EXTRACTION AND SEPARATION OF ZIRCONIUM AND HAFNIUM USING OCTANOL

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Declaration

I hereby declare that the matter embodied in the thesis entitled **"Extraction and separation of zirconium and hafnium using octanol"** is the result of the investigations carried out by me in the Fluorine and Process Integration Group of the University of Pretoria under the supervision of Prof. Philip Crouse and co-supervisor Dr Salmon Lubbe, and that the same has not been submitted elsewhere for any other degree.

Signature………………………………………………………………………………..

Date…………………………………………………………………………………..

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Synopsis

Zirconium (Zr) and hafnium (Hf) metals have drawn considerable attention due to their various applications, especially in the nuclear industry where zirconium is used as a cladding material for nuclear reactors due its low neutron-capture cross-section and strong resistance to corrosion, whereas hafnium is used as an excellent control rod material for reactors due to its high neutron-absorption capacity. The efficiency of the reactor depends directly on the concentration of hafnium in zirconium. The zirconium should contain a very low concentration of hafnium, not exceeding 100 ppm, for use in the nuclear industry.

Due to the fact that zirconium and hafnium occur within the same mineral, there is great interest in separating them in order to produce zirconium and hafnium oxide which can be used in the production of zirconium and hafnium metals appropriate for use in the nuclear industry. Hence, the separation and purification of these elements is of great importance. Solvent extraction techniques are employed to separate and purify these elements on an industrial scale. However, the separation of zirconium and hafnium is a difficult task as both elements exhibit similar chemical and physical properties.

The main objective of this investigation was therefore to evaluate the potential of octanol as an alternative extractant to the conventional extractants methyl isobutyl ketone (MIBK) and tributyl phosphate (TBP) due to the problems associated with the latter two extractants.

The effect of the different parameters affecting the extraction and separation of these two elements (Zr and Hf) were studied in terms of the initial feed concentration, contact time, extractants, loading capacity, temperature, diluents and stripping agents.

It was determined from the results obtained that the different parameters investigated all have important effects on the extraction and separation of zirconium from hafnium. The results indicate that zirconium ions were preferentially extracted over hafnium with undiluted 1-octanol and 2-octanol in 10 % hydrochloric acid and 1.5 M potassium fluoride as feed concentration at a ratio of 1:2. The McCabe-Thiele diagram indicates that four equilibrium stages are required for almost complete extraction of zirconium from the aqueous solution. Sulfuric acid was found to be the most desirable agent for stripping zirconium from the loaded organic solution.

A mixture of oxalic acid and nitric acid was considered to be a good stripping agent for hafnium as it could lead to good separation of hafnium from the remaining zirconium.

Zirconium and hafnium were neutralized using 25 % ammonium hydroxide solution. After filtration and calcination, the products obtained were characterised using XRD and SEM-EDS analysis.

A packed column was also used to compare the effectiveness of the extraction and separation of zirconium from hafnium. It was observed that in order to achieve the optimum mass transfer, greater column height is required.

Acknowledgements

Research outputs emanating from this thesis

Kabangu, M.J., Lubbe, S.J., Postma, C.J. and Crouse, P.L. 2017. *Selective extraction of zirconium and hafnium with 1-octanol in a HCl/KF system.* Paper presented at the Conference of the Precious Metals Development Network (PMDN), 17–19 October 2017, Protea Hotel Ranch Resort, Polokwane, South Africa.

Kabangu, M.J., Lubbe, S.J., and Crouse, P.L., 2019, Separation of zirconium and hafnium by extraction with 2-octanol., *Journal of chemical Engineering Transactions,* 75, 631–636 DOI:10.3303/CET1975106.

Kabangu, M.J, Lubbe S.J., and Crouse, P.L., 2019, Solvent extraction studies of zirconium and hafnium with 1- and 2-octanol: a Comparative study. *Journal of Chemical Engineering Transactions*, 75, 607 – 612 DOI:10.3303/CET1975102.

M.J. Kabangu, M.J., S.J. Lubbe., and P.L. Crouse. 2019. Extraction and separation of zirconium using 1-octanol. *Journal of Mining, Metallurgy and Exploration. https://doi.org/10.1007/s42461-019-0089-z.*

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List of abbreviations

CEZUS	Compagnie Europeenne du Zirconium
D2EHPA	Di-2 ethylhexylphosphic acid
DIBK	Diisobutyl ketone
EDS	Energy dispersive spectroscopy
HETS	The height equivalent to a theoretical number of stages in an extraction column
HFSE	High field strength element
HSAB	Hard Soft Acid Base
ICP-OES	Inductively coupled plasma optical emission spectroscopy
MIBK	Methyl isobutyl ketone
SEM	Scanning electron microscope
TBP	Tributyl phosphate
TBBP	Tributyl butylphosphonate
TEHA	Tri 2-ethylhexyl amine
TOPO	Trioctylphosphine
XRD	X-ray diffractometry

List of symbols

A/O	Aqueous to organic phase ratio
D	Distribution coefficient
d_{32}	The Mean drop size
E	Extraction percentage

K_d	Mass transfer coefficient
K_{oc}	Mass transfer coefficient for the continuous phase
β	Separation factor
V_{aq}	Volume of the aqueous phase
V_{org}	Volume of the organic phase
V_c	Volume of the continuous phase
V_d	Volume of the dispersed phase
φ	Hold up
Sh_{oc}	Sherwood number
Sc_C	Schmidt number
Re	Reynolds number
ε	Packing porosity
Q_c and Q_d	Continuous and dispersed phase volumetric flow rate
μ	Viscosity
ϱ	Density
υ	Velocity
n_s	Theoretical number of stages
x_f	Concentration of solute in the feed,
x_n	Concentration of solute in the raffinate,
y_s	Concentration of solute in the solvent,
$S\%$	Stripping percentage

Chapter 1: INTRODUCTION

1.1 Background

The predominant commercial source of zircon is beach deposits which are recovered from heavy-mineral-bearing sand. These deposits are found in Australia, Brazil, South Africa, Ceylon, India, Madagascar, the USA and Egypt (Saberyan et al, 2010). Australia is the major world producer and exporter of zircon sand (Hoddinott, 1995), followed by South Africa (Tyler et al, 2004). Zirconium metal production is based almost exclusively on the treatment of two ore minerals. Zirconium silicate (zircon, $ZrSiO_4$), which generally contains 49 % zirconium and 0.4 - 1.5 % hafnium, is the principal industrial mineral. Baddeleyite (ZrO_2), an impure zirconium oxide, is commercially important but less abundant, and contains as much as 75 % zirconium and 0.4 - 1.7 % hafnium (Suriyachat, 1992). Zirconium has many industrial applications, e.g. as ceramics, enamels, refractory materials, glazes, foundry moulds abrasive grits, dye pigments, and catalysts in organic reactions (Rejmane et al, 2006). The major use of zirconium metal is in the nuclear industry, as a structural material for reactors, due to its excellent corrosion resistance, high melting point, and low neutron-capture cross-section (De Beer et al, 2016). It is also used extensively for fuel rods in nuclear reactors. On the other hand, hafnium has a high neutron-capture cross-section and is used as a control material in water-cooled nuclear reactors and rectifiers (Nayl et al, 2009). The efficiency of the reactor core and the generation of power depend directly on the concentration of hafnium in the zirconium. For use in nuclear reactors, zirconium should have a very low hafnium concentration – less than 100 ppm. The separation of hafnium from zirconium is thus extremely important in nuclear science and technology (Banda et al, 2013).

Different methods have been used to separate hafnium from zirconium. These include fractional crystallisation, fractional precipitation, ion exchange, solvent extraction, molten salt distillation, and selective reduction. However, only two methods, namely solvent extraction and molten salt distillation (the CEZUS process developed by Compagnie Europeenne du Zirconium, Paris, France), have been used industrially. At present solvent extraction is the separation method of choice. Different solvents have been studied as extractants for zirconium and hafnium separation, but only three commercially available extractants are used in the production of nuclear-grade zirconium and hafnium metals, namely methyl-iso-butyl ketone (MIBK), tri-butyl phosphate (TBP) and the high-molecular tertiary alkyl amine. These processes present several technological disadvantages and environmental problems.

In the TBP process, the disadvantages are: low metal concentration in the aqueous and organic phases because of third phase formation; large consumption of chemicals; a low Zr/Hf separation

factor; and the inability to produce high-grade Hf for use as control rods in nuclear reactors (Da Silva & Distin, 1998). For MIBK the disadvantages are as follows: the waste stream contains high concentrations of ammonium cyanides and other organic by-products that lead to environmental concerns; the solvent itself is volatile and is slightly soluble in water, leading to significant losses by evaporation, thus requiring extra care in handling and recycling the organic stream and in discarding the effluent (Synder & Lee, 1990); there is high cost involved due to the consumption of expensive chemicals by decomposition; and the thiocyanates and thiocyanic acid have a low flash point in the presence of HCl (Da Silva & Distin, 1998). In the Toyo zirconium process, many equilibrium stages are required, which is time consuming. The starting complex must be produced prior to the extraction process. Xu et al, 2015) The CEZUS process requires highly corrosion-resistant alloys and sophisticated technologies to pump and handle the vapour streams, and to avoid any contamination by air moisture (Da Silva & Distin, 1998). The disadvantages of these processes could be largely avoided by using more benign extractants for the separation of Zr and Hf.

A large number of researchers have demonstrated that the extraction and separation of Zr and Hf is possible using different extractants. For example, Jaykishon et al (2018) developed a process of extracting Zr(IV) from sulphuric acid medium using tri-n-octyl amine in kerosene. Elizabeth et al. (2019) reported on selective extraction of hafnium from a zirconium(hafnium) heptafluoride ammonium solution using organosphosphorus-based extractant. Yadollahi et al (2018) have reported the use of mixture of cyanex-272 and TBP on the extraction and separation of Zr and Hf from nitric acid. Taghizadeh et al (2009) reported the extraction and separation of Zr and Hf using bis(2, 4, 4-trimethylpentyl) phosphoinic acid (Cyanex 272) as extractant in a nitric acid medium. MacDonald (1980) patented the separation of Zr from Hf by solvent extraction with a tertiary amine from a sulfuric acid solution. The separation factor of this process was improved by the addition of water-soluble α-hydroxycarboxylic acid. Banda et al (2013) developed a process to separate Zr and Hf by solvent extraction with tri(2-ethylhexyl) amine (TEHA). El-Yamani et al (1978) investigated the extraction and separation of Zr and Hf using Primene JMT (a long-chain primary amine) in sulfuric acid. Van der Westhuizen et al (2007) demonstrated that it is possible to extract and separate Zr and Hf using acid-pre-treated Alamine 336 in a hydrochloric medium. Voit (1992) patented on the separation of hafnium-free nuclear-grade Zr from acidic chloride solutions in the presence of thiocyanate using MIBK as an extractant. James & Jeff (2004) provided a method for optimising the separation of Zr from Hf by extraction of a feed mix including $(Zr+Hf)OCl_2$ with a thiocyanate-containing organic phase. Lawrence et al (1993) patented a

process of separating Zr values from Hf values in an aqueous solution of zirconium tetrachloride ($ZrCl_4$) and hafnium tetrachloride contacted with NH_4SCN, feeding the resultant solution into a solvent extraction system containing MIBK. Saberyan et al (2008) conducted a study on a liquid-liquid extraction to separate Hf from Zr, using Cyanex 301 in kerosene. Ling & Man (2016) developed a separation process for the selective extraction of Hf (IV) over Zr (IV) from moderate sulfuric acid solutions using di-2ethylhexylphosphic acid (D2EHPA). De Beer, Van der Westhuizen & Krieg (2016) investigated the possibility of selective extraction and separation of Hf over Zr using Lonquest 801. Xu et al (2012) developed a process for the separation of Hf from a thiocyanic acid medium using a mixture of diisobutyl ketone (DIBK) and tributyl phosphate (TBP) as the extractant. Ling et al (2013) performed a solvent extraction process of Zr and Hf from hydrochloric acid solution by using acidic organophosphorus extractants and their mixtures with trioctylphosphine (TOPO). Nayl et al (2009) carried out a solvent extraction study to extract and separate Zr and Hf from nitrate mediums using phosphine oxide extractants (Cyanex 921, Cyanex 923 and Cyanex 925) in kerosene. Da Silva et al (2000) demonstrated that Cyanex 925 is an efficient and selective extractant for getting the maximum separation factor of about 37 between Zr and Hf in hydrochloric acid. Poriel et al (2006a) studied the extraction of Zr and Hf from aqueous HCl solutions with Aliquat 336 in organic diluents.

The constraints of the conventional technologies, namely MIBK and TBP, and the Toyo Zirconium processes, (e.g. the often dangerous and unsuitable extractants used) have necessitated the search for new alternative extractants.

As an alternative method for a safer and more effective technology, octanol was used in the present investigation as an extractant based on its main advantages which include low solubility in water, sufficiently low volatility and reduced danger because of the higher flash point (81 ℃). Despite its low extracting ability, octanol has a number of advantages over the conventional extractants, TBP and MIBK, its higher flash point making it safer to use. In addition, octanol has a lower viscosity and is cheaper than TBP and MIBK. Octanol also has a very low solubility in aqueous media and has a particular commercial potential as an alternative extractant for the extraction and separation of Zr and Hf.

The choice of octanol was also based on the similar crystal-chemical properties of Zr, Hf, Ta and Nb, i.e. high charge and ionic radii. The high field strength elements (HFSE: Ti, Zr, Hf, Nb and Ta) are considered to behave as a coherent group of substituents in rock-forming silicates minerals (Sun & McDonough., 1989). The choice of octanol was also based on the previous work by

Kabangu & Crouse, (2012), in which the "Separation of niobium and tantalum from Mozambican tantalite by ammonium bifluoride digestion and octanol solvent extraction" was demonstrated. Despite the fact that Mayorov & Nikolaev (2002) and He et al (1998) demonstrated that the efficiency of extraction and separation of tantalum from niobium with octanol was comparable with MIBK commonly used in the industrial technology of Ta, Nb, Zr and Hf (Babkin et al (1998); Fischer et al (1947) and Hure et al (1956). Octanol has not been used before as an extractant in the separation of Zr from Hf. 1-octanol has only been used as a modifier to eliminate the formation of emulsions by Van der Westhuizen et al (2007) and by El-Yamani et al (1978). The focus of this investigation was on the extraction and separation of zirconium from hafnium, speciation or complexation in relation of the extraction and stripping behaviour was not part of this study. But explanations were given according to the literature and previous study.

1.2 Problem statement

Zirconium and hafnium metals have wide application in the nuclear industry because of their unique thermal neutron-absorption cross-section, mechanical strength and resistance to the corrosion associated with nuclear reactor operation at elevated temperatures. Hafnium has a very high neutron absorption capacity and acts as a control material in water-cooled nuclear reactors and rectifies.

The separation of Zr and Hf is very difficult because of the fact that these two elements are so similar in terms of their chemical and physical properties. Different methods, such as fractional crystallisation, fractional precipitation, ion exchange, solvent extraction, molten salt distillation and selective reduction, have been used to separate Zr from Hf. However, only two methods, namely solvent extraction and molten salt distillation, have been used industrially. Various solvents have been studied as extractants for Zr and Hf separation, but only three have been used commercially in the production of nuclear-grade Zr and Hf metals, namely methyl-isobutyl ketone (MIBK), tributyl phosphate (TBP) and high-molecular tertiary alkyl amine.

At the end of the 1950s, the USA abandoned the TBP process, as did France in the 1970s, because of its inability to produce high-grade Hf (which is used for control rods in nuclear reactors), its low Zr and Hf separation factor, its large consumption of chemicals, and its low metals concentration in the aqueous and organic phases because of the third phase formation. Sophisticated technologies and the energy consumption required for the extractive distillation process led to the search for new Zr and Hf separation process.

Recently, increasing environmental concerns have been raised with regard to the MIBK process due to the solubility of MIBK in water, and the low flash point and decomposition of the thiocyanate in the presence of hydrochloric acid. The Toyo Zirconium process also has a number of disadvantages.

In view of the numerous advantages of solvent extraction, it will nevertheless be the process of choice for this study. A current constraint of this process, i.e. the often dangerous and unsuitable extractants used, has necessitated the search for alternative extractants. Thus, this study will entail the extraction and separation of Hf and Zr by solvent extraction with the purpose of using an alternative extractant to the conventional MIBK and TBP in order to arrive at a more economical and environmentally friendly process.

1.3 Project aim and objectives

The aim is to find an alternative extractant for the extraction and separation of Zr and Hf, compared with conventional extractants such as MIBK, TBP and the high-molecular tertiary alkyl amine. The choice of potassium fluoride (KF) was based on the strong complexes that Zr forms with fluoride, without forming the Zr-oxy type of complexes. It is also known that K_2ZrF_6 or $2KF \cdot ZrF_4$ crystals and can easily be precipitated, but it is not as easy to precipitate Na_2ZrF_6. Preliminary experiments indicated that HCl-KF solutions were viable. The use of KF presents an interesting opportunity for exploiting local resources such as calcium fluoride (CaF_2). The process selected as a result of the research consisted of the following steps which constituted the aims of this research:

(1)   Four different acids, namely sulfuric acid (H_2SO_4), hydrochloric acid (HCl), nitric acid (HNO_3) and hydrofluoric acid (HF), were investigated to determine the most suitable acid for the digestion of the ore and the extraction of zirconium and hafnium.

(2)   The extraction conditions of zirconium and hafnium from the digested mass with an organic solvent such as 1-octanol and 2-octanol were evaluated. In this step the effect of contact time, potassium fluoride (KF) concentration and acid concentration in the feed solution were evaluated. The relative extraction and separation efficiencies of 1-octanol and 2-octanol as solvents were also evaluated.

(3)   Separation of zirconium and hafnium batchwise using shake-out tests was investigated. The distribution and separation coefficients were determined. A McCabe-Thiele diagram for the

extraction of zirconium and hafnium was constructed in order to determine the number of equilibrium stages needed for complete extraction and stripping of both metals.

(4)   Stripping of the zirconium and hafnium from their solvent, and regeneration of the solvent was studied. The effects of different stripping agents were investigated and then a McCabe-Thiele diagram for the stripping of zirconium was constructed.

(5)   Precipitation of zirconium and hafnium using ammonium hydroxide and high-temperature calcination was carried out in order to produce zirconium and hafnium oxide.

(6)   Characterisation of the final product was performed.

(7)   Extraction and separation of zirconium from hafnium was done using a continuous system (i.e. use of a countercurrent column).

1.4 Outlines of the thesis

This thesis is composed of six chapters.

Chapter 1 is the introduction to the study. The project aims and objectives are stated, followed by the problem statement and the outline of the thesis.

Chapter 2 is an overview of the beneficiation processes of zircon for the production of zirconium chemicals, including various uses of zirconium and hafnium, the techniques that have been used to unlock the inert zircon ore, extraction, separation, purification of zirconium from hafnium, and reduction to produce zirconium and hafnium metal. It also includes an explanation of the general chemistry of zirconium and hafnium.

Chapter 3 contains general information about liquid-liquid extraction and its theory. It describes different classes of systems involving compound formation, ion association and solvation. It also describes the different items of equipment used in the solvent extraction process.

Chapter 4 describes the two different experimental methods used for the extraction and separation of Zr from Hf in this study.

Chapter 5 discusses the results obtained after digestion, extraction, separation, stripping, precipitation and characterization of the final product produced.

Chapter 6 presents the conclusions and makes recommendations on possible additional work and plant design.

**Chapter 2: BENEFICIATION OF ZIRCON FOR THE PRODUCTION
OF ZIRCONIUM AND HAFNIUM CHEMICALS**

2.1 Introduction

The major and cheapest source of zirconia is zircon sand. Zircon is a highly refractory mineral on account of its geological stability. Zircon sand generally contains 1 - 3 % of hafnium oxide related to zirconium oxide, sometimes even more. Due to its neutron cross-section, hafnium must be separated from zirconium for nuclear use. The beneficiation of zircon is not easy due to its stability. The ore is cracked with aggressive reagents under high temperature conditions. In recent years numerous zircon beneficiation processing methods have been developed, owing to the different purity levels required and the cost of manufacture. Methods that have been used for the decomposition of zircon include the following: caustic fusion, thermal dissociation, carbothermic reduction, fluorosilicate fusion and chlorination. In the following sections these methods will be discussed in more detail.

2.2 Chlorination processes

2.2.1 Carbide intermediate

The preparation of zirconium chlorides from zircon on an industrial scale include, as an intermediate step, the production of zirconium carbide or carbonitride in a graphite-lined arc at 1800 ℃ (Kroll et al, 1948) according to Equation 2.1.

$$ZrSiO_4 + 4C \rightarrow ZrC + SiO + 3CO \tag{2.1}$$

This reaction involves the liberation of silicon monoxide, which is volatile at high temperatures (Jamrack, 1963). The solid product is chlorinated to form zirconium (hafnium) tetrachloride as shown in reaction 2.2. and can be separated from major impurities (iron and aluminium) by sublimation.

$$ZrC + 2Cl_2 \rightarrow ZrCl_4 + C \tag{2.2}$$

The intermediate step (Equation 2.1) is used to facilitate the removal of silicon compounds and other impurities which are difficult to separate from the volatile chlorides produced in direct chlorination processes. In addition, the subsequent chlorination of the carbide is exothermic at a lower temperature (500 ℃), whereas direct chlorination is endothermic at temperatures between 800 - 1200 ℃. Alternatively, the carbonitride is prepared by introducing air into the arc furnace.

The carbonitride formed contains 82 - 84 wt.% of zirconium, 3 - 5 wt.% carbon and 8 - 10 wt.% nitrogen. It gives a higher exothermic reaction at $500\,℃$ during chlorination (Jamrack, 1963) than the carbide. The advantage of this process is that it is completely dry. However, there is an environment concern related to the production of the airbone silicate produced during the process. (Farnworth, et al, 1980; Nielsen & Chang, 1996; Blumenthal, 1998)

2.2.2 Direct chlorination

Numerous methods have been proposed in the attempt to simplify the above route. In this process chlorine is used as a fluidising gas. Direct chlorination takes place without producing ZrC as an intermediate. This can be achieved by using a mixture of zircon sand, carbon (coke) and chlorine. The reaction takes place at 1100 ℃ and produces zirconium tetrachloride ($ZrCl_4$), silicon tetrachloride ($SiCl_4$) and carbon monoxide as shown in Equation 2.3.

$$ZrSiO_4 + 4C + 4Cl_2 \rightarrow ZrCl_{4(g)} + SiCl_{4(g)} + 4CO_{(g)} \tag{2.3}$$
$$ZrCl_4 + H_2O \rightarrow ZrOCl_2 + 2\,HCl \tag{2.4}$$

$ZrCl_4$, $SiCl_4$ and CO are removed from the reactor as gases. Zirconium chloride evaporates and is subsequently condensed at between 150 and $180\,℃$, and separated from silicon tetrachloride which condenses at a lower temperature of $10\,℃$. Zirconium tetrachloride can be hydrolysed in water to form a saturated solution of zirconium oxychloride ($ZrOCl_2$) as shown in Equation 2.4. This zirconyl chloride can be crystallised by cooling the solution to $20\,℃$. The crystal are separated and dried at $85\,℃$. They can then be calcined at $> 800\,℃$ to zirconia. (Heimann, 2010)

2.3 Fusion processes

2.3.1 Fusion with sodium hydroxide

This is the method most used for the decomposition of zircon. The fusion is conducted at temperatures between $550\,℃$ to $650\,℃$ with an excess of sodium hydroxide. The reaction varies according to the proportions of the reactants and other conditions, but can be represented by the following Equations 2.5 and 2.6:

$$ZrSiO_4 + 4NaOH \rightarrow Na_2 ZrO_3 + Na_2SiO_3 + 2 H_2O \tag{2.5}$$

$$ZrSiO_4 + 6NaOH \rightarrow Na_2 ZrO_3 + Na_4SiO_4 + 3 H_2O \tag{2.6}$$
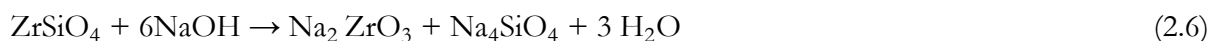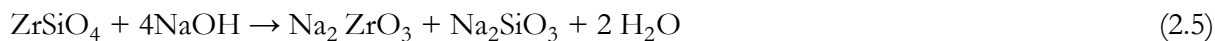
The products formed by fusion are sodium zirconate and sodium silicate or orthosilicate, depending on the mole ratios of the alkali. The frit was then leached with water to remove sodium silicate and excess alkali. Cox et al (1958) examined the problem of silica removal in more detail and devised the flow-sheet shown in Figure 2-1. The insoluble residue contains most of the zirconium in the form of sodium zirconate, water-insoluble silicate and hydroxides as the most common impurities. The washed frit was dissolved in sulfuric acid, the solution filtered, and the zirconium hydroxide precipitated using ammonia. The hydroxide was partially dried and shattered into sand-like grains when water was added, allowing the material to be washed free of silica quite readily. Zirconium nitrate feed material for solvent extraction was prepared by adding nitric acid to the washed hydroxide.
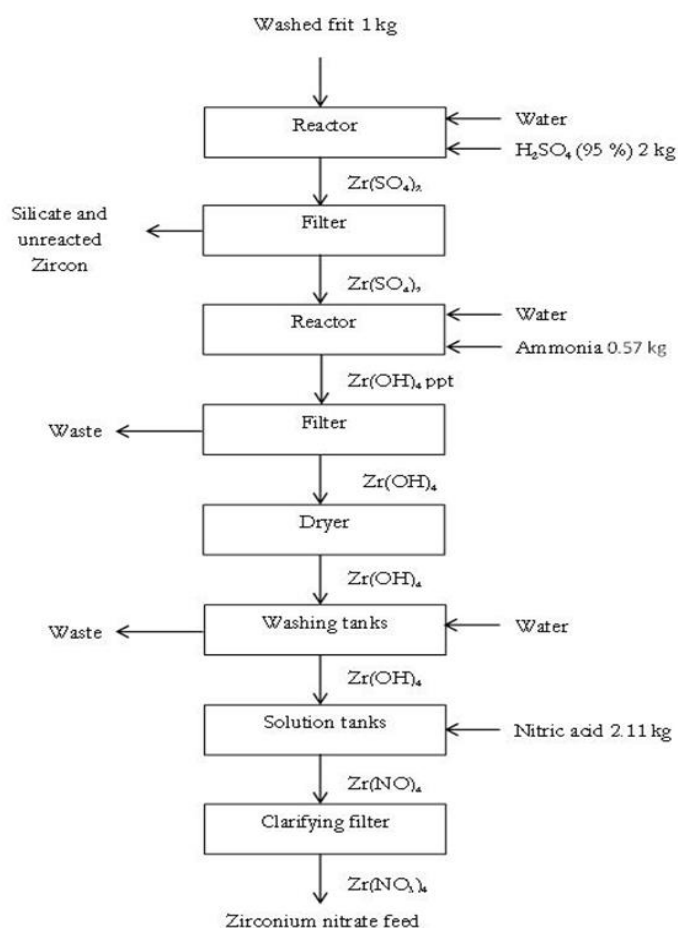
Figure 2-1: Zirconium nitrate feed preparation from caustic frit (Cox et al, 1958)

Hyung Sup Choi (1965) described the preparation of pure zirconyl compounds suitable for feed to a TBP-nitric acid solvent extraction process from zircon caustic frit. The washed frit was dissolved directly in 70 % nitric acid at 80 °C and acidified gelatine was added to the solution, causing mutual precipitation of gelatine and silica as a flock. This flock was readily filtered and the zirconyl nitrate solution contained less than 50 ppm silicon and 20 ppm iron. The final product contained traces of silica which was thoroughly removed to provide a suitable feed for solvent extraction.

2.3.2 Fusion with sodium carbonate

In contrast to sodium hydroxide fusion, in this process the temperatures must exceed $1000\,°C$ to produce sodium zirconium silicate as reaction product, which is water-insoluble. Therefore, 32 % HCl is used to dissolve the sodium zirconium silicate compound. The following chemical reactions 2.7 and 2.8 are used in this process (Nielsen & Chang, 1996).

$$ZrSiO_4 + Na_2CO_3 \rightarrow Na_2ZrSiO_5 + CO_2 \qquad\qquad (2.7)$$
$$Na_2ZrSiO_5 + 4HCl \rightarrow ZrOCl_2 + 2NaCl + SiO_2 + 2H_2O \qquad\qquad (2.8)$$
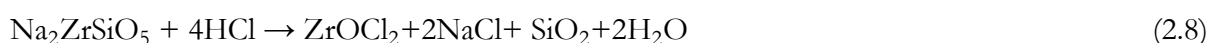
At higher sodium carbonate ratios, sodium zirconate and sodium silicate can also be formed. This can be achieved according to the following chemical reaction 2.9 (Farnworth et al, 1980).

$$Na_2ZrSiO_5 + Na_2CO_3 \rightarrow Na_2 ZrO_3 + Na_2SiO_3 + CO_2 \qquad\qquad (2.9)$$
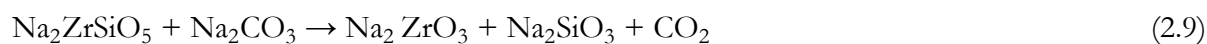
2.3.3 Fusion with calcium oxide and magnesium oxide

In this process, calcium zirconium silicate, calcium zirconate and calcium silicate are formed according to reaction 2.10 and 2.11. A mixture of zirconium dioxide and calcium silicate can be produced. The final product depends on the molar ratio of the reactant and on the temperature of the process (Farnworth et al, 1980; Welham, 2002).

$$ZrSiO_4 + 2CaO \rightarrow Ca_2 ZrSiO_5 \qquad\qquad (2.10)$$
$$ZrSiO_4 + 2CaO \rightarrow Ca_2 SiO_4 + ZrO_2 \qquad\qquad (2.11)$$

In the same way magnesium can replace the calcium and produce magnesium zirconium silicate and magnesium silicate according to reaction 2.12 and 2.13.

$$ZrSiO_4 + 2MgO \rightarrow Mg_2ZrSiO_5 \qquad\qquad (2.12)$$

$$ZrSiO_4 + 2MgO \rightarrow Mg_2SiO_4 + ZrO_2 \qquad\qquad (2.13)$$

Due to the high solubility and negligible rates of hydration and carbonation of magnesium oxide, make it the most preferable "fondant" for the reaction using alkaline earth oxides (Welham, 2002).

2.3.4 Fusion with potassium fluorosilicate

A mixture of zircon and potassium hexafluorosilicate (K_2SiF_6) was roasted at 700℃ to yield water-soluble potassium hexafluorozirconate and insoluble silica. The product of this reaction was then crushed and the fluoride salt was dissolved with hot water. The saturated hot solution was filtered to remove the insoluble silica and then allowed to cool to crystallise the potassium hexafluorozirconate according the reaction 2.14 (Kwela, 2000).

$$K_2SiF_6 + ZrSiO_4 \xrightarrow{600\text{-}700\ ℃} K_2ZrF_6 + 2SiO_2 \qquad\qquad (2.14)$$

The fused product was milled and leached in 1 % HCl at 85 ℃ for two hours. Potassium hexafluorosilicate is preferred to sodium hexafluorosilicate because of a lower tendency to dissociate and form silicon tetrafluoride by sublimation. Potassium chloride or carbonate can be added to the fusion product to promote completion of the reaction; they also reduce the tendency to dissociation of the potassium compound (Blumenthal, 1998).

2.4 Plasma-dissociated zircon

The thermal dissociation of zircon was conducted in an arc plasma furnace or an advanced electric arc reactor to form zirconium oxide in droplets of liquid silica. The mixture must be quenched rapidly in order to minimize recombination to zircon. This results in the production of zirconium oxide in amorphous silicon dioxide. The amorphous silica can be dissolved in solution of boiling sodium hydroxide (NaOH) to yield a soluble sodium silicate and an insoluble zirconium oxide residue (Blumenthal, 1998; Kwela, 2000).

The insoluble product obtained can be leached with sulfuric acid to produce a soluble zirconium sulfate, and insoluble silica gel. Sodium hydroxide can also be used to leach the solution. In this case, sodium silicate solution and insoluble zirconium oxide are produced (Blumenthal, 1998; Manhique, 2003).

Plasma processing offers several distinct advantages over conventional methods (Ananthapadmanabhan et al, 1993)

- The high temperature and energy density associated with the process makes it possible to promote reactions which are not possible by conventional means. The maximum temperature attainable in conventional furnaces is 3300 K, whereas temperatures of the order of 10000 – 20000 K are achievable in plasma reactors.

