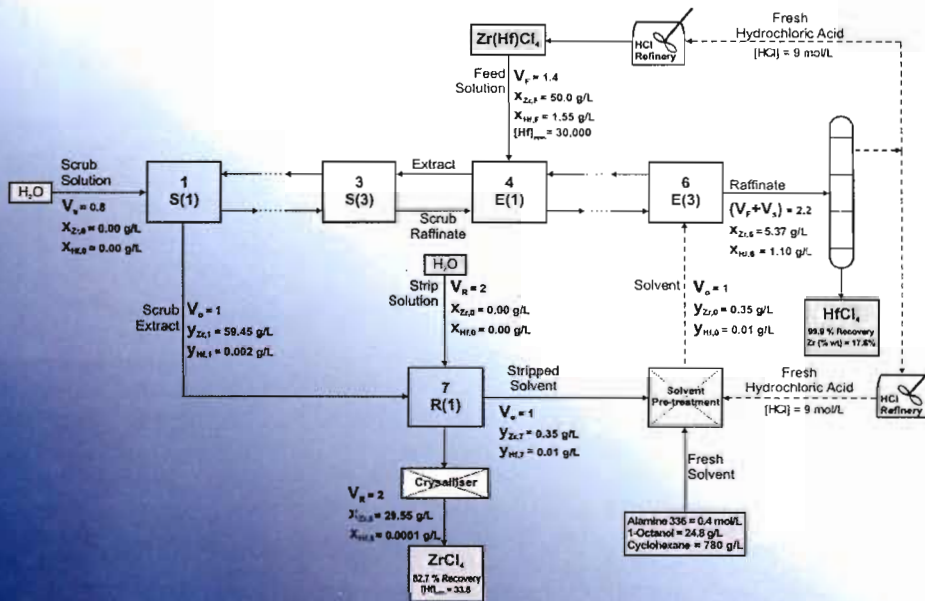




Separation of Zirconium and Hafnium via Solvent Extraction



Derik van der Westhuizen
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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 organiese 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 coefficient 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 (HNO₃) 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 Européenne 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 tetrachloride (Zr(Hf)Cl₄) by carbochlorination from the zircon ore. This Zr(Hf)Cl₄ still contains 1-3% wt of HfCl₄. Prior to the separation process the Zr(Hf)Cl₄ is converted to its oxychlorides and is then processed through a multiple-step SX process in the presence of ammonium thiocyanide (NH₄SCN). 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 (ZrO₂). Pure ZrCl₄ is produced by a second carbochlorination of the ZrO₂^[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 $\text{Zr}(\text{Hf})\text{Cl}_4$ vapours rise in a counter flow against a descending solution of AlCl_3/KCl saturated with $\text{Zr}(\text{Hf})\text{Cl}_4$ 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.

