978, 1985

Table 5.1 Summary of methods for the extraction of Zr(IV) in  $CI^{\circ}$ ,  $SO_x^{2^{\circ}}$ ,  $NO_3^{\circ}$ media.

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	Aliquat 336	Strict temperature control and 10- min shaking required for extraction	El-Yamani et al., 1978 and Sato & Watanabe, 1982
	Primene JMT	At 22 °C, 1-h contact required	El-Yamani et al., 1978
	TOA	-	Yagodin & Chakmarev, 1962, 1964 Yagadin et al., 1969
Nitrate	TOA	•	Roy, 1964
	ΤΙΟΑ	Partition coefficient is appreciable only at higher nitrate activities	Knoch, 1961
	Trilaurylamine	•	Souka & Alien, 1966

( data summarized from Sundaramurthi & Shinde, 1989)

## 5.3 Effect of Hydrochloric Acid Concentration

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The effect of hydrochloric acid level on zirconium extraction has been studied for various initial zirconium contents of the aqueous phase and several Cyanex concentrations. The extraction of zirconium was carried out at initial concentrations of 0.002 M, 0.02 M &  $0.0^{-5}$  and acidities in the range 1-6 M HCI. Concentrations of Cyanex were 1%, 2.3% & 5% (v/v) in kerosene (as diluent), which correspond to about 0.022 M, 0.055 M and 0.12 M respectively. All tests were carried out at a phase ratio of 1 and a contact time of 30 minutes. The results are shown in Figures 5.3 to 5.8. In all cases, the general trend is an increase in zirconium extraction with increasing hydrochloric acid level. This shows that zirconium is not loaded through a cation exchange reaction, since extraction would decrease as acidity increases. The results are consistent with the

expectation that zirconium is extracted as a chloride complex through a solvation reaction. The optimum hydrochloric acid concentration cannot readily be deduced from the results using 0.05 M zirconium aqueous feed (Figures 5.3, 5.4), since the loading capacity is reached in each case. At this point, it should be noted that data for extraction from 0.05 M zirconium into 1% Cyanex 925 are not available (Figure 5.4). This is because large amounts of zirconium remained in the raffinate, a condition that led to precipitation during the analytical procedure, which required ammonium hydroxide addition for pH control.



Figure 5.3 Effect of [HCI] on zirconium extraction from 0.05 M Zr solutions into 1%, 2.5%, 5% (v/v) Cyanex 923 in kerosene.



Figure 5.4 Effect of [HCI] on zirconium extraction from 0.05 M Zr solutions into 2.5%, 5% (v/v) Cyanex 925 in kerosene.



Figure 5.5 Effect of [HCI] on zirconium extraction from 0.02 M Zr solutions into 1%, 2.5%, 5% (v/v) Cyanex 923 in kerosene.



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Figure 5.6 Effect of [HCI] on zirconium extraction from 0.02 M Zr solutions into 1%, 2.5%, 5% (v/v) Cyanex 925 in kerosene.



Figure 5.7 Effect of [HCI] on zirconium extraction from 0.002 M Zr solutions into 1%, 2.5%, 5% (v/v) Cyanex 923 in kerosene.

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Figure 5.8 Effect of [HCI] on zirconium extraction from 0.002 M Zr solutions into 1%, 2.5%, 5% (v/v) Cyanex 925 in kerosene.

In contrast, when extracting from 0.002 M zirconium (Figure 5.7, 5.8), a large excess of reagent was always present. These latter results suggest that about 6 M hydrochloric acid is the optimum level for zirconium extraction in the 1% - 5% Cyanex range. At 5% Cyanex concentration, quantitative recovery was approached at 6 M hydrochloric acid. However with only 1% Cyanex, extractions approach a maximum of 80% - 85% at 6 M hydrochloric acid, consuming only about 15% of the loading capacity. It should also be noted that, for comparable conditions, Cyanex 923 is a better extractant than Cyanex 925.

