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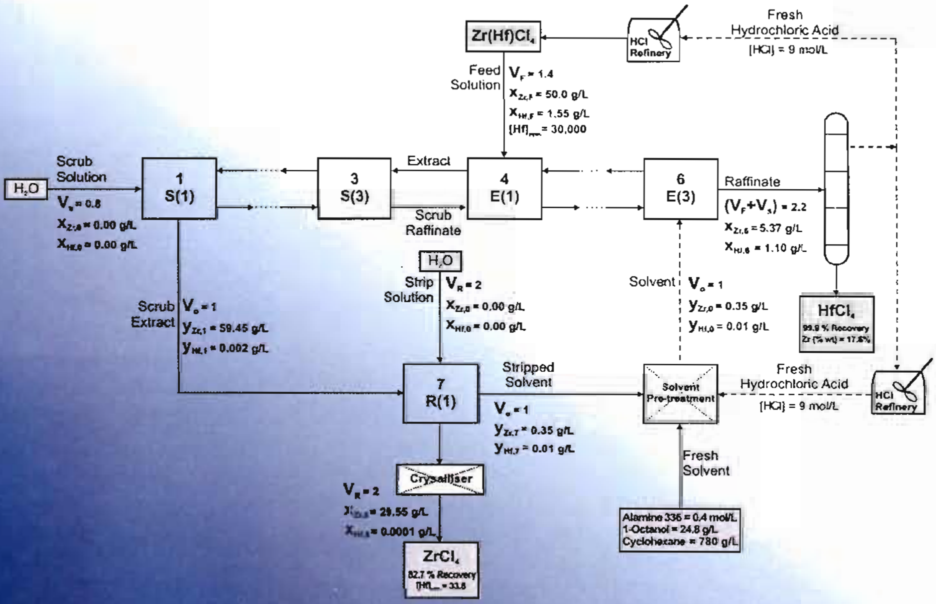

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Separation of Zirconium and Hafnium via Solvent Extraction

by

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"I have strength for all things in Christ Who empowers me."

Philippians 4:13

Amplified Bible

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ABSTRACT

Zirconium metal (Zr) is highly desirable as a cladding material for nuclear fuel rods in nuclear power plants, because of its very low nuclear absorption cross-section for thermal neutrons, however to use this Zr metal it has to be purified (<100 ppm) from the contained (1 – 3% wt) hafnium metal (Hf), occurs in zircon ore ($ZrSiO_4$) in nature. Because of the extensive beach deposits, rich in zircon minerals, located along the South African coasts, there is a great opportunity for zircon beneficiation in South Africa to convert the country's mineral output into high added value products rather than selling the basic mineral to countries like China.

Due to the significantly similar chemical properties of these two elements, the purification of the Zr metal is a complicated process. The separation of Zr and Hf, as currently practiced, is mostly conducted through solvent extraction in which the aqueous chloride solution of metal species is contacted with an immiscible organic phase containing a reagent that selectively removes one of the two metals from the aqueous phase. The conventional multi-stage industrial approach, in production since the 1950s, presented several technological disadvantages and environmental problems that were considered acceptable when these processes were developed, but have become a serious problem as legislation became more stringent. Thus, the main objective for this study is to develop an innovative, environmentally friendly and cost-efficient solvent-extraction process that makes use of Hf-containing Zr compounds, produced by NECSA (Pty) Ltd from zircon ore by means of plasma technology, for the separation of Zr and Hf in order to produce nuclear-grade Zr metal. Results obtained from this study show that the extraction of Zr and Hf from chloride-based compounds ($Zr(Hf)Cl_4$) proceeds via an anion-exchange mechanism through the extraction with amine extractants (Alamine 336 and Aliquat 336), while the Zr species could be successfully recovered from the organic solutions. However, the extraction from fluoride-based compounds ($K_2Zr(Hf)F_6$) was unsuccessful for both Zr and Hf species. The new proposed process for Zr and Hf separation from chloride-based Zr compounds seems to be an improvement from the conventional separation processes.

OPSOMMING

Sirkonium (Zr) is 'n metaal wat 'n baie lae absorpsievermoë vir termiese neutrone besit. Hierdie chemiese eienskap maak dit 'n gesogte konstruksiemateriaal vir brandstofelemente in kernreaktore. Die primêre bron van Zr is sirkoonerts ($ZrSiO_4$) wat ongeveer (1 - 3%) gewig Hafnium (Hf), relatief tot Zr bevat. Maar om Zr in kernreaktore te kan gebruik, moet dit eers gesuiwer (<100 dpm) word van Hf. As gevolg van die wyd verspreide mineraal afsettings, reik aan sirkoonerts, wat aangetref word regoor die Suid Afrikaanse kusgebiede, is daar 'n groot geleentheid vir Suid Afrika om die land se mineraaluitvoere om te skakel na hoë waarde produkte eerder as om die grondstof na lande soos China uit te voer.

Hf is baie nou verwant aan Zr in chemiese gedrag en dus is dit moeilik om hulle chemies te skei. Vloeistof-vloeistof ekstraksie is tans die mees gebruikte metode vir die skeiding van Zr en Hf. In dié proses word die waterige metaalchloried oplossing in kontak gebring met 'n onoplosbare organiese fase wat 'n reagens bevat wat selektief die een metaal van die ander metaal skei. Bestaande industriële aanlegte, wat in produksie is sedert die 1950's, het verskeie tegnologiese nadele en omgewingsprobleme, wat aanvaarbaar was gedurende die ontwikkelingsperiode van die prosesse. Omgewingswetgewing het egter strenger geword en meer omgewingsvriendelike en koste-effektiewe prosesse moet ontwikkel word. Die hoofdoel van hierdie ondersoek was die ontwikkeling van 'n proses wat van Hf bevattende Zr verbindings soos geproduseer word deur NECSA (Edms.) Bpk. vanaf sirkoon erts met behulp van plasma tegnologie, gebruik te maak. Resultate vanuit hierdie studie toon dat die ekstraksie van Zr en Hf vanaf chloriedgebaseerde verbindings ($Zr(Hf)Cl_4$) met tersiêre en kwaternêre amiene as ekstraheermiddels (Aliquat 336 en Alamine 336) via 'n anioonuitruilmeganisme uitgevoer kan word. Die herwinning van die Zr spesies vanaf die organies fase is ook suksesvol uitgevoer. Die ekstraksie vanaf fluoriedgebaseerde verbindings ($K_2Zr(Hf)F_6$) was egter onsuksesvol. Die nuwe voorgestelde skeiding proses vanaf chloriedgebaseerde verbindings word beskou as 'n verbetering op die bestaande skeidingsprosesse.

NOMENCLATURE

Section 2.5.2 (a)

M^{n-}	Metal ion
n	Stoichiometric coefficient
K	Equilibrium constant
D_M	Distribution coefficient of metal (M) between the organic and aqueous phase
$\% E_M$	Percentage extraction of metal (M) from the aqueous phase
V_{aq}	Aqueous phase volume
V_{org}	Organic phase volume
D_{rel}	Relative distribution coeffiecient between metals (M_i and M_j)
SF	Separation factor

Section 2.5.2 (b)

k	Forward reaction rate constant

Section 2.5.2 (c)

N_a	Flux of component through the interface
k_m^+	m^{th} Order forward reaction rate constant
k_n^-	n^{th} Order reverse reaction rate constant
C_x^{im}	Metal concentration on the x-phase side of the interface
C_y^{in}	Metal concentration on the y-phase side of the interface
k_a^i	Ratio of forward and reverse reaction rates

Section 2.5.3 (a)

s	Rate of extraction
k	Constant
N	Impeller speed
D	Mixer diameter

Section 2.5.3 (b)

h	Dispersion band thickness
k	Constant
Q	Dispersion flow rate
A	Settler cross-sectional area
y	Constant (range between 2.5 and 5.0)

r	Droplet radius

Section 5.1.3

n	Number of extraction stages
V_a	Aqueous phase volumetric flow rate
V_o	Organic phase volumetric flow rate
x_0	Solute concentration in the aqueous feed solution fed to stage (1)
x_n	Solute concentration in the aqueous raffinate solution exiting stage (n)
y_0	Solute concentration in the organic solvent solution fed to stage (1)
y_n	Solute concentration in the organic extract solution exiting stage (n)
E	Extraction factor
D_M	Distribution coefficient of metal (M) between the organic and aqueous phase
φ	Fraction of solute remaining in the raffinate after (n) stages
i	Desirable component
j	Undesirable component

Section 5.2.1

N_e	Number of extraction stages
N_{sc}	Number of scrubbing stages
S	Scrubbing factor
D_{sc}	Distribution coefficient for the scrubbing section
V_s	Scrub solution volumetric flow rate
V_F	Feed solution volumetric flow rate
V_o	Solvent solution volumetric flow rate

Section 5.2.2

V_R	Strip solution volumetric flow rate
R	Stripping factor
D_R	Distribution coefficient for the recovery section

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CHAPTER 1

1. INTRODUCTION

1.1. General Introduction

In 1789, Klaproth[1] announced that he had found 68% of an unknown earth in the mineral zircon ($ZrSiO_4$), which he called "zirkonde". Vauquelin[2] studied this unknown earth, which Klaproth had discovered and to which the name zirconia was given, in 1797. He worked on the preparation and properties of some of the zirconia compounds. The first crude zirconium metal (Zr) was produced in 1824 by Berzelius[3] by heating potassium (K) and potassium hexafluorozirconate (K_2ZrF_6) to produce a black powder (Zr metal). It was only a century later that the first high purity Zr metal was produced by van Arkel and de Boer[4]. They vaporised zirconium tetraiodide (ZrI_4) into a bulb containing a hot tungsten filament which caused the tetraiodide to dissociate, depositing Zr on the filament.

A few years later, it was discovered that this Zr metal is highly desirable as a cladding material for nuclear fuel rods in nuclear power plants, because of its very low nuclear absorption cross-section for thermal neutrons[5].

However, to use Zr metal in nuclear reactors it must be essentially hafnium (Hf) free (<100 ppm Hf), due to the fact that Hf has an absorption cross-section for thermal neutrons 600 times larger than Zr and thus has different nuclear properties[6]. Hf is always present with Zr in natural minerals and has very similar chemical properties to those of Zr (Hf and Zr have more similar chemical properties than any other pair of elements in the Periodic Table, apart from the inert gases), which complicates the separation of the two elements.

1.1.1. *Conventional technologies for zirconium production*

After discovering that Zr metal has desirable properties, however, it first had to be separated from the contained Hf. The American Nuclear Navy programme boosted half a dozen American companies to start producing Zr and Hf metals in the early 1950s[7].

Initially, two different solvent-extraction (SX) techniques were used for the separation of Zr and Hf: (a) the methyl isobutyl ketone (MIBK)-thiocyanic-hydrochloric acid (HCl) process [7-10] and (b) the tributyl phosphate (TBP)-nitric acid (HNO_3) process[7,8,10-12]. The MIBK process was optimised in a pilot plant at the US Bureau of Mines, Albany, Oregon in 1953 when the first commercial operation began. The TBP process was developed in 1954 by the French Nuclear Agency and was subsequently improved at Iowa State University[8]. In 1978, a French state company, CEZUS (Compagnie Europèene Du Zirconium, Paris, France), that formerly also produced nuclear-grade Zr with the MIBK process, developed a completely different (c) pyrometallurgical process (CEZUS)[7,8,10,13] from which continuous production was possible.

The three processes mentioned above presented several technological disadvantages and environmental problems. This led many separation scientists over the following years to try and create new Zr and Hf separation processes, which would be innovative, efficient, environmentally friendly and cost effective.

a) The MIBK process

In the early years of Zr and Hf separation there were a large number of processes issued and patented in the world, but the three main producers (Teledyne Wah Chang, Western Zirconium and Cezus) all used the same MIBK SX process, only with minor variations, at that time. The standard MIBK process, proposed by Fisher and Chalybaeus[14], produces zirconium tertrachloride ($Zr(Hf)Cl_4$) by carbochlorination from the zircon ore. This $Zr(Hf)Cl_4$ still contains 1-3% wt of $HfCl_4$. Prior to the separation process the $Zr(Hf)Cl_4$ is converted to its oxychlorides and is then processed through a multiple-step SX process in the presence of ammonium thiocyanide (NH_4SCN). The Hf is preferably extracted as hafnyl thiocyanate using MIBK. The remaining solution reacts with sulfuric acid to form pentazirconyl sulfate, which is precipitated by adjusting the pH with ammonium hydroxide. The zirconium hydroxide obtained is dried and calcined to give Hf-free zirconium dioxide (ZrO_2). Pure $ZrCl_4$ is produced by a second carbochlorination of the ZrO_2[10,14]. Later this thiocyanate extraction was improved by the same authors by developing a repeated stepwise fractionation in which the distribution of the thiocyanate compounds of Zr and Hf was carried out at low concentrations of chloride ions instead of sulphate ions[15,16] (see Figure 1).

Separation factors of up to 7 could be achieved and 99.6% pure Hf species were obtained after eight stages[15]. However, this method encountered several problems, such as rising costs due to consumption of expensive chemicals by decomposition, the low flash point of thiocyanates and thiocyanic acid in the presence of HCl and high solubility losses of MIBK[8], exacerbated by the corresponding quantities of by-products and the reagents needed for their destruction. The Hf is concentrated in the organic extract and these waste extract streams contained high concentrations of ammonium, cyanides and organic compounds that led to environmental concerns in recent years. These waste streams also have offensive odours which are difficult to control.

b) The TBP process

In the TBP process, sodium zirconate (Na_2ZrO_3), obtained from caustic soda fusion with zircon sand, is dissolved in concentrated HNO_3. This solution is mixed with TBP in kerosene and the Zr is selectively extracted[10,13]. Unlike the MIBK process, the separation of Zr and Hf with TBP as extractant is selective for Zr. The purified Zr product is concentrated in the organic extract and therefore stripping of the metal is required. High quality Hf was not produced by this process (see Figure 1).

Separation factors of up to 10 could be achieved[11], however, the TBP process presented several technological disadvantages, such as the low metal concentration in the aqueous and organic phases because of third phase formation, the large consumption of chemicals, and the inability to produce nuclear-grade Hf which is used as control rods in nuclear reactors. The TBP process is even more costly and produces nuclear-grade Zr at about twice the cost of the MIBK process[8].

c) The CEZUS process

The CEZUS process makes use of pyrometallurgical technology based on extractive distillation with potassium chloroaluminate ($AlCl_3/KCl$) as the solvent. The $Zr(Hf)Cl_4$ vapours rise in a counter flow against a descending solution of $AlCl_3/KCl$ saturated with $Zr(Hf)Cl_4$ at 350°C. The separation of the two metals takes place when the solvent stream is going downwards and progressively loses its $HfCl_4$. The $ZrCl_4$ is stripped with nitrogen and is then cooled and condensed[10,13].

Despite of all the advantages of using this new distillation process, separation factors of only up to 2 could be achieved, which means that about 90 stages are necessary to produce the desired nuclear-grade Zr. The CEZUS process requires highly corrosion-resistant alloys and sophisticated technologies to pump and handle the vapour streams, avoiding any air moisture contamination[8].

Figure 1 summarises the established conventional processes for the separation of Zr and Hf which are still mainly in use today. Nevertheless, the increasing energy demand and the establishment of nuclear power plants around the world will push the nuclear industry into adopting more cost-efficient and environmentally attractive technologies.

According to the specifications of these three conventional processes, any new technology for Zr and Hf separation must be compatible with or preferably improve on these processes to have any chance of success.

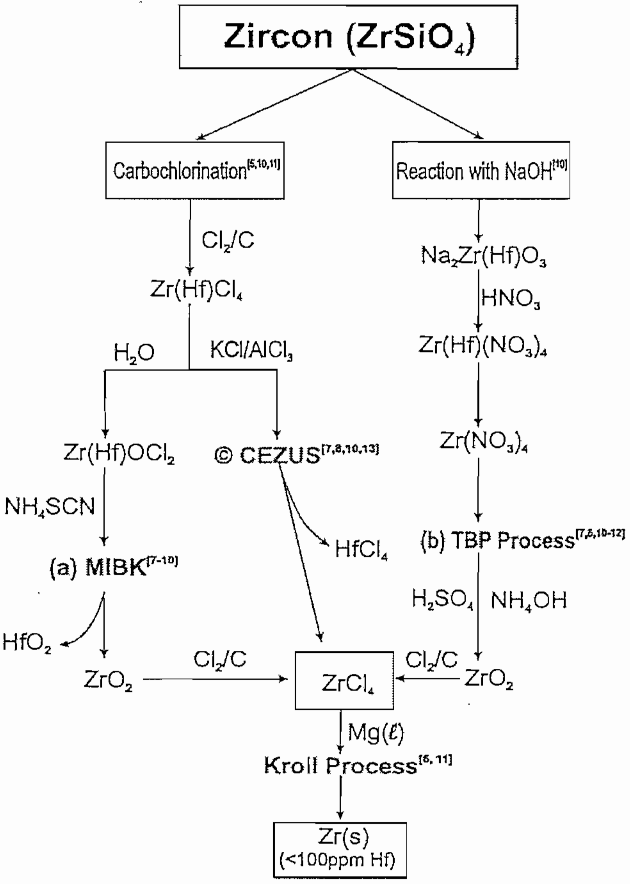

Figure 1: Conventional methods for the production of nuclear grade zirconium

In 1944, Dr. W.J. Kroll suggested to the US Bureau of Mines in Washington, D.C., that he would be in a position to produce Zr in a similar way as the processes that he used for the production of ductile titanium back at the early 1930s in Luxembourg[17]. That year, Dr. Kroll and his co-workers at Albany developed a method to produce spongy Zr by reducing $ZrCl_4$ (see Figure 1). Later this technology, known as the "Kroll process", was implemented at various commercial production plants and is still being used today[6,18].

1.1.2. *Present work*

The present work was initiated by the South African Department of Science and Technology (DST), which launched the Advanced Metals Initiative (AMI). The Nuclear Energy Corporation of South Africa (NECSA) (Pty) Ltd[19], due to existing expertise and infrastructure, was entrusted to investigate the manufacturing of the metals Zr, Hf, Ta and Nb, thereby establishing the New Metals Development Network (NMDN) Hub of the AMI.

This study deals with the development of a SX process based on the use of organic extractants and diluents for the separation and purification of Zr and Hf by using a Zr component produced by NECSA as feedstock in an acidic aqueous medium. This process must be both innovative and productive in order to contribute to economic growth of NECSA in producing nuclear-grade Zr, which should meet the nuclear industry's specifications, while minimum waste generation, based on the extraction process, is kept in mind. Results obtained from this study are compared with results obtained from other studies where traditional techniques like the MIBK and TBP processes were used.

The motive for the current study was to use chemically amenable potassium hexafluorozirconate ($K_2Zr(Hf)F_6$) as the feedstock in the SX process with Alamine 336 or Aliquat 336 as extractants. Zirconium(IV) chloride ($Zr(Hf)Cl_4$) and zirconium oxochloride ($Zr(Hf)OCl_2$), which can be produced by the plasma process, were used as the basis for the design of the experiments. Although Zr/Hf-salts, which can also be produced by the plasma process, were used in this research; the plasma processing itself was not part of the study. The extraction of $K_2Zr(Hf)F_6$ with Alamine 336 and/or Aliquat 336 could be an alternative separation process to the widely used traditional TBP, MIBK and CEZUS processes.

Figure 2 gives a clear illustration of the experimental design and possible Zr/Hf separation paths for this research.

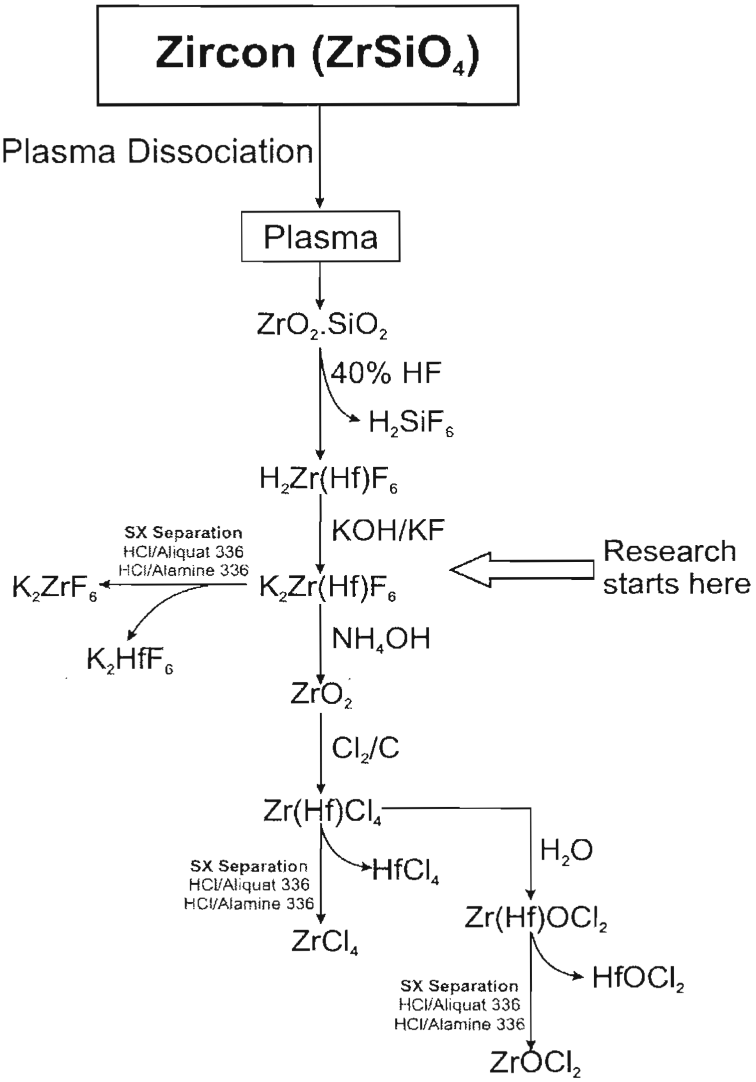

Figure 2: Research path adopted for the separation of zirconium and hafnium

$K_2Zr(Hf)F_6$ can be produced from zircon ore at NECSA by means of plasma technology[20]. This method makes use of non-transfer a.c. plasma technology to dissociate the chemically very inert feedstock ore, zircon, into so-called Plasma Dissociated Zircon (PDZ). During this process the zircon is transformed into a chemically amenable product that exothermically reacts with, for example, diluted hydrofluoric acid (HF). However, during the plasma process no purification is effected: the main change is only the transformation of crystalline to amorphous silica. Therefore the plasma process only produces a PDZ feedstock that is more amenable to subsequent chemical processing, but negligible purification is effected.

1.2. Motivation

Zr and Hf are abundantly present in the earth's crust as zircon sand (zirconium silicate - $ZrSiO_4$) and baddeleyite (zirconium oxide - ZrO_2), with zircon ore being the main source. Zircon ore is found in South Africa, Australia, North America, Brazil and many parts of Asia[21]. South Africa is rich in zircon minerals and is presently supplying 40% of the 1.05 million tonnes global demand for this mineral and possesses 60% of global reserves[22,23].

In South Africa, zircon is produced from extensive beach deposits located along the eastern, southern and north-eastern coasts. Smaller deposits are located along the west coast, north of Cape Town. Important mining operations in zircon production are Richards Bay Minerals, Exxaro's KwaZulu-Natal Sands and Namakwa Sands.

Richards Bay Minerals (RBM)[24], the largest zircon producer in South Africa and second largest zircon producer in the world, has enormous reserves along the KwaZulu-Natal coastline situated along the eastern coast of South Africa. Richards Bay Minerals is the trading name for two registered companies, Tisand (Pty) Ltd and Richards Bay Iron and Titanium (Pty) Ltd (RBIT). Tisand undertakes the dune mining and mineral separation operations, while the smelting and beneficiation processes are carried out at RBIT. The company is jointly owned by Rio Tinto plc and BHP Billiton and is one of the largest stand-alone mining operations in South Africa.

In third place of the world's top suppliers of zircon is Exxaro Sands (Pty) Ltd after the acquisition of Namakwa Sands (formerly owned by Anglo American) was approved by Exxaro shareholders early in 2007[25]. In addition, Exxaro Sands currently comprises KZN Sands (previously known as Ticor SA), which houses the South African operations, and Australia Sands, which houses the Australian operations. Namakwa Sands' mining operations are located at Brand-se-Baai, approximately 60 km west of Koekenaap on the west coast of South Africa.

After refinement by the above-mentioned companies, the zircon ore is exported mainly in unbeneficiated form, leading to very substantial losses in potential profits.

In 2006, Geratech Ltd in Krugersdorp became South Africa's only beneficiator of zircon[26]. This was the company's first year of commercial production of significance, when it produced between 4.5 and 5 kt (only 1.2% of South Africa's exported zircon) of value-added zircon chemicals and oxides. Thus, there is a great opportunity for zircon beneficiation in South Africa to convert the country's mineral output into high added value products rather than selling the basic mineral to countries like China.

1.3. Objectives

The main objective for this study is:

The development of a cost-efficient SX process that makes use of Hf-containing Zr compounds produced by NECSA for the separation of Zr and Hf in order to produce nuclear-grade Zr metal.

For this, the following key points will be followed:

1. An extensive literature survey to determine the optimum chemical compositions with respect to acids and diluents for dissolution, stripping and extraction;
2. Development of an analytical technique for Zr(IV) and Hf(IV) in the aqueous and organic phases;
3. Determination of the distribution coefficients of Zr(IV) and Hf(IV) for a selected number of extractants and acids;
4. Up-scale and design of the SX process to make comparative conclusions with regard to the extraction selectivity;
5. Determination of the cost efficiency of the proposed process and thus an economic evaluation.

1.4. Scope of Investigation

The following methodology will be used to achieve the objectives mentioned above:

a) Literature study

A comprehensive literature study will be performed on the chemistry of Zr and Hf, conventional technologies for nuclear-grade Zr production, other research activities involving SX separation techniques for Zr and Hf and, in general, the principles and chemistry of SX processes in hydrometallurgy in order to define the methods offering an optimum chance of success.

b) Analytical techniques

The most suitable analytical technique for analyzing Zr and Hf in the aqueous and organic phases will be developed as part of this study. This will include tests to measure the repeatability and sensitivity of the method. It is of great interest that the analytical results should be accurate and reliable because of the decisions and conclusions that have to be drawn according to these results.

c) Distribution coefficients

The distribution coefficients of Zr and Hf between the solvent and the aqueous phase in an extraction system, which are needed for the development of an extraction process, will be determined by a limited number of experiments. Hf-containing Zr compounds produced by NECSA, dissolved in different acids and extracted with different extractants, will be used to find comparative conclusions with regard to the extraction conditions. This will be done by means of shake-out tests in the laboratory with well chosen reagents and appropriate SX apparatus.

d) Design of the SX process

The equilibrium data obtained in (c) are used to conceptually design the mixer-settler set-up, including scrubbing, extraction and stripping stages, to make essential conclusions with regard to the extraction selectivity and the separation factor of the SX process and hence the cost efficiency for the overall multi-stage process.

e) Technical evaluation

The predicted process efficiency will then be determined in terms of stages required, solvent losses and waste generation for the production of nuclear-grade Zr and it will then be compared with results obtained from other studies where traditional techniques like the MIBK, TBP and CEZUS processes were used.

The research path adopted in this dissertation is shown in Figure 3:

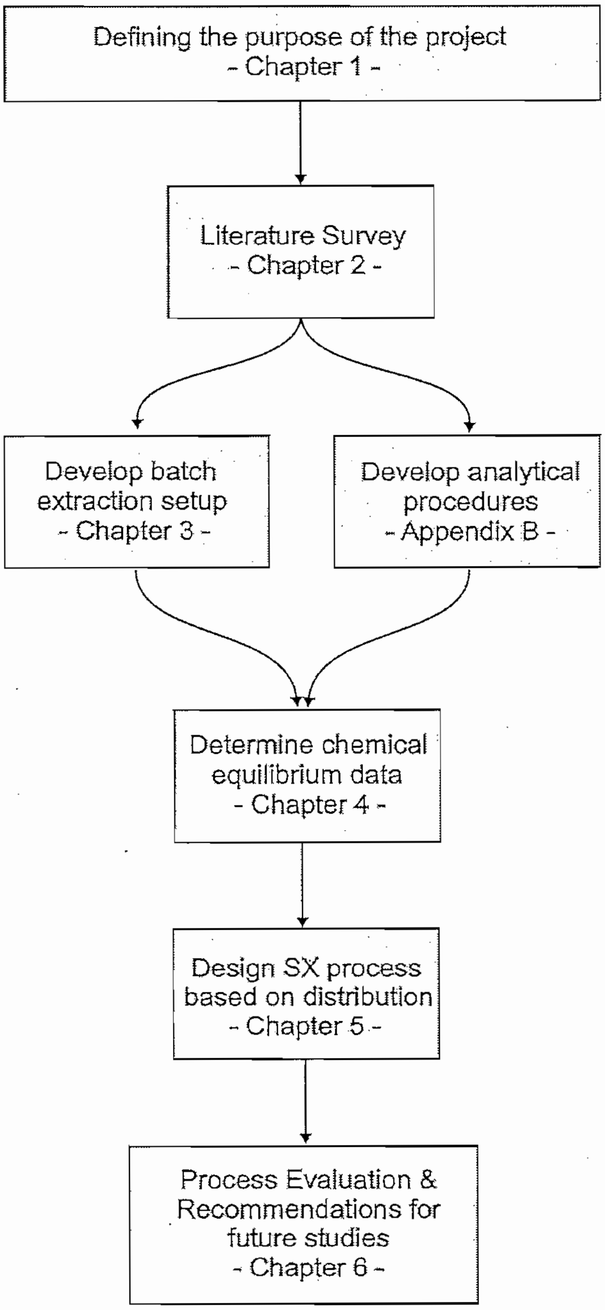

Figure 3: Research path followed in the investigation

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CHAPTER 2

2. LITERATURE SURVEY

2.1. Chemistry of Zirconium and Hafnium

2.1.1. *Introduction*

Thorough knowledge of speciation is crucial for the development of SX processes. In the case of Zr and Hf the speciation is insufficiently described and trial-and-error methods are partly used to develop SX techniques for the separation of Zr and Hf.

The main obstacle is the lack of knowledge of the possible solvolysis reactions. In aqueous solutions extensive hydrolysis is expected, together with a degree of catenation of zirconate (hafnate) species. Additionally, the rates of those possible reactions are not known. This makes it difficult to select promising extraction systems from basic principles. Experimental reaction results are difficult to explain and a degree of speculation cannot be avoided.

2.1.2. *Hydrolysis and polymerisation of zirconium and hafnium species*

In 1963, Pearson[1] introduced the concept of the "Hard-Soft-Acid-Base (HSAB)" theory. When this theory is applied to Zr and Hf, it is possible to understand why these compounds have a higher attraction for water than chloride ions and thus have a high degree of hydrolysis.

Pearson categorized atoms, molecules, ions and free radicals as "hard" or "soft" Lewis acids or bases, according to his considerations and collection of experimental data. This is based on the concept that the "hard" species in general have a small atomic radius, a high effective nuclear charge and low polarizability, whereas "soft" species possess the opposite characteristics. This principle states that acids show greater affinity for bases of the same class and *vice versa*. Thus hard acids (acceptors) tend to form strong bonds with hard bases (donors), but bind reluctantly or weakly to soft bases. The latter class of compounds interacts preferably with soft acids. In other words, a hard-soft combination is destabilised[2].

According to this theory, zirconium (Zr^{4+}) and hafnium (Hf^{4+}) ions are classified as hard Lewis acids, because of the small ionic radii of Zr (0.084 nm) and Hf (0.083 nm)[3] and their high ionic charge (M^{4+}). On the other hand, water (H_2O) and hydroxyl ions (OH^-) are classified as hard bases and chloride ions (Cl^-) are on the borderline between the hard and soft bases. Thus Zr and Hf have a higher attraction for water than for chloride and therefore have a high degree of hydrolysis in an aqueous chloride solution.

Some authors assume that Hf presents a higher tendency than Zr to polymerise in aqueous solutions. In the work of Peralta-Zamora and Martins[4], some observations about non-specific interactions between Zr and Hf are presented. The chemistry of Zr and Hf is closely connected to their capability to form polymeric species, such as $[Zr_x(OH)_y]^{4x-y}$ and $[Hf_x(OH)_y]^{4x-y}$, which can modify the reactivity of the elements to the complexing agent. Peralta-Zamora and Martins assume, according to their experimental evidence, that Hf presents a higher tendency to polymerise in aqueous solutions, forming polymeric species that hinder its complexation with the organic extractant, favouring the subsequent reaction of the Zr ion and the complexing agent.

Veyland *et al.*[5] explained the aqueous chemistry of Zr(IV) by the formation of the soluble species $Zr(OH)^{3+}$, $Zr_2(OH)^{7+}$ and $Zr(OH)_4$ in KNO_3 media, in the pH range of 1.5 to 3.5 and for Zr concentrations varying from $8x10^{-5}$ to $8x10^{-3}$ mol/L. The formation constants of the species $Zr(OH)^{3+}$, $Zr_2(OH)^{7+}$, and $Zr(OH)_4$ as well as the solubility product of zirconium hydroxide were determined in KNO_3 media at four ionic strengths. According to these authors, a useful evaluation of the solubility of Zr(IV) in aqueous medium is obtained by plotting the total Zr concentration (on a logarithmic scale) as a function of pH. Such a plot shows that the insoluble species $Zr(OH)_4$ are predominant between a pH of 5 and 12.

Another investigation of Zr and Hf was done by Johnson and Kraus[6] using equilibrium ultracentrifugation. The results reported show, in general, an increase in polymerisation with decreasing acidity for both Zr(IV) and Hf(IV), with relatively minor differences between the two elements. The most marked difference is the greater tendency for Zr(IV) to polymerise at low acidities. According to these authors, polymeric reactions of Zr(IV) and Hf(IV) become complicated at low acidities. Most of the low acidity solutions attained equilibrium distribution after about one week of centrifugation, which implies a very slow approach to equilibrium. This was, however, in contrast to the behaviour in the more acidic solutions. Ageing of zirconium oxychloride ($ZrOCl_2$) solutions, or heating, increased the degree of polymerisation significantly but did not produce very large polymers.

Other predicted data of Zr polymerisation are cited by Elison and Petrov[7], and are summarised in Table 1.

Table 1: Ionic state of zirconium in hydrochloric acid

[HCl] (mol/L)	Dominatnt Zr ion
0.1	$Zr(OH)_3^+$
0.5 - 1.5	$Zr(OH)_3^{2+}$
2.0	$Zr(OH)_3^{3+}$
0.5 - 2.0	Cations
6.0	Neutral complexes
7.0	Anions

2.2. Quantitive Determination of Zirconium and Hafnium

The quantitative determination of Zr and Hf was an important stepping stone in this study. Decisions and conclusions are drawn from analytical results and these should thus be accurate and reliable.

In the past, techniques like titrimetry (back-titration of ethylenediaminetetraacetic acid (EDTA)) and spectrophotometry (atomic absorption spectrophotometry, AAS) were used to determine elements quantitatively. However, these methods are not completely suitable where both Zr and Hf are present because their chemical similarity makes it difficult to distinguish between the two elements. For this reason, inductively coupled plasma-optical emission spectrometry (ICP-OES) was selected.

ICP-OES is an advanced modern technique of metal determination and with its high detection power it is a quantitative multi-element analytical technique that can easily distinguish between Zr and Hf in aqueous and organic solutions.

