

Selective membrane based solvent extraction of Hf from a $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$ solution

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"Chaos isn't a pit. Chaos is a ladder. Many who try to climb it fail, and never get to try again — the fall breaks them. And some are given a chance to climb, but they refuse. They cling to the realm, or the gods, or love ... illusions. Only the ladder is real, the climb is all there is." — Petyr 'Littlefinger' Baelish

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Abstract

Zr and Hf, which co-exist in nature, have similar chemical properties, except for their absorbance of neutrons which implies that Zr must contain $< 100 \text{ mg.L}^{-1}$ before it can be used as fuel cladding in nuclear reactors. In a newly proposed process, where Necsa uses a plasma and fluoride chemical process to produce Zr from Zircon, a $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$ complex is formed. It was the aim of this study to investigate the solvent extraction (SX) based separation of Zr and Hf using the $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$ complex as feed stock.

The following parameters were investigated in this study: i) the acid type (HNO_3 , HCl , H_2SO_4), and concentration ($0 - 8 \text{ mol.dm}^{-3}$), ii) the extractant type (amine- and phosphorus-based extractants) and concentration ($0 - 10 \text{ wt } \%$), iii) the stripping compound (H_2SO_4 and NaCl for the amine-based extractions and H_2SO_4 , $(\text{NH}_4)_3\text{CO}_3$, CaCl_2 and $\text{C}_2\text{H}_2\text{O}_4$ for the phosphorus-based extractions) and concentration ($0 - 2 \text{ mol.dm}^{-3}$), iv) the ageing of the feed solution, v) the time to reach equilibrium during SX experiments and vi) the influence of single vs binary metal complexes on extractions. Finally the suitability of membrane based solvent extraction (MBSX) was investigated for the phosphorus-based extraction process.

For the amine-based extractions, Alamine 336, Alamine 300, Alamine 308, Aliquat 336 and Uniquat 2280 were selected and evaluated. While Alamine 336 and Aliquat 336 yielded the highest extractions, the most promising combinations of solvent extraction (Zr = 60 %, Hf = 41 %) and selectivity (19 %) was obtained when extracting with 9 wt% Alamine 336 from a $0.5 \text{ mol.dm}^{-3} \text{ H}_2\text{SO}_4$ solution. When stripping from the loaded Alamine 336, it was found that nearly 100 % of the Zr and 95 % of the Hf could be recovered when stripping with $0.01 \text{ mol.dm}^{-3} \text{ H}_2\text{SO}_4$. On the other hand, a highly selective 46 % of the Hf and almost no Zr was stripped when using $2 \text{ mol.dm}^{-3} \text{ NaCl}$ confirming the suitability of both these stripping liquors depending on the required need.

D2EHPA, Dio-PA and Ionquest 801 were selected as examples of the phosphorus-based extractants. For all three extractants both in HCl and H_2SO_4 , more than 90 % Zr and Hf was extracted. Ageing of the feed solution had no effect on the extraction efficiency while the equilibrium time was found to be 30 minutes. When optimising the E/M ratio, it was found that 9 wt% D2EHPA gave the best results (82 % Hf and 48 % Zr extraction) when extracting from a $4 \text{ mol.dm}^{-3} \text{ H}_2\text{SO}_4$ solution. When stripping from this loaded organic phase, the best results were obtained with $1.2 \text{ mol.dm}^{-3} (\text{NH}_4)_2\text{CO}_3$, which gave a

stripping of 53 % Zr and nearly 100 % Hf, 2.0 mol.dm^{-3} CaCl_2 , which gave a stripping of 75 % Zr and < 1 % Hf and 1.2 mol.dm^{-3} $\text{C}_2\text{H}_2\text{O}_4$, which gave a stripping of 93 % Zr and nearly 100 % Hf. When extracting with 9 wt% D2EHPA using MBSX, a 69 % Zr and 83 % Hf extraction was obtained. The membrane based stripping with CaCl_2 yielded 54 % Hf and almost 0 % Zr stripping, while $\text{C}_2\text{H}_2\text{O}_4$ yielded 74 % of both Zr and Hf. However, both the extraction and the stripping took considerable longer time to reach equilibrium when using MBSX.

From these results it is clear that it was possible to extract Zr and Hf from the $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$ complex. Both the amine- and phosphorus-based extractants have specific advantages. For example, the amine process is Zr-selective, while the phosphorus process is Hf-selective. When combining the extraction, scrubbing and stripping steps using Alamine 336, 53.3 % of Zr with a purity of 99.0 % was obtained. When combining the extraction, scrubbing and stripping steps using D2EHPA, a combined 97.2 % Zr yield, again with a purity of 99 % in both product streams, were obtained showing that the D2EHPA based extraction yielded significantly more of the purified Zr. When using MBSX, 4.5 % less Zr product was obtained over the two product streams while the purity decreased with 3 % compared to the traditional SX when using D2EHPA.

Keywords: Solvent extraction, membrane based solvent extraction, amine-based extractants, phosphorus-based extractants, zirconium, hafnium.

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Nomenclature and symbols

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Zr	Zirconium
Hf	Hafnium
SX	Solvent extraction
MBSX	Membrane based solvent extraction
Å	Armstrong
TBP	Tributyl phosphate
Necsa	Nuclear Energy Corporation South Africa
D2EHPA	Di-(2-ethylhexyl)phosphoric acid
Ionquest 801	2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester
Dio-PA	Diisooctylphosphinic acid
Alamine 336	N,N-dioctyl-1-octanamine
Aliquat 336	Trioctylmethylammonium chloride
Uniquat 2280	Didecyl dimethyl ammonium chloride
LIX-84 IC	2-hydroxy-5-nonylaceto- phenone oxime

Chapter 2

MIBK	Methyl isobutyl ketone
Aq.	Aqueous
Org.	Organic
M	Metal

M^{n-}	Negative charges metal
MX	Metal bond to halogen
R	Alkyl groups
K	Equilibrium constant (-)
D_m	Distribution ratio between metals (-)
Ex%	Percentages extraction (%)
V	Volumes (mL)
k	rate constant (-)
PP	Polypropylene

Chapter 3 and 4

E/M ratio	Extractant to metal ratio
ICP-OES	Inductively coupled plasma optical emission spectrometry

Chapter 5

SF	Separation factor (-)
Ψ_{Zr}	Zr yield (%)
β_{Zr}	Zr purity (%)
[M]	Metal concentration (mg.L^{-1})
D_m	Distribution ratio between metals (-)

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Chapter 1

Introduction

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Preface

This work was initiated by the Department of Science and Technology (DST), South Africa, via the Advanced Metals Initiative (AMI), with the purpose to develop novel, or improve existing technologies for the beneficiation of South African resources. Within the AMI, the South African Nuclear Energy Corporation SOC Limited (Necsa), due to its existing expertise and infrastructure, was entrusted with the investigation of the beneficiation of Zr, Hf, Ta, Nb and U, thereby establishing the Nuclear Materials Development Network (NMDN) of the AMI.

1.1 Background

1.1.1 Historical perspective

Zirconium (Zr) was first discovered in 1789 by Martin Heinrich Klaproth, a German chemist, who, while analysing jargonite, discovered a Zr containing mineral. [1] The isolation of the impure Zr mineral was accomplished some years later (1824) by Jöns Jacob Berzelius [2], while the separation and purification of pure Zr was achieved in 1925 by Van Arkel and De Boer. [3] To obtain nuclear grade Zr, Zr must be separated from Hafnium (Hf), which always co-exists with it (1 - 3 %) in the ore and has similar chemical properties including atom radii ($Zr = 1.45 \text{ \AA}$, $Hf = 1.44 \text{ \AA}$) and valence electron configuration (Zr: $[Kr]4d^25s^2$ and Hf: $[Xe]4f^{14}5d^26s^2$). The need for the purification of Zr from Hf arises due to their significantly different nuclear properties. Zr has a low thermal neutron cross-section and is used as fuel-cladding material in nuclear reactors whereas Hf is used in the nuclear reactor as control rods and has a 640 times higher thermal cross-section for neutrons than Zr. [4] For the nuclear application of Zr, it should contain less than 100 mg.L^{-1} Hf, which has prompted the development of various separation techniques. With the successful purification and isolation of Zr metal, the first commercial nuclear power station was commissioned in England in 1956. [5]

1.1.2 Extraction and separation

While the separation of Zr and Hf has been achieved successfully using ion exchange [6] and distillation [7], solvent extraction (SX) is currently one of the most applied techniques available. [7, 8] These various techniques will be further

discussed in Chapter 2. SX has been used extensively not only to separate valuable minerals but also to purify natural essential oils from fresh fruit [9]. SX also generally reduces the environmental (energy and agro-solvents) impact of a separation process. [10]

In 1958 Cox *et al.* published a paper on the SX-based removal of Zr from Hf from a HNO_3 environment using tributyl phosphate (TBP) as extractant. [11] This led to the TBP process that is used to this day (see Section 2.3.3.3). In 2006 Poriel *et al.* investigated the suitability of the amine extractants, Alamine 336 and Aliquat 336, for the separation of Zr and Hf from an HCl acidic solution. [12] This will be discussed in more detail in Chapter 3. Apart from HCl, the stronger acid, H_2SO_4 , has also been investigated as a possible extraction feed phase. In 1971, H. Meider-Goričan presented a paper on the selective extraction of Zr and Hf from a H_2SO_4 solution which was followed by numerous papers presenting the optimisation of various different experimental SX conditions. [13-17]

In line with this study, there have been some recent studies investigating the suitability of incorporating membrane contactors into the SX process to act as a physical barrier between the organic phase and the aqueous phase. While this membrane-based SX (MBSX) has also been used for the separation of Zr and Hf [18], the technology is still novel and further confirmation is required to establish its suitability.

Problem statement

While various Zr(Hf) salts have been separated using SX, the plasma and fluoride chemical process developed by Necsa [19] produces a $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$ complex which, according to our knowledge, has never been used as the starting material for separation studies to date. This has led to the development of the research questions pertaining to this study.

Research questions

- Is it possible to selectively extract either Zr or Hf from a $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$ acid solution using amine- and/or phosphorus-based extractants?

- Can Hf be extracted preferentially from the $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$ acid solution?
- Can selective stripping of the organic phase be achieved?
- Which experimental variables will influence the extraction and selectivity?
- How will batch extraction and stripping perform when compared to MBSX?

1.1.3 Limitations

While it would be beneficial to obtain the exact speciation of the $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$ complex, previous studies have shown that speciation of these bimetallic species are both complex and difficult and will hence fall beyond the scope of this study. While it is assumed that the heptafluoride complex is stable in the solid state, it will most certainly convert to other species once dissolved. In addition to the various species, polymerisation is known to occur [3], which further complicates the system. In addition, Zr and Hf species are not UV active, placing limitations on the analytical methods available for the determination of the possible metal complexes. While some studies have focussed on MBSX, it remains a fairly novel technology, which could contribute to gaps when attempting to explain specific deviations in results when comparing with SX data.

1.2 Aim and objectives

The aim of this study was to investigate the selective extraction and separation of Hf from an $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$ acid solution by using SX and MBSX. Since the aim was to preferentially extract Hf rather than Zr, amine- and phosphorus-based extractants were chosen based on their demonstrated Hf selectivity in previous studies, albeit for other Zr(Hf) salts. [14] This led to the following objectives:

- Screening of possible feed solutions of HNO_3 , HCl and H_2SO_4 in concentration ranges of 0 - 8 mol.dm⁻³.
- Comparison of SX-based extraction data of single- and binary metal complex feed solutions.

- Determination of the best amine-based extractants over the concentration range of 0.1 - 10 wt%.
- Determination of the best phosphorus-based extractants over the concentration range of 0.1 - 10 wt%.
- Evaluation of stripping liquors for both loaded amine- and phosphorus-based organic phases.
- Evaluation of MBSX while using a phosphorus-based extraction and oxalic acid ($C_2H_2O_4$) and calcium chloride ($CaCl_2$) as stripping liquor.

1.3 Overview of chapters

In Chapter 1, a brief history on Zr and Hf and their separation is presented, followed by the problem statement which leads to the research questions and limitations. This is followed by the aim and objectives of this study.

In Chapter 2, a literature study on Zr and Hf is presented focussing on different separation methods for industrial and research purposes. Extended information on the chemistry of Zr and Hf formation, extraction and behaviour in different solutions is discussed. Lastly, SX and MBSX are explained in the light of Zr and Hf separation, presenting a new and possibly greener and more effective alternative for the production of nuclear grade Zr metal.

In Chapter 3, the extraction of Zr and Hf using amine-based extractants (Alamine 336, Aliquat 336, and Uniquat 336) is presented. The extraction from H_2SO_4 and HCl is discussed, followed by a study on the influence of the E/M ratio. Subsequently, stripping data using H_2SO_4 and NaCl is presented.

In Chapter 4, the extraction of Hf over Zr using phosphorus-based extractants (D2EHPA, Ionquest 801, and Dio-PA) is discussed. After optimising the extraction from HCl and H_2SO_4 aqueous solutions, the stripping with H_2SO_4 , $C_2H_2O_4$, $CaCl_2$ and $(NH_4)_2CO_3$ was investigated. This is followed by a discussion on MBSX.

In Chapter 5, the results and conclusions drawn from Chapter 3 and 4 are evaluated and related to the research questions and the aim and objectives. Based on this evaluation, the chapter is concluded with recommendations, including possible topics for further research.

In Appendix 1 the experimental results of the extraction with LIX-84 IC in HCl, H₂SO₄ and HNO₃ that was not used in the discussions of Chapter 3 and 4 are presented. LIX-84 IC was included in the initial screening of possible extractants and acids for the separation of Zr and Hf from (NH₄)₃Zr(Hf)F₇. Supplementary data on Cyanex 301 in all three acid solutions is also included in this Appendix. In Appendix 2, results relating to Chapter 3 are presented, including the data for the amine-based extractions from HNO₃ as well as the data on Alamine 300 and Alamine 308 from H₂SO₄. E/M ratio results of Aliquat 336 in H₂SO₄ solutions is also included. In Appendix 3, related to Chapter 4, results on the E/M ratio of the phosphorus-based extractants (Dio-Pa and Ionquest 801) in H₂SO₄ and HCl as well as the equilibrium studies and ageing of the feed solution, are presented. Lastly, Appendix 3 contains the HNO₃ data of D2EHPA, Dio-PA and Ionquest 801 extraction of the single metal complexes.

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Chapter 2

Literature study

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2.1 Introduction

Over the centuries metals and metal complexes have been separated by many processes and methods. While the separation of metals that co-exist in nature is often difficult because of their chemical similarities, SX has been used successfully for the separation of various metals. [1] Other processes that are currently used for the separation of chemically similar metals include distillation and ion exchange, as discussed further in Sections 2.3.1 and 2.3.2.

For the separation of Zr and Hf for the production of nuclear grade Zr ($< 100 \text{ mg.L}^{-1}$), SX methods are commonly used. Various Zr and Hf salts such as oxychlorides, tetrachloride and sulfates have been separated using a variety of extractants such as the Cyanex group extractants [2, 3], amine-based extractants [4-6], Ionquest 801 [7] and phosphorus-based extractants. [3, 8] These separations have been achieved from HCl, H_2SO_4 and HNO_3 solutions at different concentrations, temperatures, equilibrium times and organic to aqueous phase ratios.

The focus of this literature study will be to provide background related to the aim of this study, which was to separate Hf from Zr from a $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$ complex using SX and MBSX (Chapter 1). As in any SX process, the subsequent stripping that is required to regenerate the organic phase, thereby creating a viable SX process, will be discussed.

2.2 Zirconium and hafnium complexes

2.2.1 Introduction

While it is known that Zr and Hf have many naturally occurring species that can be present in a solution, limited speciation data or methods to produce speciation data for the complex SX systems are available to date. This is made more difficult by the fact that Zr and Hf undergo various hydrolysis and polymerisation reactions in different acids at different temperatures and time intervals (ageing of aqueous Zr(Hf) complex solutions). [8] It is thus important when studying the SX of Zr and Hf to maintain as many of the external factors as possible at constant levels. These include temperature, acid concentration and ageing of the metal solution.

2.2.2 Formation of different zirconium and hafnium complexes

While numerous salts are known for Zr and Hf, only the formation and chemistry of those mostly used for SX, including fluorides, chlorides, oxychlorides and sulfates, will be briefly mentioned. Due to the chemical similarity of the Zr and Hf salts, only the Zr salts will be discussed.

Zirconium Fluoride

Zirconium tetrafluoride (ZrF_4), which can be prepared by the fluorination of Zr metal, is the best-known fluoride Zr complex. [9] It is a white powder with a melting point of $932\text{ }^\circ\text{C}$ and a density of 4.43 g.cm^{-3} . The crystalline structure is monoclinic (B) and the average length between the Zr and F bonds is 0.210 nm .

ZrF_4 can be dissolved without hydrolysis in dilute and concentrated acids (HCl , H_2SO_4 , and HNO_3) from which it can be recovered as $\text{ZrF}_4\cdot 3\text{H}_2\text{O}$. By adding 10 – 35 wt% hydrofluoric acid (HF), $\text{H}_2\text{ZrF}_6\cdot 2\text{H}_2\text{O}$ can be crystallised out. [10] From this material, several different sodium salts of Zr can be produced. For example, when adding high concentrations of sodium fluoride, Na_3ZrF_7 is formed. To prevent the formation of oxyfluorides, the solution must remain acidic. Other stable sodium fluoride compounds of Zr are those in which the following numbers of F atoms can coordinate around the metal centre: F_{19} , F_{31} , F_{11} , F_4 , F_{13} and F_8 .

Zirconium Chloride

Zirconium tetrachloride (ZrCl_4) has a tetrahedral monomer structure in the gas phase. From the gas phase the ZrCl_4 can be polymerised in an octahedral zigzag chain, where each Zr will have two bridging pairs of chlorine anions and two terminal chlorine anions. The bond lengths of the Zr-Cl internal connection are 0.2498 nm and 0.2655 nm for the two separate Zr-Cl bonds. [10] Similar to ZrF_4 , ZrCl_4 is also a white powder with a melting point of $437\text{ }^\circ\text{C}$ and a monoclinic crystalline structure.

When ZrCl_4 reacts with water, two Cl^- ions are replaced with two OH^- ions. This hydrolysis occurs immediately, resulting in the formation of $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$. ZrCl_4 combines readily with many Lewis bases such as phosphorus oxychloride, ammonia, and sulfoxide, forming different Zr species. [10]

Zirconium Oxychloride

The zirconium oxychloride (ZrOCl_2) can be formed as described above by adding ZrCl_4 to a water solution for hydrolysis to occur. The ZrOCl_2 is important as it is a precursor for other Zr compounds including Zr sulfate, Zr phosphates and Zr linked to different halogens.

Zirconium Sulfate

Zirconium sulfate ($\text{Zr}(\text{SO}_4)_2$) is formed when ZrOCl_2 is dissolved in aqueous sulfuric acid as SO_4^{2-} is a strong anion able to remove OH groups from a Zr complex, which then forms anionic complexes with the SO_4^{2-} . In this case mostly $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ is formed, which has an orthorhombic structure. $\text{Zr}(\text{SO}_4)_2$ forms chains of $[\text{Zr}(\text{OH})_2]_n^{2n+}$, joined by bridging sulfates resulting in $\text{Zr}(\text{OH})_2^n - (\text{OH})(\text{SO}_4)^n \cdot n\text{H}_2\text{O}$ where n is bridging anions. [10] $\text{Zr}(\text{SO}_4)_2$ are used as precursors for the production of high-purity Zr oxides and ammonium Zr carbonates, and many other Zr compounds.

2.3 Separation methods of zirconium and hafnium

In Figure 2 - 1, a general depiction of a hydrometallurgy process is shown where the metal in the leach solution is extracted by a specific extractant. Subsequently, the organic phase is washed, scrubbed and stripped to regenerate the organic phase, which is again contacted with the leach solution. In this section the most prominent separation methods will be discussed. The following terms used to describe the SX process procedures are also relevant for the other processes discussed in this section and will be used in these sections as well as in the chapters to come:

1. Feed: The water or aqueous phase that consists of the metal that is dissolved in an acid solution such as H_2SO_4 , HCl or HNO_3 .
2. Extractant: The extractant is the compound that is chosen to form a selective complex with the metals from the feed solution.
3. Diluent: The diluent is the solvent for the extractant which, with the modifier, makes up the organic phase. While the diluent can contribute to the extraction, it is mostly used as the solvent to contain or dilute the extractant.

4. Modifier: The modifier is added to the extractant and diluent in the organic phase mainly to reduce emulsion formation as will be explained in Section 2.4.4.

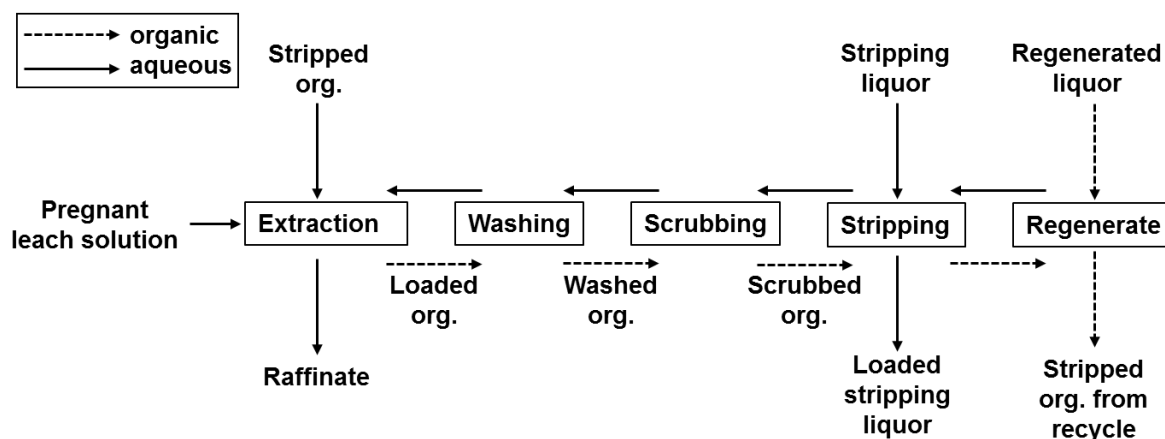


Figure 2 - 1: Adapted general hydrometallurgy extraction, scrubbing, stripping and regenerating scheme. [11]

2.3.1 Ion exchange

Ion exchange is an effective method for the separation of ionic complexes in an aqueous solution as patented in 2002 by Komatsu and Tsurubou. [12] The more selectivity is required during the separation, the more precise (selective) the exchanger that is used has to be. Other factors that influence the separation include the type of acid (concentrations) and the competition occurring (different metals, affinities for exchangers) in the solution.

For the separation of Zr and Hf, different cation and anion exchange systems have been proposed. For example, research has shown that Zr is replaced by anion exchange complexes in high concentrations of HCl or low concentrations of H₂SO₄, while Hf is replaced by cation exchange complexes only in low concentrations of H₂SO₄. [10] While ion exchange can provide a continuous and environmentally friendly extraction for Hf and Zr, the cost of an ion exchange plant is high due to the high cost of the precision ion exchange resins required.

2.3.2 Cezus – fractional distillation

The Cezus process is a known fractional distillation process for the production of nuclear grade Zr. In this process, Zr and Hf are separated from each other using the differences in their evaporation temperatures after having formed a complex with MgCl_2 . [10, 13]

The process starts with the anhydrous Zr(Hf)Cl_4 complex, which is dissolved in KCl-AlCl_3 . The solution is kept at 3 – 4.5 MPa pressure at 437 °C. Subsequently, all the HfCl_4 is distilled over. Pure nuclear grade ZrCl_4 is retained as the product, requiring no further purification. Although the disadvantage of this process is that it is a slow, discontinuous process with a low product yield at the end, the chemical consumption is small and the operation is fairly easy when the production plant is installed and maintained correctly.

2.3.3 Solvent extraction

2.3.3.1 Introduction

During most SX studies, the equilibrium data, in which the Zr and Hf species are distributed between the organic and aqueous phases, are determined, focussing on the differences in the complexation of the Zr and Hf species present in the aqueous phase with the organic based extractant to attain separation. In view of the importance of the appropriate extractants, as well as the Zr and Hf species, SX studies have investigated numerous extractants (organic phase) and acids (aqueous phase) with significantly varying results. Therefore, instead of attempting to describe all variations that have been presented in literature, only the most established processes will be discussed in this section.

2.3.3.2 MIBK process

The methyl isobutyl ketone (MIBK) process is one of the best-known processes for the production of nuclear grade Zr (< 25 mg.L⁻¹ Hf present), as well as pure Hf (< 1 % Zr present), requiring 12 – 15 stages (separation, extraction and stripping). [14]

The MIBK process, which is known for its Hf selectivity, was proposed by Fischer and Chalybaeus in 1947. [14] The starting material for this process is the $\text{Zr(Hf)OCl}_2 \cdot 8\text{H}_2\text{O}$

complex, which is firstly contacted with ammonium thiocyanate to produce the Zr and Hf thiocyanate ($\text{Zr(Hf)-[S=C}\equiv\text{N}^-]$) complexes. Lastly, the Zr and Hf thiocyanate complexes is counter-currently contacted with a thiocyanic acid-MIBK solution. During this stage, Hf is selectively extracted into the organic phase due to the difference in the solubility of the Zr and Hf thiocyanate complexes.

The major disadvantage of this process is the dangerous working environment created by the MIBK solutions, which have a low flash point, high vapour pressure and high solubility in water. In addition, the process is not self-sustainable, because of the continuous make-up of the organic phase, requiring more than 50 % new organic phase after each extraction and stripping stage. [13]

2.3.3.3 TBP process

The tributyl phosphate process (TBP process) is another well-known SX process where, in this case, Zr is preferentially extracted from a HNO_3 solution. This process was developed at the Ames Laboratory of Iowa State University. [15] The starting metal complex is the Zr(Hf)O_2 that is dissolved in $2 \text{ mol.dm}^{-3} \text{ HNO}_3$ and contacted with a TBP/kerosene organic phase. During extraction the Zr is extracted into the organic phase while the Hf and other impurities remain in the aqueous phase. Since the Zr is extracted, this process requires stripping stages to recover the Zr from the organic phase while simultaneously regenerating the organic phase. The advantage of the TBP process is that the TBP extracts most of the Zr into the organic phase, creating a process requiring fewer stages than the MIBK-process. The disadvantages, however, include the corrosive nature of TBP and the possible formation of emulsions during extraction, which can bring the production process to a halt. [16]

2.3.3.4 Toyo Zirconium Co, Ltd process

In 1979 the Japanese company, Toyo Zirconium Co, industrialised an amine-based process for the production of nuclear grade Zr by addressing some of the disadvantages of the MIBK process. The process starts with the $\text{H}_2\text{Zr(Hf)O(SO}_4)_2$ metal complex which is dissolved in H_2SO_4 and counter-currently contacted with a high-molecular alkyl amine solvent solution. During the SX, the $\text{H}_2\text{ZrO(SO}_4)_2$ is extracted into the organic phase with a separation factor of 10 – 20. Some of the improvements of this process are firstly, the low solubility of the solvent in water,

creating a more environmentally friendly process and secondly, the extractant can be reused more often than in the MIBK process, creating a more economical and environmentally friendly process.