In this system, the acid is performing a dual role. A high chloride ion content is necessary to promote formation of an extractable zirconium complex. Also, a high hydrogen ion concentration is required to suppress hydrolysis and polymerization, which would cause unextractable species to form.

### 5.4 Zirconium Extraction Isotherm and McCabe-Thiele Diagram

While single stage batch 'shake-out' tests, such as those represented by the data of Figures 5.3 to 5.8, yield distribution coefficients at equilibrium, fullscale commercial solvent extraction usually operates as a continuous countercurrent multistage process. The McCabe-Thiele diagram is the link between data from single stage extraction tests and the expected performance characteristics when the solvent extraction process is run in countercurrent multistage mode. This diagram is a plot of g/l metal in the organic phase vs g/l metal in the aqueous phase, and contains 2 sets of information.

Firstly, the distribution (extraction) isotherm must be established, this being a series of distribution coefficients determined from batch contacts. Secondly, the 'operating line' for the actual process must be defined. The position of this line is fixed by specifying operating parameters such as metal concentrations in the incoming leach solution, outgoing raffinate and incoming stripped organic, as well as the aqueous/organic flow rate ratio. The most important information obtained from this diagram is an estimate of the number of stages required to achieve the desired results. Also, the effect on the staging requirements of changing operating conditions can readily be determined.

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An example of a McCabe-Thiele diagram based on present laboratory-scale shake-out tests and a hypothetical operating line is shown in Figure 5.9. Here, the distribution isotherm is constructed from batch 'shake-out' tests carried out at various phase ratios using 0.02 M zirconium in 2 M hydrochloric acid as aqueous feed and 10% Cyanex 923 in kerosene as the organic phase. Although about 6 M hydrochloric acid is required for high extraction into 5% Cyanex 923 (Figure 5.5), similar results are obtained with a combination of 10% Cyanex 923 and 2 M hydrochloric acid.



Figure 5.9 McCabe-Thiele diagram for Zr extraction (0.02 M / 2 M HCI) into 10% (v/v) Cyanex 923 in kerosene.

For the operating line, it is assumed that the leach solution contains 1.3 g/l Zr and the final loaded organic will contained 4.50 g/l Zr (coordinates of point A). The coordinates of point B represent zirconium concentrations in the final raffinate and the incoming stripped organic (0.10 g/l and 0.90 g/l respectively). These results would be obtained at an aqueous/organic flow ratio (phase ratio) of 3, as given by the slope of the line AB. Starting at point A, the dashed lines show the graphical construction required for calculation of the number of stages needed, which in this case amounts to 5. Since it is assumed that equilibrium is reached in every stage, it is necessary to continue the construction such that the last vertical dashed line falls to the left of point B.

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Figure 5.10 shows the distribution isotherm for Cyanex 925 determined for the same conditions as for Cyanex 923 (Figure 5.9). Distribution coefficients in Figure 5.10 are significantly less than in Figure 5.9 so confirming that Cyanex 925 is a poorer extractant than Cyanex 923 in the present application.



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Figure 5.10 Distribution isotherm for Zr extraction from 0.02 M /2 M HCl into 10% (v/v) Cyanex 925 in kerosene.

### 5.5 Zirconium Stripping

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Stripping is the reverse of extraction in that metal is returned to an aqueous phase. With solvating systems where high acid concentrations are required, as for zirconium extraction, stripping agents such as water or an alkaline reagent are suitable for decomposing the loaded chloride complex and driving zirconium into the aqueous phase. The stability of the extracted species will govern the type and concentration of stripping solution required. In the present research, a cloudy third phase appeared between the clear aqueous and organic phases when using water as strip solution. It was found that third phase formation could be avoided by using a weak ammonium carbonate strip solution to shift the pH from 7 at which emulsion and phase separation problems are commonly encountered. This latter approach has been used successfully for Cyanex 272 (Witte & Frey, 1985). Zirconium can then be precipitated from the strip solution through ammonium hydroxide addition.