- The plasma process is characterised by a high quench rate which prevents recombination and ensures the completion of the desired reaction.

-    Further processing and treatment steps are often simplified.

-    The reaction environment can be controlled, thus ensuring high purity of the products.

2.5 Zirconium-hafnium separation processes

The separation of zirconium and hafnium is not a simple operation. This can be attributed to their close chemical properties, that is reflected by the similar physical properties of the compounds. Although many separation methods have been investigated in the past, only a few have been implemented successfully on industrial scale (Skaggs et al, 1984; Poriel et al, 2006a; Poriel et al, 2006b; Vinarov et al, 1967; Da Silva & Distin, 1998). Separation by solvent extraction using either the methyl isobutyl ketone (MIBK)-thiocyanic-hydrochloric acid (HCl) or the tributyl phosphate (TBP)-nitric acid processes have been applied industrially (Vinarov, 1967; Da Silva & Distin, 1998; Synder & Lee 1990; Hure & Saint-James, 1956; Nandi et al, 1983). The MIBK process was developed by the Oakridge National Laboratory in 1949 and optimised in a pilot plant at the US Bureau of Mines, Albany, Oregon in 1953 where the first commercial operation took place. The TBP process was developed in 1954 by the French Nuclear Agency, CEA, and was subsequently improved at the Iowa State University to use aqueous HNO_3 solution. This modification process provides opportunities to recycle the respective acid solutions (Da Silva & Distin, 1998).

The CEZUS process (Compagnie Europeenne du Zirconium) was developed in 1978 by this French company to eliminate the number of process steps involved in the solubilisation, extraction, precipitation and calcination during the production of ZrO_2 (Banda & Lee, 2014).

Separation by fractional crystallisation has been used industrially in the Russian Federation and in pilot plant operations in India and the U.S.A. In the Russian Federation and India, potassium fluozirconate with hafnate, $K_2Zr(Hf)F_6$, was used as feed material. The process examined in the U.S.A made used of $(NH_4)_2Zr(Hf)F_6$, but an overall flowsheet was not developed (Royston & Alfredson, 1970).

The products after solvent extraction are usually converted into an oxide. The oxide is chlorinated to the tetrachloride for reduction to metal by the Kroll process with magnesium chloride. Where a chloride head-end process is used, it would be advantageous to eliminate this second chlorination step by using a separation process based on chlorides. However, zirconium tetrachloride reacts readily with water to form the oxychloride and consequently separation methods using chlorides must be non-aqueous (Royston & Alfredson 1970).

Three important non-aqueous separation techniques, namely selective partial reduction, distillation and sublimation are reviewed in this thesis. Other techniques such as phase dechlorination, ion exchange and fractional precipitation, which have shown limited development, will not be described (Royston & Alfredson 1970).

2.5.1 Solvent extraction and separation processes

2.5.1.1 MIBK-thiocyanic process

In the chlorination of a mixture of zircon sand and carbon, the silicon dioxide (SiO_2) is sublimed as $SiCl_4$. The resulting $Zr(Hf)Cl_4$ is then processed through a multiple-step chemical process. Firstly, the mixture of zirconium chloride ($ZrCl_4$) and hafnium chloride ($HfCl_4$) is dissolved in an aqueous solution, whereby the tetrachlorides are converted to oxychlorides, $Zr(Hf)OCl_2$. An initial extraction is performed using MIBK for the removal of the ferrous impurities from the oxychloride solution. The purified oxychloride solution is then mixed with NH_4SCN and NH_4OH, which causes the formation of zirconyl thiocyanate ($ZrO(SCN)_2$) and hafnyl thiocyanate ($HfO(SCN)_2$) to form the feed solution. The latter is then contacted in a series of countercurrent

stages with MIBK as the extractant. Thereafter the hafnium complex is preferentially extracted into the organic phase by (MIBK) and removed from the aqueous solution. The aqueous solution enriched with Zr is treated with hydrochloric acid in order to yield an aqueous zirconium oxychloride solution which reacts with sulfuric acid to form the pentazirconyl sulfate. By adjusting the pH of the solution using NH_4OH, pentazirconyl sulfate is precipitated. The product is then either calcined to produce zirconia, or is neutralised with an ammonia solution to form $Zr(OH)_4$, which is filtered, rinsed and calcined to form the oxide (Nielsen & Chang, 2001; Stephens , 1984; Moulin et al, 1984; Da Silva & Distin, 1998).

A second carbochlorination is required in order to obtain a hafnium-free zirconium tetrachloride. Due to the use of many chemical reagents, this chloride requires purification by sublimation in order to purify the zirconium tetrachloride for the Kroll reaction as, shown in Figure 2-2.

This process presents some disadvantages. The waste stream contains a high concentration of ammonium cyanides and other organic by-products that lead to environment concerns. The solvent itself is volatile and slightly soluble in water, leading to significant losses by evaporation. Thus extra care is needed to handle and recycle the organic stream and in discarding the effluent (Snyder & Lee, 1990). The process also involves high cost due to consumption of expensive chemicals by decomposition, and costly equipment maintenance due to the corrosion caused by acids and the organic solvent, and the low flash point of thiocyanates and thiocyanic acid in the presence of HCl (Da Silva & Distin, 1998).

The MIBK process also has some advantages. Since Hf is in effect stripped from the desired component, Zr, efficient separation can be attained which enables the production of both Zr and Hf metal according to the nuclear specifications. MIBK also has a high load capacity and excellent settling characteristics which is advantageous when using a mixer-settler type solvent extraction setup (Da Silva & Distin 1998).

2.5.1.2 The TBP process

In this process, sodium zirconate (Na_2ZrO_3) is used as the feed material. It is obtained from the caustic soda fusion process with zircon sand. It is dissolved in concentrated nitric acid. The product after dissolution is contacted with a 50 % solution of TBP in n-heptane or kerosene as the organic extractant. The zirconium nitrate-TBP complex is preferentially extracted into the

organic (TBP) phase (Poriel et al, 2006a, Besson et al, 1977). Unlike in the MIBK process, the separation of Zr and Hf with TBP is selective for zirconium. Sodium nitrate ($NaNO_3$) is added as a salting agent. Most of the impurities remain in the aqueous phase together with Hf, while Zr is stripped into a suitable aqueous solution. Nitric acid is recycled from both streams by distillation, and the solutions are neutralised to precipitate the metal hydrates. The hydroxides are then calcined to yield the oxide (Stephens, 1984). The obtained separation factor of this process is around 10 (Hure & Saint-James, 1956).

Nevertheless, this process has some technological disadvantages such as the low metal concentration in the aqueous and organic phases because of the formation of a third phase, the large consumption of chemicals, and the inability to produce nuclear-grade Hf (Benedict et al, 1980). In financial terms, the TBP process is twice as expensive than the MIBK process (Da Silva & Distin, 1998).
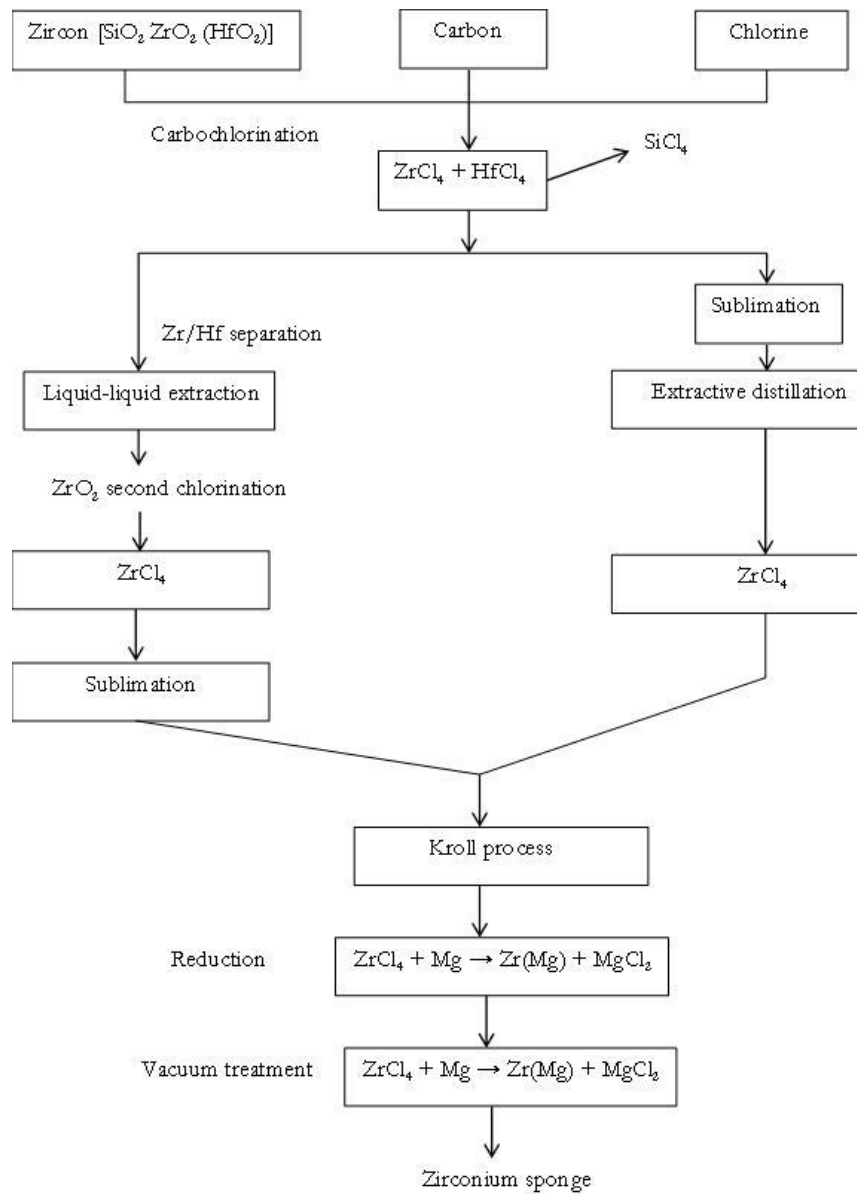
Figure 2-2: Liquid-liquid extraction versus extractive distillation for zirconium sponge production (Moulin et al. 1984)
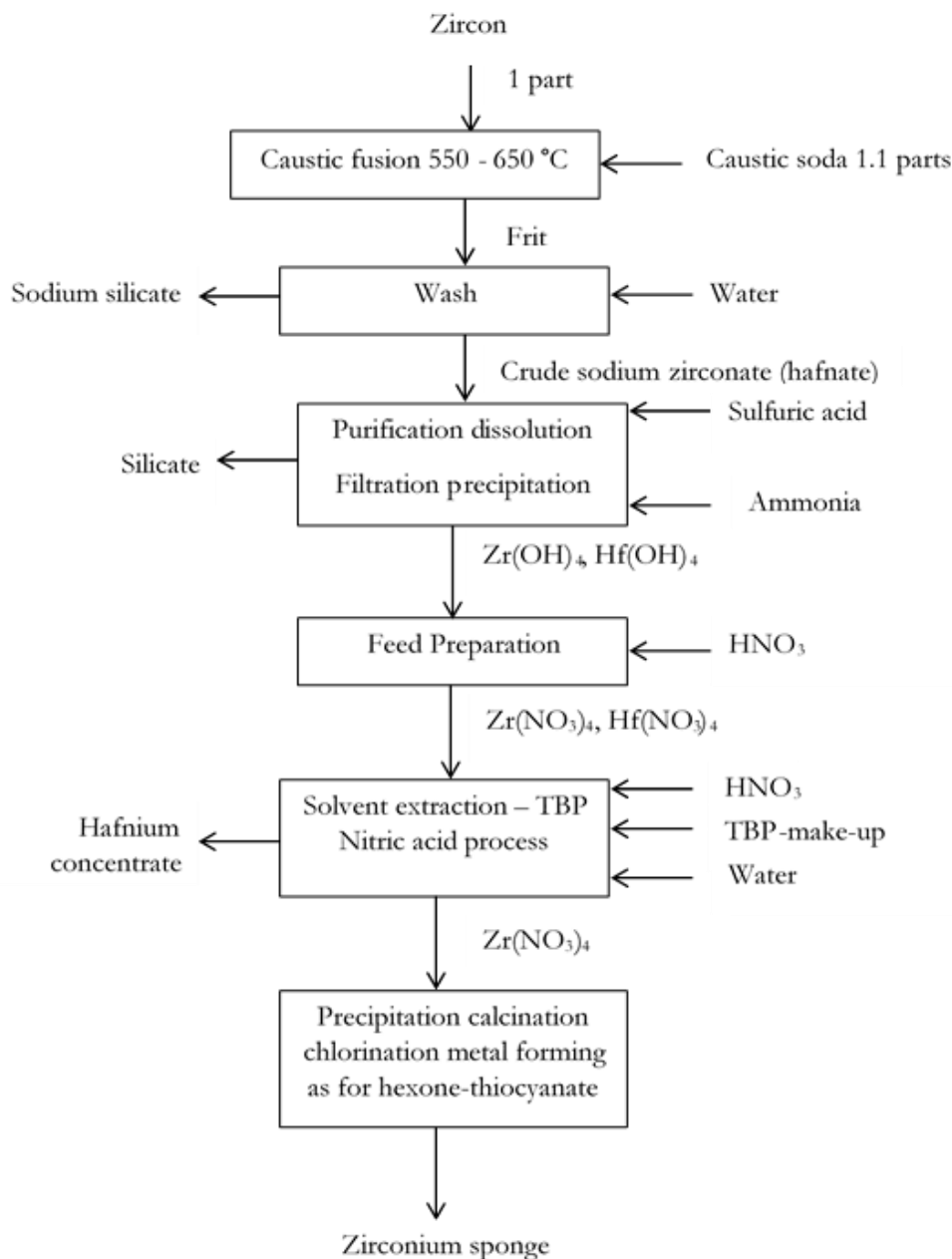
Figure 2-3: Hafnium-free zirconium production, TBP-nitric acid process by (Cox et al, 1958).

2.5.1.3 Toyo zirconium Co, Ltd process

The problems related to the continued use of the MIBK process, especially in Japan, where regulation of environmental pollution is very strict, led to the development of a new process for separating zirconium and hafnium, using solvent extraction with a high-molecular tertiary alkyl

amine. This process is more cost-efficient, less corrossive, and is free from environmental pollution problems. (Moulin et al, 1984)

The feed solution of the process is $H_2Zr(Hf)O(SO_4)_2$ metal complex which is counter-currently contacted with a high-molecular alkyl amine solvent solution. During the extraction, all zirconium and a part of the hafnium are extracted into an organic solvent, as shown by the following chemical reactions 2.15 and 2.16:

$$2R_3NH+ H_2SO_4 \rightleftharpoons 2(R_3NH)HSO_4 \tag{2.15}$$

$$4(R_3NH)HSO_4 + H_2Zr(Hf)O(SO_4)_2 \rightleftharpoons (R_3NH)_4ZrHf(SO_4)_4 + 2H_2SO_4 \tag{2.16}$$
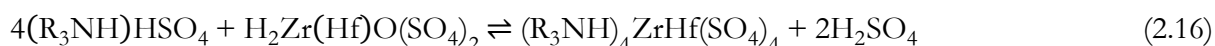
The organic solvent from the scrub operation is stripped with a solution of sodium chloride. Zirconium sulfate in the organic solvent is recovered and concentrated into the aqueous phase according to the following reaction 2.17:

$$(R_3NH)_4Zr(SO_4)_4 + 4NaCl \rightleftharpoons 4(R_3NH)Cl + 2Na_2SO_4 + Zr(SO_4)_2 \tag{2.17}$$
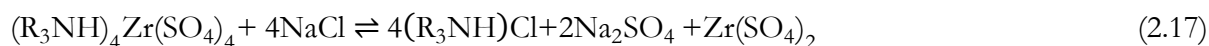
The amine in the organic solution is converted from sulfate to chloride, and then the organic solvent is neutralised with sodium carbonate solution, according to the following reaction 2.18:

$$2R_3NHCl+ Na_2CO_3 \rightarrow 2R_3N + 2NaCl + CO_2 + H_2O \tag{2.18}$$
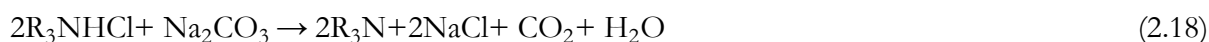
From the above reaction, the amine in the solvent is regenerated from chloride to free amine, and recycled to the extraction operation (Moulin et al, 1984). The improvements of this process, compared to the MIBK process, are the low solubility of the solvent in water, which result in a more environmentally friendly process, and the fact that the extractant can be reused more times compared to the MIBK, leading to a more economical process.

As in most of the cases, this process also has disadvantages: it requires many equilibrium stages which is time consuming; the starting complex has to be produced before extraction; and the stripping operation of the organic solvent to regenerate the extractant requires Hf-free Zr sulfate, which somehow makes the process self-defeating (Xu et al, 2015).

2.5.1.4 The CEZUS process

In 1978 the French state company CEZUS started a process of producing zirconium and hafnium using the Besson process, involving distillation in molten salts (Besson et al, 1977). The process uses pyrometallurgical technology based on extractive distillation with chloroaluminate (mixture of $AlCl_3$ and KCl) as the solvent. The vapours of $Zr(Hf)Cl_4$ rise in a counter-flow against a descending solution of potassium chloroaluminate saturated with $Zr(Hf)Cl_4$ at 350 ℃ (Poriel et al, 2006a, Besson et al, 1977). The rising vapour is steadily enriched with $HfCl_4$ whereby the solvent stream is depleted of the impurity. The Zr(IV)-enriched solvent is stripped with nitrogen, cooled and condensed to produce a solid $ZrCl_4$. The produced $ZrCl_4$ can be used directly in the Kroll process to produce Zr sponge. In this process, a separation factor of approximately two was obtained, which means that about 90 stages are required to achieve the desired separation to produce both zirconium and hafnium according to nuclear specifications. (Monnahela, 2008)

The disadvantages of the process are the requirements for highly corrosion-resistant alloys and for sophisticated technologies to pump and handle the vapour streams while avoiding any moisture contamination (Da Silva & Distin , 1998). The process is slow, discontinuous with low product yield at the end. It also presents some advantages: distillation is performed at atmospheric pressure, which is permitted by the use of the molten salt mixture, as opposed to the high-pressure liquid vapour distillation of $Zr(Hf)Cl_4$, no hazardous organic solvents are used and consequently no by-products are produced and purified $ZrCl_4$ can be produced with improved yield, due to a reduction in the number of stages required (Moulin et al, 1984, Staggs et al, 1984). The cost of the process is reported to be much lower than that of the MIBK route (El-ammouri & Distin, 1996).

2.5.2 Fractional crystallisation

Fractional crystallisation and fractional precipitation techniques were the first methods used to produce small quantities of hafnium-free zirconium. This process was operated for many years on industrial scale (Sajin & Pepelyaeve, 1956). Despite its multi-step character and the simplicity of each individual crystallisation process, it suffers from low process efficiency and need to be operated in batch mode (Vinarov et al, 1967, Li et al, 2011) . The process is based on small differences in the solubility of potassium hexafluorozirconate (K_2ZrF_6) and potassium hexafluorohafnate (K_2HfF_6) in aqueous solutions (Zelikman et al, 1966). In general, the solubility

of hafnium salts is greater and depending on the hafnium-zirconium solubility ratio, and thus the separation will be more successful. Early process studies were based on the crystallisation of ammonium fluorozirconate and fluorohafnate. However the unstable nature of the ammonium salts and the corrosive conditions, which require the use of highly acidic solutions to suppress this decomposition, limited the use of the process. In spite of these problems, potassium fluoro-zirconate gave a higher separation factor with a larger change in solubility between room temperature and 100 ℃ (Royston and Alfredson, 1970).

In general, the problem of handling the numerous liquid and solid fractions generated during fractional crystallisation, has prevented the commercial exploitation of the process (Flengas and Dutrizac, 1977).`

2.5.3 Distillation

Zirconium and hafnium can also be separated by either direct distillation or extractive distillation (Makhofane, 2014). Direct distillation requires a high operating pressure, ranging from 2.5 - 3 MPa to achieve the separation of zirconium tetrachloride and hafnium tetrachloride in the liquid phase (McLaughlin et al, 1989; Niselon et al, 2009), while extractive distillation with a fused salt solvent, is considered as a serious alternative to the solvent extraction route. In this technique, the separation is achieved via sublimation of $Zr(Hf)Cl_4$ from a molten salt solution, which selectively decreases the activity of one of the tetrachlorides and permits separation at ambient pressure and a reasonably lower temperature (Niselon et al, 2009; Tangri et al, 1995).

Due to the optimisation of the tetrachloride distillation conditions and by selecting an appropriate solvent, extractive distillation can be achieved almost at atmospheric pressure, which makes it an industrially viable process compared to the direct distillation method (Niselon et al, 2009; Tangri et al, 1995). Zirconium-rich mixtures can be recovered as either a liquid at the column depending on the solvent used, or as a hafnium-rich mixture the other way round (Delons et al, 2002).

2.5.4 Process production of zirconium metal

The production of pure zirconium metal is not an easy task; it requires the best equipment and skill to ensure that the metal produced is not unduly contaminated. The consumption of zirconium ores for the production of pure zirconium metal represents only about 4 % of the total use of the ores. The USA is the largest producer of zirconium metal, followed by France and the Ukraine.

(Nielsen and Chang, 1996) Two methods of zirconium metal production namely: reduction methods, and electrolytic methods are summarised below.

2.5.4.1 Reduction methods

This method was first used by Lely and Hamburger to produce the first malleable zirconium metal by reduction of the tetrachloride with sodium (Miller, 1957). The commercial zirconium metal is produced in two steps (Itsuno et al, 1988). In the first stage of the process, zirconium tetrachloride is slowly fed into a stirred argon-filled reactor containing sodium chloride. It is then reduced to zirconium dichloride by the sodium. The process is very exothermic. The product formed, which is a mixture of $ZrCl_2$ and NaCl, is then transferred to a second loaded reactor, sealed and heated to 800℃ (Nielsen & Chang, 1996). The $ZrCl_2$ is reduced to zirconium metal with Na and NaCl as impurities according to the following chemical reaction 2.19:

$$ZrCl_2 + 2Na \rightarrow Zr + 2NaCl \tag{2.19}$$

Sodium chloride is removed from the zirconium by leaching the solution with water (Nielsen and Chang, 1996).

2.5.4.2 Electrolytic method

This method has been considered as an alternative to the Kroll process (Nielsen and Chang, 1996; Blumenthal, 1998). Electrolysis of an all-chloride molten-salt synthesis is normally inefficient because of the instability of the lower chlorides in these melts. Adding a small amount of fluoride salts to the melt increases the stability of the zirconium (IV) ions in solution, thereby decreasing the concentration of the lower valence zirconium ions, resulting in a much higher current efficiency yield (Nielsen and Chang, 1996; Blumenthal, 1998; Kyoung et al, 2012). The recovery of zirconium metal by electrolysis of aqueous solutions is not thermodynamically feasible, although efforts have been made in this direction (Nielsen et al, 2001).

Zirconium powder can be fabricated by the reduction of zirconium oxide with calcium (Neikov et al, 2009). The final Zr powder is separated from the CaO by leaching with cold hydrochloric acid. Because of the large surface area involved, the production can ignites spontaneously and is hazardous.

The Zr preparation processes described above require costly equipment and apparatus. These multistage processes occur at elevated temperature (800 ℃ - 1000 ℃) with high energy consumption. For these reasons, their production efficiency is low and cannot provide low-cost Zr sponge (Kyoung et al, 2012).

2.5.5 Kroll process

The main commercial process for producing Zr metal, is the Kroll reduction process (Kroll, 1937; Kroll et al, 1948). Zircon is charged into a chlorinator reactor with carbon and reacted with $Cl_{2(g)}$ at 900 ℃. In this way, zirconium and hafnium tetrachlorides and carbon dioxide are produced. Zirconium tetrachloride vapour is collected in a nickel condenser below 200℃. The zirconium and hafnium are then separated by means of liquid-liquid extraction. For the production of nuclear-grade zirconium, the $ZrCl_4$ is reduced with molten magnesium or sodium in an inert atmosphere, whereby zirconium sponges and $MgCl_2$ are produced as products. There are two routes for removing the $MgCl_2$, namely leaching with water and vacuum distillation. The choice of the method involves a compromise between cost and quality. While vacuum distillation is generally considered expensive, it yields a zirconium metal of a higher quality than leaching. Magnesium chloride and the excess magnesium are separated from zirconium sponge by vacuum distillation at 920 - 980℃. (Manhique, 2003; Kyoung et al, 2012) After cooling and conditioning, the sponge is removed from the reaction chamber using vacuum arc melting and crushed into small pieces (0.5 - 1 cm in diameter) (Kyoung et al, 2012).

The disadvantages of the Kroll process are: the use of $ZrCl_4$ which is a solid at room temperature; batch operating steps, resulting in low efficiency; high energy consumption; and high cost of the product. $MgCl_2$ is electrochemically converted to magnesium metal for recycling. (Jackson and Dring 2006) It also consists of a primary reduction, sponge handling and a purification process that is expensive and complex (Xu el al, 2015).

The advantage of the Kroll process is the removal of oxygen, hence effectively avoiding the presence of oxygen following the metal extraction steps. This is an important measure for product quality control because all group IV metals have a very high affinity for oxygen. However, in the context of the on-going global industrial effort to reduce energy consumption and carbon emissions, the multistep Kroll process is attracting increasing criticism due to its much higher

energy consumption compared to steel production (45 - 55 kWh/kg Ti and 25 - 30 kWh/kg Zr versus ca. 5 kWh/kg for steel). (Junjun et al, 2009)

Zirconium sponge produced by the Kroll process has adequate purity and ductility for most uses. For better understanding of the basic process as originally developed, a flowsheet is shown as Figure 2-4. Various changes to this process have since been made to comply with environmental pollution regulations and pressures, rather than improving the process itself. (Suriyachat, 1992)

For nuclear reactor applications, high purity reactor-grade Zr-metal can be made from any of the three processes, namely (Kapoor & Padmapradu, 2008)

- Magnesium-thermic reduction (Kroll's process) followed by pyro-vacuum distillation
- Molten-salt electrolysis and
- Van Arkel iodide process.
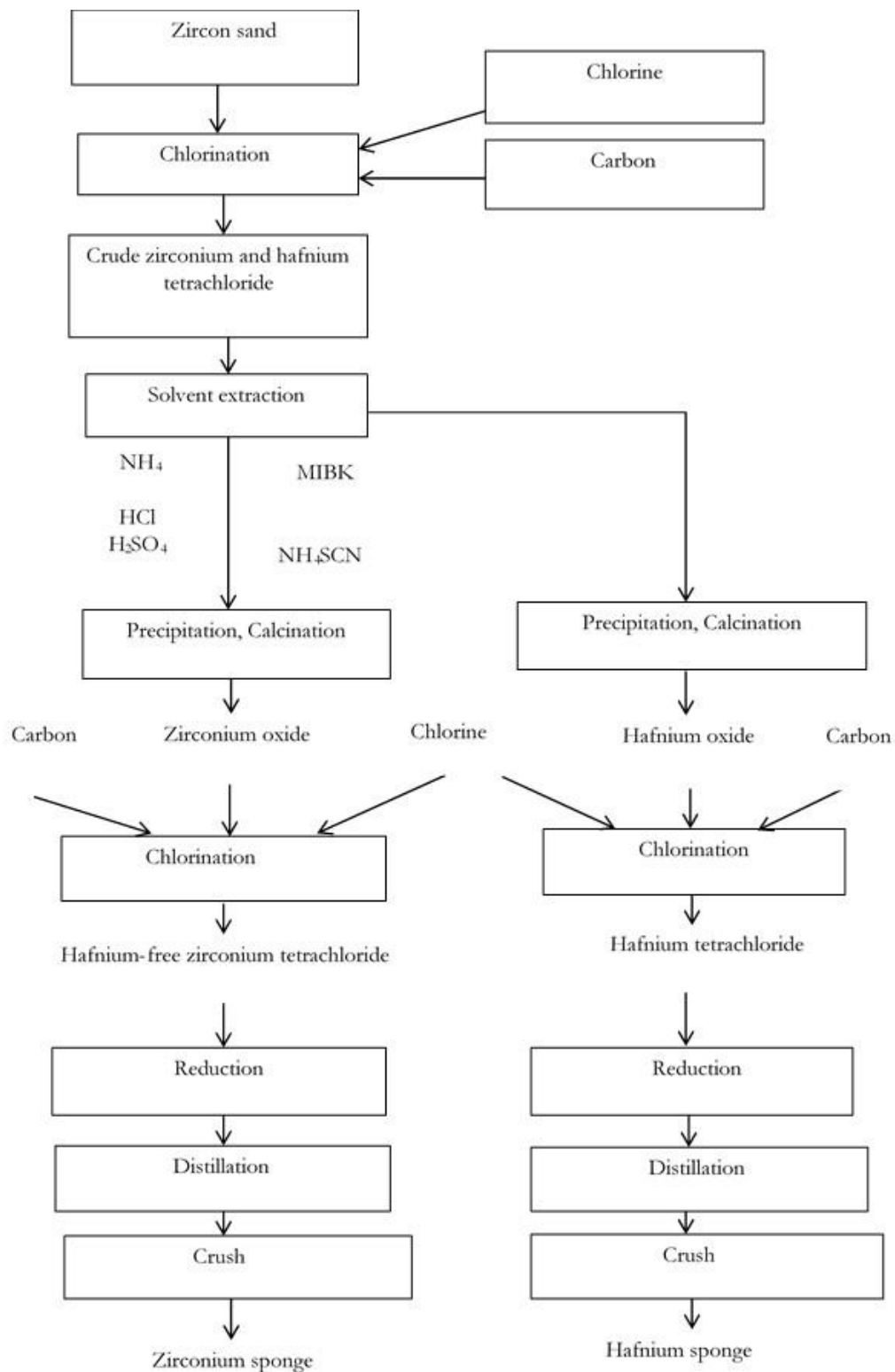
Figure 2-4: Zirconium and hafnium sponge production flowsheet (conventional method) (Suriyachat, 1992)

2.5.6 Magnesium-thermic reduction

The magnesio-thermic reduction occurs according to the following reaction 2.20 (Ganguly, 2002):

$$ZrCl_{4(v)} + 2Mg_{(l)} \rightarrow Zr_{(s)} + 2MgCl_{2(l)} \qquad\qquad (2.20)$$

The reduction is carried out at 899.85 ℃ in a closed retort vessel made of refractory steel. $ZrCl_4$ and Mg are loaded in separate containers inside the retort. The Mg is placed at the bottom of the retort with a slight argon overpressure. The retort is put in a furnace which has two heating zones: a lower heating zone in which magnesium is melted, and an upper zone allowing the progressive sublimation of zirconium tetrachloride. During the process, the chlorides sublime and travel to the bottom of the retort where the reduction reaction takes place with molten Mg, and the formation of globules of zirconium occurs. (Kapoor and Padmapradu, 2009; Vignes, 2011) The zirconium globules fall to the bottom of the retort, dragging liquid magnesium with them. At the end of the operation, all the zirconium tetrachloride will have been converted into zirconium which contains a pseudo-alloy Zr 30 % Mg layer, a layer of $MgCl_2$ and a few residual sub-chlorides (Vignes, 2011). The retort is then opened and the different phases are separated mechanically. Pressure inside the retort which is due to the subliming chloride vapours, is monitored by measuring the back pressure of the argon gas purged into the retort (Kapoor and Padmapradu, 2009). The separation of Zr from Mg is performed by vacuum distillation and Mg is recovered in a condenser and recycled, leaving behind a Zr sponge (Vignes, 2011). Figure 2-5 shows the reduction setup for the production of crude reactor-grade sponge.
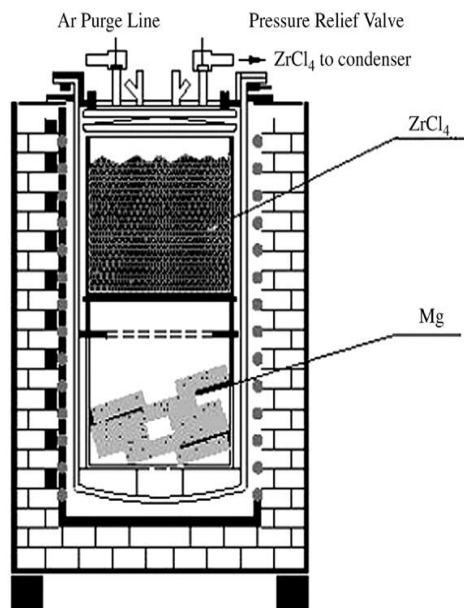
Figure 2-5: Kroll's reduction cell for the production of zirconium (Kapoor and Padmapradu, 2009)

2.5.7 Pyro-vacuum distillation

Pyro-vacuum distillation of the Zr sponge is carried out in a closed retort at 979.85℃ under a very low pressure of less than 13.3 Pa for distillation. The vapour pressures of Mg and $MgCl_2$ at 899.85 ℃ K being 13.3 and 1.1 Pa respectively ensure complete removal during distillation. (Kapoor and Padmapradu, 2009) The vacuum distillation assembly consists of a top retort into which the zirconium mass is loaded, and a bottom retort externally cooled with water to condense Mg and $MgCl_2$ vapours. The vacuum in the retort is generated by a combination of a rotary piston pump and a Roots pump connected in series. The furnace is held under vacuum by means of the rotary piston pump to avoid buckling of the retort. Figure 2-6 shows the distillation setup for the production of reactor-grade Zr sponge. (Kapoor and Padmapradu, 2009)
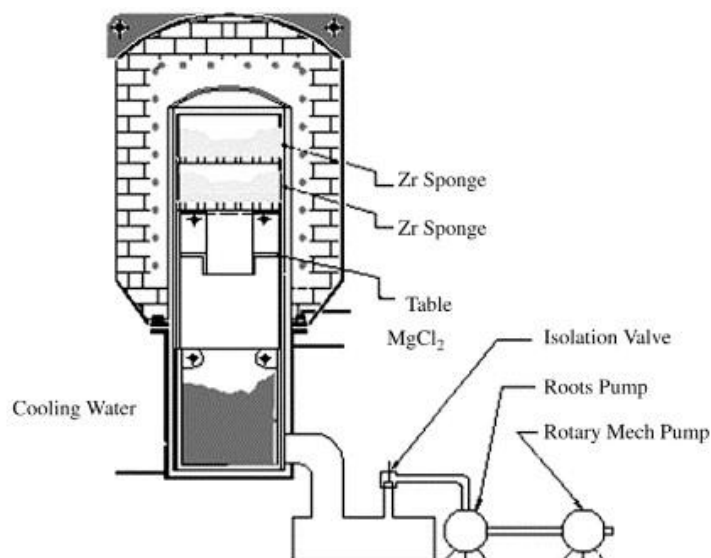
Figure 2-6: Vacuum distillation cell for purification of reduced sponge (Kapoor & Padmapradu, 2009)

2.5.8 Molten salt electrolysis

Molten salts electrolysis has wide application, and the production of metals by molten salt electrolysis has become a large industrial process. Examples of such important processes are the production of aluminium from a fluoride-alumina melt at 960℃, magnesium from a chloride melt at 700 ℃ and sodium from a chloride melt at 750 ℃ (Haarbert and Thonstad, 1989). Smaller quantities of zirconium, titanium, lithium, potassium, rubidium, calcium, beryllium and tantalum are also produced by molten salt electrolysis either directly or indirectly by metallothermic reaction using aluminium, magnesium or sodium as reducing agent. (Haarbert and Thonstad, 1989)

In this process, the electrolysis is performed in a reactor called an electrochemical cell, which enables the electrical energy to do the chemical work i.e. the extraction of elemental metal from one of its compounds. The compound must first be dissolved in a fused-salt solution from which the metal is recovered by the passage of an electrical current.