As is often the case, this process has disadvantages, as it requires many stages that are time consuming. In addition, the starting complex has to be produced before extraction. The stripping procedure of the organic phase to regenerate the extractant requires Hf-free Zr sulfate, which somehow makes the process self-defeating. [13]

2.3.3.5 *Kroll process*

The Kroll process is another established process where pure Zr is obtained from an Zr(Hf)Cl_4 complex. HfO_2 is removed by means of SX and HfCl_4 with extractive distillation. [13] For the production of nuclear grade Zr, the Zr(Hf)Cl_4 is reduced with molten magnesium in an inert atmosphere, whereby Zr sponges and MgCl_2 are produced as products. After reduction, the Zr is purified in two stages. Firstly, the bulk MgCl_2 is removed mechanically and secondly, the unreacted Mg is removed using vacuum distillation. The pure Zr that remains in the reactor is thereafter removed using vacuum arc melting. The disadvantage of this process is that it consists of a primary reduction, sponge handling and purification process that is expensive and complex. [13]

2.3.3.6 *The Necsa plasma process*

The last process to be mentioned is the Necsa-based plasma process which forms the basis of this study. In 2014, Necsa patented the Necsa plasma process for the production of nuclear grade Zr, which was the first industrial process for the production of pure Zr in South Africa. [17] Figure 2 - 2 gives a diagrammatic representation of the Necsa process which starts with the mined zircon (Zr(Hf)SiO_4) that is treated with a plasma to produce a plasma-dissociated zircon complex ($\text{Zr(Hf)O}_2\cdot\text{SiO}_2$). This complex is subsequently treated with HF and ammonium fluoride to produce the ammonium zirconium hafnium heptafluoride complex ($(\text{NH}_4)_3\text{Zr(Hf)F}_7$) that was chosen as starting material in this study. After sintering at 700 °C, Zr(Hf)F_4 is formed, which is converted to ZrCl_4 before being reacted with MgCl_2 (Kroll process). Using SX, the Zr can be separated from the Hf and nuclear grade Zr is produced.

The disadvantages of the process are the number of stages and the high temperature (700 °C) necessary to produce the ZrF₄. The advantages are that it is a local process which ultimately will help the South African economy while creating novel research subjects.

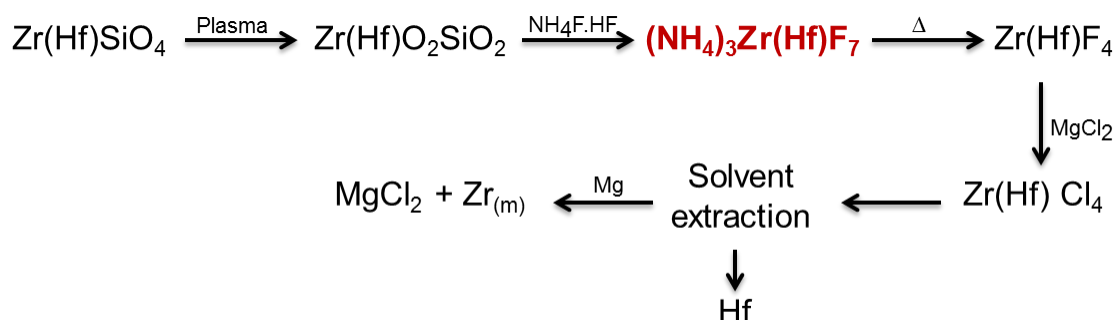


Figure 2 - 2: Schematical representation of the Necsa plasma process.

2.4 Solvent extractants and modifiers

2.4.1 Introduction

While numerous extractants, modifiers and diluents are available for SX and have been used extensively, some aspects of their chemistry, such as the active position, stability, lifetime and the orientation of some extractants in the water-immiscible phase, are still often ill-defined. To further improve extraction or selectivity, extractants, modifiers and/or diluents are combined to create a more stable organic phase with faster phase disengagement properties, which unfortunately complicate the underlying chemistry of extraction even more. [18]

Generally extractants partake in one of three mechanisms; i) metal cation extraction, where the metal cation M^{n+} is transferred from the aqueous phase by replacing an H^+ on the extractant, ii) metal anion extraction, where the metal anion, MX^{n-} , can be extracted by a neutral or positive extractant and iii) metal salt extraction, where the metal cation and its attendant anions are transported from the aqueous phase to the organic phase as a salt. In view of the focus of this study, the following section will elaborate on the amine- and phosphorus-based extractants that have been studied extensively for the extraction and separation of Zr and Hf from the different complexes discussed in Section 2.2.2.

2.4.2 Amine-based extractants

Amine extractants are used when a metalate anion is present, which forms a neutral complex with the extractant before extraction into the organic phase. [11] According to literature, high molecular weight amines extract Zr and Hf in the order of tertiary amine > secondary amine > primary amine due to the gradual increase in the basicity of the nitrogen. [19] When considering amines as possible extractants for a process such as the one discussed in Section 2.3.3.4, it is important to determine whether emulsions and third phases are formed, which has been reported for amines. [20-22] Unlike the 4° amines, the 1°, 2° and 3° amines have to be preconditioned in an acid to ensure that the amine group is positively charged.

Although most studies have focussed on 3° and 4° amines, a few studies have investigated 1° and 2° amines. For example, Schrotterová and Nekovar investigated Primene JMT for the extraction of Fe(III) in a H₂SO₄ environment and found that complex formations become more complex at higher H₂SO₄ concentrations. [23] Cerrai and Testa included a secondary amine (di-cyclohexylamine) in their study on the separation of Zr and Hf and found that the tertiary amine used (Alamine 336) gave a higher extraction of Zr and Hf than the secondary amine. [5]

Tertiary amines such as the well-known Alamine 336 have been studied extensively for the SX of numerous metals [21] including Zr and Hf. Alamine 336 has been investigated for the extraction and separation of Zr and Hf from HNO₃, HCl and H₂SO₄ solutions. [4, 6, 22, 24] When extracting the metalate anion complex, it was found that the extractants active position does not reach the inner coordination sphere of the metal complex where bonding takes place, resulting in lower selectivity and not being able to exploit the coordination around the metal centre for improved extraction. [11] When using tertiary amines, this problem is overcome, as a result of less steric hindrance. [11]

Quaternary ammonium salts, of which Aliquat 336 is probably best known, have a positive charge and hence do not require a preconditioning step. The effect of Aliquat 336 on the extraction of various Zr and Hf salts such as Zr(Hf)Cl₂ and H₂Zr(Hf)O(SO₄)₂ has been well documented. [6, 13, 25] In a recent study within the NWU, Conradie *et al.* showed that both Aliquat 336 and Uniquat 2280 were suitable in selectively

extracting high percentages (above 90%) of Zr and Hf from both HCl and H₂SO₄ solutions. [24] These results are presented in Chapter 3.

2.4.3 Phosphorus-based extractants

Since the discovery of phosphine in 1763 by Gengembre, numerous phosphorus-based extractants have been investigated for the separation of many different metals. [26] Since the 1960s, phosphorus-based extractants have been studied for the separation of Zr and Hf from H₂SO₄, HCl as well as HNO₃ solutions where it was shown, as is the case for various other metals, that the type of acid influences the extraction attained. [3, 8]

When considering phosphorus-based extractants, it is important to note that phosphorus (P) has a low electronegativity and therefore bonds easily to oxygen and halogens. In addition, P has a strongly reactive lone pair of electrons as well as vacant d-orbitals available for bonding by forming pentavalent (5 bonds) stable phosphorus compounds like phosphine oxide, phosphinic acid, phosphonic acid and phosphoric acid. [27] Of these, the phosphinic, phosphonic and phosphoric acids are most widely used for the extraction and separation of Zr and Hf from tetrachloride [7], tetrafluoride, sulfate [28] and now ammonium heptafluoride salts. [24] In Table 2 - 1 the general structures of these three extractant types are presented. According to Kislik, the metal extraction decreases from phosphinic acid > phosphonic acid > phosphoric acid. [29] However, recently Wang and Lee obtained higher extraction of Zr and Hf using D2EHPA (phosphoric acid based) and TBP than when using phosphinic acids. [28] Extraction with D2EHPA has been studied on Zr and Hf [28], uranium [30], zinc [2] and water purification [31], to name a few.

Table 2 - 1: Structures of phosphorus-based extractants. [11]

	Phosphinic acid	Phosphonic acid	Phosphoric acid
General structure	$\begin{array}{c} \text{O} \\ \\ \text{HO}-\text{P}-\text{R} \\ \\ \text{R} \end{array}$	$\begin{array}{c} \text{O} \\ \\ \text{HO}-\text{P}-\text{OR} \\ \\ \text{R} \end{array}$	$\begin{array}{c} \text{O} \\ \\ \text{HO}-\text{P}-\text{OR} \\ \\ \text{OR} \end{array}$
Substituents	Dio-PA: R = $\text{CH}_3(\text{CH}_2)_6\text{CH}_2-$	Ionquest 801: R = $\text{C}_4\text{H}_9(\text{C}_2\text{H}_5)\text{CHCH}_2-$	D2EHPA: R = $\text{C}_4\text{H}_9(\text{C}_2\text{H}_5)-\text{CHCH}_2-$ TBP: R = $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$

Phosphorus-based extractants form strong hydrogen bonds between extractant molecules, giving rise to the formation of dimers as shown in Figure 2 - 3 for phosphinic acid. When contacted with a metal complex, an 8-membered ring is typically formed as the product. During complexation, the hydrogens of two extractants are replaced with a metal cation (M^{2+}), thereby forming a tetramer. According to Wilson *et al.*, the electron donor can be replaced by oxygen or sulfur to complement the hard-soft properties of the metals to be extracted. [11] They also confirmed the formation of the stable dimeric structure, for example in cyclohexane (non-polar solvent). Accordingly, phosphinic, phosphonic and phosphoric acid would generally give complexes consisting of 4 extractant molecules to 1 metal atom provided that the extractant is in excess.

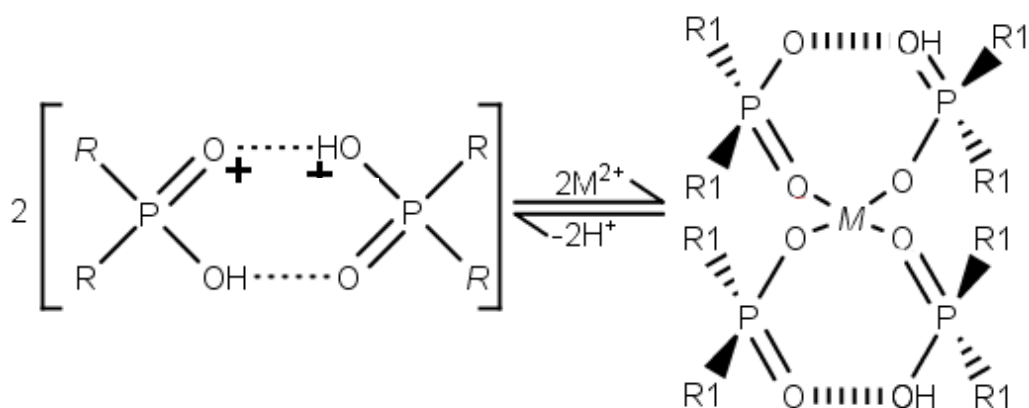


Figure 2 - 3: Tetramer metal complex formation with phosphinic acid. [11]

When diphenylphosphinic acid was used, Tasker *et al.* identified the formation of an 8-membered ring using X-ray crystallography. [32] In the absence of a metal, a 4-membered ring (stable dimer) combines with a second tetramer in the presence of the metal, forming the metal-containing 8-membered ring. The O-M-O bonds in the 8-membered ring can have angles $>90^\circ$, which can influence the selectivity towards, for example, base metals and Zr and Hf. Even more complex structures are expected with other combinations of extractants and metal complexes. For example, when extracting with D2EHPA as the phosphorus-based extractant from a concentrated H_2SO_4 environment, it was shown that the metal complex is negatively charged and that a hydrogen bond is formed between the MSO_4^{2-} ($\text{M} = \text{Zr/Hf}$) and the hydrogen of the D2EHPA. [33]

Phosphorus-based extractants are generally stable extractants with a long operational lifespan, which makes stripping of the metal from the loaded phosphorus-based extractants essential to obtain a clean and reusable extractant. Similar to extraction, stripping liquors have to be screened as their stripping ability differs for each loaded extractant, depending on, amongst others, the acid, metal and the concentrations thereof. For example, in the TBP process, Na_2CO_3 is used as the stripping liquor. [14] In other cases the same acid that was used for extraction can be used for stripping, albeit usually at other pH values. The change in pH creates a reverse reaction whereby the extracted metal is stripped back into the acidic stripping solution.

2.4.4 Modifiers

According to IUPAC, a modifier in solvent extraction is:

“A substance added to a solvent to improve its properties e.g. by increasing the solubility of an extractant, changing interfacial parameters or reducing adsorption losses. Additives used to enhance extraction rates should be called accelerators or catalysts.” [34]

Accordingly, the main reason for adding a modifier to a SX process is to decrease the time for phase entanglement and to decrease the probability of emulsification. [35] When adding a modifier it should ideally either improve or at least not participate in the extraction of the metals. In addition, the modifier should be i) soluble in the organic phase, ii) stable and iii) non-volatile to prevent the loss of the modifier. Löfström-Engdahl *et al.* stated that the modifier, diluent and extractant often participate together in the extraction of the metal, which, according to them, gives an explanation of the perceived extraction, without considering either of these three to be incomplete. [18] Various modifiers have been studied. In this study, 1-octanol ($\text{CH}_3(\text{CH}_2)_7\text{OH}$) was used, which is water immiscible while making the organic phase less polar and thereby decreasing third phase and emulsion formation.

2.5 Solvent extraction principles

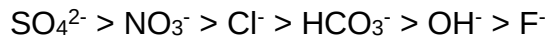
2.5.1 Introduction

As mentioned previously, SX is based on the separation of different metals using two phases separated by the density differences in the two liquids. While the terms pertaining to SX (feed, extractant, diluent and modifier) were discussed in Section 2.3, this section will aim to briefly elaborate on the most important equilibrium and kinetic principles relating to the SX process.

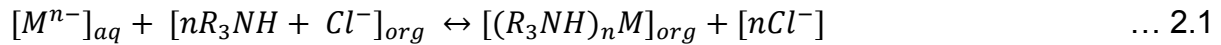
2.5.2 Equilibrium

SX is usually an equilibrium based process. To determine whether equilibrium had been reached, time studies can be used. The equilibrium in SX is influenced by many factors such as the organic phase, feed composition, temperature, agitation time,

agitation rate and the type of anion present, which can be arranged in the order of strong to weak according to acid strength:



The general Equation for an anion exchange mechanism as is found for amine-based extractants is:



where aq. and org. refer to the aqueous and organic phases, respectively, M is the metal and R₃NH the 3° amine. For equation 2.1 the equilibrium constant (K) can be derived from Equation 2.2:

$$K = \frac{[Cl^-]^n [R_3(NH)_nM]}{[R_3NH^+ Cl^-] [M^{n-}]^n} \quad \dots 2.2$$

In addition, the extraction distribution ratio (D_M) of the metal between at equilibrium the two phases can be determined using Equation 2.3:

$$D_m = \frac{M_{org}}{M_{aq}} \quad \dots 2.3$$

where M_{org} and M_{aq} are the metal concentrations in the organic and aqueous phases, respectively.

Lastly, another important parameter, i.e. the percentage extraction (Ex%), can be determined using Equation 2.4:

$$Ex\% = \frac{D_{mi} \frac{V_{aq}}{V_{org}}}{D_{mi} + \frac{V_{aq}}{V_{org}}} \times 100 \quad \dots 2.4$$

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

2.5.3 Kinetics

In SX the rate at which a reaction occurs can be measured by the rate of extraction and stripping. [36] In addition to the distribution mentioned above, the rate is also influenced by, amongst others, the viscosity of the various solutions, the agitation rate

and the temperature of the reaction. [29, 36] When determining the order of the kinetics using the rate laws considering Equation 2.1, it follows that:

$$Rate = k \times [M^{n+}] \times [RH] \quad \dots 2.5$$

where k is the rate constant in L/mol.s. According to Equation 2.5, it is clear that the rate constant will change when the concentrations of the extractant or metal change.

2.6 Membrane-based solvent extraction

2.6.1 Introduction

MBSX is a relatively new method which aims at improving on the traditional SX method. Here the mass transfer occurs between two immiscible liquids from the liquid-liquid immobilized interface at the rim of the pores in the hollow fibre membrane wall. [36] During MBSX the membrane does not physically participate in the extraction, it rather acts as a separator (barrier) between the two phases.

Initially membrane technology was developed for the water purification industry to remove particles and macromolecules. Since then membranes have been used in ever-increasing areas of application ranging from their use in slow-release drugs, [37], haemodialysis (artificial kidneys) [38], fuel cells and in osmotic power plants. [39, 40] One of the first commercial hollow fibre membrane contactors was used to remove aromatic compounds from water. [41] In this study, SX was combined with hollow fibre membrane contactors to determine its influence on the separation of Zr and Hf. Previous work focussing on this combination will briefly be highlighted in this section.

2.6.2 Liqui-Cel contactor

In this study, a Liqui-Cel membrane contactor consisting of 10200 Celgard® microporous polypropylene (PP) fibres, as shown in Figure 2 - 4, was used. PP fibres are used as they have a low density (light weight), high stiffness, heat resistance, chemical inertness, stretchability and recyclability. [42] These properties help create a membrane with an extended life cycle in a chemical environment that can be recycled when it has to be substituted.

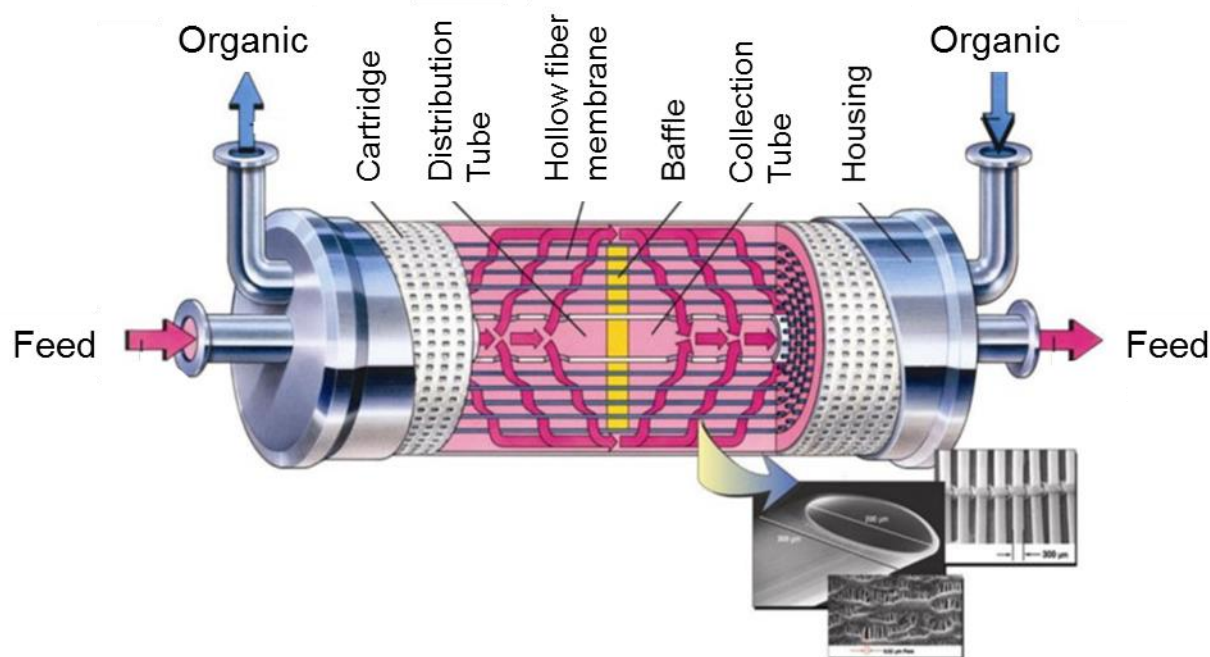


Figure 2 - 4: Depiction of the Liqui-Cel membrane contactor used in this study. [43]

For these contactors the feed, which can either be aqueous or organic, can be fed to the shell or lumen side of the membrane (maximum flow rate of Liqui-Cel unit = $124.9 \text{ m}^3\text{hr}^{-1}$). The “Organic” inlet pressure (Figure 2 - 4) must be lower than that of the “Feed” pressure to prevent breakthrough (when the “Organic” solution breaks through the PP pores contaminating the “Feed” solution). The feed and organic solutions are typically circulated counter currently through the uniform PP fibres (30 nm) which, in the case of the Liqui-Cel, have a pore diameter of 40 nm.

During MBSX, an extractant-containing organic phase and the aqueous feed solution are contacted non-dispersively while typically flowing in different directions, where the membrane non-wetting phase will have a higher pressure than the wetting phase. The wetting phase fills the pores while the non-wetting phase flows over these filled pore openings where the extraction of the metals occurs. [44]

One of the disadvantages of this technology is the occurrence of membrane fouling, [45] which increases the cost of an industrial process due to the required cleaning and eventually the replacement of the membrane. In addition, membranes are not 100 % chemically resistant to all possible solvents and acids, which makes the material choice important when selecting a membrane. In addition, the membrane will also increase the inherent resistance to mass transfer. [46]

Advantages of MBSX are listed below:

- No emulsification occurs in the module due to the physical barrier between the two phases. This can help specifically when using amine extractants whose tendencies to form emulsions have been recorded. [4, 24]
- Due to the physical barrier between the two phases, it is no longer necessary for the aqueous and organic phase to have a density difference as in traditional SX the phases must, however, remain immiscible.
- To increase the extraction capacity of the system, more modules can be added. An MBSX set-up can be small and compact, while a larger set-up can be installed when higher efficiencies are required. [47]
- The equilibrium-limited chemical reaction typically found for all SX processes can be exploited by continuous contact and circulation of the two phases in the system. [48]
- Continuous contact and circulation also make it possible to replace the extracted product at any time interval with a clean organic phase. This will help to shift the reaction equilibrium to favour the product; thereby increasing productivity while preventing product inhibition. [48, 49]
- The contact area of the Liqui-Cel module used in this study was is 1.4 m², which is significant for such a small module.
- Extraction capabilities remain constant at high and low flow rates due to the independence of flow between the two fluids. [47]
- In addition to the different flow rates that can be maintained, different aqueous and organic volumes can also be used for extraction. [49]
- Due to the standard contact area and constant module performance, predictions on extraction can be made accurately, which is more difficult with traditional SX due to the constant changeability of the contact area. [48]
- When using expensive extractants in the organic phase, membranes can be used which have a low solvent hold-up. [47]
- MBSX has no moving part such as a rotating incubator, resulting in a decrease in maintenance cost.
- Finally, MBSX is a clean technology using a set-up that is easy to design and maintain, requiring little alterations for up- or down- scaling.

2.7 Conclusion

In this chapter a literature overview was presented on the subject of Zr and Hf separation. Firstly, different complexes in which Zr and Hf have been separated were discussed, followed by an overview of the industrial processes that are commonly used for the production of nuclear grade Zr.

Since SX is the technology used in this study, a detailed description of this technology was subsequently presented, focussing on the process, terms used and the mechanism of the process. Both amine- and phosphorus-based extractants were discussed in more detail, thereby providing the required background to facilitate the discussions in Chapters 3 and 4. After briefly discussing the important SX principles of equilibrium and kinetics, the concept of MBSX was explained in terms of hollow fibre membrane contactors, followed by a summary of the disadvantages and advantages of this technology.

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Chapter 3

The separation of zirconium and hafnium from $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$ using amine-based extractants

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3.1 Introduction

As mentioned in Chapter 1, Zr and Hf co-exist in nature and have similar chemical properties such as ionic radii (0.074 nm for Zr^{4+} and 0.075 nm for Hf^{4+}) and valence electrons in the outer orbitals. [1, 2] Although both elements can be found in group 4 of the periodic table, their properties as regards nuclear application differ, the thermal neutron capture cross-section being much higher for Hf than that for Zr. [3, 4] Zr also has a high corrosion resistance, which improves the lifetime of cladding materials in nuclear reactors. Hence, for Zr to be used as fuel-cladding material and water-cooled components in nuclear reactors, the Hf content must be reduced from the naturally occurring 1 - 3 % to $< 100 \text{ mg.L}^{-1}$. [5]

Several processes are currently in use for the extraction and purification of Zr and Hf, such as the MIBK process proposed by Fischer and Chalybaeus. [6] In this process, Zr and Hf form complexes with thiocyanate that have different solubilities, resulting in Hf being preferentially extracted into the organic phase. The disadvantages of this process are the high concentrations of ammonium and cyanides in the waste stream. The formation of cyanides from thiocyanate can occur in various ways, but in the case of the MIBK-process the thiocyanate (SCN^-) is converted to OCN^- by the ammonium and to HCN by nitric acid solutions also present in the mixtures. [7] The low flashpoint of the solvent is also a disadvantage. Other processes known to the industry are the TBP and Cyanex 923 processes, in which selective extraction is attained in a nitric acid solution as proposed by Taghizadeh *et al.* [8] In 1974, Sato and Watanabe investigated the extraction of Zr in a sulfate medium using different types of amine extractants, showing that secondary amines are superior to tertiary amine extractants. [9] In 2014, Wang and Lee reported on the preferential extraction of Zr in a sulfate medium using Aliquat 336, Alamine 336, Alamine 300 and Alamine 308. [10] All of the above-mentioned methods and processes use Zr and Hf chloride salts as the starting reagent.