This analytical method was studied by various authors for the determination of Zr and Hf in aqueous or organic solutions. Shariati and Yamini[8] proposed a simple versatile separation method using a cloud-point procedure for the extraction of trace levels of Zr and Hf. The extraction of analytes from aqueous samples was performed in the presence of quinalizarine as chelating agent and Triton X-114 as a non-ionic surfactant. The enriched analytes in the surfactant-rich phase were determined by ICP-OES. The different variables affecting the complexation and extraction conditions were optimised. Under the optimum conditions (3.4×10^{-5} mol/L quinalizarine, 0.1% (w/v) Triton X-114, 55°C equilibrium temperature) the calibration graphs were linear in the range of 0.5–1000 µg/L with detection limits (DLs) of 0.26 and 0.31 µg/L for Zr and Hf, respectively. In the presence of foreign ions no significant interference was observed. The precision (% Relative standard deviation (RSD)) for 8 replicate determinations at 200 µg/L of Zr and Hf was better than 2.9% and the enrichment factors were obtained as 38.9 and 35.8 for Zr and Hf, respectively. This proposed method was verified with real samples and was proven satisfactory for the simultaneous determination of trace levels of Zr and Hf in a variety of aqueous matrixes.

Baluch *et al.*[9] studied the determination of Hf down to 100 mg/L and less in Zr matrix using ICP-OES. The standard addition method was applied for the determination of Hf at different Hf wavelengths. Additionally, Hf was determined after it was separated from the Zr matrix using AG 1-X8 Biorad anion exchange resin. Zr and Hf were estimated spectrophotometrically to supplement the ICP data. A calibration curve was constructed from known Hf standards of 0.25, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 mg/L in 2 mol/L HCl. It was observed that the Hf content determined following the standard addition method using the Hf line at 356.166 nm compared well with the results obtained using spectrophotometry.

In the current case it was necessary to determine Zr and Hf in greater quantities than trace levels. Thus, a relatively simple but effective method for determining these two elements in aqueous and organic solutions was developed, as discussed in Appendix B.

2.3. Solvent-Extraction Separation of Zirconium and Hafnium

SX processes are concerned with the removal of one or more components of a leach or other solution by transfer of a metallic species from the aqueous *phase into an* immiscible organic phase. The extracted species are generally re-extracted (stripped) into an aqueous phase by a suitable change in chemical conditions. By favouring the extraction of one component in a multi-component system at specific conditions, separation can be achieved between those components. For more technical information about SX, please refer to Section 2.5.

2.3.1. *Single extraction studies of zirconium and hafnium*

Many groups have worked on the extraction of Zr or Hf individually without taking the separation of the two metals into account. These data are also seen as useful for separation studies.

a) Zirconium

Reddy and Kumar[10] carried out extraction of Zr from low acidity chloride solutions, containing 1.0 x 10^{-3} mol/L $ZrOCl_2.8H_2O$, with 1.0 x 10^{-1} mol/L 2-hydroxy-5-nonylacetophenoneoxime (LIX 84-IC) as an extractant. A variation of temperature in the range of 30 - 60°C increased the extraction from 49 to 90%.

The effects of different donors, like trioctyl phosphine oxide (TOPO), triphenyl phosphine oxide (TPPO), tributyl phosphine oxide (TBPO), tributyl phosphate (TBP), trioctyl amine (TOA) and Amberlite LA-2 were investigated by Banerjee and Basu[11]. It was observed that the 2.0 x 10^{-4} to 8.0 x 10^{-4} mol/L amine donors extract better than the phosphorus donors with a Zr extraction of 88 to 95% from a 1.1 x 10^{-3} mol/L Zr(IV) acidic solution that was spiked with a ^{95}Zr tracer.

Sato and Watanabe first investigated the extraction of Zr with Aliquat 336 and HCl[12], Alamine 336 and HCl[13], and then with Aliquat 336 and sulphuric acid (H_2SO_4) solutions[14]. It was found that the efficiency of extraction increases with the chain length of the alkyl group and was enhanced when the alkyl chain in the amine was branched.

Al-Ani and Masoud[15] also used Alamine 336 (extractant and feed concentration not stated) and obtained an extraction of 14% from low HNO_3 acidic solutions (2.0 mol/L), while Mishra *et al.*[16] used 1.15 x10^{-1} mol/L Alamine 336 and 1.11 x 10^{-1} mol/L Aliquat 336 together with 3.7 x 10^{-2} mol/L TBP as extractant and obtained 99%

and 100% extraction from a 1.0 x 10^{-3} mol/L $ZrOCl_2.8H_2O$ and 8.0 mol/L HCl solution, respectively.

Schrotterova and Mrnka[17] examined the extraction of Zr from H_2SO_4 solutions by primary, secondary and tertiary amines, and found that it could be extracted by all amines studied. When using primary amines, it can be extracted at a lower pH.

b) Hafnium

It is also found in literature that a number of extractants have been used for the extraction of Hf, such as bis(2,4,4-trimethylpentyl)monothiophosphinic acid (Cyanex 302), by Reddy *et al.*[18], that indicates the transfer of Hf from a 1.0 x 10^{-3} mol/L $HfCl_4$ acidic chloride solution following a cation-exchange reaction with 98% extraction by 2.0 x 10^{-3} mol/L Cyanex 302 diluted in chloroform.

Khan and Ali[19] concluded that Hf can be extracted almost quantitatively (>98%) in two extractions using 1.2 x 10^{-3} mol/L di-n-butyl sulfoxide (DBSO) in cyclohexane from 8.0 mol/L HNO_3 solutions.

The distribution of Hf was studied by Navratil[20-22] between aqueous solutions and solutions of dialkylphosphoric acids (di(2-ethylhexyl)phosphoric acid (HDEHP)) from different mediums. It was found that at higher initial concentrations of Hf (3.4 x 10^{-8} mol/L), polymeric complexes are formed in the aqueous phase, which caused a decrease in the value of the distribution ratio of the Hf.

2.3.2. *Different extractant applications for solvent-extraction separations*

Various authors have proved that Zr and Hf can be separated by SX utilising various types of extractants and diluents. Although a number of SX process models for Zr and Hf separation have been developed in the past, not one of them featured SX with $K_2Zr(Hf)F_6$ as the feedstock.

a) Solvent-extraction separation with β-diketones

β-diketones are widely used for extraction of many metals. Extraction of Zr and Hf by 444-trifluoro-1-(2-thienyl)-1,3-butanedione (TTA) was studied by Weginwar *et al.*[23].

According to these authors, other studies on Zr and Hf separation with TTA provide little information on the co-extraction of other elements. The trifluoromethyl group in TTA makes the enolic form acidic, enabling extractions at low pH values. Both TTA and the Zr chelates have low solubility in aqueous acid solutions, but are soluble in organic diluents such as benzene, toluene, xylene, *etc*. It was concluded that TTA-decalin separated Zr and Hf well, while other carrier-free radionuclides remained in the aqueous phase. The separation of Zr and Hf with TTA was, however, studied from multitracer solutions containing carrier-free radioisotopes of very low concentrations of Zr and Hf, which are suitable for analytical techniques but not for nuclear-grade Zr metal production.

b) Solvent-extraction separation with organophosphorus extractants

Brown and Healy[24] studied the separation of Zr from Hf in a HNO_3 solution by dibutylbutylphosphonate (DBBP) as a function of acidity, extractant and metal concentration. Separation factors obtained with single extractions were in the 15 – 30 range for most Zr concentrations. They also tested the data obtained from the batch extraction with a 10-stage Croda mixer-settler[25]. The Hf content of the Zr could be reduced below 100 mg/L and the Hf could be recovered if desired.

Irgolic *et al.*[26] investigated the extraction of several metal ions with a HCl- tris(n-octyl) arsine oxide (TOCASO)-C_6H_6 system, including Zr and Hf. The phosphorus analogue of TOCASO and tris(n-octyl)phosphine (TOPO) were found to be superior to tributylphophate (TBP) for several metal extractions. The extraction of Zr and Hf by TOCASO differs considerably from that by TOPO. They postulated that these differences in the extraction properties of TOCASO and TOPO may be a result of the exceptional stability of the "tocasonium" ion, the formation which is favoured by high acidities. However, the separation of the metals was successful. Very low concentrations of radioactive tracers were used in this study (5×10^{-5} mol/L and 7.0×10^{-4} mol/L for zirconium (^{97}Zr) and hafnium (^{181}Hf), respectively). The use of arsine-containing extractants can lead to major environmental problems.

Zr and Hf separation were studied by Da Silva and Distin in 1998 and 1999 by using Cyanex 923[27] and Cyanex 925[28] diluted in kerosene. The two phosphines were extensively tested. The alkyl groups R in Cyanex 923 have straight chains whereas those of Cyanex 925 are branched. Cyanex 925 selectively extracts Zr over Hf from HCl solutions, but without the formation of thiocyanate complexes as with the MIBK process and a separation factor of 37 was observed.

In the past year (2008), new attempts at the selective separation of Zr and Hf were reported. Taghizadeh *et al.*[29] used Taguchi's method to determine the optimum conditions for the separation of Zr from Hf by SX.

According to Antony and Antony[30], the Taguchi method (Tm) can be a powerful problem-solving technique applied by industrial engineers for improving process performance, yield and productivity. By applying the Tm, the number of experiments can be reduced if there is a wide range of variable parameters by focusing on the mathematical aspects of probability. In the study of Taghizadeh *et al.,* three factors at three levels, i.e., acid concentration, acid type and extractant were considered. For three parameters, each at three levels, the traditional full factorial design would require 3^3, i.e., 27 experiments. However, in their new design (Taguchi L9 orthogonal array), only nine experiments are required.

The experimental conditions were studied in the range of 0.1 to 2.0 mol/L for three different acids and TBP, D2EHPA or Cyanex 272 as extractant. The optimum conditions were acid concentration of 2.0 mol/L using 7.92×10^{-4} mol/L Cyanex 272, whereas mixing HNO_3 and HCl had a minor positive effect. Under these conditions, the extraction of Zr was about 71% from a 1.29×10^{-4} mol/L $ZrOCl_2.8H_2O$ acidic solution, with a separation factor of 8.1. More detailed experiments showed that the optimum conditions for selective Zr extraction were extraction by Cyanex 272 from >2 mol/L HNO_3 when Zr extraction was about 80% and the separation factor was 34.

c) Solvent-extraction separation with amines

Usually the high molecular weight amines (primary, secondary and tertiary) and the quaternary ammonium compounds are used as liquid anion exchangers.

Primary amines

Primene JMT, a long chain primary amine, was used by Schotterova *et al.*[31] in 1992 as an extractant in the application of amine extraction to the production of pure Zr salts. Another primary amine, Armeen 18-D, has been applied by Cerrai and Testa[32] to the extraction and separation of Zr and Hf from solutions containing various concentrations of HCl, and giving separation factors in the range of 10 - 17.

Secondary amines

According to Cerrai and Testa[32], di-cyclohexylamine, which is a secondary amine, gives a greater extraction than the corresponding primary amine. Amberlite LA-1 gave similar separation factors in the range of 4 to 16. Armeen 2C, a mixture of secondary amines with a mean molecular weight of 400, also gave fairly good results with separation factors between 8 and 15.

Tertiary amines

Some preliminary experiments from various authors[32-40] showed that tri-n-octylamine (TOA), also known as Alamine 336, presented many interesting characteristics: it is very selective in several separation processes and easily soluble in most organic diluents in a wide temperature range. When mixed with the aqueous phase, the separation time is very short (about 30 s in most cases) and no addition of octanol or rise in temperature is required. Very high separation factors of 200+ were obtained by the addition of other acids, like HNO_3 (5% v/v) with the HCl-TOA-cyclohexane system.

Quaternary ammonium compounds

Although excellent results can be obtained by the tertiary amines, a drawback to the use of such amines is their high cost. The use of tricaprylyl-monomethyl ammonium chloride[41-46], also known as Aliquat 336, as a metal extractant in SX gained great popularity in the last few years as a more advantageous compound than the amines mentioned above, because of its lower cost and outstanding extraction features.

2.4. Other Zirconium and Hafnium Separation Techniques

2.4.1. *Separation studies using fractional crystallization*

Fractional crystallization is used as a separation method by making use of comparatively small differences in the solubilities of individual compounds of Zr and Hf[47-49]. In the work of Branken *et al.*[50], fractional crystallization of Zr and Hf was studied using computational and experimental techniques. Molecular modelling of $K_2Zr_{(1-z)}Hf_zF_6$ solid solutions was used to predict the separation efficiency of K_2ZrF_6 and K_2HfF_6 by crystallization. It was shown that the predicted efficiency of separation is low due to the low enthalpy changes associated with solid solution formation. Therefore many recrystallization steps would be needed to sufficiently purify the Zr salt (<100 ppm Hf) to be applicable for nuclear applications. The separation efficiency via crystallization of $K_2Zr(Hf)F_6$ was also investigated experimentally using small-scale crystallization experiments and enhancement of the purity of K_2ZrF_6 was observed.

2.4.2. *Separation studies using extractive distillation*

The extractive distillation method of separation is based on the use of the difference in the boiling points of various Zr and Hf compounds. Van Arkel and de Boer[51] investigated the fractional distillation of complex compounds – products of the reaction of zirconium and hafnium tetrachlorides with phosphorus(V) chloride and, more particularly, phosphoryl(V) chloride. The compositions of the Zr complexes were $2ZrCl_4.PCl_5$ after the $ZrCl_4$ reacted with PCl_5, and $2ZrCl_4.POCl_3$ after reacting with $POCl_3$. The compositions of the Hf complexes are analogous to those of the Zr complexes. These authors stated that, although the difference in the boiling points of the complexes formed by phosphoryl(V) chloride with $Zr(Hf)Cl_4$ is comparatively small (360°C and 355°C, respectively), effective separation of Zr and Hf can be achieved when the number of plates in the fractionating column is sufficiently large.

2.4.3. *Separation studies using solid ion-exchange resins*

Zr and Hf form anionic complexes with different stabilities in a sufficiently low pH range. Industrial applications of ion exchange for the recovery and separation of metal ions is usually carried out in a fixed bed. Extractant-impregnated resin[52] and both cation- and anion-exchange resins have been used to study Zr and Hf separation[53-67]. Ion exchange is also considered, together with SX, to be a very effective separation technique for Zr and Hf.

Some of the latest work done on the separation of Zr and Hf using ion exchange were the studies of Poriel *et al.*[68] testing the sorption behaviour of Zr and Hf on different commercial anion-exchange resins with different amine functionalities: ammonium (Amberjet 4200 Cl), pyridine (PVP) and pyridinium (HPQ) functional groups were investigated in HCl in 2006. The highest separation factor (SF = 10.4), at equilibrium conditions, was obtained by PVP with a 9.5 mol/L HCl solution. In 2007, Favre-Reguillon and his co-workers[69] studied the influence of the concentration of HCl and the initial Zr/Hf ratio on Zr and Hf extraction by Amberjet 4200 Cl. In this work, binary equilibrium isotherm data of Zr and Hf systems were predicted using different mathematical models. Separation factors of up to 9, under equilibrium conditions, were obtained with a 9.5 mol/L HCl solution. In the early '90s, Murty *et al.*[70] tested some advantages of using an acid mixture by digesting Zr wet cake (residue obtained after water leaching of alkali-fused zircon) with concentrated HCl, and then efficiently ageing and filtering the slurry. The residue was then leached with 6 mol/L HCl- 2 mol/L H_2SO_4 mixtures. After the slurry was further aged and finally filtered, the filtrate was passed through an anion-exchange resin. A high-purity zirconium dioxide was obtained. Some of the important advantages they discovered by using a mixture of acids were an increase in solubility of the Zr, thus a lesser volume of effluent generation becomes possible, and an increase in the distribution, hence the capacity of the resin increases. In 2002 Mohammed and Daher[71] used almost the same technique to purify Zr from Egyptian zircon with anion-exchange resins. They leached with a 6 mol/L HCl- 1 mol/L H_2SO_4 mixture and found that it is possible to produce high quality zirconia powder with simplicity and low costs.

2.4.4. *Separation studies using membrane technology*

a) Supported liquid membranes

In the Supported Liquid Membrane (SLM)[72] option, the organic extractant is located inside the wall of a porous hydrophobic hollow fibre membrane. The two aqueous streams, being the feed and the stripping liquor, are on the lumen and the shell side of the membrane. The allure of SLM is in the fact that the loading and the stripping occur in one step.

Yang *et al.*[73] studied the separation of Zr and Hf with this technique, using TOA and Aliquat 336 as the carriers (Part 1). They reported that the selectivity of SLM is equivalent to a single SX stage. Separation factors of up to 38 were found in a 6 mol/L HCl-TOA SLM system. In Part 2[74], they stated that liquid chromatography has a very high efficiency among the traditional separation methods, since it is a multi-stage rather than a single-stage process and a very high number of separation stages can be achieved in a low volume unit. However, despite the SF of 60 they found with an HCl-TOA liquid chromatography system, this technology has been only useful for laboratory and pilot-plant scale production to produce small amounts of nuclear-grade Zr. The main reason why the SLM method is not applied in an industrial setting is the fact that pressure shocks at either the lumen or the shell side lead to loss of the organic solvent in the wall[72,75].

b) Nanofiltration

In the past two years, Poriel *et al.*[76] used membrane filtration equipment to evaluate Zr and Hf separation efficiency by a membrane separation process. EDTA, a soluble organic ligand with a high thermodynamic stability constant towards Zr and Hf, was introduced to a HCl aqueous solution and enhanced the transport of both Zr and Hf across membranes. The data found from this were then used to demonstrate that the ligand-enhanced separation of Zr and Hf from aqueous solution using membranes was applicable. Separation factors of up to 5 were obtained.

2.4.5. *Separation studies using selective reduction*

In the early years of Zr and Hf separation various authors[77,78] reported a scheme using Zr metal powder as the oxidant and aluminium as the reductant for the separation of Zr and Hf based on possible differences in their chemical behaviour. Some years later, research workers turned their attention to the marked difference in the abilities of $ZrCl_4$ and $HfCl_4$ to undergo reduction. This indicated the possibility of using selective reduction of the tetrachlorides to separate Zr and Hf. In the work of Newnham[79], a mixture of $Zr(Hf)Cl_4$ containing 1.5% HfO_2 in $Zr(Hf)O_2$ was reduced with Zr in an evacuated vessel at 300 - 550°C. $ZrCl_4$ was reduced to $ZrCl_3$, with $HfCl_4$ several times smaller. The $HfCl_4$ and unreduced $ZrCl_4$ were sublimed off at a temperature of 420°C. The concentrates obtained were converted into Hf dioxide by ion exchange or SX [78].

2.4.6. *Separation studies using flotation*

Eriochrome cyanine R (ECR) was investigated by Akl *et al.*[80] as a collector for separation and flotation of Zr and Hf through the use of an oleic acid surfactant. Distilled water, acidified with HCl, containing known concentrations of Zr(IV), Hf(IV) and ECR, were introduced into a flotation cell, where the surfactant (HOL) was added. The flotation cell was turned upside-down twenty times by hand. The Hf(IV) liquor was completely rinsed into another flotation cell. The Zr(IV)-containing scum layer was dissolved in HNO_3 and then spectrophotometrically measured with Arsinazo III. These authors stated that selective separation of Zr(IV) was achieved at pH 2 with maximum efficiency, whereas Hf(IV) was completely separated at pH 7.0 - 7.5. The self-floatable species that formed was indicated as M-ECR-HOL, with M = metal (Zr/Hf), ECR = Eriochrome cynine R and HOL = oleic acid. Excess ECR was used to avoid interferences from foreign ions without any effect on the separation efficiency.

2.5. Solvent-extraction

Hydrometallurgy involves a series of interlinked unit operations for the recovery and purification of metals using aqueous solutions. Despite the fact that each plant is almost unique in the way in which the various unit operations are combined into an overall process, many of the operations can be combined into a single group of related operations as shown in Figure 4.

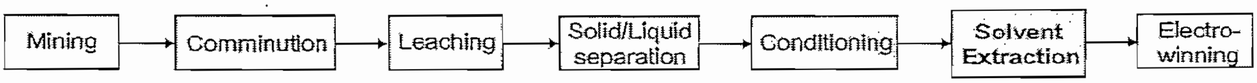


Figure 4: Process route in hydrometallurgy using solvent extraction for metal separation

First, the ore goes through a leaching process that involves the selective dissolution of the valuable component(s) of the ore, concentrate, calcine or other intermediate product. The active chemical species responsible for the dissolution is known as the lixiviant or leaching agent (i.e., H_2SO_4, HCl, sodium cyanide (NaCN) or sodium hydroxide (NaOH))[81].

After leaching the ore, the resulting solution (leachate) must be subjected to one or more of the chemical process steps designed to remove the impurities and/or concentrate the solution so that the desired metal can be successfully recovered in a pure form. These unit operations can involve selective precipitation, crystallization, cementation, adsorption, ion exchange or SX. As mentioned before, SX is studied as the unit operation in this research.

To use SX as the unit operation for the separation, concentration and/or purification of metals, the overall hydrometallurgical route has to be considered. The choice of extraction process is influenced by processes downstream of solution purification, especially where the operation is intended to fit into an existing flowsheet. The SX process can also impose restrictions on the upstream unit operations. In particular, the presence of surfactants (flocculants to aid solid-liquid separation or mist suppressants in tankhouses) can have a deleterious effect on extractant performance. Thus, it is important not to consider the SX operation in isolation, but to base it on the fullest knowledge of both the upstream and downstream processes with which it will be interfaced.

2.5.1. *Principles of solvent-extraction*

Some of the SX terms used to describe the process streams in this research are as follows[82]:

• Feed:	The feed to a SX process is the aqueous solution that contains the metals to be separated.
• Solvent:	The solvent is the immiscible organic liquid mixture, containing the extractant, diluent, modifier and any other organic components.
• Extractant:	The extractant is diluted in the solvent for the purpose of extracting the desired metal from the feed by complexation or solvation.

• Diluent:	The diluent is used to dilute the extractant to an appropriate concentration in the solvent.
• Extract:	The solvent phase leaving the SX process, containing the metal.
• Raffinate:	The raffinate is the aqueous phase left from the feed after being contacted by the solvent.

The basic SX circuit in hydrometallurgy typically consists of a series of interconnecting loops, illustrated in Figure 5.

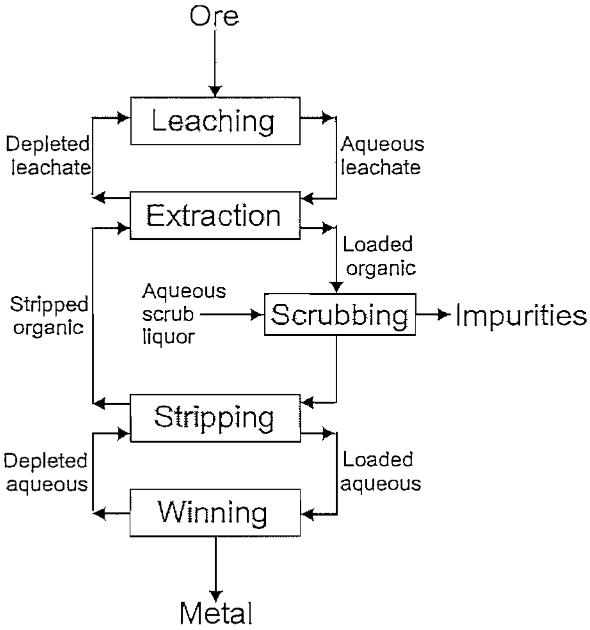


Figure 5: Typical SX flowsheet for the purification of metals from a leach solution

The desired metal is transferred into an immiscible organic phase, which may then be contacted with a series of aqueous solutions designed to strip any impurities co-extracted with the desired metal, which is called scrubbing. From the scrubbing section, the resulting aqueous scrub raffinates (containing impurities) may then be further treated to remove any valuable elements. Finally, the purified organic phase is contacted with an appropriate strip solution to return the chosen element to an aqueous phase from which it can be recovered, thereby regenerating the organic extractant solution for recycling.

2.5.2. *Chemistry of solvent-extraction*

a) Solvent-extraction equilibria

Consider a generic anion-exchange reaction,

$$\left[M^{n-}\right]_{(aq)} + \left[nR_3NH^+Cl^-\right]_{(org)} \rightleftharpoons \left[(R_3NH)_nM\right]_{(org)} + \left[nCl^-\right]_{(aq)} \tag{1}$$

where (aq) and (org) represents the aqueous and organic phases, respectively.

Assuming ideal solutions, the equilibrium expression can then be derived from Equation 1:

$$K = \frac{\left[Cl^-\right]^n\left[(R_3NH)_nM\right]}{\left[R_3NH^+Cl^-\right]\left[M^{n-}\right]^n} \tag{2}$$

and, by taking logarithms,

$$\log K = \log\left[(R_3NH)_nM\right] + n\log\left[Cl^-\right] - \log\left[M^{n-}\right] - n\log\left[R_3NH^+Cl^-\right] \tag{3}$$

Thus, by rearranging Equation 3

$$\log\frac{\left[(R_3NH)_nM\right]}{\left[M^{n-}\right]} = \log D_M = \log K + n\log\left[R_3NH^+Cl^-\right] + n\log\left[Cl^-\right] \tag{4}$$

with D_M defined as the distribution ratio, which is the ratio between the concentration of the metal ion in the extract $[M]_{(org)}$ and the raffinate $[M]_{(aq)}$:

$$D_M = \frac{[M]_{(org)}}{[M]_{(aq)}} \tag{5}$$

The distribution coefficient can be used to calculate the percentage extraction (%E) of the desired metal (M).

$$\%E_M = \frac{D_M}{D_M + \frac{V_{aq}}{V_{org}}} \times 100 \tag{6}$$

where V_{aq} and V_{org} are the volumes of the aqueous and organic phases, respectively.

When considering the separation of two metal ions M_i and M_j, the relative distribution coefficient (D_{rel}) can be calculated from Equation 5:

$$D_{rel} = \frac{D_{M_i}}{D_{M_j}} \tag{7}$$

This leads to the separation factor (SF) for the two metals which can be described as:

$$SF = \frac{1}{D_{rel}} \tag{8}$$

The SF gives an indication of how selective the extraction is regarding the purification of the desired metal ion (M_i). For any given system there are factors affecting the value of the distribution ratio and thus the separation factor, for example, the concentration of the extractant in the solvent and the pH of the feed.

b) <u>Solvent-extraction kinetics</u>

One of the desirable features of an extractant in SX is speed of reaction, defined in terms of rates of extraction and stripping. The kinetics of SX are complex, involving mass transfer with chemical reaction in a mixed heterogeneous system. However, the kinetic behaviour of an extraction system influences important economic parameters such as residence time in the mixer and thus the size of plant and volume of reagents. For this reason it is important to evaluate the time it takes for the chemical system to reach equilibrium.

Metal extraction with extractants in SX involves three steps[83]:

- diffusion of reagents to the reaction zone;
- chemical reaction;
- diffusion of products away from the reaction zone.

Any one of these can be the rate-determining step.

Most of the chemical reactions in SX, involving complex formation with the metal ion, except chelate formation, are special cases of ionic-type nucleophilic substitution reactions (S_N1 and S_N2), which are rapid most of the time. These are only limiting cases and an entire range of intermediate situations exists[84]. However, there are other factors like viscosity of the phases, amount of agitation, and the temperature of the system that affect extraction rates.

Consider the equilibrium in (9):

$$\left[M^{n-}\right]_{(aq)} + \left[nR_3NH^+Cl^-\right]_{(org)} \rightleftharpoons \left[(R_3NH)_nM\right]_{(org)} + \left[nCl^-\right]_{(aq)} \qquad (9)$$

The reactions show second-order kinetics, with the rate law[85]:

$$\text{Rate} = k \times \left[M^{n+}\right] \times \left[\ RH\ \right] \qquad (10)$$

The constant (k) is called the rate constant for the reaction and has units of liters per mole second (L/mol.s). Hence, according to this kinetic relation, it is clear that if either the metal or the extractant concentration changes, the rate of the reaction changes proportionally.

c) <u>The mass transfer process of solvent-extraction</u>

The mass transfer of a metal solute between two immiscible liquids is an important aspect in SX used in hydrometallurgical applications. Numerous mechanisms and models were proposed by Davies and Rideal[86] to clarify the complicated aspects of the mass transfer during SX. The most commonly used models are based on film and penetration theories and consider that the equilibrium is established at the interface, so that the interfacial resistance can be considered negligible. However, there are some researchers like Brener and Leal[87,88] who developed a theory, based on Brownian transport of the solute between the immiscible phases, that proves that such an interfacial resistance exists. Some authors[89-91] observed the presence of an interfacial resistance with a comparable value to that of the liquid bulk.

As mentioned in the previous section, in most cases the SX examples of inorganic systems in hydrometallurgy are special cases of ionic-type nucleophilic substitution reactions (S_N1 and S_N2) and thus examples of heterogeneous reactions between metal solutes and extractants. In these particular cases, the metal ionic species (cations and anions) can only exist in an aqueous phase. It is therefore necessary for them to react with an appropriate organic compound (extractant) to form a neutral complex before they can enter an organic phase and, since such extractants normally have a very slight solubility in water; the reaction generally takes place at the interface itself.

In the following discussion of mass transfer, explained in Kirk-Othmer Encyclopedia of Chemical Technology[92], the interfacial resistance is taken into account.

According to Kirk-Othmer[92], the effect of heterogeneous reactions can conveniently be described in terms of the "two-film" theory. The result is that the concentrations at the interface are no longer in equilibrium, but can be related via an m^th order forward and n^th order reverse reaction with rate constants k_m^+ and k_n^- as follows:

$$N_a = k_m^+ C_x^{im} - k_n^- C_y^{in} \tag{11}$$

$$= k_m^+ \left[C_x^{im} - \frac{k_n^-}{k_m^+} C_y^{in} \right] \tag{12}$$

The parameter N_a is the flux of component through the interface and at equilibrium the net reaction rate is zero. So,

$$k_a^i = \frac{k_n^-}{k_m^+} = \frac{C_x^{im}}{C_y^{in}} \tag{13}$$

where k_a^i is the ratio of forward and reverse reaction rates and C_x^{im} is the concentration on the *x*-phase side of the interface in equilibrium with C_y^i on the *y* side. This can be used to derive the resistance in series to give

$$\frac{1}{k_{ax}} = \frac{1}{k_x} + \frac{1}{m_y k_y} + \frac{1}{k_m^+} \left[\frac{C_x^i - C_x^{ix}}{C_x^{im} - C_x^{imx}} \right] \tag{14}$$

This is essentially equivalent to introducing an extra resistance at the interface. In many hydrometallurgical applications, the reaction term in Equation 14 can be rate controlling.

These mass transfer coefficients can be experimentally determined by Lewis-type cells[93] that work on the principle of mixing of the individual phases and creating a flat contact interface.

2.5.3. *Equipment and processes*

The contact of the two phases that is required for this extraction or stripping to be effected is achieved by special extraction equipment such as[94]:

- Mixer-settlers
- Spray columns
- Pulsed columns (packed or plate)
- Centrifugal contactors

In hydrometallurgy, the recovery, concentration or purification of major metals by SX usually makes use of the mixer-settler contactor design. This type of contactor is well established with literally hundreds of operating units. It further has excellent mixing characteristics and the prediction of capital and operating costs are accurate, while phases are readily accessible for sampling and examination *in situ*[95].

In mixer-settlers, the two liquid phases are first mixed and then separated by settling. These two sfeatures of the SX process equipment are characterised below.

a) Mixer characteristics

The performance of a mixer-settler is affected by two issues: 1) the effectiveness of mass transfer between phases and 2) the entrainment of fine droplets.

The rate of extraction(s) is generally proportional to the interfacial surface area which can be related to agitation[81]

$$s = kN^3D^2 \tag{15}$$

where N is the impeller speed, D is the mixer diameter, and k is a constant. The term N^3D^2 is referred to as the "mixing intensity", with units m^3/s^2.

If the agitation speed is too high, droplets of extremely small diameter will be formed resulting in fine droplets of the aqueous phase in the organic phase and *vice versa*. This can lead to the formation of an emulsion or third phase.

b) Settler characteristics

Settlers are usually characterised by the thickness of the dispersion band (h) at the outlet as a function of the flow rate (Q) of the dispersion[81]:

$$h = k\left(\frac{Q}{A}\right)^y \tag{16}$$

where k is a constant, A is the cross-sectional area of the settler and y is a constant in the range 2.5 to 5.

The following points have been noted regarding settlers[81].

- This relationship results in settlers operated with the same dispersion band thickness having a capacity directly proportional to the surface area of a horizontal longitudinal section of the settler.
- The height of the settler is generally kept between 1 and 2 meters during scale up.
- The settling rate decreases as the agitation intensity increases.
- In general, coalescence time is proportional from r^{-1} to r^{-3} where r is the droplet radius.
- The nature of the continuous phase affects the settling time.
- The presence of fine solid particles can lead to the formation of very stable emulsions.

2.5.4. *Dispersion and coalescence*

When the two liquid phases are mixed in a SX process, the result is called ***dispersion*** because of the one phase that is dispersed into the other, while the process of phase disengagement is referred to as ***coalescence***.

In mass transfer of a metal between two different liquid phases the contact area across which the transfer can take place is one of the controlling parameters for mass transfer rates and hence for efficiency of utilization of equipment. However, the physical aspects of the system, such as the dispersion of the phases on mixing, the type of droplet formation, and the rate and completeness of coalescence, are not less important[96]. These parameters are used to find suitable contacting equipment and the design and operation of the SX plant are based on them.

The rate of mass transfer is a function, among other variables, of the drop size distribution or interfacial area between the phases. The drop size is governed by the surface tension, densities of the two phases and type of agitation and design of the contactor. Up to a point, the smaller the drop, the greater the rate of mass transfer[97]. Thus, poor coalescence and phase separation in a multi-stage counter-current system will tend to cause a decrease in efficiency of the mass transfer. In order to achieve practically useful coalescence of two dispersed phases, the dispersion must be of a temporary nature[98].

2.6. Extraction with High Molecular Weight Amines

2.6.1. *Introduction*

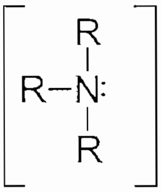
High molecular weight alkyl amines have a wide variety of uses in the mining industry for the purification and recovery of various metal species by means of flotation (primary and secondary amines) and SX (tertiary and quaternary amines). The latter were developed as SX reagents for the uranium industry in the 1950s[99] and are applied to different hydrometallurgical uses. Apart from the mining industry, these tertiary and quaternary amines are also used in citric acid extractions, inorganic acid production, such as phosphoric acid, and phase transfer catalysis.

2.6.2. *Structure of amine extractants*

The structure of extractants used in SX determines the extraction efficiency by means of the way they effectively compete against water and other anions (Cl^-, F^-, SO_4^- and NO_3^-, *etc.*) for the available coordinating positions around the complex metal ion. The stronger the extractant basicity, the more able it is to replace water and other anions around the metal ions.

The structure of tertiary and quaternary alkyl amines is, to a large extent, related to the structure of ammonia with the hydrogen atoms replaced by hydrocarbon chains.

Figure 6 gives an indication of a tertiary amine, where R represents hydrocarbon chains. Tri-octylamine (R = C_8H_{17}) is produced by using moderate pressure catalytic reactions and is commercially available under the trade name **Alamine® 336**, where the alkyl groups (R) are a mixture of C8 to C10 hydrocarbon chains, with C8 the most dominant. (See Appendix A1 for the Technical Specifications Sheets (Tech Spec Sheets) of Alamine 336).

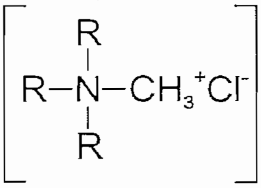


$$\left[R-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{N}}: \right]$$

Figure 6: Lewis presentation of a tertiary amine

The tertiary amine has a tetrahedral structure with three alkyl groups on the corners of the tetrahedron while the fourth corner contains the unshared pair of electrons that provide the amine with its basicity, shown in Figure 6. The bond angles between the alkyl chains are approximately 108 degrees[99].