A prototypical molten salt electrolysis cell is composed of the electrolyte, the electrodes and the container. The electrolytes are multicomponent melts, either chlorides or fluorides. Chlorides offer the advantages of a lower operating temperature and of greater choice of electrode and container materials. With regard to the disadvantages, chlorides react with moisture: some are hygroscopic, even deliquescent, while others decompose by hydrolysis. (Sadoway, 1991)

Fluorides on the other hand, have the advantage of being less reactive with moisture. Additionally, fluorides can dissolve oxide directly. With regard to disadvantage the higher melting point and corrosiveness of fluorides severely limit the choice of materials of construction in the plant. Another disadvantage is the relatively low solubility of refractory metal oxide in molten fluorides. (Sadoway, 1991)

2.5.9 Van Arkel iodide process

This process, also known as the iodide process or the van Arkel de Boer process, was developed by Anton Eduard van Arkel and Jan Hendrik de Boer in 1925. It was the first industrial process used for the production of pure ductile metallic zirconium. In this method crude metal reacts with iodine in an evacuated vessel to form volatile iodides which are decomposed on a heated filament to form a coherent deposit of high-purity metal. The success of this process in producing pure metal from crude metal containing large quantities of oxygen and nitrogen lies in the fact that neither the nitrides nor the oxides are attacked appreciably by iodine under the operating conditions and, hence, oxygen and nitrogen are transferred only to a very limited extent. (Nash et al, 1953)

In the case of zirconium, the zirconium that is to be purified, together with a small amount of iodine or zirconium tetra-iodide, is loaded into a reaction chamber or "de Boer bottle". This bottle contains two sealed-in electrical leads capable of carrying a substantial current, and a long, thin "seed" filament which joins these leads within the bottle. The bottle is then evacuated and heated to a certain temperature to allow the iodine to react with zirconium in order to form the tetra-iodide at an appreciable rate. A current is then passed through the seed filament, sufficient to heat it between 1300 and 1500℃. The volatile zirconium tetra-iodide diffuses to the hot filament, where it is decomposed to metallic zirconium and iodine. The iodine thus liberated, diffuses back to the crude zirconium, reacts with more zirconium to form the tetra iodide, which is in turn decomposed upon the hot filament, and so on. In this manner a heavy rod of ductile zirconium is built up on the seed filament. (Robert and Bernard, 1953)

2.6 Chemistry of zirconium and hafnium

2.6.1 Introduction

The chemistry of zirconium and hafnium has been the subject of numerous investigations since these metals were discovered, but there is still a lack of information about the exact species existing in the aqueous phase. The aqueous chemistry of hafnium has not been as extensively studied as that of zirconium, particularly after 1970. However, the behaviour of these two metals in aqueous solution is very similar. This means that the expected solution chemistry of hafnium must be inferred from known data for zirconium (El-Ammouri, 1994). Knowledge of the state of the ions in aqueous solutions is essential in predicting the relative importance of different complexes of zirconium and hafnium. The traditional belief was that the Zr^{4+} ions do not exist in solution, but rather as the zirconyl ions. Due to the lack of understanding, and the considerable confusion that exists in the literature regarding the ion species present in aqueous solution, the denominations "zirconyl" and "hafnyl" appear to be a suitable way of naming more complex and not completely defined chemical species, as noted by Elison and Pedrov (1969), despite the fact that the existence of zirconyl in solution is without much experimental evidence. Kharitonov and Rozarov (1962) have clearly shown the existence of the $Zr=O$ double bond using infrared adsorption spectra. However, no study has yet demonstrated unequivocally that the zirconyl ion does not exist in any aqueous solution. It is therefore necessary to consider the effect of the zirconyl ion on zirconium aqueous chemistry.

Zirconium and hafnium compounds are characterised by their high degree of hydrolysis, and by their tendency to form various complex ions and polymer compounds (Muha & Vaughan, 1960). The complexity of this behaviour is increased by the fact that in many cases the solutions take a long time to reach a state of equilibrium (Vianna, 1996). Data collected up to now show very similar physical and chemical behaviour of the same compounds of zirconium and hafnium, so the separation of these elements based on properties such as their boiling and melting points is impractical. The differences that could be exploited to separate these elements are differences in equilibrium constant, in the solubilities of hafnium and zirconium compounds in water, in organic solvents, in fused salts or liquid metals, and in the kinetics of the reactions that they take part in. As this question is the central issue in this thesis, the problem of separation was dealt with in detail in Chapter 2 Section 2.5 above.

2.6.2 Hydrolysis and polymerisation

Due to their high charge and small radius, the zirconium and hafnium ions exhibit a marked tendency to hydrolyse in aqueous solution. Using the concept of Hard Soft Acid Base (HSAB) introduced by Pearson (1963), it is possible to understand why zirconium and hafnium have a higher attraction for water than chloride ions, and thus have a high degree of hydrolysis. Based on a variety of chemical information and his collection of experimental data, Pearson (1963) formulated this simple concept to categorise atoms, molecules, ions and free radicals as "hard" or "soft" Lewis acids or bases. The useful rule proposed is that hard acids bind strongly to hard bases, and soft acids bind strongly to soft bases.

According to the proposed rule, zirconium (Zr^{4+}) and hafnium (Hf^{4+}) ions can be classified as hard Lewis acids. This is due to the small ionic radii of zirconium (0.084 nm) and hafnium (0.083 nm) and their high ionic charge (X^{4+}). Water (H_2O) and hydroxyl ions (OH^-) are classified as hard bases, and chloride is classified as between a hard and a soft base. Consequently this explains why zirconium and hafnium have a higher affinity towards water than chloride, and will therefore have a high degree of hydrolysis in aqueous chloride solutions (Derik, 2010).

In order to avoid difficulties arising from hydrolysis, experimental processes are always conducted in a strongly acidic solution and at a low concentration of metal ions. Because of extensive hydrolysis and polymer formation, even in a solution of high acidity, the aqueous chemistry of zirconium and hafnium is extremely complex (Suriyachat, 1992).

Elison and Petrov (1969) stated that an increase in the extent of hydrolysis with time, temperature and metal concentration, is a general rule for zirconium and hafnium aqueous chemistry. The hydrolysis of zirconium and hafnium compounds in solution is directly connected to their capability to form polymeric species such as $[Zr_x(OH)_y]^{4x-y}$ and $[Hf_x(OH)_y]^{4x-y}$, which can modify the reactivity of the elements to the complexing agent.

Zielen and Connick (1956) suggested that Zr^{4+} is not extensively hydrolysed below 0.0001 M in 1 M acid, and concluded that unhydrolysed Zr^{4+} monomers predominate in such a solution. By contrast, Hf^{4+} can be hydrolysed even at a pH below 1, where $Hf(OH)^{3+}$ complexes appear to exist (Cotton and Wilkinson, 1980). However, under the same operational conditions, hafnium has a lower tendency to polymerise than zirconium. According to Peralta Zomora and Martins (1999),

hafnium presents a greater tendency to polymerise in aqueous solutions, forming a polymeric species that hinder its complexation with the organic extractant, favouring the subsequent reaction of the zirconium ion and the complexing agent. Table 2-1 summarises other predicted data on zirconium polymerisation, cited by Elison and Petrov(1969).

2.6.3 Sulfate complexes

Of all acceptors, zirconium and hafnium are complexed more strongly by sulfate ions (SO_4^{2-}) than by chloride ions (Cl^-). In acidic solutions, complexation to form monomers can be represented by the following chemical reaction 2.21

$$Zr^{4+} + nHSO_4^- \rightarrow Zr(SO_4)_n^{(4-2n)-} + nH^+ \tag{2.21}$$

It should be noted that under acidic conditions, HSO_4^- is the reacting species rather than SO_4^{2-}, due to the following reaction 2.22:

$$H^+ + SO_4^{2-} \rightarrow HSO_4^- \tag{2.22}$$

Hydroxyl ions attached to Zr^{4+} as a result of hydrolysis, are readily replaced by SO_4^{2-}, giving a species distribution in which neutral and anionic complexes predominate. It has been proven that it is difficult to determine the equilibrium constant for the formation of different complexes, because the latter takes a long time to achieve. This is because bridges form slowly between hafnium atoms, effectively giving polymeric species.(Mukherji, 1970)

Tribalat and Schriver 1976 determined the equilibrium and it is constant for reaction 2.23

$$ZrOH^{+3} + nHSO_4^- \rightleftharpoons Zr(SO_4)_n^{4-2n} + H_2O + nH^+ \tag{2.23}$$
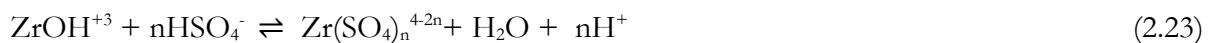
Table 2-1: Ionic state of zirconium in hydrochloric acid

HCl , M	Dominant Zr ion	Reference
0.1	$Zr(OH)_3^-$	Beliyavskaya, 1959
0.5 - 1.5	$Zr(OH)_2^{+2}$	Beliyavskaya, 1959
2	$Zr(OH)^{+3}$	Beliyavskaya, 1959
0.5 - 2	Cations	Lister, 1952
6	Neutral complexes	Lister, 1952
7 - 12	Anions	Krous, 1956

2.6.4 Nitrate complexes

Nitrate ion exhibit less tendencies to form complex ion with zirconium or hafnium than sulphate. The reaction involved in the formation of complex with nitrate ion is expessed as in 2.24. However, they forms stronger complexes with Zr(IV) and Hf(IV) when compared to perchlorate which is quite a weak complexing agent (Ling et al, 2016). Electro migration studies of the ligands, SO_4^{2-}, NO_3^-, Cl^-, and ClO_4^- reveal relative stability constants in the following order: $SO_4^{2-} > NO_3^- > Cl^- > ClO_4^-$ (Elinson and Petrov, 1969).

$$Zr^{4+} + nNO_3^- \rightleftharpoons ZrNO_{3n}^{4-n}. \tag{2.24}$$

2.6.5 Chloride complexes

Chloride complexation of zirconium is based on the following chemical reaction 2.25:

$$Zr^{4+} + nCl^- \rightleftharpoons ZrCl_n^{4-n}. \tag{2.25}$$

Complexation of zirconium and hafnium by the chloride ion is qualitatively similar to the nitrate ion (Ling et al, 2016). The experiment conducted by Prasilova and Havlicek (1970) in order to determine the stability constants of zirconium chloride complexes by an ion exchange method using dinonyl naphthalene sulphonic acid in heptane as liquid and in a solution of 2 M $HClO_4$ at 20 ℃, shows consistent formation of $ZrCl^{3+}$, $ZrCl_2^{2+}$ and $ZrCl_3^{+}$.

2.6.6 Fluoride complexes

The study of fluoride complexes indicates that zirconium forms relatively stable fluoride complexes, with evidence of the species ZrF^{3+} to ZrF_6^{2-}. The studies have used either ammonium perchlorate, sodium perchlorate or perchloric acid as the ionic medium. (Paul, 2005) The step-wise reaction of zirconium with hydrogen fluoride can be represented by the following Equation 2.26:

$$ZrF_{q-1}^{5-q} + HF \rightleftharpoons ZrF_q^{4-q} + H^+ \tag{2.26}$$

2.6.7 Hydroxide complexes

The highly charged Zr^{4+} and Hf^{4+} are strongly hydrated in aqueous solution as a result of the formation of $Zr(OH)_4$ or $Hf(OH)_4$ according to the following general chemical reaction 2.27:

$$mZr^{4+} + qH_2O \rightleftharpoons Zr_m(OH)_q^{4m-q} + qH^+ \tag{2.27}$$

There is an increase in the number of species in the system at the expense of the evolution of free water molecules from the Zr^{4+} or Hf^{4+} hydration shells. The pH range for these complexes is very acidic. The ligation number, as expected for hydroxyl ions, increases with the increase in pH. (Suriyachat, 1992). The complexation of Zr(IV) with OH^- depends on the solution pH, increasing with the increase of pH (Ling et al, 2016).

2.7 Zirconium and hafnium applications

2.7.1 Zirconium

Due to their chemical, physical and nuclear properties which are unique to both zirconium and hafnium, these metals have several applications in modern industry.

Zirconium has a very low corrosion rate in nitric, hydrochloric and sulfuric acids, in dry chlorine, sodium and potassium hydroxide, sea water, halide salts and sodium hypochlorite. The

combination of these factors with its mechanical properties had led to the development of many applications as a construction material in the chemical industry. Some of these applications are (Miller, 1957):

- Zirconium metal plates are employed in pulse columns, operating alternatively with hydrochloric acid and sulfuric acid.
- Zirconium is used in the construction of tanks to treat operational residues like zirconium tetrachloride, which decomposes during processing to hydrochloric acid.
- High speed agitators which operates successfully in zirconium phthalate production.
- One of the main uses of zirconium alloys is in nuclear technology, as cladding of fuel rods in nuclear reactors (Eagleson, 1994).
- Because of zirconium's corrosion resistance, zirconium alloys can be used for body implants (George et al, 2002).

Zirconium metal has been used as a heat shield in a grid-controlled mercury vapour rectifiers, with excellent results. It has also been used in sleeves over filament supports, and various arrangements have been devised for using the metal in close proximity to filaments or cathodes so that it will act as a getter for scavenging oxygen and nitrogen atoms whenever the tube is in operation, regardless of anode load and temperature. (Miller, 1957) Table 2-2 lists the most common zirconium chemical applications.

2.7.2 Hafnium

Hafnium has few commercial uses owing to the difficulty in separating it from zirconium. However, it has become more available as a by-product of reactor-grade zirconium.

Hafnium is used to fabricate control rods which are used in water-cooled nuclear reactors (Nayl et al, 2009). It has an adequate absorption cross section for thermal neutrons, resistance to corrosion, and has excellent mechanical properties. All these have made hafnium a very useful material in nuclear reactors where high cross section and high-temperature corrosion resistance are required.

Table 2-2: Major zirconium application (Charles, sa)

Zirconium Chemicals	Chemical formula	Typical applications
Zirconium oxychloride hexahydrate	$ZrOCl_2 \cdot 8H_2O$	Feed material for catalyst, or other zirconium compounds, like high polymer hardener. Titania coating, antiperspirant, oil field oxidising agent.
Zirconium basic sulfate	$Zr_2SO_4/$ $Zr_5O_7(SO_4)_3 \cdot xH_2O$	Feed material for zirconium compounds, raw material for catalyst. Pigment surface processor. Leather tanning reagent. Titania coating.
Zirconium basic carbonate	$Zr_2CO_3/$ $(ZrO)_2(OH)_yCO_3 \cdot xH_2O$	Feed for other Zr chemicals. Paint driers (siccative). Antiperspirant. Catalyst.
Ammonium zirconium carbonate	$(NH_4)_2ZrO(CO_3)_2$	Paper surface processor, binder, high polymer bridging agent, metal surface processor. Paper coating (insolubiliser). Fungicidal treatment of textiles
Potassium hexafluorozirconate	K_2ZrF_6	Grain refiner - Mg/Al alloys. lame proofing of textiles.
Zirconium acetate	$H_2ZrO_2(C_2H_3O_2)_2$	Manufacture of other Zr chemicals, water repellent in textiles/paper. Catalyst production.
Zr metal	Zr	Chemicals processing plant. Nuclear fuel rod/core components. Explosives. Alloys. Pyrotechnics. Military. Orthopaedics.

Zirconium oxide	ZrO_2	Refractories. Ceramics colour. Abrasives. Electronics. Oxygen sensors. Glass/gemstones. Catalyst. Advanced ceramics.

In point of fact, more hafnium is now used for alloying purposes than in reactor applications (El-Ammouri, 1994). It is largely used as an alloying additive (1 - 2 %) in the production of high temperature nickel-based super-alloys due to its high melting point (2150℃) and is also used in the manufacturing of turbine blades in the combustion zone of jet aircraft engines (Nielsen et al, 2001). Hafnium fluoride glass is used in fibre optics since they provide a high rate of transmission. Hafnium is also used in vacuum tubes as a getter, a material that combines with and removes trace gases from vacuum tubes. (El-Ammouri, 1994)

Hafnium tetrafluoride has been used in the preparation of catalysts that produce high yields of high-molecular mass isostatic polypropylene, known as a metallocene Ziegler-Natta-type catalyst. Hafnium tetrafluoride can also be used in the glass cladding of some heavy metal fluorides. (Nielsen et al, 2001)

Hafnium oxide has been used as a special refractory oxide due to its high refractive index and low absorption. The metal oxide is also suitable to be used as a hard, scratch-free coating for optical elements such as metal mirrors which are used in the near ultraviolet to infrared part of the spectrum. (Malefo, 2016). The major applications of hafnium-containing chemical are summarized in the Table 2-3.

Table 2-3: Major applications of hafnium (Charles, sa)

Hafnium chemicals	Chemicals formula	Typical applications
Hf metal	Hf	Aerospace alloys, nuclear refractories, control rods, cutting tips, sputtering agent, plasma coating
Hf dichloride	$HfCl_2$	Catalyst
Hf dibromide	$HfBr_2$	Special refractories
Hf oxide	HfO_2	Optical coating, electronics
Hf carbide	HfC	Nuclear control rods
Hf nitride	HfN	Cutting tools, coatings

Chapter 3: LIQUID-LIQUID EXTRACTION

3.1 Introduction

Liquid-liquid extraction is an important chemical engineering technique used in many industrial processes such as the petroleum industry, food processing, separation and purification of pharmaceutical and natural products, extraction of metals, and processing of nuclear fuel. Liquid-liquid extraction is based on the principle that a solute can distribute itself in a certain ratio between two immiscible solvents, one of which is usually water (aqueous phase) and the other an organic solvent. The two immiscible liquids are called the feed (F) and the extractant or extraction solvent (S) respectively. The feed solution contains the components that need to be separated, and the extractant is the immiscible solution added to the process in order to extract a solute from the feed. The extraction solvent that leaves the extraction system contains a solute, also called an extract (E) and a raffinate (R), which is left over from the feed from which the solute has been removed. In this operation, the feed and the extractant are brought into contact with each other in order to facilitate the extraction of the solute from the feed, separation of the phases, and finally the removal and recovery of the solvent from each other phase. In certain cases, the solute can be more or less completely transferred into the organic phase. This technique is used for purposes of preparation, purification, enrichment, separation and analysis, or all scales of use, from microanalysis to production processes. (Suriyachat, 1992)

Liquid-liquid extraction is the only method available for the separation of rare earth group elements to obtain the individual metals. This method is very effective for the separation of dissolved compounds and enables the production of high-purity products, in addition to its advantages of being a low cost and simple method. (Agulyansky, 2004)

This process can be made selective for one metal over another, under suitable conditions. The feed solution (aqueous phase) is mixed with a suitable solvent (extractant, diluent and modifier if required), resulting in the extraction of the metal. The co-extracted undesired metal can be removed by scrubbing the solution with water, dilute acid or base. The loaded organic solvent is then contacted with a strip solution to cleave the metal-extractant species, providing an aqueous

solution of the metal. On going from the feed solution to the strip solution, the concentration of the desired metal may be substantially increased. (Clarke, 1991)

An integrated solvent extraction scheme might be expected to operate in a counter current manner (Hughes, 1975), as shown in Figure 3-1. The closed-loop operation produces only the metal of interest, the leached residues and the final aqueous raffinate. The solvent and the strip reagent are recycled, with the acid often being diverted to the acid leaching process. In some systems, the metal may be recovered as the hydroxide precipitate, which may be suitable for recycling through the furnace. (Clarke, 1991)
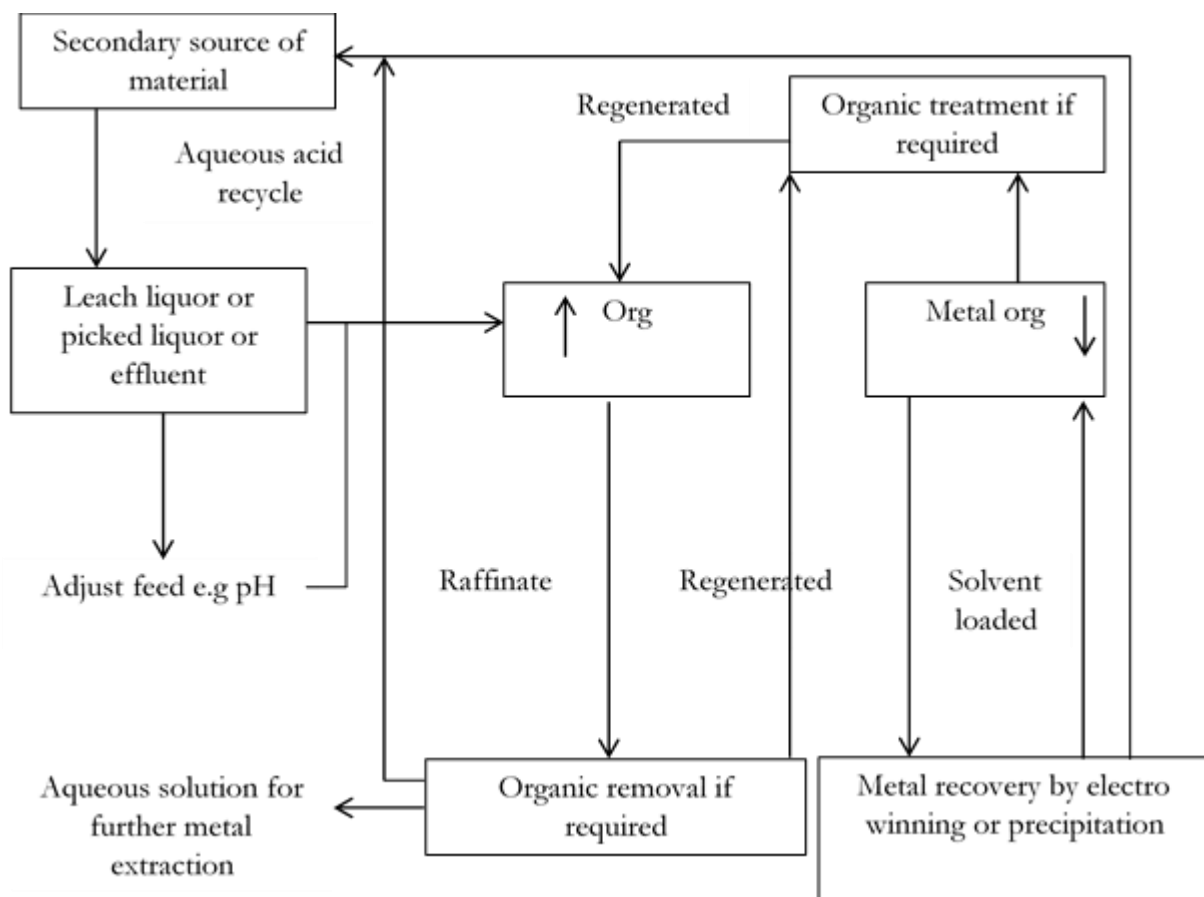
Figure 3-1: An integrated solvent extraction process for the recovery of a metal from secondary source (Hughes, 1975).

In hydrometallurgy systems, chemical interactions are usual in metal extraction and the distribution law is more applicable. The distribution ratio of a metal between an aqueous phase and an organic phase is known as the extraction coefficient, or the distribution coefficient, (D), and is defined as the ratio of the concentration of metal present in the organic phase to that in the aqueous phase at equilibrium see Equation 3.1.

$$D = \frac{\text{concentration of metal in the organic phase}}{\text{concentration of metal in the aqueous phase}} \tag{3.1}$$

This simple formula provides much of the data on which solvent extraction processes are based and is the basic for all solvent extraction studies. Calculation of (D) assumes that equilibrium of the metal ion is obtained. However there are conditions that must be taken into consideration in the use of this approach for the determination of (D) (Fathi, 1999. These conditions are: no volume change occurs on shaking the two phases; no third phase is formed; and so-called crude (an emulsion between the aqueous and organic phases) should not be formed. The presence of crude, or a third phase, in any shake-out will mean that the system is unsuitable for a solvent extraction process (Osman, 2006).

The distribution coefficient is also quoted as a measure of how well-extracted a species is. It is a function of temperature, the concentration of chemical species in the system, the phase ratio (A/O), the pH and a large number of other parameters depending on the system. The higher the value of (D) at equilibrium, the higher is the extractability of the metal ions in question by that particular extractant (Fathi, 1999). The distribution coefficient is related to the percentage extraction, (E), by the Equation 3.2:

$$E = \frac{100\,D}{D + \frac{V_{aq}}{V_{org}}} \tag{3.2}$$

where V_{aq} and V_{org} are the volume of the aqueous and organic phases respectively. The effectiveness of separation is usually expressed by means of the separation factor or separation coefficient (Morrison and Freiser, 1957). The separation factor, (β), is calculated as the ratio between two distribution coefficients. It is a measure of the ability of the system to separate two solutes. It is calculated by means of following formula 3.3:

$$\beta = \frac{D_1}{D_2} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (3.3)$$

The separation factor gives an indication of how selective the extraction is regarding the purification of the desired metal.

3.2 Liquid-liquid system

It is evident that if a metal species is to be transferred from aqueous solution into an organic solution, there must be a chemical interaction between the two solutions. The component in the organic phase which chemically interacts with the metal is called the extractant or reagent. The requirements for a successful extractant in analytical chemistry are much different from the requirements for an extractant to be successful in large-scale metal-recovery operations, especially as they relate to process continuity and economics. In order for an extractant to be commercially successful it must (David, 2017):

- Extract the desired metal(s) selectively from the metal-containing solution
- Be strippable into a solution from which eventual metal recovery can take place
- Be stable to the circuit conditions so that it can be recycled many times
- Be non-flammable, nontoxic, noncarcinogenic, etc
- Be soluble in an inexpensive organic diluent or be able to function as the diluent
- Load and strip metal at a rate fast enough to allow for the use of economical mixing times
- Not promote stable emulsions
- Not transfer deleterious species from strip to extraction
- Have an acceptable cost

In metal extraction systems, the nature of the extractable metal species is of fundamental importance. Based on this fact, Ritcey and Ashbrook (1984) classified extractants into three classes or groups as indicated below:

- Extractant involving compound formation
- Extractant involving ion association
- Extractant involving solvation

The first group consists of acidic extractants that extract metal by either chelating or a cation exchange mechanism, and includes organophosphoric acid derivatives or carboxylic acids or hydroximes (Trevor et al, 2015). In this process the cation may be extracted by exchanging with the H-atom of an OH-group in the extractant, giving a compound whose nature is defined by the particular reagent used (El-Ammouri, 1994). The second group consists of amine extractants, which are either strong (quaternary amines) or weak (secondary and tertiary amines) anion exchangers. The third group includes ethers, esters, ketones, aldehydes and alcohols, together with organophosphoric acid derivatives with oxygen or sulfur as an electron donor atom. The mechanism involves the solvation of neutral inorganic molecules or complexes (Trevor et al, 2015). Cation and anion exchange are based on chemical reaction, while solvation relies on physical interactions between the extractant and metal complexes.

3.2.1 Extractants involving compound formation

The simplest form of the extraction process with an acid extractant is expressed by the following chemical reaction 3.4:

$$M^{n+} + \overline{nHA} \rightleftharpoons \overline{MA_n} + nH^+ \tag{3.4}$$

where M^{n+} refers to the metal cation with positive charge n, HA is the extractant and MA_n is the metal complex of the extractant, and the bars refers to the organic phase (Ritcey and Ashbrook, 1984).

This class of extractant can be divided into two sub-classes, namely chelating extractants and acidic extractants. The former are those that chelate with metal ions, while the latter are those having reactive groups such as –COOH, >P(O)OH and SO_3H. (Ritcey and Ashbrook, 1984)

3.2.1.1 Chelating extractants

Chelating extractants are those which contain at least two donor atoms that are coordinated to the same metal such as nitrogen, sulfur or oxygen as the basic atom capable of forming bidentale complexes (Ritcey, 1973; Roundhill, 2013).

Commercially available chelating extractant are of two types; the 2-hydroxybenzophenone oximes produced by (Henkel Corporation under the name LIX reagents and Shell Ltd under the name

SME) and the 8-hydroxyquinolines produced by Sherex and marketed under the name Kelex. Also, available are the β-diketones LIX 54 and Hostarex DK16. The chemical structural of these are illustrated overleaf. Most of these extractants were developed for the specific extraction of copper from acidic leach liquors and from alkaline solutions (Swanson and Agers, 1964; Ritcey, 1973). LIX and Kelex extractants are able to remove copper selectively from copper-ferric ion solutions due to the slow kinetics of iron extraction (Clarke, 1991).

Dialkyl pyrophosphoric acid
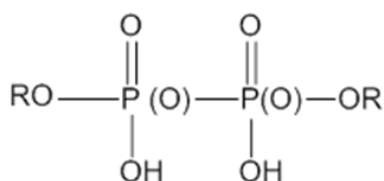
e.g. R = ethyl hexyl, bis-ethyl, hexyl pyrophosphoric acid, (BEHPPA).