Necsa has patented a plasma and fluoride process for the manufacture of Zr metal starting from the mineral zircon ($ZrSiO_2$). [11] According to the patent, plasma-dissociated zircon is reacted with ammonium bifluoride and an $(NH_4)_3Zr(Hf)F_7$ complex is formed and isolated for downstream processing, *i.e.* separation of Zr and Hf. It was the purpose of this study to determine the suitability of

amine extractants (Alamine 336, Aliquat 336 and Uniquat 2280) for the separation of Zr and Hf from $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$ complex solution (97 mg.L^{-1} Zr and 3 mg.L^{-1} Hf) in HCl and H_2SO_4 solutions ($0.01 - 8 \text{ mol.dm}^{-3}$). Since the extraction from this metal complex has not been published previously, limited comparison of the data to literature data was possible. The parameters investigated were the type of acid and acid concentration, the type of extractant, extractant concentration and the effect of the two metals (Zr and Hf) on one another. Subsequently, two stripping agents (NaCl and H_2SO_4) were evaluated to regenerate the organic phases and to serve as possible scrubbing liquors.

3.2 Materials and Methods

Tri-octyl/decyl amine (98 % Alamine 336, Cognis Corporation), tricaprylmethylammonium chloride (97 % Aliquat 336, Cognis Corporation) and didecyl dimethyl ammonium chloride (Uniquat 2280, 80 %, Lonza) were diluted with cyclohexane (98 %, Labchem) to 10 wt%. Lastly, 5 v/v% 1-octanol (98 %, Sigma Aldrich) was added to the solvent to prevent the formation of a third phase. All chemicals were of analytical grade and were used as received.

Fresh stock solutions of sulfuric- (98 % H_2SO_4 , Labchem) or hydrochloric acid (32 % HCl, LabChem) were prepared containing $(\text{NH}_4)_3\text{ZrF}_7$ and $(\text{NH}_4)_3\text{HfF}_7$ obtained from Necsa. The pure Zr and Hf salts were prepared by simulating the Necsa plasma fluoride process, proposed by Nel *et al.* in 2014, using a single metal feed of zirconium oxide (99.9 % ZrO_2 , Sigma-Aldrich) and hafnium oxide (99.9 % HfO_2 , Sigma-Aldrich). The prepared $(\text{NH}_4)_3\text{ZrF}_7$ and $(\text{NH}_4)_3\text{HfF}_7$ were analysed at Necsa to ensure the correctness and purity (97 %) of the compounds. Pelindaba Analytical Laboratories (PAL) performed ICP-OES (Inductively coupled plasma – optical emission spectroscopy) analyses to verify the metal concentrations. Distillation methods were used to obtain the relevant fluoride data. An ion selective electrode was used to analyse the fluoride concentration in the distillate. Acid concentrations varied from $0.001 - 8 \text{ mol.dm}^{-3}$, while the metal concentrations for single metal complex extractions were fixed at 100 mg.L^{-1} Zr/Hf and for binary complex extractions at 97 mg.L^{-1} and 3 mg.L^{-1} for Zr and Hf, respectively. Aqueous phase dilutions were made with deionized water (Millipore Milli-Q Plus® Q-pack

CPMQ004R1). H_2SO_4 and NaCl (98 % NaCl, LabChem) were diluted with deionized water to concentrations ranging from $0.001 - 2 \text{ mol.dm}^{-3}$.

The extraction and stripping experiments were done by contacting equal volumes of the organic and aqueous phase (25 mL; A/O = 1) at 25°C for 60 minutes in a rotary shaker and incubator at 310 r.min^{-1} . Although equilibrium was reached after 25 minutes (Appendix 2) all samples were shaken for 60 minutes to ensure sufficient equilibrium. After achieving equilibrium and separating the phases in standard separation funnels, inductively coupled plasma – optical emission spectrometry (ICP-OES, Thermo Scientific iCAP 6000 SERIES ICP + CETACASX- 520 Auto sampler) was used to analyse the metal concentration in the aqueous phase. The concentration of the metal in the organic phase was assumed to be in accordance with the mass balance.

3.3. Results and Discussion

3.3.1. Extraction

3.3.1.1. Influence of acid concentration on single metal complex extraction

The initial experiments were designed to observe the effect and correlation of single and binary metal complex extractions. Both single and binary systems were evaluated using HCl and H_2SO_4 solutions, while keeping the concentration range as wide as possible for the initial screening ($0.1 - 8 \text{ mol.dm}^{-3}$). In subsequent experiments more data points in narrower ranges were selected. Three different amine-based extractants were used. Alamine 336 is a tertiary amine with three carbon chains extended from the nitrogen atom ($\text{C}_{24}\text{H}_{51}\text{N}$). Both Aliquat 336 and Uniquat 2280 are quaternary ammonium salts with a positively charged nitrogen bonded to a methyl group, with three additional carbon chains in the case of Aliquat 336 and two methyl groups and two carbon chains in the case of Uniquat 2280. [12-14]

In the single metal complex experiments, emulsions were observed and hence no analysis was possible when extracting with Uniquat 2280 in $4 - 8 \text{ mol.dm}^{-3} \text{H}_2\text{SO}_4$, as well as when using Alamine 336 in $0.1 \text{ mol.dm}^{-3} \text{H}_2\text{SO}_4$. Banda *et al.* observed similar emulsions and third phase formations while using Alamine 336 in HCl. [15]

Figure 3 - 1 and Figure 3 - 2 display data on the single metal complex extraction of Zr and Hf from HCl and H₂SO₄ respectively, using the experimental conditions described.

No significant extraction was obtained above 1 mol.dm⁻³ acid, irrespective of the type of acid or extractant used. The highest extraction values (>85 %) were attained at 0.1 mol.dm⁻³, with a slightly higher extraction from an HCl environment. The only noteworthy selectivity at high enough extraction values was obtained using Aliquat 336 (Figure 3 - 1b), where a 27 % Hf selectivity was observed at 0.1 mol.dm⁻³. The percentage selectivity was calculated by dividing the lesser extracted metal from the greater extracted metal.

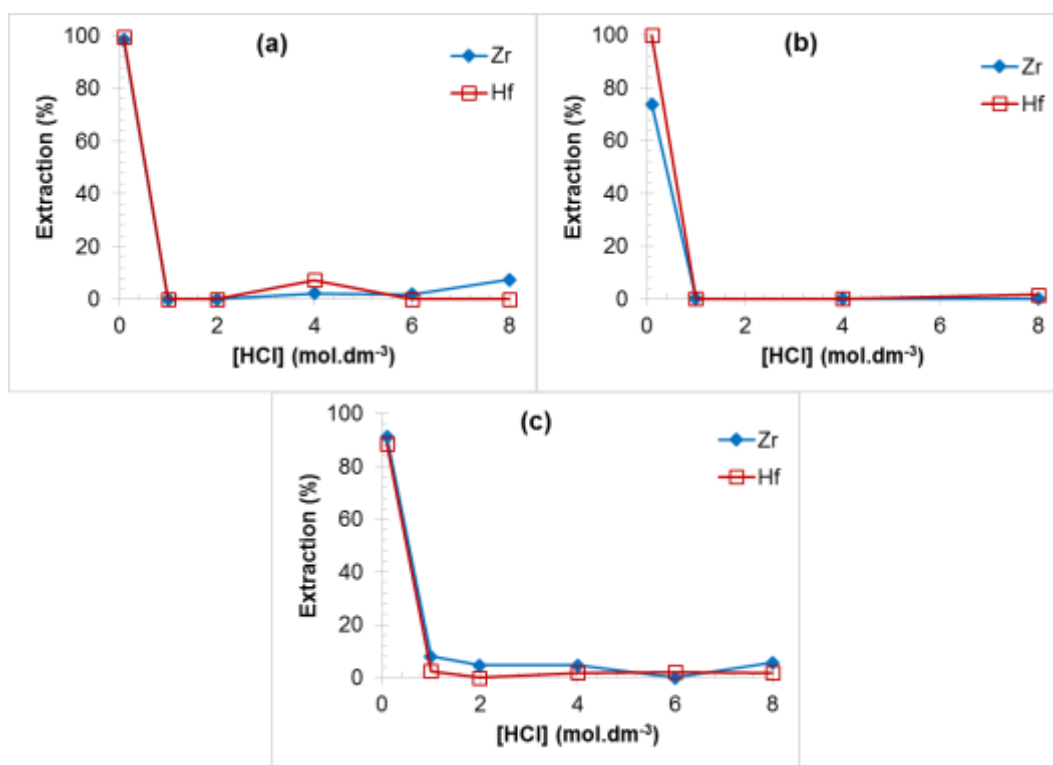


Figure 3 - 1: Effect of HCl concentration with single metal complex extraction using (a) Alamine 336, (b) Aliquat 336 and (c) Uniquat 2280. Conditions: 10 wt% extractants, 100 mg.L⁻¹ Zr, 100 mg.L⁻¹ Hf, A/O = 1, equilibrium time = 60 minutes.

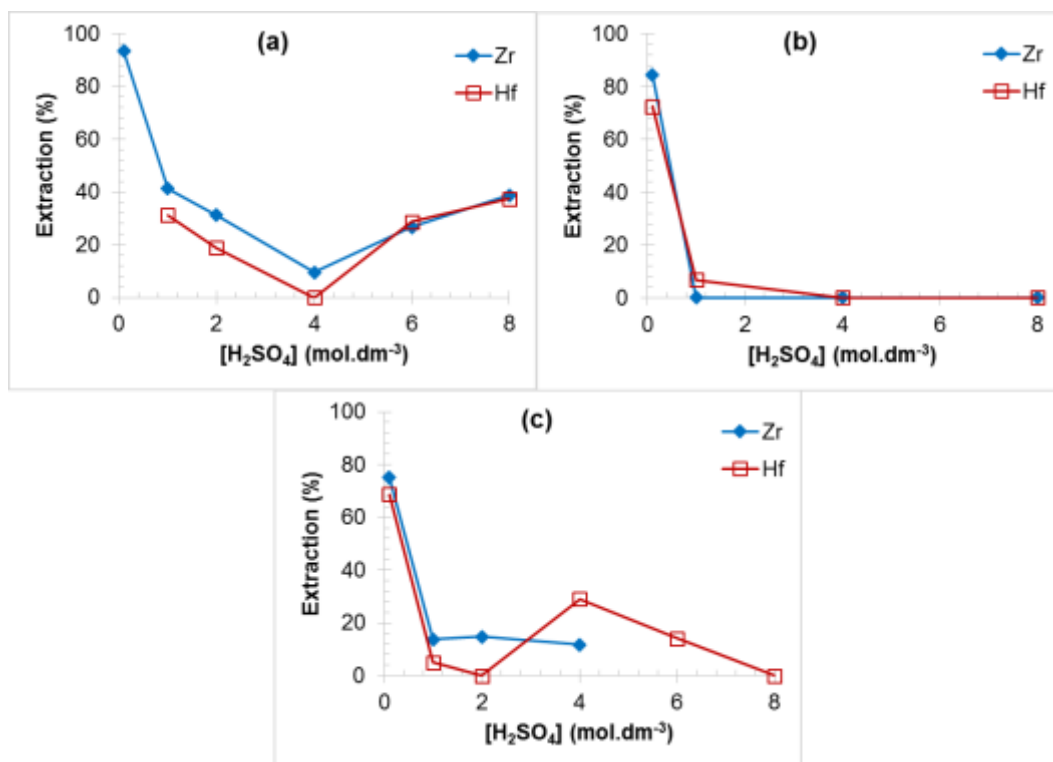


Figure 3 - 2: Effect of H₂SO₄ concentration with single metal complex extraction using (a) Alamine 336, (b) Aliquat 336, (c) Uniquat 2280. Conditions: 10 wt% extractants, 100 mg.L⁻¹ Zr, 100 mg.L⁻¹ Hf, A/O = 1, equilibrium time 60 minutes.

3.3.1.2. Influence of acid concentration on binary complex extractions

Using the same parameters that had been used for single salts, binary metal complex (97 mg.L⁻¹ Zr and 3 mg.L⁻¹ Hf) experiments were performed to correlate single and binary metal complex extractions, thereby determining whether the metals affected each other; for example, due to mutual inhibition during extraction. Binary metal complex extractions with the three amine-based extractants and the two acids were evaluated. HCl and H₂SO₄ solutions with a concentration range of 0.01 – 8 mol.dm⁻³ were used.

Similar to the discussion in the previous section, Figure 3 - 3 and Figure 3 - 4 illustrate the results on the binary metal complex extractions of Zr and Hf from HCl and H₂SO₄ solutions. When attempting extraction from HCl, no extraction was attained when using Alamine 336 between 0.1 – 4 mol.dm⁻³ HCl (Figure 3 - 3a), increasing to just over 20 % extraction at 6 mol.dm⁻³ HCl. With Aliquat 336, 48 % extraction was obtained at 0.1 mol.dm⁻³ HCl with a 4 % Hf selectivity (Figure 3 - 3b).

Although Uniquat 2280 (Figure 3 - 3c) showed some extraction in the range of 1 – 8 mol.dm⁻³ HCl, the extraction remained less than 20 %. It is known that amine-based extractants can form emulsions when extracting from an HCl environment (Barnabas and Treadway, 2010); this was also observed in the present study when using Alamine 336 combined with H₂SO₄ at 0.1 mol.dm⁻³ and Uniquat 2280 at 6 – 8 mol.dm⁻³. [14] Emulsions were observed in HCl solutions of 8 mol.dm⁻³ for Alamine 336 and 0.1 mol.dm⁻³ for Uniquat 2280.

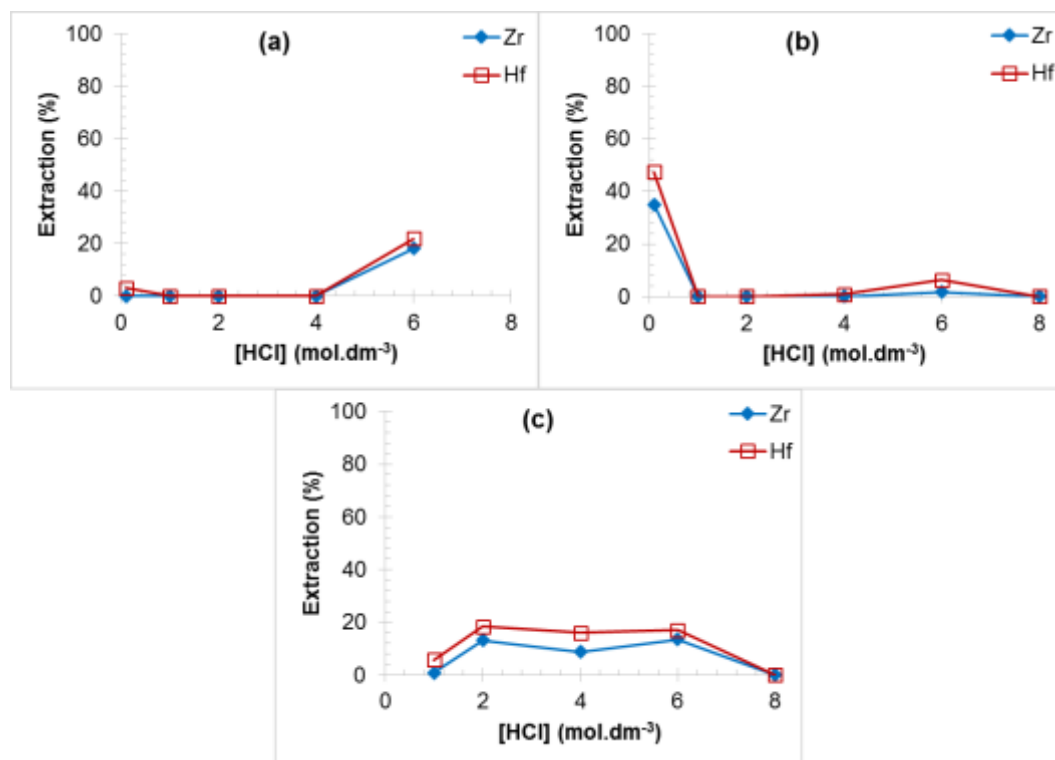


Figure 3 - 3: Effect of HCl concentration with binary metal complex using (a) Alamine 336, (b) Aliquat 336, (c) Uniquat 2280. Conditions: 10 wt% extractants, 97 mg.L⁻¹ Zr and 3 mg.L⁻¹ Hf, A/O = 1, equilibrium time 60 minutes.

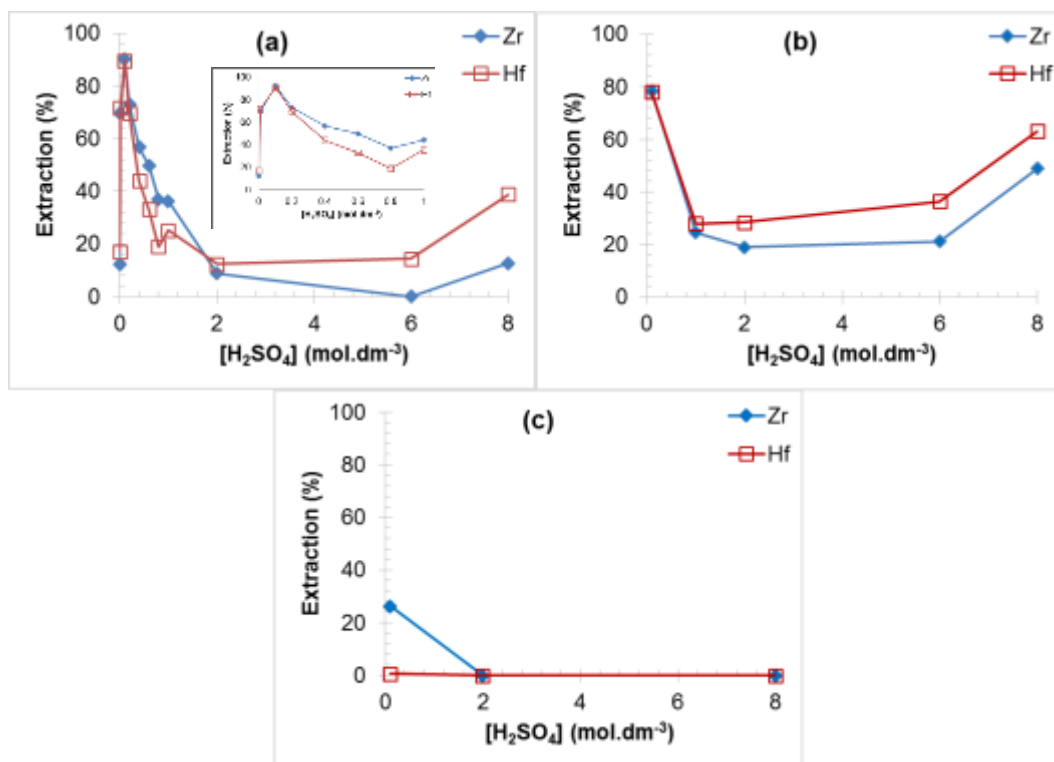


Figure 3 - 4: Effect of H_2SO_4 concentration with binary metal complex using (a) Alamine 336, (b) Aliquat 336, (c) Uniquat 2280. Conditions: 10 wt% extractants, 97 mg.L^{-1} Zr and 3 mg.L^{-1} Hf, A/O = 1, equilibrium time = 60 minutes.

Due to the high extraction with Alamine 336, seven extractions were completed at less than 1 mol.dm^{-3} H_2SO_4 (0, 0.01, 0.1, 0.2, 0.4, 0.6, 0.8 mol.dm^{-3}) to obtain more comprehensive results. When considering the extraction of the binary metal complex from a H_2SO_4 solution (Figure 3 - 4), significant extraction for Alamine 336 and Aliquat 336 was observed when extracting from a low acid concentration, while no significant extraction was observed when using Uniquat 2280. Extraction with both Alamine 336 and Aliquat 336 increased at high ($>6 \text{ mol.dm}^{-3}$) and low ($<2 \text{ mol.dm}^{-3}$) H_2SO_4 concentrations. For both Alamine 336 and Aliquat 336 the extractions decreased from above 80 % to 20 – 30 % between 0.1 and 2 mol.dm^{-3} , remained practically constant between 2 and 4 mol.dm^{-3} and then gradually increased again from 4 – 8 mol.dm^{-3} H_2SO_4 . The highest extractions with Alamine 336 and Aliquat 336 were 91 % and 78 %, respectively, at 0.1 mol.dm^{-3} H_2SO_4 . This trend has been observed in previous studies – when increasing HCl above 6 mol.dm^{-3} a similar increase in extraction occurred. [15, 16]

When comparing the single (Figure 3 - 1 and Figure 3 - 2) and binary metal complex (Figure 3 - 3 and Figure 3 - 4) extractions, both correlations and differences become apparent. In HCl (Figure 3 - 1 and Figure 3 - 3), the same negligible extraction was observed above 1 mol.dm⁻³ HCl. However, at 0.1 mol.dm⁻³ the extraction with Aliquat 336 was >80 % for single salts, which is significantly higher than the 50 % attained for binary metal complexes. No significant extraction was attained when using either Alamine 336 (where emulsion formation was observed above 6 mol.dm⁻³) or Uniquat 2280 when extracting binary metal complex compared to the >90 % extraction achieved when using single salts. The differences in extractions for the various extractants could be related to the fact that tertiary amines (Alamine 336) have a neutral charge, whereas quaternary amines have a positive charge. The Zr salt used for extraction ((NH₄)₃Zr(Hf)F₇) probably has a negative charge in solution (Zr(Hf)F₇³⁻, or possibly Zr(Hf)F₆²⁻). In spite of some protonation of the tertiary amine in the acid environment, it can be assumed that this will still be less charged than the quaternary amine where all extractants remain positively charged irrespective of the acid concentration. Assuming the negatively charged Zr salt (ZrF₆²⁻/ZrF₇³⁻ anion) in solution, a higher extraction can be expected with the quaternary amine due to its positive charge. This expectation is corroborated in Figure 3 - 4 when comparing (a) tertiary amine and (b) quaternary amine. While higher extraction for the quaternary amine (Aliquat 336) occurred only above 2 mol.dm⁻³ H₂SO₄, higher extraction was observed with lower acid concentrations (<1 mol.dm⁻³) for Alamine 336. This is preferential in view of the lower amount of acid used, which has both economic and environmental advantages.

While most results correlate between the single and binary metal complex, it is clear that the two complexes influence each other's extractions, specifically at low HCl concentrations (<1 mol.dm⁻³). While the competitive behaviour is influenced by the speciation, which due to its complexity falls beyond the scope of this study, the changed extraction behaviour, specifically of Hf in the binary complex, could be related to the change in the Hf concentration from 100 mg.L⁻¹ to 3 mg.L⁻¹ from the single to the binary metal complex. It was shown that Cl⁻ inhibits extraction at higher concentrations in both the single and binary metal complexes. Hence, when the Hf concentration was decreased from the single to the binary metal complex experiments, the Cl to Hf ratio increased, implying that at 3 mg.L⁻¹ Hf the Cl⁻, even at

low HCl concentrations, was sufficiently in excess to inhibit the extraction of Hf. It remains, however, unclear why this would also result in such a significant decrease in the Zr extraction.

In H_2SO_4 (Figure 3 - 2 and Figure 3 - 4) similar tendencies for single and binary metal complex were observed irrespective of the acid concentration ($0.1 - 8 \text{ mol.dm}^{-3}$), which again confirms the role of the Cl^- ion during extraction from an HCl environment. Some differences were observed; for example, the Alamine 336 formed no emulsions during the extractions with binary metal complex while emulsions did occur when using single salts. A reason for this is not apparent. In addition, Aliquat 336 yielded 20 % higher extraction from $1 \text{ mol.dm}^{-3} \text{ H}_2\text{SO}_4$, which increased gradually with the increase in acid concentration with binary complexes. Uniquat 2280, on the other hand, formed emulsions at 4 and 6 mol.dm^{-3} (Figure 3 - 4c). Comparing the data with Figure 3 - 2b, where emulsions were formed only in the presence of Zr, it seems that the Zr is responsible for these emulsions. [2]

3.3.1.3. Influence of extractant to metal_{Zr+Hf} ratio on binary metal complex extraction

According to the previous section, the best results for binary metal complexes were attained when extracting from a low H_2SO_4 concentration using Alamine 336 as extractant (Figure 3 - 4). Accordingly, the influence of the extractant to metal (E/M) ratio was determined by changing the Alamine 336 concentration between 0.01 – 10 wt% at $0.01, 0.1$ and $0.5 \text{ mol.dm}^{-3} \text{ H}_2\text{SO}_4$.

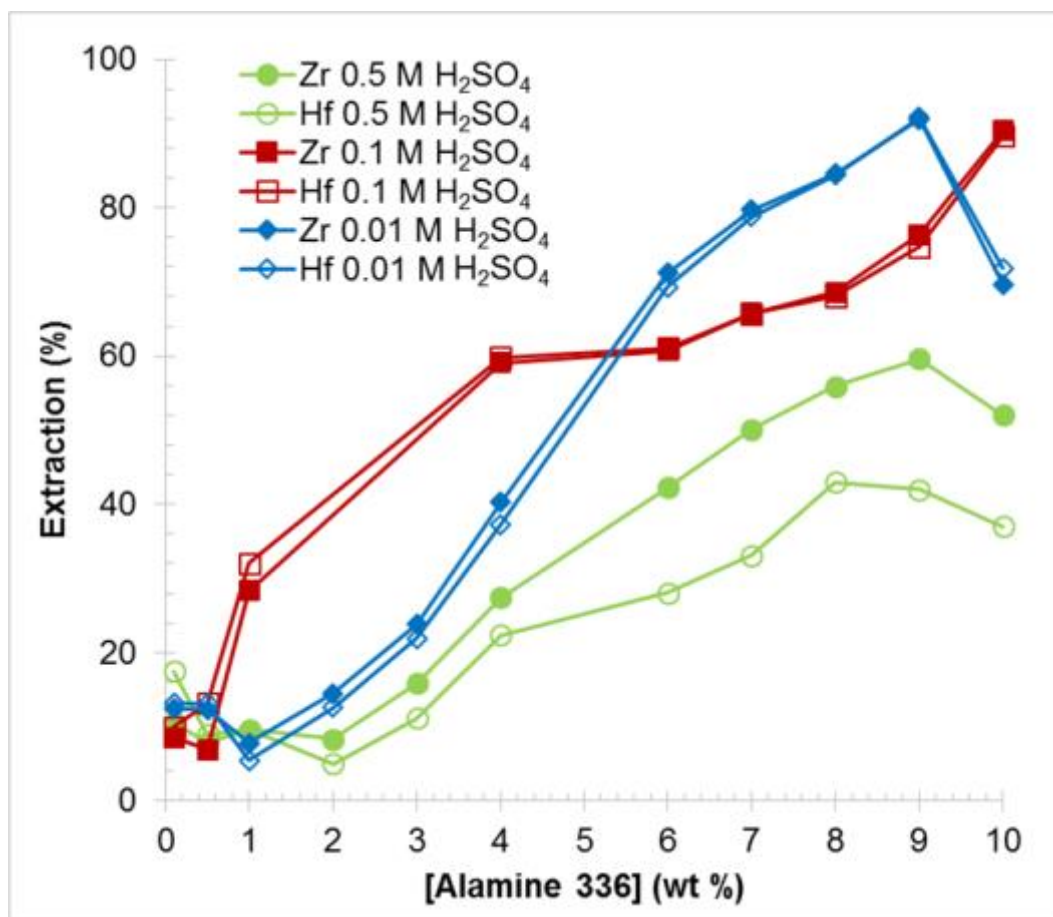


Figure 3 - 5: Effect of extractant concentration changes with binary metal complex in H_2SO_4 using Alamine 336. Conditions: 0.001 – 10 wt% extractant, [Acid]: 0.01, 0.1 and 0.5 mol.dm^{-3} , 97 mg.L^{-1} Zr and 3 mg.L^{-1} Hf, A/O = 1, equilibrium time = 60 minutes.