Figure 7 showes the Lewis presentation of a quaternary amine.



$$\left[R-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{N}}-CH_3{}^+Cl^- \right]$$

Figure 7: Lewis presentation of a quaternary amine

For the quaternary amine the unshared pair of electrons is replaced with a methyl group. In this case the four alkyl groups are covalently bonded to the nitrogen atom, which results in a positively charged ion which is paired with a chloride anion, showed in Figure 7. The bond angles between the alkyl chains are also approximately 108 degrees[99]. (See Appendix A2 for the Tech Spec Sheets of Aliquat 336).

This quaternary amine (tricaprylyl methyl ammonium chloride), is produced by reacting Alamine 336 with methyl chloride (CH_3Cl)[100] and is commercially available under the trade name **Aliquat® 336**. These two extractants are widely available from the major chemical suppliers like Sigma Aldrich and Merck, but they are trademarks of **Cognis©** Corporation based in Cincinnati, OH, which has a long history of the production and marketing of alkyl amines for mining industry applications.

2.6.3. *Physical properties and chemical stability*

a) Physical and chemical properties

Although the structures of the two amines are closely related to each other, the chemical and physical properties differ from Alamine 336 to Aliquat 336. These properties are summarised in Table 2:

Table 2: Chemical and physical properties of Alamine 336 and Aliquat 336[20]

Property	Unit	Alamine 336	Aliquat 336
Molecular formula	-	R_3N	$R_3R'N^+Cl^-$
Chemical formula	-	$C_{24}H_{51}N$	$C_{22}H_{54}N^+Cl^-$
Molecular mass	kg/mol	353.7×10^{-3}	404.2×10^{-3}
Specific gravity	kg/m^3	8.15×10^2	8.87×10^2
Pour point (ASTM)	°C	-54	-14
Flash point (ASTM)	°C	179	132
Surface Tension	N/m	0.053	0.028
Viscosity (4°C)	Pa.s	23×10^{-3}	6300
Viscosity (30°C)	Pa.s	11×10^{-3}	1450
Viscosity (60°C)	Pa.s	6×10^{-3}	197

with the alkyl chains $R = C_8H_{17}$ and $R' = CH_3$.

Another important property of the extractant used in SX is the solubility of the reagent in the diluent used in the extraction process.

In the case of Alamine 336 and Aliquat 336, the length of the alkyl chain has an effect on the solubility of the amine in water and in organic diluents. The longer the alkyl chain, the more soluble the amine will be in organic diluents and less soluble in aqueous solutions[99]. The solubility of the extractant used in SX has a direct effect on the solubility of the extractant-metal anion complex in the diluent. Large extractant-metal anion complexes can have limited solubility in the organic phase and can separate out as a third phase at the organic–aqueous interface. This third phase can be countered by using longer chain alkyl amines and/or by adding a modifier.

Alamine 336 and Aliquat 336 are C8-C10 alkyl amines and therefore completely miscible in diluents like cyclohexane, toluene, o-, p- and m-xylene, chloroform, kerosene, benzene, carbon tetrachloride, diisobutyl ketone, ethanol, isopropanol, n-butanol and n-decanol, amongst others.

b) Chemical stability

Tertiary amines (exemplified by **Alamine 336**) are very stable compounds when in contact with both acid and alkali aqueous solutions. However, under highly oxidizing conditions and in the presence of nitrate ions they can degrade to form nitrosamines. Besides reducing the amine concentration, nitrosamines are also carcinogenic.

Tertiary alkyl amines are more stable than secondary amines and these are more stable than primary amines. Thus, high quality tertiary amines are compulsory when extracting with anion extractants. Alamine 336 has a low secondary amine content.

On the other hand, quaternary amines (such as **Aliquat 336**) are less stable in alkaline aqueous solutions than tertiary amines but are relatively stable in acidic aqueous solutions. Aliquat 336 can undergo elimination reactions (Hofmann Elimination)[99,100] and decomposes into an alkene, a tertiary amine and water when heated in the presence of alkali, or when it is reacted with strong alkali (approx. 1.0 mol/L NaOH)[99] a quaternary ammonium hydroxide is formed.

2.7. Conclusion

According to the literature, the application of SX for the separation of Zr and Hf is clearly the most effective separation technique among others such as crystallisation, sublimation, distillation, reduction, use of solid ion-exchange resins and flotation. It seems to be the most promising way for various reasons (recovery of acids and diluents, good separation factors, higher throughput, continuous operation, *etc.*)

Since the establishment of the MIBK and TBP processes, none of the many SX techniques described in section 2.3 have reached industrial production due to many technological and environmental problems. These problems include: low separation efficiency, thus larger amount of stages required; low metal concentration in the aqueous feed, thus low production turnover; high cost and solubility losses of extractants; large consumptions of extractants and reagents; the use of volatile diluents, energy consumption, and waste production, which have to be solved. No indication in literature could be found of any attempt at an economical evaluation of these processes.

In recent years, however, attention is converging on the use of liquid anion exchangers, comprising of high molecular weight amines like Alamine 336 and Aliquat 336. These extractants, together with different diluents, gave promising results for the separation of Zr and Hf, and they have a low solubility in the aqueous phase, good stability and good coalescence properties when mixed with a diluent and modifier, and hence conform to requirements of extractants used in hydrometallurgy.

Thus, according to this conclusion, it was decided to follow the amine route for the current study. An integrated investigation was necessary, because there was no certainty of how the $K_2Zr(Hf)F_6$ feed material would extract from acid chloride solutions with these amines.

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CHAPTER 3

3. EXPERIMENTAL METHODS

3.1. Experimental Design

3.1.1. *Materials and reagents*

a) Aqueous phase:

All chemicals used in this research were of analytical reagent grade. Zr(IV) and Hf(IV) salts were tested in the three different forms; potassium hexafluorozirconte ($K_2Zr(Hf)F_6$) with a 1-3% Hf(IV) content, zirconium tetrachloride ($ZrCl_4$) and hafnium tetrachloride ($HfCl_4$) that were mixed to the desired Hf(IV) content, and zirconium oxochloride ($ZrOCl_2$) with a 1-3% Hf(IV) content, all obtained from Sigma-Aldrich. Hydrochloric acid (32% HCl), sulphuric acid (95% H_2SO_4) and nitric acid (55% HNO_3), obtained from Merck (Saarchem products), were used to adjust the pH of the feed solution. Deionized water with a resistivity of >18 MΩ/cm (Milli-Q system, Millipore) was used throughout the experiments.

b) Organic phase:

The two amine extractants (Alamine 336 and Aliquat 336) were commercial samples of Cognis Corporation, in Cincinnati, Ohio, and kindly supplied by Anglo Platinum, South Africa. The diluents used to dilute the extractants were cyclohexane, toluene, m-xylene and kerosene, all analytical-grade reagents, supplied by Merck. 1-Octanol, obtained from Sigma Aldrich, was used where necessary as a modifier in the organic phase.

3.1.2. *Apparatus*

Shake-out tests were carried out in separation funnels in the laboratory to narrow the wide range of possible reagents and extraction conditions for the selective extraction of the metals. The batch SX setup is shown in Figure 8.

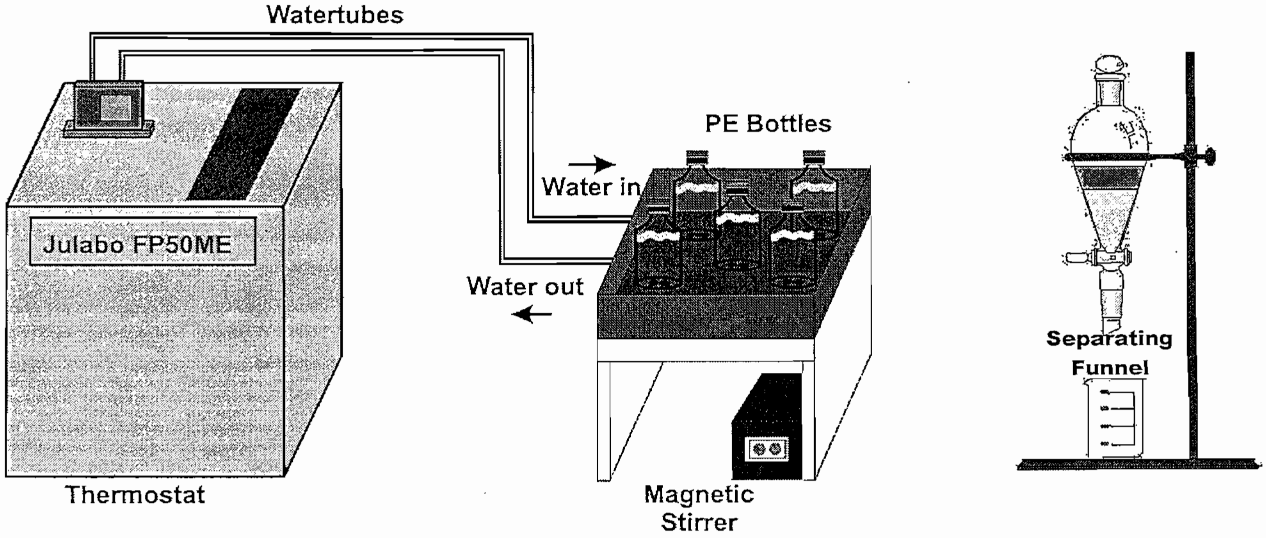

Figure 8: Experimental setup for the bench-scale SX of Zr and Hf

A magnetic stirrer was used for mixing the two liquid phases. A thermostatted bath was used to keep the extraction solution at constant temperature during phase separation. After extraction, phase separation proceeded via centrifugation and separating funnels, with the analysis immediately thereafter.

3.2. Extraction Procedure

Different acid concentrations were made up by volume from commercial, concentrated 10.2 mol/L HCl (32%). The aqueous phases were prepared by dissolving 10 g/L $K_2Zr(Hf)F_6$ and 1 g/L $Zr(Hf)Cl_4$ with different Zr/Hf ratios in solutions of 0-10 mol/L HCl and deionised water in volumetric flasks. Known masses of Aliquat 336 or Alamine 336 were added to the volumetric flasks and the cyclohexane was weighed to obtain the organic phase, which contained an additional 1-octanol (3% v/v) as modifier. The organic phase was then saturated with HCl solutions having the same concentration as that from which the extraction was carried out, in order to prevent HCl absorption by the extractant during the extraction process, ensuring constant chloride ion concentrations in the aqueous phase. Extraction experiments were carried out by taking a constant volume phase ratio of 1:1 (50 ml from both the aqueous and organic phases) placed in a 150 ml polypropylene flask and stirred mechanically with a custom-built magnetic stirrer at 25°C until equilibrium was reached. The temperature was controlled by a FP50-ME Julabu thermo bath. The liquid phases were then left to separate in separation funnels at 25°C. The concentrations of Zr(IV) and Hf(IV) in the aqueous phase were determined by ICP-OES.

When the tests for equilibrium were done, more shake-outs were necessary to determine the following:

- Specificity of the extractant for Zr and Hf
- Loading capacity
- pH and temperature dependency
- Requirements of modifiers or special diluents
- Scrubbing and stripping characteristics

All the extraction experiments were basically performed in the same manner. Specific detail for the different experiments is given together with the results in Chapter 4. The data obtained in the bench-scale shake-outs were utilised to construct flow ratio- and number of stages-diagrams, which are useful in the process design for estimating the number of theoretical extraction stages required to obtain complete separation according to standards for the nuclear industry, and were prepared for both extraction and stripping operations (see Chapter 5).

CHAPTER 4

4. RESULTS & DISCUSSION

4.1. Initial Studies

4.1.1. *Modifier requirements*

Initial studies were carried out to test the behaviours of the two extractants, Alamine 336 and Aliquat 336. During testing the Aliquat 336, it was observed that the organic phase has a tendency for emulsification with an increase in chloride concentration by HCl addition to adjust the pH of the aqueous feed solution. 1-Octanol was tested as a modifier, and it was found that it completely eliminated the formation of emulsions. However, the amount of modifier to be added to the solvent was uncertain, hence formation of a third phase was observed at higher concentrations of amine (>10% wt of the organic phase) in the organic phase, for both Alamine 336 and Aliquat 336, as shown in Figure 9.

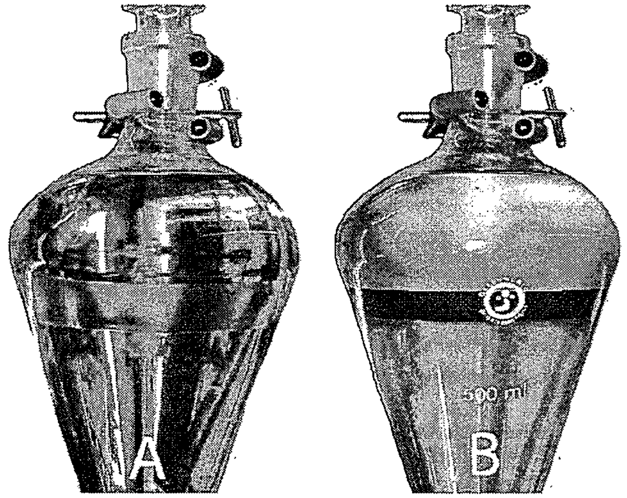

Figure 9: Third phase formation of a) 10%wt Alamine 336 and b) 10%wt Aliquat 336

The amount of modifier required to avoid the third phase formation was determined by contacting the aqueous and organic phases without the modifier to obtain the third phase. The three phases were allowed to settle out and then the lower aqueous phase was drawn off and discarded. 1-Octanol was then added from a burette in small increments to the two organic phases and the mixture shaken after each addition. 1-Octanol has a solubility of ~0.1% in water and the water does not substantially affect the formation of the two organic layers. 6.5 ml 1-octanol (2.6% v/v of the organic phase) was required to produce a 250 ml single organic phase. Thus ~3% v/v 1-octanol was necessary as a modifier to be added to the solvent in the extraction studies that continued. No effects of the modifier on the kinetics and equilibria of metal extraction and stripping were tested further; it was assumed that there were no effects.

4.1.2. *Establishment of equilibrium*

Poriel *et al.*[1] tested the kinetics of metal extraction with a Zr(Hf)Cl_4 solution containing high levels of Hf, Zr/(Zr + Hf) = 0.71 ([Zr] = 10.83 x 10^{-3} mol/L and [Hf] = 3.89 x 10^{-3} mol/L) in 7 mol/L HCl using 10.9 x 10^{-3} mol/L Aliquat 336 (5% wt) in toluene at 25°C as the solvent. The extraction conditions used in the work of Poriel *et al.* were repeated and a moderate approach to equilibrium was confirmed, as illustrated in Figure 10.

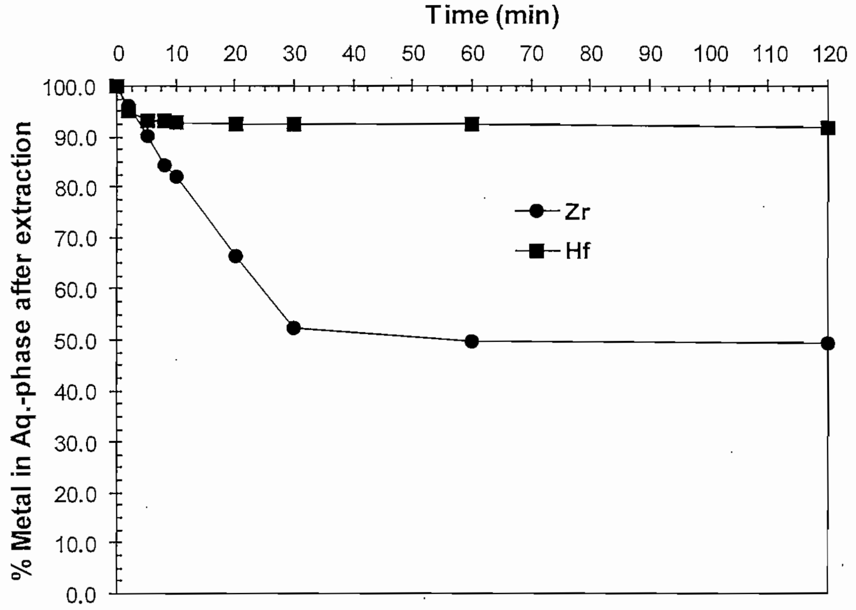

Figure 10: Rate of establishment of equilibrium, using 10.9 x 10^{-3} mol/L Aliquat 336 in cyclohexane, [HCl] = 8 mol/L at 25°C, phase ratio = 1:1. Zr/(Zr + Hf) = 0.71

The Zr "plateau" was achieved in less than 40 minutes, and for Hf, this equilibrium was achieved in less than 5 minutes. In the present work, the contact time of the batch extraction experiments was set at 60 min to be conservative, this also being the conditions chosen by the above-cited workers.

4.1.3. *Solvent pre-treatment*

Almost all solvent solutions used in SX processes require treatment, sometimes referred to as solvent equilibration, either prior to their initial use or after being stripped of the extracted metal species[2,3]. This is done by contacting the organic solution, containing the extractant, modifier and diluent in appropriate amounts, with a suitable aqueous solution prior to entering the extraction stage. The objective of this pre-treatment is to provide an extractant which will effectively extract the required metal ions, either because of the form of the active constituent of the extractant or by maintaining the necessary extraction pH prior to extraction. This ensures that the equilibration process of the extractants does not skew the experimental observations.

The extraction of metal species by Alamine 336 and Aliquat 336 occurs via ion association, whereby a large, positively charged organic molecule causes the extraction of a large anionic metal complex into the organic-phase with associated removal of a small common anion to the aqueous-phase. In order for the Alamine 336 to act in this manner it must be first converted to an amine salt (Eq. 17):

$$\left[R_3N\right]_{(org)} + \left[H^+\right]_{(aq)} + \left[A^-\right]_{(aq)} \rightarrow \left[R_3NH^+A^-\right]_{(org)} \qquad (17)$$

This is accomplished by contacting the solvent with an appropriate aqueous acid. In this case, HCl is used (Eq. 18):

$$\left[R_3N\right]_{(org)} + \left[HCl\right]_{(aq)} \rightarrow \left[R_3NH^+A^-\right]_{(org)} \qquad (18)$$

In the case of Aliquat 336, the active constituent is already in the form of a salt (see Chapter 2, Figure 7). However, in the present study the solvent was also contacted with HCl, to maintain the necessary extraction pH prior to extraction. This also helps to prevent HCl absorption by the extractant during the extraction process, ensuring constant chloride ion concentrations in the aqueous phase. The need for pretreatment of Aliquat 336 was confirmed by Poriel *et al.*[1].

4.1.4. *Extractant conditioning*

Commercially produced extractants are not pure and sometimes contain residual starting materials, by-products formed during manufacture or degradation products[2]. The presence of these impurities in the solvent system can produce cruds, good or poor phase separation and enhanced or poor loading characteristics. However, no extractant conditioning for the purification of Alamine 336 or Aliquat 336 was effected in the present study. It was assumed that, according to the manufacturer, Cognis[4], the two amine extractants were pure enough.

4.1.5. *Solubility studies*

The solubility of K_2ZrF_6 in water at different temperatures was determined as it was envisaged to use the data in further SX experiments to quantify the maximum amount of loading in the aqueous feed. The method used to determine the solubility of K_2ZrF_6 in H_2O is described below.

The solubility was determined at discrete temperatures of 25°C to 75°C at intervals of 10°C. An excess of K_2ZrF_6 was weighed in four separate polyethylene bottles. The same mass of salt was used for each bottle. 100 ml of deionised H_2O was measured using volumetric flasks and added to each of the four bottles. A magnetic stirrer bar was added to each mixture and the containers were sealed tightly using the screw cap. The bottles were then immersed in a waterbath that was used to keep the temperature constant for 24 hours at the desired temperature setting. The waterbath was placed on top of four magnetic stirrers of the same type and the same agitation speed was used on each stirrer whereby the mixtures in each bottle could be kept well mixed. One hour was allowed after the bottles were placed in the waterbath to allow the mixture to achieve thermal equilibrium; thereafter the 24 hour period was commenced.

Just before the 24 hour period was completed, the masses of four different filter papers were determined. After the mixtures were held at a constant temperature for 24 hours, the mixtures were filtered as quickly as possible using a Büchner funnel and ethanol was used to wash the remainder of the undissolved salt from the inside of the containers. The filtered products and filter papers from each of the four cases were dried overnight in an oven at 50°C. The mass of the dried product and filter papers were determined. Using this mass, the mass of the undissolved salt could be determined. The data from the four measurements were then used to determine the average solubility as well as the standard deviation, as shown in Figure 11.

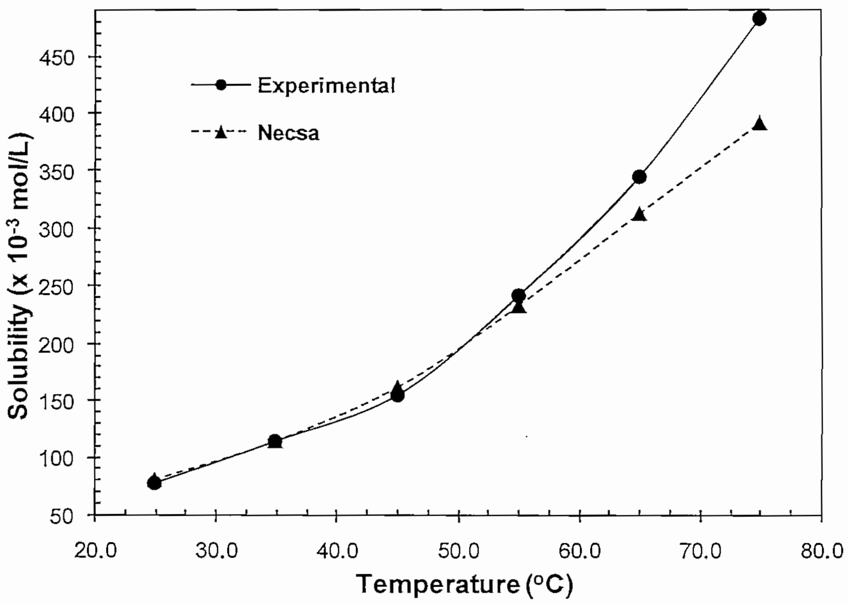

Figure 11: Solubility of potassium hexafluorozirconate ($K_2Zr(Hf)F_6$)

The results shown in Figure 11 indicate a relatively low solubility (20 g/L at 25°C) which increases with temperature. The % RSD for each of the measured datapoints did not exceed 0.11%.

These results were compared with data obtained by Nel[5] at the former Atomic Energy Cormporation of South Africa (AEC-AEK), now known as NECSA. The solubility of K_2ZrF_6 was well supported by these data obtained from literature.

4.2. Chloride Route for Zirconium and Hafnium Separations

4.2.1. *Solvent-extraction kinetics*

As stated in Chapter 2, the kinetics of SX governs, amongst other things, the throughput of the process.

Amine extractants are classified as surface-active extractants[2]. Hence, in the case of Alamine 336 and Aliquat 336, desorption of these surface-active extractants from the organic-aqueous interface can be the rate-determining step of the metal extraction process. This kinetic effect was tested by contacting a $Zr(Hf)Cl_4$ acidic solution, dissolved in 8 mol/L HCl, with 12.1 x 10^{-3} mol/L Alamine 336 or 10.9 x 10^{-3} mol/L Aliquat 336 (5% wt), diluted in cyclohexane, at 25°C with an agitation speed of 350 rpm and a phase ratio of 1:1. 3% v/v 1-Octanol was added as a modifier. This was repeated eight times for different contacting time periods, varying between 1 and 120 minutes. Results are shown in Figures 12 and 13.

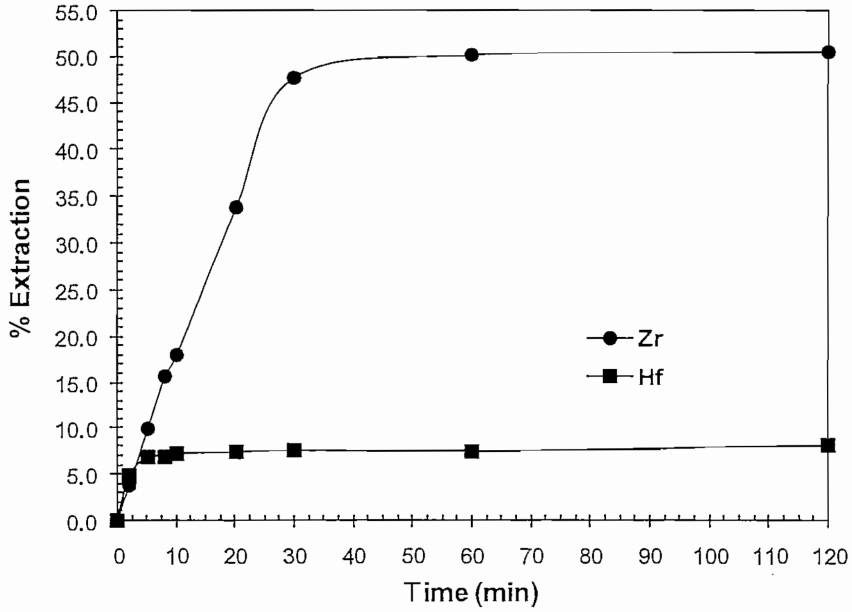

Figure 12: Kinetics of zirconium and hafnium extraction using 10.9 x10^{-3} mol/L Aliquat 336 in cyclohexane, [HCl] = 8 mol/L at 25°C, phase ratio = 1:1. Zr/(Zr + Hf) = 0.71 as Zr(Hf)Cl_4

According to Figures 12 and 13, for both Alamine 336 and Aliquat 336, the maximum extractions of 37% and 51%, respectively, were achieved after 30 minutes. However in the case of Alamine 336, it is better to not exceed a contact time of 30 minutes because a decrease in Zr extraction was observed when extracting beyond this point.

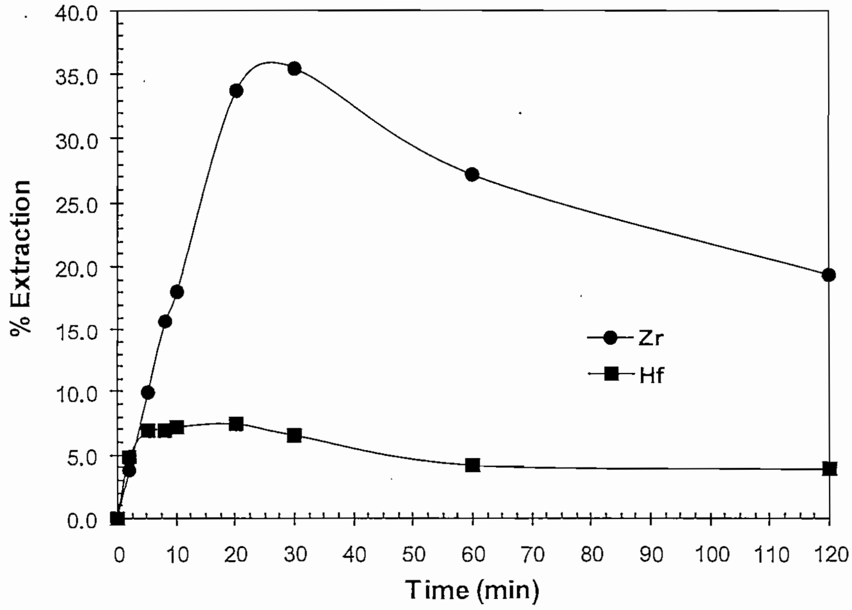

Figure 13: Kinetics of zirconium and hafnium extraction using 12.1 x 10^{-3} mol/L *Alamine* 336 in cyclohexane, [HCl] = 8 mol/L at 25°C, phase ratio = 1:1. Zr/(Zr + Hf) = 0.71 as Zr(Hf)Cl_4

A satisfactory explanation could not be found. Slow changing in metal speciation might be the cause of this observation. Data on the speciation of Zr(IV) and Hf(IV) and especially the rate of equilibration were not available and the explanation remains speculative.

The desorption effect reduces the rate of transfer of Zr(IV) and Hf(IV) species apparently as a result of "mechanical blocking", especially if the interfacial area is large due to excessive mixing. It is understood that this mechanical blocking refers to the interference of the miscibility and transportation (mass transfer rates) of the complex-containing phase. Thus, extraction with excessive mixing may be significantly different from that obtained with gentler mixing with the same system. Therefore an agitation speed of 300 rpm was used in continuing extraction studies. On the other hand, this agitation speed could not be reduced further because of the lack of contacting area between the two phases and thus poor mass transfer of the Zr-amine species into the organic phase.

4.2.2. *The effect of hydrochloric acid concentration*

All extractants of the chelating or acidic types used in SX processes liberate hydrogen ions on the extraction of a metal,

$$\left[M^{n-}\right]_{(aq)} + \left[nRH\right]_{(org)} \rightleftharpoons \left[R_nM\right]_{(org)} + \left[nH^+\right]_{(aq)} \tag{19}$$

The greater the amount of metal extracted, the more hydrogen ions are produced.

This effect results in a decrease in pH of the system and consequently a decrease in the further amount of metal that can be extracted. Thus, the pH of the system affects both the metal ion and the extractant, because if the pH is increased, the metal will eventually hydrolyse and will not extract. Above the pKa of the acidic extractant the extent of dissociation of the extractant is reduced. On the other hand, a decrease in pH will increase the hydrogen ion concentration, which may result in the formation of non-extractable metal species as a result of complexation with components of the aqueous phase[2].

In the case of metal extraction by ion-association or solvating extractants (like Alamine 336 and Aliquat 336), this oversimplification of pH dependence does not hold because these extractants are not primarily dependent on pH for metal complex formation, but rather on factors such as anion concentration in the aqueous phase. The extraction of metals by amines that are present as organic ammonium ions (anionic exchange) generally requires the formation of anionic metal species in the aqueous phase, which is achieved by the use of high salt or acid concentration.

Thus, in this particular case, the purpose of addition of high concentrations HCl in the aqueous phase is not only to adjust the pH but also to increase the chloride ion concentration.

The extraction of Zr and Hf as a function of chloride concentration was investigated using 12.1 x 10^{-3} mol/L Alamine 336 and 10.9 x 10^{-3} mol/L Aliquat 336 (5% wt), respectively, diluted in cyclohexane with the addition of 3% v/v 1-octanol to the organic phase. Aqueous phase acidities were varied from 1 – 10.2 mol/L HCl at 25°C. This was carried out at a phase ratio of 1:1 using mixtures of $ZrCl_4$ (10.8 x 10^{-3} mol/L) and $HfCl_4$ (3.9 x 10^{-3} mol/L) to obtain a metal ratio of Zr/(Zr + Hf) = 0.71 in the aqueous phase. The agitation speed did not exceed 300 rpm.

The effect of the chloride concentration on the extraction of Zr and Hf, when using the two different amine extractants, is illustrated in Figures 14 and 15.

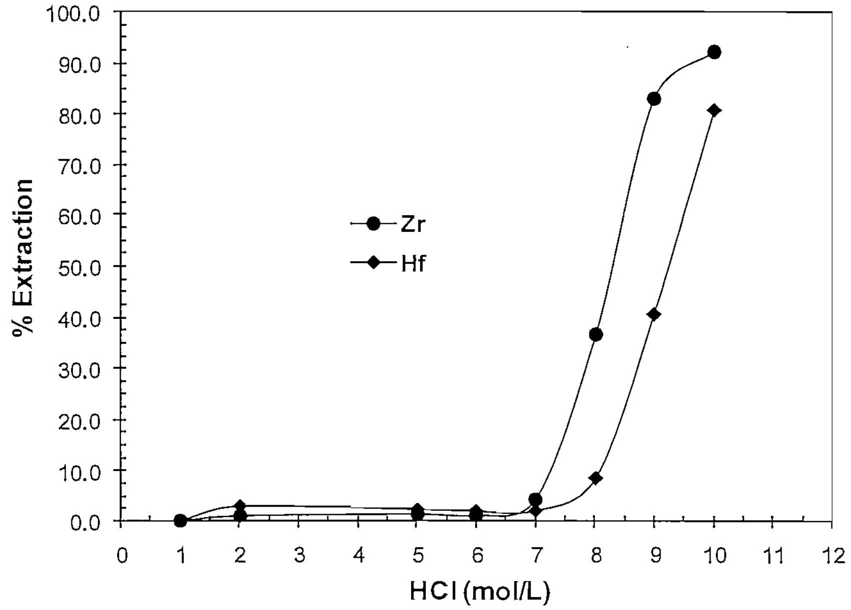

Figure 14: Effect of HCl concentration on the extraction of $Zr(Hf)Cl_4$ using 10.9 x 10^{-3} mol/L Aliquat 336 in cyclohexane at 25°C, phase ratio = 1:1. Zr/(Zr + Hf) = 0.71 as $Zr(Hf)Cl_4$

Poriel and co-workers[1] investigated the extraction of Zr and Hf with 5% wt Aliquat 336 in toluene over a range of aqueous phase acidities from 0 – 12 mol/L HCl at

25°C. They stated that Zr and Hf extraction increased with an increase in chloride concentration up to 8 mol/L for Zr and up to 11 mol/L for Hf.

The authors proposed the following extraction stoichiometry:

$$\left[nR_3R'N^+Cl^-\right]_{(org)} + \left[ZrCl_i^{(i-4)}\right]_{(aq)} + \left[(i-4)H^+\right]_{(aq)} \rightleftarrows \left[\left(R_3R'NH_{(i-4)}\right)_n ZrCl_{i+n}\right]_{(org)} \qquad (20)$$

Where n represents the stoichiometric coefficient, with R and R' the alkyl groups (C_8H_{17}) and (CH_3), respectively.

According to Figure 14, the extraction of Zr and Hf increases with increasing the chloride concentration up to 10.2 mol/L for both Zr and Hf. A remarkable difference between Zr and Hf is that Hf has a lower tendency than Zr to form anionic complexes, confirmed by Poriel *et al.*[1]. Thus, at 9 mol/L HCl the maximum amount of Zr (83.2% extraction) with the least amount of Hf (40.7% extraction) was extracted. This leads to a separation factor of up to 7.2. As described in Section 2.5.2(a), this separation factor is represented by the raffinate and not the extract stream.