LIX 64

Substituted o-hydroxybenzophenone
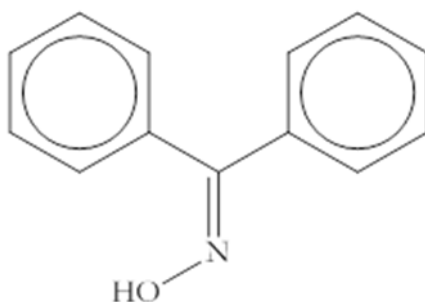
Kelex 100

7-[3-(5,5,7,7-tetramethyl-1-octenyl)]-8-hydroxyquinone
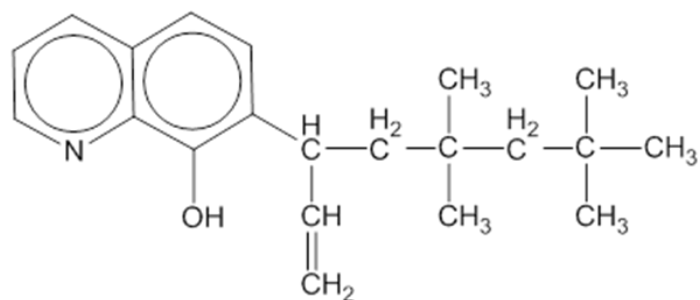
SME 529

2-hydroxy-5-nonyl acetophenone oxime
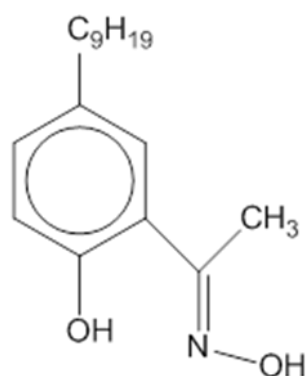
LIX 54
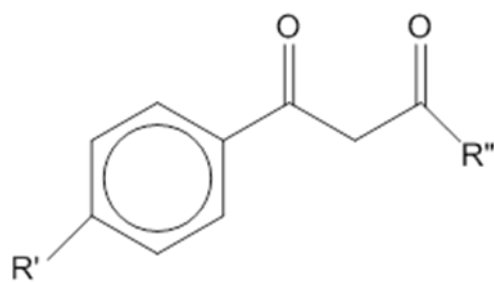
If R = $C_{12}H_{25}$ and R" = CH_3

 Hostarex DK 16
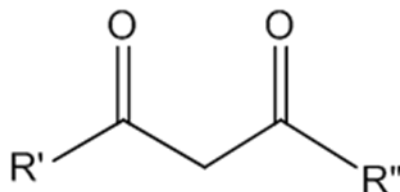
3.2.1.2 Acidic extractants

In a general way the extraction mechanism involving acidic extractants is more complicated to describe than the chelating extractants. The extraction by acidic extractants is similar to that by chelating extractants in that the basic extraction equilibrium is as expressed in Equation 3.4, although extraction is affected more by solvent phase properties than it is with chelating extractants. (Clarke, 1991; Ritcey and Ashbrook, 1984). Acidic extractants are cationic liquid ion exchangers which have ionisable hydrogem atoms that can be replaced by metal ions to generate a neutral species. (Jack et al., 2016). They extract metal ions by a cation exchange mechanism, where the extractant proton is substituted by a metal. Equation 3.4 indicates the extraction of a metal; it describes that the reaction is heavily dependent on the equilibrium pH of the aqueous phase. Thus, as the pH is decreased (and the hydrogen ion concentration increased), metal extraction will decrease since the equilibrium will shift towards the left. Conversely, as the pH is increased, metal extraction will increase. The extraction is also dependent on the stability of the extractable metal complex formed, which is partly a function of the extractant. The metal extractants of acid type that have been found useful in commercial operations are organic derivatives of phosphorus acids and monocarboxylic acids. (Ritcey and Ashbrook, 1984) Organophosphorus acid extractants: this type of extractant includes the following:

   (a) Phosphoric acid
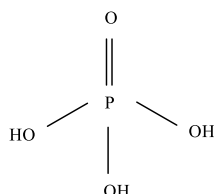
1. Mono-2-ethylhexyl phosphoric acid (M2EHPA)
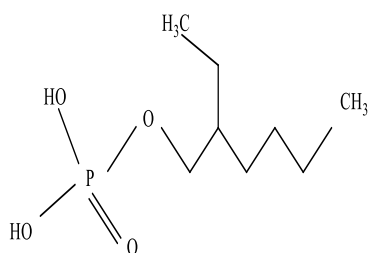
2. Di-ethylhexyl phosphoric acid (DEHPA, D2EHPA, EHPA)
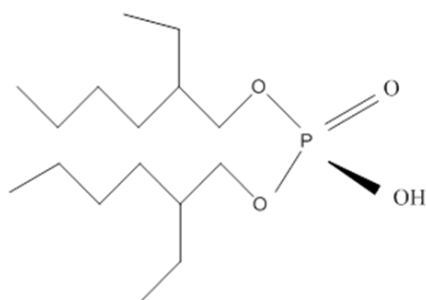
3. Di-p-octylphenyl phosphoric acid (OPPA)
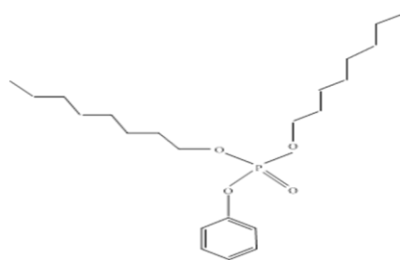
(b) Phosphonic acids
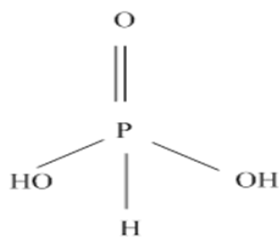
1. 2-Ethylhexyl phosphonic acid or mono-2-ethylhexyl ester
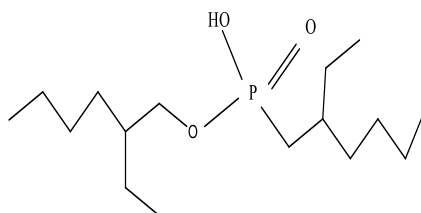
2. Di-2,4,4-trimethylpentyl (Cyanex 272)
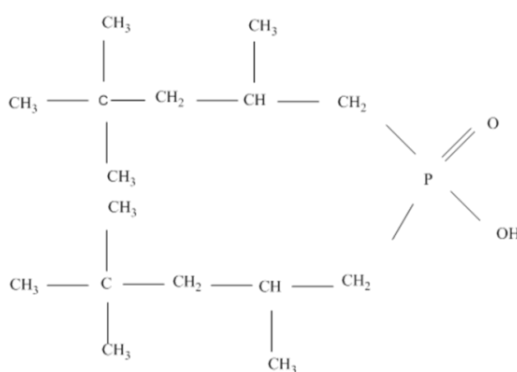
3   Di-2-ethylhexylphosphonic acid (P-229)
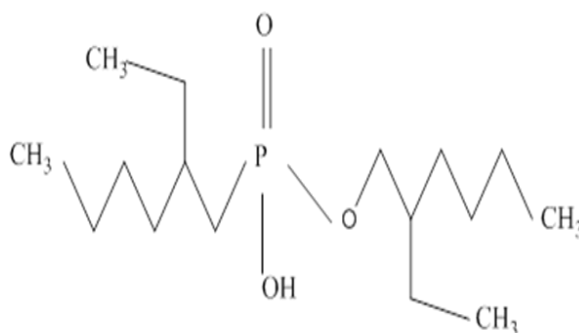
Among these extractants, phosphoric acid have proved to be the most versatile, especially di-2-ethylhexyl phosphoric acid (DEHPA). It has been used in many applications with a broad range of metals, including uranium (Brown and Coleman, 1958), cobalt and nickel (Cook and Szmokaluk, 1971), rare earths (Kolarik and Pankova, 1966) and vanadium (Blake et al, 1955). Among the esters

of phosphonic acid, 2-ethylhexyl phosphonic mono-2-ethylhexyl ester (EHEHPA) has been widely used for the extraction and separation of rare earths, cobalt and nickel (Reddy et al, 1993; Ando et al, 1983). Various dialkyl phosphonic acid extractants, such as bis(2,4,4-trimethylpentyl) acid (Cyanex 272) have been proved to be important for rare earth, cobalt and nickel extraction and separation (Sabbot and Rollat, 1985).

The use of D2EHPA present some advantages in solvent extraction processing such as its chemical stability, generally good kinetics of extraction, good loading and stripping characteristics, low solubility in the aqueous phase and its availability in commercial quantities. It is still being considered as the most versatile of all the extractants commercially available. (Ritcey and Ashbrook, 1984)

Carboxylic acids: Included in this class of acidic extractants are Versatic acid (shell Ltd) and Naphthenic acid which are produced from the distillation of crude oil. Naphthenic acid is the name given to a group of cyclic aliphatic monocarboxylic acids. Versatic acids and naphthenic acids having the general structure shown below are the most common carboxylic acids in use.
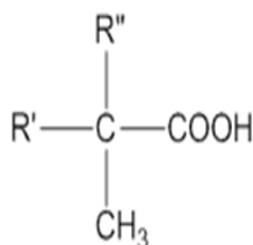
Versatic acid   Naphthenic acid
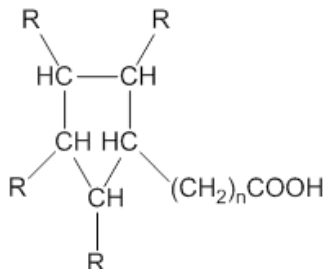
Versatic 911 acid (R_1, $R_2 = C_4 - C_5$)

Versatic 10 acid (R_1, $R_2 = C_6$

The solubility of carboxylic acid extractants in aqueous solution is a function of temperature, pH, and salt concentration. Most of the information on the solubility of these reagents is limited to their solubility in water, and not much practical information is available on actual leach liquors and similar solutions (Rydberg et al, 2004).

Naphthenic acid has been widely used for separating yttrium from lanthanides in China. However, the extractant composition changes with use and its high solubility in water leads to significant

reagent losses. (Li et al, 1994) The carboxylic acids have been used by others in their processes. The Krupp Company has used carboxylic acid at a pH of 6 to extract cobalt and nickel from copper-free ammonium carbonate solution (Jacobs et al, 1984). The carboxylic acid compounds which are usable include perlargonic acid, 2,2-dimethyl propionic acid, caproic acid, butyric acid and 3,5-dinitro benzoic acid.

A carboxylic acid extractant that can be used to great advantage in the process is an organic acid sold under the trade name "Versatile" 911R (Versatile 911R acid is a Shell Chemical Company trademark for a saturated synthetic tertiary monocarboxylic acid having C_9, C_{10} and C_{11} chain length).

3.2.2 Extractants involving ion association

These systems include the extraction of metals with liquid anionic exchangers, also known as basic extractants. Quaternary ammonium compounds with high molecular weight (e.g. Aliquat 336) behave chemically as strong base anion exchangers and require lower concentrations of salting-out reagents. Commercial processes have been developed which use primary (RNH_2) (Spink & Okuhara,1973), secondary (R_2NH) (Bozec et al, 1974), and tertiary (R_3N) (Meyburgh, 1970) amines and quaternary ammonium salts (R_4N^+) (Lewis and House, 1960).

Amine cations are formed with an acid as part of an ion association complex, and are soluble in the organic phase as shown in Equation 3.5.

$$R_3N_{org} + HX_{aq} \leftrightarrow R_3NH^+X^-_{org} \tag{3.5}$$

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

The amine salt is the extracting agent, not the free amine. The solubility of amine salts depends on the chain length and the degree of branching, and can be significant if the molecular weight is below 250. The molecular weight of amines tends to be in the range of 250 - 400 (Clarke, 1991).

The usefulness of amines as extractants depends essentially on the ability of ions to form anionic species in the aqueous phase, these ions are extracted by the amines in an anion exchange process (Ritcey and Ashbrook, 1984). The extraction of M^{n+}, which forms anionic complexes with an anion A^- in the aqueous phase, by amine salt $R_3N \cdot HA$, can be represented as an anion exchange process such as shown in Equation 3.6:

$$MA_m^{-n} + n(R_3N^+ \cdot HA^-) \leftrightarrow (R_3N^+H)n\, MA_m^{-n} \tag{3.6}$$

In order to achieve this exchange, the amine is first converted to the appropriate amine salt to provide an anion to exchange with the metal species Equation 3.7:

$$R_3N + HX \leftrightarrow R_3N^+HX^- \tag{3.7}$$

One of the most important factors influencing the extraction of metals by amines is the aggregation of the amines in the organic phase, which is determined by the nature of the diluent Equation 3.8.

$$R_3N^+HX^- \leftrightarrow (R^3N^+HX^-)_2 \leftrightarrow (R_3N^+HX^-)_n \tag{3.8}$$

Another factor influencing metal extraction by amines is the nature of carbon chain and also the number of carbon atoms in the chain. Primary, secondary, and tertiary amines are all good metal extractants for sulfate systems, while quaternary ammonium characteristically extracts metals only from neutral alkaline solutions. (Ritcey and Ashbrook, 1984)

3.2.3 Extractants involving solvation

Extractants involving solvation constitute another important group of solvent extraction systems which is based on the solvation of neutral inorganic molecules or complexes by extractant containing electron donor (Ritcey and Ashbrook, 1984).

Solvating extractants operate by replacing the solvating water molecules around the aqueous metals complex, making the resulting species lipophilic. (El-Nadi, 2017) There are two main groups of extractants involving solvation: the first group are those containing oxygen bonded to carbon, such as ethers (C-O-C), esters (COOR), alcohols (C-OH) and ketones (C=O). Commercial exploitation has been restricted to alcohols and a ketone, namely methyl isobutyl ketone (MIBK). Alcohols are used mainly for the extraction of phosphoric acid and MIBK is used in the separation of tantalum from niobium and of zirconium from hafnium. The second group is extractants containing oxygen bonded to phosphorus, such as alkyl-phosphate esters (P=O). Examples in this group include: trialkyl phosphate, e.g. tributyl phosphate (TBP); dialkyl alkylphosphonate e.g. Tributyl butylphosphonate (TBBP); alkyl dialkylphosphinates and trialkyl phosphine oxides e.g. tri-n-octylphosphine oxide (TOPO). (Ritcey and Ashbrook, 1984)

The most well known and most used of organophosphorus esters is undoubtedly TBP because of its wide use in the processing of nuclear materials. Examples include: uranium extraction from nitrate-nitric acid systems; separation of zirconium from hafnium and tantalum from niobium; chromic acid recovery; and iron removal from chloride solutions containing cobalt and nickel. TOPO has been used in the recovery of vanadium from phosphate solutions. (Ritcey and Ashbrook, 1979)

The major difference between these two groups of extractants involves the role played by water. The strongly polar organophosphorus compounds compete with water and replace water molecules on the first hydration sphere of metal ions. With ethers and ketone, water is a necessary part of the complex, probably forming bridges between the organic and metal components of the complex through hydrogen bonding. These extractants by virtue of solvation, can extract both acids and metals. (Ritcey and Ashbrook, 1984)

Table 3-1: General structure of esters of organophosphorus acids (Ritcey and Ashbrook, 1979)

Structure	Ester	Examples
RO—P=O with RO, RO substituents	Trialkyl phosphate	Tri-n-butyl phosphate (TBP)
RO—P=O with R, RO substituents	Dialkyl alkylphosphate	Dibutyl butylphosphonate (TBBP)
R—P=O with R, RO substituents	Alkyl dialkylphosphinate	Tri-n-octylphosphine oxide (TOPO)
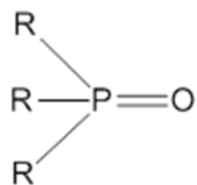
Trialkyl phosphine oxide   Tri-n-octylphosphine   oxide
(TOPO)

3.2.4 Scrubbing

The objective of scrubbing a loaded solvent is to saturate the extract with the desired product, by removing as much as possible of any unwanted co-extracted metal. There are many possible ways of accomplishing this by varying the scrub solution. The scrubbing of unwanted metal may be achieved by water, dilute acid, base, or by an aqueous solution of the salt of the metal of primary interest in the solvent. The scrubbing tests are carried out in the same manner as the stripping process, whereby the loaded solvent is contacted with the scrub solution at an appropriate concentration, pH, phase ratio, contact time and temperature. (Kilambi, 2013) After equilibrium has been reached, the organic and aqueous phase are separated. The solution is then analysed in order to determine whether the unwanted metal, and how much of the desired metal of interest, have been removed. The final product from the scrubbing process can be recycled to the aqueous feed because it may contain a substantial amount of valuable metals. (Rydberg et al, 2004)

3.2.5 Stripping

Stripping of a metal from a loaded solvent is the second most important step after extraction in the solvent extraction process. It is the reverse of the extraction process. (Ritcey and Ashbrook, 1984) It is generally the removal of the extracted solute from the organic phase for further precipitation before the estimation step of the analysis. The solute is usually stripped from the solvent in the extraction process by shaking the solvent with a water-containing acid or base reagent under specific conditions. The loaded solvent is contacted with a suitable strip solution (e.g. base, acid, etc.) at an appropriate phase ratio until equilibrium is attained in order to drive the metal into the aqueous phase. (Robbins, 1999) It is conducted under specific conditions with the aim of producing strip liquor containing a high concentration of the metal value. The extraction of a metal from the loaded feed solution does not mean that it will be easily stripped. For example cobalt (III), although extracted at pH 6, cannot be stripped by even concentrated acids. However,

Co (III) may be removed as the sulphide by sparging the solution with hydrogen sulphide. (Ritcey and Ashbrook, 1979)

Stripping can equally be done in single-stage, cross-flow or counter-current systems. The stripping isotherm may be drawn and a McCabe-Thiele diagram constructed in order to determine the number of theoretical strip stages required. Note that the stripped extract may contain some traces of the desired component. This is a slight nuisance as the stripped extract will, in the normal course of events, be recycled to the extraction stages where it will reduce the extraction efficiency. (Kislik, 2012)

3.3 Solvent extraction contactors

Liquid-liquid extraction is a technique used to separate ions in solution via distribution between two immiscible liquid phases. These two phases are brought into intimate contact in order to extract, separate and purify the product. Contacting the two immiscible liquids may be accomplished in any of the several types of equipment, such as a baffle-plate mixer, impinging jets of the two liquid streams, agitating vessels containing the liquids, in plate columns, or even in packed towers. Separation my be accomplished by simple settling tanks or by means of centrifugation. (Robbins, 1999) The most important part of the equipment for any solvent extraction technique is the contactors in which the two immiscible phases are mixed together. The purpose of the contactors is to mix intimately the two phases to provide sufficient interfacial area across which the transfer of the required solutes takes place (Osman, 2006). Over the years different solvent extraction contactors have been developed for use in the mineral processing industry these include mixer-settlers, pulsed columns, and centrifugal types (Drain et al, 2003).

3.3.1 Mixer-settler

Mixer-settlers are simple stage wise liquid-liquid contactors. The settler consists of two parts, namely a stirred mixing tank in which the solvent and the aqueous pregnant liquor solution are intimately mixed together, and a settling tank into which the two phase solution flows where the components are allowed to separate by gravity due to the difference in their density, Figure 3-2. The separate phases exit the settling tank by flowing over a weir (organic phase) or through an underflow weir (aqueous phase). Each mixer-settler unit provides a single stage extraction. The mixer may also consist of multiple stage extractions. In this case multiple mixer-

settlers are installed with mixing tanks located at alternating ends of each stage since the outlet of the settling tank feeds the inlets of the adjacent mixing section. (Colven, 1956; Davidson, 1957) The mixer-settler remains the most commonly used contactor today. It has been suggested that this is as a result of it being (a) a proven technology, (b) simple to construct, operate and maintain, (c) able to process high throughput volumes, and (d) simple to assess its performance (Thunaes & Colbone 1969; Hanson, 1982).
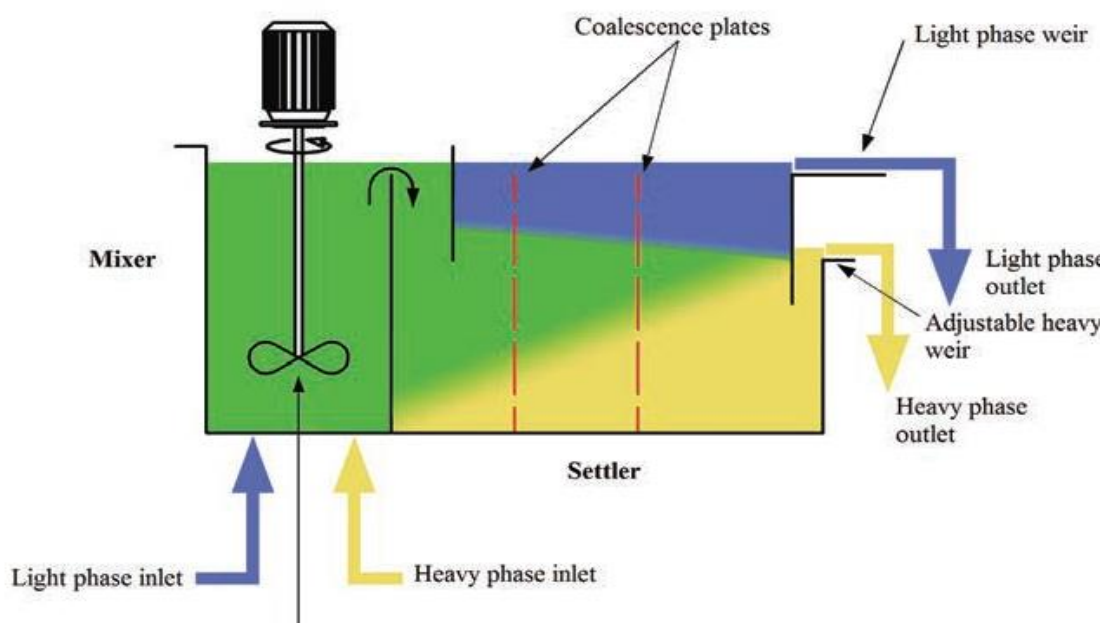
Figure 3-2: Flow diagram of a mixer-settler unit (courtesy of Rousselet-Robatel, Annonay France).

3.3.2 Pulsed column

Pulsed column, in constrast to mixer-settlers, are contactors without individual extraction stages. The pulsed column is basically an enclosed vertical column containing either perforated plates in the case of a sieve-plate pulsed column as shown in Figure 3-3, or a series of rings and donuts in the case of the proprietary Bateman pulsed column, and a pulsing mechanism which is often a piston pump at the bottom of the column (Marc, 2011).

A solvent (light phase) is circulate in a cylindrical tube from the bottom to the top, with an aqueous solution (heavy phase) flowing in counter-current, thus ensuring that the two phases are in constant contact. Owing to the difference in density between the solvent and the aqueous phase, the latter will settle to the bottom and the solvent will rise to the top. The aqueous phase, which disperses in droplets, is immiscible with the solvent. To generate and maintain this emulsion, the liquids are moved back and forth to create turbulence as they encounter obstacles positioned along the column. The obstacles are usually referred to as trays. (Drain et al, 2003)

The efficiency of liquid-liquid contractors depend on the degree of turbulence imparted to the system and the interfacial area available for mass transfer (Torab-Mostaedi et al., 2010) Therefore, in pulsed columns, rate of mass transfer can be increases by pulsation to liquid phase that decreases the size of the droplets. One of the advantage of pulsed columns is the absence of moving parts to make poper contact between dispersed and continues pahse in entire column that cuases a decrease in maintenance costs and finally a decrease in total costs. (Adel et al., 2015)
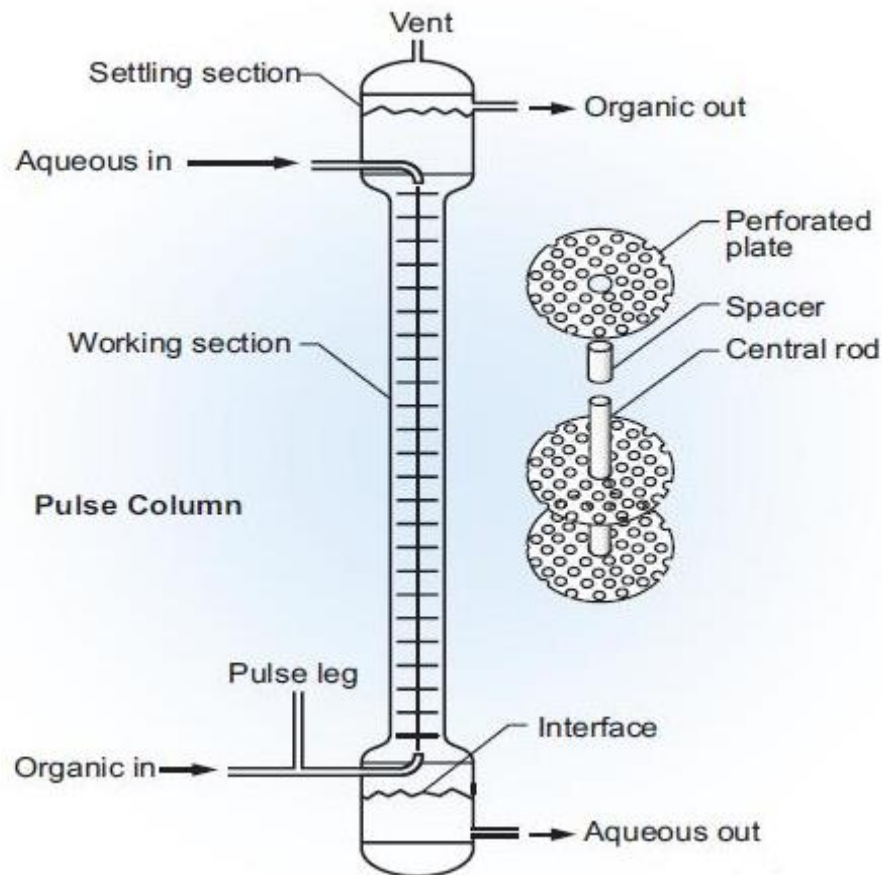
Figure 3-3: Pulsed column (McKetta and Weismantel, 1998).

3.3.3 Centrifugal extractor

Centrifugal extractors, also known as annular centrifugal contactors, are ideal for a system in which the density difference between the two phases is small. In this extractor system, two immiscible liquids with different densities, are fed to separate inlets and are mixed in the annular space between the spinning rotor and the stationary housing. The mixed phases are directed towards the centre of the rotor by radial vanes in housing bases. As the liquids enter the central opening of the rotor, they are accelerated towards the wall. The mixed phases are accelerated to rotor speed. The separation takes place as the liquids are displaced upwards. (Michael and Jack, 2010; Vedantam and Joshi, 2006)

A system of weirs at the top of the rotor allows each phase to exit the rotor where it enters a collector apparatus and exits the stage. The separated phases exit the extractor by overflow and underflow weirs, almost similar to those in mixer-settlers. (Michael and Jack, 2010)

Their main advantage is the compact footprint, which means that maintenance operations can be performed using appropriate shielded containments (Drain et al, 2003). They also present other advantages such as short residence times, low holdup volumes, flexible phase ratio, and centrifugal acceleration settling. However, as centrifugal extractors are finely machined, they tend to be the most expensive type of extractor in capital investment terms. (Lo, 1983) The performance of centrifugal extractor is characterised by the following parameters: flooding, holdup, pressure, backmixing and efficiency.

Their compact nature also means that liquid hold-up is very small, ensuring that chemical equilibrium is attained rapidly (Drain et al, 2003).

3.3.4 Spray and packed extractor

In a non-agitated extraction column, such as the spray and packed column, separation takes place continuously and simultaneously without stage contacts. The simplest column among the liquid-liquid extractor is the spray column. Packed colums are similar, in principle, to spray columns but are more efficient because of improved contacting and reduced backmixing. The lighter liquid is fed in at the bottom of the column and distributed as small droplets. The droplets rise and flow through the heavier liquid, which flows down as a continuous stream. The heavier stream exit at the bottom of the column. The heavier liquid can also be the dispersed phase. In this case the direction of the flows is reversed. The heavier liquid is dispersed into the light phase at the top of the column and the droplets flow down through the lighter liquid, which is now a continuous stream. (McCabe et al, 1993)

The column is filled with a packing material such as Rasching or Berl saddles, which cause the droplets to coalesce at frequent intervals. The packing element promotes the breakup of the droplets and reduces back mixing of the continuous phase, with the effect of further enhancing mass transfer. (Frank and James, 1988)

In order to design an optimum extractor, both the hydrodynamic and mass transfer behaviour of the system should be well understood (Moutasem et al, 2011). In liquid-liquid extraction, the dispersed phase undergoes changes and loses its identity continuously as the drops break and coalesce. This makes the study of the hydrodynamic quite complex (Mohanty and Vogelpohl,

1997). Therefore, in the following section, some of the terminologies involved in the hydrodynamic process are elaborated on.

3.4 Hydrodynamic basic of liquid-liquid extraction

For the description of an extraction column, the key parameters for determining column capacity are the hydraulic characteristics being hold-up, drop size and residence time distribution and, therefore, the required column diameter in order to provide the desired throughput (Karolina, 2012).

3.4.1 Hold-up

Hold-up is defined as the ratio of the volume of the dispersed phase to the total working volume of the column. It can be experimentally determined by measuring the total volume ($V_c + V_d$) and the volume of the dispersed phase (V_d) after settling has been completed according to Equation 3.8:

$$\varphi = \frac{V_d}{V_c + V_d} \tag{3.8}$$

V_c and V_d are the volume of the continuous and dispersed phases respectively.

In an extraction column, the mass transfer between the flowing liquid phase depends, among other factors, on the interfacial area between the continuous and dispersed phases. The interfacial area available for mass transfer in a counter-current extraction depends upon the volume fraction or hold-up, of the dispersed phase, as well as on the mean droplet size. It is therefore important, at the design stage, to be able to predict the dispersed liquid hold-up for a given system, column geometry and set of operating conditions. (Sa et al, 2010)

The performance of an extraction unit operated continuously, depends on the amount of solvent present in the extractor. If the amount of solvent is high, compared to the feed, mass transfer of the solute is favoured (Sa et al, 2010). Knowledge of the liquid hold-up hydrodynamic behaviour is very important in liquid-liquid extraction since it enables the determination, not only of the mass transfer, but also of the flooding (Aravamudan and Malcolm, 1999). The hold-up of the dispersed phase increases gradually, then rapidly as the dispersed phase flow input increases at a fixed rate

of the continuous phase, until it reaches a maximum value at flooding in a column, which corresponds to the maximum permissible velocity of the discontinuous phase (Richard, 1962).

3.4.2 Mass transfer

3.4.2.1 Dispersed phase mass transfer coefficient for a single droplet

There are several theoretical and empirical equations to predict the mass transfer coefficient of a single droplet system; most of them are time dependent. These equations are generally based on the model describing the mass transfer into, or out of, droplets rising or falling in a continuous medium. The mechanism used to determine the mass transfer rates of solutes in droplets may be classified into categories of stagnant, circulating and oscillating. (Kumar and Hartland, 1999)

Stagnant droplet

This situation was analysed by Gröber (1925) for the resistance in both phases, which resulted in the following Equation 3.9:

$$K_d = -\frac{d}{6t} \ln \left[6 \sum_1^\infty B_n \, \exp \frac{-4\lambda^2 \, D_d \, t}{d^2} \right] \tag{3.9}$$

Where B_n and λ are functions of $K_c d / D_d$. Where there is no resistance in the continuous phase, the Equation 3.10 is reduced to

$$K_d = -\frac{d}{6t} \ln \left[\frac{6}{\pi^2} \sum_1^\infty \frac{1}{n^2} \exp \frac{-4n^2\pi^2 \, D_d \, t}{d^2} \right] \tag{3.10}$$

By retaining only the first term of the series, the mass transfer coefficient for long time intervals may be derived in simple form the above Equation:

$$K_d \cong \frac{2\pi^2 D_d}{3d} \tag{3.11}$$

Circulating droplets

For the case of zero external resistance and droplets, with Reynolds number (Re) values less than unity, Kronig and Brink (1950) developed a model for mass transfer in circulating droplets. The result for the mass transfer coefficient is given below 3.12:

$$K_d = -\frac{d}{6t}\ln\left[\frac{3}{8}\sum_{n=1}^{\infty} B_n{}^2 \exp\frac{-64\lambda\,D_d\,t}{d^2}\right] \tag{3.12}$$

The solution for long contact times can be obtained from the above equation by using only the first term of the series to give Equation 3.13:

$$K_d \cong 17.7\,\frac{D_d}{d} \tag{3.13}$$

The rate of mass transfer is enhanced by a factor of about 2.7 compared with the stagnant-drop case.

Oscillating droplets

The model of oscillation and mixing intensity in oscillating droplets is not well understood. The values of the mass transfer coefficient are numerically similar to those precticted by the simple model of Handlos and Baron (1957). This might well be the reason why the oscillating droplet and vigorously circulating droplet have often been treated under the same heading.