A few ammonium carbonate stripping tests were performed using loaded Cyanex 923 (Figure 5.11). Cyanex 923 was chosen over Cyanex 925 because of the superior extraction performance. Zirconium was first loaded from a 0.02 M solution into 5% Cyanex 923 at acidities that gave > 95% extraction. Subsequent stripping with 0.005 M ammonium carbonate recovered about 75% of the original 0.02 M zirconium feed. This yield was not increased by increasing the stripping time of 1 hour. The data of Figure 5.3 to 5.8 indicate that weak acid at about pH 3, might be a satisfactory stripping agent, provided that precipitation effects are not encountered. The search for improved stripping conditions or

alternative stripping agents was not pursued further, since the main focus of this work was on zirconium loading.

It should be noted that, in addition to the inferior extraction performance of Cyanex 925, phase separation problems were more severe than with Cyanex 923 when either water or 0.005 M ammonium carbonate solution was used as stripping agent.

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Figure 5.11 Stripping of zirconium-loaded 5% Cyanex 923 in kerosene using  $0.005 \text{ M} (\text{NH}_4)_2 \text{ CO}_3$ . Zirconium initially loaded from 0.02 M.

## 5.6 Hydrochloric Acid Extraction during Zirconium Loading

It is frequently observed that inorganic acids are coextracted with metal ions during solvent extraction. In particular, neutral organophosphorus compounds may extract acids as shown, for example, by the extraction of hydrochloric acid by TBP (Peppard, et al., 1956 & Baldwin, et al., 1959). Since the present system involves zirconium extraction from 'high' hydrochloric acid solutions, it is necessary to determine how much of the loading capacity is taken up by acid extraction.

Four series of tests were carried out in which zirconium was loaded from 0.05 M solutions, containing 1 M to 6 M hydrochloric acid, into either 2.5% Cyanex 923 or Cyanex 925 or 5% of these extractants. In each case, the contact time was 30 minutes at an A/O of 1. The acid contents of the feeds and corresponding raffinates were measured by titration with 1 M NaOH using methyl orange as indicator. The results, given in Figures 5.12 and 5.13, show that the acid content of each raffinate is essentially the same as that of the matching feed, indicating that only zirconium chloride complexes are extracted with insignificant acid coextraction. Thus, although Hcl is not significantly extracted, it is not possible to assume zero Hcl extraction, since this conclusion would rely on detecting small differences in large numbers obtained from the titrations.



Figure 5.12 HCl extraction from 1 M - 6 M HCl containing 0.05 M Zr into 2.5% (v/v) Cyanex 923 or 925 in kerosene.



Figure 5.13 HCl extraction from 1 M - 6 M HCl containing 0.05 M Zr into 5% (v/v) Cyanex 923 or 925 in kerosene.

## 5.7 Chloride Extraction during Zirconium Loading

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While section 5.6 has shown that there can only be minor HCI extraction at levels required for zirconium loading, some coextraction of chloride ion would be expected during zirconium extraction itself since zirconium is expected to be loaded as a chloride complex. Thus, using the silver nitrate titration procedure described in chapter 4, chloride ion levels in the feed and raffinate were compared when zirconium was loaded from 0.02 M solutions in nominally 4 M or 5 M Hcl into 5 vol% Cyanex 923. The chloride contents of the strip solutions ( $0.005 M (NH_4)_2CO_3$ ) were also determined, as shown in Table 5.7.1.

It is difficult to obtain meaningful conclusions from a comparison of chloride contents of feed and raffinate, since not only are small differences in large titration volumes being sought (as for the acid / base titration of the preceding section), but also chloride from HCI greatly exceeds that from the zirconium present. Indeed, for both loading tests, chloride concentrations in the feed and raffinate are essentially the same. Thus it was not possible, through this comparison, to find the relatively small amount of chloride ion that would be expected to accompany zirconium extraction.