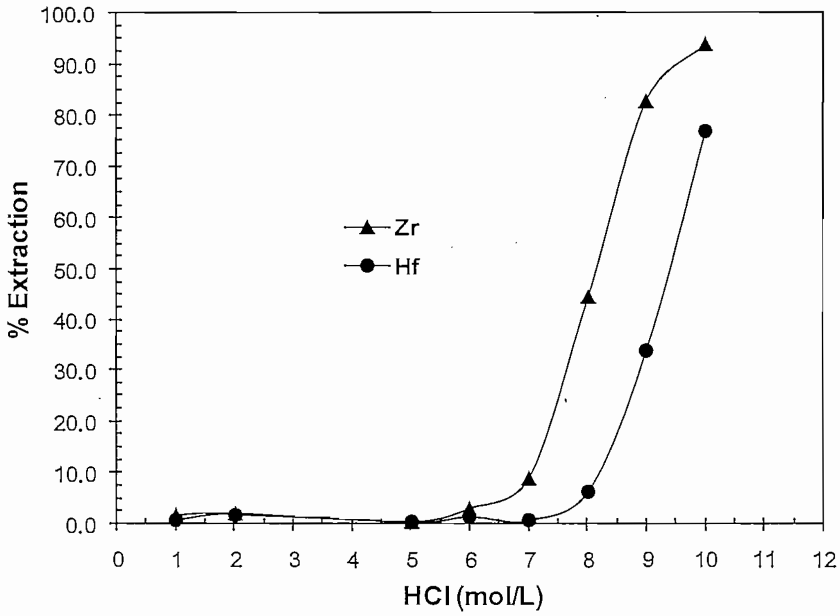

Figure 15: Effect of HCl concentration on the extraction of Zr(Hf)Cl_4 using 12.1 x 10^{-3} mol/L Alamine 336 in cyclohexane at 25°C, phase ratio = 1:1. Zr/(Zr + Hf) = 0.71 as Zr(Hf)Cl_4

In the case of Alamine 336, Zr and Hf were extracted in almost the same manner as Aliquat 336. Here, Hf has an even lower tendency to form anionic complexes than in the former case. Separation factors up to 15.2 were found with a maximum at 7 mol/L HCl, however the best extraction of Zr (44.4% extraction) with least amount of Hf (6.3% extraction) was obtained at 8 mol/L HCl which gave a separation of SF = 11.2. At 9 mol/L HCl, there was an increasing amount of Zr (82.9% extraction) extracted, however, a great amount of Hf (40.7% extraction) was simultaneously extracted which leads to a poorer separation factor of up to 9.4. The overall separation efficiency of Alamine 336 was better than that of Aliquat 336. The extraction reaction, as proposed by Poriel *et al.*[1] is indicated with Equation 21.

$$\left[nR_3N^+Cl^-\right]_{(org)} + \left[ZrCl_i^{-(i-4)}\right]_{(aq)} + \left[(i\text{-}4)H^+\right]_{(aq)} \rightleftharpoons \left[\left(R_3NH_{(i-4)}\right)_n ZrCl_{i+n}\right]_{(org)} \tag{21}$$

Poriel *et al.*[1] describe the lower tendency of Hf to form anionic complexes with the Hard-Soft Acid-Base theory (HSAB), discussed in Section 2.1.2. They stated that Zr and Hf are regarded as hard acids, however values of absolute hardness calculated for Zr and Hf indicate that Hf is less hard than Zr. Thus, in the SX process using liquid anion extractants, the hard base (Cl^-) will preferably form inner-sphere anionic complexes with Zr that are extracted to the organic phase by Alamine 336 and Aliquat 336.

4.2.3. *The effect of extractant concentration*

The extractant concentration required to extract Zr species, at a phase ratio of 1:1, will depend essentially on the Zr concentration in the aqueous feed solution, hence it will depend on the stoichiometry of the proposed anion-exchange reaction (shown in Equations 22 and 23) and the formation constants of the extractable species.

Tertiary amines, Alamine 336:

$$\left[nR_3N^+Cl^-\right]_{(org)} + \left[ZrCl_i^{-(i-4)}\right]_{(aq)} + \left[(i\text{-}4)H^+\right]_{(aq)} \rightleftharpoons \left[\left(R_3NH_{(i-4)}\right)_n ZrCl_{i+n}\right]_{(org)} \tag{22}$$

Quaternary ammonium compound, Aliquat 336:

$$\left[nR_3R'N^+Cl^-\right]_{(org)} + \left[ZrCl_i^{-(i-4)}\right]_{(aq)} + \left[(i\text{-}4)H^+\right]_{(aq)} \rightleftharpoons \left[\left(R_3R'NH_{(i-4)}\right)_n ZrCl_{i+n}\right]_{(org)} \tag{23}$$

It is assumed that all of the above is also valid for Hf[1].

The influence of extractant concentration in the organic phase on Zr extraction, and thus Zr and Hf separation, was examined for 9 mol/L HCl with cyclohexane as the diluents, as illustrated in Figures 16 and 18. Mixtures of $ZrCl_4$ (10.8×10^{-3} mol/L) and

$HfCl_4$ (3.9 x 10^{-3} mol/L) were contacted for 60 minutes with eight different organic solutions at 25°C, each containing a different concentration of the extractant for both Aliquat 336 and Alamine 336 varying from 0 to 17% wt. 3% v/v 1-Octanol was added as modifier at every extraction.

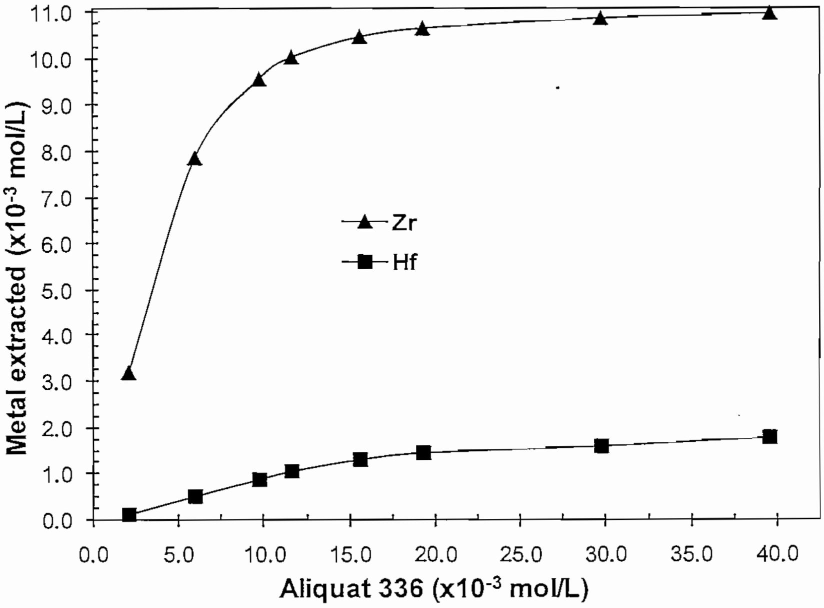

Figure 16: Effect of Aliquat 336 concentration on the extraction of Zr(Hf)Cl_4, using cyclohexane as diluent at 25°C, [HCl] = 9 mol/L, phase ratio = 1:1. Zr/(Zr + Hf) = 0.71 as Zr(Hf)Cl_4

It was expected that an increase in extractant concentration in the organic phase will ensure that there was an increase in the extraction of Zr-amine complexes from the aqueous phase. This expectation was confirmed according to Figure 16. Almost complete extraction of 10.76 x 10^{-3} mol/L Zr(IV) (99.1%) was atchieved with 39.7 x 10^{-3} mol/L Aliquat 336 (16.6% wt). Unfortunately the Hf extraction also increased (up to 87.6% extraction) with an increasing extractant concentration which causes a decrease in separation efficiency. Nevertheless, a separation factor of 15.2 with 39.7 x 10^{3} mol/L Aliquat 336 was obtained, even though the extraction of Hf was also high.

The circumstances of this high separation factor together with high Hf extraction can be explained by presenting the equilibrium data in terms of the distribution ratio of Zr and Hf, as illustrated in Figure 17 and 19.

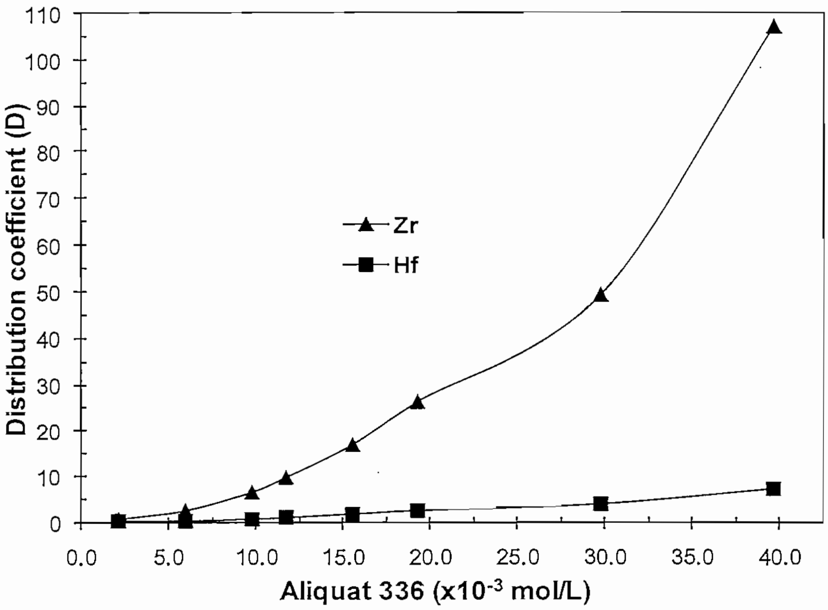

Figure 17: Effect of Aliquat 336 concentration on zirconium and hafnium distribution ratio, using cyclohexane as diluent at 25°C, [HCl] = 9 mol/L, phase ratio = 1:1. Zr/(Zr + Hf) = 0.71 as $Zr(Hf)Cl_4$

One would expect, when examining Figure 16, that the separation efficiency is at its best between 6.0 and 15.6 x 10^{-3} mol/L Aliquat 336 (between 3 and 7% wt) in the organic phase, however, according to Figure 17, a practically constant distribution of Hf was obtained when the Aliquat 336 concentration was varied from 1 – 16.6% wt, although a large increase in Zr distribution was observed because of the distribution coefficient that is directly dependent on the molar concentration of the Zr species that predominate in the aqueous phase and are then transferred to the organic phase, in relation to the Hf species.

The influence of Alamine 336 concentration in the organic phase on Zr extraction, and thus Zr and Hf separation, was examined under the same experimental conditions as the extraction with Aliquat 336. Mixtures of $ZrCl_4$ and $HfCl_4$, were dissolved in 9 mol/L HCl and contacted for 30 minutes with eight different organic solutions at 25°C, each containing different concentrations of Alamine 336 varying from 0 to 16.5% wt. 3% v/v 1-Octanol was added as modifier to prevent emulsions or third-phase formation.

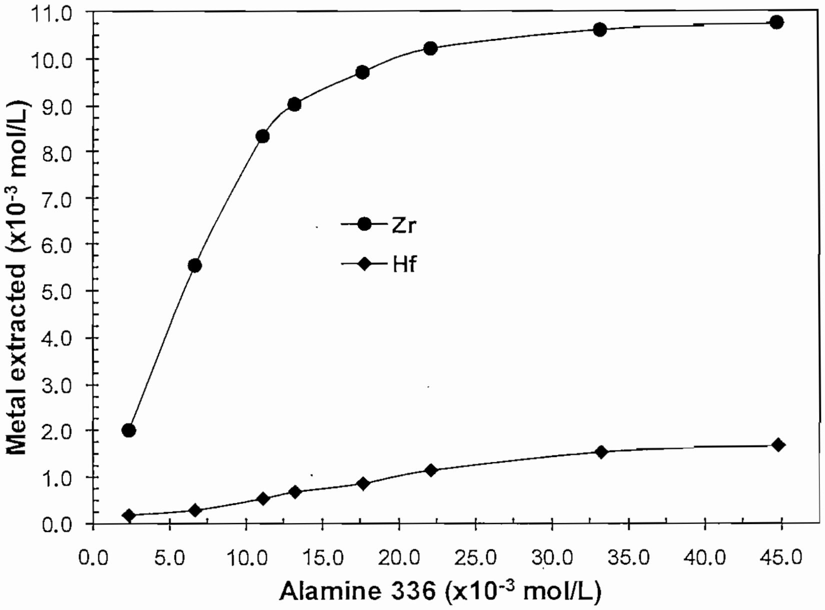

Figure 18: Effect of Alamine 336 concentration on the extraction of $Zr(Hf)Cl_4$, using cyclohexane as diluent at 25°C, [HCl] = 9 mol/L, phase ratio = 1:1. Zr/(Zr + Hf) = 0.71 as $Zr(Hf)Cl_4$

According to Figure 18, the extraction of Zr-amine complexes from the aqueous phase into the organic phase increased with an increase in Alamine 336 concentration as expected. In this case, the Zr extracted even more (99.4% extraction) at 44.9 x 10^{-3} mol/L Alamine 336 in the organic phase, than in the case of Aliquat 336. With 44.9 x 10^{3} mol/L Alamine 336 (16.5% wt) in the organic phase, 84.5% of the Hf extracted from the aqueous phase which leads to a separation factor of up to 30.2, double that of the Aliquat 336 extraction.

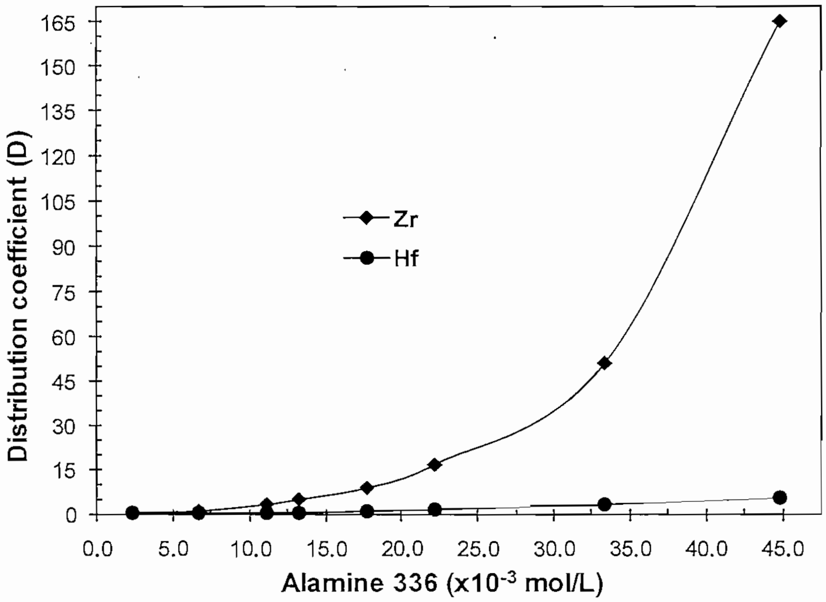

Figure 19: Effect of Alamine 336 concentration on zirconium and hafnium distribution ratio, using cyclohexane as diluent at 25°C, [HCl] = 9 mol/L, phase ratio = 1:1. Zr/(Zr + Hf) = 0.71 as $Zr(Hf)Cl_4$

Again, these phenomena can be explained with the expression of the separation efficiency in terms of the distribution ratios of Zr and Hf, as illustrated in Figure 19. The distribution of the Zr species into the organic phase increased largely with increasing Alamine 336 concentration in the organic phase, while a practically constant distribution of Hf was obtained when the Alamine 336 concentration was varied from 1 – 17% wt.

From these results, it is clear that the separation of Zr and Hf is stoichiometry dependent and, with the extractant concentration in the organic phase fixed, fluctuations in the Zr and Hf feed of the multi-step process will ensure co-extraction of the Hf species. Therefore, in order to inhibit excessive co-extraction of Hf, it was decided that the multi-step process should be operated at as close to saturation loading of the solvent as is practical with the Zr ion; in this way co-extraction of Hf will be depressed.

4.2.4. *Choice of diluent*

Ritcey and Ashbrook[6] describe all of the general requirements and properties governing the choice of diluent in SX processes. The most important factor, amongst many others, to be considered in this research was the effect of type of diluent on the extraction efficiency.

The diluents used to dilute the extractants were cyclohexane, toluene, m-xylene and kerosene, all supplied by Merck.

The effect of diluent on the extraction and separation of Zr and Hf was tested by performing four different extractions of Zr and Hf, each with a different diluent. Mixtures of $ZrCl_4$ (10.8 x 10^{-3} mol/L) and $HfCl_4$ (3.9 x 10^{-3} mol/L) were dissolved in 9 mol/L HCl and contacted for 30 minutes with four different organic solutions containing 12.0 x 10^{-3} mol/L Alamine 336 (5% wt), each diluted in cyclohexane, toluene, m-xylene or kerosene, respectively, at 25°C. 3% v/v 1-Octanol was added as modifier to prevent emulsions or third-phase formation.

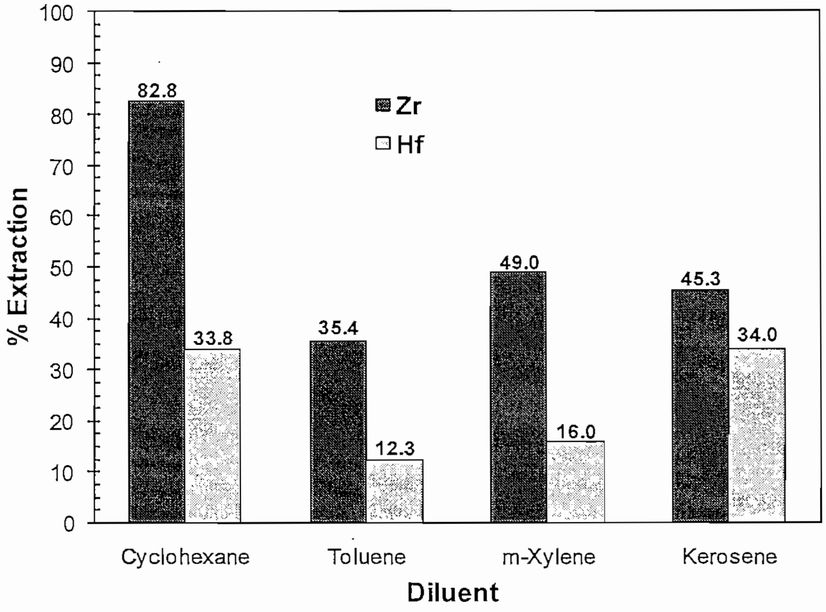

Figure 20: The effect of type of diluent on the extraction/separation efficiency, using 12.0 x 10^{-3} mol/L Alamine 336 at 25°C, [HCl] = 9 mol/L, phase ratio = 1:1. Zr/(Zr + Hf) = 0.71 as $Zr(Hf)Cl_4$

As seen in Figure 20, all four diluents have a greater tendency for complex formation of Alamine 336 with the Zr species. A higher extraction yield was obtained with cyclohexane, while a separation factor of 9.5 exists for this cycloalkane nonpolar diluent, in contrast with the low separation factor of the aromatic hydrocarbon diluents (3.9, 5.0 and 1.6 for toluene, m-xylene and kerosene, respectively). This selectivity and extractability favours cyclohexane as a diluent, in contrast to the third phase formation in the case of cyclohexane. However, this problem can be avoided by employing a modifier as discussed earlier, and thus could cyclohexane be used.

4.2.5. *Ageing of aqueous solution containing the zirconium and hafnium*

As discussed in Section 2.1.2, the hydrolysis and polymerisation of Zr and Hf species in acidic aqueous solutions are considered very important factors in Zr and Hf chemistry and thus in the extraction/separation studies of these two elements. For this reason, it was decided to examine the effect that ageing the aqueous feed solution has on the extraction efficiency, hence on the separation of Zr and Hf.

The following experiment was carried out. The extraction of Zr and Hf from a "fresh solution" was compared with the extraction of these elements from "old solutions". The "fresh solution" refers to a solution that was prepared just before the contacting of the two phases, while "old solutions" refers to solutions with a storage time of between one and seven days (24 – 168 hours). The maximum ageing period of seven days was assumed to be enough time for the aqueous solution to age, because it is unlikely for a commercial acidic solution to stay more than one week in the tanks of an industrial facility.

Four different acidic aqueous solutions, each containing the same ratio of mixtures of $ZrCl_4$ and $HfCl_4$, dissolved in 9 mol/L HCl, were prepared at different times before the day of extraction. At a certain day, all four aqueous solutions were contacted under the same extraction conditions with an organic solution containing 12.0 x 10^{-3} mol/L Alamine 336 and 3% v/v 1-octanol diluted with cyclohexane for 30 min at 25°C. A phase ratio of 1:1 was maintained constant during each run.

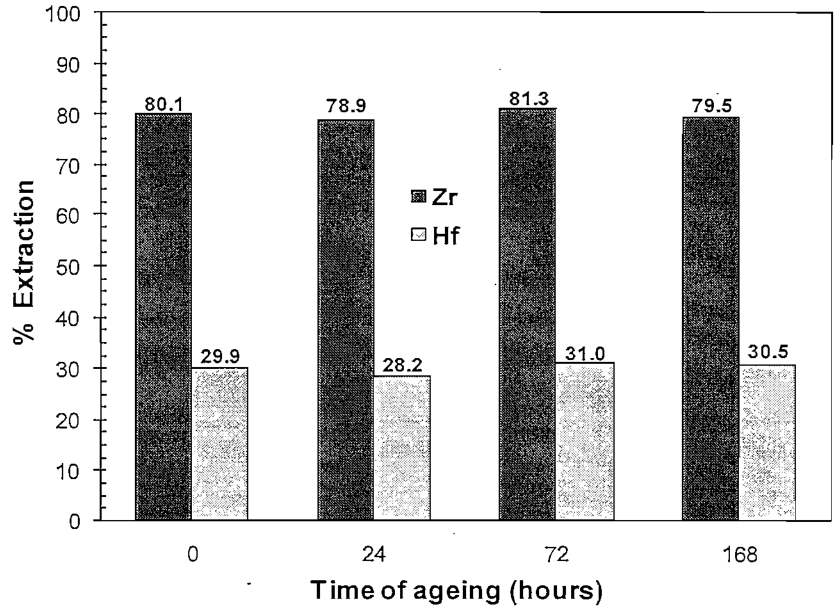

Figure 21: Effect of ageing the acidic aqueous solution on the extraction, using 12.0 x 10^{-3} mol/L Alamine 336 diluted with cyclohexane at 25°C, [HCl] = 9 mol/L, phase ratio = 1:1. Zr/(Zr + Hf) = 0.71 as $Zr(Hf)Cl_4$

According to results obtained, shown in Figure 21, no major differences in the extraction of either Zr or Hf between the "fresh" and "old" solutions were observed. The separation factors of these four extractions varied between 8.8 and 9.7, which are in good correlation with the results obtained in previous extraction experiments with Alamine 336. It is uncertain if there were any solvolysis reactions of Zr and Hf in the acidic aqueous solutions after seven days, however it is satisfying to know that there were no observed effects after a week of ageing the acidic aqueous feed solution.

4.2.6. *The effect of hydrochloric acid concentration on stripping*

Good extraction/separation results are of no use when stability of the extracted complex is so great that the recovery of the chosen element from the organic phase back into the aqueous phase is prohibited.

The stripping ability at a series of different concentrations was tested for HCl as stripping agent. The solvent was loaded by extracting the maximum quantity of Zr-amine complexes from a 9 mol/L HCl acidic aqueous solution, containing mixtures of $ZrCl_4$ (10.83 x 10^{-3} mol/L) and $HfCl_4$ (3.89 x 10^{-3} mol/L), with 44.9 x 10^{-3} mol/L Alamine 336 diluted in cyclohexane at 25°C. 10.77 and 3.87 x 10^{-3} mol/L Zr and Hf species were loaded respectively in the solvent. This loaded solvent was then contacted with eight different strip solutions with composition varying between 0 and 10.2 mol/L HCl for 60 minutes at 25°C and a phase ratio of 1:1.

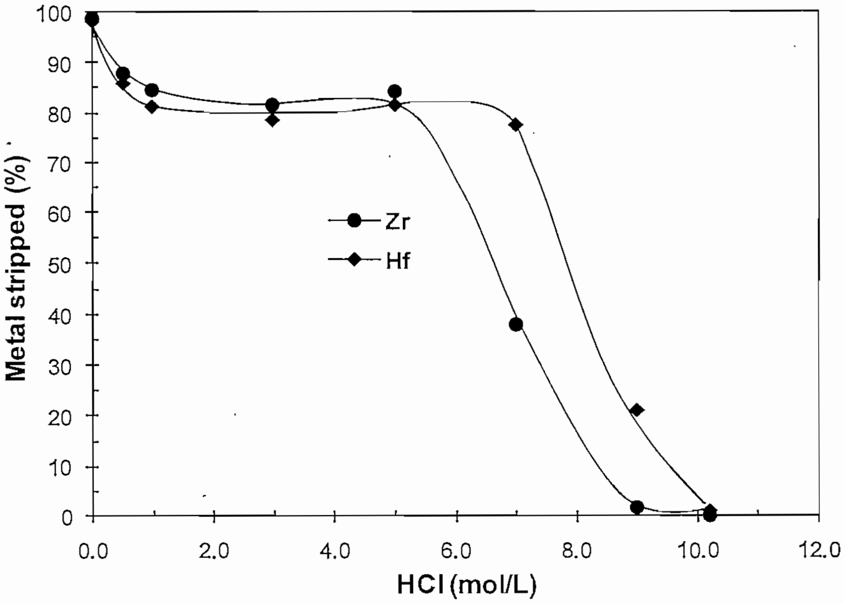

Figure 22: Effect of hydrochloric acid concentration on the stripping efficiency, using 0 – 10.2 mol/L HCl as stripping agent at 25°C, 10.77 x 10^{-3} mol/L Zr and 3.87 x 10^{-3} mol/L Hf as $ZrCl_4$, phase ratio = 1:1

It is clear from the results in Figure 22 that for anion-exchange systems, stripping with water will result in shifting the equilibrium far to the left. Thus, complete recovery (back extraction/stripping) of Zr and Hf species into the aqueous phase was obtained. Another important factor is that Hf has a greater tendency to be stripped from the solvent with 7 to 9 mol/L HCl. However, the stripping does not have any contribution to the selective separation of the Zr and Hf species.

4.3. Fluoride Route for Zirconium and Hafnium Separations

Now that the separation technique and analysis were established by obtaining satisfying extraction and stripping results from the chloride route for Zr and Hf separation, the next step was to verify the relevance of the fluoride route for Zr and Hf separation because of the significance of fluoride chemistry at NECSA. If the fluoride route could also deliver satisfying results, it would be more favourable because of the current fluoride production at NECSA.

4.3.1. *The effect of hydrochloric acid on the extraction*

The influence of HCl concentration was studied for both Aliquat 336 and Alamine 336 as extractants. 15.10 x 10^{-3} mol/L $K_2Zr(Hf)F_6$ was dissolved in eight different HCl solutions (0.1- 8.0 mol/L) to obtain the aqueous phase (the maximum solubility at 8 mol/L HCl is 4.28 g/L). The Aliquat 336 and Alamine 336 were diluted with cyclohexane to 30.20 x 10^{-3} mol/L to obtain the organic phase. 3% v/v 1-octanol was added as a modifier to eliminate third phase formation. The two phases were contacted for 60 minutes at 25°C. The effect of HCl concentrentration with Alamine 336 can be observed in Figure 23.

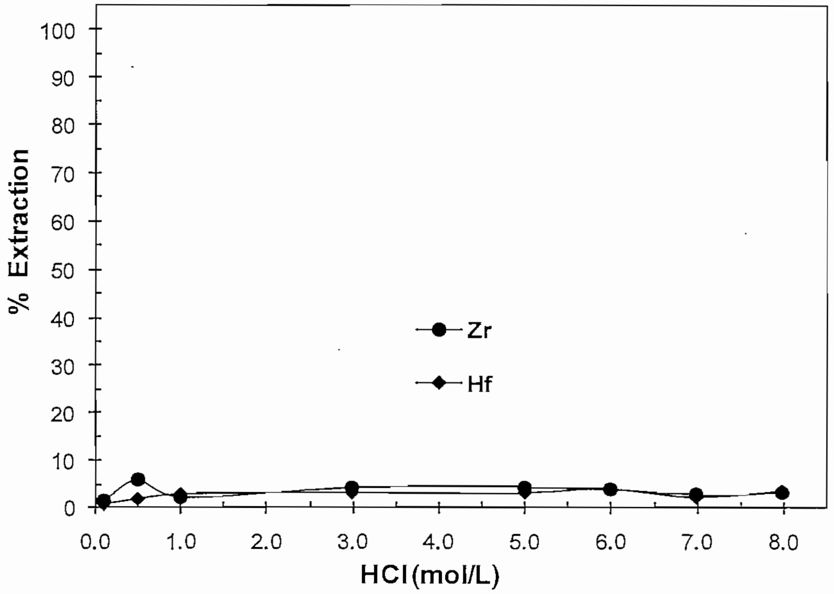

Figure 23: Effect of HCl concentration on the extraction of $K_2Zr(Hf)F_6$, using 30.20 x 10^{-3} mol/L Alamine 336 in cyclohexane at 25°C, [HCl] = 0.1 – 8.0 mol/L, phase ratio = 1:1

The extraction of Zr and Hf from $K_2Zr(Hf)F_6$ with Alamine 336 and Aliquat 336 proceeds via an anion-exchange reaction. The interaction of HCl with Alamine 336 (R_3N) can be described by the reaction:

$$\left[R_3N\right]_{(org)} + \left[HCl\right]_{(aq)} \rightleftharpoons \left[R_3NH^+Cl^-\right]_{(org)} \tag{24}$$

The extraction of Zr can be described by the following proposed reaction:

$$\left[ZrF_6^{2-}\right]_{(aq)} + \left[2R_3NH^+Cl^-\right]_{(org)} \rightleftharpoons \left[(R_3NH)_2ZrF_6\right]_{(org)} + \left[2Cl^-\right]_{(aq)} \tag{25}$$

The effect of HCl concentrentration with Aliquat 336 can be observed in Figure 24.

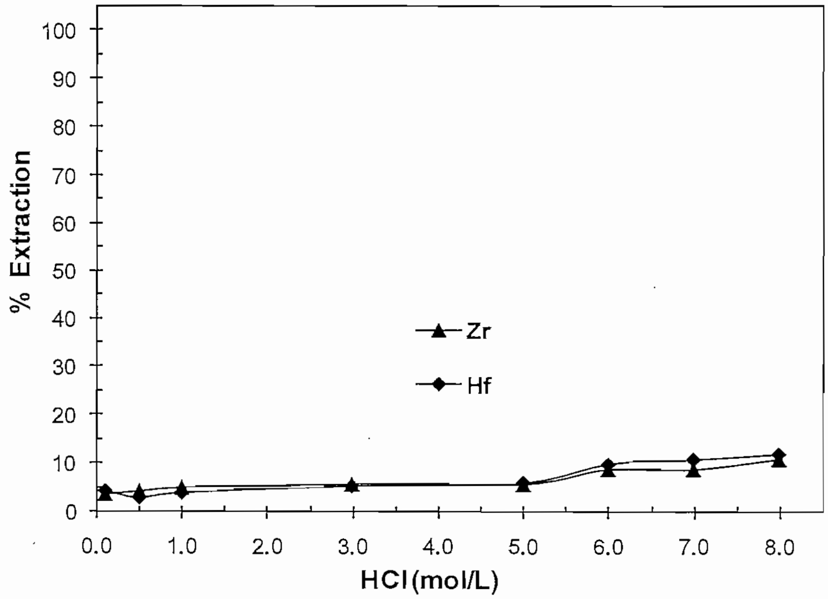

Figure 24: Effect of HCl concentration on the extraction of $K_2Zr(Hf)F_6$, using 30.20 x 10^{-3} mol/L Aliquat 336 in cyclohexane at 25°C, [HCl] = 0.1 – 8.0 mol/L, phase ratio = 1:1

For Aliquat 336, the extraction of Zr can be described by the following proposed reaction:

$$\left[ZrF_6^{2-}\right]_{(aq)} + \left[2R_3R'N^+Cl^-\right]_{(org)} \rightleftharpoons \left[(R_3R'N)_2ZrF_6\right]_{(org)} + \left[2Cl^-\right]_{(aq)} \tag{26}$$

According to Figures 23 and 24, a slight difference between Aliquat 336 and Alamine 336 could be obtained, however, the HCl concentration had no influence on the extraction of Zr and Hf, with the extraction efficiency not exceeding 10%. The minimal extraction of both Zr and Hf delivered no separation selectivity between the two metals. Although in the case of Aliquat 336, there was a minor increase between 5 and 6 mol/L HCl, extraction still did not exceed 10%.

4.3.2. *The effect of sulphuric acid on the extraction*

The influence of SO_4^{2-} ions, instead of Cl^- ions, in the aqueous phase was tested as a function of metal extraction for both Aliquat 336 and Alamine 336 as extractants. The amount of $K_2Zr(Hf)F_6$ in the acidic aqueous feed solution was kept constant at 15.10×10^{-3} mol/L – the same as the previous experiment. The acidic concentration of the aqueous solution was varied between 0.1 and 8.0 mol/L H_2SO_4. Cyclohexane was used to dilute the extractants to 30.20×10^{-3} mol/L, with an addition of 3% v/v 1-octanol as modifier. Extraction was carried out for 60 minutes at a constant temperature of 25°C.

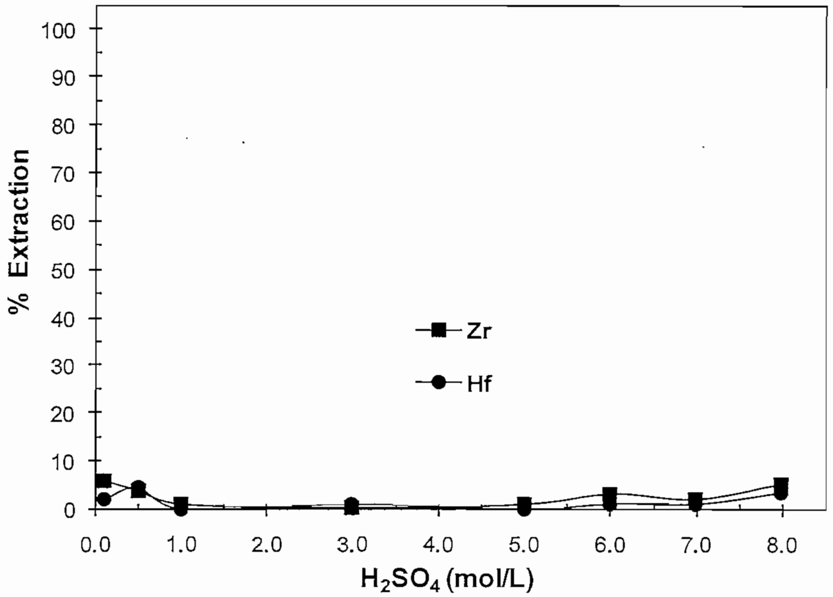

Figure 25: Effect of H_2SO_4 concentration on the extraction of $K_2Zr(Hf)F_6$, using 30.20×10^{-3} mol/L Alamine 336 in cyclohexane at 25°C, $[H_2SO_4]$ = 0.1 – 8.0 mol/L, phase ratio = 1:1

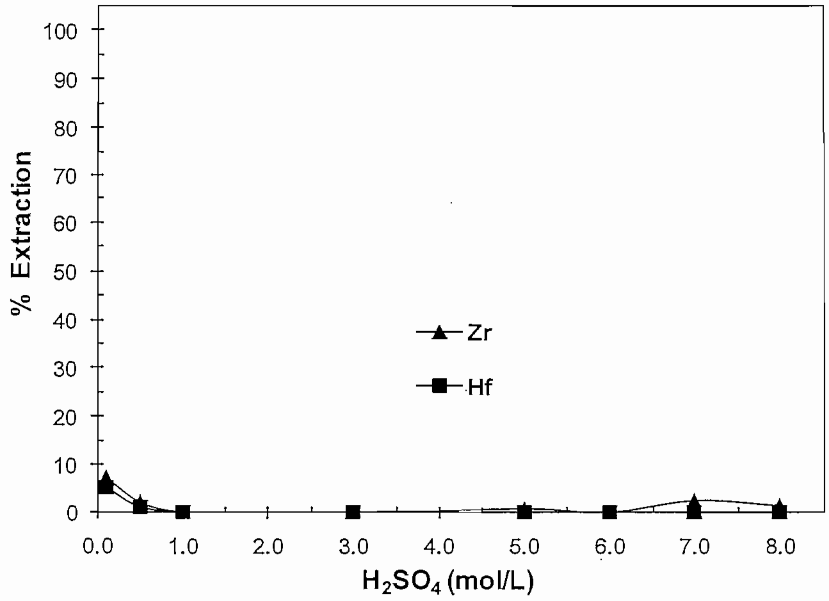

Figure 26: Effect of H_2SO_4 concentration on the extraction of $K_2Zr(Hf)F_6$, using 30.20 x 10^{-3} mol/L Aliquat 336 in cyclohexane at 25°C, [H_2SO_4] = 0.1 – 8.0 mol/L, phase ratio = 1:1

H_2SO_4 had little to no influence on the extraction of Zr and Hf, as seen in Figures 25 and 26. No difference in the extraction ability of Aliquat 336 and Alamine 336 could be found. A slightly higher extraction value was present at lower concentrations (0.1 mol/L H_2SO_4), but was still under 10%, and therefore the use H_2SO_4 was eliminated from consideration.