3.4.2.2 Mass transfer coefficient based on the continuous phase

The prediction of the overall mass transfer coefficient based on the continuous phase around the droplets is generally affected by the combination of molecular diffusion, and convection in the continuous phase. For the continuous phase mass transfer, there are many empirical correlations. According to Kumar (1999), the correlation for predicting the overall mass transfer coefficient for the continuous phase (K_{oc}) is given by Equation 3.14 and 3.15:

$$Sh_{oc} = \frac{K_{oc}\,d_{32}}{D_c} \tag{3.14}$$

$$Sc_c = \frac{\mu_c}{\varrho_c D_c} \tag{3.15}$$

Equation 3.14 predicts the value of the mass transfer coefficient for all flow regimes within the droplet, and assumes upper and lower bounds for the Sherwood number (Sh), which is determined by the limiting values for the Sherwood number for the oscillating droplets and the stagnant droplets. The Sherwood number (Sh), based on the continuous phase, is considered to be a function of the droplet, Reynolds number, the capillary number, the viscosity ratio and the Schmidt

number. The Schmidt number (Sc) is considered to be the measure of the ratio of the velocity and the thicknesses of the concentration boundary layers.

Lochiel & Calderbank (1964), considered a quadratic velocity in the boundary layer and calculated the thickness of this layer at a high Reynolds number. This resulted in the following Equation 3.16:

$$Sh_{oc} = 0.7Re^{1/2} Sc^{1/3} \qquad\qquad (3.16)$$

Clift et al (1978) correlated the available experimental data in the form of Equation 3.17

$$Sh_{oc} = 1+0.724Re^{0.48}Sc_c^{1/3} \qquad\qquad 100 < Re < 2000, \text{ and } Sc_c > 200 \quad (3.17)$$

The Reynolds number (Re) of the immiscible phases and the slip velocity (U_{slip}) between two phases through the column are calculated as follows Equation 3.18:

$$Re = \frac{\varrho_c U_{slip} d_{32}}{\mu_c} \qquad\qquad (3.18)$$

For extraction columns without packing, (U_{slip}) is given by the following Equation 3.19

$$U_{slip} = \frac{Q_d}{\varphi} + \frac{Q_c}{1-\varphi} \qquad\qquad (3.19)$$

For a packed column of voidage (ε) by Equation 3.20:

$$U_{slip} = \frac{Q_c}{\varepsilon(1-\varphi)} + \frac{Q_d}{\varepsilon\varphi} \qquad\qquad (3.20)$$

Where d_{32} is the Sauter mean diameter , ϱ_c and μ_c are respectively the density and viscosity of the continuous phase, φ, and ε are respectively the dispersed phase hold-up and the packing porosity and Q_c and Q_d are respectively the continuous and dispersed phase volumetric flow rates.

Different mathematical correlations can be estimated for the diffusivity of a solute in a liquid medium at a particular temperature. These mathematical correlations link the diffusivity to solute and liquid properties (molar volume, molecular weight and liquid viscosity). According to Torab-Mostaedi et al, (2008) the volumetric overall mass transfer cofficient K_c based on the continuous phase concentration can be obtained by the following Equation 3.21:

$$K_c = \frac{Q_c \, (x_{in} - x_{out})}{V_M (x_{in} - x^*_{out})} \tag{3.21}$$

Where Q_c is the continuous flow rate, x_{in} and x_{out} are the solute mass fraction in and out of the continuous phase respectively, V_M is the column volume, and $x^* = \frac{y}{k}$ is the aqueous phase concentration in equilibrium with the organic phase.

The correlation mostly used for the calculation of the diffusion coefficient are Equation 3.22, 3.23 and 3.24:

- Correlation for dilute mixture according to Wilke and Chang (1955)

$$D_{AB} = \frac{1.173 \times 10^{-16} (\emptyset M_B T)}{\mu V_A^{0.6}} \tag{3.22}$$

- Correlation for colloidal particles in solution by Polson, (1950).

$$D_{AB} = \frac{9.40 \times 10^{-15} T}{\mu V_A^{1/3}} \tag{3.23}$$

- Stokes-Einstein correlation

$$D_{AB} = \frac{9.96 \times 10^{-16} T}{\mu V_A^{1/3}} \tag{3.24}$$

Where M_A and M_B are the molecular weight of the solute and liquid medium respectively (kg/kmole), V_A is the solute molar volume at its normal boiling point (m³/kmole), μ is the viscosity of the liquid medium (kg/ms), $\emptyset$ is the association parameter and has a value of 2.6 for water and 1 for solvents, and T is the temperature (K).

3.4.3 Droplet size and coalescence

Knowledge of the droplet size is a very important variable, as it affect the hydrodynamic and mass transfer processes.

The mean droplet size (d_{32}) in a dispersion is expressed as the Sauter mean diameter, or volume surface mean diameter, and is given by the following Equation 3.25:

$$d_{32} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$$ (3.25)

Where n_i is the number of droplets of mean diameter d_i within a narrow size range i, and d_{32} represents the ratio of the total volume to the total surface area of a droplet swarm.

As a general trend, the Sauter mean diameter decreases everywhere in the extraction column with agitation, while the droplet size distribution becomes narrower. On the other hand, an increase in the flow rate results in a larger droplet, an effect which has been found to be more significant for the dispersed phase flow rate in comparison with the continuous one.(Tsouris et al, 1990) Providing that the mean void size in the packing is equal to the mean droplet size, the size of the packing has little effect on the exit of a packed column. However, a large droplet introduced into a packed column emerges as smaller droplets. Conversely, in the packed column small droplets coalesce to an equilibrium size. However, local distortions in the flow patterns, and hold-up at the interstices of the packing, may cause greatly increased internal turbulence when the droplets are released, leading to a higher mass transfer coefficient (Davies, 1972).

3.5 Commercial considerations

There are many parameters to be considered in the development of a commercial extraction system. These include the parameters that may be controlled, namely the extractant concentration, phase ratio, pH and temperature. In order to improve the extraction characteristics, such as the extraction rate and solvent losses, it is important to consider the pre-treatment of the solvent, and the selection of the diluent and modifiers. (Clarke, 1991) These parameters used in solvent extraction process are discussed below.

3.5.1 Extractant concentration

The formation of a stoichiometric metal extractant depends essentially upon the extraction concentration, is shown in Equation 3.26. According to this expression, the loading capacity of the solvent increases linearly with the concentration of the extractant, until extractant aggregation takes place. At higher extractant concentrations, the loading capacities increase only slightly.

$$D = K_D \frac{[HA_{org}]^n}{[H^+]_{aq}}$$ (3.26)

Metal extraction increases with an increase in the extractant concentration.

Dimerisation and polymerization of the extractant take place at high extractant concentrations, which will affect the extraction negatively. Similarly, the $pH_{1/2}$ of the extraction will decrease with an increase in the extractant concentration as expressed in the following Equations 3.27 and 3.28 (Clarke, 1991):

$$pH = \frac{1}{2}\log D - \frac{1}{n}\log K_D - \log[HA]_{org} \qquad (3.27)$$

$$pH_{\frac{1}{2}} = -\frac{1}{2}\log K_D - \log[HA]_{org} \qquad (3.28)$$

The quantitative mathematical treatment of systems expressed, is for dilute solutions, but holds qualitatively for concentrated solutions (Clarke, 1991).

3.5.2 Loading capacity and phase ratio

It is advisable to determine the loading capacity when a high concentration is used in the process. This is done either by contacting the aqueous and organic phase several times, or by using a concentrated solution of the metal with a high aqueous to organic ratio, until maximum loading is achieved. For the extraction of metal, the quantity of extractant used depends on the phase ratio (A/O). In order to achieve a high solvent loading under specific experimental conditions of contact time, temperature, pH, etc. the phase ratio (A/O) and the extractant concentration should be optimised. The optimisation process is very necessary and it can be done either by experimental work, or by mathematical modelling to determine the level of extractant and the volume of solvent in each stage, in order to obtain the maximum amount of the product. A high level of free extractant may favour the co-extraction of an unwanted metal, or the extraction may be so high that the extracted species exceeds its solubility in the organic phase and is observed as a third phase. In solvent extraction processes, the use of a required solvent flow rate is economically important. The loading capacity depends on the amount of free extractant available and on the organic solubility of the metal-extract and species, which is affected by the diluent and modifier.

3.5.3 Diluent and modifier

In the solvent extraction of metals, the solvent is generally made up of an extractant dissolved in a diluent since many extractants are viscous materials in their undiluted form. (Pardon et al, 2002) In practice, the extractant is dissolved in an inert diluent, which plays a important role in improving the physical properties of the organic phase that affect the separation between the organic and aqueous phases. It was thought earlier that the diluent in solvent extraction was inert, but it is now accepted as having an important bearing on the solvent mixture. (Ritcey et al, 1974) Most extractants require diluent, but some of them can be used at full strength. The diluent is generally a combination of aliphatic and aromatic hydrocarbons. An aliphatic diluent has some good properties to provide better extraction, a good separation factor, faster equilibrium and ease of phase separation, which makes it preferable to aromatic diluents (Mohapatra et al, 2007).

The choice of diluent is determined by a number of desirable properties. These include low aqueous solubility, low density and viscosity to aid dispersion and coalescence for phase disengagement. The extractant, modifier, and metal extractant species must have high solubilities in the diluent and low surface tension to reduce the emulsification tendencies of a system. Other desirable properties of a diluent related to environmental and safety considerations are a high flash point, low volatility, and of considerable importance, low cost and easy availability. In this investigation, different types of diluents were used, but unfortunately none of them significantly changed the extraction of the metals.

High solvency of the extracted metal minimises the problem of third phase formation and enhances loading capacity. Third phase formation is essentially the splitting of the organic phase into two different parts: the new phase has an intermediate density between that of the organic and the aqueous phases. It is usually caused by the limiting organic solubility of the metal extractant species, under specific conditions of high metal loading. This phenomenon can be avoided or prevented by the addition of a modifier. A modifier is just an additional organic species which is added to the extractant to improve its properties. Usually modifiers are alcohols such as isodecanol, 2-ethylhexanol, etc. They increase the solubility of the extracted metal in the solvent phase by changing some of the physical and chemical properties of the extractant, and also inhibit the formation of a stable emulsion. The choice of diluent and modifiers will influence the selectivity of the extractant. The latter can either enhance or depress the selectivity of the extraction. In this investigation, no modifier was used because no formation of the third phase was viable.

3.5.4 pH

All extractants of the chelating or acidic type used in solvent extraction processes, liberate hydrogen ions on the extraction of metal according to the Equation 3.4. The equation indicates that the extraction of metal described by this equation is heavily dependent on the equilibrium pH of the aqueous phase. Thus, as the pH is decreased, metal extraction will decrease since the equilibrium will be shifted towards the left. Conversely, as the pH is increased, metal extraction will increase (Ritcey and Ashbrook, 1984). The extraction also depend on the stability of the extractable metal complex formed, which is partly a function of the extractant. The greater the amount of metal complexed, the greater will be the drop in pH, which will have a consequent effect on the distribution coefficient.

3.5.5 Temperature

Temperature has a significant effect on the extraction and stripping properties of a solvent extraction system. The equilibrium constant for metal-extractant interactions will be affected by temperature. Consequently it also affect the distribution coefficient. (Rydberg et al, 2004; Ritcey and Ashbrook, 1979) According to Equation 3.4, when there is an increase in temperature, the equilibrium equation, being endothermic, will be moved to the right. This is used to advantage in metal extraction, but for metal stripping, a higher temperature will have a detrimental effect on the equilibrium position. Raising the temperature will increase the rate at which equilibrium is reached, and can considerably improve contact time. It will also reduce viscosity, which will improve coalescence and promote the rate of phase transfer. (Hanson, 1972)

3.5.6 Solvent losses

Solvent losses in a solvent extraction system is one of the most important issues. It can have a significant implications for the economics of the process. The losses of solvents may occur in several ways. These include solubility in the aqueous phase, entrainment, evaporation/vaporisation, degradation and crud formation. The loss of solvent due to aqueous solubility is usually small. Solubility depends on temperature, pH and salt concentration in the aqueous phase. (Ritcey and Ashbrook, 1979)

The solubility of the solvent in the aqueous phase can usually be enhanced by increasing the temperature of the system. The solubility of the polar solvent is affected by the variation in the

pH. An increase in the salt concentration usually decreases the solubility of the solvent due to the salting effect (Rydberg et al, 2004). The serious cause of solvent loss in the strip liquor, or in crude, is the entrainment of solvent in the raffinate. This can occur as a result of insufficient settling area or time allowed for phase disengagement, poorly designed or operated mixers, too much energy input into the mixing stage, lack of additive to suppress emulsion formation, poor of diluent, and high extractant concentration in the solvent (Ritcey and Ashbrook, 1984). Solvent losses due to vaporisation or evaporation generally take place when the extraction process is operated at high temperatures. Usually, one would expect that the most volatile component to evaporate or vaporise, first would probably be the diluent (Rircey and Ashbrook, 1984). Degradation of the solvent can arise from differents sources: these include the oxidizing properties of the aqueous phase, the systems operating at temperature that is too high, ageing and oxidation by atmospheric oxygen, and general instability of the components over a prolonged period of use (Ritcey and Ashbrook, 1984). The problem of stable emulsions and eventually the formation of crud is common to most solvent extraction systems in the mining industry. Crud arises from the agitation of an organic and aqueous phase and fine solid particles. It is usually collected at the interface between the organic and aqueous phases (Ritcey and Ashbrook, 1984).

3.5.7 Perfomance of liquid-liquid extraction

A key understanding of the performance of liquid-liquid extraction is gained by determinating the theoretical number of stages. Once the concentration of the solute is known for the feed and solvent inlets, and the extract and raffinate outlets, the theoretical number of stages can be determined. One of the standard methods of determining the number of stages is via a graphical solution, whereby the liquid-liquid extraction curve and the operating line are plotted on the same graph, and the number of stages "stepped off" using the McCabe-Thiele diagram. (Robbins, 1999)

When the distribution coefficient is constant for all concentrations of solute between the feed and the final raffinate, then the Kremser equation 3.30 can be used to calculate the theoretical number of stages. If the distribution coefficient changes significantly with the concentration, then the McCabe-Thiele diagram is the method of choice. The Kremser Equation 3.30 is calculated as follows:

$$n_s = \frac{Log\left[\left(\frac{x_f - y_s/K}{x_n - y_s/K}\right)\left(1 - \frac{1}{E}\right) + \frac{1}{E}\right]}{Log\ E} \qquad (3.30)$$

Here: n_s is the theoretical number of stages

   x_f is the concentration of solute in the feed,

   x_n is the concentration of solute in the raffinate,

   y_s is the concentration of solute in the solvent,

   E is the extraction factor (E = KS/F),

   S/F is the mass ratio of solvent rate to feed rate.

According to Cusack (1999), the equation for the calculation of the number of mass transfer unit based on the overall raffinate n_{or} is identital to Kremser equation 3.31 for a straight operating line and straight equilibrium line.

$$n_{or} = \frac{Log\left[\left(\frac{x_f - y_s/k}{x_n - y_s/K}\right)\left(1 - \frac{1}{E}\right) + \frac{1}{E}\right]}{1 - \frac{1}{E}} \qquad (3.31)$$

When the extraction factor is higher than 1.5, especially if the theoretical number of stages is low, the staged equipment can be modelled best by the number of mass transfer units. The height equivalent to a theoretical number of stages (HETS) in an extraction column can be calculated from the contacting height, (Z), and the theoretical number of stages is then achieved as follows Equation 3.32:

$$HETS = \frac{Z}{n_s} \qquad (3.32)$$

Likewise, the height of a mass transfer unit based on the raffinate phase composition, H_{or}, can be calculated from the height of the column, (Z), and the number of mass transfer units n_{or} according to the following Equation 3.33:

$$HETS = \frac{Z}{n_{or}} \qquad (3.33)$$

The implementation of the extraction process is limited by the mass transfer from the raffinate phase. This is typical of the performance of many devices, including actual staged equipment.

Chapter 4: EXPERIMENTAL METHODS

4.1 Introduction

A number of experiments were performed in order to determine the optimal conditions for the extraction and separation of zirconium from hafnium. These optimal conditions depend on different factors. They include the effect of the initial acidity of the feed solution, the nature of the solvent, the nature of the stripping agent and the nature of the precipitating agent.

By varying certain parameters, the separation factor, percentage of extraction, and stripping efficiency of zirconium and hafnium were determined. Two different types of experiment were carried out: firstly, a batch process, using a mixer-settler process; and secondly a continuous process using a column. The extraction and separation technique were performed using different pieces of apparatus, methods and experimental set-up as described below.

4.2 Materials and Methods

4.2.1 Materials

All chemicals used were of analytical grade. Zirconium basic carbonate $(ZrO)_2(OH)_yCO_3 \cdot xH_2O$ (ZBC), which contained approximately 40 % ZrO_2 by mass and 1 - 2 % HfO_2 by mass, was purchased from Sigma Aldrich and was used for all extraction and separation experimental studies without further purification. Hydrochloric acid (HCl) with a purity of 32 % by mass, purchased from Sigma Aldrich, and potassium fluoride (KF) with a minimum purity of 98.5 %, purchased from Merck, were used to prepare the aqueous solutions that were used for all the extraction and separation experiments. 1-octanol $(C_8H_{18}O)$ with a purity of ≥ 99.0 %, purchased from Merck, and 2-octanol purchased from ACE (Associated Chemical Enterprises) with a purity of 97 %, were used as extractant in all the extraction experiments. Toluene (C_7H_8) with a purity of 99.5 %, kerosene and cyclohexane (C_6H_{12}) with a purity of 98.5 % all of them purchased from ACE were used as diluent in the extraction process. Sulfuric acid (H_2SO_4) with a purity of 98 % by mass, purchased from Sigma Aldrich, hydrofluoric acid (HF) purchased from Sigma Aldrich with a purity of 40 % by mass and nitric acid (HNO_3) from Merck with a purity of 70 % by mass were used respectively for the decomposition of zirconium basic carbonate and as a stripping agents for Zr and Hf from the loaded organic solution. Ammonium sulfate $[(NH_4)_2SO_4]$ from Sigma Aldrich with a purity of ≥ 99.0 % and ammonium hydroxide (NH_4OH) from Sigma Aldrich with a purity of 28 % were used respectively as a stripping and precipitation agent for Zr and Hf. Oxalic acid

($C_2H_2O_4$) with a purity of 99 % was from Merck used as a stripping agent of Hf. Zirconium oxychloride (ZOC) $ZrOCl_2 \cdot 8H_2O$ was prepared in our laboratory with Zr and Hf contents of 3967 mg/l and 81.3 mg/l repectively were determined via inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis. Deionised water prepared in our laboratory was used in all aqueous preparations. The ICP calibration standards were obtained from Monitoring and Control Laboratories, South Africa.

4.2.2 Apparatus and instruments

Different pieces of apparatus and instruments were used in this investigation. All samples were kept in polytetrafluorethylene (PTFE), perfluoroalkoxyl (PTA) or polyethylene flasks and bottles to avoid any corrosion which could occur from using potassium fluoride.

A mixer-settler magnetic stirrer was used for mixing the phases (organic and aqueous). A Rodwag analytical balance, model PS 8000/X, with accuracy of ± 0.01 g was used for weighing all samples used in this work. A programmable rheometer was used for the determination of viscosity.

A packed column was used to compare the batch process and the continuous system. The column was equipped with pumps to pump the aqueous and organic phases. The column consists of the organic phase (octanol) circulating from the bottom to the top of a cylindrical tube, with an aqueous zirconium/hafnium phase flowing counter-current to ensure that the organic and aqueous phase were in contact. After extraction, phase separation proceeded via a centrifugation process and separating funnels, with the analysis done immediately thereafter.

The following instruments were used for analysis: a Spectro Arcos model inductively coupled plasma optical emission spectrometer (ICP-OES) was used for the elemental analysis of the aqueous solution. A PANalytical X'Pert Pro diffractometer, in θ-θ configuration, equipped with Fe-filtered Co-Kα radiation, with an X'Celerator detector, was used for X-ray diffractometry (XRD). A Jeol JSM IT300 scannning electron microscope (SEM), equipped with an Oxford energy dispersive spectroscopy (EDS) add-on, was used for imaging and analysis of the product.

4.2.3 Experimental methods using a mixer settler setup

As stated in Chapter 1 section 1.3, the aim of this study was to investigate the possibility of replacing MIBK or TBP for zirconium and hafnium separation with octanol as the main extractant.

The mixer-settler process was used. All the experiments were conducted batch-wise. ZBC was dissolved using different acids, such as HCl, H_2SO_4, HF and HNO_3 at different concentrations. The acidity of the dissolved solution was adjusted with a solution of potassium fluoride (KF) or a mixture of potassium fluoride and hydrofluoric acid (HF) at different concentrations. The extraction experiments were carried out by vigorously shaking equal volumes (50 ml) of the organic solvent (either 1- or 2-octanol) with the previously prepared zirconium/hafnium aqueous solutions at different time intervals. After equilibration, the contents were allowed to disengage. A separation funnel was used to separate the aqueous from the organic phase. All extraction experiments were carried out at ambient temperature (20 - 25 ℃).

Analyses of the aqueous phase were carried out to determine the concentration of Zr and Hf using an ICP-OES. The metal concentrations of the Zr and Hf in the organic solution were inferred from a mass balance analysis. After extraction and separation, the organic solution was stripped using different stripping agents. The distribution ratio (D) was considered as the ratio of the concentration of metal present in the organic phase to that in the aqueous phase at equilibrium and was calculated according to the following Equation 3.1

$$D = \frac{C_i - C_f}{C_f} \qquad (3.1)$$

Where C_i is the initial concentration in the aqueous phase before extraction and C_f is the final metal ion concentration in the aqueous phase after extraction. D_{Zr} and D_{Hf} represent the distributions coefficient of zirconium and hafnium respectively. From the distribution coefficient the extraction percentage (% E) and the separation factor (β) were calculated.

The extracted percentage (E %) was calculated according to Equation 3.2

The hafnium-to-zirconium separation factor was calculated according to Equation 3.3:

The stripping percentage (S %) was calculated by using the relationship 4.1:

$$S \% = \frac{(C_s \times 100)}{(C_o - C_f)} \qquad (4.1)$$

where C_o is the original concentration of metal in the aqueous phase before extraction, C_f is the metal concentration in the aqueous phase after extraction, and C_s is the metal concentration in the aqueous phase after stripping. The results reported are the mean values of at least three samples at each set of experimental conditions for each process parameter variable. It must also be noted that the feed solution containing both Zr and Hf metals was freshly prepared for each experiment.

The strip solution was neutralised using ammonium hydroxide as the precipitating agent. The zirconium and hafnium were precipitated and washed, followed by calcination. The zirconium and hafnium oxides obtained were identified and quantified by XRD and SEM-EDS.

4.2.4 Experimental method using a packed column

A photo of the experimental apparatus is shown in Figure 4-1. The essential equipment used for continuous extraction of zirconium and hafnium consist of the extraction column, two feed reservoirs, one for the aqueous phase and the second one for the organic phase, with two peristaltic pumps. The effective zone of the column was made of a Perspex^R pipe of 2.2 cm internal diameter, and 120 cm length. The column had a packed length of 110 cm with two disengaging spaces at the top and bottom where the aqueous phase and organic phase respectively were withdrawn. The organic phase was fed from a 1 L flask to the column through a distributor at the bottom of the column. The distributor consisted of a diffuser having a pore size of 0.45 cm. The diffuser of the polytetrafluoroethylene (PTFE) tube was attached to a peristaltic pump so that the flow rate of the organic phase could be controlled. The continuous phase (aqueous phase) was fed from the top of the column through a PTFE tube, connected to a peristaltic pump to control the flow rate of the aqueous phase. The column was randomly packed with 2716 beads having a diameter of 49 mm. The experiments were conducted at ambient temperature. The feed streams were introduced counter-current. The aqueous phase, namely zirconium basic carbonate (ZBC), containing 40 % ZrO_2 and 2 % HfO_2, was dissolved using HCl at different concentrations. KF at different concentrations was added to this solution in order to obtain the feed for the liquid-liquid extraction experiment. This solution was introduced at the top of the column, and the solvent (octanol) inlet stream at the bottom of the column.
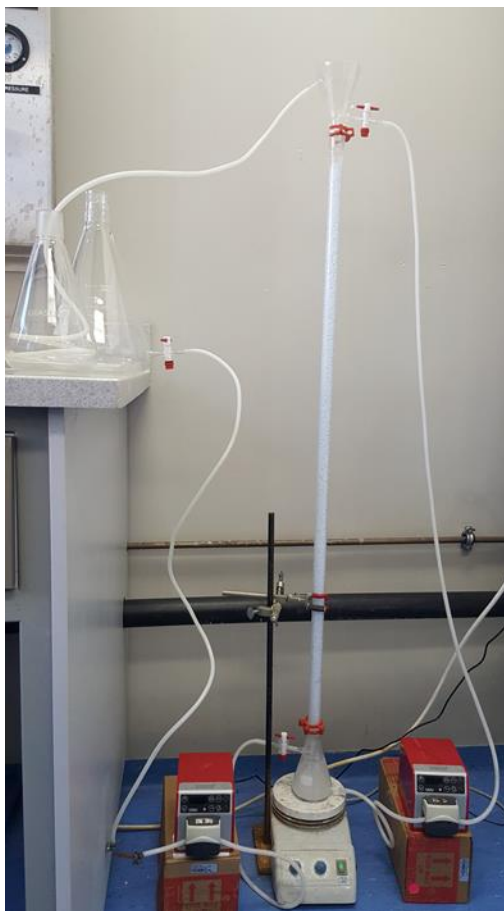
Figure 4-1: Photo of the packed column setup

4.2.5 Selection of stripping agent

The stripping process was carried out in order to choose an appropriate stripping agent that could successfully strip zirconium or hafnium from the loaded organic solvent. For this purpose different stripping agents, such as distilled water, sulfuric acid, ammonium sulfate and hydrochloric acid, were used. The experiments were conducted at different contact times between 10 and 60 min and at an A/O ratio of 1:1. The organic phase was washed with distilled water and then with dilute sulfuric acid to obtain zirconium by selective stripping. The aqueous phase contains the hafnium complex. Ammonia was added to the aqueous solutions obtained from the stripping process to precipitate zirconium and hafnium.

4.2.6 Precipitation

One of the most widespread methods of separation is precipitation. The method is based on the difference in the solubility of the metal compounds in the aqueous phase. In this investigation precipitation agent was added, to precipitate zirconium and hafnium from the pregnant stripped solution. The precipitate was allowed to settle and was then filtered. Thereafter it was washed with boiling distilled water and dried in the oven. The dried precipitate was put into a porcelain crucible and then placed in a muffle furnace. Calcinations were done at 600 ℃ for three hours. The zirconium and hafnium oxides were obtained. The products were sent for XRD and SEM analysis for characterisation.

Chapter 5: RESULTS AND DISCUSSION

5.1 Mixer-settler results and discussion

5.1.1 Introduction

This section presents the results of the extraction, separation, stripping, precipitation and characterisations of the products. It also discusses further treatment required in order to produce a pure zirconium and hafnium oxide. In order to optimise the extraction, separation and stripping process, the influence of experimental parameters such as HCl, KF, H_2SO_4, HNO_3 and HF concentrations in the aqueous phase, the contact time, and concentrations of H_2SO_4, $(NH_4)_2SO_4$, HCl, and distilled water as stripping agents, were examined.

5.1.2 Selective extraction of zirconium and hafnium with 1-octanol in a HCl/KF system

The extraction and analytical methods followed in this investigation for the selective extraction of zirconium and hafnium with 1-octanol in the HCl/KF system were described in Section 4.2.3.

5.1.2.1 Effect of contact time

To make a valid interpretation of the effect of different experimental parameters, it must be ensured that equilibrium between the organic and aqueous phases is reached in all experiments. Thus it is necessary to determine the minimum time required to establish equilibrium. This was investigated by vigorously shaking 50 mL of organic solvent (1-octanol) with 50 mL of aqueous solution containing Zr and Hf for different time intervals between 5 and 20 min. The percentage metal extraction as a function of time is shown in Figure 5-1. The minimum contact time required to achieve equilibrium between the organic and aqueous phases was found to be 5 min. A maximum time of 15 min was selected for all subsequent experiments, because extending this time did not greatly affect the extraction of either the Zr or Hf species according to Figure 5-1. The preliminary tests indicated that there was no formation of a third phase which would have required the addition of a modifier in this investigation. Separation of the two phases (organic and aqueous) was fast, and the separated phases were clear without the presence of a modifier.
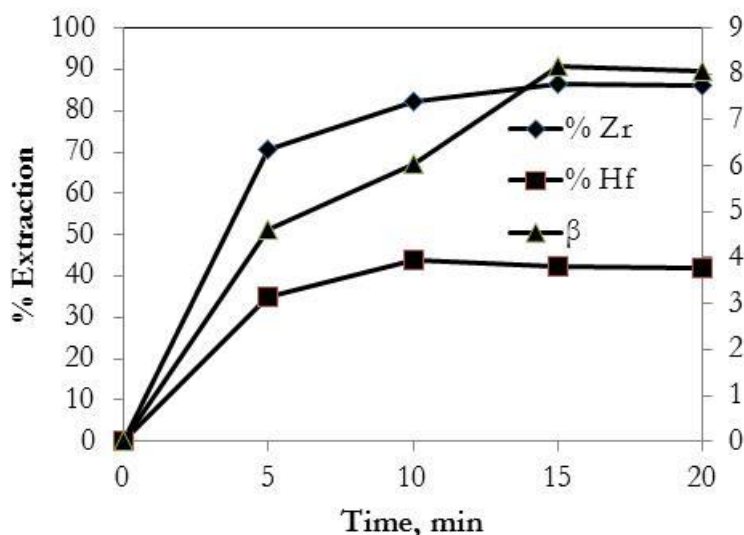
Figure 5-1: Effect of contact time on extraction of Zr and Hf. Experimantal conditions: organic phase: 100 % 1-octanol, [HCl] = 10 %, [KF] = 1.5 M in solution, A/O ratio = 1:1

5.1.2.2 Effect of HCl concentration

The influence of hydrochloric acid concentration on the extraction of Zr and Hf was investigated. Zirconium basic carbonate was dissolved in hydrochloric acid at various concentrations from 5 % - 20 %. After dissolution, a predetermined concentration of potassium fluoride was added to the solution. The solution obtained was then contacted with 1-octanol for the extraction of Zr and Hf. The tests were carried out at an A/O ratio of 1:1 and a contact time of 15 min. The results in Figure 5-2 indicate that the extraction of both Zr and Hf increases with increasing acid concentration. These results are consistent with the expectation that both Zr and Hf are extracted as a chloride complex through a solvation reaction. The high chloride ion and high hydrogen ion contents are respectively necessary to promote the formation of extractable Zr and Hf complexes and to supress hydrolysis and polymerisation. The increase in hydrochloric acid concentration promotes depolymerisation, while, simultaneously, hydroxide ions attached to Zr or Hf are displaced by chloride ions to form inner-sphere complexes Equation 5.1(Johnson and Krous, 1956 ; El-Ammouri and Distin, 1996), with M = Zr or Hf:

$$[M(OH)_n](4-n) + iCl- +nH^+ \rightleftharpoons [MCli](4-i) +nH_2O \qquad (5.1)$$

83
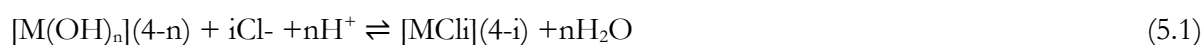
At high hydrochloric acid concentrations, the extraction of Zr or Hf with 1-octanol was improved. The results obtained from this process could be rationalised by the Hard Soft Acid-Base theory. Zirconium and hafnium are known to be hard acids (Ho, 1975). Nevertheless, the values of hardness calculated for Zr and Hf indicate that Hf is less hard than Zr (Pearson, 1988). In this extraction process where octanol was used as extractant, the hard base Cl$^-$ will preferentially react with the hard acid Zr to form an inner complex which will be extracted in octanol. As also established in the conventional process: in the MIBK, NCS$^-$, which is a soft base, preferentially forms a complex with Hf. The Hf complex is then extracted by the MIBK into the organic phase, whereas in the TBP process, the hard TBP ligand preferentially forms a complex with Zr which is then extracted into the organic phase (TBP). The increase in HCl concentration showed a positive effect on the extraction of Zr and Hf. For this reason 10 % HCl was chosen for the extraction and separation of zirconium and hafnium.
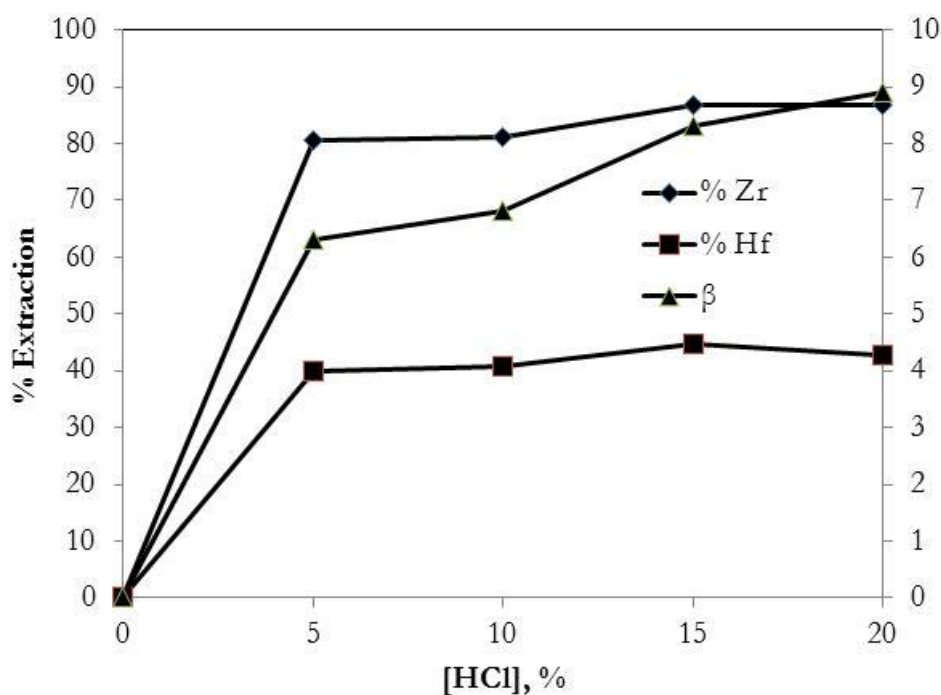
Figure 5-2: Effect of HCl concentration on extraction of Zr and Hf with 1-octanol. Experimental conditions: 100 % 1-octanol, [HCl], = 5 - 20 %, A/O ratio = 1:1, [KF] = 1.5 M

5.1.2.3 Effect of KF concentration

Zirconium basic carbonate was dissolved in 10 % HCl. A predetermined potassium fluoride concentration, between 0.5 M and 2 M, was added in order to find the optimum concentration for the extraction and separation of Zr and Hf. Table 5-1 shows the effect of KF concentration on the extraction and separation of zirconium and hafnium. Increasing the KF concentration increases the extraction and separation efficiency of both Zr and Hf, with the highest separation efficiency obtained at 1.5 M KF in solution. This shows that the extraction of both Zr and Hf depend strongly on the concentration of KF in the aqueous phase. This peculiar behaviour is probably connected with a change in the nature of complexes formed with the increase of the concentration of fluoride and potassium ions. It is postulated that a $(Zr,Hf)F_4 \cdot 2KF$ compound is formed in aqueous solution. At low KF concentration, the hexafluoride complex $[(Zr,Hf)F_6]^{2-}$ formed has a lower affinity for 1-octanol. At a higher KF concentration, it is possible that there is formation of heptafluoride complex $[(Zr,Hf)F_7]^{3-}$ which is probably the reason for the significant selectivity observed between Zr and Hf. The heptafluoride complex might be less selective towards Hf and more selective towards Zr, which helps to explain the high extraction and separation obtained at this particular concentration, although in-depth molecular species studies are required to investigate this issue. When KF was replaced by sodium fluoride (NaF), no extraction was observed. Beyond this value of 1.5 M KF, a small increase was observed. This concentration was regarded as the optimum value. From Table 5-1 it is clear that the Hf concentration decreases with an increase in the KF concentration. On the other hand, the distribution coefficient of Zr increases with an increase in the KF concentration. Therefore, the separation of Hf relative to Zr in the solution also increased, or, in other words, at a higher KF concentration, more Hf remained in the aqueous phase with respect to Zr, while more Zr was transferred to the organic phase, which led to better separation of the two metals with respect to the two phases.