Sample	Cl <sup>-</sup> (g/l.)	CI <sup>-</sup> (mole/l.)
Feed	138.6	3.91
Raffinate	138.9	3.92
Strip	4.99	0.141
Blank	0.356	0.010

 Table 5.7.1 Chloride extraction during zirconium loading.

a) 4 M HCI feed

b) 5 M HCI feed

Sample	Cl' (g/l.)	Cl <sup>-</sup> (mole/l.)
Feed	174.9	4.94
Raffinate	176.0	4.97
Strip	6.59	0.186
Blank	0.356	0.010

Loading: 0.02M Zr into 5 vol% Cyanex 923 with 30 minutes contact at A/O = 1 Stripping: 0.005M (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> with 60 minutes contact at A/O = 1

An alternative method is to measure the chloride content of the strip solution. The blank values shown in Table 5.7.1 refer to titration of the strip solution before contact with loaded organic. After allowing for these blank values, the Cl/Zr ratios in the strip solution were 8.73 and 10.5 for the 4M and 5M HCl feed solutions respectively. It is possible that zirconium is extracted as a ZrCl<sub>4</sub> complex through a solvation reaction similar to that reported for TBP (Sato, 1970 & Levitt and Freund, 1956). Thus the chloride in excess of that required for a CI/Zr ratio of 4 is probably due to minor HCl transfer that was too small, relative to 4M-5M HCl feed solutions, to be found when comparing either the acidities of feed and raffinate, or their chloride contents.

A further attempt to determine the CI/Zr ratio in the organic extract was made using organic phase pre-equilibrated with 2 4M HCl solution in the absence of zirconium. The results are shown in Table 5.7.2. Here, the chloride and zirconium contents of the organic phase, calculated as differences in feed and raffinate values, are equivalent to a CI/Zr ratio of 4.11. Although this value is close to the expected ratio of 4, the validity of the measured ratio is again dependent on precise determination of a small difference between large chloride levels in feed and raffinate. Values for zirconium and chloride in the strip solution were not used in inferring CI/Zr ratio in loaded organic since the small amount of HCl loaded during pre-equilibration may also be stripped.

Sample	Zr (g/l)	Zr (mole/l)	Distribution (%)	<b>Ci</b> (g/l)	CI (mole/l)
Feed	1.80	0.0197	100	140.0	3.944
Raffinate	0.042	0.0005	2.42	137.2	3.865
Organic	1.76	0.0192	97.6	2.80	0.079

Table 5.7.2Coextraction of zirconium and chloride into pre-equilibrated<br/>Cyanex 923.

CI/Zr in organic = 4.11

0.02 M Zr / 4M HCl contacted with 5 vol% Cyanex 923 pre-equilibrated with 4 M HCl, 30 minutes loading time at A/O = 1

## 5.8 Effect of Chloride Source on Zirconium Extraction

If zirconium is extracted as a chloride complex, the controlling factor should be chloride level rather than acidity, provided sufficient acid is present to prevent hydrolysis and polymerization reactions. To examine this hypothesis, tests were carried out in which zirconium was loaded into 5 vol% Cyanex 923 or 925 from 0.02 M solutions containing 2 M total chloride at various LiCl/HCI ratios. The results, given in Figure 5.14, show that zirconium extraction is constant at LiCl/HCI ratios between 0 and 1.

Since there must be a minimum acidity below which either unextractable zirconium species or zirconium-containing precipitates will form, further experiments were conducted where the LiCI/HCI ratio was extended beyond the maximum of 1.0 applicable to Figure 5.14. This was done for total chloride concentrations of 1.5 M, 2.0 M and 3.0 M, and the results are shown in Figure 5.15. It can be seen that zirconium extraction decreases if the HCI level drops below a value characteristic of the total chloride concentration. The higher the total chloride level, the lower may the minimum HCI concentration be before zirconium extraction decreases.