Figure 3 - 5 illustrates the extraction behaviour of Zr and Hf with increasing Alamine 336 concentration at three different H_2SO_4 concentrations. Apart from yielding the best results in the previous section, low concentrations of acids are also more cost-effective and leave a smaller chemical footprint. It is interesting to note that the extraction curve with 0.01 and 0.5 mol.dm^{-3} H_2SO_4 has a near S-shape, while extraction at 0.1 mol.dm^{-3} first increases logarithmically ($R^2 = 0.9082$) before levelling off. This might be related to the change in extraction between 0 and 1 mol.dm^{-3} H_2SO_4 (shown in the insert in Figure 3 - 4a) where the 0.01 mol.dm^{-3} data point was to the left of the inclining slope while the 0.5 mol.dm^{-3} data point was to the right of the descending slope with 0.1 mol.dm^{-3} on the peak of the graph. This, however, only confirms that there is a change in speciation in the vicinity of 0.1 mol.dm^{-3}

H₂SO₄, but not what this change might be. Irrespective of the variation in the shape of the curves, however, extraction increased in all cases with increasing Alamine 336 concentration from 2 to 9 wt%.

An extraction of 92 % was attained at 9 wt% Alamine 336 when extracting from 0.01 mol.dm⁻³ H₂SO₄, and 87 % at 10 wt% Alamine 336 when extracting from 0.1 mol.dm⁻³ H₂SO₄. Extraction from 0.5 mol.dm⁻³ H₂SO₄, while also increasing with increasing extractant concentration, had the smallest gradient, resulting in the lowest extraction, reaching a maximum of 60 % Zr and 41 % Hf at 9 wt% Alamine 336. In spite of the lower extraction, the experiment at 0.5 mol.dm⁻³ was the only one that displayed any selectivity between the two metals, in this case favouring the extraction of Zr with a 19 % selectivity at 9 wt% Alamine 336.

3.3.2. Stripping

In the work described in the previous sections the extractions were optimised. In order to be able to reuse the extractants for subsequent extractions in a solvent extraction process, the stripping of the metal complexes (Zr and Hf) from the loaded Alamine 336 has to be investigated. While stripping has been demonstrated in literature with various stripping liquors, the best results in this study were attained when using NaCl and H₂SO₄. [15, 17]

Figure 3 - 6 indicates the stripping of a loaded organic phase attained by a 60-minute extraction from a 0.5 mol.dm⁻³ H₂SO₄ solution using 9 wt% Alamine 336. The stripping liquor concentrations were varied from 0 – 2 mol.dm⁻³ for both H₂SO₄ and NaCl. According to Figure 3 - 6, both stripping liquors achieved stripping of the Zr and Hf, with decreasing stripping with increasing stripping liquor concentration. However, when using H₂SO₄ as stripping liquor, a 42 % Hf selectivity was achieved at 2 mol.dm⁻³. NaCl yielded favourable stripping results at 2 mol.dm⁻³ NaCl with a 46 % Hf stripping and 0 % Zr stripping. Although 2 mol.dm⁻³ NaCl was not able to strip all the Hf, it did result in a selective removal of Zr, leaving pure Zr in the organic phase, which can be stripped in a second stripping step, for example using H₂SO₄.

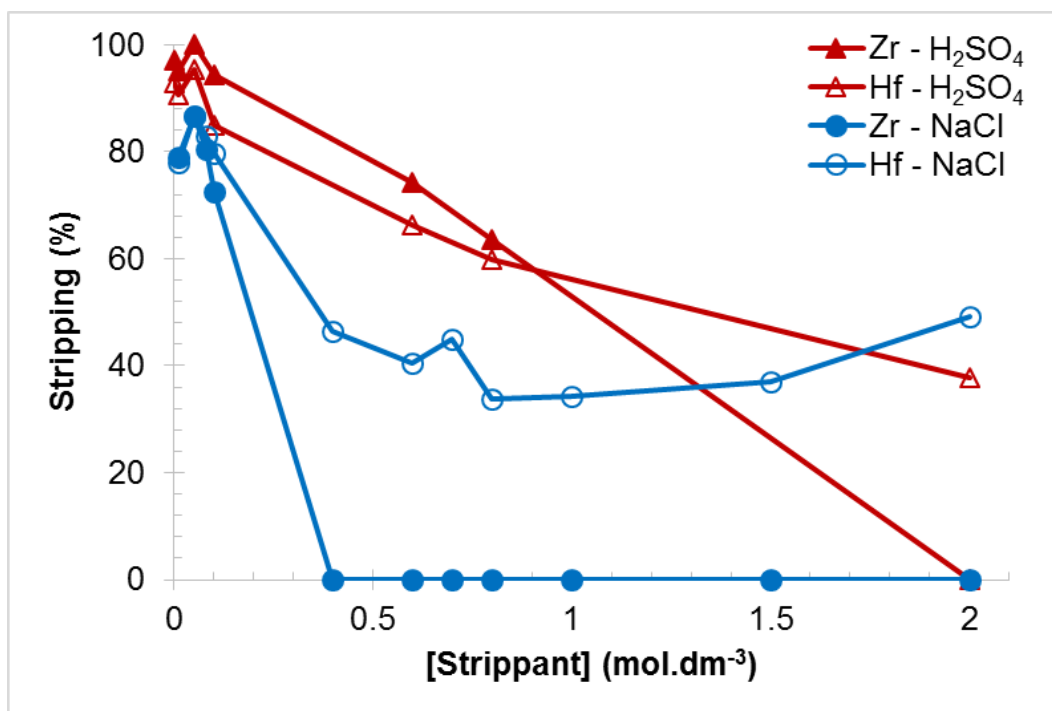


Figure 3 - 6: Effect of sodium chloride and H₂SO₄ as stripping liquor on loaded Alamine 336. Extraction conditions: 9 wt% Alamine 336, 0.5 mol.dm⁻³ H₂SO₄, 97 mg.L⁻¹ Zr and 3 mg.L⁻¹ Hf, O/A = 1, contact time 60 minutes. Stripping conditions: 9 wt% Alamine loaded, [Stripping liquor] = 0 – 2 mol.dm⁻³, O/A = 1, equilibrium time = 60 minutes.

3.3.3. Proposed extraction, scrubbing and stripping scheme

Using the extraction and stripping data obtained in this study, a possible scheme with various stages of extraction and stripping can be proposed (Figure 3 - 7), which could ultimately lead to a process for the manufacturing of nuclear-grade Zr if designed correctly. In the extraction step, the aqueous feed (0.5 mol.dm⁻³ H₂SO₄) and the aqueous scrubbing liquor (2.0 mol.dm⁻³ NaCl) are contacted with the organic solution (Alamine 336, 9 wt%) and the loaded organic solution. During this extraction an excess of Zr is extracted into the organic phase. During the scrubbing of the loaded organic phase most of the extracted remaining Hf is scrubbed to the aqueous phase. Thereafter the Zr is stripped from the organic phase using 0.05 mol.dm⁻³ H₂SO₄. Subsequently, the solvent is regenerated, water being used to remove any residual Zr or Hf from the organic phase. Finally, the depleted solvent is recirculated to the solvent make-up where any lost extractant is replenished, completing the process.

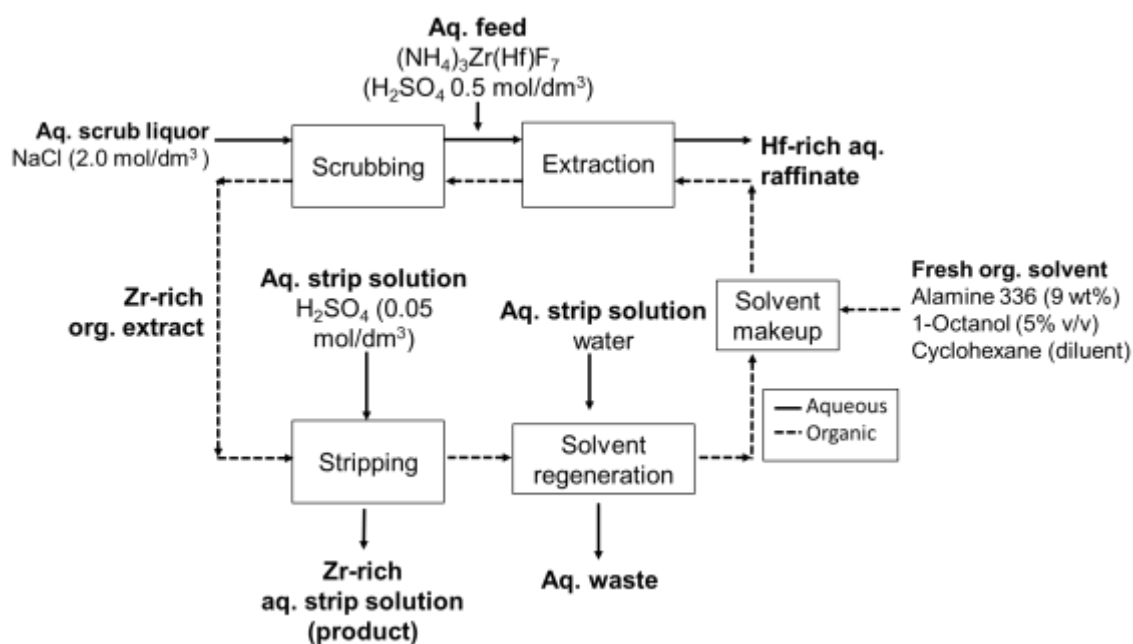


Figure 3 - 7: Proposed extraction, scrubbing and stripping scheme for Zr purification.

3.4. Conclusion

A solvent extraction study was done to determine the extraction and separation of Zr and Hf as $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$ from HCl and H_2SO_4 environments ($0.01 - 8 \text{ mol.dm}^{-3}$) using three amine-based extractants (Alamine 336, Aliquat 336 and Uniquat 2280). While similar extractions were attained for single and binary metal complex, both the Zr and Hf extractions were significantly lower when using binary metal complex at low HCl concentrations. Of the three amines tested, Alamine 336 exhibited the best extraction and selectivity for the separation of Zr from Hf at both low (86 %) and high (39 %) H_2SO_4 concentrations. Varying the E/M ratio of Alamine 336 at three low H_2SO_4 concentrations (0.01 , 0.1 and 0.5 mol.dm^{-3}) led to a 19 % selective extraction of Zr over Hf with 9 wt% Alamine 336 in $0.5 \text{ mol.dm}^{-3} \text{ H}_2\text{SO}_4$. Complete stripping of Zr and Hf from loaded Alamine 336 was achieved using $2 \text{ mol.dm}^{-3} \text{ NaCl}$. A proposed extraction, scrubbing and stripping scheme was presented showing the possibility for the development of a process for the separation of Zr and Hf from $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$ in a H_2SO_4 environment using amine-based extractants such as Alamine 336. With the current data it is possible to purify Zr from 97 % to 99 %. By combining further extraction, scrubbing and stripping steps, it should be possible to

reduce the Hf concentration in the Zr metal to below 100 mg.L^{-1} as required by the nuclear industry.

3.4 References

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Chapter 4

The hafnium-selective extraction from $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$ solution using phosphorus-based extractants

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4.1 Introduction

For the nuclear industry the separation of Zr and Hf is vital because of their opposite chemical nuclear properties. For Zr's use as cladding material in nuclear reactors, the Zr should contain less than 100 mg.L⁻¹ Hf. [1] Nuclear graded Zr is currently produced using various routes including ion exchange [2], distillation [3] and solvent extraction as intermediate step. [4]

An important commercial process used for the separation of Zr is the TBP/HNO₃ process, where 3 mol.dm⁻³ HNO₃ containing 30 g.L⁻¹ Zr and Hf is counter-currently contacted with 60 v/v% TBP and 2 mol.dm⁻³ HNO₃. Distribution coefficients of 1.5 and 0.15 were obtained for Zr and Hf, respectively. [5] Taghizadeh *et al.* [6] suggested that TBP combined with Cyanex 923 can yield higher separation factors, improving the extraction of Zr(Hf)Cl₄ while using a lower HNO₃ concentration (2.5 mol.dm⁻³). In addition to a separation factor of 186, no third phase formations were seen for this proposed process. In 1979 the Toyo Zirconium Co. Ltd. developed a SX-based process using alkyl amines to extract Zr from H₂Zr(Hf)O(SO₄)₂ into the organic phase, yielding a separation factor of between 10 and 20. [7] The advantages of this process include the extractants' stability and low water solubility, thereby reducing the environmental impact. The drawbacks, however, include the length of the process and the need to scrub the organic phase with a pure Zr solution to purify the Zr in solution. [1]

Over the years other processes have been proposed. For example, the selective extraction of ZrOCl₂ from 2 mol.dm⁻³ HCl was achieved by Reddy *et al.* in 2003 using PC-88A / Ionquest 801. [8] Biswas and Hayat [9], when investigating the performance of D2EHPA with ageing of the HCl feed solution, observed that Zr extraction increases with the ageing of the metal-chloride solution. Another new process was patented by Necsa in 2014 for the production of Zr metal using a plasma and fluoride process. According to the patent, the starting material is zircon (ZrSiO₂), which is transformed into plasma dissociated zircon (ZrO₂.SiO₂), which in turn is reacted with ammonium bifluoride to form (NH₄)₃Zr(Hf)F₇. [10] It is accordingly the purpose of this paper to selectively extract Hf or Zr from an ammonium zirconium hafnium heptafluoride ((NH₄)₃Zr(Hf)F₇) complex (97 mg.L⁻¹ Zr and 3 mg.L⁻¹ Hf) from H₂SO₄ or HCl (0.01 - 8 mol.dm⁻³) solutions. Phosphorus extractants such as

D2EHPA, Dio-PA and Ionquest 801 were evaluated. The effect of the type and concentration of the acids were tested both for single and binary metal complexes. In addition, the effect of extractant concentration on the extraction of mixed complex systems was investigated. Subsequently, four stripping agents (H_2SO_4 , ammonium carbonate $((\text{NH}_4)_2\text{CO}_3)$, calcium chloride (CaCl_2) and oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) were assessed to recover the metals and regenerate the organic phase. Hollow fibre membrane based solvent extraction (MBSX) was also investigated using D2EHPA in a 4 mol.dm^{-3} H_2SO_4 mixed metal complex solution, while the membrane based stripping and scrubbing were verified using two of the best stripping agents found during the SX studies. Since no literature was found for the extraction of $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$, only limited comparisons with literature was possible.

4.2 Materials and methods

4.2.1 Extraction

The extractants di-2-ethylhexylphosphoric acid (97 % D2EHPA, Sigma Aldrich), diisooctylphosphinic acid (90 % Dio-PA, Sigma Aldrich) and Ionquest 801 (95 % pure, SNF Flomin) were diluted with cyclohexane (95 %, LabChem) to 10 wt%. 1-Octanol (99.5 %, Sigma Aldrich) was added (5 v/v%) as a phase modifier. All chemicals were of analytical grade and used without further purification.

The freshly prepared aqueous feed solution consisted of 100 mg.L^{-1} $(\text{NH}_4)_3\text{ZrF}_7$ and 100 mg.L^{-1} $(\text{NH}_4)_3\text{HfF}_7$ for single metal complexes and 97 mg.L^{-1} $(\text{NH}_4)_3\text{ZrF}_7$ and 3 mg.L^{-1} $(\text{NH}_4)_3\text{HfF}_7$ for binary metal complexes in $0.01 - 8 \text{ mol.dm}^{-3}$ sulfuric acid (98 % H_2SO_4 , Merck) or hydrochloric acid (32 % HCl , LabChem). The pure metal complexes were produced at Necsa using a single metal complex feed solution from ZrO_2 (99.9 %, Sigma Aldrich) and HfO_2 (99.9 %, Sigma Aldrich). After the preparation of the two metal complexes, analytical results (ICP-OES analysis for the metal concentration, distillation methods to obtain fluoride data and ion specific electrodes to analyse the fluoride concentration) were used to verify and validate the structure of the complexes. All aqueous phase dilutions were prepared with deionised water (Millipore Milli-Q Plus® Q-pack CPMQ004R1).

4.2.2 Stripping

Ammonium carbonate (99.9 % $\text{NH}_4(\text{CO}_3)_2$, LabChem), calcium chloride (98 % CaCl_2 , LabChem), H_2SO_4 (98 %, Sigma Aldrich) and oxalic acid (99 %, $\text{C}_2\text{H}_2\text{O}_4$, Merck) were prepared to concentrations of 0 - 2 mol.dm^{-3} as the stripping liquors.

4.2.3 Method

4.2.3.1 Solvent Extraction

The extraction and stripping experiments were carried out with equal volumes of organic and aqueous phases (25 mL) in polypropylene bottles (Kartell). Extraction was done in a circular auto-shaker and incubator (Labcon, 3081U) after 60 minutes at 25 °C (+/- 2 °C) and 300 rpm. The solution was left after equilibrium for phase disengagement to take place. Subsequently the concentrations of the metals in the aqueous phases were measured with ICP-OES (Inductively coupled plasma – optical emission spectroscopy, Thermo Scientific iCAP 6000 SERIES ICP + CETAC ASX-520 Auto sampler). The concentration of the metals in the organic phase was obtained by mass balance. [11]

4.2.3.2 Membrane based solvent extraction

MBSX was carried out with equal volumes (1 L) of organic (9 wt% D2EHPA) and aqueous phases (4 mol.dm^{-3} H_2SO_4 , 97 mg.L^{-1} Zr, 3 mg.L^{-1} Hf) contacted for 180 minutes using a hydrophobic hollow fibre membrane (Liqui-Cel® Extra-Flow module, 1.4 m^2). The module consisted of pores (diameter = 240 μm) made from polypropylene (PP) fibres with a wall thickness of 30 μm . The organic (lumen) flow rate and pressure were 350 mL.min^{-1} and 70 kPa, respectively, while the aqueous (Shell) flow rate and pressure were 450 mL.min^{-1} and 100 kPa, respectively. In Figure 4 - 1 the basic experimental set-up of the MBSX that was adapted from van der Westhuizen *et al.* can be observed. [12]

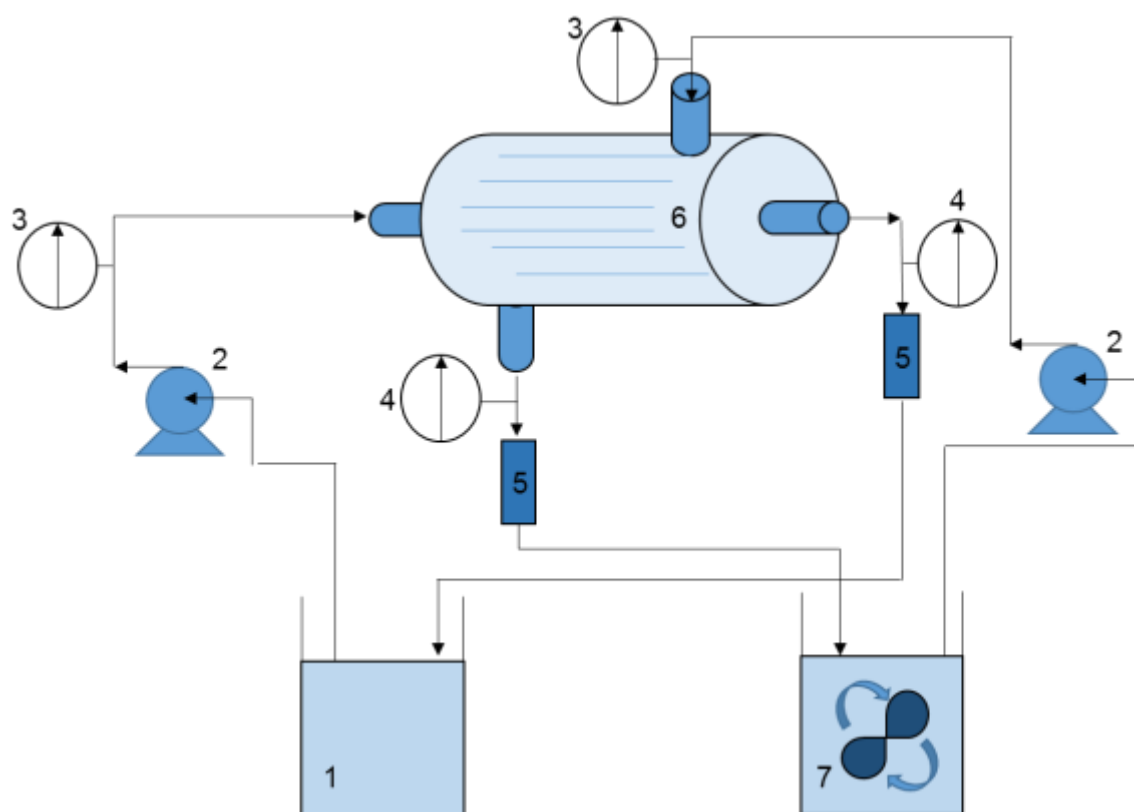


Figure 4 - 1: Experimental MBSX set-up: 1) organic solution, 2) pumps, 3) inlet pressure gauges, 4) outlet pressure gauges, 5) flow meter, 6) hollow fibre membrane, 7) agitated aqueous solution. [12]

4.3 Results and discussion

4.3.1 Dispersive solvent extraction

4.3.1.1 Influence of acid concentration on single and binary metal extraction

The extraction experiments were designed to determine the effect of SX on single and binary metal complex systems, and to ensure that if any correlation is observed, it would be considered when deliberating on the results. The effects were evaluated both on the single and binary extraction using $0.1 - 8 \text{ mol.dm}^{-3}$ HCl and H_2SO_4 . In addition, three different phosphorus-based extractants were selected, based on their structural and extraction properties. D2EHPA ($(\text{C}_8\text{H}_{17}\text{O})_2\text{PO}_2\text{H}$ – a phosphoric acid) has four oxygen bonds, one of which is double bonded, attached to the phosphorus atom. Ionquest 801 ($\text{C}_{16}\text{H}_{35}\text{PO}_3$ – a phosphonic acid) only has three oxygens bonded to the phosphorus atom, while Dio-PA ($\text{C}_{16}\text{H}_{35}\text{PO}_2$ – a phosphinic acid) only has two

oxygens bonded to the phosphorus atom, one of which is double bonded. While all three extractants can form hydrogen bonds, the chemical support differs on these active bonding positions. All the Dio-PA and D2EHPA in H₂SO₄ SX experiments, as well as all the E/M ratios and the stripping experiments were repeated, for which an experimental error below 5 % was obtained.

Since similar data was obtained for the single and binary complex extractions for all three extractants when extracting from both HCl and H₂SO₄ solutions, only the extraction using D2EHPA will be presented for HCl (Figure 4 - 2) and H₂SO₄ (Figure 4 - 3) as representative of the three extractants tested; in each case showing the extraction using (a) single salts and (b) binary salt mixtures. According to the results shown in Figure 4 - 2(a), complete extraction was obtained with no selectivity when extracting single salts from HCl, while a slightly more selective extraction towards Zr (20 %) was observed in the mixed complex above 4 mol.dm⁻³ HCl. Although Wang *et al.* used a different salt complex (ZrOCl₂, HfOCl₂), similar results (80 % extraction, 5 % selectivity) were observed in 4 mol.dm⁻³ HCl solutions with D2EHPA. [13] Similarities were also observed in the data of Reddy *et al.*, who used lonquest 801 in a 1 mol.dm⁻³ HCl solution. [8] Although the metal ratio differed from 100 mg.L⁻¹ Zr and Hf for single complexes ((Figure 4 - 2(a)) to 97 mg.L⁻¹ Zr and 3 mg.L⁻¹ Hf for binary complex systems (Figure 4 - 2(b)), the extraction of single and binary complexes was near identical below 4 mol.dm⁻³ HCl, showing slightly less extraction for the mixed salts above 4 mol.dm⁻³ HCl. This correlation indicates that both phosphinic (Appendix 3, Figure A3 – 6 and A3 - 7) and phosphonic acids in HCl solutions show no significant preference for the two chemically similar metals in the (NH₄)₃Zr(Hf)F₇ complex solution.