4.3.3. *The effect of nitric acid on the extraction*

The influence of HNO_3 concentrations (NO_3^- ions in the aqueous phase) was studied for both Aliquat 336 and Alamine 336 as extractants. The amount of $K_2Zr(Hf)F_6$ in the acidic aqueous feed solution was kept constant at 15.10 x 10^{-3} mol/L. $K_2Zr(Hf)F_6$ was dissolved in eight different HNO_3 solutions (0.1- 8.0 mol/L) to obtain the aqueous phase. Both extractants were diluted with cyclohexane to 30.20 x 10^{-3} mol/L, with an addition of 3% v/v 1-octanol as a modifier. Extraction was carried out for 60 minutes at a constant temperature of 25°C.

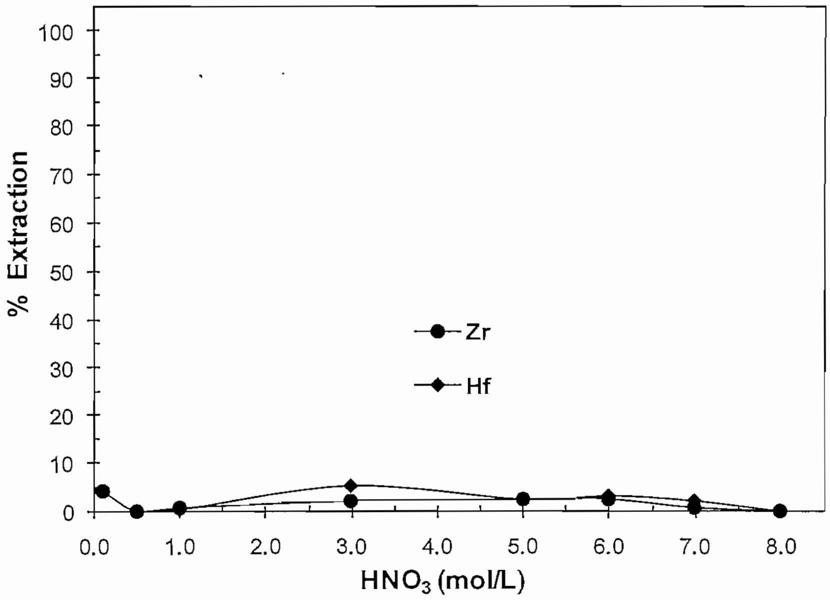

Figure 27: Effect of HNO_3 concentration on the extraction of $K_2Zr(Hf)F_6$, using 30.20 x 10^{-3} mol/L Alamine 336 in cyclohexane at 25°C, $[HNO_3]$ = 0.1 – 8.0 mol/L, phase ratio = 1:1

In this case, where NO_3^- ions are present in the aqueous phase, the tendencies of Alamine 336 and Aliquat 336 to form complexes with Hf were slightly greater than those for Zr. However, no separation using either of the extractants was observed and the extraction ability was less than 5%.

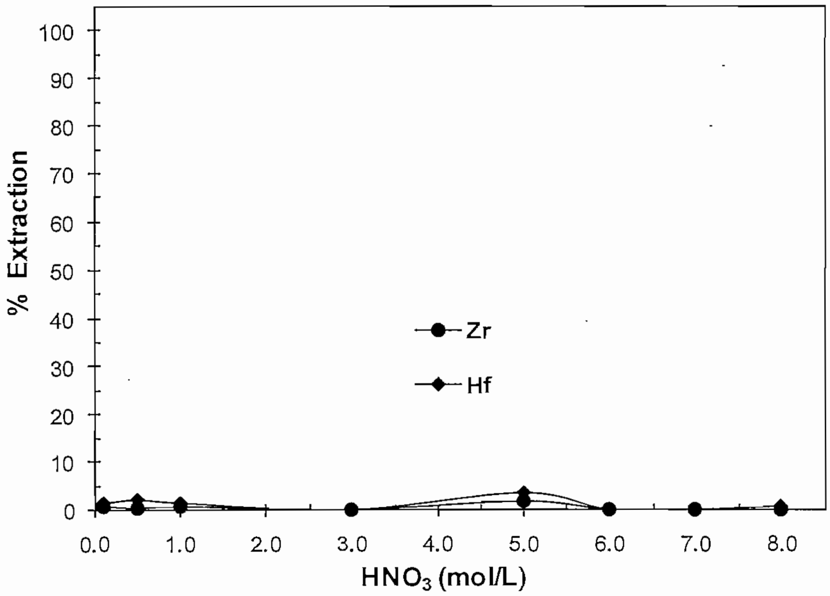

Figure 28: Effect of HNO_3 concentration on the extraction of $K_2Zr(Hf)F_6$, using 30.20 x 10^{-3} mol/L Aliquat 336 in cyclohexane at 25°C, $[HNO_3]$ = 0.1 – 8.0 mol/L, phase ratio = 1:1

Thus, none of the above-mentioned ions (Cl^-, SO_4^{2-} of NO^{3-}) present in the acidic aqueous feed solution had any influence on the extraction of Zr or *Hf. Due to the* presence of ZrF_6^{2-} species in the aqueous solution, the possibility of using hydrofluoric acid (HF), to increase the F^- ions and to eliminate the Cl^- ions in the aqueous solution could be the answer. However, due to the corrosiveness and toxicity of this reagent, extractions from acidic aqueous solutions containing high concentrations of HF were not considered.

4.3.4. *The effect of extractant concentration on the equilibrium*

The influence of excess extractants in the extraction process was tested by varying the quantities of Alamine 336 and Aliquat 336 between 1.0 x 10^{-3} and 30.0 x 10^{-3} mol/L in the organic phase.

The maximum amount of $K_2Zr(Hf)F_6$ that can be dissolved at 25°C in the amount of water needed to dilute 10.2 mol/L HCl to 7 mol/L HCl for the aqueous phase is 6.25 g/L (22.05 x 10^{-3} mol/L), after the acid is added. The organic phase was obtained by the dilution to 8 different Aliquat 336 and Alamine 336 concentrations with cyclohexane. 3% v/v Octanol was added as modifier. The two phases were contacted for 60 minutes at 25°C.

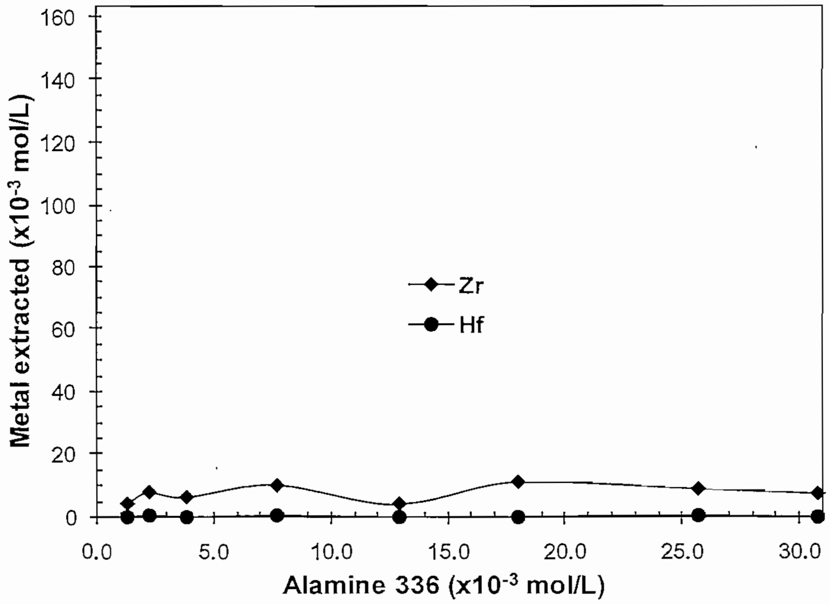

Figure 29: Effect of Alamine 336 concentration on the extraction with K_2ZrF_6, using cyclohexane as diluent at 25°C, [HCl] = 7 mol/L, phase ratio = 1:1

According to results obtained, shown in Figures 29 and 30, the excess extractant had no significant increase on the extraction of Zr or Hf. Both extractants did not exceed an extraction of 10% for both metals. The separation selectivity, when extracting with Alamine 336, was small but still insignificant. Little to no difference between the extraction with Alamine 336 and Aliquat 336 was observed, as seen from Figure 30.

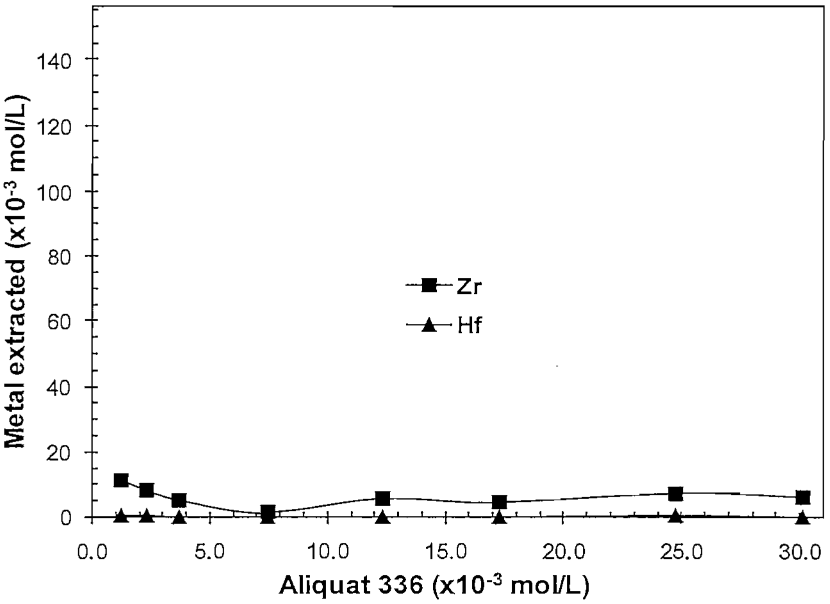

Figure 30: Effect of Aliquat 336 concentration on the extraction with K_2ZrF_6, using cyclohexane as diluent at 25°C, [HCl] = 7 mol/L, phase ratio = 1:1

4.3.5. *The effect of solvent pre-treatment on the extraction*

In previous cases of Zr and Hf extraction from fluoride-based compounds ($K_2Zr(Hf)F_6$), the organic solution, containing the extractant, modifier and diluent, was contacted with a suitable aqueous solution prior to entering the extraction stage. This is called solvent equilibration or solvent pre-treatment. However, the extraction ability of the two amine extractants on the ZrF_6^{2-} species was tested without "treating" the solvents prior to extraction.

22.05 x 10^{-3} mol/L $K_2Zr(Hf)F_6$ was dissolved in 7 mol/L HCl, contacted with an organic solution containing eight different Alamine 336 and Aliquat 336 concentrations between 1.0 x 10^{-3} and 30.0 x 10^{-3} mol/L, diluted in cyclohexane. 3% v/v 1-Octanol was added as a modifier. The two phases were contacted for 60 minutes at 25°C. No solvent pre-treatment was applied prior to extraction.

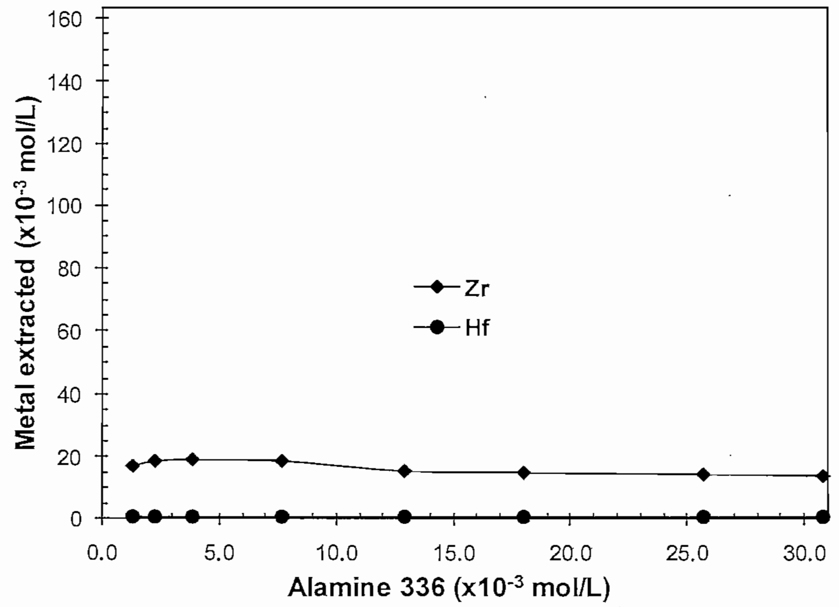

Figure 31: Effect of Alamine 336 concentration on the extraction with K_2ZrF_6 without solvent pre-treatment, using cyclohexane as diluent at 25°C, [HCl] = 7 mol/L, phase ratio = 1:1

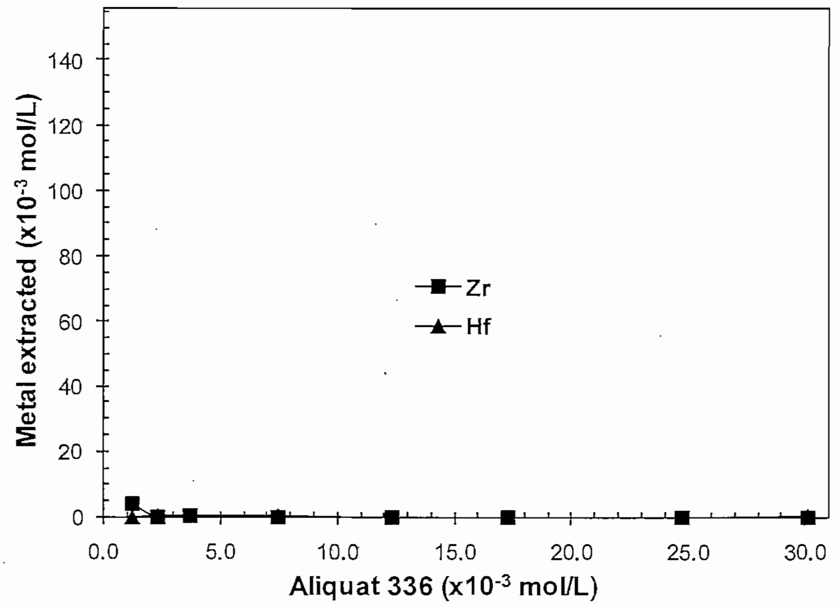

Figure 32: Effect of Aliquat 336 concentration on the extraction with K_2ZrF_6 without solvent pre-treatment, using cyclohexane as diluent at 25°C, [HCl] = 7 mol/L, phase ratio = 1:1

In Figure 31, the Zr extraction exceeded 10% between 0.5 and 9.0 mol/L Alamine 336, but was still unproductive: 13% is still too low with no selectivity. In the case of Aliquat 336, shown in Figure 32, there was a slight difference in the extraction of Zr and Hf with Alamine 336 and Aliquat 336, but no significant results were obtained and thus it can be assumed that the solvent pre-treatment has no effect on the extraction or on the selectivity.

4.3.6. *The effect of type of diluent on the extraction*

The effect of diluent on the extraction and separation of Zr and Hf via the fluoride route was tested by performing four different extractions of Zr and Hf, each with a different diluent. 22.05 x 10^{-3} mol/L (6.25 g/L) $K_2Zr(Hf)F_6$ was dissolved in 7 mol/L HCl and contacted for 60 minutes with four different organic solutions, each containing 12.0 x 10^{-3} mol/L Alamine 336 or 10.9 x 10^{-3} mol/L Aliquat 336 (5% wt), diluted in cyclohexane, toluene, m-xylene or kerosene, respectively, at 25°C. 3% v/v 1-octanol was added as a modifier to prevent emulsions or third-phase formation.

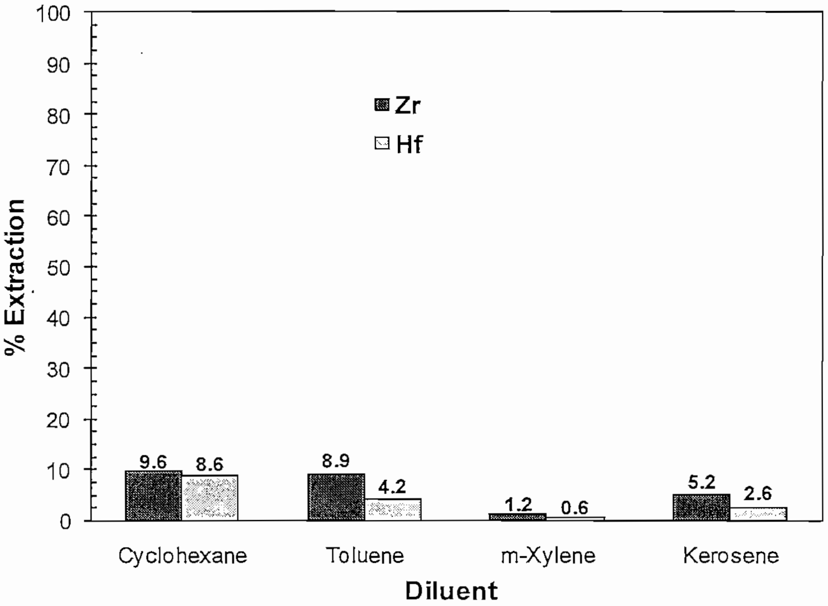

Figure 33: The effect of type of diluent on the extraction/separation efficiency, using 12.0 x 10^{-3} mol/L Alamine 336 at 25°C, [HCl] = 7 mol/L, phase ratio = 1:1

According to Figures 33 and 34, both Alamine 336 and Aliquat 336 extracted Zr and Hf better when diluted with cyclohexane, but the overall extraction of the two extractants did not improve when diluted in any of the above-mentioned diluents. There was no selectivity in the extraction between Zr and Hf. Thus, none of the four diluents tested gave any reason to believe that the effect of a different diluent will extract the Zr or Hf species.

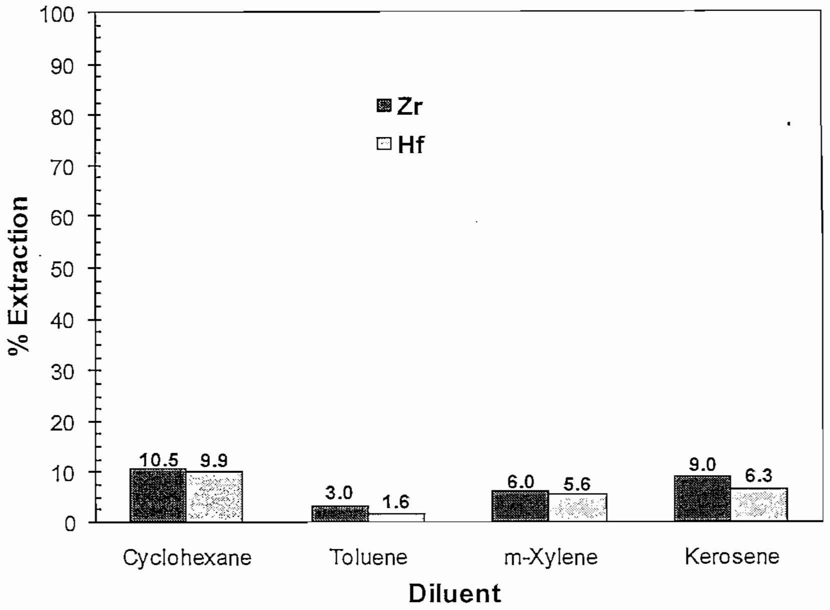

Figure 34: The effect of type of diluent on the extraction/separation efficiency, using 10.9 x 10^{-3} mol/L Aliquat 336 at 25°C, [HCl] = 7 mol/L, phase ratio = 1:1

4.3.7. *The effect of temperature on the equilibrium*

Temperature can have a considerable effect on the extractive properties of a SX process with respect to equilibrium, kinetics and metal separation The extraction of Zr and Hf was carried out with 22.05 x 10^{-3} mol/L $K_2Zr(Hf)F_6$ dissolved in 7 mol/L HCl as the aqueous phase and for the organic phase 12.0 x 10^{-3} mol/L Alamine 336 was diluted with cyclohexane and 1-octanol (3% v/v). The temperature was varied between 15 and 55°C to observe any changes on the extraction yield when operating at other temperatures than 25°C.

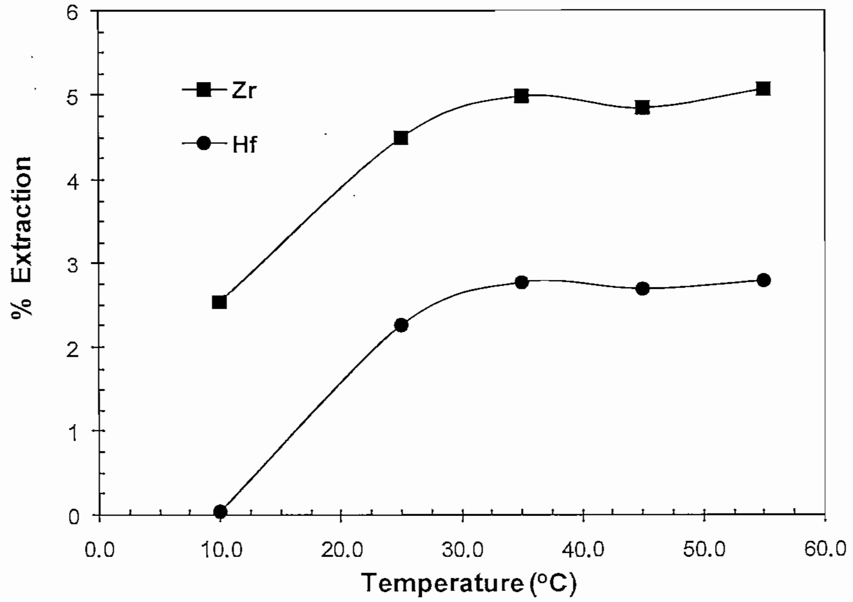

Figure 35: Close-up effect of temperature on the extraction with $K_2Zr(Hf)F_6$, using 12.0 x 10^{-3} mol/L Alamine 336 at 25°C, [HCl] = 7 mol/L, phase ratio = 1:1

In the case of zirconium fluoride compounds (ZrF_6^{2-}) there was no effect with respect to the above-mentioned factor. As seen from Figure 35, the extraction yield increased with an increase in temperature, but according to Figure 36, the overall extraction yield, temperature had little (<6%) effect on the extraction.

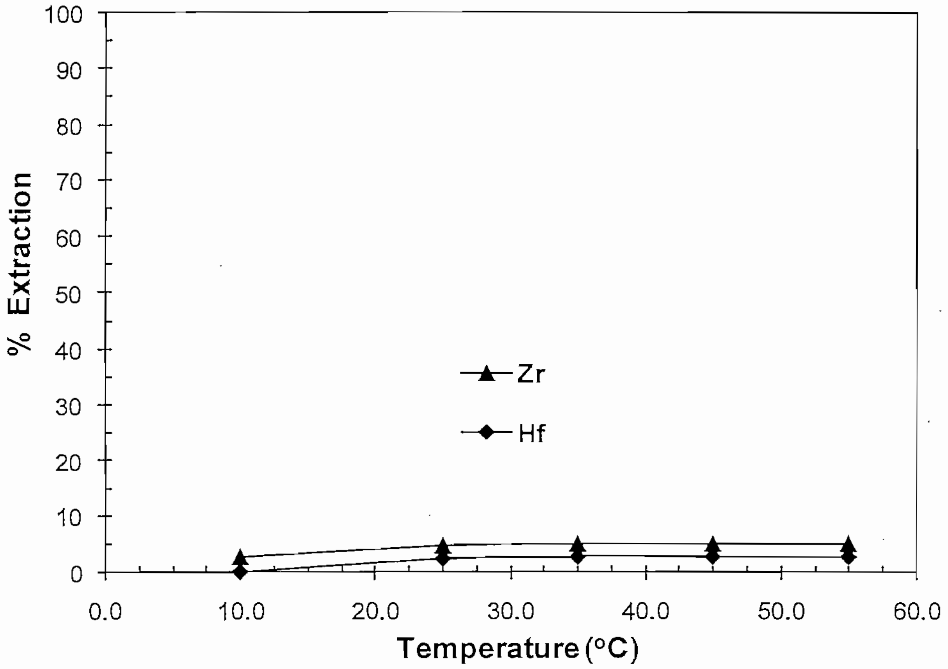

Figure 36: Effect of temperature on the extraction with $K_2Zr(Hf)F_6$, using 12.0 x 10^{-3} mol/L Alamine 336 at 25°C, [HCl] = 7 mol/L, phase ratio = 1:1

4.3.8. *Solvent-extraction kinetics*

The kinetics of SX is dependent on the various chemical reactions occurring in the system during contact and the rates of diffusion of the various species that control the chemistry of the SX process. This is one more reason why it is exceptionally important to understand the complex formation (speciation) regarding this study of Zr and Hf extraction from fluoride compounds.

The kinetics of the metal extraction with Alamine 336 and Aliquat 336 was tested by dissolving 22.05 x 10^{-3} mol/L K_2ZrF_6 in 7 mol/L HCl for the aqueous phase and 12.0 x 10^{-3} mol/L Alamine 336 or 10.9 x 10^{-3} mol/L Aliquat 336, diluted with cyclohexane, with an addition of 3% v/v 1-octanol as modifier to obtain the organic phase. Eight different time intervals for phase contact, varying between 1 - 120 minutes, were chosen for extraction.

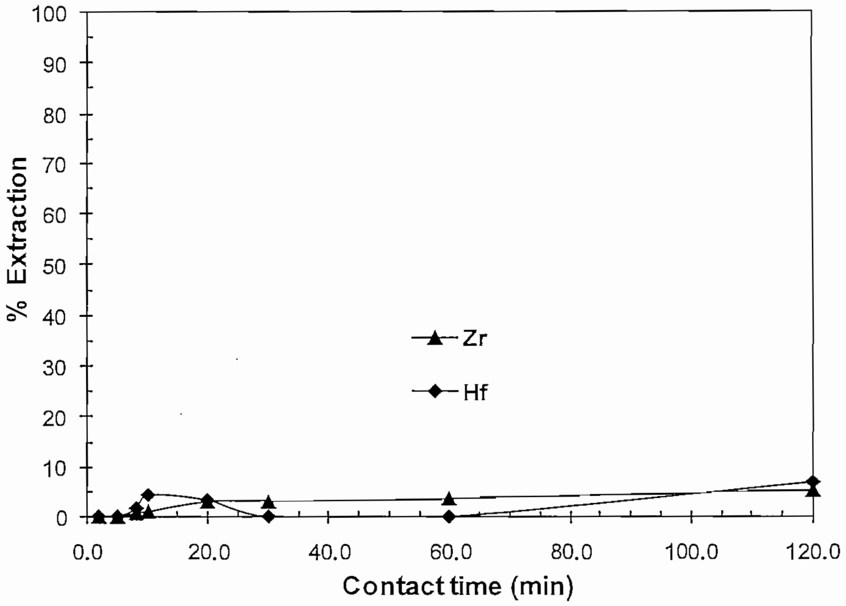

Figure 37: Kinetics of zirconium and hafnium extraction using 12.0 x10^{-3} mol/L Alamine 336 in cyclohexane, [HCl] = 7 mol/L at 25°C, phase ratio = 1:1

When using Alamine 336, shown in Figure 37, Hf showed a greater tendency extract within the first 20 minutes, whereas the extraction of Zr increased over time, although both metal extractions remained below 10%, and this phenomenon could be within analytical error. In Figure 38, Aliquat 336 extracted less Zr and Hf than Alamine 336 and no selectivity was observed. Hence, by exposing the two metals over a long period of time, no improvement in extraction yield was gained.

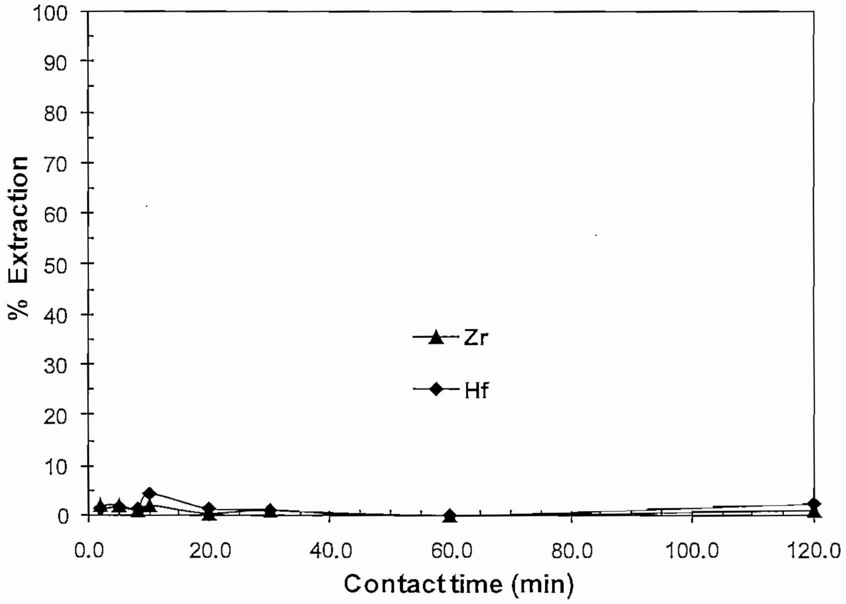

Figure 38: Kinetics of zirconium and hafnium extraction using 10.9 x10^{-3} mol/L Aliquat 336 in cyclohexane, [HCl] = 7 mol/L at 25°C, phase ratio = 1:1

4.3.9. *Ageing of aqueous solution*

Four different acidic aqueous feed solutions, each containing 22.05 x 10^{-3} mol/L $K_2Zr(Hf)F_6$ dissolved in 7 mol/L HCl, were prepared at different times before the day of extraction. On a certain day, all four aqueous solutions were contacted under the same extraction conditions with an organic solution containing 13.3 x 10^{-3} mol/L wt Alamine 336 and 3% v/v 1-octanol diluted with cyclohexane for 60 min at 25°C. A phase ratio of 1:1 was kept constant during each run.

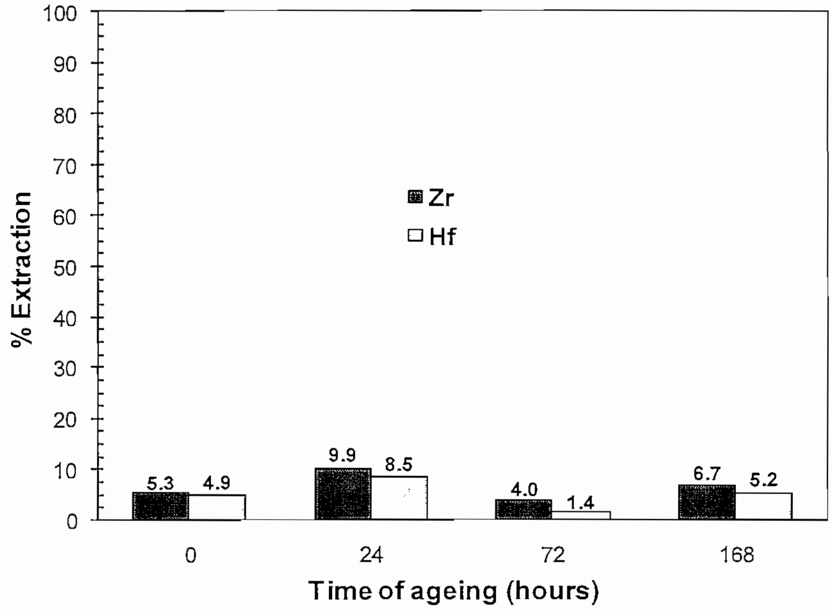

Figure 39: Effect of ageing the acidic aqueous solution on the extraction with Alamine 336

After leaving the acidic aqueous feed solution for 24 hours, the extraction yield increased to almost 10%, but decreased to less than 4% when left for 72 hours. After storing the aqueous solution for seven days (168 hours), extraction again increased. The actual metal concentrations are so low that it can be assumed that the difference is within experimental error. Therefore, there is no clear inclination of an effect on the extraction yield with ageing of these feed solutions.

The unfortunate results obtained in the extraction of Zr and Hf from fluoride compounds leads us back to the discussion of Zr and Hf speciation in aqueous solutions. This is due to the lack of knowledge of the complex formation reactions. It is therefore difficult to choose a promising extractant and integrated extractive conditions for the selective extraction of the Zr or Hf species.

This study shall be continued in the future. However it is not part of the current investigation.

4.4. Other Routes for Zirconium and Hafnium Separations

Before finalising the choice of extractant, we tried to observe any additional differences and preferable improvements in the extraction and purification of Zr metal with the two amine extractants by using other sources of aqueous feed solutions. This was done with two other Zr compounds, zirconium oxychlorides ($ZrOCl_2.8H_2O$) and zirconium nitrates ($ZrO(NO_3)_2$). Both of these compounds can be derived from zircon ore in the same way as the chloride- and fluoride-based compounds with only minor variations in the process route. The effect of two additional kinds of Zr- and Hf- containing salts were examined over a range of HCl solutions.

4.4.1. *Zirconium oxychlorides*

The extraction of Zr and Hf as a function of chloride concentration was investigated using 12.0 x 10^{-3} mol/L Alamine 336 and 10.9 x 10^{-3} mol/L Aliquat 336, respectively, diluted in cyclohexane with the addition of 3% v/v 1-octanol to obtain the organic phase. 15.52 x 10^{-3} mol/L $ZrOCl_2.8H_2O$ was dissolved in a range of aqueous phase acidities varying from 1 – 10.2 mol/L HCl, to obtain the aqueous phase. The extraction was carried out at a phase ratio of 1:1 at 25°C for 60 minutes.