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It is well established that several effects take place at low acid or chloride level, and these would be expected to be detrimental to zirconium solvent extraction in the present system. Firstly, the proportion of unextractable cationic species increases with decreasing acid concentration. Secondly, hydrolysis is promoted at low acidity, while at low chloride levels, polymerization is encouraged through breakage of Zr-Cl bonds and displacement of chloride ions by hydroxyl ions. Reactions such as the following have been proposed to represent hydrolytic polymerization at low acid and chloride concentrations.

$$[Zr(OH)_{2}.4 H_{2}O]_{4}^{B+} = [Zr(OH)_{2+x}.(4-x) H_{2}O]^{(\mathcal{E}-4x)+} + 4 xH^{+}$$
(5.1)

## 5.9 Mechanism of Zirconium Extraction

#### 5.9.1 Effect of Cyanex Concentration

From the effects of chloride ion and acid levels on zirconium extraction, as discussed previously, it is probable that zirconium is extracted as a neutral chloride complex through a solvation reaction. The overall process may be represented as neutral complex formation in the aqueous phase, followed by extraction:

$$Zr^{4+} + 4 Cl^{-} \longrightarrow ZrCl_4$$
 (5.2)

$$ZrCl_4 + n.R_3(P=0) \longrightarrow ZrCl_4 [R_3(P=0)]_n$$
 (5.3)

The 'slope analysis' method is widely used in studies of the stoichiometry of reactions such as 5.3, where n is the unknown quantity. From equation 5.3 :

$$K_{1} = \frac{[ZrCl_{4}[R_{3}(P-O)]_{R}]}{[ZrCl_{4}].[R_{3}(P-O)]^{n}}$$
(5.4)

where equilibrium constant  $K_1$  is expressed as final concentrations.

Thus	log K <sub>1</sub>	=	$\log D - n \log [R_3 (P=0)]$	(5.5)
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so that  $\log D = n \log [R_3(P=0) + \log K_1]$  (5.6)

A plot of log D vs log  $[R_3(P=O)]$  would therefore give a straight line of slope n if the following important conditions are met:

- 1) Equilibrium is reached.
- 2) Activity coefficients remain constant.
- 3) Only one zirconium species is extracted, with no polymeric species formed in either phase.
- 4) Formation of intermediate non-extractable complexes is negligible.
- 5) Hydrolysis reactions are insignificant.

Figures 5.16 and 5.17 are plots of log D vs log  $[R_3(P=O)]$  for Cyanex 923 and 925 respectively, two initial zirconium concentrations (0.002 M and 0.004 M) being shown in each case. A large molar excess of Cyanex over zirconium was present in each case, so that the free Cyanex concentration remains essentially constant during extraction. It is evident that approximate straight lines of slope 1.5 to 1.7, are followed up to about 2.5 vol% Cyanex, above which increasing slopes are observed. In general, these steepening slopes can be explained by an increase in solvation number, n, with increasing amounts of excess extractant present.






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With the tendency for polymerization and hydrolysis in this system, it would be surprising if Figures 5.16 and 5.17 had yielded straight lines except within a narrow range of conditions. Indeed, the decrease in D with increasing initial zirconium concentration at constant HCI and Cyanex concentrations (Figures 5.16 and 5.17) suggests some polymerization occurs in the aqueous phase, and to a greater extent than in the organic phase. However, straight lines were apparently obtained in equivalent plots described in earlier work with TBP (Levitt and Freund 1956, and Sato 1970). Given the assumptions made, it can reasonably be concluded that, under the conditions of Figures 5.16 and 5.17, zirconium is extracted as the disolvate, except at large excess extractant concentrations.

## 5.9.2 Effect of HCI Concentration

Levitt and Freund (1956), working on the extraction of zirconium from HCI solutions into TBP, expressed the complexation of zirconium with chloride ion in the aqueous phase, and subsequent zirconium extraction as analogous to:

$$ZrCl_n^m + x Cl^m = ZrCl_{(n+x)}^{(m-x)}$$
 (5.7)

$$ZrCl_{(n+x)}^{(m-x)} + 2 [Cyanex] = ZrCl_{(n+x)}^{(m-x)} [Cyanex]_2$$
 (5.8)

where [Cyanex] is written in place of [TBP], and extraction of the disolvate is assumed. If the initial Cyanex concentration remains essentially constant, then from equation 5.8,

$$[ZrCl_{(n+x)}^{(m-x)} [Cyanex]_2] = K_2 [ZrCl_{(n+x)}^{(m-x)}]$$
(5.9)  
where K<sub>2</sub> is a constant.