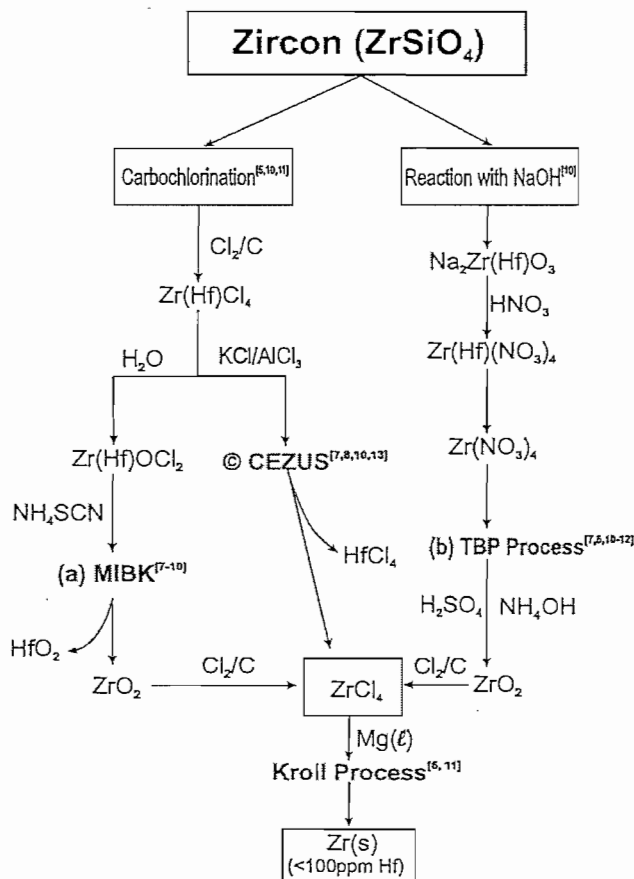


Figure 1: Conventional methods for the production of nuclear grade zirconium

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.

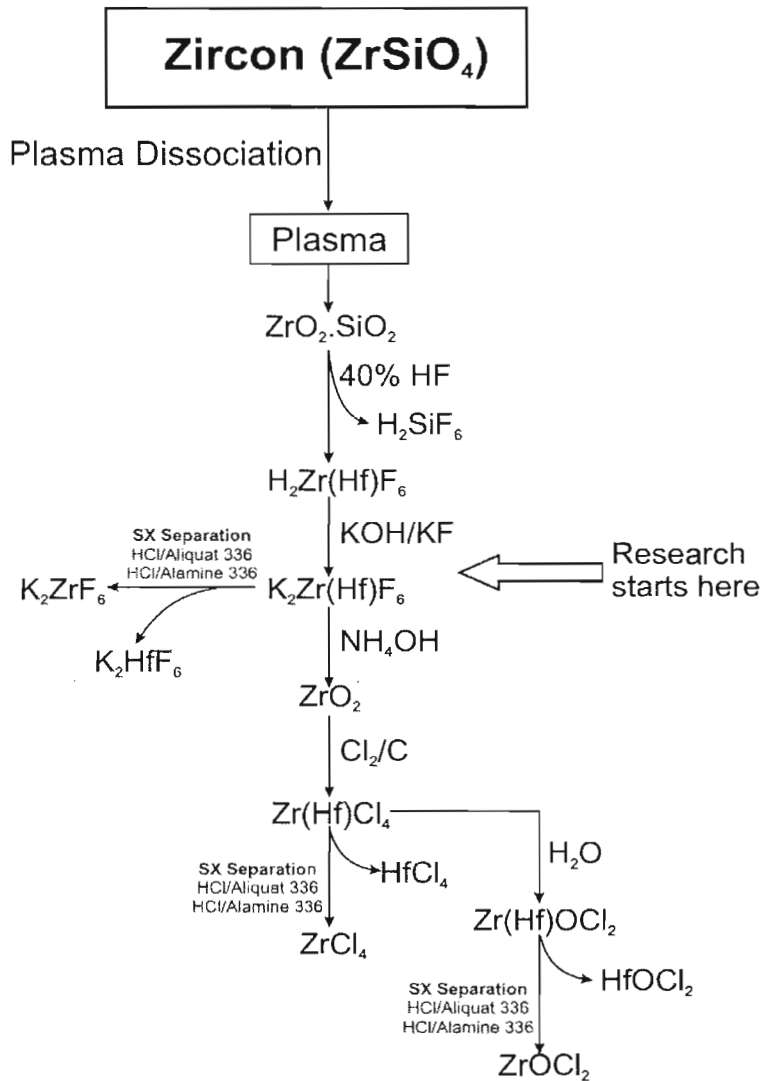


Figure 2: Research path adopted for the separation of zirconium and hafnium

$K_2Zr(Hf)F_6$ 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:

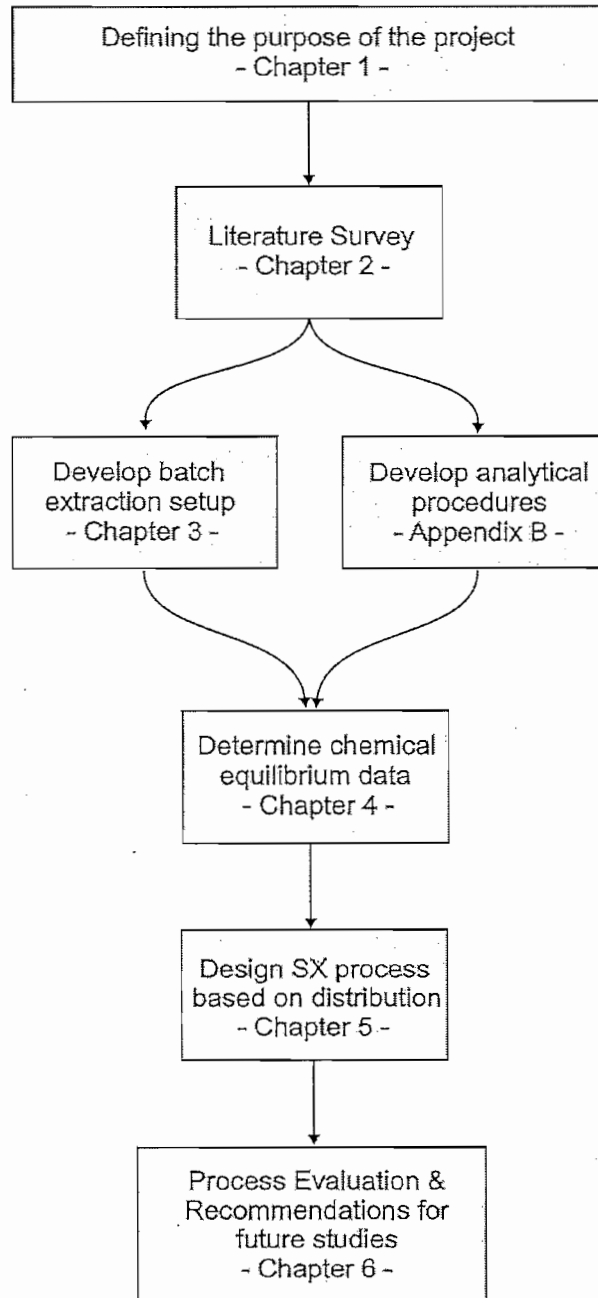


Figure 3: Research path followed in the investigation

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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 8×10^{-5} to 8×10^{-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)	Dominant 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. Quantitative 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 1.0×10^{-3} mol/L $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, with 1.0×10^{-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 2.0×10^{-4} to 8.0×10^{-4} mol/L amine donors extract better than the phosphorus donors with a Zr extraction of 88 to 95% from a 1.1×10^{-3} mol/L Zr(IV) acidic solution that was spiked with a ⁹⁵Zr 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 1.15×10^{-1} mol/L Alamine 336 and 1.11×10^{-1} mol/L Aliquat 336 together with 3.7×10^{-2} mol/L TBP as extractant and obtained 99%

and 100% extraction from a 1.0×10^{-3} mol/L $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ 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 1.0×10^{-3} mol/L HfCl_4 acidic chloride solution following a cation-exchange reaction with 98% extraction by 2.0×10^{-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 1.2×10^{-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 (3.4×10^{-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 $\text{K}_2\text{Zr}(\text{Hf})\text{F}_6$ 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 HNO₃ 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)-C₆H₆ system, including Zr and Hf. The phosphorus analogue of TOCASO and tris(*n*-octyl)phosphine (TOPO) were found to be superior to tributylphosphate (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 (⁹⁷Zr) and hafnium (¹⁸¹Hf), 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 HNO₃ 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 ZrOCl₂.8H₂O 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 HNO₃ 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 HNO₃ (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 $2ZrCl_4 \cdot PCl_5$ after the $ZrCl_4$ reacted with PCl_5 , and $2ZrCl_4 \cdot POCl_3$ 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 H₂SO₄ 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 H₂SO₄ 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.