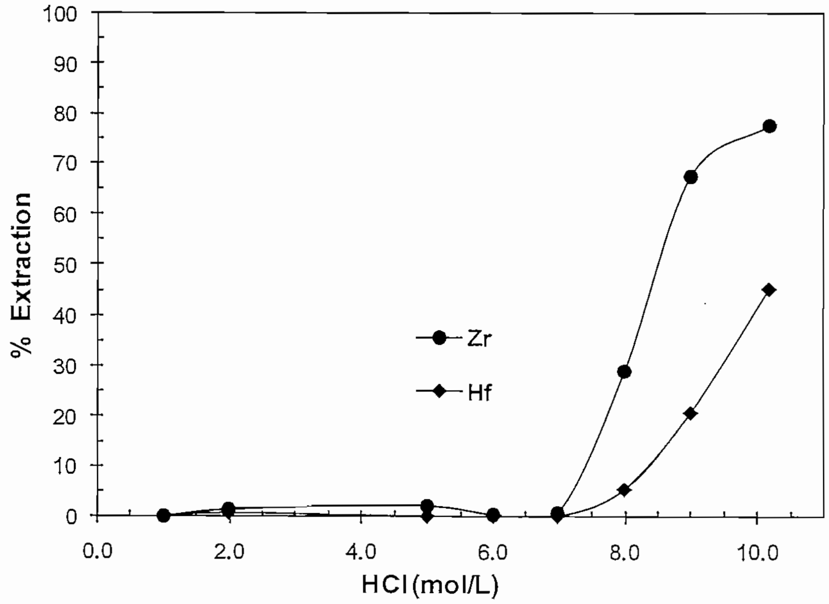

Figure 40: Effect of HCl concentration on the extraction of $ZrOCl_2.8H_2O$, using 12.0 x 10^{-3} mol/L Alamine 336 in cyclohexane at 25°C, [HCl] = 0.1 – 10.2 mol/L, phase ratio = 1:1

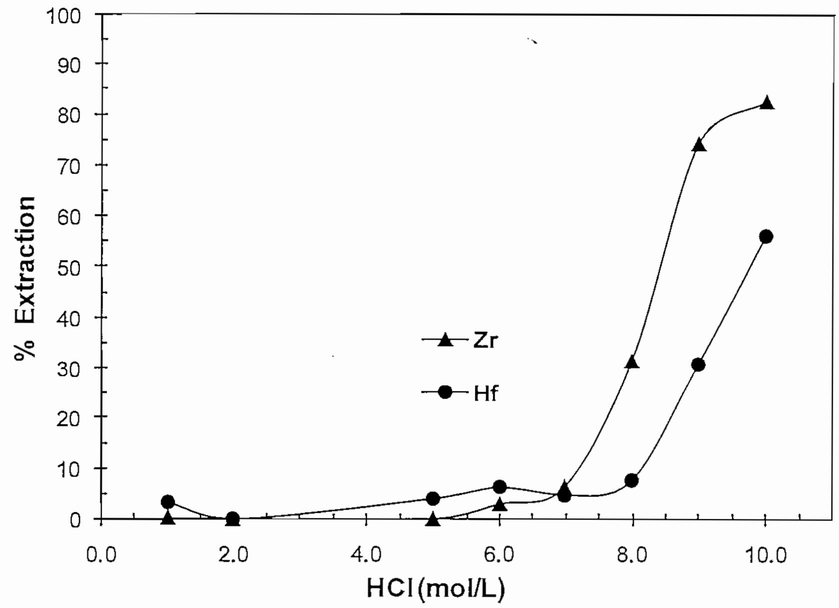

Figure 41: Effect of HCl concentration on the extraction of $ZrOCl_2.8H_2O$, using 10.9 x 10^{-3} mol/L Aliquat 336 in cyclohexane at 25°C, [HCl] = 0.1 – 10.2 mol/L, phase ratio = 1:1

As shown in Figures 40 and 41, there was insignificant extraction of Zr and Hf of below 10% when extracting from aqueous solutions of less than 7 mol/L HCl. The extraction of both metals increased with increasing chloride concentration up to 10.2 mol/L for both Alamine 336 and Aliquat 336. As seen in the case of the extraction from Zr chloride compounds, the Hf showed a lower tendency than Zr to form anionic complexes. Thus, at 9 mol/L HCl the maximum amount of Zr (67.2% extraction) with the least amount of Hf (21.0% extraction) was extracted with Alamine 336. This leads to a separation factor of up to 7.7. In the case of Aliquat 336, the maximum amount of Zr (74.2% extraction) with the least amount of Hf (30.8% extraction) was extracted at 9 mol/L HCl. This leads to a separation factor of up to 6.5. Thus, higher Zr extraction could be obtained with Aliquat 336, but better selectivity could be observed with Alamine 336.

4.4.2. *Zirconium nitrates*

For the effect of chloride concentration on the zirconium nitrate extraction, 21.62 x 10^{-3} mol/L $ZrO(NO_3)_2$ was dissolved in a range of aqueous phase acidities varying from 1 – 10.2 mol/L HCl, to obtain the aqueous phase. 12.0 x 10^{-3} mol/L Alamine 336 and 10.9 x 10^{-3} mol/L Aliquat 336, respectively, were diluted in cyclohexane with the addition of 3% v/v 1-octanol to obtain the organic phase. The extraction was carried out at a phase ratio of 1:1 at 25°C for 60 minutes.

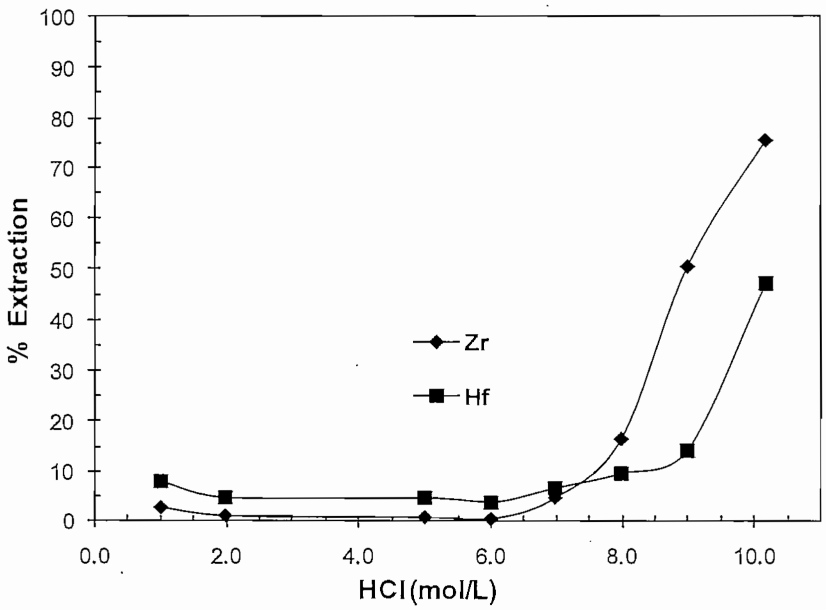

Figure 42: Effect of HCl concentration on the extraction of $ZrO(NO_3)_2$, using 12.0 x 10^{-3} mol/L Alamine 336 in cyclohexane at 25°C, [HCl] = 0.1 – 10.2 mol/L, phase ratio = 1:1

According to results obtained, shown in Figures 42 and 43, the behaviour of Zr and Hf extraction, when extracting from nitrate solutions, was to a large extent the same as in the case of chloride and oxychloride compounds previously discussed. At 9 mol/L HCl the maximum amount of Zr (50.5% extraction) with the least amount of Hf (14.3% extraction) was extracted with Alamine 336. This leads to a separation factor of up to 6.1. In the case of Aliquat 336, the maximum amount of Zr (63.5% extraction) with the least amount of Hf (23.7% extraction) was extracted at 9 mol/L HCl. This leads to a separation factor of up to 5.7.

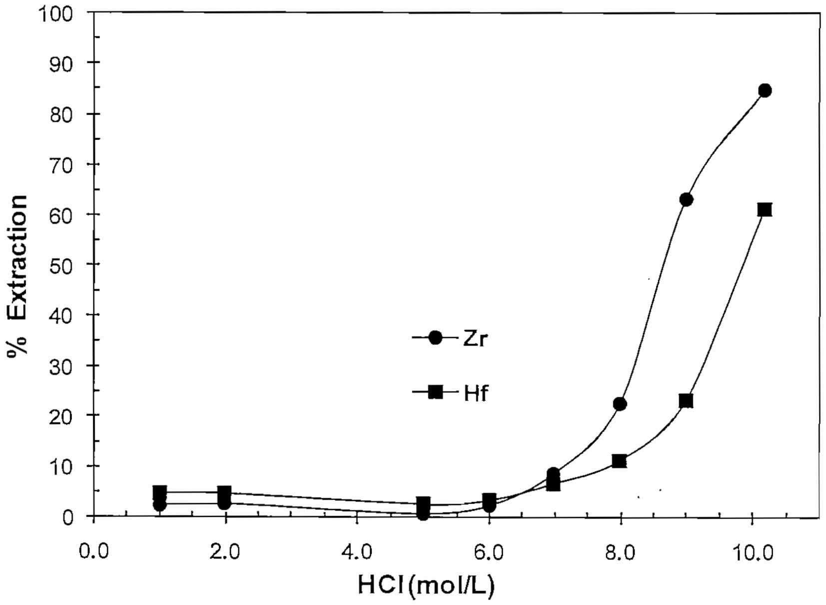

Figure 43: Effect of HCl concentration on the extraction of $ZrO(NO_3)_2$, using 10.9 x 10^{-3} mol/L Aliquat 336 in cyclohexane at 25°C, [HCl] = 0.1 – 10.2 mol/L, phase ratio = 1:1

The extraction yields and separation efficiencies of Alamine 336 and Aliquat 336, applied to different acidic aqueous feed solutions, are summarised in Table 3.

Table 3: Percentage extraction and separation efficiency of different Zr/Hf salts

Zr/Hf Feed	Extractant	%E (Zr)	%E (Hf)	D_{Zr}	D_{Hf}	D_{Hf}/D_{Zr}	SF
Zr(Hf)Cl_4	Alamine 336	82.9	33.8	4.83	0.51	0.106	9.4
Zr(Hf)Cl_4	Aliquat 336	83.2	40.7	4.95	0.69	0.138	7.2
K_2Zr(Hf)F_6	Alamine 336	3.2	2.5	0.03	0.03	0.777	1.3
K_2Zr(Hf)F_6	Aliquat 336	5.7	5.2	0.06	0.05	0.904	1.1
Zr(Hf)$OCl_2.8H_2O$	Alamine 336	67.2	21.0	2.05	0.27	0.129	7.7
Zr(Hf)$OCl_2.8H_2O$	Aliquat 336	74.2	30.8	2.88	0.44	0.155	6.5
Zr(Hf)$O(NO_3)_2$	Alamine 336	50.4	14.3	1.02	0.17	0.164	6.1
Zr(Hf)$O(NO_3)_2$	Aliquat 336	63.6	23.6	1.75	0.31	0.177	5.7

As seen from Table 3, by using $ZrOCl_2.8H_2O$ or $ZrO(NO_3)_2$ as the feedstock material, the extraction of Zr could not be improved in terms of recovery of the product. Also, the difference of Zr and Hf distribution between the organic and aqueous phases was the highest when extracting with Alamine 336 from Zr(Hf)Cl_4.

4.5. References

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CHAPTER 5

5. PROCESS EVALUATION

As part of the closure of this project, prior to the final remarks and recommendations, the separation efficiency and economic viability of the proposed process for the separation of Zr and Hf via SX are evaluated. This is done by means of a numerical method to determine the number of stagewise contacts for both the enrichment (extraction) and metal recovery (stripping) sections that would be necessary to obtain nuclear-grade Zr (<100 ppm Hf).

The first part of this Chapter (5.1 and 5.2) is concerned with the mathematical engineering optimisation of experimental results obtained in Chapter 4, aiming at determining the best process conditions for the main variables in SX with Alamine 336 and Aliquat 336 solubilised in cyclohexane for maximum Zr recovery and minimum Hf impurity from aqueous acidic feed solutions.

In Section 5.3 an alternative and optimised SX process for the purification of Zr will be presented, starting with a $Zr(Hf)Cl_4$ solution and containing an extraction, a scrubbing and a stripping section, and an evaluattion thereafter.

5.1. Zirconium Purification by Extraction

As described in Chapter 2, it is recommended that mixer-settler contactors be used because of factors like good contacting of phases, ability to handle a wide range of flow ratios, high efficiency, many stages and low cost[1]. For these contactors, the number of stagewise contacts, stage efficiency and the flow capacity are determined from bench data obtained in Chapter 4.

Multistage contacting with mixer-settlers, commonly used in hydrometallurgical applications, can be arranged in a (a) co-current, (b) cross-current or (c) counter-current configuration, discussed in the following section. The sequence of stages is sometimes referred to as a cascade[2].

5.1.1. *Co-current extraction*

The co-current extraction scheme is shown in Figure 44. As mixer settlers have the ability to reach virtually 100% stage efficiency[1,3,4], co-current stagewise contact is usually not necessary, because equilibrium is reached between the streams after the first stage.

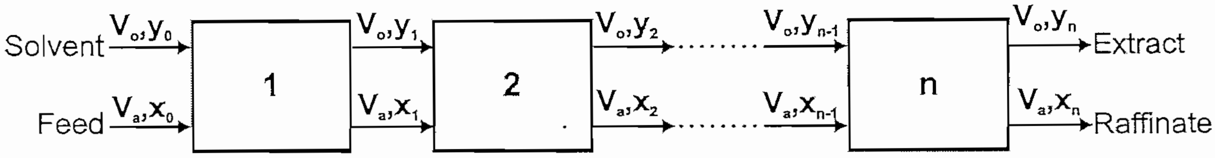

Figure 44: Co-current stagewise contact scheme

V_a is the volume flow rate of the aqueous phase, V_o the volume flow rate of the organic phase, x_0 the metal concentration in the aqueous feed, x_n the metal concentration in the aqueous raffinate stream after extraction, y_0 the metal concentration in the organic solvent feed solution and y_n the metal concentration in the organic extract stream after extraction.

5.1.2. *Cross-current extraction*

In the cross-current extraction scheme, illustrated in Figure 45, the raffinate stream, remaining from the feed solution after extraction in the previous stage, is contacted again with fresh organic solvent. This procedure can be seen as a multiple batch process. By employing this procedure in the laboratory, the extract and raffinate phases can be analysed after each stage. This generates comprehensive equilibrium data of the extraction cascade by varying the phase volume ratio, which can then be used to obtain the equilibrium isotherm experimentally.

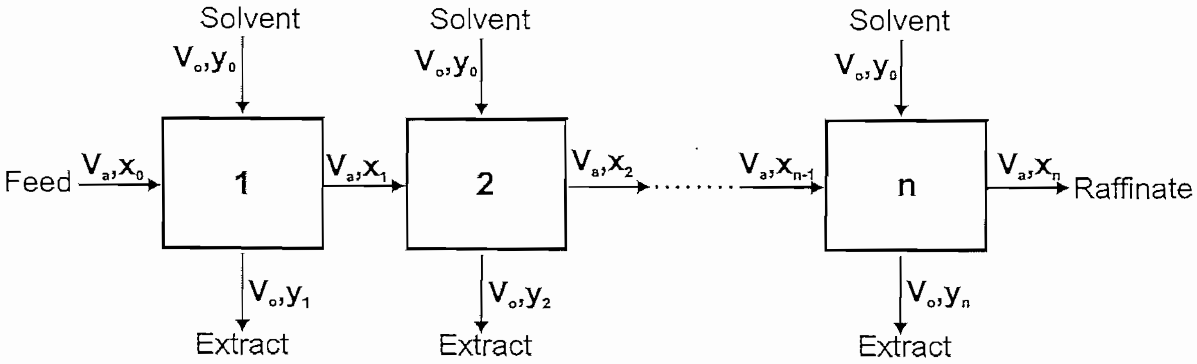

Figure 45: Cross-current stagewise contact scheme

In the case of a multi-component separation system, this method can be used to selectively separate one component from the other. However, the cross-current scheme is not generally economically attractive for large commercial processes because solvent usage is high and solute concentration in the combined extract is low[2,4,5].

5.1.3. *Counter-current extraction*

In the counter-current extraction scheme, illustrated in Figure 46, the aqueous phase is extracted with successive volumes of solvent such that the fresh organic phase always extracts from the weakest aqueous phase and the most concentrated solvent extracts from the strongest aqueous phase. This provides the lowest residual concentration of solute in the raffinate and at the same time produces maximum solute loading of the organic phase.

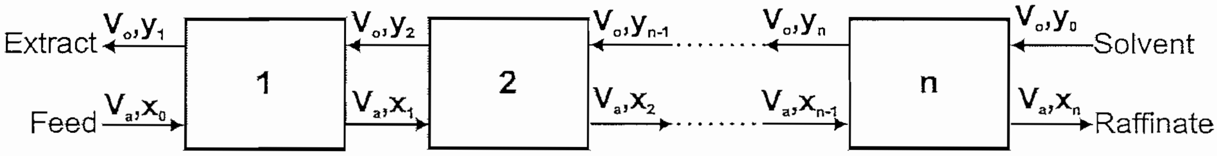

Figure 46: Counter current stagewise contact scheme for extraction

For a simple multi-stage extraction process, having only one aqueous feed stream and assuming no volume changes on mixing, shown in Figure 46, the fraction of solute remaining in the raffinate (φ) after a finite number of stages (N) can be calculated, with analogy to absorbers, with the Kremser Group method[6] as described by Smith and Brinkley[7,8].

From Figure 45, assuming no volume changes on mixing, because of minimal solvent losses *etc.*, a mass balance over a single stage, gives:

$$V_a(x_0 - x_n) = V_o(y_n - y_0) \qquad (27)$$

The organic extract leaving the cross-current extraction cascade can be recovered by stripping/back extracting the metal with an appropriate stripping solution. If, as in the case of this study, it is assumed that the metal is completely stripped from the organic solution, $y_0 = 0$. Hence, the mass balance should give:

$$V_a(x_0 - x_n) = V_o y_n \qquad (28)$$

Thus, from Equation 28, it can be seen that the extraction factor (E) can be derived as follows[4]:

$$E = \frac{V_o y_n}{V_a x_n} = \frac{V_o}{V_a} D_M \tag{29}$$

By using a mass balance over a single stage (Eq. 28), with the distribution coefficient (D_M) (Eq. 5) in place of the K-value and the extraction factor (E) (Eq. 29) in place of the absorption factor, (φ) can be calculated as follows:

$$\varphi = \frac{(y_0)E + (1 - y_0)(E - 1)}{E^{(n+1)} - 1} \tag{30}$$

Thus, for a component entering only in the feed, assuming that it is completely stripped from the recovered organic solvent, $y_0 = 0$, and

$$\varphi = \frac{x_n}{x_0} = \frac{E - 1}{E^{(n+1)} - 1} \tag{31}$$

Hence, the concentration of the solute in the extract stream is,

$$y_1 = (1 - \varphi)x_0 \tag{32}$$

Thus, in case of a multi-component system, the same procedure can be followed for the other component(s) and therefore the concentration of the solutes in the extract stream ($y_{i,1}$) leads to a purity of the desired component (*i*) in the final product after recovery from the organic extract of:

$$Y_i = \frac{y_{i,1}}{\sum_{m=1}^{j} y_{i,1}} \tag{33}$$

and a purity of the undesired component (*j*) in the aqueous raffinate:

$$X_i = \frac{x_{i,n}}{\sum_{m=1}^{j} x_{i,n}} \tag{34}$$

The recovery of the desired component can also be calculated:

$$\text{\% recovery of (i) in the extract} = \left[\frac{x_{i,n}}{x_{i,0}}\right] \times 100 \qquad (35)$$

The production of nuclear-grade Zr (< 100 ppm Hf), can be evaluated by calculating the parts of Hf per million parts Zr in the Zr-rich organic stream, according to:

$$[\mathrm{Hf}]_{\mathrm{ppm}} = \left[\frac{y_{\mathrm{Hf},1}}{y_{\mathrm{Hf},1} + y_{\mathrm{Zr},1}}\right] \times 10^{6} \qquad (36)$$

By varying extraction and process conditions, such as extractant and extractant concentration, organic-to-aqueous volumetric flow ratios and the number of equilibrium stages, the conditions can be optimised to obtain the required separation of the two components.

According to Venkatachalam[9], it is desirable that the geometric mean of the distribution coefficient does not depart greatly from unity, because the optimum organic-to-aqueous volumetric flow ratio is given approximately by:

$$\left(\frac{V_a}{V_o}\right)_{\mathrm{opt}} = \sqrt{D_{M,i} \times D_{M,j}} \qquad (37)$$

With the optimum volumetric flow ratio, the number of extraction stages can be varied. As the number of extraction stages is increased indefinitely, the organic extract approaches equilibrium with the aqueous feed, so that, in the limit[9],

$$\left(\frac{V_o}{V_a}\right)_{\mathrm{min}} = \frac{1 - \varphi}{D_M} \qquad (38)$$

Thus, by operating above the minimum flow ratio, with a large number of extraction stages, it becomes possible to approach complete extraction with a finite amount of solvent.

The distribution data for the extraction section, together with the optimum and minimum organic-to-aqueous flow ratios, used in these calculations, are shown in Table 4.

Table 4: Distribution data used in the calculations for the design of a Zr/Hf extraction setup

Alamine 336 ($x10^{-3}$ mol/L)	D_{Zr}	D_{Hf}	D_{Zr}/D_{Hf}	$(V_o/V_F)_{opt}$	$(V_o/V_F)_{min}$
44.91	165.27	5.47	30.2	0.03	0.01
22.17	16.56	1.35	12.3	0.21	0.06
13.27	5.05	0.50	10.1	0.63	0.17
6.69	1.04	0.17	6.1	2.38	0.49

According to these results, the optimum organic-to-aqueous feed flow ratio is V_o/V_F = 0.03, when extracting with high concentration of Alamine 336. Also, it is therefore important to operate above a flow ratio of 0.01.

The most advantageous extractant concentration was tested at a constant organic-to-aqueous flow ratio of 1:1, with a variation in number of extraction stages, by calculating the Hf impurity and Zr recovery as indicated before. These results are shown in Figure 47.

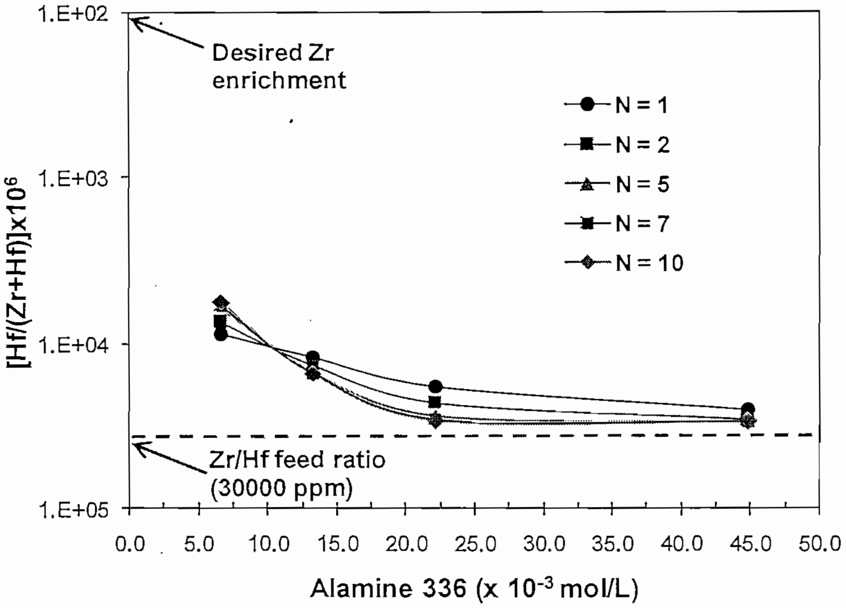

Figure 47: Effect of Alamine 336 concentration and number of stages for Zr and Hf separation

As illustrated in Figure 47, it seems to be impossible to reach the target of 100 ppm Hf, relative to Zr, in the extract, even if the number of extraction stages and the extractant concentration are varied. In relation to the Zr recovery results, presented in Table 5, this counter-current scheme is ideal for concentrating metal solutes in, for instance, a chemical waste water stream.

Table 5: Effect of Alamine 336 concentration and number of stages for Zr recovery in the organic extract

Alamine 336 ($\times 10^{-3}$ mol/L)	Zirconium recovery in the organic extract (%)				
	N = 1	N = 2	N = 5	N = 7	N = 10
44.91	99.4	100.0	100.0	100.0	100.0
22.17	94.3	99.7	100.0	100.0	100.0
13.27	83.5	96.8	100.0	100.0	100.0
6.69	51.0	68.0	84.9	89.1	92.6

For separation of the two solutes, the ratio of their distribution coefficients should differ from unity as far as possible or the extraction conditions should be altered. According to results obtained in Figure 47, it seems that the separation of the two metals increases with a decrease in extractant concentration. Thus, the extractant concentration was reduced to 6.69×10^{-3} mol/L Alamine 336. This was tested over a wide range of solvent flow ratios to the extraction stage, as illustrated in Figure 48.

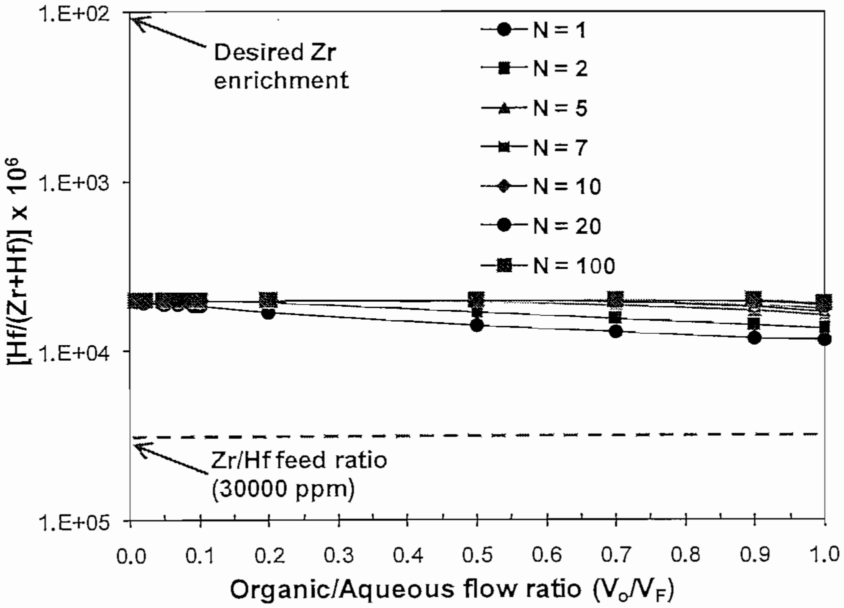

Figure 48: Effect of organic/aqueous flow ratio and number of stages at 6.69×10^{-3} mol/L Alamine 336.

It was found that the Hf-to-Zr ratio was almost kept constant at 5000 parts Hf per million parts of Zr. The recovery of Zr solutes in the organic extract can be seen in Table 6.

Table 6: Effect of organic/aqueous flow ratio for Zr recovery in the organic extract

V_o/V_F Ratio	Zirconium recovery in organic extract (%)						
	N = 1	N = 2	N = 5	N = 7	N = 10	N = 20	N = 100
0.01	1.0	1.0	1.0	1.0	1.0	1.0	1.0
0.02	2.0	2.1	2.1	2.1	2.1	2.1	2.1
0.05	4.9	5.2	5.2	5.2	5.2	5.2	5.2
0.07	6.8	7.2	7.3	7.3	7.3	7.3	7.3
0.09	8.6	9.3	9.4	9.4	9.4	9.4	9.4
0.1	9.4	10.3	10.4	10.4	10.4	10.4	10.4
0.2	17.2	20.1	20.8	20.8	20.8	20.8	20.8
0.5	34.2	44.1	51.0	51.7	52.0	52.0	52.0
0.7	42.1	55.7	68.0	70.5	71.9	72.8	72.8
0.9	48.3	64.4	80.5	84.4	87.6	91.5	93.6
1.0	51.0	68.0	84.9	89.1	92.6	96.9	99.9

Reasonable recoveries were obtained with $V_o/V_F > 0.7$ and $N > 5$.

The same procedure was followed for the extraction of Zr with 44.91 x 10^{-3} mol/L Alamine 336, for different numbers of equilibrium stages, as shown in Figure 49, in order to evaluate the amount of extractant to be contacted with the aqueous feed solution.

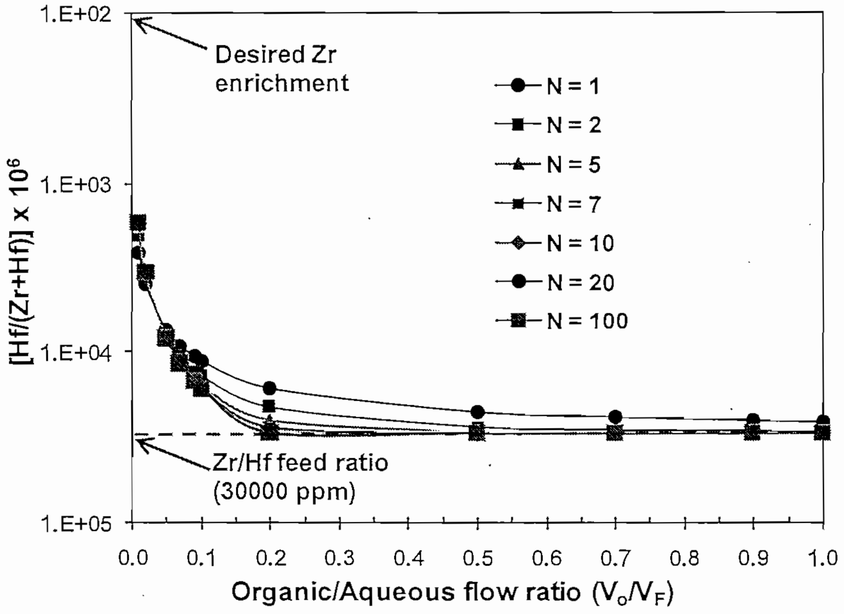

Figure 49: Effect of organic/aqueous flow ratio and number of stages at 44.91 x 10^{-3} mol/L Alamine 336

With full recovery of the Zr solutes in the organic extract after five equilibrium stages, a slight improvement in the separation of Zr and Hf was obtained at 44.91 x 10^{-3} mol/L Alamine 336, although still inefficient for the production of nuclear-grade Zr. In order to improve the fractional extraction (product ratio in the extract stream) of the multi-component system, a scrubbing section can be combined with the extraction section, as will be discussed in the next section.

5.2. Zirconium Purification by Extraction, Scrubbing and Stripping

For the selective "back-extracting" of Hf, a scrubbing section was combined with the extraction section. In the scrubbing section, the loaded organic extract solution obtained from the extraction section is contacted with an aqueous scrub solution designed to scrub any impurities co-extracted with the desired metal into the aqueous scrub raffinate. This aqueous scrub solution normally consists of water or dilute acid or base[1] and, particularly for hydrometallurgical applications, often a scrub liquor can be a very concentrated metal solution. It depends on the mechanism of extraction and what exactly is to be achieved. A general metal purification system thus exists of three sections: extraction, scrubbing and stripping, as shown in Figure 50.

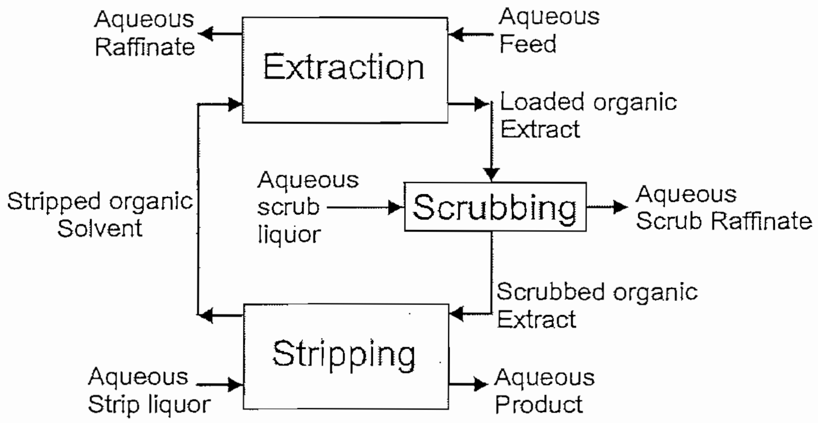

Figure 50: Typical flowsheet for combining scrubbing with extraction

5.2.1. *Counter-current extraction/scrubbing for Zr/Hf separation*

A schematic diagram for the design calculations of an extraction/scrubbing train is shown in Figure 51.

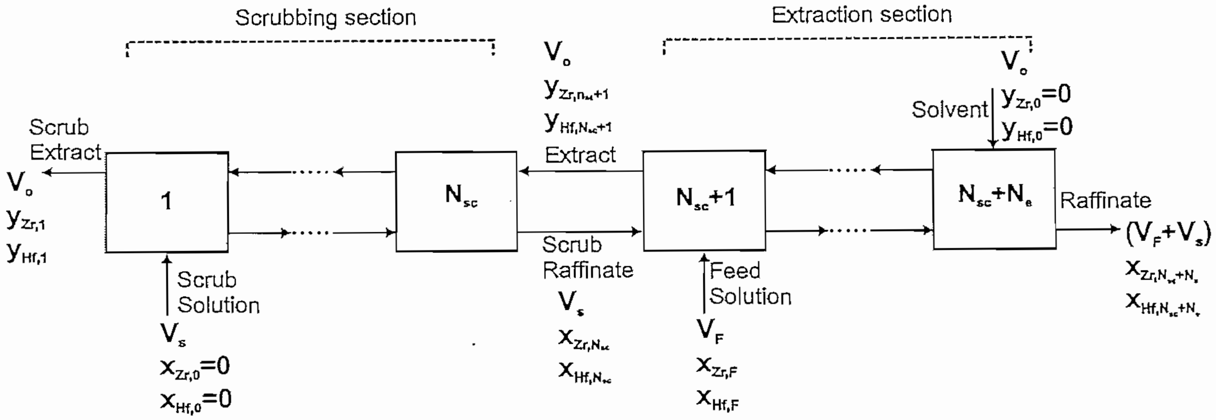

Figure 51: Counter-current extraction scheme for zirconium and hafnium separation

The extraction/scrubbing train consists of N_e extraction stages and N_{SC} scrubbing stages. The acidic aqueous feed solution with the scrub raffinate enters the first extraction stage (N_{SC} +1) and the Zr is selectively extracted in the counter-current extraction section. The aqueous raffinate, exiting stage (N_{SC} + N_e), is thus enriched in Hf and the organic extract, exiting stage (1), in Zr. In order to remove Hf to below 100 ppm relative to Zr, a scrub solution is added at stage (1). The Zr-rich organic extract can then be sent to a recovery section, where the Zr solute is recovered and a clean organic solvent is produced to be recycled to stage (N_{SC} + N_e), as discussed in Section 5.2.2.

Assuming no volume changes on mixing, an overall mass balance over N_{SC} scrubbing stages gives:

$$V_o\left(y_{N_{sc}+1}-y_1\right)=V_a\left(x_{N_{sc}}-x_0\right) \tag{39}$$

with $y_{n_{sc}+1}$ the solute concentration in the loaded organic feed solution, obtained from the extraction section, and $y_{n_{sc}}$ the solute concentration in the aqueous scrub raffinate.