Thus 
$$D = \frac{K_2 [ZrCl_{(n+x)}^{(m-x)}]}{[ZrCl_n^m]}$$
 (5.10)

and 
$$\log D = \log K_2 + \log [ZrCl_{(n+x)}^{(m-x)}]$$
 (5.11)  
[ZrCl\_m^m]

Hence,  $\log D = \log K_2 + \log K_3 + x \log [CI]$  (5.12) where  $K_3$  is the equilibrium constant for reaction 5.7.

Thus,  $\log D = A + x \log [Cl]$  (5.13) where A is a constant. A plot of log D vs log Cl should give a straight line of slope x.

In Figures 5.18 and 5.19, the slopes of log D vs log CI (taken as log HCI) have values between 1.9 and 2.5. Taking a value of 2 for x means that both m and n must also equal 2 to be consistent with extraction of the  $ZrCl_4$  neutral complex. Thus, equations 5.7 and 5.8 become:

$$ZrCl_2^{2+} + 2Cl^2 = ZrCl_4$$
 (5.14)

$$ZrCl_4 + 2 [Cyanex] = ZrCl_4.[Cyanex]_2$$
(5.15)

A value of 3 for x has been found for the equivalent system involving zirconium extraction from HCI solutions into TBP (Levitt and Freund, 1956). This difference in the value of x for the aqueous phase may be partly due to the different concentration ranges of HCI and zirconium for the two studies (6.4 M to 11.3 M HCI, 0.03 M to 0.05 M Zr for Levitt and Freund, 1.0 M to 6.3 M HCI, 0.002 M Zr for the present work). In addition, the assumptions enumerated in the previous section, 5.9.1, on the effect of Cyanex concentration also apply to the present section 5.9.2.



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Figure 5.18 Effect of HCl concentration (log D vs log [HCl]) for Zr extraction from 0.002 M / 1-6 M HCl into 1%, 2.5%, 5% (v/v) Cyanex 923 in kerosene.





## **CHAPTER 6**

## CONCLUSIONS AND RECOMMENDATIONS

With Cyanex 923 or 925 as extractant, zirconium is loaded as a chloride complex by a solvation reaction. This conclusion follows firstly from the increase in zirconium extraction with increasing hydrochloric acid concentration. Secondly, the extraction level is maintained if, at constant total chloride, hydrochloric acid is partially replaced by lithium chloride, provided sufficient acid is present to prevent zirconium hydrolysis.

Zirconium is extracted as its tetrachloride complex forming a disolvate, except at high excess extractant concentration where the solvation number increases. There is evidence of polymerization, especially in the aqueous phase, because  $D_{zr}$  decreases with increasing zirconium concentration under otherwise identical conditions. For both extractants, apparent equilibrium is reached in 5 to 10 minutes with the mechanical shaking procedure used, and there is insignificant co-extraction of hydrochloric acid. A small number of experiments has shown that an aqueous solution of ammonium carbonate may be a potential stripping agent.

Under given conditions, zirconium extracts more readily into Cyanex 923 than Cyanex 925. The major difference in structures of the two reagents is the straight chain alkyl groups of Cyanex 923 in contrast to the branched chain structure of Cyanex 925. Thus, it appears that the latter arrangement offers

'steric hindrance' to the loading of zirconium leading to lower  $D_{zr}$  values than with Cyanex 923.

For this study, zirconium was analyzed in the aqueous phase using a titrimetric technique in which EDTA in excess of that required to complex zirconium was titrated against bismuth nitrate. This method was found to be faster, simpler and more dependable than atomic absorption spectrophotometry.

Further work should be directed towards studying hafnium extraction from chloride solution in to Cyanex 923 or Cyanex 925 to determine if conditions exist for potential separation of these metals. In addition, more data are needed for the ammonium carbonate stripping system briefly investigated in the present study. It may also be necessary to investigate alternative stripping agents, especially if 1 hour is required to reach equilibrium using ammonium carbonate solutions.

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