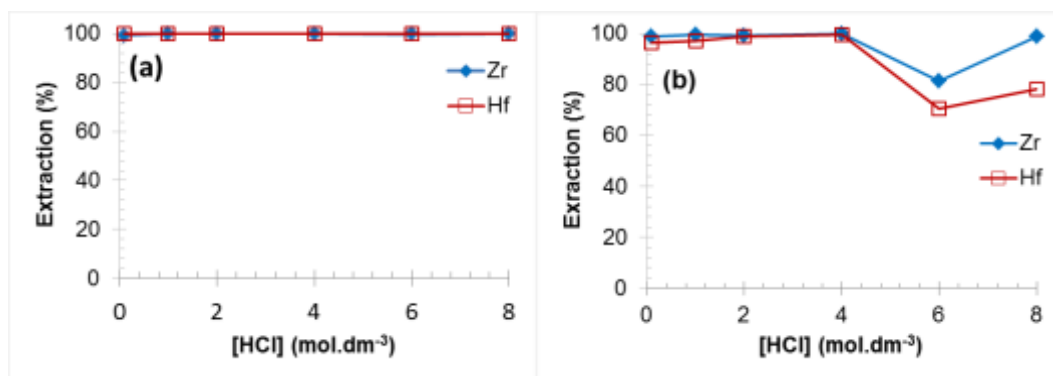


Figure 4 - 2: Effect of HCl concentration on the extraction of Zr and Hf from (a) single metal complex extraction = 100 mg.L⁻¹ Zr and 100 mg.L⁻¹ Hf and (b) binary metal complex extraction = 97 mg.L⁻¹ Zr and 3 mg.L⁻¹ Hf using D2EHPA. Conditions: 10 wt% extractant, A/O = 1, equilibrium time = 60 minutes

Biswas and Hayat [9] showed that Zr extraction with D2EHPA from HCl is influenced by the ageing of the metal complex solution. To verify this, ageing was also investigated in this study (Appendix 3, Figure A3 - 15), but even an ageing of 7 days did not influence the extraction results. It is clear from comparing the single complex (Figure 4 - 2 (a)) and binary complex (Figure 4 - 2 (b)) data that no competition was observed for the D2EHPA between the metal (ZrF₅⁻, HfF₅⁻) and the Cl⁻ ions at low acid concentrations, as was confirmed by Kovalev *et al.* [14] However, a slight difference between the two systems' extraction was observed between 6–8 mol.dm⁻³ HCl. A possible explanation for this difference in extraction could be due to the higher concentration of Cl⁻ ions at higher HCl concentrations. In solution, D2EHPA has a slightly positively (δ^+) charged oxygen that participates in the extraction by forming a hydrogen bond with the metal complexes. [15] At low HCl concentrations, all ions in solution (Cl⁻, ZrF₅⁻, and HfF₅⁻) can be extracted because of the amount of available active sites on the D2EHPA. However, with increasing Cl⁻ concentration, the competition for D2EHPA active sites increases. This could explain why ZrF₅⁻, being second highest in concentration (highest anions were Cl⁻), extracted more than HfF₅⁻ at elevated Cl⁻ concentrations, which would imply that the 10 – 20 % selectivity observed above 4 mol.dm⁻³ HCl (Figure 4 - 2(b)) is not due to a chemical selectivity but due to a concentration competition between Zr and Hf complexes in the presence of higher Cl⁻ concentrations. This was confirmed by the fact that, if the selectivity had been based on a chemical preference, selectivity would have been

observed during the single complex extractions. For chemical selectivity, a variation should exist in the bond length between the metal atom (Zr or Hf) and the D2EHPA active position. [16] Since the Cl^- ions will probably not replace the F^- ions on the metal complex (ZrF_5^- , HfF_5^-), no chemical changes and hence changes in bond lengths will occur in the metal complex which could contribute to a chemical selectivity.

In Figure 4 - 3(a) and (b) the extraction for D2EHPA from H_2SO_4 solutions for single and binary complex systems, respectively, is shown. Accordingly, almost 100 % Hf extraction was observed from 0.1 – 8 mol.dm^{-3} H_2SO_4 for the single complex extraction (Figure 4 - 3 (a)), while the Zr extraction was 100 % between 0.1 – 2 mol.dm^{-3} H_2SO_4 , before decreasing to 79 % at 8 mol.dm^{-3} H_2SO_4 , resulting in a 21 % preferential extraction of Hf. A similar behaviour was observed when using a mixed salt system (Figure 4 - 3(b)) where the Zr extraction decreased between 6 mol.dm^{-3} (Hf = 100 %, Zr = 76 %, selectivity = 26 %) and 8 mol.dm^{-3} (Hf = 95 %, Zr = 65 %, selectivity = 30 %). Lee *et al.* [17] obtained similar results (98 % Zr and 100 % Hf extraction in 2 mol.dm^{-3} H_2SO_4 at 0.07 mol.dm^{-3} D2EHPA) when using ZrOCl_2 and HfOCl_2 as initial complexes. According to these results, D2EHPA at higher H_2SO_4 concentrations resulted in Hf selectivity, both in the single and binary systems. In contrast to the results obtained with the HCl study, this implies that the selectivity is based on a chemical selectivity, which can occur when the bond length between the metal and the extracted compound differs for the Zr and Hf. [16] It is therefore possible that the SO_4^{2-} in solution is either replacing a F^- ion on, or associating with, the ZrF_5^- or HfF_5^- compound, thereby changing the length of the D2EHPA to metal complex bond. The slightly higher selectivity observed for the mixed salt experiments could be indicative of additional competition between Zr and Hf for the D2EHPA extractant. It is known that D2EHPA follows a cation exchange mechanism, which means that the $\text{Zr}(\text{SO}_4)_3^{2-}$ that forms at high H_2SO_4 concentrations is less likely to be extracted than the more stable $\text{Hf}(\text{SO}_4)_2$ neutrally charged complex at high H_2SO_4 concentrations. [18]

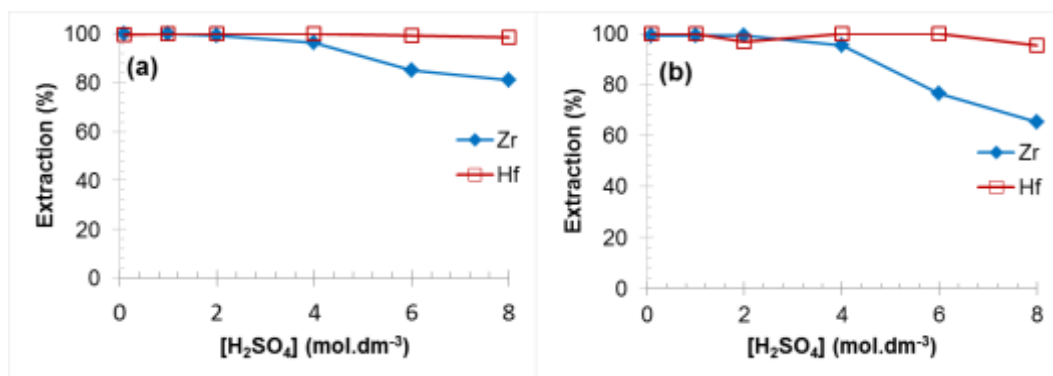


Figure 4 - 3: Effect of H_2SO_4 concentration on the extraction of Zr and Hf (a) single metal complex extraction = 100 mg.L^{-1} Zr and 100 mg.L^{-1} Hf and (b) binary complex extraction = 97 mg.L^{-1} Zr and 3 mg.L^{-1} Hf using D2EHPA. Conditions: 10 wt% extractant, A/O = 1, equilibrium time = 60 minutes.

4.3.1.2 Influence of extractant to metal_{Zr+Hf} ratio on binary complex extraction

According to Section 4.3.1.1, high extraction of Zr and Hf was obtained irrespective of the acid concentration ($0.1 - 8 \text{ mol.dm}^{-3}$, H_2SO_4 and HCl) and the extractant used (D2EHPA, Dio-PA and Ionquest 801). As no significant differences were obtained when comparing single and binary metal complexes, the influence of extractant concentration on the metal concentration was done using binary salts only (Zr = 97 mg.L^{-1} , Hf = 3 mg.L^{-1}). To determine the influence of the extractant to metal (E/M) ratio, the extractant concentration was varied from 0.1 – 10 wt% and equilibrated with 0.1, 4 and 8 mol.dm^{-3} H_2SO_4 and HCl.

In Figure 4 - 4 the E/M ratio data for Dio-PA (similar for Ionquest 801 – Appendix 3, Figure A – 13 and A - 14) in HCl (similar to H_2SO_4 – Appendix 3) is presented. When extracting from HCl, low extraction of Zr and Hf is observed at low extractant concentrations due to the limited amount of extractant available. De Beer *et al.* [19], obtained similar results with $ZrCl_4$ and $HfCl_4$ in HNO_3 when varying Ionquest 801 concentrations. As the extractant concentration increased, an increase in extraction was observed, reaching nearly a 100 % extraction at 4 wt% Dio-PA, giving rise to a steep slope between 0.1 and 2 wt%, confirming that a low concentration of Dio-PA is required for this extraction. The highest selectivity was attained in 8 mol.dm^{-3} HCl when using 0.5 and 1 wt% Dio-PA, resulting in a selectivity of 19 % and 14 % Hf,

respectively. No significant difference was observed when varying the acid concentration (0.1, 4 and 8 mol.dm⁻³) as a function of the E/M ratio.

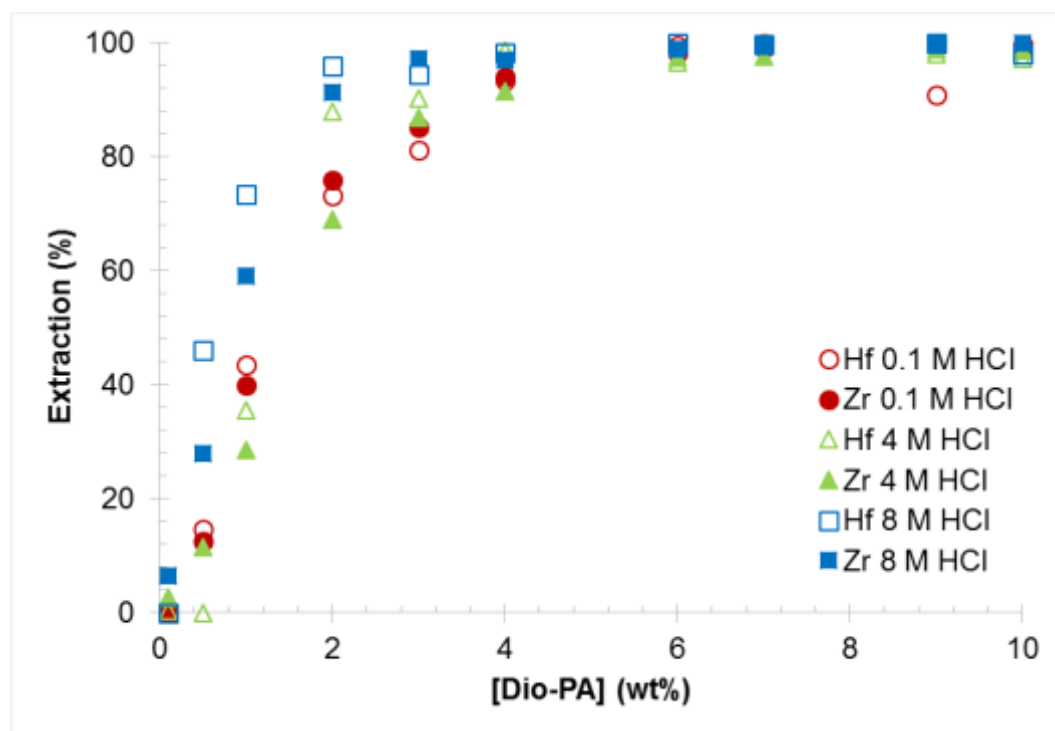


Figure 4 - 4: Effect of Dio-PA concentration on the extraction of mixed metal complexes from HCl solutions. Conditions: 0.001 - 10 wt% extractant, [Acid]: 0.1, 4 and 8 mol.dm⁻³, 97 mg.L⁻¹ Zr and 3 mg.L⁻¹ Hf, A/O = 1, equilibrium time = 60 minute.

The D2EHPA extraction from HCl and H₂SO₄ as a function of the E/M ratio is presented in Figure 4 - 5 and Figure 4 - 6, respectively. The extraction from HCl (Figure 4 - 5) was similar to the results obtained with Dio-PA (and Ionquest 801), showing an increase in extraction with an increase in the D2EHPA concentration for all three acid concentrations (0.1, 4 and 8 mol.dm⁻³). Optimum extractions occurred at 6 wt% D2EHPA, compared with the 4 wt% optimum observed when extracting with Dio-PA (and Ionquest 801). Due to the two bonding possibilities on the extractant (1- OH hydrogen bond and 2- O hydrogen bond), bonding competitions may arise with D2EHPA in HCl, resulting in the higher E/M ratio required for complete extraction of the metal complexes. This bonding competition might be due to dipole-dipole effects as investigated by Varnek *et al.* [20] for Zr and Hf in a TBP (phosphoric acid) and HNO₃ environment. In addition, D2EHPA has branched chains that can cause steric hindrance when the chains obscure the entrance of the metal

complex to the binding position. While Watarai *et al.* [21] stated that phosphorus-based extractants that are more branched should yield higher liquid–liquid extractions, no data was presented to indicate whether this might imply that more extractant might be required for the enhanced extraction.

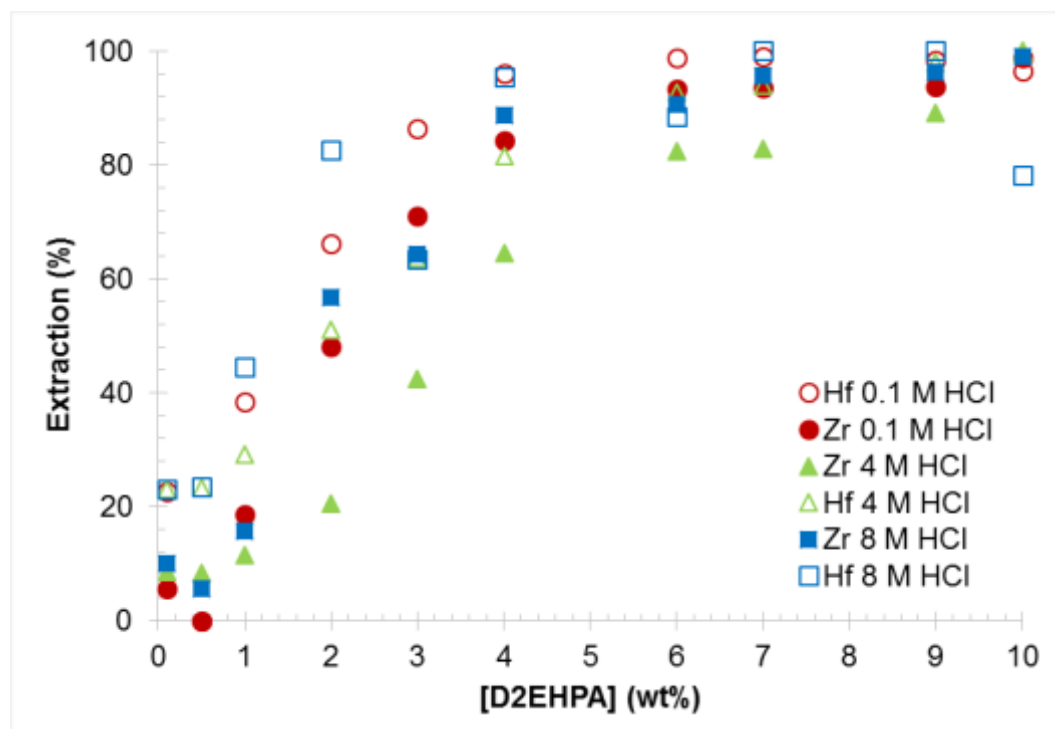


Figure 4 - 5: Effect of D2EHPA concentration on the extraction of binary metal complexes from HCl solutions. Conditions: 0.001 - 10 wt% extractant, [Acid]: 0.1, 4 and 8 mol.dm⁻³, 97 mg.L⁻¹ Zr and 3 mg.L⁻¹ Hf, A/O = 1, equilibrium time = 60 minute.

It is apparent that the extraction as a function of the E/M ratio changed remarkably when extracting with D2EHPA from an H₂SO₄ environment (Figure 4 - 6), where the extraction with D2EHPA at low and high H₂SO₄ concentrations seems to follow different mechanisms as suggested by Juang and Lo. [22] At 0.1 mol.dm⁻³ H₂SO₄, the extraction followed the same trend as had been observed for the Dio-PA, lonquest 801 and D2EHPA from an HCl environment (Figure 4 - 5 and Figure 4 - 6). At 0.1 mol.dm⁻³ H₂SO₄, a small amount of SO₄²⁻ is present in solution, limiting the competition between the SO₄²⁻, ZrF₅²⁻ and HfF₅²⁻ for D2EHPA extraction positions. As the D2EHPA concentration was increased, an increase in extraction was observed with the 97 % extraction optimum at 6 wt% D2EHPA, which is similar to the extraction observed from HCl while differing from the 80 % Hf and 40 % Zr extraction

Wang and Lee [11] observed when extracting with 0.2 g.L^{-1} D2EHPA from a 1 mol.dm^{-3} H_2SO_4 solution, confirming the influence of the type of salt used for extraction. However, at 4 and 8 mol.dm^{-3} H_2SO_4 , there was initially a decline in extraction, followed by a plateau and then an increase with increasing E/M ratio. It seems that at these higher concentrations of H_2SO_4 (4 and 8 mol.dm^{-3}), the higher concentration of SO_4^{2-} influenced the extraction behaviour of Zr and Hf.

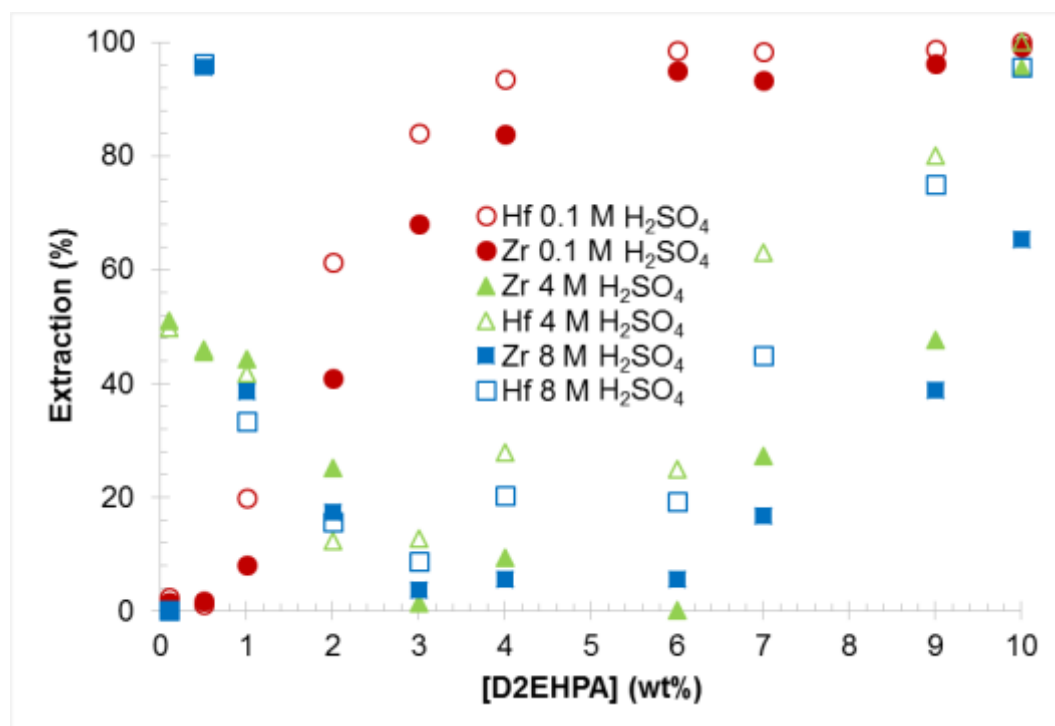


Figure 4 - 6: Effect of D2EHPA concentration on the extraction of mixed metal complexes from H_2SO_4 solutions. Conditions: 0.001 - 10 wt% extractant, [Acid]: 0.1, 4 and 8 mol.dm^{-3} , 97 mg.L^{-1} Zr and 3 mg.L^{-1} Hf, A/O = 1, contact time = 60 minute.

Small differences were observed in the tendencies of the extractions from 4 and 8 mol.dm^{-3} H_2SO_4 . At 8 mol.dm^{-3} H_2SO_4 , no extraction was observed with 0.1 wt% D2EHPA, which increased to a 97 % Zr and Hf extraction when using 0.5 wt% D2EHPA. Accordingly, 0.5 wt% D2EHPA would seem sufficient to extract all the ZrF_5^{2-} and HfF_5^{2-} in solution. However, above 1 wt% D2EHPA, a decrease in Zr and Hf extraction was observed, decreasing to 10% extraction at 3 wt% D2EHPA. It seems that above 1 wt%, D2EHPA forms dimers and polymers in the presence of H_2SO_4 , with the result that the D2EHPA does not complex the metal from the aqueous solution but complexes with itself, resulting in a decreased extraction. [23]

Above 4 wt% D2EHPA, a steady increase in extraction was once again observed, reaching a 95 % Hf and 65 % Zr extraction at 8 mol.dm⁻³ H₂SO₄. At 7 wt% D2EHPA a 29 % Hf selectivity was observed (see explanation of Figure 4 - 3(b) Section 4.3.1.1) with a 33 % selectivity at 9 wt% and a 30 % selectivity at 10 wt% D2EHPA.

At 4 mol.dm⁻³ H₂SO₄, a 50 % extraction was observed at 0.1 wt% D2EHPA, before declining with increasing D2EHPA content, reaching a minimum extraction of no Zr and 10 % Hf at 3 wt% D2EHPA, which correlates with the minimum (albeit lower) observed at 8 mol.dm⁻³ H₂SO₄. With further increase from 4 – 10 wt% in the D2EHPA concentration, an increase in extraction was observed, reaching a 100 % Hf and 98 % Zr extraction at 10 wt% D2EHPA. Both at 7 and 9 wt% D2EHPA, a 32 % Hf selectivity was observed. According to Smitha *et al.* [24], Hf will be extracted preferentially when a cation exchange extractant like D2EHPA is used when extracting from a H₂SO₄ solution.

4.3.1.3 Stripping

In Section 4.3.1.2, the extraction of (NH₄)₃Zr(Hf)F₇ was optimised with three extractants (D2EHPA, Dio-PA and Ionquest 801) in HCl and H₂SO₄ from 0.1 – 8 mol.dm⁻³. According to the results, the optimum compromise between extraction and selectivity was attained when extracting with 9 wt% D2EHPA from a 4 mol.dm⁻³ H₂SO₄ solution. Using these extraction conditions, loaded organic solutions were obtained for stripping experiments. Based on the various stripping liquors that have been investigated for the stripping of Zr and Hf salts from loaded D2EHPA, H₂SO₄ [11], (NH₄)₂CO₃, NaCl [25], C₂H₂O₄ [26], chlorides (NaCl) [27]), (NH₄)₂CO₃, CaCl₂, H₂SO₄ and C₂H₂O₄ were investigated in this study.

In Figure 4 - 7, the stripping data using four different stripping agents (0 – 2 mol.dm⁻³) are presented. While it was not possible to dissolve the (NH₄)₂CO₃ and C₂H₂O₄ above 1.0 mol.dm⁻³ and 1.2 mol.dm⁻³, respectively, the calcium chloride (CaCl₂) formed emulsions below 1.0 mol.dm⁻³. Hence, no results were obtainable for these conditions.

As can be seen from to Figure 4 - 7, no stripping was attained when using H₂SO₄, confirming previous studies. [28] When using (NH₄)₂CO₃ and C₂H₂O₄ there was no

stripping initially (at 0.01 mol.dm⁻³). However, the stripping increased with increasing stripping liquor concentration. This correlates with the observations made by Wang and Lee. [11] With C₂H₂O₄ a maximum stripping of 99 % Hf and 92 % Zr was attained at 1.2 mol.dm⁻³. While Pandae *et al.* [28] also observed a 100 % Zr and Hf stripping when using 1.2 mol.dm⁻³ C₂H₂O₄, they observed high extractions at low C₂H₂O₄ concentrations (0.1 mol.dm⁻³ C₂H₂O₄ resulted in 82 % Zr and 57 % Hf stripping), which again confirms the influence of the starting metal complex, which in this case was ZrCl₄. With these results, it is clear that a clean organic phase can be produced, which can be inserted back into the extraction stage of the process. (NH₄)₂CO₃ at 1.2 mol.dm⁻³ and CaCl₂ at 2 mol.dm⁻³ both yielded Hf selective stripping of 48 % and 75 %, respectively. Survachat obtained a 75 % Zr stripping with 0.005 mol.dm⁻³ (NH₄)₂CO₃, compared to the 52 % obtained in this study, which can again be ascribed to the difference in the starting material. [29]

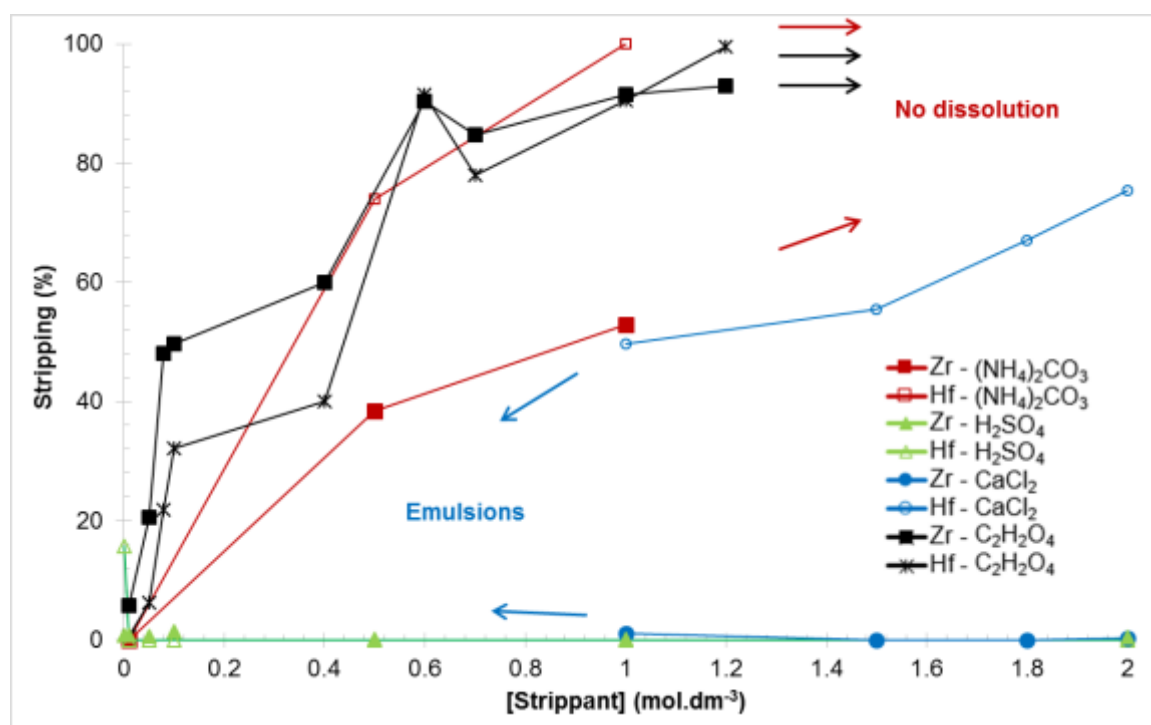


Figure 4 - 7: Effect of (NH₄)₂CO₃, H₂SO₄, CaCl₂ and C₂H₂O₄ concentrations as stripping liquors on the stripping of Zr and Hf from loaded D2EHPA. Extraction conditions: 9 wt% D2EHPA, 4 mol.dm³ H₂SO₄, 97 mg.L⁻¹ Zr and 3 mg.L⁻¹ Hf, O/A = 1, contact time = 60 minutes. Stripping conditions: 9 wt% loaded D2EHPA, [Stripping liquor] = 0 – 2 mol.dm⁻³, O/A = 1, equilibrium time = 60 minutes.