The aqueous scrub feed solution contains none of the solutes, thus, with x_0 = 0, the overall mass balance reduces to:

$$V_o\left(y_{N_{sc}+1}-y_1\right)=V_a x_{N_{sc}} \tag{40}$$

By changing the conditions in the scrubbing solution, the distribution coefficient is no longer constant for "back-extracting". Thus, a new distribution should be derived for the scrubbing section. This was obtained from equilibrium data in batch experiments. This batch scrubbing procedure is similar to the batch stripping procedure by contacting the loaded organic phase with the scrub solution at the appropriate strength, pH, phase ratio, contact time and temperature. The distribution coefficient for the scrubbing section (D_{sc}) can be calculated as follows:

$$D_{Zr,sc}=\frac{[Zr]_{(\text{scrub raffinate})}}{[Zr]_{(\text{scrub extract})}}=\frac{x_{Zr,n_{sc}}}{y_{Zr,1}} \tag{41}$$

with $D_{Zr,sc}$ the reciprocal of $D_{Zr,e}$ for the extraction section. By using this distribution coefficient and the mass balance over the scrubbing section, the scrubbing factor (S_{Zr}) can be calculated:

$$S_{Zr}=\frac{V_a x_{Zr,n_{sc}}}{V_o y_{Zr,1}}=\frac{V_a}{V_o}D_{Zr,sc} \tag{42}$$

Thus, with analogy to the extraction section (described with Eq. 30 and 31), the Kremser equation can be manipulated to obtain the fraction of metal remaining in the organic scrub extract, i.e. fraction not scrubbed (φ_{sc}):

$$\varphi_{Zr,sc}=\frac{(x_{Zr,0})S_{Zr}+(1-x_{Zr,0})(S_{Zr}-1)}{S_{Zr}^{(n_{sc}+1)}-1} \tag{43}$$

and, for a component entering only in the loaded organic extraction extract stream, assuming that the scrubbing solution contains no solute, $x_o = 0$,

$$\varphi_{Zr,sc}=\frac{y_{Zr,1}}{y_{Zr,n_{sc}+1}}=\frac{S_{Zr}-1}{S_{Zr}^{(n_{sc}+1)}-1} \tag{44}$$

From Figure 51, a mass balance over the extraction section leads to the mass of Zr extracted into the organic extract stream:

$$V_o y_{Zr,n_{sc}+1}=(1-\varphi_{Zr,e})(V_s x_{Zr,n_{sc}}+V_F x_{Zr,F}) \tag{45}$$

and thus, the mass of Zr not extracted in the aqueous raffinate stream:

$$(V_s+V_F)x_{Zr,n_{sc}+n_e}=\varphi_{Zr,e}(V_s x_{Zr,n_{sc}}+V_F x_{Zr,F}) \tag{46}$$

A mass balance over the scrubbing section can lead to the mass of Zr scrubbed into the aqueous scrub raffinate stream:

$$V_s x_{Zr,n_{sc}} = \left(1 - \varphi_{Zr,sc}\right) V_o y_{Zr,n_{sc}+1} \tag{47}$$

hence, the mass of Zr not scrubbed in the organic scrub extract stream:

$$V_o y_{Zr,1} = \varphi_{Zr,sc}\left(V_o y_{Zr,n_{sc}+1}\right) \tag{48}$$

The overall Zr mass balance can be written as follows:

$$V_F x_{Zr,F} + V_s x_{Zr,0} + V_o y_{Zr,0} = \left(V_s + V_F\right) x_{Zr,n_{sc}+n_e} + V_o y_{Zr,1} \tag{49}$$

By assuming that the recycled organic solvent is completely stripped and the scrub liquor contains no solute, the overall mass balance can be simplified as follows:

$$V_F x_{Zr,F} = \left(V_s + V_F\right) x_{Zr,n_{sc}+n_e} + V_0 y_{Zr,1} \tag{50}$$

Thus, with four unknown solute concentrations ($y_{Zr,1}$, $y_{Zr,n_{sc}+1}$, $x_{Zr,n_{sc}}$ and $x_{Zr,n_{sc}+n_e}$) and five equations (Eq. 46 – 49, 51), the degree of freedom is zero and thus can be solved as follows:

Substitute Eq. 46 and Eq. 48 in Eq. 49:

$$\begin{aligned} V_F x_{Zr,F} &= \varphi_{Zr,e}\left(V_s x_{Zr,n_{sc}} + V_F x_{Zr,F}\right) + \varphi_{Zr,sc}\left(V_o y_{Zr,n_{sc}+1}\right) \\ &= \left(\varphi_{Zr,e}\right) V_s x_{Zr,n_{sc}} + \left(\varphi_{Zr,e}\right) V_F x_{Zr,F} + \left(\varphi_{Zr,sc}\right) V_o y_{Zr,n_{sc}+1} \end{aligned} \tag{51}$$

And from Eq. 47:

$$\begin{aligned} V_F x_{Zr,F} &= \left(\varphi_{Zr,e}\right)\left(1 - \varphi_{Zr,sc}\right) V_o y_{Zr,n_{sc}+1} + \left(\varphi_{Zr,e}\right) V_F x_{Zr,F} + \left(\varphi_{Zr,sc}\right) V_o y_{Zr,n_{sc}+1} \\ \therefore \left[\left(\varphi_{Zr,e}\right)\left(1 - \varphi_{Zr,sc}\right) + \left(\varphi_{Zr,sc}\right)\right] V_o y_{Zr,n_{sc}+1} &= V_F x_{Zr,F} - \left(\varphi_{Zr,e}\right) V_F x_{Zr,F} \\ &= \left(1 - \varphi_{Zr,e}\right) V_F x_{Zr,F} \end{aligned} \tag{52}$$

Thus, by solving for $y_{Zr,n_{sc}+1}$, the Zr mass concentration in the organic extract stream after (N_e) extraction stages is:

$$y_{Zr,n_{sc}+1} = \frac{\left(1 - \varphi_{Zr,e}\right)V_F x_{Zr,F}}{V_o\left[\left(\varphi_{Zr,e}\right)\left(1 - \varphi_{Zr,sc}\right) + \left(\varphi_{Zr,sc}\right)\right]} \qquad (53)$$

and by substituting Eq. 53 back into Eq. 48, the Zr mass concentration in the organic scrub extract stream, after (N_{sc}) scrubbing stages is:

$$y_{Zr,1} = \frac{\varphi_{Zr,sc}\left(1 - \varphi_{Zr,e}\right)V_F x_{Zr,F}}{V_o\left[\left(\varphi_{Zr,e}\right)\left(1 - \varphi_{Zr,sc}\right) + \left(\varphi_{Zr,sc}\right)\right]} \qquad (54)$$

From Eq. 46, the Zr mass concentration in the aqueous scrub raffinate stream, after (N_{sc}) scrubbing stages, is:

$$x_{Zr,n_{sc}} = \frac{\left(1 - \varphi_{Zr,sc}\right)\left(1 - \varphi_{Zr,e}\right)V_F x_{Zr,F}}{V_s\left[\left(\varphi_{Zr,e}\right)\left(1 - \varphi_{Zr,sc}\right) + \left(\varphi_{Zr,sc}\right)\right]} \qquad (55)$$

and by substituting Eq. 55 in Eq. 46, the Zr mass concentration in the aqueous raffinate stream, after (N_e) extraction stages and (N_{sc}) extraction stages, is:

$$x_{Zr,n_{sc}+n_e} = \frac{\dfrac{\varphi_{Zr,e}\left(1 - \varphi_{Zr,sc}\right)\left(1 - \varphi_{Zr,e}\right)V_F x_{Zr,F}}{\left[\left(\varphi_{Zr,e}\right)\left(1 - \varphi_{Zr,sc}\right) + \left(\varphi_{Zr,sc}\right)\right]} + (\varphi_{Zr,e})V_F x_{Zr,F}}{\left(V_s + V_F\right)} \qquad (56)$$

This procedure can also be followed for Hf mass balances, and hence, the performance of the separation process can be evaluated as follows:

The Hf impurity of the Zr-rich organic extract:

$$Y_{Hf} = \frac{V_o y_{Hf,1}}{V_o y_{Hf,1} + V_o y_{Zr,1}} \qquad (57)$$

$$\%\ \text{Recovery of Zr in the org.} = \left[\frac{V_o y_{Zr,1}}{V_F x_{Zr,F}}\right] \times 100 \qquad (58)$$

The Zr impurity of the Hf-rich aqueous raffinate:

$$X_{Zr} = \frac{\left(V_s + V_F\right)x_{Zr,n_{sc}+n_e}}{\left(V_s + V_F\right)x_{Zr,n_{sc}+n_e} + \left(V_s + V_F\right)x_{Hf,n_{sc}+n_e}} \qquad (59)$$

$$\%\ \text{Recovery of Hf in the aq.} = \left[\frac{(V_s + V_F)x_{Hf,n_{sc}+n_e}}{V_F x_{Hf,F}}\right] \times 100 \qquad (60)$$

The production of nuclear-grade Zr (< 100 ppm Hf), can be evaluated by calculating the parts of Hf per million parts Zr in the Zr-rich organic stream according to:

$$[Hf]_{ppm} = \left[\frac{V_o y_{Hf,1}}{V_o y_{Hf,1} + V_o y_{Zr,1}}\right] \times 10^6 \qquad (61)$$

Thus, by varying the extraction conditions, the optimum process conditions can be evaluated for maximum Zr recovery and minimum Hf impurity by Eq. 58 and Eq. 61.

The targets for this setup are:

1. Extract/Scrub extract composition in the organic phase of $Hf/(Zr + Hf) = 10^{-4}$ (100 ppm), and
2. 70% recovery of the Zr solutes into the organic extract. (The Zr that is lost to the aqueous raffinate is further processed and will be used in the production of pigments.)

The variables for this setup are:

1. Type and concentration of extract in organic solvent
2. Type and concentration of acid in aqueous scrub feed solution
3. The number of extraction stages (N_e)
4. The number of scrubbing stages (N_{sc})
5. Organic solvent-to-aqueous scrub volumetric flow rates (V_o/V_S), and
6. Organic solvent-to-aqueous feed volumetric flow rates (V_o/V_F)

The constraints selected for this setup are:

1. Organic-to-aqueous flow ratio in the range $0.1 < V_o/V_F < 10$, in order to maintain appropriate contact between the two phases, and
2. Minimum aqueous feed to scrub flow ratio of $V_F/V_S = 0.1$, in order to prevent the raffinate being diluted or increased too much.

The Zr recovery and Hf impurity of the Zr-rich organic extract stream were calculated as shown above at different process conditions. A Hf-to-Zr feed ratio ($x_{Hf,F}/x_{Zr,F} + x_{Hf,F}$) of 0.03 was used in all design calculations for a counter-current extraction scheme as described in Figure 51.

a) V_o/V_F ratio and number of extraction stages (N_e)

By varying the organic solvent-to-aqueous feed solution flow ratios between 0.01 and 10 for 44.91 x 10^{-3} mol/L Alamine 336, the number of extraction stages was tested at a constant number of scrubbing stages of three, N_{sc} = 3, as shown in Figure 52.

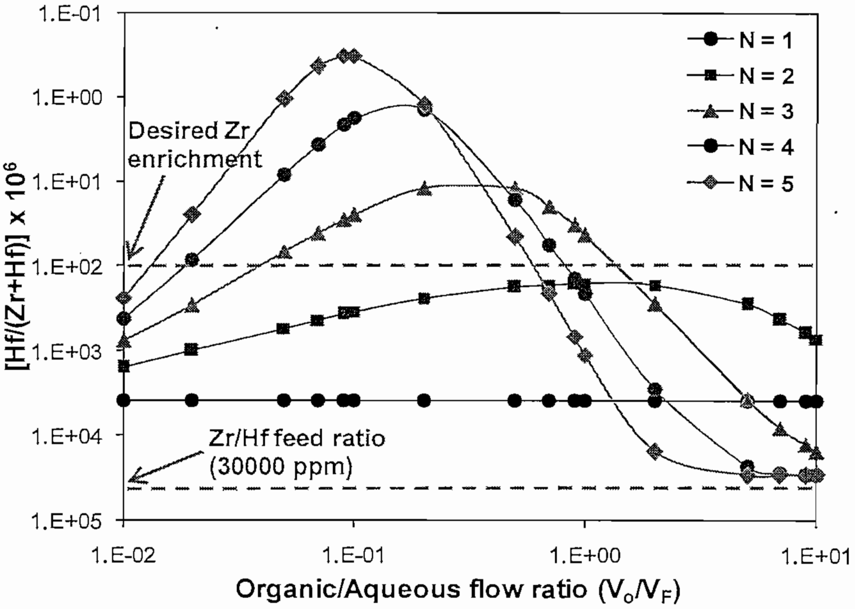

Figure 52: Effect of organic-to-aqueous flow ratio at different numbers of extraction stages, V_o/V_s = 1, N_{sc} = 3, 44.91 x 10^{-3} mol/L Alamine 336

The results in Figure 52 show that:

- the minimum number of extraction stages required for $[Hf]_{ppm} \leq 100$ is N_e = 3,
- the required V_o/V_F ratio for N_e = 3 ranges from $0.06 \leq V_o/V_F \leq 1.0$,
- the optimum purification, $[Hf]_{ppm}$ ~ 10 is obtained at $0.2 \leq V_o/V_F \leq 0.7$,
- although for more than three extraction stages the purification is even better, the fact that $V_o/V_F < 0.1$ creates a problem regarding phase contacting,
- the observation that the purification has a maximum at a given V_o/V_F ratio is easily understood. At high V_o/V_F ratio, both metals are extracted completely

and $[Hf]_{ppm}$ = 30,000, the feed value. At the extremely low V_o/V_F value $[Hf]_{ppm}$ = 7000, the result obtained without scrubbing.

The second target, to recover more than 70% of the Zr, can be met for V_o/V_F ratios larger than 0.7. This and more detailed results are given in Table 7.

Table 7: Effect of organic-to-aqueous flow ratios on the zirconium recovery at different numbers of extraction stages (N_{sc} = 3)

V_o/V_F Ratio	Zirconium recovery in organic extract (%)				
	$N_e = 1$	$N_e = 2$	$N_e = 3$	$N_e = 4$	$N_e = 5$
0.01	0.00	0.00	0.00	0.0	0.0
0.02	0.00	0.00	0.01	0.0	0.1
0.05	0.00	0.01	0.10	0.9	6.7
0.07	0.00	0.02	0.28	3.1	27.0
0.09	0.00	0.04	0.57	7.9	56.0
0.1	0.00	0.05	0.78	11.5	68.2
0.2	0.01	0.18	5.73	66.8	98.5
0.5	0.01	1.12	48.25	98.7	100.0
0.7	0.02	2.16	71.82	99.7	100.0
0.9	0.02	3.51	84.39	99.9	100.0
1.0	0.03	4.29	88.11	99.9	100.0
2.0	0.05	15.17	98.34	100.0	100.0
5.0	0.13	52.74	99.89	100.0	100.0
7.0	0.19	68.62	99.96	100.0	100.0
9.0	0.24	78.32	99.98	100.0	100.0
10.0	0.27	81.69	99.99	100.0	100.0

As seen from Table 7, the optimum recovery of Zr solutes into the organic extract stream, within desired enrichment, is obtained at an organic-to-aqueous feed ratio larger than 0.7 when extracting with three or more stages. The conclusion therefore is that with three scrubbing stages and 44.91×10^{-3} mol/L Alamine 336, the optimum number of extraction stages is three with a $V_o/V_F = 0.7$.

b) V_o/V_F ratio and number of scrubbing stages (N_{sc})

Similarly, the number of scrubbing stages was tested at a constant number of extraction stages (N_e = 3), as is illustrated in Figure 53.

It is evident from Figures 52 and 53 that the extraction section was mainly responsible for the Zr recovery, while the scrubbing section was largely responsible for the Zr purification, although in the counter-current extraction scheme, the one section is insufficient without the other.

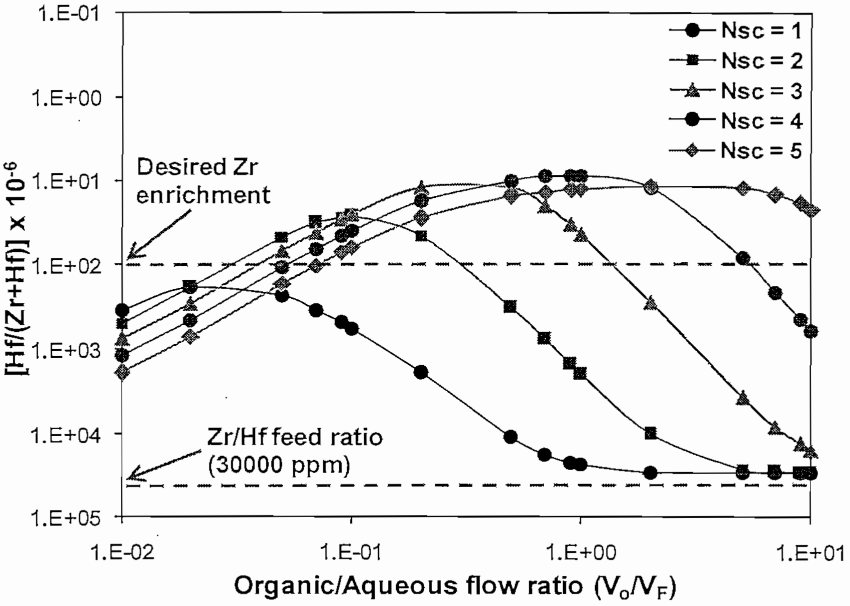

Figure 53: Effect of organic-to-aqueous flow ratio at different numbers of scrubbing stages, $V_o/V_s = 1$, $N_e = 3$, 44.9×10^{-3} mol/L wt Alamine 336

Figure 53, for the Zr purity, together with Table 8, for the Zr recovery, shows that the optimum number of scrubbing stages, $N_{sc} = 3$. A larger number of scrubbing stages leads to reduced Zr recovery, whereas a smaller number leads to problems regarding the purity specifications.

Table 8: Effect of organic-to-aqueous flow ratio on the zirconium recovery at different numbers of scrubbing stages ($N_e = 3$)

V_o/V_F Ratio	Zirconium recovery in organic extract (%)				
	$N_{sc} = 1$	$N_{sc} = 2$	$N_{sc} = 3$	$N_{sc} = 4$	$N_{sc} = 5$
0.01	9.4	0.1	0.0	0.0	0.0
0.02	37.0	0.7	0.0	0.0	0.0
0.05	88.2	8.1	0.1	0.0	0.0
0.07	95.2	19.0	0.3	0.0	0.0
0.09	97.6	32.7	0.6	0.0	0.0
0.1	98.2	39.9	0.8	0.0	0.0
0.2	99.8	83.7	5.7	0.1	0.0
0.5	100.0	98.7	48.2	1.1	0.0
0.7	100.0	99.5	71.8	2.9	0.0
0.9	100.0	99.8	84.4	6.0	0.1
1.0	100.0	99.8	88.1	8.1	0.1
2.0	100.0	100.0	98.3	41.1	0.8
5.0	100.0	100.0	99.9	91.6	11.4
7.0	100.0	100.0	100.0	96.8	26.1
9.0	100.0	100.0	100.0	98.5	42.9
10.0	100.0	100.0	100.0	98.9	50.7

c) V_o/V_F ratio and V_o/V_S ratio

With a selective separation of Zr and Hf and fulfilling Zr recovery over three extraction stages combined with three scrubbing stages, the organic-to-aqueous flow ratios were tested for the scrubbing section in order to reduce the chemical consumption and thus the amount of raffinate exiting the extraction section. The results are shown in Figure 54 and Table 9.

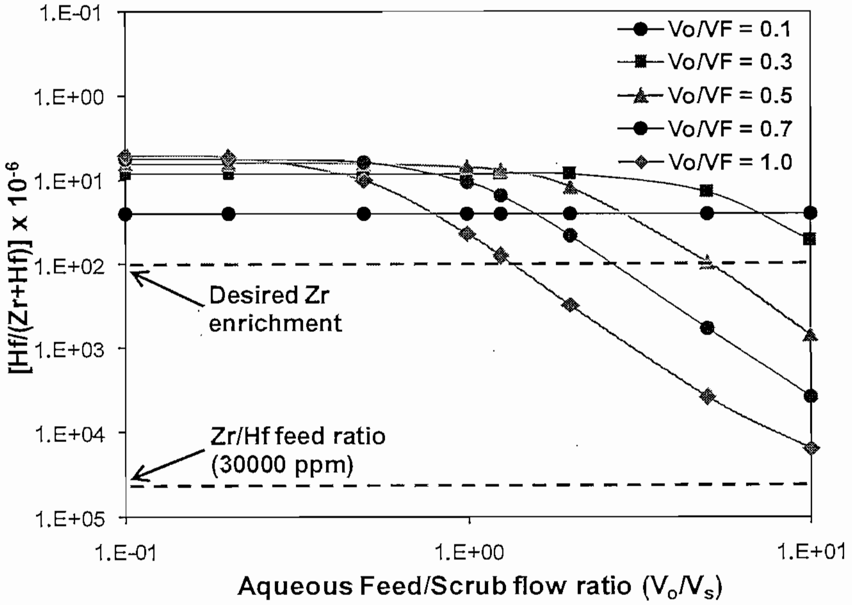

Figure 54: Effect of organic-to-aqueous scrub flow ratio at different feed ratios

Table 9: Effect of organic feed-to-scrub flow ratio on the zirconium recovery at different organic-to-aqueous feed flow ratios

V_F/V_s Ratio	Zirconium recovery in organic extract (%)				
	$V_o/V_F = 0.1$	$V_o/V_F = 0.3$	$V_o/V_F = 0.5$	$V_o/V_F = 0.7$	$V_o/V_F = 1.0$
0.1	0.00	0.00	0.01	0.1	0.7
0.2	0.00	0.00	0.09	0.7	5.6
0.5	0.00	0.07	1.45	9.9	48.2
1.0	0.00	0.55	10.49	46.6	88.1
1.3	0.00	1.07	18.61	63.0	93.5
2.0	0.01	4.24	48.25	87.4	98.3
5.0	0.10	40.66	93.47	99.1	99.9
10.0	0.78	84.33	99.11	99.9	100.0

As can be seen in Table 9, the recovery of the Zr in the organic extract increased with an increase in the organic extract flow and a decrease in the aqueous scrub flow. However, by simultaneously decreasing the organic solvent flow fed to the extraction section and decreasing the scrub liquor flow to the scrubbing section, the outcomes did not improve but were limited to $2 \leq V_F/V_S \leq 10$. Therefore, slightly decreasing the scrub solution to V_o/V_S = 1.25, with V_o/V_F = 0.7, results in a V_F/V_S ratio of 2.5, which is acceptable within the selected constraints.

The input process conditions and outcomes for the conceptual design stage, for optimum Zr and Hf separation with maximum Zr recovery are summarised in Table 10.

Table 10: Selected process conditions for optimum zirconium and hafnium separation with maximum zirconium recovery

Extraction Section		Scrubbing Section		Product specifications	
N_e	3	**N_{sc}**	3	**$[Hf]_{ppm}$**	33.7
V_o/V_F	0.7	**V_o/V_S**	1.25	**% Zr recovery**	83.2
Extractant	44.91 x 10^{-3} mol/L Alamine 336	**Scrub Solution**	Water		

For peace of mind, the purification ability was again tested for both of the solvating extractants, Alamine 336 and Aliquat 336, at different solute concentrations in the organic solvent, which was fed to the extraction section at stage (N_{sc} + N_e), at the process conditions selected above.

Figure 55 and 56 indicates the Zr enrichment in terms of extractant concentration, varying from 6 to 45 x 10^{-3} mol/L, for both Alamine 336 and Aliquat 336.

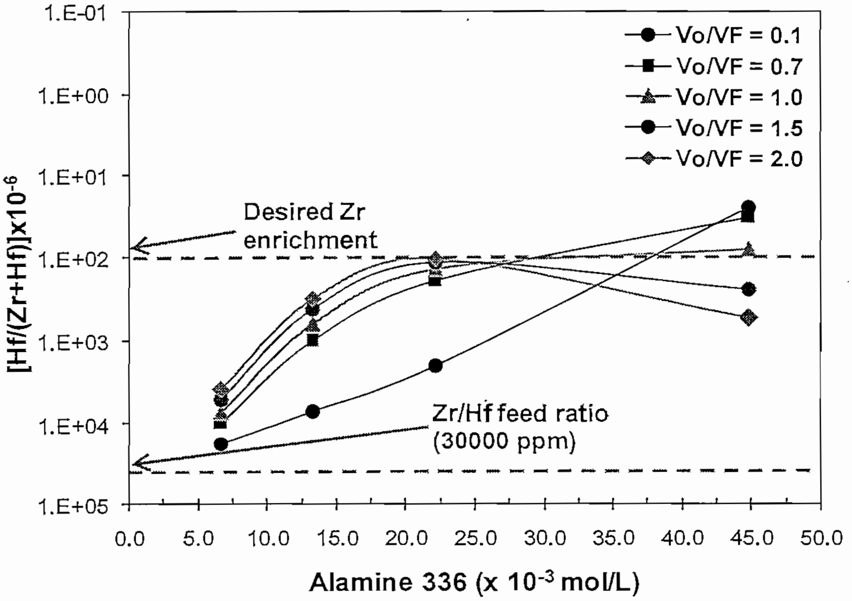

Figure 55: Effect of Alamine 336 concentration in the solvent at different feed ratios

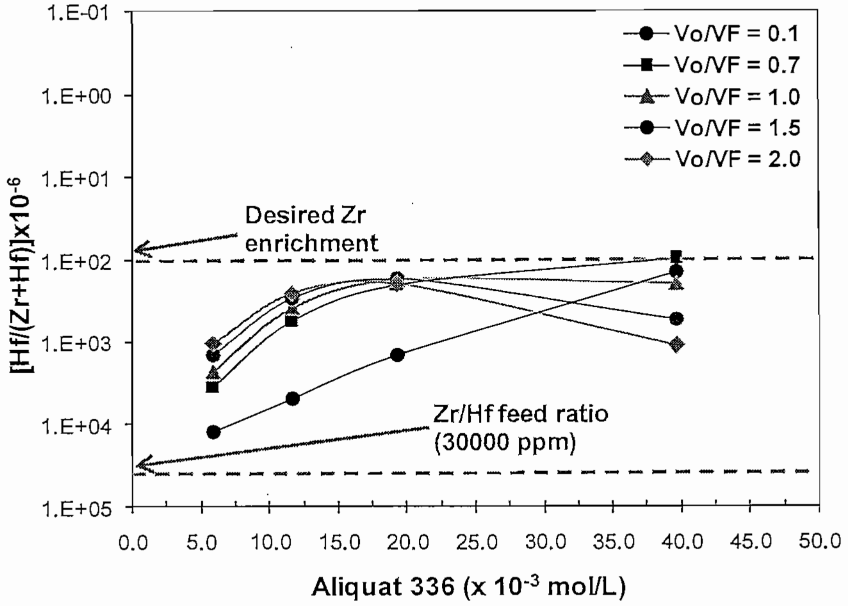

Figure 56: Effect of Aliquat 336 concentration in the solvent at different feed ratios

When comparing the two extractants at a specific organic-to-aqueous feed ratio (V_o/V_F = 0.7), it can be seen from Figures 55 and 56 that extraction with Alamine 336 enhanced the purification and recovery of Zr solutes in the organic extract stream. It is also evident from Figure 55 that the organic solvent can be reduced to V_o/V_F = 0.1, however as seen before, the recovery of Zr solutes will decrease to 1.5%. The recovery of Zr is summurised in Table 11, which corresponds to the extraction of Zr and Hf by Alamine 336 and Aliquat 336 and the purification by scrubbing Hf from the extract stream.

Table 11: Zirconium recovery for Alamine 336 and Aliquat 336 at different feed ratios

Amine Extractant	Extractant (x 10^{-3} mol/L)	$D_{Zr,sc}$	$D_{Hf,sc}$	$D_{Zr,e}$	$D_{Hf,e}$	Zirconium recovery in organic extract (%)				
						$V_o/V_F = 0.1$	$V_o/V_F = 0.7$	$V_o/V_F = 1.0$	$V_o/V_F = 1.5$	$V_o/V_F = 2.0$
Alamine 336	44.91	84.60	53.91	165.27	5.47	1.50	83.23	93.52	97.98	99.14
Alamine 336	22.17	84.60	53.91	16.56	1.35	0.00	0.54	1.51	4.83	10.64
Alamine 336	13.27	84.60	53.91	5.05	0.50	0.00	0.02	0.05	0.16	0.34
Alamine 336	6.69	84.60	53.91	1.04	0.17	0.00	0.00	0.00	0.00	0.00
Aliquat 336	39.66	84.60	53.91	107.16	7.05	0.43	57.62	79.79	93.00	96.92
Aliquat 336	19.33	84.60	53.91	26.03	2.54	0.01	1.99	5.51	16.26	31.37
Aliquat 336	11.72	84.60	53.91	9.57	1.03	0.00	0.11	0.31	1.00	2.29
Aliquat 336	5.96	84.60	53.91	2.43	0.32	0.00	0.00	0.01	0.02	0.05

According to these results it was clear that Alamine 336 is more efficient than Aliquat 336 in the counter-current extraction/scrubbing train for Zr and Hf separation. By keeping the Alamine 336 concentration at 44.91 x 10^{-3} mol/L of the solvent, the target of $[Hf]_{ppm} < 100$ is reached and the loading of Zr solute into the organic extract stream is maximised and maximum recovery of Zr is guaranteed.

5.2.2. *Stripping of the loaded organic solvent*

In the recovery section, Zr is stripped from the loaded and scrubbed organic solvent to an aqueous phase that can be further treated for the production of the metal sponge. This section simultaneously regenerates the organic solvent which can then be recycled to the extraction section at stage (N_{sc} + N_e).

As seen from stripping results obtained from batch experiments, presented in Figure 22, deionised water can be used to strip Zr, together with trace amounts of Hf, from the loaded organic extract solution. Thus, a single equilibrium stripping stage would be justified for the recovery of the Zr solute product from the organic phase into the aqueous phase. Therefore, no counter-current stripping would be necessary for this section. A schematic diagram for the design calculations of the stripping train for Zr recovery from the organic extract stream is shown in Figure 57.

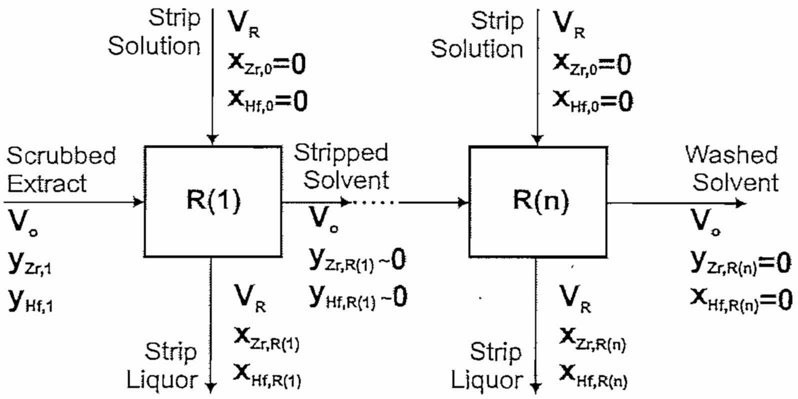

Figure 57: Cross-current stripping scheme for zirconium recovery

The same procedure as in the case of cross-current scrubbing, described in Section 5.2.1(a), was used for the calculation of the solute concentration ($x_{Zr,R(1)}$ and $x_{Hf,R(1)}$) in the aqueous strip liquor stream that is exiting the recovery stage R(1).

The equilibrium data obtained in Chapter 4, when varying the strip acid type and concentration, can be used to obtain the distribution coefficient ($D_{Zr,R}$) for the stripping of Zr from the organic scrub extract into the strip liquor. This coefficient can then be used to calculate the stripping factor (R_{Zr}) with analogy to the scrubbing section, where Eq. 41 is used:

$$R_{Zr} = \frac{V_R x_{Zr,R(1)}}{V_o y_{Zr,1}} = \frac{V_R}{V_o} D_{Zr,R} \qquad (62)$$

The fraction of solute not stripped, after (N_R) stripping stages, can be calculated with analogy to the extraction section, as described by Eq. 28:

$$\varphi_{Zr,R} = \frac{y_{Zr,R(1)}}{y_{Zr,1}} = \frac{1}{\left(1 + R_{Zr}\right)^{n_R}} \tag{63}$$

With the fraction of solute not stripped ($\varphi_{Zr,R}$), the solute concentration of the Zr exiting through the organic stripped solvent $y_{Zr,R(1)}$, can be calculated with a mass balance over stage R(1):

$$\begin{aligned} V_o y_{Zr,R(1)} &= \varphi_{Zr,sc} V_o y_{Zr,1} \\ \therefore y_{Zr,R(1)} &= \varphi_{Zr,sc} y_{Zr,1} \end{aligned} \tag{64}$$

and the Zr solute concentration that is recovered through the aqueous strip liquor:

$$\begin{aligned} V_R x_{Zr,R(1)} &= \left(1 - \varphi_{Zr,sc}\right) V_o y_{Zr,1} \\ \therefore x_{Zr,R(1)} &= \frac{\left(1 - \varphi_{Zr,sc}\right) V_o y_{Zr,1}}{V_R} \end{aligned} \tag{65}$$

This procedure can also be followed for Hf mass balances and, hence, the performance of the separation process can be evaluated according to:

$$Y_{Zr} = \frac{V_R x_{Hf,R(1)}}{V_R x_{Hf,R(1)} + V_R x_{Zr,R(1)}} \tag{66}$$

$$\%\ \text{Stripping of Zr in the aq.} = \left[\frac{V_R x_{Zr,R(1)}}{V_o y_{Zr,1}}\right] \times 100 \tag{67}$$

The production of nuclear-grade Zr (<100 ppm Hf) can be evaluated by calculating the parts of Hf per million parts Zr in the Zr-rich aqueous stream as follows:

$$\left[Hf\right]_{ppm} = \left[\frac{V_R x_{Hf,R(1)}}{V_R x_{Hf,R(1)} + V_R x_{Zr,R(1)}}\right] \times 10^6 \tag{68}$$

The organic solvent to aqueous stripping solution flow ratio was varied for a single stripping stage in order to recover the Zr ($y_{Zr,1}$) from the organic solvent exiting the scrubbing section that is fed to the stripping section.

As presented in Table 12, the overall stripping of Zr from the organic solvent was considered successful over a single stripping stage. The increase in the stripping solution flow rates presented a minor increase in the stripping of Zr and thus a V_o/V_R ratio was considered to be the optimum for recovery.

With more than 99% of Zr and Hf stripped from the organic solvent, this is rather common and it is accepted that less than 1% of the solutes is retured to the extraction section.

Table 12: Effect V_o/V_R flow ratio over the stripping, $N_R = 1$, Feed = $y_{Zr,1}$ and $y_{Hf,1}$

V_o/V_R ratio	% Zr Stripping	% Hf Stripping	$[Hf]_{ppm}$
0.1	89.4	84.4	31.8
0.2	94.4	91.5	32.7
0.5	97.7	96.4	33.3
0.7	98.3	97.4	33.4
0.9	98.7	98.0	33.5
1.0	98.8	98.2	33.5
2.0	99.4	99.1	33.6
5.0	99.8	99.6	33.7
7.0	99.8	99.7	33.7
9.0	99.9	99.8	33.7
10.0	99.9	99.8	33.7

The final outcomes are given in Table 13. This shows that for a single stage stripping section, it was possible to meet the selected targets for both Zr purity and recovery.

Table 13: Final process conditions for optimum zirconium and hafnium separation with maximum zirconium recovery

Extraction Section		Scrubbing Section		Stripping Section		Product specifications	
N_e	3	N_{sc}	3	N_R	1	$[Hf]_{ppm}$	33.6
V_o/V_F	0.7	V_o/V_s	1.25	V_o/V_R	0.5	% Zr recovery	82.7
Extractant	44.91 x 10^{-3} mol/L Alamine 336	Scrub Solution	Water	Strip Solution	Water		

5.3. Complete Zirconium Purification Plant Flowsheet

Figure 58 shows the flowsheet for the enrichment process for nuclear-grade zirconium tetrachloride ($ZrCl_4$ <100 ppm Hf) by a seven-stage SX process involving complex formation with Alamine 336.