Table 5-1: Effect of KF on the extraction and separation of Zr from Hf, with [KF] = 0.5 - 2.0 M , O/A= 1:1, 1-octanol as the organic solvent

[KF], M	D_{Zr}	D_{Hf}	% Zr	% Hf	β
1.0	3.97	0.82	79.87	39.66	6.04
1.5	6.32	0.77	86.35	43.40	8.25
2.0	6.18	0.77	86.08	43.58	8.01

5.1.2.4 Effect of phase ratio on the extraction of Zr and Hf

The effect of different volume ratios of aqueous phase to organic phase (A/O) was investigated. In this study, the volume ratio of aqueous to organic was varied from 1:5 - 1:1. The organic solution was contacted with zirconium basic carbonate dissolved in 10 % HCl and 1.5 M KF with a concentration of 3573.46 mg/L Zr and 63.93 mg/L Hf, which were kept constant throughout the entire experiment. Under the given set of experimental conditions, the results in Table 5-2 indicate that the preferred (A/O) ratio in this investigation is 1:2 or even higher. It shows that the percentage extraction of Zr and Hf increases with an increase in the volume ratio of organic to aqueous phase. The separation factor between Zr and Hf also increases from 8.11 - 8.69 from the ratio 1:1 to 1:2, and then remains constant up the volume ratio of 1:5.

Table 5-2: Effect of phase ratio on the extraction of Zr and Hf with 1-octanol. Experimental conditions: 100 % 1-octanol, KF, = 1.5 M , [HCl] = 10 %

A/O	D_{Zr}	D_{Hf}	% Zr	% Hf	β
1:1	4.99	0.62	83.31	48.88	8.11
1:2	6.77	0.78	93.13	60.92	8.69
1:3	5.15	0.60	93.92	64.09	8.66
1:4	3.86	0.46	93.91	64.55	8.47
1:5	3.16	0.37	94.05	64.67	8.63

5.1.2.5 McCabe-Thiele Diagrams

McCabe-Thiele diagrams were constructed to determine the number of stages needed to reach the desired separation of Zr from Hf. In this study, the equilibrium data were obtained at different A/O volume ratio, using optimum extraction conditions as determined above. The initial concentration of Zr was kept constant during the experiment. From the McCabe Thiele diagram in Figure 5-3, four equilibrium stages are required for almost 94 % Zr extraction.
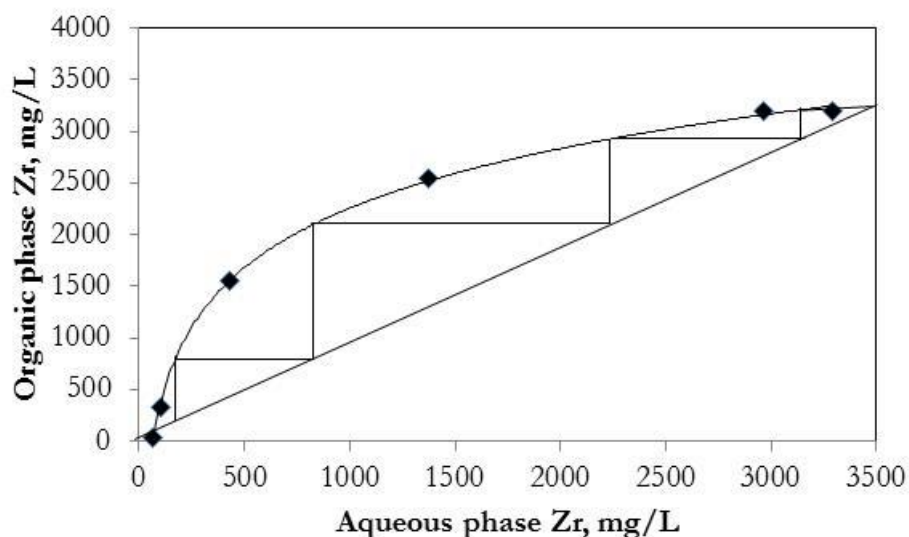
Figure 5-3: McCabe-Thiele diagram for Zr extraction. Experimental conditions: 100 % 1-octanol, A/O 1:1 to 1:5, 15 min contact time, 10 % HCl and 1.5 M KF

5.1.2.6 Zirconium stripping

In order to obtain an efficient and economical stripping process, it was necessary to study the relevant factors affecting the stripping process to determine the optimum conditions. The stripping process depends on a number of factors, which have to be investigated in order to obtain the best stripping efficiency and at the same time also matches the economic considerations. The factors under consideration are: the effect of different stripping agents such as H_2SO_4, HCl, H_2O and $(NH_4)_2SO_4$, the effect of contact time, the effect of the stripping agent concentration and the construction of the McCabe-thiele diagram for Zr stripping.

5.1.2.7 Effect of stripping agent

The effect of different stripping agents, such as distilled H_2O, H_2SO_4, $(NH_4)_2SO_4$, and HCl, was studied by using a constant concentration value of 1 M and keeping other factors constant. The results obtained are given in Figure 5-4 and shows that the stripping efficiency of Zr and Hf depends on the stripping agent. The highest stripping percentage of 38.87 % was obtained using H_2SO_4 as a stripping agent, and the lowest was 24.38 %, using HCl as a stripping agent.
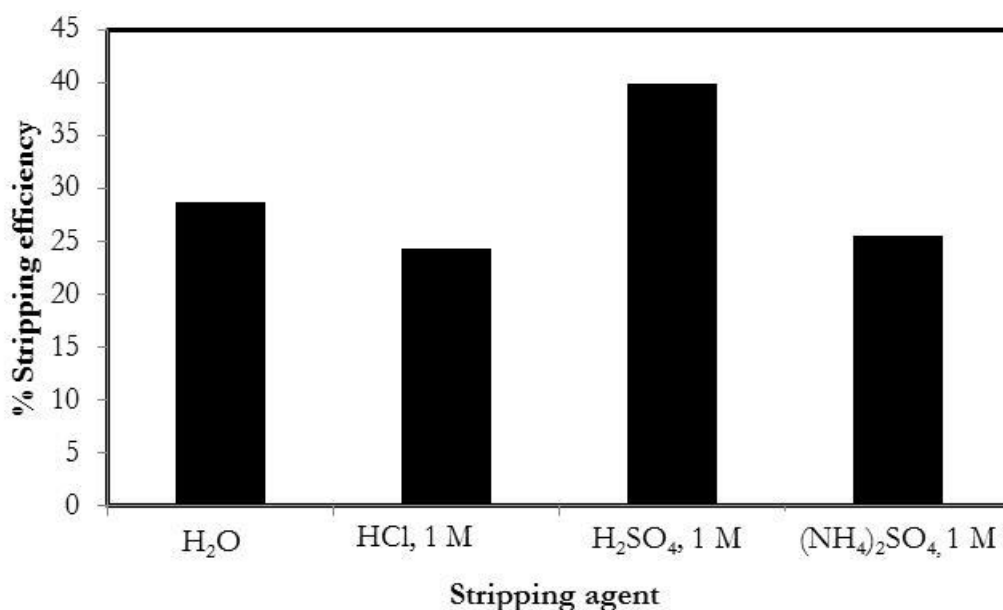
Figure 5-4: Effect of stripping agent on the stripping of Zr from loaded 1-octanol. Contact time 15 min, A/O 1:1

5.1.2.8 Effect of contact time

The effect of contact time on the stripping of Zr from the loaded organic solution was studied at time intervals between 10 - 60 min, while other parameters were kept constant. The results obtained show that the stripping percentage increases with the increase in contact time. The results given in Figure 5-5 indicated that the optimum stripping efficiency was achieved at approximately 40 min.

In order to investigate the stripping behaviour of Zr in the loaded extract solution, stripping experiments were conducted. The extracted solution obtained from the HCl/KF 1-octanol system was stripped with sulfuric acid at concentrations between 1 M - 5 M. The results indicate that the stripping percentage of Zr increases with an increase of H_2SO_4 up to 3 M, then starts to decrease. The decreasing stripping efficiency at higher H_2SO_4 concentrations could be due to the successive formation of highly charged anionic species of Zr and Hf complexes in aqueous solutions (Pershina et al, 2002). The results in Figure 5-6 indicate that the highest stripping efficiency of Zr

was obtained at a sulfuric acid concentration of 3 M. H_2SO_4 was also reported to be a great stripping agent of zirconium (Reddy et al., 2004 ; Shafie et al., 2004).
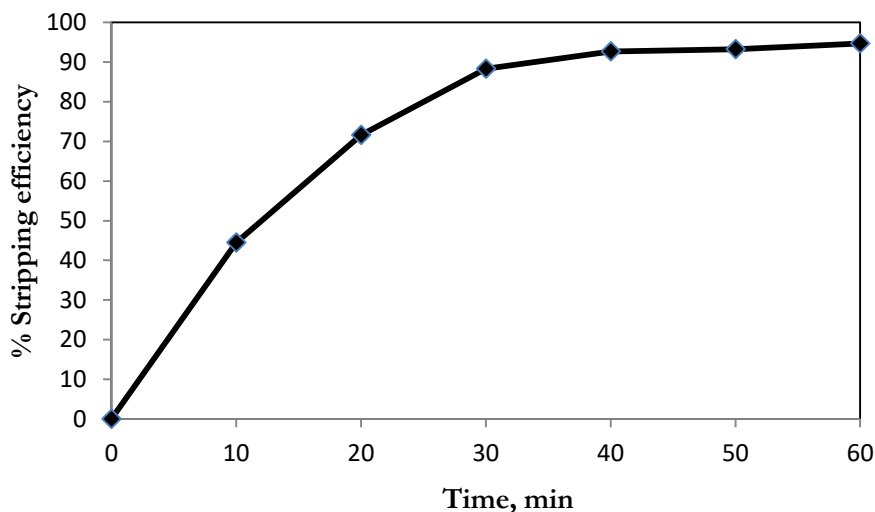
Figure 5-5: Effect of contact time on stripping efficiency of Zr. Contact time 0 - 60 min, A/O 1:1, stripping agent 3 M H_2SO_4
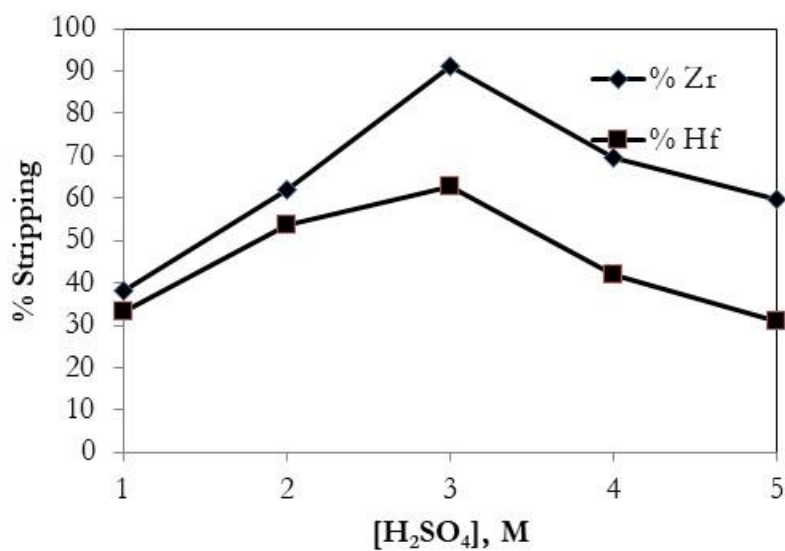
Figure 5-6: Effect of sulfuric acid concentration on the stripping of Zr and Hf from loaded 1-octanol. Experimental conditions: A/O ratio 1:1, $[H_2SO_4]$ = 1 - 5 M

5.1.2.9 McCabe-Thiele diagram for stripping of zirconium

In order to determine the number of equilibrium stages required to strip Zr from the loaded extractant, a McCabe-Thiele diagram was constructed. The data were obtained by shaking the loaded organic solution with a fixed volume of 3 M sulfuric acid until equilibrium was obtained. It was found (Figure 5-7) that five equilibrium stages would be sufficient for the stripping of Zr from the loaded extract.
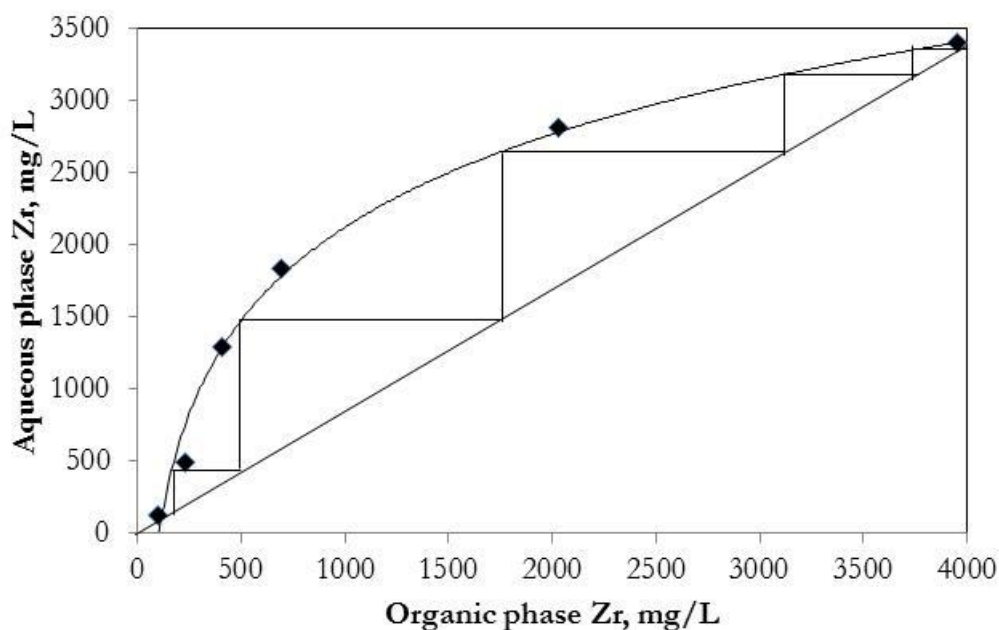
Figure 5-7: McCabe-Thiele diagram for Zr stripping from loaded 1-octanol. Experimental conditions: contact time 40 min, $[H_2SO_4] = 3$ M

5.1.3 Extraction and separation of zirconium and hafnium using 2-octanol

A literature survey indicated that three extractant processes, namely TBP, MIBK and a high-molecular alkyl amine, have been used industrially for the extraction of zirconium and hafnium. The use of a neutral organosphosphorus extractant such as in TBP has some disadvantages like third phase formation and poor disengagement (Da Silva and Distin, 1988). Hence a modifier has to be introduced into the organic phase. The Toyo process requires many equilibrium stages which are time consuming (Xu et, 2015). The MIBK process uses high concentrations of ammonium cyanide which leads to environmental concerns. In order to overcome the above limitations, in the

present study, 2-octanol was explored for the extraction and separation of zirconium from hafnium. The results are presented below.

The liquid-liquid extraction and the analytical method used for the extraction of zirconium from hafnium were the same as described previously. Preliminary results indicated the extraction equilibrium is attained within 15 min for all the metal ions, and that the highest separation efficiency was obtained at 1.5 M KF in solution, as shown in Figure 5-8.
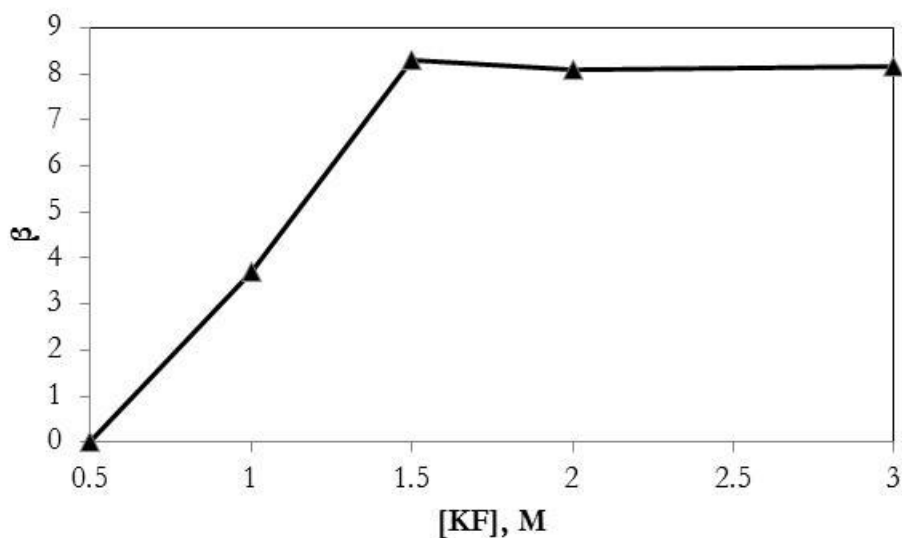
Figure 5-8: Effect of KF on the extraction and separation of Zr and Hf. Experimental conditions: A/O ratio 1:1, 100 % 2-octanol, [KF], = 0.5 - 3 M.

5.1.3.1 Effect of HF concentration

The experiments were conducted by dissolving zirconium basic carbonate in different HF concentrations between 5 % - 20 %. The extraction experiments were conducted using the aqueous solution by varying the HF concentration with or without KF at a constant concentration of 1.5 M. After dissolution, the solution obtained was contacted with the organic solvent. The extraction of Zr and Hf was then investigated by vigorously shaking the mixture for 15 min. The two phases were then separated and the aqueous phase was analysed by ICP-OES. When the extractions were done without the addition of KF, no extraction or separation took place. This can be interpreted as showing that it is not only the fluoride complex that plays a role in the extraction of Zr and Hf,

but also the presence of potassium ions, because when NaF was used in place of KF, no extraction was observed.

The results obtained with 1.5 M potassium fluoride in solution, with different HF concentrations ranging between 5 % - 20 %, are shown in Table 5-3. Increasing the concentration of HF increases the extraction of Zr and Hf, but separation decreases. The highest extraction and separation obtained were 66.84 % and 49.24 % zirconium and hafnium respectively at 20 % HF, and 3.5 as separation factor between zirconium and hafnium with 5 % HF.

Table 5-3: Effect of HF on the extraction and separation of Zr from Hf. Experimental conditions: 2-octanol, A/O ratio: 1:1, [HF] , = 5 - 20 % , [KF] = 1.5 M

[HF], %	D_{Zr}	D_{Hf}	% Zr	% Hf	β
5	0.98	0.28	49.50	21.61	3.56
10	1.38	0.39	57.93	28.14	3.52
15	1.67	0.65	62.60	39.43	2.57
20	2.02	0.97	66.84	49.24	2.08

5.1.3.2 Effect of mixture of KF and HF

The effect of mixtures of KF and HF was investigated. ZBC was dissolved in 10 % HCl and then a constant concentration of 1.5 M KF in solution and variable concentrations of HF over a range of 1 - 4 M HF were added to the aqueous solution prior to the extraction and separation. According to the results obtained (Figure 5-9), the distribution coefficients of both Zr and Hf increased, and therefore the separation factor decreased with increasing HF concentration, compared to the ZBC/HCl/KF system. But the extraction increased up to 1 M HF concentration. With a further increase in the HF concentration, however, the distribution coefficient of both Zr and Hf

increased, indicating a rapid decrease in the extraction and separation. The highest separation factor of 7.40 was observed at 1 M HF.
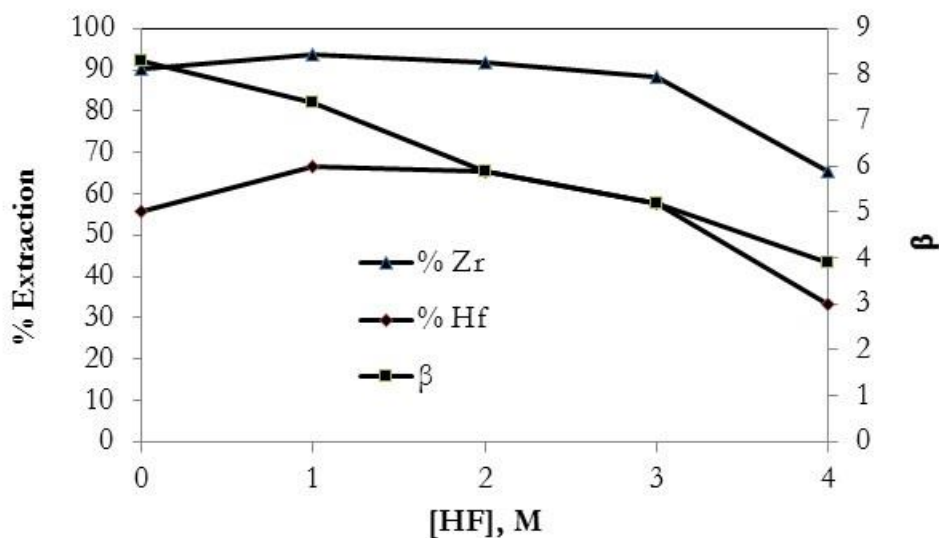
Figure 5-9: Effect of mixture of KF and HF on the extraction and separation of Zr from Hf. Experimental conditions: 100 % 2-octanol, A/O ratio 1:1, [KF], = 1.5 M, [HF], = 1 - 4 M.

5.1.3.3 Influence of HCl, H₂SO₄ and HNO₃ with constant KF concentration on extraction efficiency

In this set, the extraction of Zr and Hf was done at a constant 1.5 M KF concentration. The acid concentration in the feed solution was varied from 5 - 20 %. All tests were carried out at an A/O ratio of 1:1 and a contact time of 15 min. It can be observed that the extraction of Zr and Hf increases drastically with increasing acidity for all acids, but that the effect is more profound for HCl.

In the case of HNO₃, the extraction of Zr and Hf increases with an increase in the acid concentration in the range investigated from 38.50 % - 63.64 % for Zr and from 19.98 % - 45.81 % for Hf. This behaviour can be explained by the fact that at a lower nitric acid concentration, the small amount of acid in the octanol solution cannot complete with the metal for the extractant, but at a higher acid concentration, complex formation between the acid and the extractant becomes appreciables which affects the percentage extraction of both metals from the nitric acid medium. The results in Figure 5-10 also indicated that an increase in the nitric acid concentration

resulted in a decrease in the separation factor. Foos and Wilhelm, (1954); and Cox et al., (1958) also reported a similar trend when extracting Zr and Hf from an aqueous solution containing a mixture of Zr and Hf with diluted and undiluted tibutyl phosphate.

In the case of HCl, the extraction percentage for both Zr and Hf increased at different rates with increased HCl concentration as shown in Figure 5-11. The extraction percentage of Zr increases from 44.84 % - 92.55 %, while Hf exhibits a small increase. This leads to an increase of the separation factor between Zr and Hf. The remarkable difference from extraction of Zr and Hf in the organic phase, is that Hf has a lower tendency than Zr to form anionic complexes, which confirms the findings of Poriel el al , (2006a). They stated that Zr and Hf are regarded as hard acids (Ho, 1975), but the absolute values of hardness calculated for Zr and Hf indicate that the hardness of Hf is less than that of Zr (Pearson, 1988). This indicates that in the solvent extraction process using liquid anion extractants, the hard base Cl^- will by preference form inner-sphere anionic complexes with Zr that is extracted to the organic phase by octanol. The increase in the percentage extraction of Zr and Hf with increasing HCl concentration may also imply that solvation reactions are responsible for the extraction of both metals by the extractant used.

The suggested reaction may be expressed by the following chemical expression 5.2 (Ling et al., 2013).

$$M^{x+}_{(aq)} + xCl^-_{(aq)} + y(HA)_{(org)} \rightleftharpoons MCl_x \cdot y(HA)_{(org)} \tag{5.2}$$
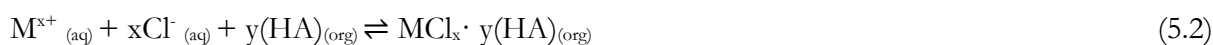
Where M^{x+} represents cationic species of Zr and Hf in HCl solution. The chloride concentration affects the speciation of the metal complexation and higher chloride concentration favours the formation of extractable metal chloro-complexes, pushing the equilibrium concentration in Equation 5.2 to the right. The extraction behaviour of Zr and Hf in the present study is in good agreement with the results reported by Ling et al., (2013) which founds an increase in HCl concentration promotes the separation of Zr over Hf. Banda et al., (2013) also reported that the extraction of Zr was selective over Hf with TOPO from chloride concentration. The extraction and separation also improve with an increase in HCl concentration.
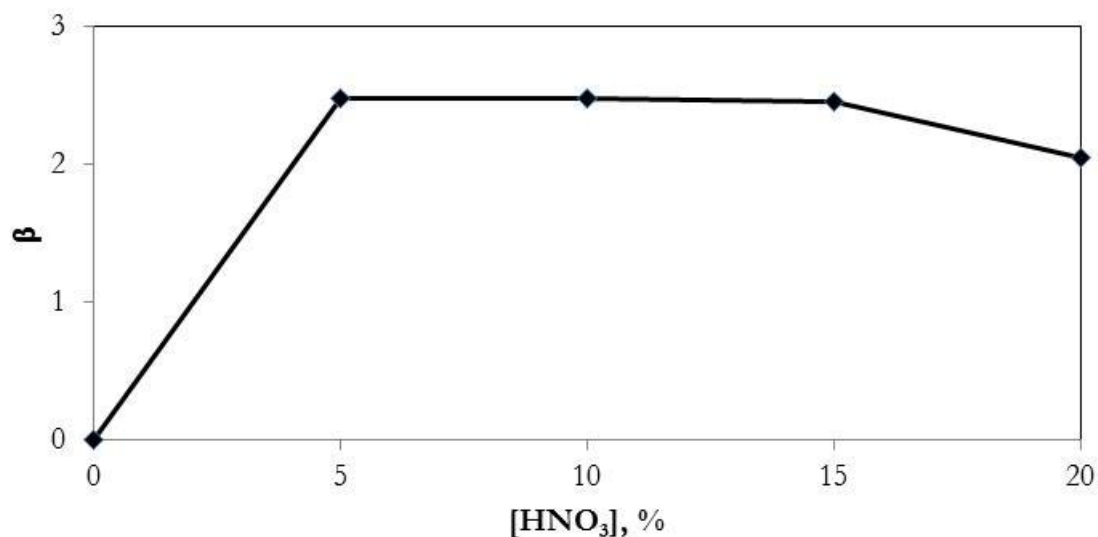
Figure 5-10: Separation factor of Zr and Hf at various nitric acic concentrations. Experimental conditions: 100 % 2-octanol, A/O ratio 1:1, $[HNO_3]$, = 5 - 20 %, [KF], = 1.5 M, contact time 15 min

In the case of H_2SO_4, the extraction of Zr and Hf increases from 40.37 % - 79.42 % for Zr and from 22.64 % - 64.16 % for Hf. The extraction of both metals increased with increasing H_2SO_4 concentration. The extraction of Zr was higher than that of Hf in the range investigated. Although octanol displays extraction ability on both metals, it is not efficient in separating Zr from Hf. The low extraction percentage of metal ions from sulfuric acid compared with hydrochloric acid may be attributed to the influence of hydrolysis on the complex formation of each metal's ions. HCl was therefore used in the rest of the investigation.

Table 5-4: Effect of H_2SO_4 and HNO_3 on the extraction and separation of Zr from Hf. Experimental conditions: 2-octanol, A/O ratio: 1:1, $[H_2SO_4]$ and $[HNO_3]$ = 5 - 20 %, [KF] = 1.5 M.