4.3.2 Non-dispersive solvent extraction

4.3.2.1 Extraction

According to Section 4.3.1.2, 9 wt% D2EHPA in 4 mol.dm⁻³ H₂SO₄ performed the most favourable for the extraction of Hf over Zr in a binary complex system (Zr = 97 mg.L⁻¹, Hf = 3 mg.L⁻¹). These experimental conditions were used to compare SX results to MBSX. In Table 4 – 1 the summarised results when using SX are indicated.

Table 4 - 1: Optimum extraction, scrubbing and stripping results for SX.

	Feed solution 97 mg.L ⁻¹ Zr 3 mg.L ⁻¹ Hf	Extraction 9 wt% D2EHPA 4 mol.dm ⁻³ H ₂ SO ₄	Scrubbing 2 mol.dm ⁻³ CaCl ₂	Stripping 1.2 mol.dm ⁻³ C ₂ H ₂ O ₄
Hf extraction (%)	-	80	75.4	99.6
Zr extraction (%)	-	48	0.0040	92.9
% selectivity	-	33	75.4	6.7

In Figure 4 - 8 , the effect of time on the extraction of Zr and Hf can be seen when using 9 wt% D2EHPA in 4 mol.dm⁻³ H₂SO₄. There was a gradual increase in extraction over time with a preferential extraction of Hf, as had been observed during the SX studies. After 180 minutes 72 % Hf and 44 % Zr had been extracted, giving a 28 % Hf selective extraction. This is similar to the results obtained by Yang *et al.* [30], who obtained a 100% Hf and 22 % Zr extraction in a supported liquid membrane configuration in an HCl solution using tri-n-octyl-monomethyl ammonium chloride (Aliquat 336) after 2.5 days. According to the SX data (Figure 4 - 6), the Hf and Zr extraction were 80 % and 47 %, respectively, when using 9 wt% D2EHPA, which implies a deviation of 8 % and 3 % for Hf and Zr, respectively, when comparing MBSX and batch SX data. While MBSX and SX cannot be compared directly in the case of this work because of the differences in volumes used in the two separation methods (25 mL and 1 L for SX and MBSX, respectively), which helps explain the longer time required for the MBSX (more salt present), the amount extracted for both methods was similar.

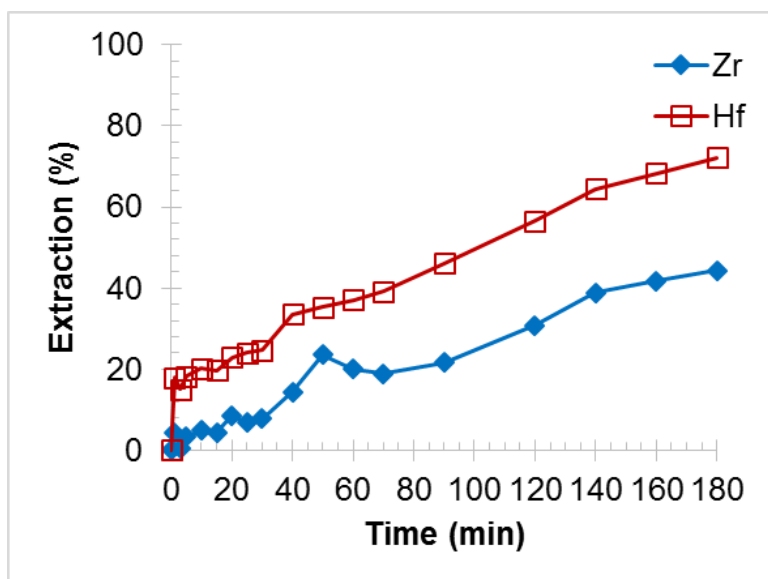


Figure 4 - 8: Effect of time (min) on extraction using MBSX. Conditions: 9 wt% D2EHPA (lumen), 4 mol.dm⁻³ H₂SO₄ (shell), Zr = 97 mg.L⁻¹, Hf = 3 mg.L⁻¹, lumen pressure: 70 kPa, shell pressure: 35 kPa, lumen flow rate: 450 mL.min⁻¹, shell flow rate: 350 mL.min⁻¹.

4.3.2.2 Stripping

In Section 4.3.2.1, MBSX was used to extract 72 % Hf and 44 % Zr in 180 minutes. For the stripping, the two most suitable stripping liquors (see Section 4.3.1.3), i.e. CaCl₂ (2 mol.dm⁻³) and C₂H₂O₄(1.2 mol.dm⁻³), were used for stripping using the above-described MBSX operation of which the results are shown in Figure 4 - 9 and Figure 4 - 10, respectively.

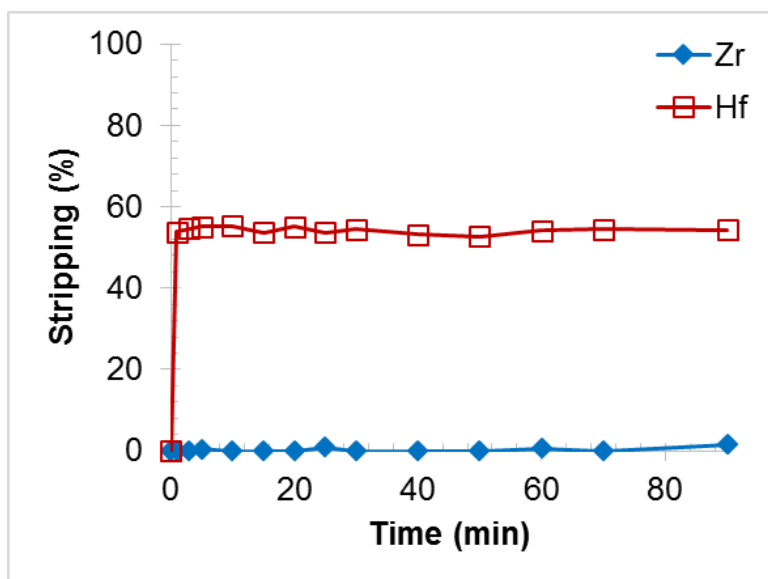


Figure 4 - 9: Effect of time (min) on stripping with CaCl_2 using MBSX. Conditions: loaded D2EHPA (72 % Hf, 44 % Zr) (lumen), 2 mol.dm^{-3} CaCl_2 (shell), lumen pressure: 70 kPa, shell pressure: 35 kPa, lumen flow rate: 450 mL.min^{-1} , shell flow rate: 350 mL.min^{-1} .

In Figure 4 - 9 the stripping data is presented when stripping with 2 mol.dm^{-3} CaCl_2 from the loaded D2EHPA that was produced by contacting 9 wt% D2EHPA with 4 mol.dm^{-3} H_2SO_4 in a Liqui-Cell membrane for 90 minutes. It is evident that a complete selective stripping was achieved with no Zr extraction and 58 % Hf extraction. The rapid equilibrium was achieved without any emulsion or precipitate forming. When comparing the stripping data obtained using SX (Figure 4 - 7) with the membrane based stripping data (Figure 4 - 9), it is clear that 22 % less Hf is extracted in this MBSX method. Since the membrane only acts as a physical barrier between the two phases, it is not clear why this difference in selectivity was observed.

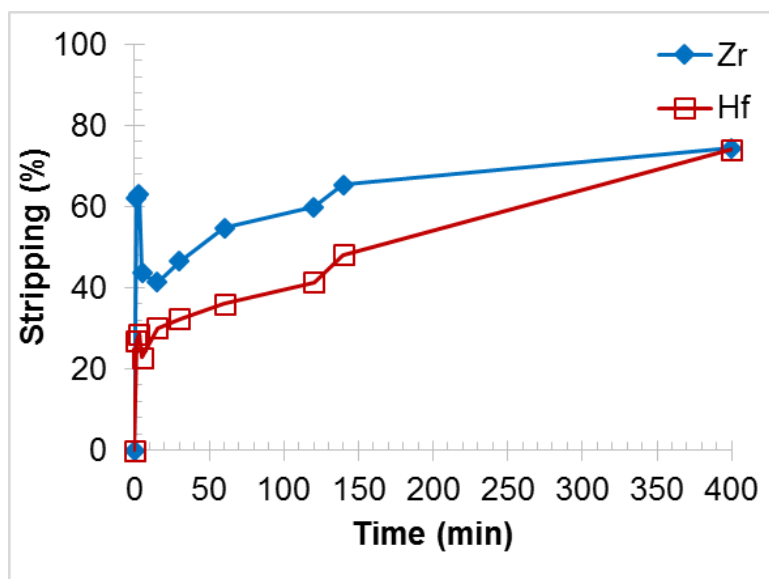


Figure 4 - 10: Effect of time (min) on stripping with $C_2H_2O_4$ using MBSX. Conditions: loaded D2EHPA (72 % Hf, 44 % Zr) (lumen), 1.2 mol.dm^{-3} $C_2H_2O_4$ (shell), lumen pressure: 70 kPa, shell pressure: 35 kPa, lumen flow rate: 450 mL/min, shell flow rate: 35 kPa, lumen flow rate: 450 mL.min^{-1} , shell flowrate: 350 mL.min^{-1} .

In Figure 4 - 10 the membrane based stripping data for 1.2 mol.dm^{-3} $C_2H_2O_4$ is shown. After 400 minutes equilibrium was reached with the co-stripping of 74 % Zr and Hf from the loaded D2EHPA. This membrane stripping value is 23 % less for the metals than when using the batch stripping (Figure 4 - 7), confirming that equilibrium had not been reached after 400 minutes. Again, it is not clear why the stripping was so slow compared with the MBSX based stripping using $CaCl_2$.

4.3.3 Proposal of a process flow sheet

Implementing the optimised extraction and stripping data for $(NH_4)_3Zr(Hf)F_7$ obtained using the results in Table 4 - 1, an extraction, scrubbing and stripping scheme with multiple stages could be as illustrated in Figure 4 - 11. Using 9 wt% D2EHPA as the extractant with 4 mol.dm^{-3} H_2SO_4 , a 32 % Hf-selective extraction can be obtained, leaving 53 % of the Zr in the aqueous phase. Subsequently, the Zr-rich organic phase can be scrubbed with 2 mol.dm^{-3} $CaCl_2$, which yields an organic phase containing 47.4 % Zr. $C_2H_2O_4$ (1.2 mol.dm^{-3}) can then be used to strip all the remaining metals (mostly Zr) from the organic phase to regenerate the D2EHPA for another cycle in the extraction stages 44.2 % of the Zr metal will be attained in the

$\text{C}_2\text{H}_2\text{O}_4$ stripping liquor. Solvent makeup should be used to replenish any lost extractant.

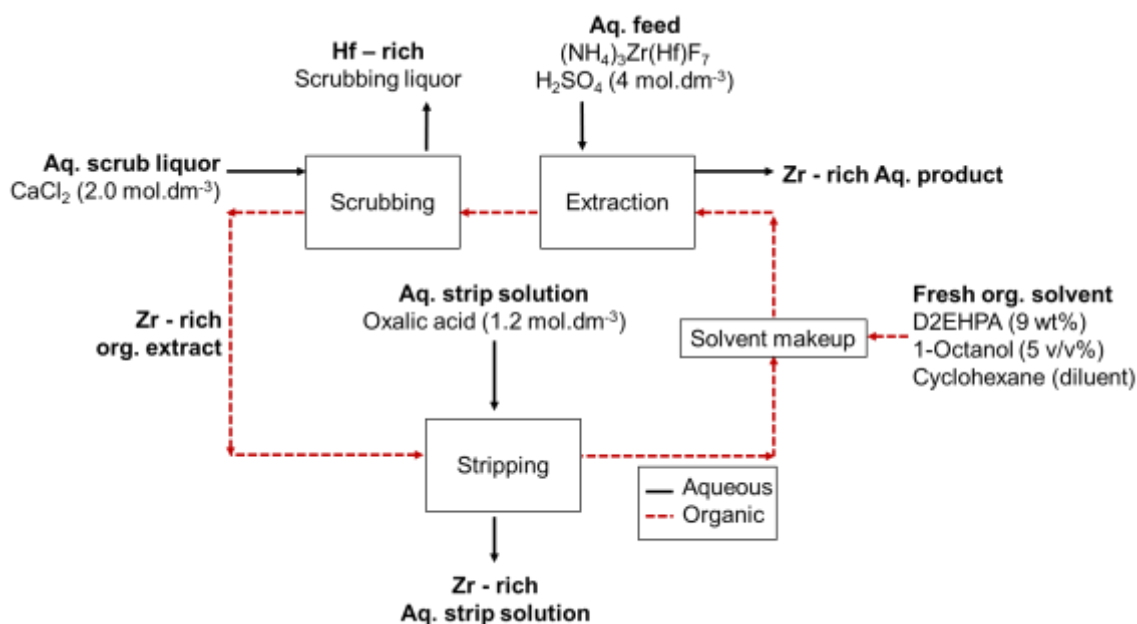


Figure 4 - 11: Proposed extraction, scrubbing and stripping scheme for Zr purification.

4.4 Conclusion

A SX and MBSX study was conducted to determine the selective extraction of Zr and Hf from a $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$ complex in HCl and H_2SO_4 (0.1 – 8 mol.dm⁻³) using the three phosphorus-based extractants: Dio-PA, Ionquest 801 and D2EHPA. When determining the effect of the acid type and concentration on extraction, similar results were obtained for single and binary complex extractions in HCl and H_2SO_4 for Dio-PA and Ionquest 801 (100 % extraction of Zr and Hf). For D2EHPA, 100 % extraction was only observed when extracting from HCl, while a 70 % Zr extraction and 30 % Hf selectivity was found at 8 mol.dm⁻³ H_2SO_4 . Subsequently, the E/M ratios were optimised for all extractants. Again similar results were obtained for Dio-PA and Ionquest 801 in both HCl and H_2SO_4 solutions. At 9 wt% D2EHPA an Hf-selective extraction (32 %) was observed when extracting from 4 mol.dm⁻³ H_2SO_4 . Stripping with $(\text{NH}_4)_2\text{CO}_3$, $\text{C}_2\text{H}_2\text{O}_4$ and CaCl_2 was evaluated using the 9 wt% D2EHPA-extracted loaded organic phase. While CaCl_2 (2 mol.dm⁻³) gave the most selective

stripping (75 % Zr selective), $\text{C}_2\text{H}_2\text{O}_4$ (1.2 mol.dm^{-3}) gave the highest yield overall (99 % Zr and 92 % Hf).

After optimising the extraction and stripping using SX, MBSX was completed with 9 wt% D2EHPA in $4 \text{ mol.dm}^{-3} \text{ H}_2\text{SO}_4$ where a 72 % Hf and 44 % Zr extraction was observed after 180 minutes with a 28 % Hf selectivity. Again two stripping liquors, i.e. CaCl_2 (2 mol.dm^{-3}) and $\text{C}_2\text{H}_2\text{O}_4$ (1.2 mol.dm^{-3}), were evaluated using a loaded D2EHPA phase, where CaCl_2 yielded a 47 % Hf-selective stripping. With $\text{C}_2\text{H}_2\text{O}_4$, a 75 % co-stripping of Zr and Hf was attained after 400 minutes.

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Chapter 5

Evaluation and Recommendations

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5.1 Introduction

It was the aim of this study to selectively separate Hf from a $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$ complex using SX and MBSX. The $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$ complex, which is produced during the Necsa plasma fluoride process, has not been studied previously as a possible starting material for the SX-based separation of Zr(Hf) salts (Chapter 1). If it were possible to separate the Zr and Hf using this metal complex, it could lead to a less costly process with a smaller chemical footprint.

To achieve this, single and binary complex systems were initially evaluated by varying the acid type (HNO_3 , HCl and H_2SO_4) and concentration ($0.001 - 8 \text{ mol.dm}^{-3}$) of the $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$ -containing feed solution. The extraction was optimised using both amine- and phosphorus-based extractants as discussed in Chapters 3 and 4, respectively. Parameters that were evaluated included the E/M ratio, ageing of the feed solution and the time required for reaching equilibrium during SX. Subsequently, the stripping from a loaded organic phase, containing either amine- or phosphorus-based extractants, was optimised. Lastly, MBSX was investigated using a phosphorus-based extractant (D2EHPA), where CaCl_2 and $\text{C}_2\text{H}_2\text{O}_4$ were used as stripping liquors.

5.2 Evaluation

For this evaluation, the results obtained from the studies on the amine-based extractants (Chapter 3) and the phosphorus-based extractants (Chapter 4) will be discussed before comparing the results obtained from the two extractants. This will be followed by a brief comparison between the SX and MBSX results. In each case it will be shown how these results have contributed to the initial aim and objectives as set out in Chapter 1.

5.2.1 Amine-based extractants

To facilitate an evaluation of the results, it would be helpful to discuss the results obtained using the distribution ratios (D_{Zr} , D_{Hf}), the separation factor (SF_{Hf}), as well as the yield (Ψ_{Zr}) and purity (β_{Zr}) in terms of the desired product, which was nuclear

grade Zr metal. As a first estimate it was assumed that D_{Zr} and D_{Hf} during scrubbing and stripping, which were calculated using the equations discussed in Chapter 2, were constant and independent of the metal concentration in the loaded organic phase. Since the aim of the study was to develop a Hf-selective process, the separation factor (SF_{Hf}) was expressed as a fraction of the distribution ratios of Hf and Zr:

$$SF_{Hf} = \frac{D_{Hf}}{D_{Zr}} \quad \dots 5.1$$

When considering that $D_M = [M]_{org}/[M]_{aq}$, it is clear that a $SF_{Hf} > 1$ implies a preferred distribution of Hf to the organic phase, while $SF_{Hf} < 1$ implies a preferred distribution of Hf to the aqueous phase (scrubbing or stripping liquor). The purity factor of the Zr (β_{Zr}) was obtained from:

$$\beta_{Zr} = \frac{[Zr]_{product\ stream}}{[Zr]_{product\ stream} + [Hf]_{product\ stream}} \times 100 \quad \dots 5.2$$

where $[Zr]$ and $[Hf]$ are the metal concentrations ($mg.L^{-1}$) in the product stream, which can either be the organic or the aqueous phase, depending on the phase of interest (organic for extraction and scrubbing and aqueous for stripping). The Zr yield (Ψ_{Zr}) was obtained by:

$$\Psi_{Zr} = \frac{[Zr]_{product\ stream}}{[Zr]_{feed}} \times 100 \quad \dots 5.3$$

where Ψ_{Zr} is the yield (%) of Zr, $[Zr]_{product\ stream}$ is the Zr concentration in $mg.L^{-1}$ in the organic or aqueous phase, and $[Zr]_{feed}$ is the metal concentration in $mg.L^{-1}$ in the initial feed solution.

According to Chapter 3 (see Chapter 3, Section 3.3.3), the best amine-based purification was attained when extracting with 9 wt% Alamine 336 from a $0.5\ mol.dm^{-3}\ H_2SO_4$ feed solution and scrubbing the loaded organic phase with $2\ mol.dm^{-3}\ NaCl$ before stripping with $0.01\ mol.dm^{-3}\ H_2SO_4$. A summary of the results, expressed in terms of D_{Zr} , D_{Hf} , SF_{Hf} , Ψ_{Zr} and β_{Zr} , is presented in Table 5 - 1. It is important to note that the β_{Zr} and Ψ_{Zr} presented for the extraction and scrubbing were expressed in terms of the Zr in the organic phase, while referring to the

aqueous phase during stripping. The aqueous and organic flow streams were equal to unity for the β_{Zr} and Ψ_{Zr} calculations in all cases.

Table 5 - 1: Extraction, scrubbing and stripping data of Zr and Hf when using Alamine 336 as extractant.

	Feed solution	Extraction (9 wt% Alamine 336) (0.5 mol.dm ⁻³ H ₂ SO ₄)	Scrubbing (2 mol.dm ⁻³ NaCl)	Stripping (0.01 mol.dm ⁻³ H ₂ SO ₄)
D _{Zr} (-)	/	1.33	64	0.052
D _{Hf} (-)	/	0.69	1.04	0.104
SF _{Hf} (-)	/	0.52	0.0162	1.99
β_{Zr} (%)	97.0	98.0 ¹	99.0 ¹	99.0 ²
$\Psi_{\text{Zr aq}}$ (%)	/	57.0 ¹	56.1 ¹	53.3 ²

¹ organic phase; ² aqueous phase

During a single-step extraction (1st step), the purity of the Zr extracted into the organic phase increased from 97.0 % to 98.0 %, with a Zr yield of 57.0 %. This is understandable when considering that $SF_{\text{Hf}} < 1$ as $D_{\text{Zr}} > D_{\text{Hf}}$, indicating a Zr-selective extraction process. During the scrubbing with NaCl (2nd step), the purity of the Zr in the organic phase increased to 98.0 %. This can be ascribed to the fact that the NaCl is highly Hf selective ($SF_{\text{Hf}} = 0.0162$), scrubbing the Hf from the organic phase, with only approximately 1 % of Zr lost to the scrubber during this stage. After the stripping step (3rd step), using a 0.01 mol.dm⁻³ H₂SO₄ solution, a purity of 99.0 % Zr in the aqueous stripping phase, with a yield of 53.3 %, was obtained. For this step, the $SF_{\text{Hf}} \approx 2$, confirming that the stripping favours Hf. In summary, it is clear that when extracting with Alamine 336, using only a single extraction, scrubbing and stripping stage, over 50% of the Zr can be recovered while increasing the purity from 97.0 % to 99.0 %. After the three-stage process, the organic phase contained a residual 2.80 % Zr and Hf, which could be recovered using further purification steps such as a scrubbing with water as proposed in Chapter 3, Section 3.3.3.

5.2.2 Phosphorus-based extractants

Similarly to the discussion on the amine-based extractions, the best results obtained from the phosphorus-based extractants (Chapter 4), which were obtained when extracting with 9 wt% D2EHPA from a 4 mol.dm⁻³ H₂SO₄ feed solution, scrubbing the loaded organic phase with 2 mol.dm⁻³ CaCl₂ before stripping with 1.2 mol.dm⁻³ C₂H₂O₄, were also expressed in terms of D_{Zr} , D_{Hf} , SF_{Hf} , Ψ_{Zr} and β_{Zr} , and are presented in Table 5 - 2.

It is clear that the proposed extraction, scrubbing and stripping process when using D2EHPA is different when compared with the extraction using Alamine 336. The most important difference is that, in this process, two separate product streams are obtained: the first one during the initial extraction and the second during the final stripping phase. Accordingly, the purity and yield of Zr, shown in Table 5 - 2, are expressed in terms of the aqueous phase for the extraction and stripping results, and in terms of the organic phase for the scrubbing results.

Table 5 - 2: Extraction, scrubbing and stripping data of Zr and Hf when using D2EHPA as extractant.

	Feed solution	Extraction (9 wt% D2EHPA) (4 mol.dm ⁻³ H ₂ SO ₄)	Scrubbing (2.0 mol.dm ⁻³ CaCl ₂)	Stripping (1.2 mol.dm ⁻³ C ₂ H ₂ O ₄)
D_{Zr} (-)	/	0.91	308	0.076
D_{Hf} (-)	/	4.02	0.326	0.00422
SF_{Hf} (-)	/	4.43	0.00106	0.055
β_{Zr} (%)	97.2	99.0 ²	99.0 ¹	99.0 ²
Ψ_{Zr} (%)	/	52.5 ²	47.4 ¹	44.2 ²

¹ Organic phase; ² Aqueous phase

According to the data in Table 5 - 2, it is clear ($SF_{Hf} = 4.43$) that D2EHPA is a Hf-selective extractant when extracting from an (NH₄)₃Zr(Hf)F₇ complex. As a result, the purity of the Zr in the raffinate was increased from 97 % to 99 % after extraction (1st step). Due to the $D_{Zr} = 0.91$, this aqueous raffinate stream contained 52.5 % of the initial Zr. The scrubbing with 2 mol.dm⁻³ CaCl₂ (2nd step) was highly Hf selective

($SF_{Hf} = 0.00106$), not only maintaining the purity of the residual Zr in the organic phase (99 %), but also ensuring that 47.4 % of the Zr was retained in the organic phase after scrubbing. During stripping (3rd step), most of the residual Zr ($D_{Zr} = 0.076$) and Hf ($D_{Hf} = 0.00422$) were recovered using $1.2 \text{ mol.dm}^{-3} \text{ C}_2\text{H}_2\text{O}_4$. As the stripping favoured Hf ($SF_{Hf} = 0.055$), the stripping liquor contained 44.2 % of the initial Zr at a purity of 99.0 %, which means that only 3.3 % of the Zr was retained in the organic phase after the scrubbing and stripping stages.

5.2.3 Amine- vs. phosphorus-based extractants

When comparing the amine- and phosphorus-based extractants for their ability to separate Hf and Zr from the $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$ stock solution (Table 5 - 3), it is clear that both processes have advantages and disadvantages.

Table 5 - 3: Comparison of amine- and phosphorus-based extraction processes

	Amine	Phosphorus
Amount of product streams	1	2
β_{Zr} (%)	99.0	99.0 (99 ¹ & 99 ²)
Ψ_{Zr} (%)	42.2	97.2 (53 ¹ & 44.2 ²)
Zr and Hf in organic phase after stripping (%)	2.8	3.3
¹ after extraction in raffinate	² after stripping	

The major difference, as mentioned previously, is that the amine-based process has only one product stream where the Zr is accumulated in a $0.01 \text{ mol.dm}^{-3} \text{ H}_2\text{SO}_4$ environment after the final stage of stripping, whereas the phosphorus-based extractant process has two product streams/outlets. The 1st extraction product stream/outlet is in a $4 \text{ mol.dm}^{-3} \text{ H}_2\text{SO}_4$ environment and the 2nd stripping product stream is in a $1.2 \text{ mol.dm}^{-3} \text{ C}_2\text{H}_2\text{O}_4$ environment. However, when attempting to combine these two streams, a white precipitate was obtained. Although this was not analysed further, it is possible that some CaCl_2 was transferred from the scrubbing step via the organic phase to the final $\text{C}_2\text{H}_2\text{O}_4$ -containing stripping phase, which, when combined with H_2SO_4 , resulted in the possible formation of CaSO_4 .