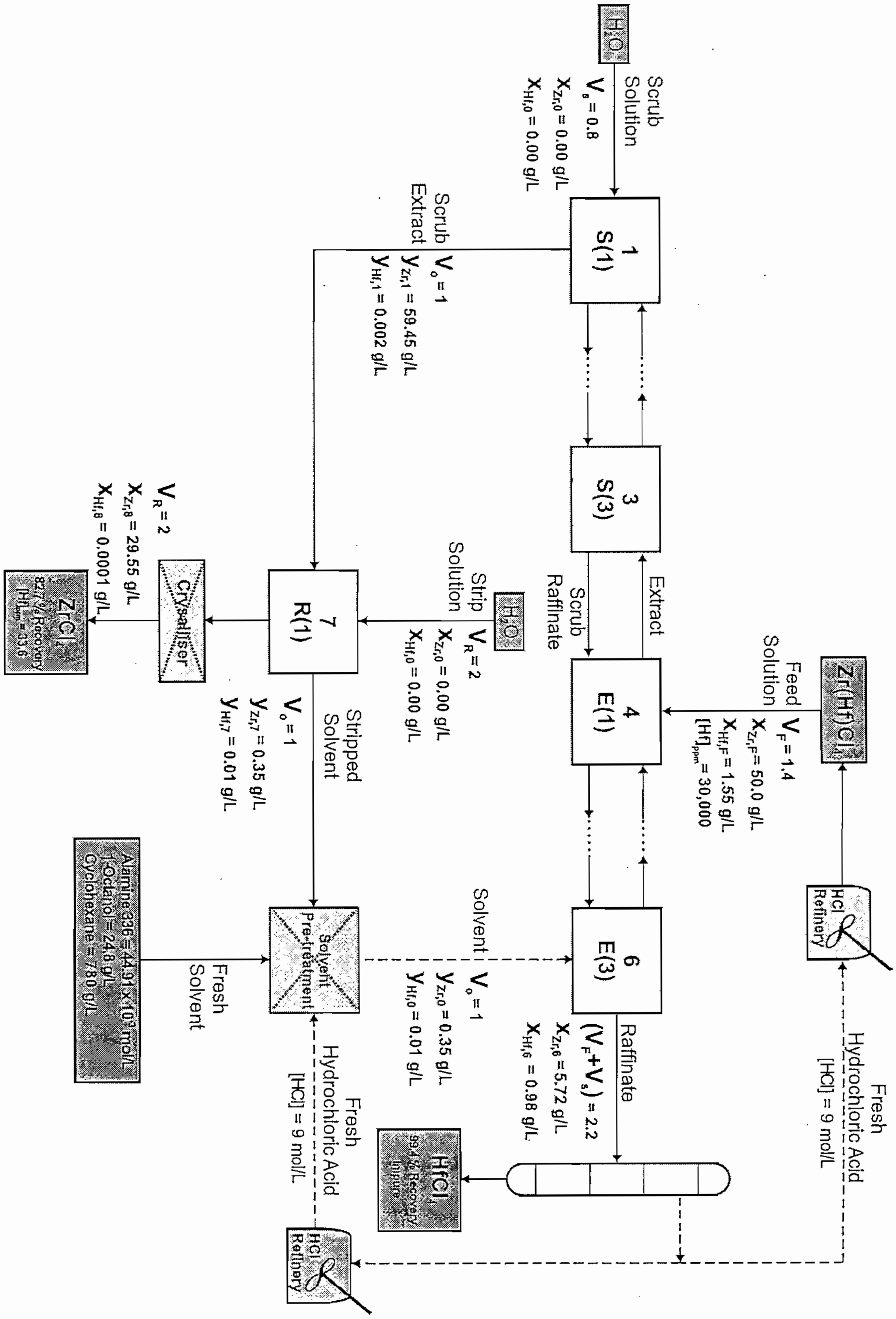

Figure 58: Proposed process flowsheet for the separation of Zr and Hf via solvent-extraction

The proposed production process for nuclear-grade Zr sponge, as shown in Figure 2, includes the main steps of (1) plasma dissociation of zircon sand, (2) production of $Zr(Hf)Cl_4$, (3) separation of Zr and Hf by SX and (4) production of Zr metal (Kroll process).

(1) Plasma dissociation of zircon sand:

Zircon ore, which is very inert, is dissociated in a so-called Plasma Dissociated Zircon process (PDZ), by making use of non-transfer a.c. plasma technology. During this process the zircon is transformed from a crystalline product into an amorphous silica product that is more amenable to subsequent chemical processing.

(2) Production of zirconium(hafnium) tetrachloride:

By following the aqueous route, the chemically amenable $ZrO_2.SiO_2$ is reacted with dilute hydrofluoric acid (40% HF) to produce H_2ZrF_6 which is then reacted with KOH or KF to produce $K_2Zr(Hf)F_6$. The $Zr(Hf)Cl_4$ is then produced by reaction with NH_4OH which is followed with carbochlorination (Cl_2/C).

(3) Separation of zirconium and hafnium via solvent extraction:

The organic solvent is 16.5% wt Alamine 336 and 3% v/v 1-octanol in cyclohexane, pre-treated with 9 mol/L HCl. The aqueous acidic feed solution containing 50 g/L $ZrCl_4$ dissolved in a 9 mol/L HCl solution with a Hf-to-Zr ratio Hf/(Hf + Zr) of 3% (maximum Hf in natural zircon ore) is fed to the extraction section of three stages. The two phases are contacted and separated in box-shaped mixer-settler extractors, in a counter-current manner at an aqueous-to-organic flow ratio of 1.4 ($V_F/V_o = 1.4$). Each mixer is designed in such a way that the two phases are in contact for at least 30 minutes. 99.4% of the Hf solute in the feed solution can be recovered after the HCl is retrieved with distillation, leaving the impure Hf solutes in the aqueous raffinate. The Zr-rich organic extract leaving the extraction section at stage E(1) is fed to a scrubbing section of three stages at S(3).

The scrub solution of pure deionised water (pH ≈ 5 - 6), containing no Zr or Hf solutes, is fed to the first scrubbing stage S(1) at an aqueous-to-organic flow ratio of

0.8 ($V_S/V_O = 0.8$), where the Zr can be enriched in the organic extract up to nuclear reactor standards, with counter-current scrubbing of Hf into the aqueous raffinate. The organic scrub extract, leaving the scrubbing section, contains 59.45 g/L Zr solutes with only 0.002 g/L Hf solutes.

This Zr-rich organic phase is then fed to a stripping section, where it is contacted with a strip solution of pure deionised water (pH ≈ 5 - 6), containing no Zr or Hf solutes, at an aqueous-to-organic flow ratio of 2 ($V_R/V_O = 2$). With this single stage cross-current stripping of Zr, 99.4% of the Zr from the organic solvent was stripped and thus 82.7% of the Zr that was fed can be recovered, with a Hf content of only 33.6 parts Hf per million parts of Zr. This solute-free organic solvent is then recycled to the solvent pre-treatment where it can be prepared for extraction.

(4) Production of zirconium metal (Kroll process):

Hf-free Zr sponge can then be prepared by reduction of Zr chloride with magnesium according to the Kroll process, mentioned in Chapter 1. The Zr and magnesium chloride are distilled and the Zr product is crushed to produce nuclear-grade Zr sponge.

5.4. References

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CHAPTER 6

6. CONCLUSION & RECOMMENDATIONS

6.1. Equilibrium Data

During initial experiments, emulsification and third-phase formation problems were solved by using 1-octanol as a modifier in the extraction system, employed in the organic solution prior to extraction. The minimum quantity of modifier to be used was determined as 3% volume of the total organic solution. Investigations of the kinetics of metal extraction proved that equilibrium was established after 30 minutes of contact time but, to be safe 60 minutes was used for contacting the two phases.

One of the key endeavours of this study was to evaluate the use of $K_2Zr(Hf)F_6$ in the production of nuclear-grade Zr metal. However, the attempt was unsuccessful because extraction of neither one of the two metals could be obtained with Alamine 336 or Aliquat 336. Encouraging data have been obtained from chloride-based compounds ($Zr(Hf)Cl_4$) in the feed solutions for both amine extractants. It was clear from the extraction results that HCl is the unsurpassed choice of acid to be used in the aqueous phase. A general trend of an increase in metal extraction with an increase in HCl concentration (Cl^- ion concentration) was obtained. Extractions from additional zirconium(hafnium) compounds ($ZrOCl_2.8H_2O$ and $ZrO(NO_3)_2$) in the aqueous feed solutions proved that Alamine 336 and Aliquat 336 have a greater tendency to form complexes with Zr than Hf and thus separation of the two metals could be achieved. The failure to extract the fluoride compound cannot yet be satisfactorily explained. There is only limited information available on the speciation or ligand-exchange reaction rates of Zr and Hf complexes. Without this information the role of hydrolysis and hydrogen ligands during the extraction remains speculative. According to Table 7, it is clear that Aliquat 336 gave a higher extraction yield for the Zr species, while Alamine 336 improved on the separation selectivity. Thus, because of this issue, the design of the process, as discussed in Chapter 5, will tell us the best choice of extractant between Alamine 336 and Aliquat 336 in terms of the economical implications. Further, it was evident from results obtained that in the case of Alamine 336, an excess of the extractant in the organic phase leads to separation factors up to 32. This loaded organic phase was successfully stripped with deionised water and the Zr metal could be fully recovered.

6.2. Process Evaluation

From the processing standpoint, the plasma dissociation of zircon to produce chemically amenable plasma dissociated zircon (PDZ) is a novel alternative in the zircon beneficiation industry. Various Zr chemicals can be produced via the reaction with more chemically reactive PDZ feedstock. Natural zircon is inert and needs severe reaction conditions.

At least three points can be highlighted from the proposed separation process for Zr and Hf. First, the possibility exists to separate these two metals according to nuclear regulations without the use of environmental unfriendly chemicals like the thiocyanates and the arsine-containing extractants that are used in some of the conventional processes. The use of an amine extractant, Alamine 336, gives both a direct advantage by reducing costs and an indirect advantage by the avoidance of environmental problems. Secondly, the long alkyl chain of Alamine 336 ensures greater solubility of the amine in cyclohexane and lower solubility in the aqueous solutions. Therefore, the near elimination of solvent loss to the aqueous phase is achieved. Finally, the stability of the extracted Zr-amine complex is of such a nature that the recovery of the Zr solutes from the organic phase back into the aqueous phase is possible with deionised water, without the addition of any stripping chemicals. These points can be achieved without making any important changes in the input or output of the extraction system, except for the solvent pre-treatment prior to extraction, which is the case in almost all of the SX processes for zircon beneficiation. Thus, the use of chemicals in the proposed process is fully compatible with conventional technologies.

From an engineering point of view, no problems are expected for the selection of materials used in the separation process. The operating conditions can be considered to be mild. The use of a weak Lewis acid, zirconium(IV) chloride ($ZrCl_4$), as the feedstock in the process has the advantage of high solubility in aqueous solutions because of the linear polymeric structure wherein each Zr is octahedrally coordinated. Thus, a high solute loading capacity relative to chemical consumption can be achieved. The extractant and diluent used in the organic phase are less volatile, harmful and aggressive, therefore minimum requirements relevant to the construction materials are necessary. However, attention should be paid to the selection of materials compatible with the high concentration of HCl. The use of box-shaped mixer-settlers has the advantage of very high stage efficiency. The most important variables in the proposed process are the acidity of the aqueous feed solution and the organic-to-aqueous flow rates to each section.

6.3. Final Remarks and Recommendations

Encouraging data have been obtained through the evaluation of the proposed process. The relatively high selectivity of zirconium(IV) chloride to hafnium(IV) chloride extraction with Alamine 336 has supported the proposed process in terms of low to moderate extraction, scrubbing and stripping conditions. The eight equilibrium stages of Zr enrichment below 35 ppm Hf and above 82% recovery can be considered to be compatible with the SX of Zr and Hf with MIBK and TBP extractants. The elimination of solvent losses, which can be attributed to the low volatility of Alamine 336 and the immiscibility of the organic phase in water, results in reducing costs in three areas: waste treatment, direct reduction in chemical expense and the reduction of solvent make-up at the organic recycling step. The volumetric flow rates of the extraction and scrubbing sections result in lower capital costs due to the smaller equipment that can be used.

In the proposed process, high separation factors arise from the selectivity for Zr, therefore the production of high grade Hf is limited to a raffinate product with no purification whatsoever, whereas, in the case of the MIBK process, the selectivity is for Hf. However, it is possible to include two extra stages in the extraction section for the purpose of Hf purification. The high acidity of the aqueous feed solution is a bit problematic for the economic and engineering factors. It is recommended that the HCl be recovered with a distillation process and then recycled back to an HCl refinery section where it can be distributed to the solvent pre-treatment and feed solution preparation.

It is, however, a great disappointment in this project that the use of $K_2Zr(Hf)F_6$, as the feedstock for the beneficiation of zircon did not succeed. Speciation data, and thus understanding of the chemistry of ZrF_6^{2-} -amine complex formation, might be able to explain why this is the case. For the future, attention should be focussed on speciation of different Zr compounds extracted with different kinds of extractant. From these data it might be possible to predict more appropriate extraction conditions for the separation of Zr and Hf.

The next step in this work is the optimisation of the proposed process in a continuous industrial-scale pilot plant, by improving the technology of both chemical equilibrium and operational levels. According to literature obtained in this study, the equilibrium data of various organic extractants for the selective separation of Zr and Hf are well established. Thus, the conventional processes should be improved by improving the method of separation and scale-up technology of the separation process.

APPENDIX A

A1: Technical Specifications Sheet of Alamine 336

Blue Line
TECHNICAL BULLETIN

Revised February 4, 2008

ALAMINE®336

Alamine 336 is a water insoluble, tri-octyl/decyl amine which is capable of forming oil soluble salts of anionic species at low pH.

APPLICATIONS :

Alamine 336 finds use as an agent for producing oil soluble salts of various anions or as a reagent in recovering and/or purifying organic or inorganic species which are capable of forming anions using a process known as solvent extraction.

CHEMISTRY:

Since **Alamine 336** contains a basic nitrogen atom, it typically can react with a variety of inorganic and organic acids to form amine salts, which are capable of undergoing ion exchange reactions with a host of other anions. The general reactions are shown below in two steps, protonation and exchange, describe this behavior.

Protonation: $[R_3N]_{org} + [HA]_{aq} \rightleftharpoons [R_3NH^+A^-]_{org}$

Exchange: $[R_3NH^+A^-]_{org} + [B^-]_{aq} \rightleftharpoons [R_3NH^+B^-]_{org} + [A^-]_{aq}$

The extent to which B^- will exchange for A^- is a function of the relative affinity of the two anions for the organic cation and the relative solvation energy of the anions by the aqueous phase.

When used as reagent in solvent extraction, the **Alamine 336** first extracts the target species from an aqueous solution and then must be regenerated (stripped) for recovery of the target species and reuse of the reagent. Amine type extractants can be stripped by a wide variety of inorganic salt solutions such as NaCl, Na_2CO_3 and $(NH_4)_2SO_4$. The type of stripping agent used depends on the overall recovery process, but in general basic stripping agents, which reverse the amine protonation reaction, give the best stripping in the fewest stages. The equation below shows the stripping action of Na_2CO_3 on the amine salt:

$$2[R_3NH^+B^-]_{org} + [2Na^+ + CO_3^{=}]_{aq} \rightleftharpoons$$

$$2[R_3N]_{org} + [H_2O]_{aq} + CO_2 + 2[Na^+]_{aq} + 2[B^-]_{aq}$$

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TECHNICAL BULLETIN

In certain cases the formation of anionic complexes, and their subsequent extraction, is dependent upon the concentration of the anion contributing to the anionic complex. Examples include the chloride complexes of copper, cobalt and iron.

SUGGESTED USES:

Alamine 336 is effective for Cadmium, Cobalt, Hafnium, Iron, Niobium, Rare Earths, Tungsten, Uranium, Vanadium and Zinc extraction. **Alamine 336** is also effective for recovery of organic and mineral acids from process and waste streams.

TYPICAL ANALYSIS:

Tertiary Amine Content	95.0-100.0%	Secondary Amine Content	≤ 1.0%
Color (APHA)	≤ 500	Clarity	Clear

CHEMICAL AND PHYSICAL PROPERTIES:

PROPERTIES			SOLUBILITY (g amine/100 g solvent)	
Specific Gravity		0.81	Acetone	13
Surface Tension(dynes/cm@25°C)		53	Water	<5ppm
Pour Point (ASTM)		-54°C	Completely Miscible in:	
Flash Point (ASTM)		179°C	Benzene, Carbon Tetrachloride	
Fire Point(ASTM)		210°C	Chloroform, Cyclohexane	
Viscosity (CPS)	40°C	23	Diisobutyl Ketone, Ethanol,	
	86°C	11	#2 Fuel oil, isopropanol,	
	140°C	6	Kerosene, n-Butanol,	
			n-Decanol.	

AVAILABILITY:

Alamine 336 is available in bulk, totes (net 1800 pounds) drums (net 360 pounds) and five gallon pails (net 30 pounds), F.O.B. Kankakee, Illinois. Pint samples of **Alamine 336** are also available on request.

SAFETY: A Material Safety Data Sheet is available on request.

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Cognis Corporation ● 2430 North Huachuca Drive ● Tucson, Arizona USA 85745-1273
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A2: Technical Specifications Sheet of Aliquat 336

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TECHNICAL BULLETIN

Revised June 1, 2000

Aliquat® 336

Aliquat 336 is a water insoluble quaternary ammonium salt made by the methylation of mixed tri octyl/decyl amine, which is capable of forming oil soluble salts of anionic species at neutral or slightly alkaline pH.

APPLICATIONS:

1) **Solvent Extraction: Aliquat** 336 has been used to recover or purify the following ionic complexes: Cadmium, Cobalt, Iron, Molybdenum, the Rare Earths, Tungsten, Uranium, Vanadium and Zinc. **Aliquat** 336 has also been used in acid purification.

2) **Waste treatment:** Aliquat 336 has been used successfully to remove and recover acids or their salts or to remove certain heavy metals from wastewater. Aliquat 336 is also effective in defoaming wastewater containing anionic surfactants.

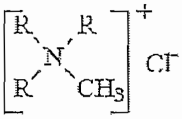
3) **Adhesion promoter and surface curing aid** for fluorocarbon elastomers.

4) **Anti-static agent:** for textile fabrics and carpeting.

5) **Decolorization and deodorization:** of fermentation broths.

Chemistry:

Aliquat 336 is composed of a large organic cation associated with a chloride ion, as shown below.



Because the ammonium structure has a permanent positive charge, it can form salts with anions over a wider pH range than primary, secondary or tertiary amines. For this reason, **Aliquat** 336 finds application in environments from acid to slightly alkaline pH.

When used as reagent in solvent extraction, the **Aliquat** 336 first extracts the target species from an aqueous solution and then must be regenerated (stripped) for recovery of the target species

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and reuse of the reagent. Quaternary ammonium extractants are more difficult to strip than amines. Usually the stripping agent must be more strongly attracted to the quaternary than the anion to be stripped. In some cases, stripping can be accomplished by using a large anion, which will crowd off the anion to be stripped. Chloride ions are frequently effective stripping agents. In certain cases the formation of anionic complexes, and their subsequent extraction, is dependent upon the concentration of the anion contributing to the anionic complex. In other cases, the chloride ion in **Aliquat 336** prevents effective extraction. This is because different anions are bound more strongly than others. It may be desirable to exchange the chloride anion to some other anion. (Request bulletin "Converting **Aliquat 336** chloride to hydrogen sulfate")

TYPICAL ANALYSIS:

% Quaternary salt content	90	Acid value	0-1.0
Amine value	1.0-2.0	Color (Gardner)	3-6
% Water	5	Appearance	amber colored, viscous liquid

Chemical and Physical Properties

PROPERTY		PROPERTY					PROPERTY				
Average Molecular Weight	442	Viscosity (Brookfield)					Thermal Stability*				
Specific Gravity(25°C/25°C)	0.88	4° C	6300cps				Temp	4 hours		8 hours	
Pour Point (ASTM)	-14°C	30° C	1450cps					III°	IV°	III°	IV°
Flash Point (ASTM)	132°C	60° C	197cps				25° C	0.28	10.1	0.37	10.0
Surface Tension (dynes/cm)	28	Solubility**	0°C	8°C	30°C	60°C	60° C	1.14	9.4	1.77	8.7
Interfacial Tension (dynes/cm)		Benzene	-	100	100	100	100° C	9.21	1.3	9.28	1.2
1.0% Nujol Solution	1.6	Chloroform	100	100	100	100	Control	0.22	10.2		
0.1% Nujol Solution	3.1	Isopropanol	100	100	100	100	(0 Hour)				
0.01% Nujol Solution	20.6	Kerosene***	100	100	100	100					
		Water ****	-	-	0.12	0.2					

* Stability tests were done by stirring equal volumes of 10w/v% Aliquat 336 in xylene and 50% aqueous NaOH at elevated temperatures. Samples were titrated for tertiary amine (III°) and quaternary salt (IV°) values.

** (g/100g solvent)

*** Increasing aromatic content of kerosene results in increased solubility.

**** The distribution of Aliquat 336 into an aqueous phase from kerosene would be much lower than the solubility of Aliquat 336 in the aqueous phase.

Availability:

Aliquat 336 is available in bulk, totes (net 1800 pounds) drums (net 390 pounds) and five-gallon pails (net 30 pounds), F.O.B. Kankakee, IL or Charlotte, NC. Pint samples of **Aliquat 336** are also available.

Safety: Material safety data sheet (MSDS) available on request.

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APPENDIX B

B: Quantitative Determination of Zr and Hf

The instrument used was a Thermo-Scientific *i*CAP 6000 Series ICP-OES (see Figure B1), utilizing the *i*TEVA software. For the analysis of Zr and Hf, ICP standards of the elements were obtained from Merck, which were the oxychlorides of Zr and Hf (Zr/HfOCl$_2$) dissolved in HCl with concentrations of 1000 mg/L (CertiPUR). The standard solutions are of high purity and the Zr solution contains less that 0.1 mg/L Hf and the Hf solution less than 0.1 mg/L Zr. Solutions with different concentrations (10, 50, 100, 500 mg/L) of both Zr and Hf were prepared from these solutions for calibration purposes.

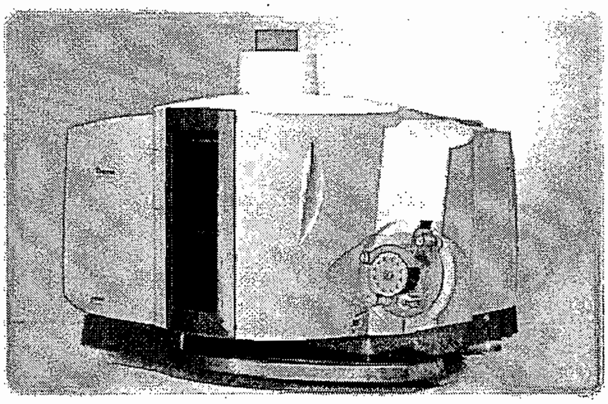

Figure B1: Thermo-Scientific *i*CAP 6000 Series ICP-OES

The instrument was calibrated for two emission wavelengths for Zr and Hf that, according to the *i*TEVA software, gave the highest sensitivity for both Zr and Hf and the least amount of interference of each element with the other as summarised in Table B1.

Table B1: Relative intensity of selected emission lines of Zr and Hf

Emmision Line (nm)	Relative Intensity	Interference with Zr/Hf	% Interference
Zr (339.1)	3500000	27059	0.77
Zr (343.8)	2500000	15000	0.60
Hf (263.9)	1000000	80000	8.00
Hf (339.9)	600000	50000	8.33

The calibration for each of the emission lines resulted in calibration curves for both Zr and Hf as shown in Figures B2 and B3, with a correlation of better than R^2 = 0.9999.

Table B2: Calibration data for Zr using the 343.8 nm emission line

Sample name	Concentration (mg/L) Stated	Concentration (mg/L) Found	% Difference
Blank	0.0000	-0.0011	0.00
STD 1	10.000	10.396	3.96
STD 2	50.000	53.340	6.68
STD 3	100.00	100.94	0.94

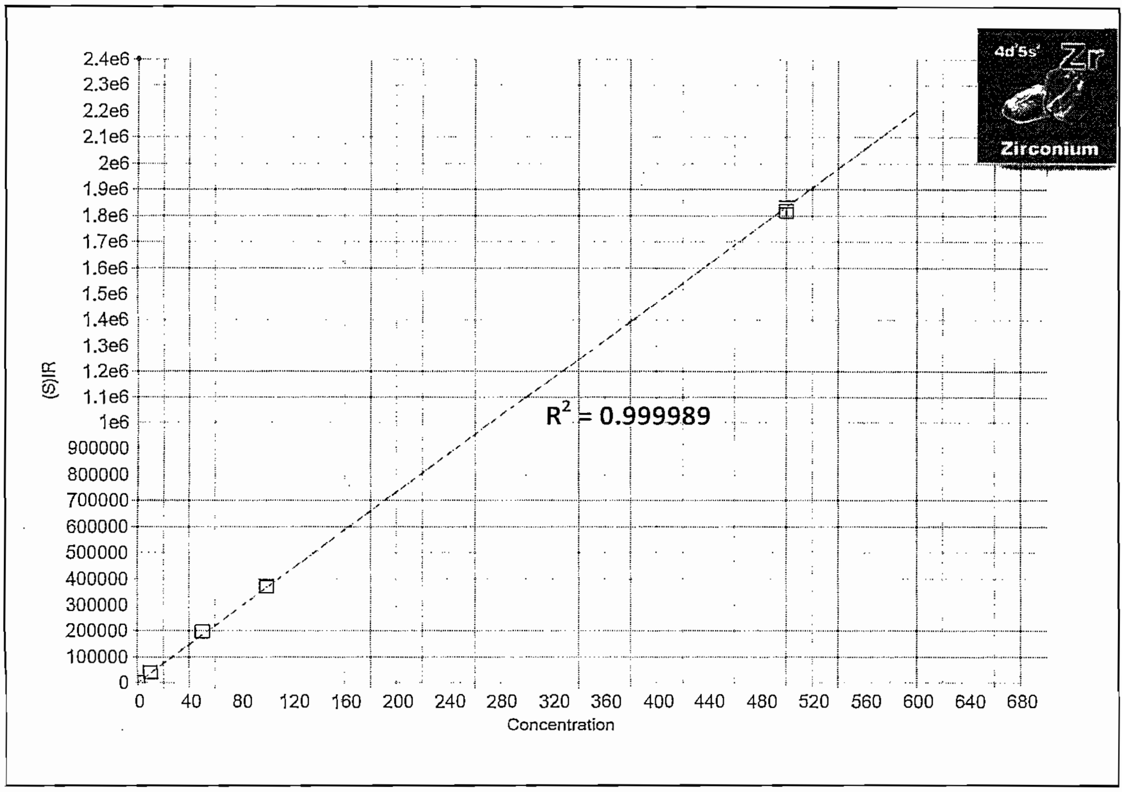

Figure B2: Representative calibration curve for Zr using the 343.8 nm emission line

Table B3: Calibration data for Hf using the 263.8 nm emission line

Sample name	Concentration (mg/L) Stated	Concentration (mg/L) Found	% Difference
Blank	0.0000	0.0020	0.00
STD 5	10.000	10.072	0.72
STD 6	50.000	48.536	-2.93
STD 7	100.00	99.855	-0.15

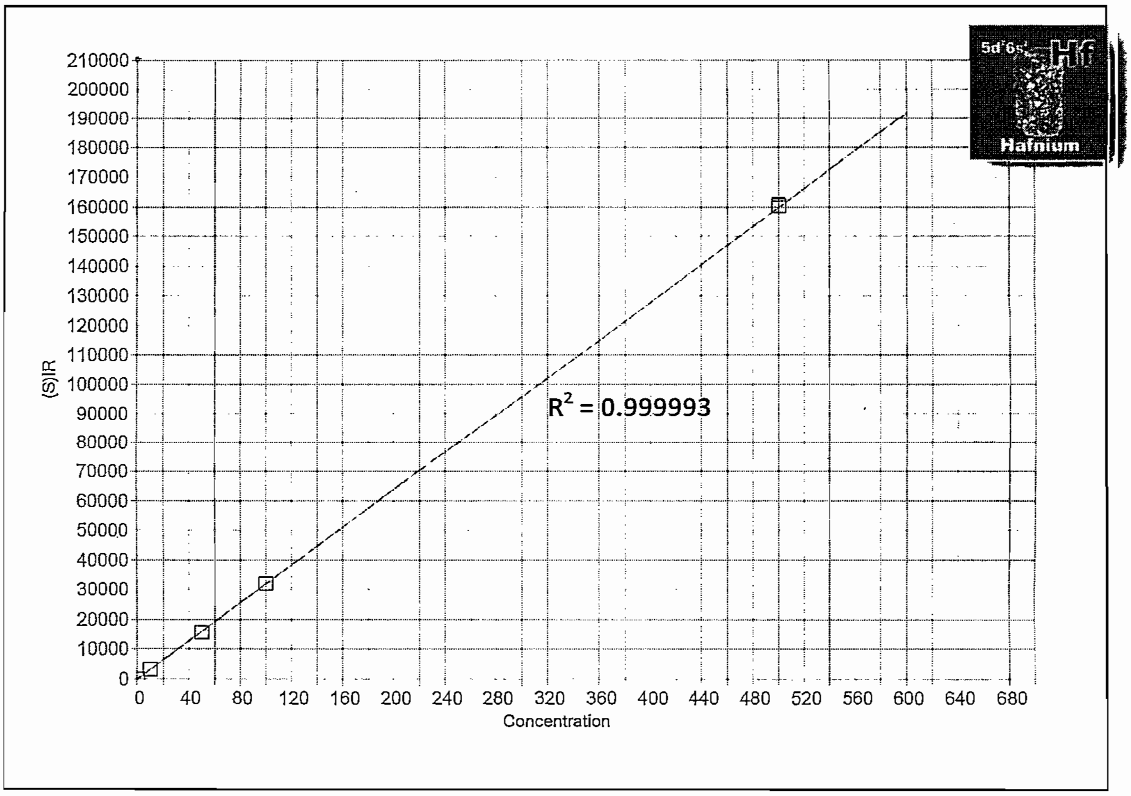

Figure B3: Representative calibration curve for Hf using the 263.8 nm emission line

Using the calibrations for each of the emission lines for Zr and Hf, the calibration standards were then analyzed again to test the accuracy of the method, the results of which are shown in Table B4. The negative values indicate that the detected line intensity is lower than the detection limit of the instrument and, as in the case of the blank solution, it can be assumed that the concentration is zero.

Table B4: Accuracy tests for calibrated emission lines of Zr and Hf

Sample name	Zr/Hf (mg/L)	Determined Concentrations (mg/L)			
		Zr (339.1)	Zr (343.8)	Hf (263.8)	Hf (339.9)
Blank	Zr & Hf = 0	-0.512	-0.4570	0.703	2.353
Zr10	10.00	10.32	10.360	0.676	2.290
Zr50	50.00	53.74	53.460	0.701	2.336
Zr100	100.0	104.4	104.90	0.712	2.624
Zr500	500.0	495.3	502.70	0.832	3.690
Hf1	1.000	-0.458	-0.4680	1.207	2.998
Hf10	10.00	0.275	0.3160	10.86	13.93
Hf50	50.00	-0.459	-0.3160	52.01	60.70
Hf100	100.0	-0.278	-0.0330	100.4	114.3
Hf500	500.0	-0.101	0.1120	494.7	557.6

From these results it was concluded that the emission lines of 343.8 nm for Zr and 263.8 nm for Hf gave the most accurate results. These were the emission lines used in further analysis. Before each analysis one or two standards were analyzed to determine whether the concentrations were accurately detected and, if so, the analysis of samples with unknown concentrations were carried out.

During the analysis of samples containing high concentrations of H_2SO_4, it was observed that there were deviations on the contained metal concentration in the aqueous phase. Accordingly, it was decided to investigate the possibility of a matrix effect in sample analysis.

An experimental study on the effect that a different matrix has on the results obtained from ICP-OES analysis was conducted and the results are shown in Figure B4. Zr and Hf ICP standards in their oxychloro form were used to calibrate the ICP-OES. After calibration, solutions containing 5 mg/L Zr and Hf were made up with different H_2SO_4 concentrations. Each of the samples were run as an unknown, and the %RSD was calculated up to 50%. Therefore, for future analysis, all samples (including those containg H_2SO_4) were ten times diluted in order to maintain the %RSD below 10%.

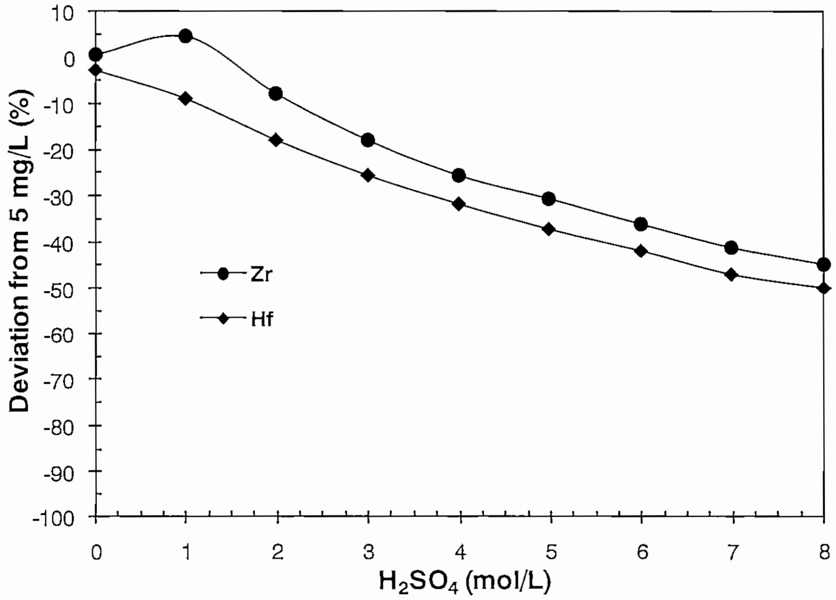

Figure B4: The effect of different matrix on ICP-OES results

Figure B5 gives an idea of the accuracy of the ICP-OES results when using an auto-sampler on many samples in a row. Samples were made up from Merck standards containing 50 mg/L Zr and Hf, respectively. Quality checks (QC's) of 50 mg/L were used to check if the results were up to standard.

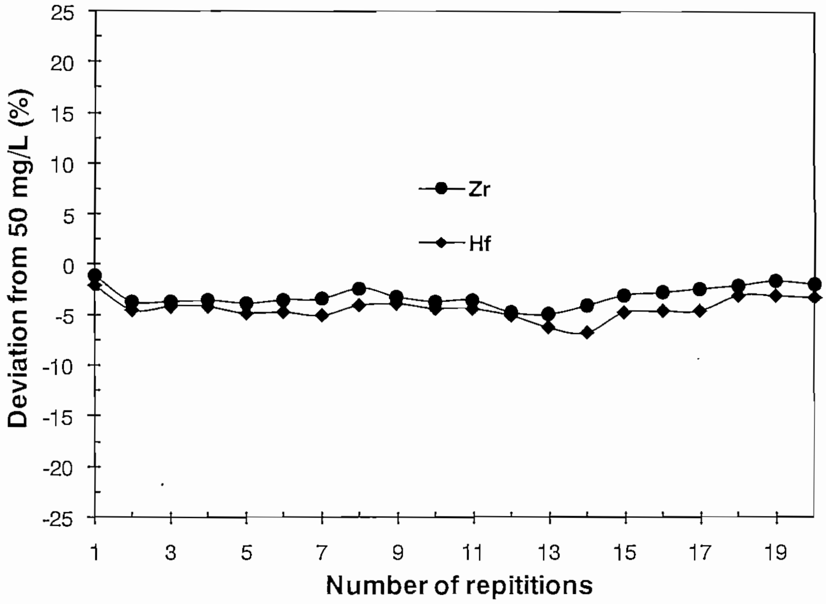

Figure B5: % Deviation when repeating sample analysis

When the known concentration of the QC sample was run 20 times in a row, the %RSD for Zr(343.8 nm) was 1.04 and for Hf(263.8 nm) 1.09. This was a good indication that the results obtained from the ICP-OES were reliable and trustworthy.