[H₂SO₄], %	Extraction (%)			[HNO₃], %	Extraction (%)		
	Zr	Hf	β		Zr	Hf	β
5	40.37	22.64	2.31	5	38.5	19.98	2.51
10	68.16	36.43	3.73	10	53.48	23.61	2.49
15	72.28	59.22	2.27	15	60.72	38.58	2.46
20	79.42	64.16	2.16	20	63.64	45.81	2.38
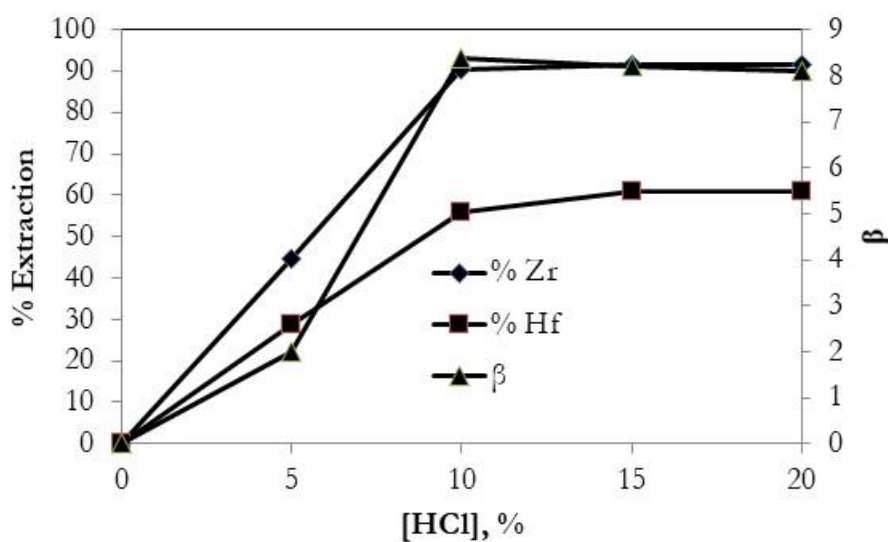
Figure 5-11: Effect of HCl concentration on the extraction of Zr and Hf. Experimental conditions: 100 % 2-octanol, A/O ratio 1:1, [HCl], = 5 - 20 % , [KF], = 1.5 M, contact time 15 min

5.1.3.4 Distribution and separation coefficients with HCl

Table 5-5 shows the effect of HCl concentration on the separation of Zr from Hf. The results obtained indicate that the distribution coefficients of both Zr and Hf increase with an increase in HCl concentration. The increase in HCl concentration also shows a positive effect on the separation of Zr from Hf, with the highest separation factor of 8.38 at 10 % HCl, and extraction of 60.54 % and 92.56 % for Hf and Zr respectively.

Table 5-5: Effect of HCl on the extraction and separation of Zr from Hf. Experimental conditions: 2-octanol, A/O ratio: 1:1, [HCl] , = 5 - 20 %, [KF] = 1.5 M

[HCl], %	D_{Zr}	D_{Hf}	% Zr	% Hf	β
5	0.81	0.40	44.84	28.78	2.01
10	9.25	1.10	90.25	52.47	8.38
15	10.92	1.33	91.61	57.06	8.22
20	12.44	1.53	92.56	60.54	8.11

5.1.3.5 Effect of temperature on the extraction process

The effect of temperature on the extraction of zirconium and hafnium was investigated between 25 - 65 ℃ for 15 min under the following conditions: 2-octanol, 10 % HCl concentration, 1.5 M KF. According to the results shown in Figure 5-12, the extraction percentage and the distribution coefficient of both elements decreases with increased temperature. Thus, the indications are that a better extraction and separation of zirconium and hafnium could be obtained only at low temperature. The results are similar to those obtained by Xu al, (2012).
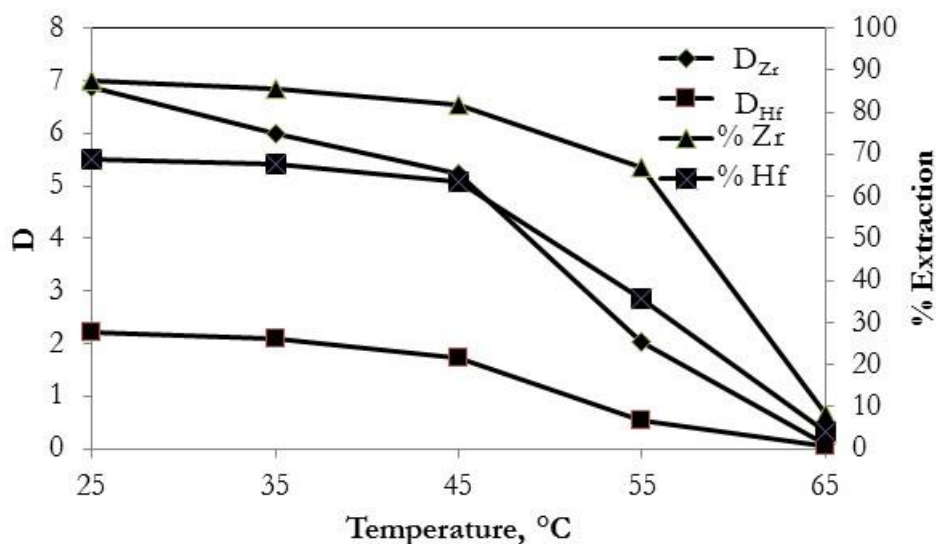
Figure 5-12: Effect of temperature on the distribution coefficient (D) and extraction percentage (% E) of Zr and Hf

5.1.3.6 Effect of phase ratio

A set of experiment was carried out to examine the effect of the aqueous to organic phase ratio (A/O). The experimental conditions were kept constant, while varying the A/O organic to aqueous ratio from 1:1 to 1:5. The results are illustrated in Figure 5-13. From this result, the percentage extraction of Zr and Hf increases in all the ranges investigated. However the percentage extraction of both metals increases at different rates, which resulted in the increase of the separation factor.

It was concluded from these experiments that an aqueous to organic volume ratio of 1:2, which gave a separation factor of 9.2, was appropriate in this investigation.
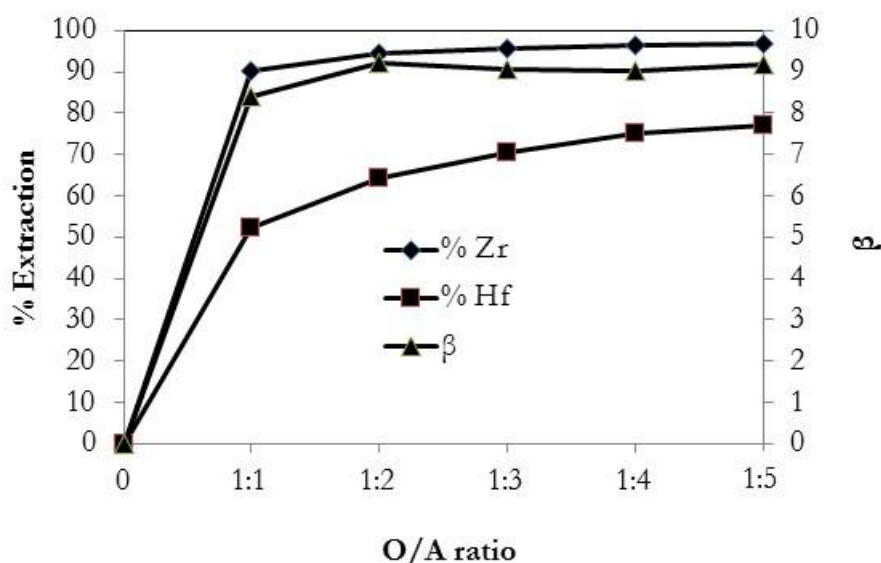
Figure 5-13: Effect of phase ratio on the extraction of Zr and Hf. Experimental conditions: 100 % 2-octanol, [KF], = 1.5 M, A/O ratio form 1:1 - 1:5

5.1.3.7 Effect of diluent

The most important factor to be considered in the liquid-liquid extraction process is the effect and type of diluent on the extraction and separation efficiency. The diluents used in this investigation were kerosene, toluene and cyclohexane, all supplied by Sigma Aldrich.

The effect of the diluents were tested by performing five different extractions of Zr and Hf. Each extractant was diluted, with different concentrations ranging between 5 % and 50 %.

Zirconium basic carbonate was dissolved in 10 % HCl, then 3 M KF was added to the solution and contacted for 15 min with five different organic solutions containing 2-octanol, each diluted in kerosene, toluene and cyclohexane at different concentrations. The volume of the A/O phase was maintained at 1:1 in order to avoid any third phase formation and emulsification.

Both Zr and Hf were quantitatively extracted with the different concentrations of the organic phase. The results Figure 5-14, Figure 5-16 and Figure 5-18 indicated that the distribution coefficient of Zr decreases with an increase in diluent concentration. There is an increase for Hf, consequently, the separation factor decreases. We assume that the addition of different

concentrations of diluent to the system increases mass transfer to the organic phase, while decreasing the hafnium-zirconium separation factors. The use of pure octanol as the organic phase resulted in higher mass transfer and separation factors, compared with the use of octanol, which was diluted with different types of diluent. The extraction efficiency also decreases with the increase of the diluent as shown in Figure 5-15, Figure 5-17, and Figure 5-19. Thus, none of the diluents investigated gave any reason to believe that the effect of different diluents would enhance extraction and separation.
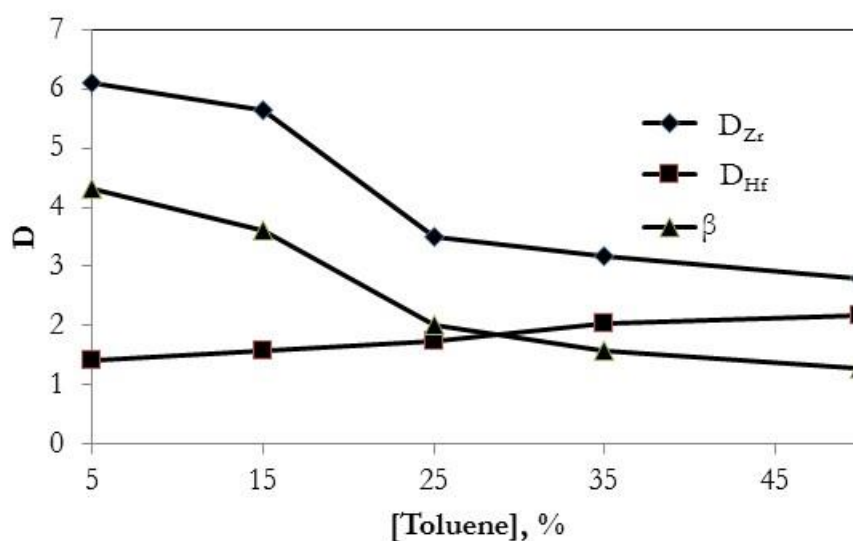
Figure 5-14: Effect of toluene concentration on the separation efficiency of Zr and Hf. Experimental conditions: [KF], = 1.5 M, [HCl], = 10 %, [Toluene], = 5 - 50 %, contact time 15 min, 2-octanol, A/O ratio 1:1.
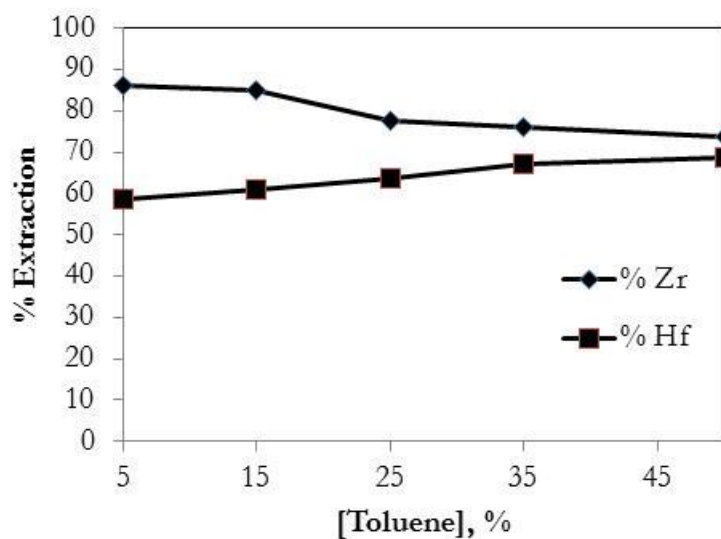
Figure 5-15: Effect of toluene concentration on the extraction efficiency of Zr and Hf. Experimental conditions: [KF], = 1.5 M , [HCl], = 10 %, [Toluene], = 5 - 50 %, contact time 15 min, 2-octanol, A/O ratio 1:1.
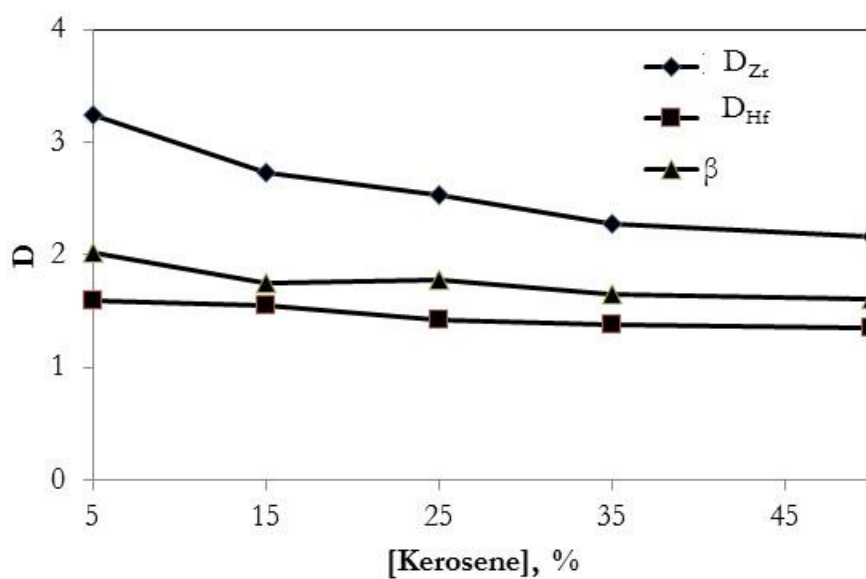
Figure 5-16: Effect of kerosene on the separation efficiency of Zr and Hf. Experimental conditions: [KF], = 1.5 M , [HCl], = 10 % , [Kerosene], = 5 - 50 %, contact time 15 min, 2-octanol, A/O ratio 1:1.
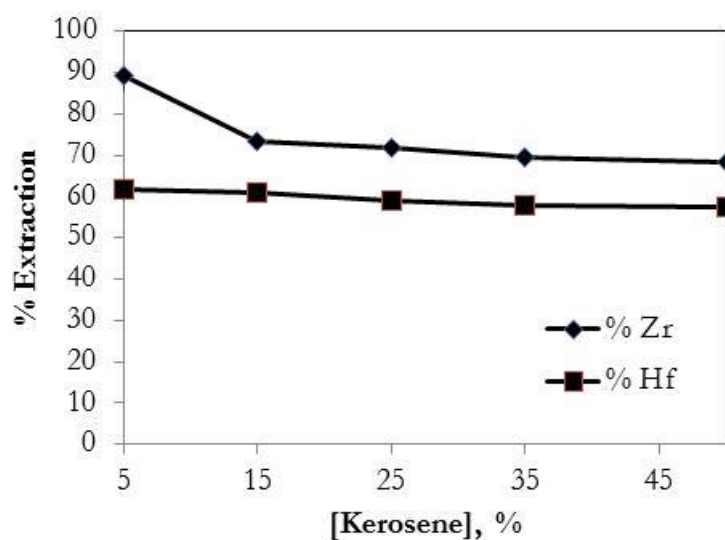
Figure 5-17: Effect of kerosene concentration on the extraction efficiency of Zr and Hf. Experimental conditions: [KF], = 1.5 M, [HCl], = 10 %, [Kerosene], = 5 - 50 %, contact time 15 min, 2-octanol, A/O ratio 1:1.
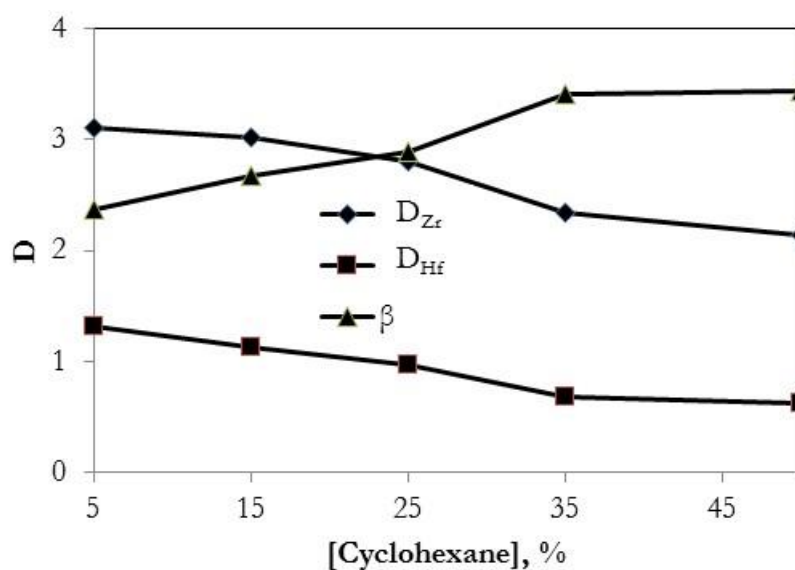
Figure 5-18: Effect of cyclohexane concentration on the separation efficiency of Zr and Hf. Experimental conditions: [KF], = 1.5 M, [HCl], = 10 %, [Cyclohexane], = 5 - 50 %, contact time 15 min, 2-octanol, A/O ratio 1:1.
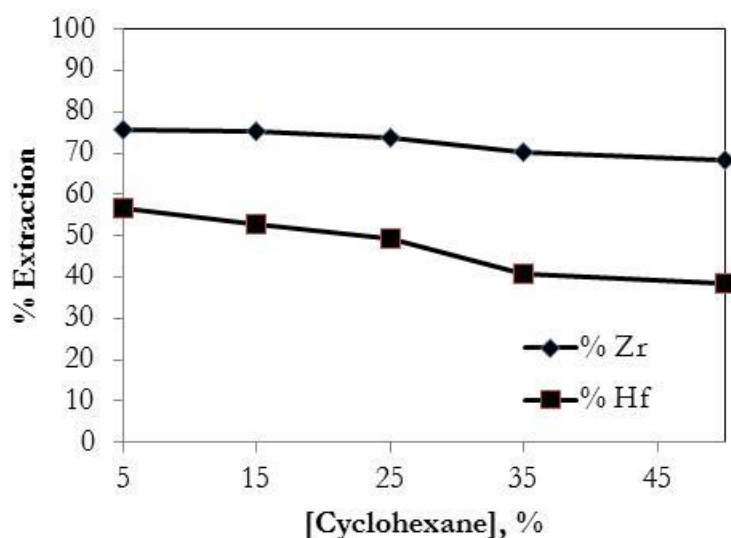
Figure 5-19: Effect of cyclohexane concentration on the extraction efficiency of Zr and Hf. Experimental conditions: [KF], = 1.5 M, [HCl], = 10 %, [Cyclohexane], = 5 - 50 %, contact time 15 min, 2-octanol, A/O ratio 1:1.

5.1.3.8 Loading capacity

The loading capacity of 2-octanol was investigated by repeatedly shaking 2-octanol with equal volumes of the aqueous solution (zirconium basic carbonate dissolved in 10 % HCl + 3 M KF) containing 3698.17 mg/L of Zr and 85.44 mg/L of Hf for 15 min. After equilibrium was reached, the organic and aqueous phases were separated. The concentrations of Zr and Hf in the aqueous phase were determined using ICP-OES. The amount of Zr and Hf transferred into the organic solvent (2-octanol) in each experiment was calculated by difference. It was found that the organic phase was nearly saturated with the metal after eleven contact stages for Zr and seven contacts stages for Hf. The extraction capacity of 2-octanol is 13712.99 mg/L for Zr and 184.07 mg/L for Hf respectively. These quantities remained constant during any further contact with other Zr and Hf aqueous phases solutions.

5.1.3.9 McCabe-Thiele diagrams

McCabe-Thiele diagrams were constructed to determine the number of stages needed to reach the desired separation of Zr from Hf. In this study, the equilibrium data were obtained at different A/O volume ratio, using optimum extraction conditions as determined above. As seen from the McCabe Thiele diagram for Zr (Figure 5-20), four equilibrium stages are required 96.58 % Zr extraction.
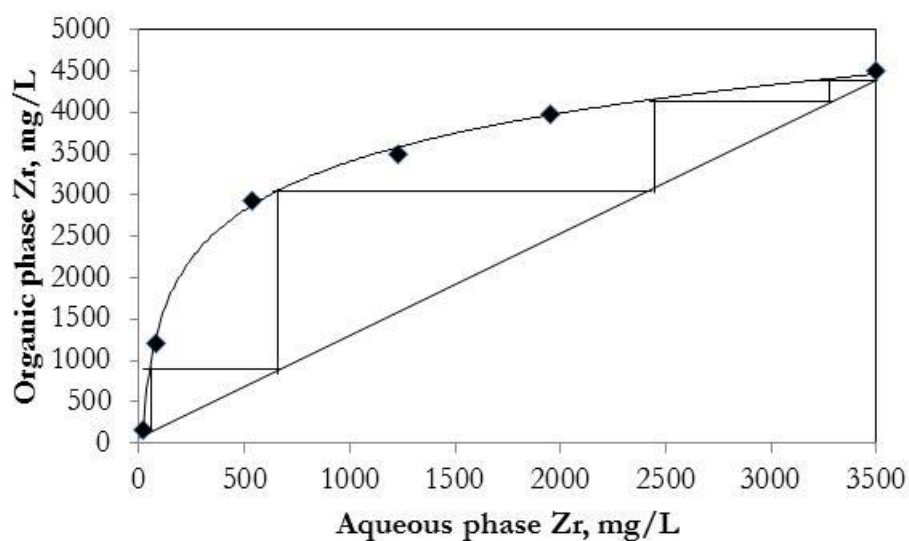
Figure 5-20: McCabe-Thiele diagram of Zr extraction. Experimental conditions: 100 % 2-octanol, A/O ratio 1:1 to 1:5, contact time 15 min.

5.1.3.10 Effect of stripping agent

The effect of stripping agents was studied using different stripping agents (distilled H_2O, H_2SO_4, $(NH_4)_2SO_4$, and HCl), at a ratio A/O of 1:1, keeping the concentration of the stripping agent and other factors constant. The results obtained are given in Figure 5-21 and show that the stripping efficiency of zirconium and hafnium greatly depend on the stripping agent used. The best stripping

agent for zirconium was found to be H_2SO_4 which around 44.48 % of Zr was stripped from the loaded 2-octanol.
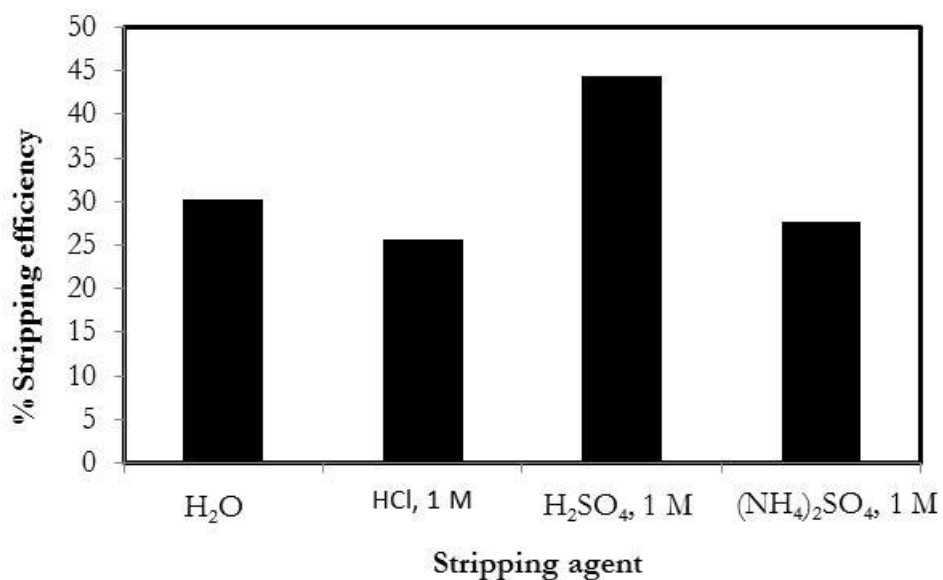
Figure 5-21: Effect of stripping agent on the stripping of Zr from loaded 2-octanol. Experimental conditions: contact time = 15 min, A/O ratio 1:1.

5.1.3.11 Effect of sulfuric acid concentration on the stripping efficiency of zirconium

The effect of sulfuric acid concentration was studied between 1 M and 5 M. Figure 5-22 shows that the stripping efficiency increases with increasing acid concentration from 1 M - 3 M (44.48 - 81.20 % S) and then decreases. Thus 3 M of H_2SO_4 was considered to be the optimum stripping concentration.
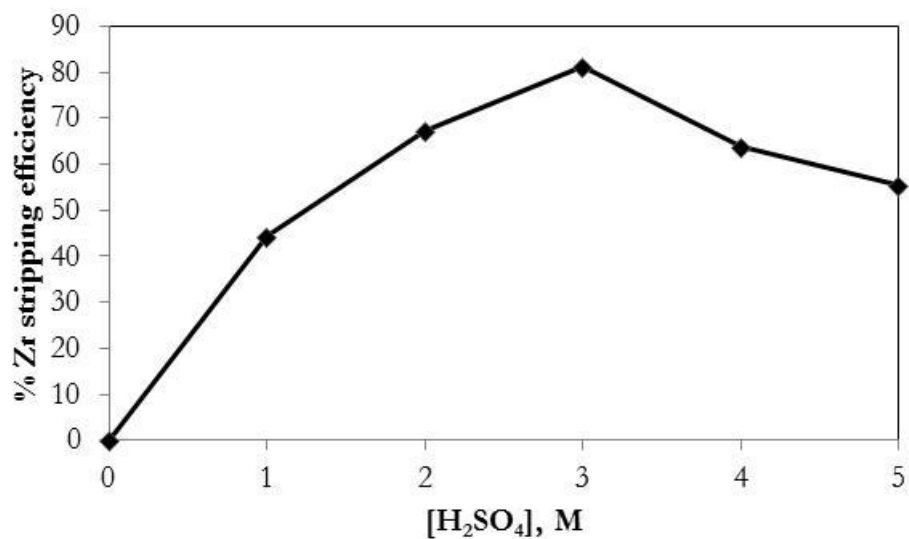
Figure 5-22: Effect of sulfuric acid concentration on the stripping of Zr from loaded 2-octanol. Experimental conditions: contact time 15 min, A/O ratio = 1:1, [H_2SO_4], = 1 - 5 M.

5.1.3.12 Effect of contact time

The effect of contact time on the stripping was studied at different contact times, between 10 and 60 min, while other factors were kept constant; i.e. using an A/O phase ratio of 1:1, and 3 M H_2SO_4 as the stripping agent. The stripping efficiency increased considerably with increased time. From the results obtained and shown in Figure 5-23, an optimum stripping efficiency is achieved after 40 min.
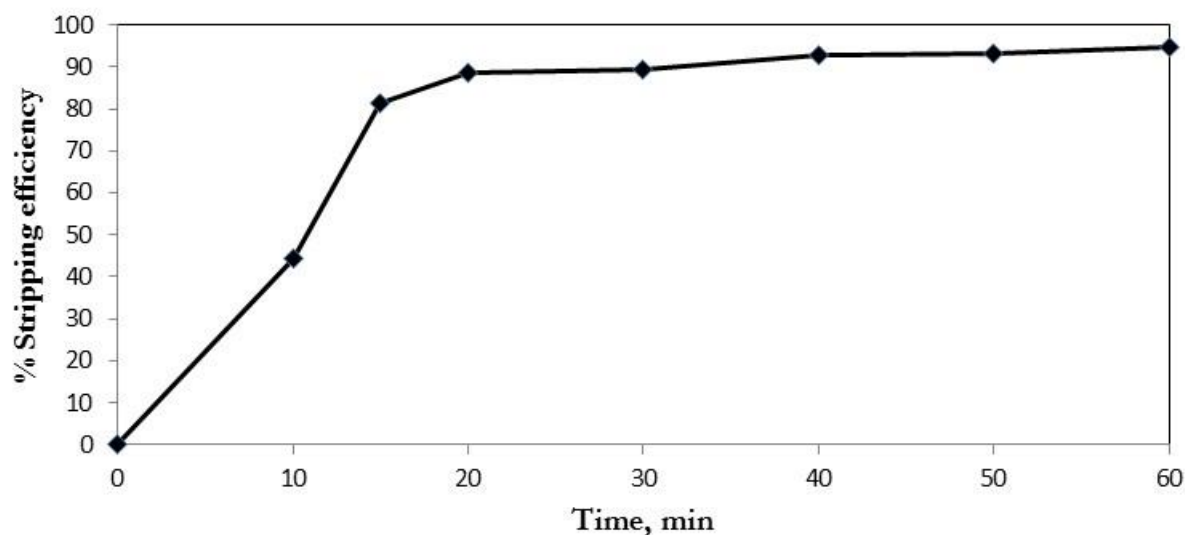
Figure 5-23: Effect of contact time on stripping efficiency of Zr. Experimental conditions: A/O ratio 1:1, contact time 0 - 60 min, [H$_2$SO$_4$], = 3 M.

5.1.3.13 McCabe Thiele for the stripping of zirconium

The data for the construction of the McCabe-Thiele diagram were obtained by shaking different volumes of Zr loaded solvent with a fixed volume of sulfuric acid (3 M) for 40 min until equilibrium was obtained. From this McCabe-Thiele diagram, presented in Figure 5-24, it is clear that five stages are sufficient for stripping around 98.52 % of Zr from loaded 2-octanol.
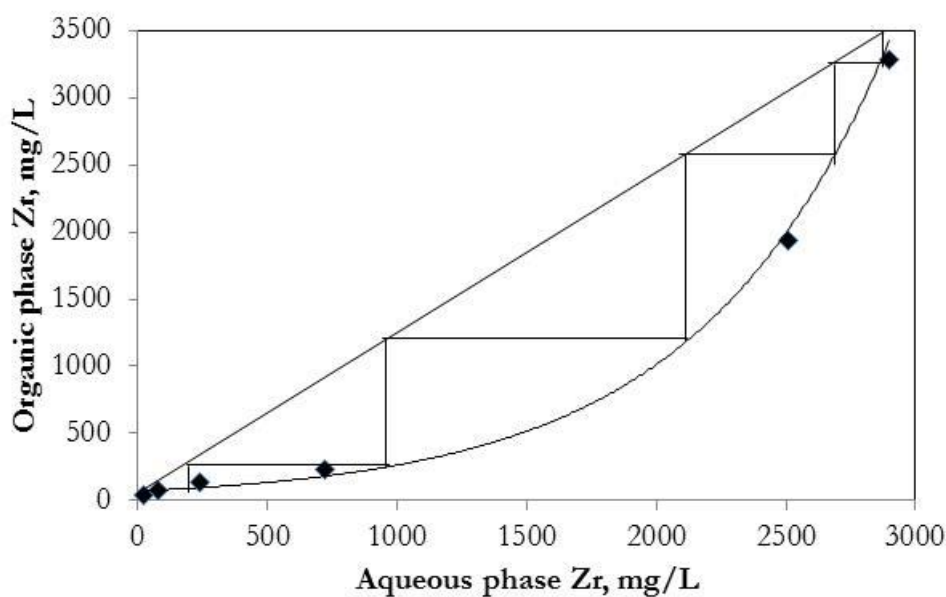
Figure 5-24: McCabe-Thiele diagram for the stripping of Zr from loaded 2-octanol

5.1.3.14 Precipitation and characterisation of zirconium

The loaded stripped zirconium solution was neutralised by adding 25 % ammonium hydroxide up to a pH 9 to precipitate zirconium hydroxide. After filtration, the precipitate was dried in the oven. The dried precipitate was then put into a porcelain crucible and placed in the furnace at 600 ℃ for 3 h. After calcination, the product obtained was characterised using XRD and SEM-EDS as shown in Figure 5-25, Figure 5-26, Figure 5-27, Figure 5-28 and Figure 5-29. XRD analysis showed that the synthesised product consisted of only three phases: zirconium oxide as the major phase and small amounts of potassium and hafnium oxides (JCPDS file 01-083-0942). The SEM-EDS result also indicates a high presence of zirconium and traces of hafnium and potassium. The presence of potassium may be attributed to the potassium fluoride used in this process which was not completely removed during the extraction and washing process.