Another significant difference is the yield of Zr, which was 43.5 % and 97 % for the amine- and phosphorus-processes, respectively, which clearly favours the phosphorus process, especially when considering that both processes resulted in a 99 % purity of Zr. On the other hand, it would seem that the two product streams obtained during the phosphorus route would have to be processed separately. However, even if only one product stream is possible, the phosphorus route still yielded a 2 % (or 11 % depending on the product stream of choice) higher Zr yield than the amine-based process at the same purity. Since both streams resulted in a residual 3 % waste in the organic phase, it seems clear that the phosphorus route is most advantageous when attempting to purify Zr from the $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$ complex.

5.2.4 SX vs. MBSX

It was illustrated, using both amine- and phosphorus-based extractants, that traditional SX yielded satisfactory and repeatable results, confirming the suitability of SX for the separation of Zr and Hf from the Necsa-produced $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$ complex. In Chapter 4, MBSX was used to repeat the SX results obtained with the phosphorus-based extractants to determine its effect on extraction and separation. While equilibrium during extraction had been reached in 30 minutes when using SX (Appendix 3, Figure A3 - 15), it is clear that equilibrium had not been reached after 180 minutes when using MBSX (Chapter 4, Section 4.3.2.1). Similarly, it took more than 400 minutes during stripping to reach equilibrium. This indicates that the membrane resistance has contributed significantly to the delay in transfer of the metals from the aqueous to the organic phase during extraction, and from the organic to aqueous phase during stripping. In the D_{Zr} , D_{Hf} , S_{Hf} , Ψ_{Zr} and β_{Zr} for the MBSX data are shown for comparison with the phosphorus-based SX data (Table 5 - 2).

Table 5 - 4: Membrane based solvent extraction, scrubbing and stripping data of Zr and Hf when using D2EHPA as extractant.

	Feed solution	Extraction (9 wt% D2EHPA) (4 mol.dm ³ H ₂ SO ₄)	Scrubbing (2.0 mol.dm ³ CaCl ₂)	Stripping (1.2 mol.dm ³ C ₂ H ₂ O ₄)
D _{Zr} (-)	/	0.34	64	0.344
D _{Hf} (-)	/	1.14	1.02	0.348
SF _{Hf} (-)	/	3.31	0.0159	1.01
β _{Zr} (%)	96.1	97.5	96.2	96.2
Ψ _{Zr} (%)	/	74.4	25.2	18.7

After 180 minutes, when using MBSX, the SF_{Hf}, Ψ_{Zr} and β_{Zr} for extraction were 3.31 %, 97.5 % and 74.4 %, respectively. When comparing this to the data in Table 5 - 2, it is clear that the SF_{Hf} decreased with 1.12 units, making the MBSX less Hf selective. Accordingly, the purity of the Zr product only increased to 97.5 %, while a 21 % increase in Zr yield was observed. For the MBSX-based scrubbing with CaCl₂, the SF_{Hf}, Ψ_{Zr} and β_{Zr} were 0.0159 %, 96.2 % and 25.2 %, respectively, which in each case was less desirable, i.e. less Hf selective, resulting in a lower purity and yield of the Zr product than the traditional SX results. After 400 minutes of the MBSX stripping step with 1.2 mol.dm⁻³ C₂H₂O₄, where no equilibrium had been reached, the SF_{Hf}, Ψ_{Zr} and β_{Zr} were 1.01 %, 96.2 % and 18.7 %, respectively. When comparing this with the stripping results presented in Table 5 - 2, it is clear that the SF_{Hf} during MBSX is no longer Hf selective, resulting in a declined purity (2 % less) and yield (25.5 % less) in comparison to SX. Accordingly, not only did the MBSX take longer during extraction and stripping to reach equilibrium (no equilibrium with stripping), but it also resulted in a 3 % lower purity combined with a significant decline in yield over the two product streams (4.5 %). These results imply that more research has to be completed on the pertraction from the (NH₄)₃Zr(Hf)F₇ solution.

5.3 Recommendations

- In this study, the aim was to find a separation process for Zr and Hf when using $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$. While the goal was achieved, there is currently no understanding of the speciation involved during the SX when using $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$. Understanding the speciation would certainly further elucidate the underlying mechanism as well as provide direction for further optimisations.
- The higher solubility of $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$ ($40\,000\text{ mg}\cdot\text{L}^{-1}$), compared with, for example $\text{Zr}(\text{Hf})\text{F}_4$, should facilitate the upscaling of such a process. However, further studies would be required to obtain SX results at these elevated concentrations, thereby establishing the influence of these conditions on the yield and purity of the Zr after extraction, scrubbing and stripping.
- Further optimisation during SX and MBSX could entail varying the organic to aqueous phase ratio, which would provide additional kinetic data while possibly improving the results obtainable using MBSX.
- In view of the slow extraction observed during MBSX, it could be helpful to investigate different types of membranes, for example to study the effect of hydrophobic and hydrophilic membranes.
- Simultaneous extraction and stripping of the metals can be investigated when using MBSX by inserting two or more membranes in parallel, which could create a faster and more effective separation and purification process.
- Another possibly important variable that might influence the suitability of this process commercially is the ageing of the feed solution for longer periods and under different environments, as storage and lifetime of chemicals can become challenging in an industrial process.
- While various extractants have been evaluated in this study, it is always possible to test more extractants, acids and modifiers on the $(\text{NH}_4)_3\text{Zr}(\text{Hf})\text{F}_7$ complex.
- Multiple-step mixture settler trains should be modelled to increase the Zr purity from the 99.2 % purity obtained in this study (using D2EHPA), where a single extraction, scrubbing and stripping was used, to the 99.99 % required for nuclear applications.

Appendix 1

LIX-84 IC and Cyanex 301

Single metal complex results in HNO_3 , HCl and H_2SO_4 with LIX-84 IC

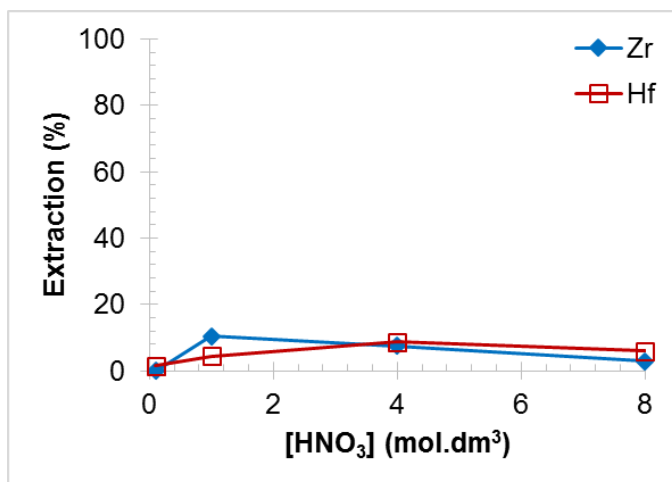


Figure A1 - 1: Effect of HNO_3 concentration with single metal complex extraction using LIX-84 IC. Conditions: 10 wt% LIX-84-IC, 100 mg.L^{-1} Zr, 100 mg.L^{-1} Hf, A/O = 1, equilibrium time = 60 minutes.

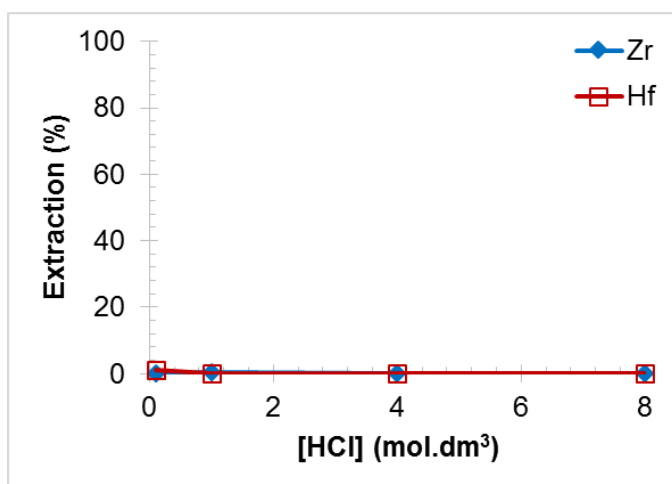


Figure A1 - 2: Effect of HCl concentration with single metal complex extraction using LIX-84 IC. Conditions: 10 wt% LIX-84-IC, 100 mg.L^{-1} Zr, 100 mg.L^{-1} Hf, A/O = 1, equilibrium time = 60 minutes.

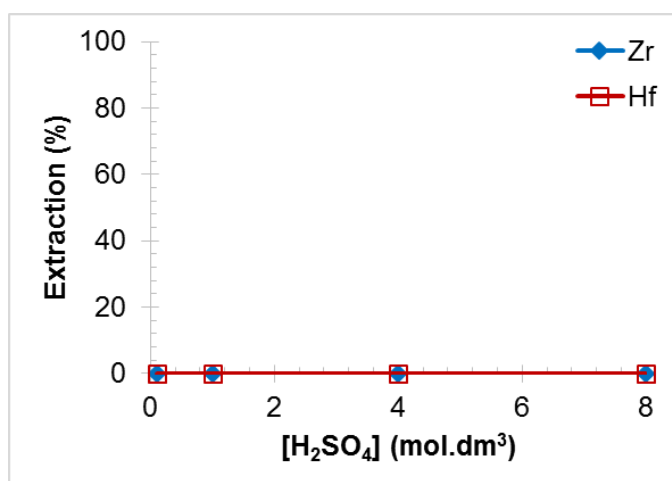


Figure A1 - 3: Effect of H_2SO_4 concentration with single metal complex extraction using LIX-84 IC. Conditions: 10 wt% LIX-84 IC, 100 mg.L^{-1} Zr, 100 mg.L^{-1} Hf, A/O = 1, equilibrium time = 60 minutes.

Single metal complex results in HNO_3 , HCl and H_2SO_4 with Cyanex 301

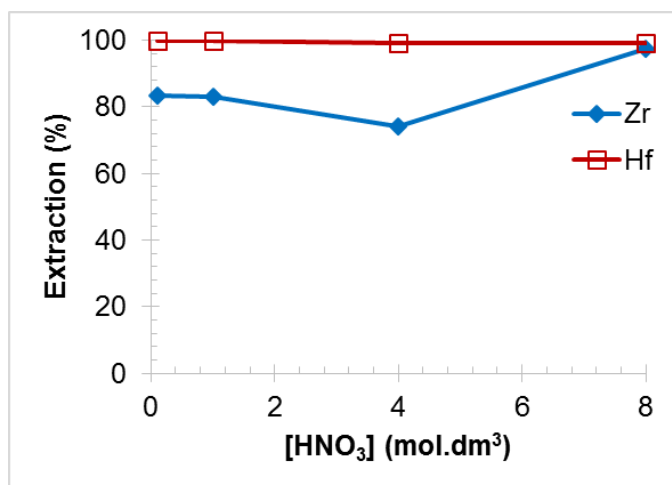


Figure A1 - 4: Effect of HNO_3 concentration with single metal complex extraction using Cyanex 301. Conditions: 10 wt% Cyanex 301, 100 mg.L^{-1} Zr, 100 mg.L^{-1} Hf, $A/O = 1$, equilibrium time = 60 minutes.

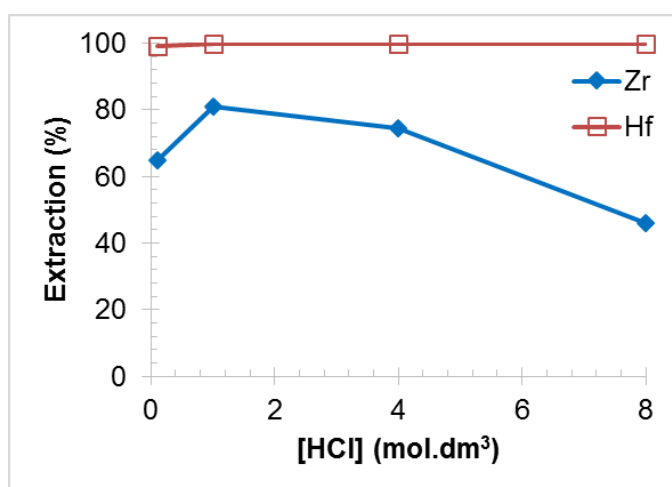


Figure A1 - 5: Effect of HCl concentration with single metal complex extraction using Cyanex 301. Conditions: 10 wt% Cyanex 301, 100 mg.L^{-1} Zr, 100 mg.L^{-1} Hf, $A/O = 1$, equilibrium time = 60 minutes.

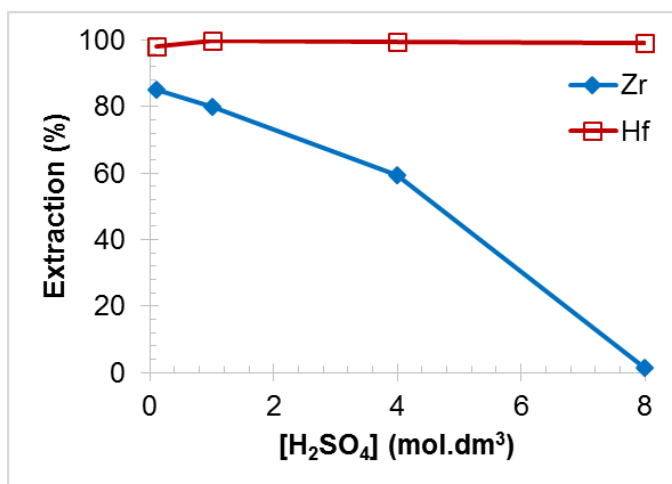


Figure A1 - 6: Effect of H_2SO_4 concentration with single metal complex extraction using Cyanex 301. Conditions: 10 wt% Cyanex 301, 100 mg.L^{-1} Zr, 100 mg.L^{-1} Hf, $A/O = 1$, equilibrium time = 60 minutes.

Appendix 2

Amine-based extractants

Single metal complex results in HNO_3 with Uniquat 2280, Aliquat 336 and Alamine 336

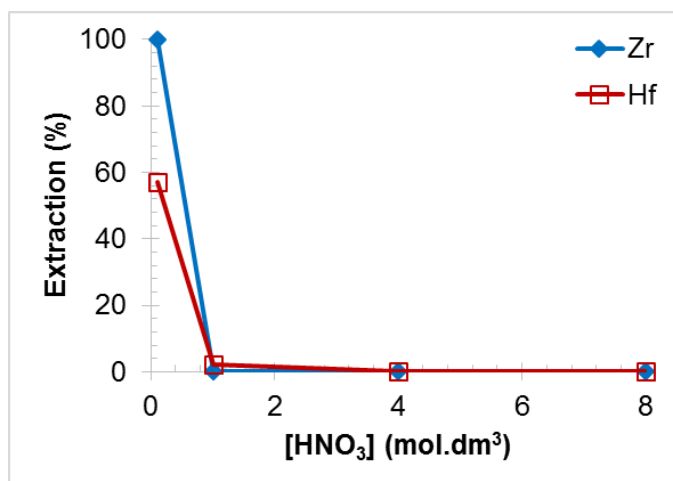


Figure A2 - 1: Effect of HNO_3 concentration with single metal complex extraction using Uniquat 2280. Conditions: 10 wt% Uniquat 2280, 100 mg.L^{-1} Zr, 100 mg.L^{-1} Hf, $A/O = 1$, equilibrium time = 60 minutes.

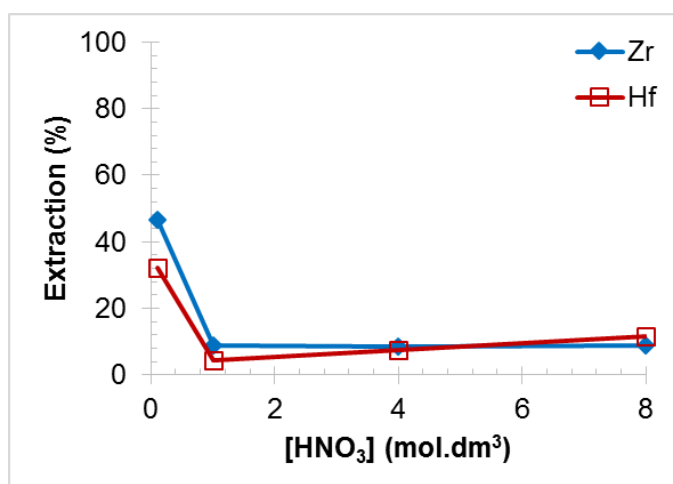


Figure A2 - 2: Effect of HNO_3 concentration with single metal complex extraction using Aliquat 336. Conditions: 10 wt% Aliquat 336, 100 mg.L^{-1} Zr, 100 mg.L^{-1} Hf, $A/O = 1$, equilibrium time = 60 minutes.

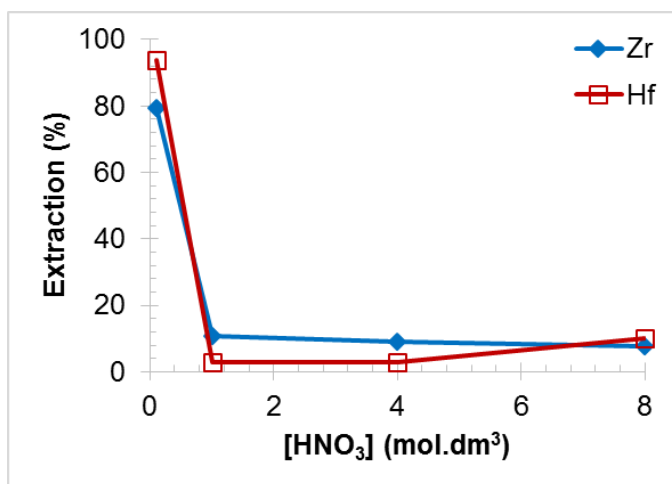


Figure A2 - 3: Effect of HNO_3 concentration with single metal complex extraction using Alamine 336. Conditions: 10 wt% Alamine 336, 100 mg.L^{-1} Zr, 100 mg.L^{-1} Hf, $A/O = 1$, equilibrium time = 60 minutes.

Binary metal complex results in HCl and H₂SO₄ with Alamine 300

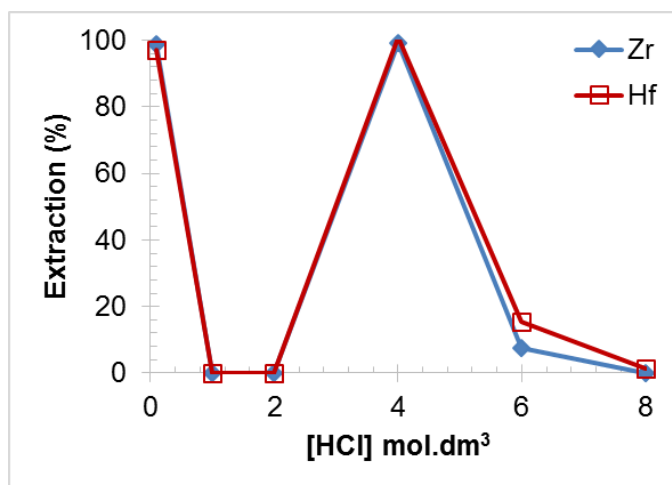


Figure A2 - 4: Effect of HCl concentration with binary metal complex extraction using Alamine 300. Conditions: 10 wt% Alamine 300, 97 mg.L⁻¹ Zr, 3 mg.L⁻¹ Hf, A/O = 1, equilibrium time = 60 minutes.

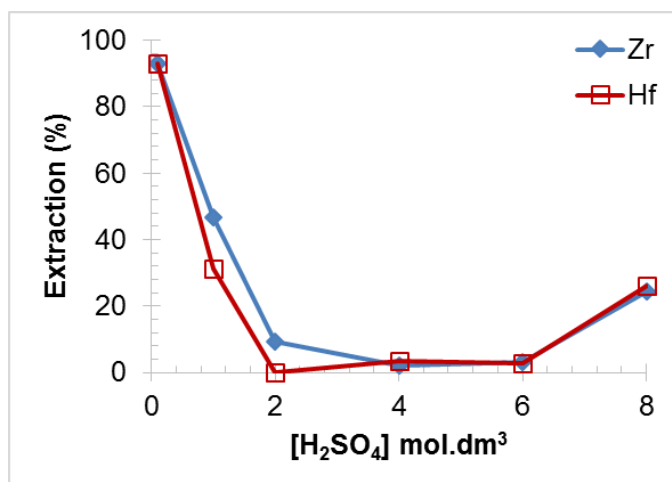


Figure A2 - 5: Effect of H₂SO₄ concentration with binary metal complex extraction using Alamine 300. Conditions: 10 wt% Alamine 300, 97 mg.L⁻¹ Zr, 3 mg.L⁻¹ Hf, A/O = 1, equilibrium time = 60 minutes.

Binary metal complex results in HCl and H₂SO₄ with Alamine 308

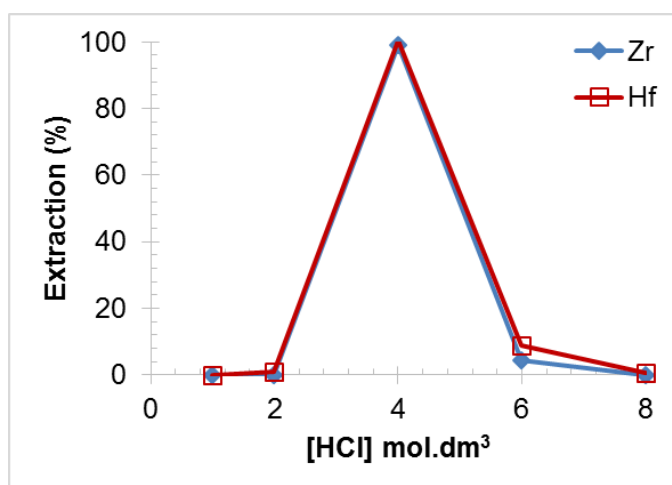


Figure A2 - 6: Effect of HCl concentration with binary metal complex extraction using Alamine 308. Conditions: 10 wt% Alamine 308, 97 mg.L⁻¹ Zr, 3 mg.L⁻¹ Hf, A/O = 1, equilibrium time = 60 minutes.

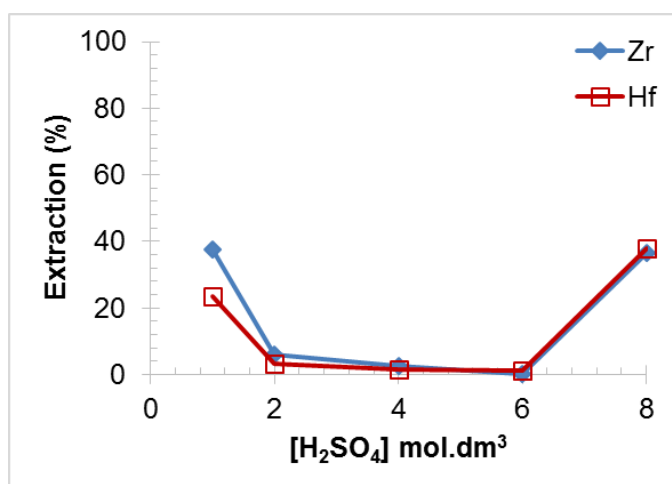


Figure A2 - 7: Effect of H₂SO₄ concentration with binary metal complex extraction using Alamine 308. Conditions: 10 wt% Alamine 308, 97 mg.L⁻¹ Zr, 3 mg.L⁻¹ Hf, A/O = 1, equilibrium time = 60 minutes.

E/M_{Zr+Hf} ratio in HCl with Aliquat 336

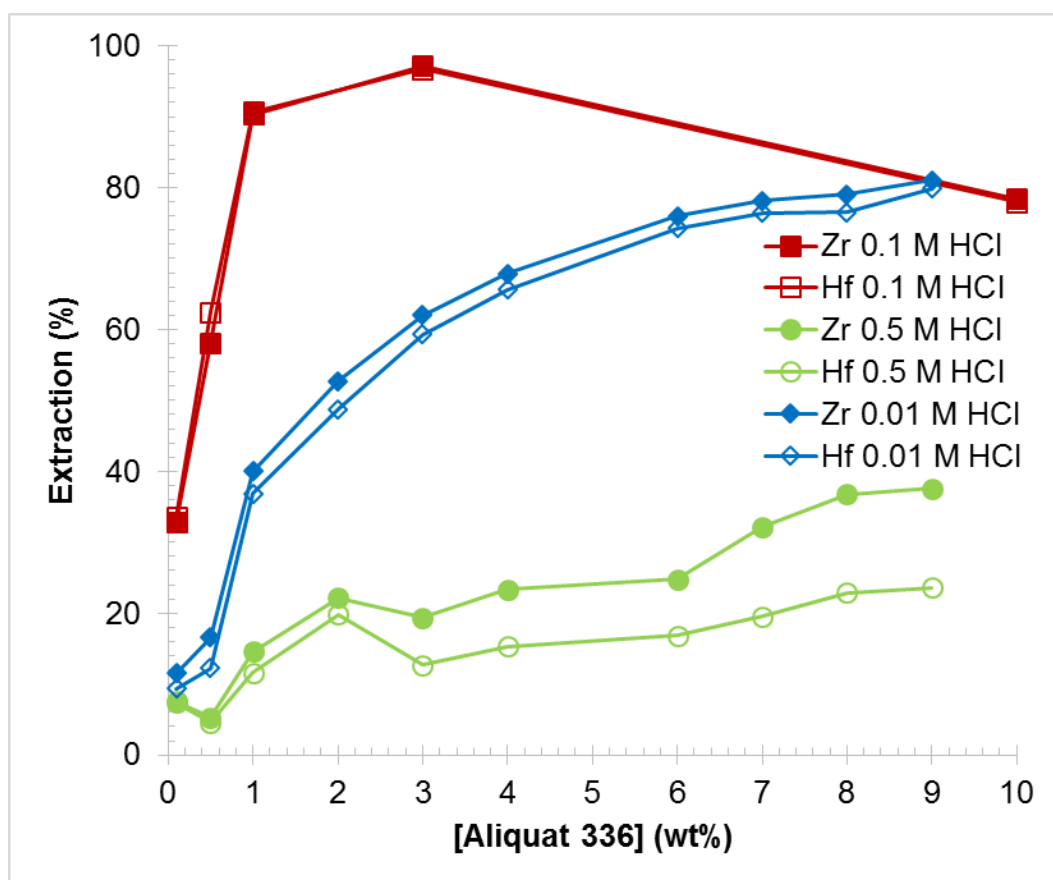


Figure A2 - 8: Effect of extractant concentration changes with mixed metal complex in H_2SO_4 using Aliquat 336. Conditions: 0.001 - 10 wt%, [Acid] = 0.01, 0.1 and 0.5 mol.dm⁻³, 97 mg.L⁻¹ Zr, 3 mg.L⁻¹ Hf, A/O = 1, equilibrium time = 60 minutes.