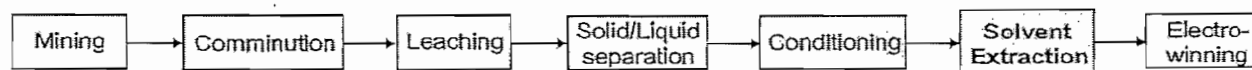


Figure 4: Process route in hydrometallurgy using solvent extraction for metal separation

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 (floculants 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.

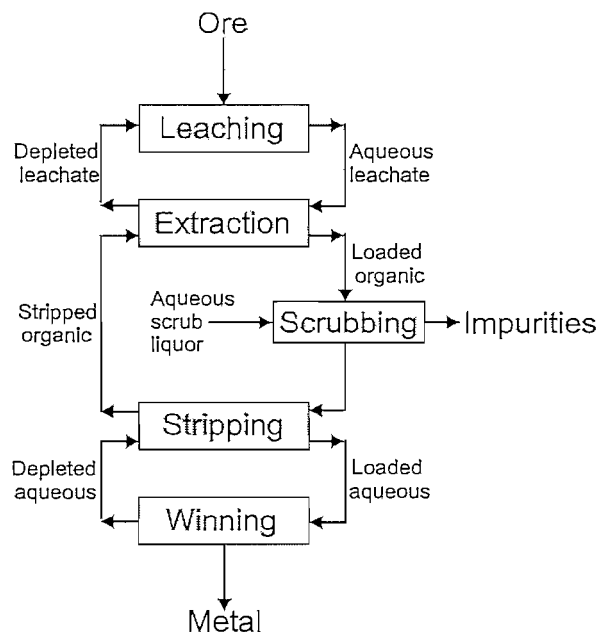


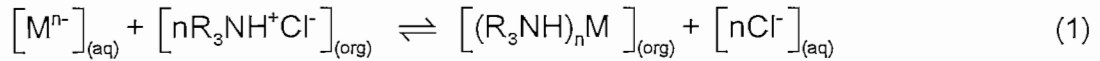
Figure 5: Typical SX flowsheet for the purification of metals from a leach solution

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,



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

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

$$K = \frac{[Cl^-]^n [(R_3NH)_n M]}{[R_3NH^+Cl^-][M^{n-}]^n} \quad (2)$$

and, by taking logarithms,

$$\log K = \log [(R_3NH)_n M] + n \log [Cl^-] - \log [M^{n-}] - n \log [R_3NH^+Cl^-] \quad (3)$$

Thus, by rearranging Equation 3

$$\log \frac{[(R_3NH)_n M]}{[M^{n-}]} = \log D_M = \log K + n \log [R_3NH^+Cl^-] + n \log [Cl^-] \quad (4)$$

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 $[M]_{(aq)}$:

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

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

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

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:

$$D_{rel} = \frac{D_{M_i}}{D_{M_j}} \quad (7)$$

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

$$SF = \frac{1}{D_{rel}} \quad (8)$$

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) Solvent-extraction kinetics

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.

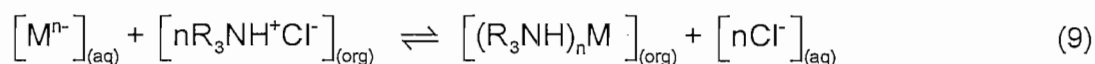
Metal extraction with extractants in SX involves three steps^[83]:

- 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):



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

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

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) The mass transfer process of solvent-extraction

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:

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

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

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

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

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

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

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 features 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]

$$s = kN^3D^2 \quad (15)$$

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]:

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

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 ($\text{R} = \text{C}_8\text{H}_{17}$) 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).

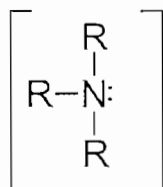


Figure 6: Lewis presentation of a tertiary amine

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 shows the Lewis presentation of a quaternary amine.

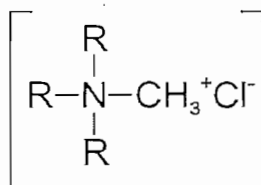


Figure 7: Lewis presentation of a quaternary amine

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,