Appendix 3

Phosphorus-based extractants

Single metal complex results in HNO_3 with Lonquest 801, Dio-PA, and D2EHPA

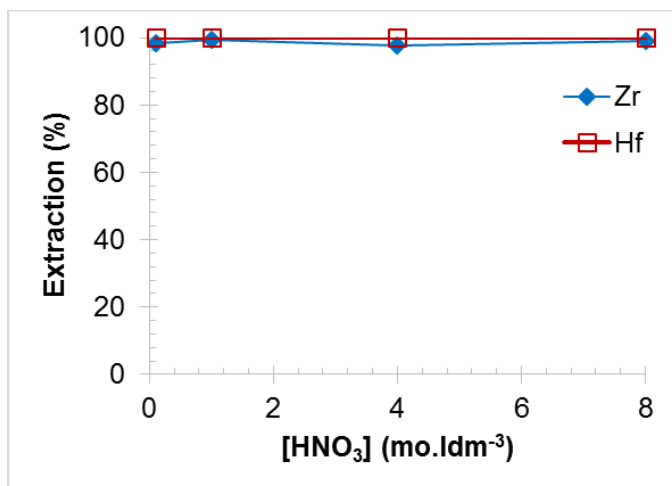


Figure A3 - 1: Effect of HNO_3 concentration with single metal complex extraction using Lonquest 801. Conditions: 10 wt% Lonquest 801, 100 mg.L^{-1} Zr, 100 mg.L^{-1} Hf, $A/O = 1$, equilibrium time = 60 minutes.

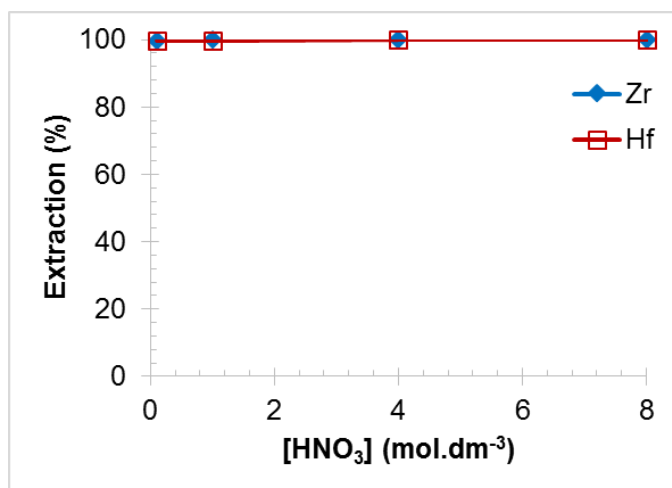


Figure A3 - 2: Effect of HNO_3 concentration with single metal complex extraction using Dio-PA. Conditions: 10 wt% Dio-PA, 100 mg.L^{-1} Zr, 100 mg.L^{-1} Hf, $A/O = 1$, equilibrium time = 60 minutes

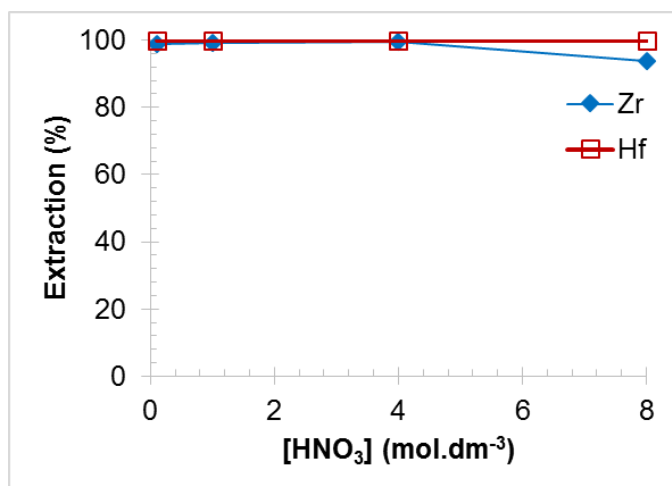


Figure A3 - 3: Effect of HNO_3 concentration with single metal complex extraction using D2EHPA. Conditions: 10 wt% D2EHPA, 100 mg.L^{-1} Zr, 100 mg.L^{-1} Hf, $A/O = 1$, equilibrium time = 60 minutes.

Single metal complex results in H₂SO₄ with lonquest 801 and Dio-PA

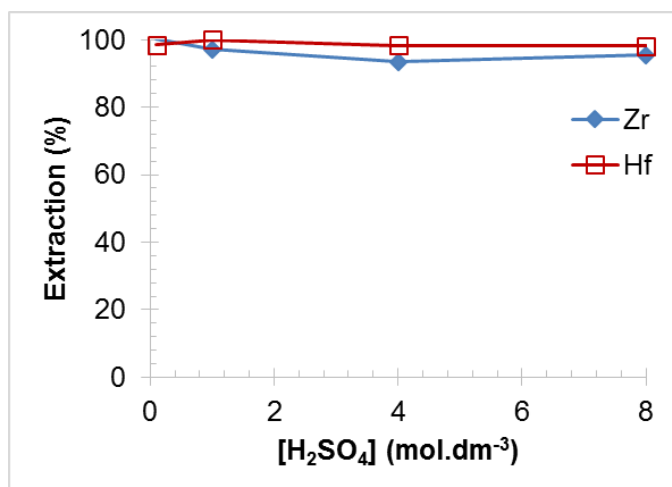


Figure A3 - 4: Effect of H₂SO₄ concentration with single metal complex extraction using lonquest 801. Conditions: 10 wt% lonquest 801, 100 mg.L⁻¹ Zr, 100 mg.L⁻¹ Hf, A/O = 1, equilibrium time = 60 minutes.

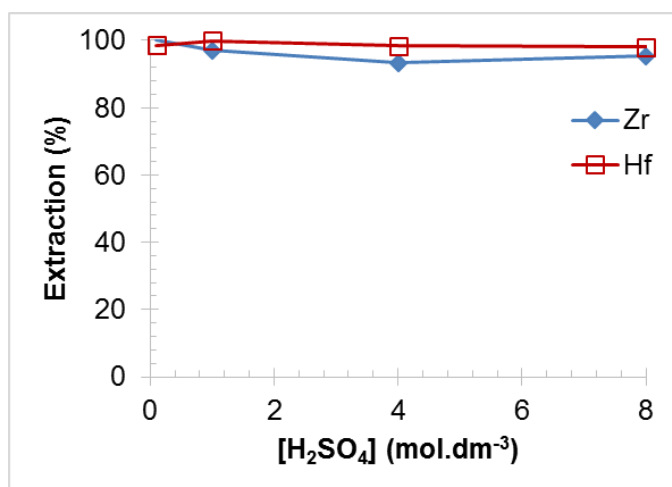


Figure A3 - 5: Effect of H₂SO₄ concentration with single metal complex extraction using Dio-PA. Conditions: 10 wt% Dio-PA, 100 mg.L⁻¹ Zr, 100 mg.L⁻¹ Hf, A/O = 1, equilibrium time = 60 minutes.

Single metal complex results in HCl with lonquest 801 and Dio-PA

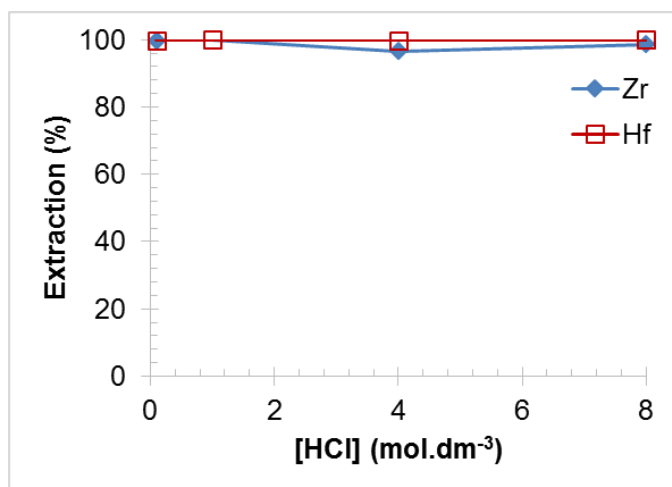


Figure A3 - 6: Effect of HCl concentration with single metal complex extraction using lonquest 801. Conditions: 10 wt% lonquest 801, 100 mg.L⁻¹ Zr, 100 mg.L⁻¹ Hf, A/O = 1, equilibrium time = 60 minutes.

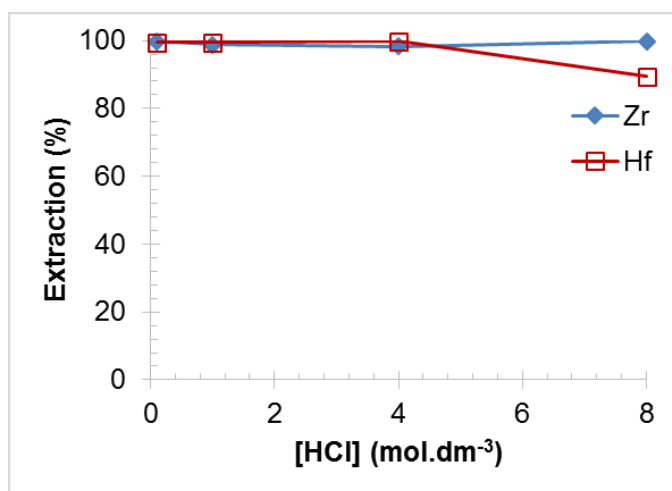


Figure A3 - 7: Effect of HCl concentration with single metal complex extraction using Dio-PA. Conditions: 10 wt% Dio-PA, 100 mg.L⁻¹ Zr, 100 mg.L⁻¹ Hf, A/O = 1, equilibrium time = 60 minutes.

Binary metal complex results in H_2SO_4 with lonquest 801 and Dio-PA

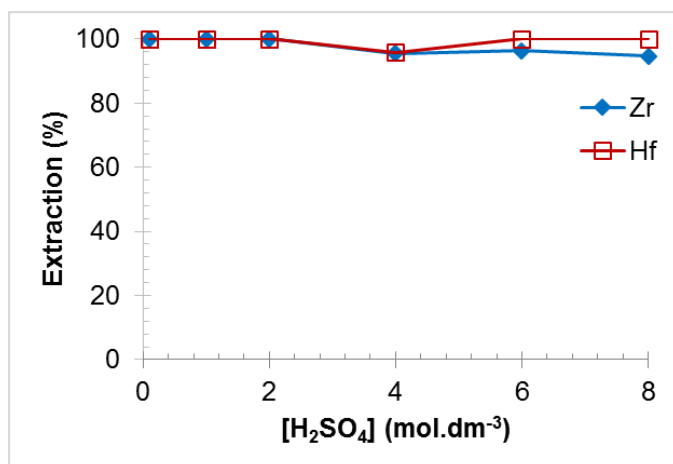


Figure A3 - 8: Effect of H_2SO_4 concentration with binary metal complex extraction using lonquest 801. Conditions: 10 wt% lonquest 801, 97 mg.L⁻¹ Zr, 3 mg.L⁻¹ Hf, A/O = 1, equilibrium time = 60 minutes.

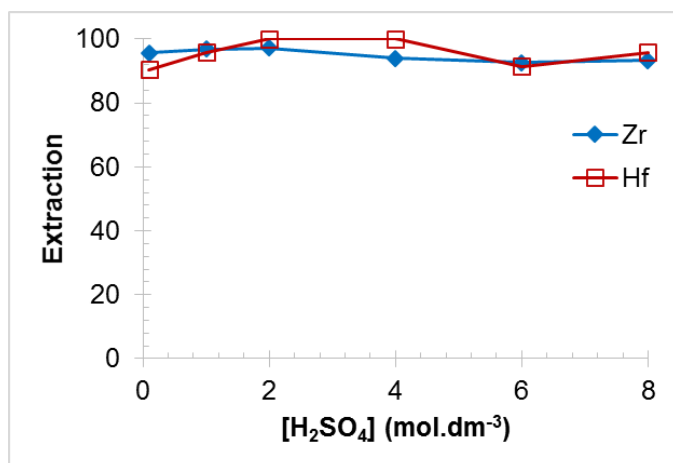


Figure A3 - 9: Effect of H_2SO_4 concentration with binary metal complex extraction using Dio-PA. Conditions: 10 wt% Dio-PA, 97 mg.L⁻¹ Zr, 3 mg.L⁻¹ Hf, A/O = 1, equilibrium time = 60 minutes.

Single metal complex results in HCl with lonquest 801 and Dio-PA

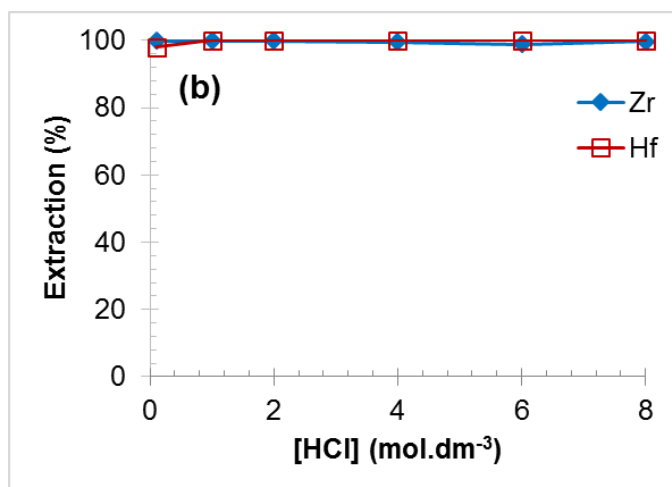


Figure A3 - 10: Effect of HCl concentration with binary metal complex extraction using lonquest 801. Conditions: 10 wt% lonquest 801, 97 mg.L⁻¹ Zr, 3 mg.L⁻¹ Hf, A/O = 1, equilibrium time = 60 minutes.

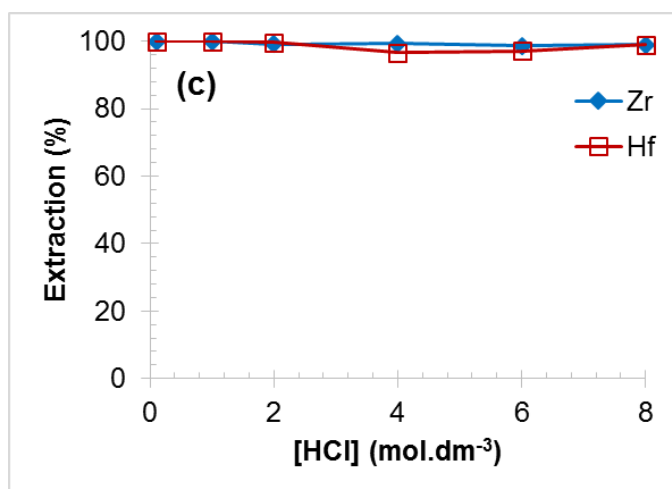


Figure A3 - 11: Effect of H₂SO₄ concentration with binary metal complex extraction using Dio-PA. Conditions: 10 wt% Dio-PA, 97 mg.L⁻¹ Zr, 3 mg.L⁻¹ Hf, A/O = 1, equilibrium time = 60 minutes.

E/M_{Zr+Hf} ratio in H₂SO₄ and HCl with lonquest 801

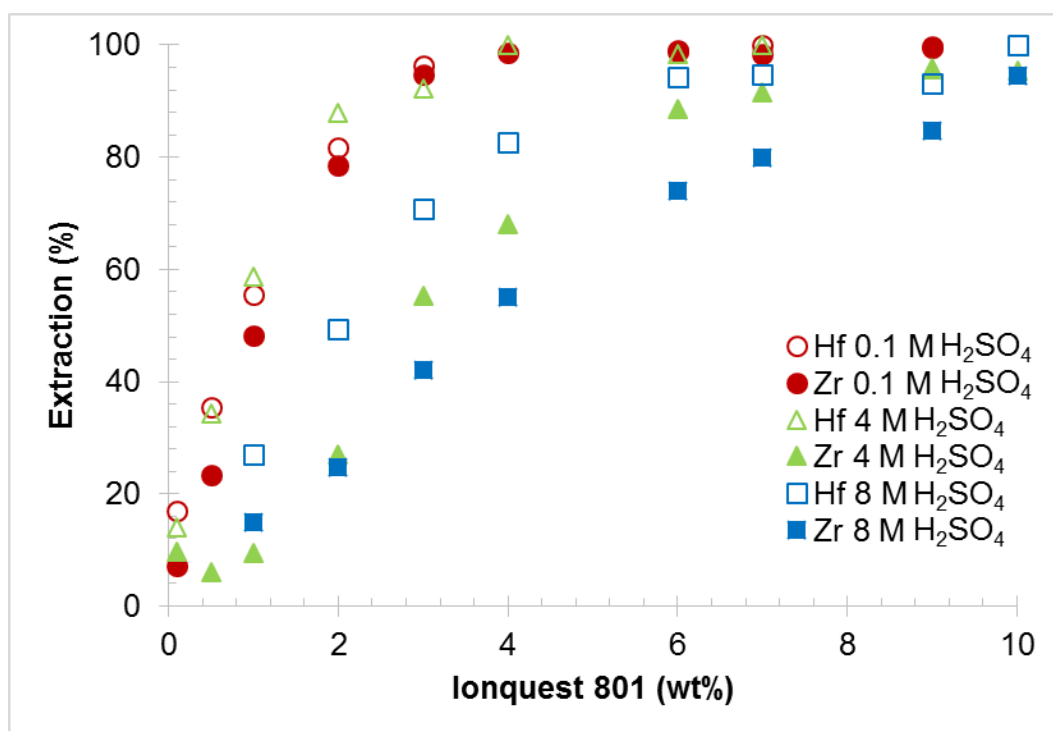


Figure A3 - 12: Effect of extractant concentration changes with binary metal complex in H₂SO₄ using lonquest 801. Conditions: 0.001 - 10 wt% lonquest 801, [Acid] = 0.01, 0.1 and 0.5 mol.dm⁻³, 97 mg.L⁻¹ Zr, 3 mg.L⁻¹ Hf, A/O = 1, equilibrium time = 60 minutes.

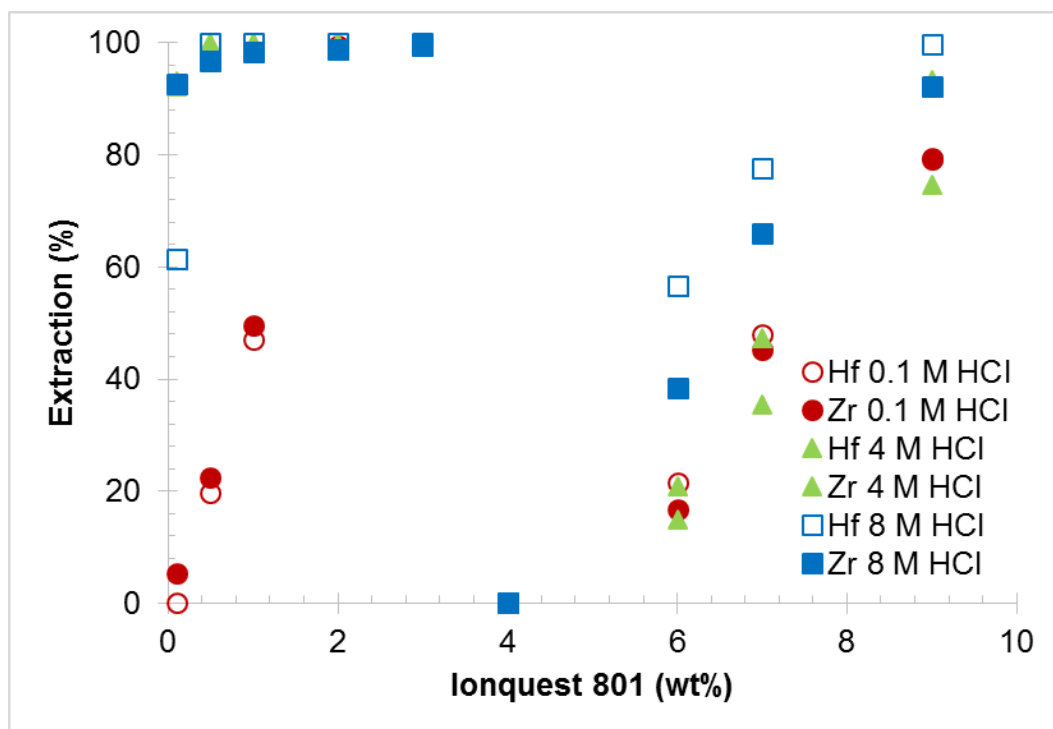


Figure A3 - 13: Effect of extractant concentration changes with binary metal complex in HCl using lonquest 801. Conditions: 0.001 - 10 wt% lonquest 801, $[Acid] = 0.01$, 0.1 and 0.5 mol.dm⁻³, 97 mg.L⁻¹ Zr, 3 mg.L⁻¹ Hf, A/O = 1, equilibrium time = 60 minutes.

E/M_{Zr+Hf} ratio in HCl with Dio-PA

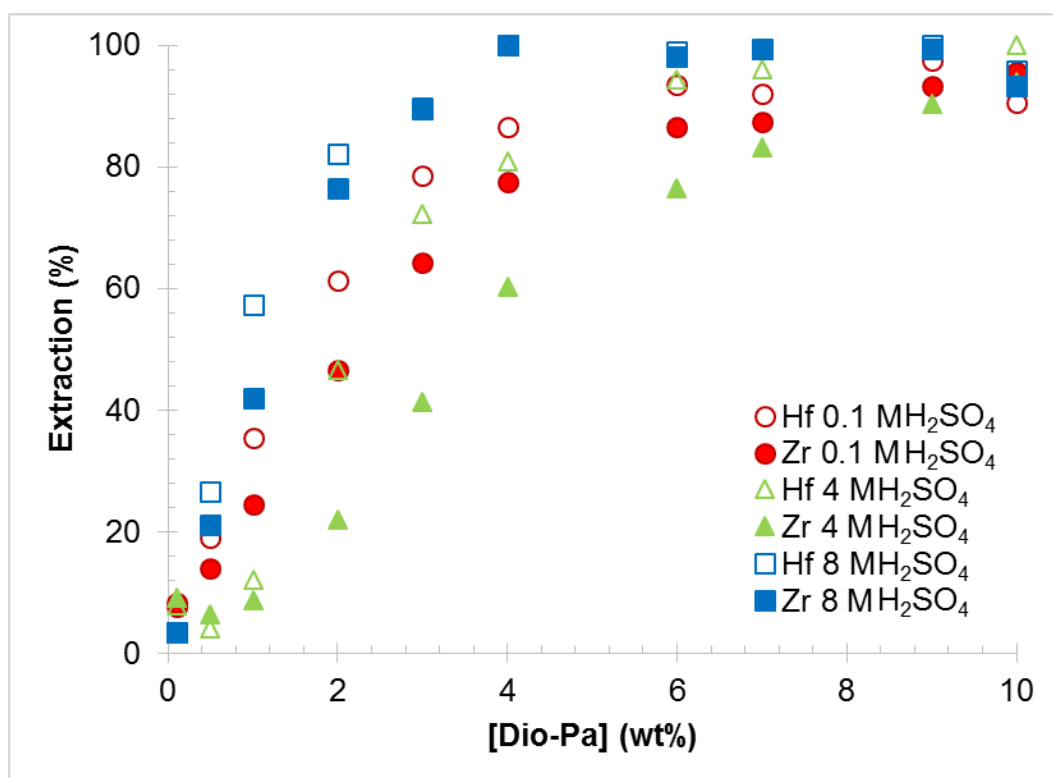


Figure A3 - 14: Effect of extractant concentration changes with binary metal complex in H₂SO₄ using Dio-PA. Conditions: 0.001 - 10 wt% Dio-PA, [Acid] = 0.01, 0.1 and 0.5 mol.dm⁻³, 97 mg.L⁻¹ Zr, 3 mg.L⁻¹ Hf, A/O = 1, equilibrium time = 60 minutes.

Effect of ageing on the feed solution

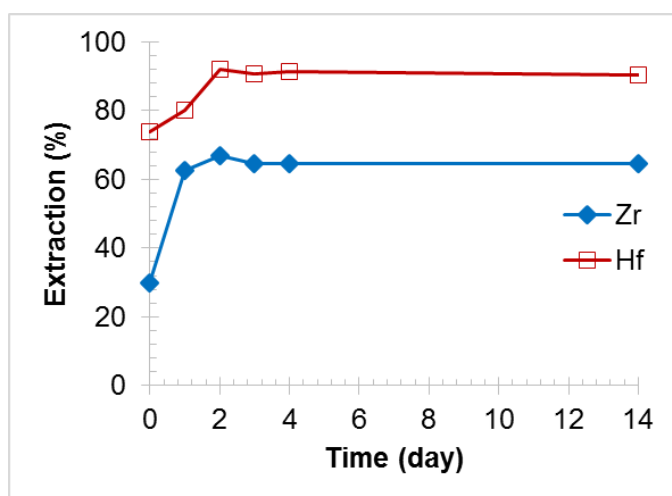


Figure A3 - 15: Effect of ageing of feed solution while extracting with 9 wt% D2EHPA in 4 mol.dm⁻³ H₂SO₄. Conditions: ageing time 0 – 14 days, 97 mg.L⁻¹ Zr, 3 mg.L⁻¹ Hf, A/O = 1, equilibrium time = 60 minutes.