Figure 5-25: X-ray patterns of synthesised zirconium oxide. The elemental symbols all refers to the oxides
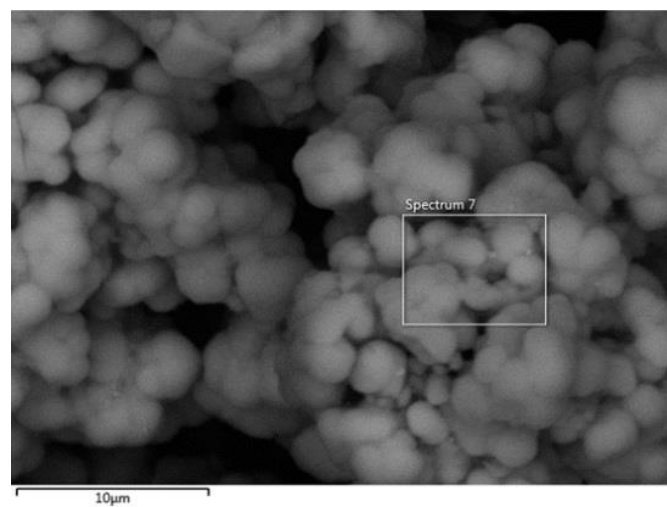
Figure 5-26: SEM results of synthesised ZrO_2
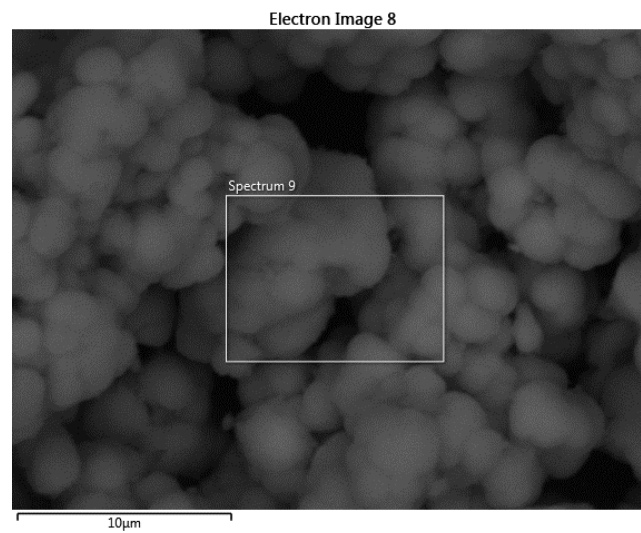
Figure 5-27: SEM result of pure ZrO$_2$
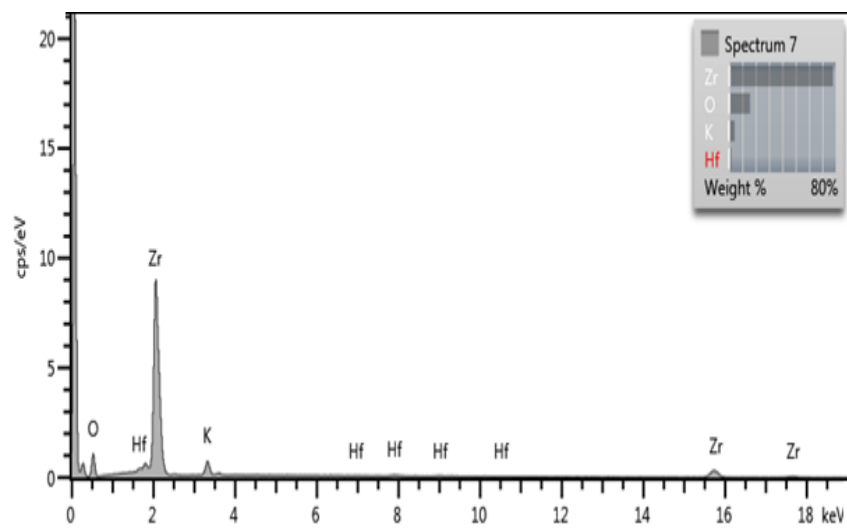
Figure 5-28: EDS spectrum of synthesised ZrO$_2$
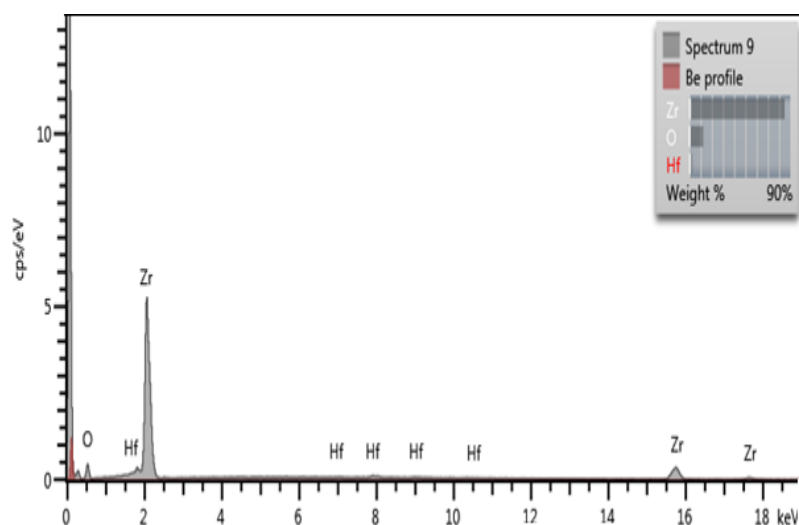
Figure 5-29: EDS spectrum of pure ZrO_2

5.1.3.15 Recovery of Hf

After Zr had been stripped from the loaded organic solvent, the solution was scubbed with 3 M H_2SO_4 at an A/O ratio of 1:1 in order to remove the traces of Zr. Thereafter Hf was recovered by stripping the remaining loaded Hf organic solution with a mixture of oxalic acid and nitric acid. The results obtained indicate that a mixture of oxalic and nitric acid can be considered as a good stripping agent for Hf as it appears to lead to a good separation of Hf from the remaining Zr. Therefore, stripping with different concentrations of a mixture of oxalic acid and nitric acid was investigated. The results obtained are shown in Table 5-6. A concentration of 0.5 M oxalic acid and concentrated nitric acid was chosen as a good stripping agent. It gave 50.68 % Hf and 23.83 % Zr after one stripping stage. After two stages, the stripping percentage increased to 73 % Hf and 28,68 % Zr, and after three stages 97.25 % Hf and 31.92 % Zr were stripped, which led to a good separation of the two metals ions.

Table 5-6: Stripping of Hf and Zr after one stripping stage with a mixture of oxalic acid 0.5 % and nitric acid M = 1 to 15.7

Oxalic acid, %	HNO$_3$, M	% Hf	% Zr
0.50	1	2.48	0.86
0.50	3	6.91	2.55
0.50	6	14.74	8.74
0.50	9	18.15	10.62
0.50	11	26.38	18.64
0.50	15.7	50.68	23.83

5.1.3.16 Precipitation and characterisation of hafnium

The loaded stripped hafnium solution and the aqueous phase after extraction of zirconium, were mixed. The solution obtained was neutralised by adding 25 % ammonium hydroxide up to a pH of 9 to precipitate hafnium hydroxide. After filtration, the precipitates were washed with hot water and dried in the oven. The dried precipitates were put into a porcelain crucible and placed in the furnace at 600℃ for 3 h. After calcination, the product obtained was characterised using XRD and SEM-EDS as shown from Figure 5-30 to Figure 5-34. XRD analysis showed that the synthesised product consists only of three phases: zirconium oxide as the major phase and small amounts of potassium and hafnium oxides (JCPDS file 01-083-0942). The SEM-EDS results also indicate a high presence of hafnium and traces of zirconium and potassium. The high presence of potassium may be attributed to the potassium fluoride solution used in the extraction process which was not removed during the extraction process or washed out completely before the precipitation process.
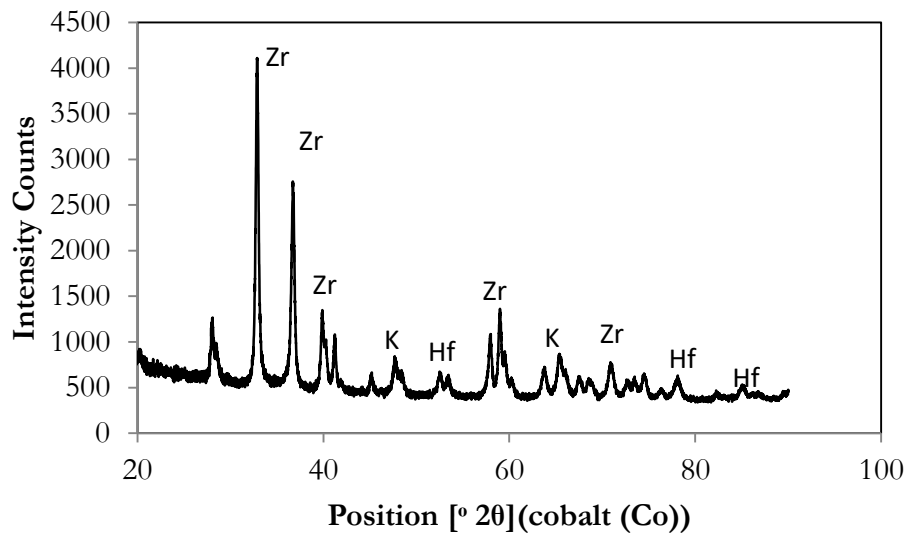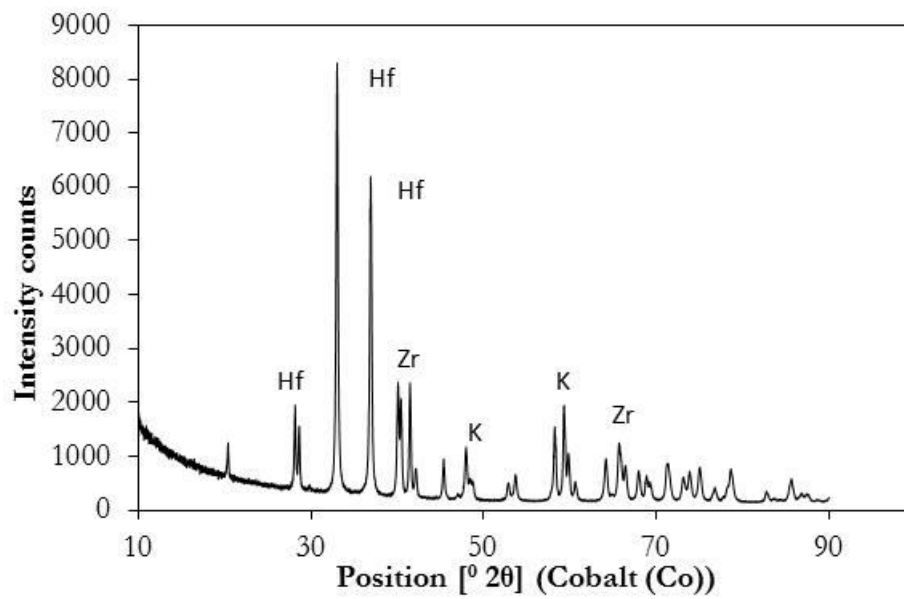
Figure 5-30: X-ray patterns of synthesised hafnium oxide. The elemental symbols all refers to the oxides
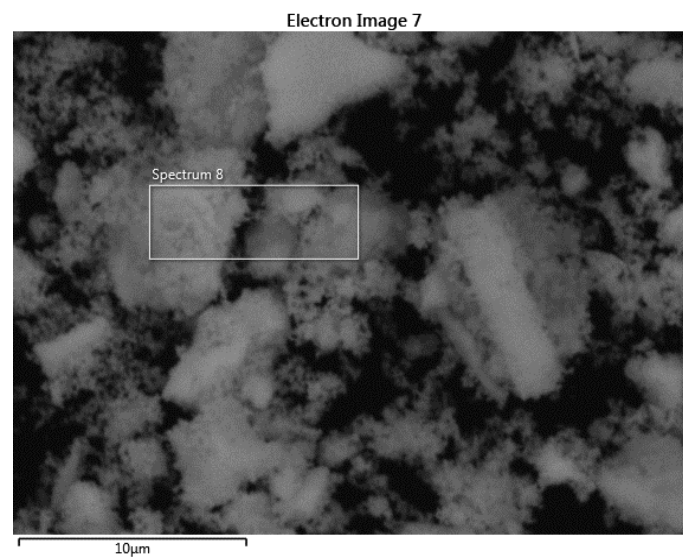

Figure 5-31: SEM results of pure HfO_2
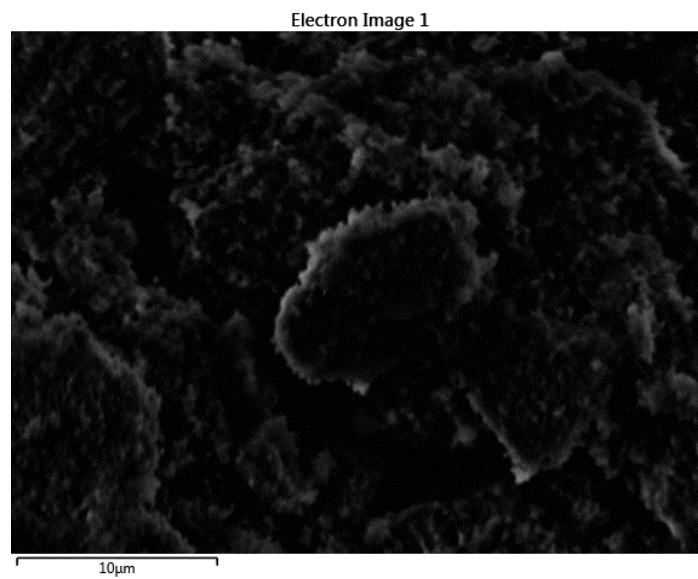
Figure 5-32: SEM results of synthesised HfO_2
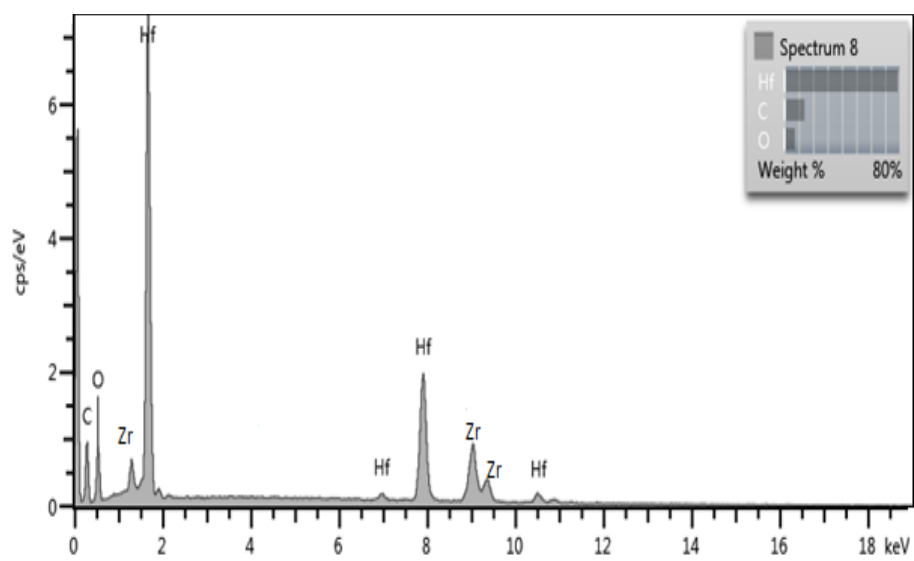
Figure 5-33: EDS spectrum pure HfO_2
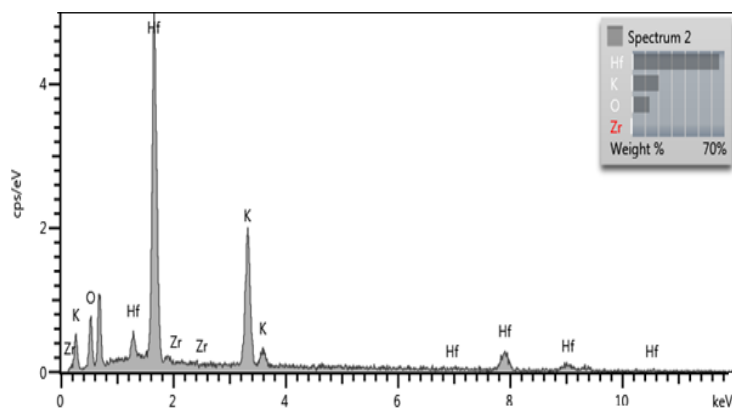
Figure 5-34: EDS spectrum of synthesised HfO_2

5.1.3.17 Summary of the process

The proposed technical flow sheet for the extraction and separation of Zr from Hf starting with zirconium basic carbonate as feed solution and using 2-octanol as extractant is summarised in the Figure 5-35.

Zirconium basic carbonate was decomposed in 10 % HCl then a predetermined concentration of 1.5 M potassium fluoride was added to the decomposed solution. The solution from the decomposition process was contacted with a 100 % 2-octanol at an aqueous and organic phase ratio of 1:2. After extraction of Zr, the solution was stripped with a solution of 3 M H_2SO_4 at a ratio of 1:1. The loaded Zr solution was then neutralised with 25 % ammonium hydroxide in order to precipitate Zr. The precipitate solution obtained was washed with water in order to remove the excess of potassium fluoride. The washed solution was then calcined at 600 ℃ for 3 h in order to obtain a pure zirconium oxide.

The loaded Hf solution from the stripping of Zr was then scrubbed with a solution of 3 M H_2SO_4 at a ratio of 1:1 to remove the remaining Zr solution. The loaded Hf solution was then stripped with a mixture of oxalic and nitric acid at a ratio A/O of 1:1. The stripped solution was then precipitated using a 25 % NH_4OH solution. After washing the precipitate with hot water the solution was calcined at 600 ℃ for 3 h. After calcination a pure hafnium oxide was obtained.
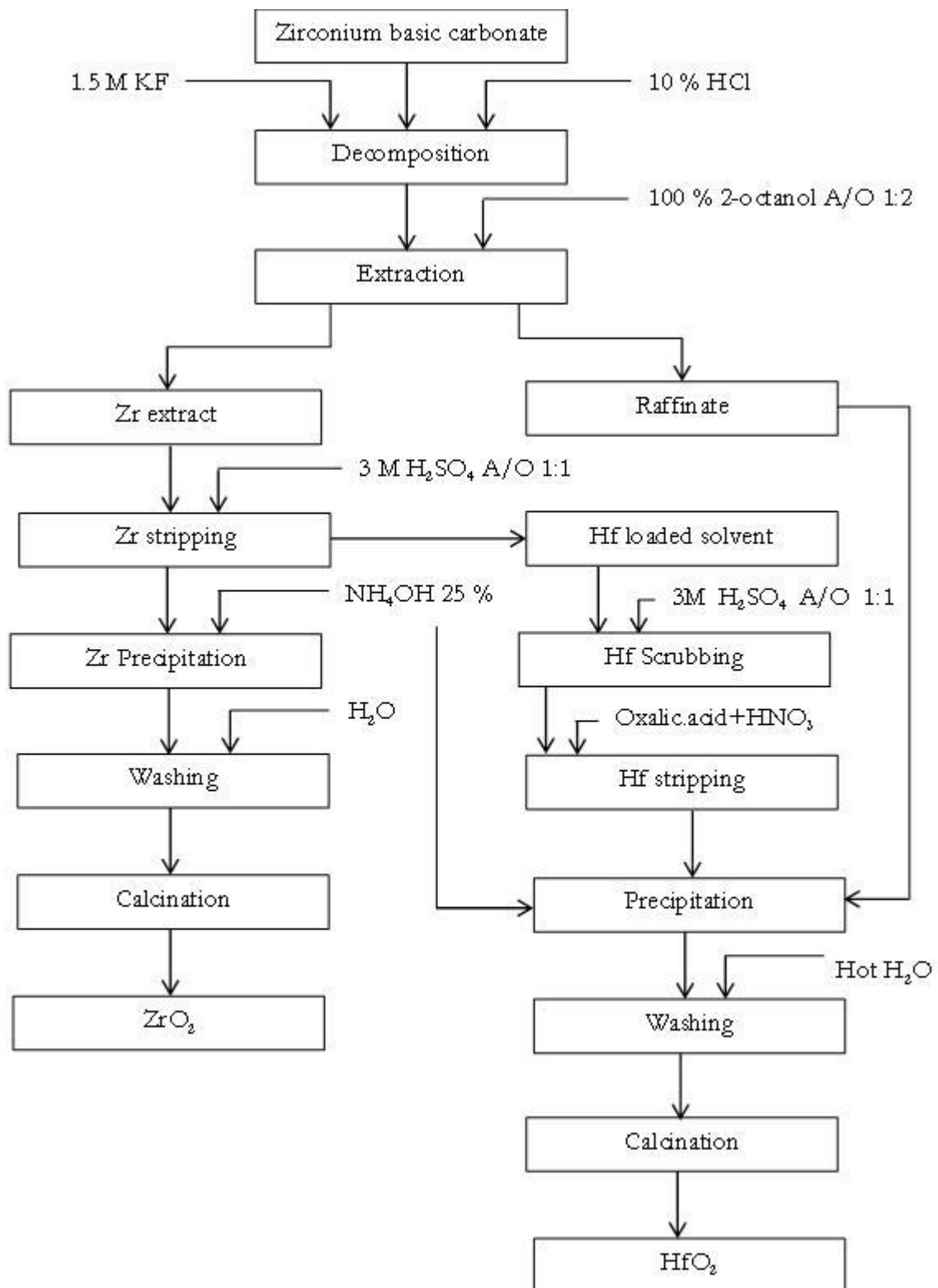
Figure 5-35: Proposed technical flow sheet for the extraction and separation of Zr/Hf

5.1.3.18 Extraction and separation of Zr and Hf using other raw materials

In order to observe any additional differences or improvements in the extraction and separation of zirconium from hafnium, another starting material was used. The feed used was zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$).

5.1.3.19 Extraction of Zr and Hf from zirconium oxychloride

Zirconium oxychloride was dissolved in distilled water. A predetermined concentration ranging from 1 - 10 M of HCl was added to the solution. The concentration of the feed solution obtained was adjusted by adding a 1.5 M of potassium fluoride in order to abtain an aqueous phase which would be ready for liquid-liquid extraction. The aqueous phase was contacted with an organic solvent (2-octanol) for the extraction. The extraction was carried out at an A/O phase ratio of 1:1 at room temperature ($\sim 25\,°C$) for 15 min. The results in Figure 5-36 indicate that at low HCl concentration, the percentage of Zr and Hf extracted increases at the same rate. Consenquently, the separation factor between the two metals decreases. At high HCl concentration, the percentages of Zr and Hf extracted increase at different rates. The extraction percentage of Zr increases faster than the percentage of Hf, which increases the separation factor between the two metals. The highest separation factor obtained was 6.35, with an extraction efficiency of 91.15 % for Zr and 62.18 % for Hf.
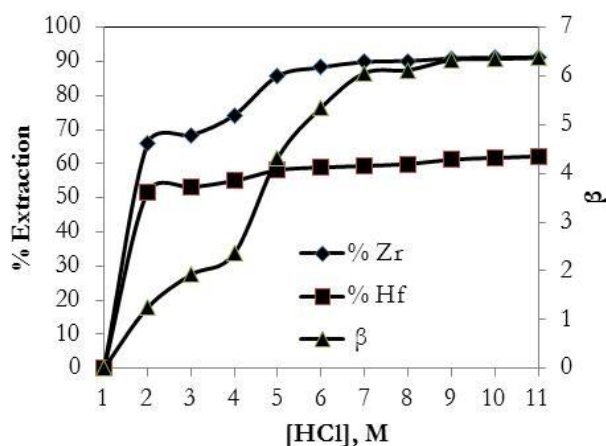
Figure 5-36: Effect of HCl concentration on the extraction of Zr and Hf from $ZrOCl_2 \cdot 8H_2O$. Experimental conditions: 100 % 2-octanol, [HCl], = 1 to 10 M, A/O ratio 1:1

5.1.3.20 Synergism and mixed extractants

The phenomenon whereby a solvent extraction process of metal chelate having an excess of coordination sites is markedly enhanced by the addition of a neutral ligand forming adduct complexes in the organic phase is known as "synergistic extraction". Synergism can be defined as co-operation between two extractant molecules to transfer metal ions from the aqueous to the organic phase in order to satisfy both the solvation and co-ordination sites of the cation and neutralise charge, while another less sterically demanding extractant or synergist, may serve to replace water, or to occupy open co-ordination sites (Roshni et al., 2014). In this way two extractants work together to improve or increase the extraction. It must be mentioned that the opposite phenomenon, i.e reduction in the extraction efficiency in the presence of mixed extractants is known as "antagonism". The first investigation into synergism was carried out by Blake et al, in 1955, who found that U(IV) is extracted synergistically by a mixture of dialkyl-phosphoric acid and a neutral organophosphorus reagent.

Many mixed extractant systems have been investigated in order to take advantage of this phenomenon, expecially for the extraction of actinide elements in the nuclear industry. Many examples of synergism have been found. For example, the synergistic extraction of Zr(IV) and Hf(IV) from 0.2 mol/dm^3 hydrochloric acid solutions with a mixture of H$_2$SbBP (4-sebacoylbis(1-phenyl-3-methyl-5-pyrazolone) (0.01 - 0.03 mol dm^{-3}) and TOPO (tri-n-octylphosphine) (0.01 - 0.03 mol/dm^3) or TBP (tri-n-butylphosphate) (0.01 - 0.03 mol/dm^3) into chloroform was investigated and the results indicated the the extraction of Zr(IV) and Hf(IV) with the above neutral organophosphorus extractant was negligible. However, with a mixture of H$_2$SbBP and a neutral organophosphorus extractant, a considerable synergistic enhancement in the extraction of Zr(IV) and Hf(IV) was observed (Janardhan et al, 2006).

The chemistry involved in most of the synergistic extractions is very complex, and not well understood. It certainly appears that mixed extractant systems can offer much in the way of enhancing the separation of metals, and increasing solvent loading. Another reason for the use of mixed extractant systems lies in the simultaneous extraction of both a cation and an anion (Osman, 2006).

5.1.3.21 Effect of MIBK on the separation factor of Zr and Hf (synergistic effect)

A solution of MIBK was added to the solution of 2-octanol in different amount from 10 % - 50 %. Table 5-7 and Figure 5-37**Error! Reference source not found.** show that with an increase in the percentage of MIBK added, there is a decrease in the distribution coefficient of both Zr and Hf, while the separation factor between the two metals also decreases. This indicates that at lower MIBK concentration, the separation factor between Zr and Hf is slightly higher when compared to the extractaion of both metals using 100 % octanol as an extractant. However, there is a decrease in the separation factor when 20 % - 50 % of MIBK solution is added. The effect of synergism was not observed.

Table 5-7: Effect of MIBK concentration on the separation factor of Zr and Hf

% MIBK	% Zr	% Hf	D_{Zr}	D_{Hf}	β
10	91.01	51.89	10.12	1.07	9.38
20	86.09	43.50	6.19	0.77	8.04
30	85.23	44.04	5.77	0.79	7.33
40	82.57	43.00	4.74	0.76	6.28
50	78.74	37.35	3.70	0.60	6.19
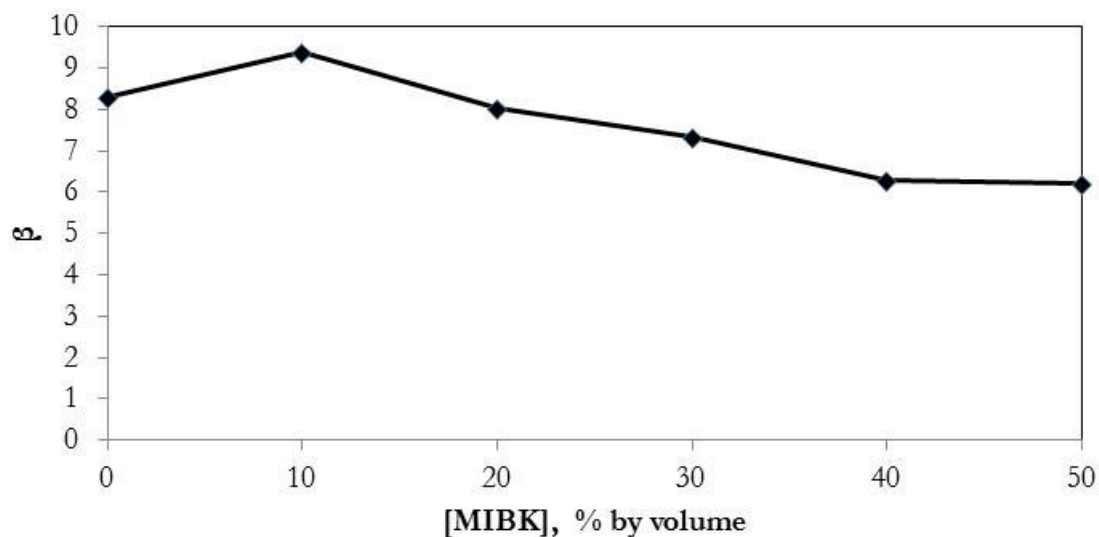
Figure 5-38: Effect of MIBK concentration on the separation of Zr and Hf. Experimental conditions: [HCl] = 10 %, contact time 15 min, A/O ratio = 1:1, [MIBK], = 10 - 50 %

5.1.3.22 Effect of TBP on the separation of Zr and Hf (synergistic effect)

A solution of TBP was added to the solution of 2 octanol in different amount from 10 % - 50 %. Table 5-8 and Figure 5-39**Error! Reference source not found.** show that when the percentage of TBP added is increased, there is a very low distribution coefficient for both Zr and Hf, which also reduces the separation factor between the two metals compared to the MIBK process.

The extraction percentages of both zirconium and hafnium are very low compared to the MIBK process. This indicates that TBP is antagonistic at the concentration investigated.

Table 5-8: Effect of TBP concentration on the separation factor of Zr and Hf

% TBP	% Zr	% Hf	D_{Zr}	D_{Hf}	β
10	68.15	55.89	2.14	1.27	1.69
20	56.72	48.53	1.31	0.94	1.39
30	51.28	45.64	1.05	0.84	1.25
40	47.59	42.68	0.91	0.74	1.23
50	40.86	38.35	0.69	0.62	1.11
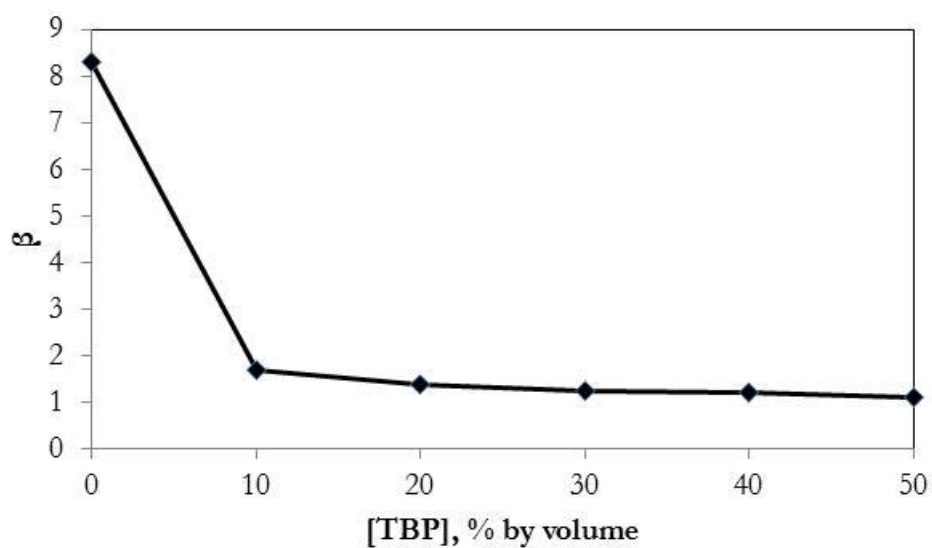
Figure 5-39: Effect of TBP concentration on the separation of Zr and Hf. Experimental conditions: [HCl], = 10 %, contact time 15 min, A/O ratio = 1:1, [TBP], = 10 - 50 %

5.2 Packed column results and discussion

This section presents the results on the extraction and separation of Zr and Hf using a packed column. In order to optimise the extraction process, different parameters, such as the effect of time, the effect of flow rate were investigated and empirical equation were used to determine the mass transfer of the dispersed and the continuous phase.

5.2.1 Effect of time

As stated previously in Section 5.2.1, it is important to ensure that equilibrium between the phases is reached in all the experiments. Therefore, it is necessary to determine the time required to established equilibrium. This is done by investigating the feeding rate into the column, the light solvent phase at the bottom, and the heavier pregnant liquor stream at the top. Due to the difference in density between the two phases, the heavier pregnant stream will settle to the bottom and the solvent will rise to the top. The counter-current flow of these phases, together with the applied pulsation action, will create turbulence within the column, resulting in intimate contact between the two phases. After a predetermined interval of time, the aqueous solution is collected and analysed to determine the amount of zirconium and hafnium extracted. According to the results shown in Figure 5-40 and Figure 5-41, both the extraction percentage and the separation factor between zirconium and hafnium increases with the increases in time. The required minimum time to achieve equilibrium was found to be 180 min, resulting in an extraction percentage of 91.75 % Zr and 54.41 % Hf, with a separation factor of 9.34. Extending the time did not significantly affect the extraction of either zirconium or hafnium. The highest separation factor between zirconium and hafnium obtained was 10.41.
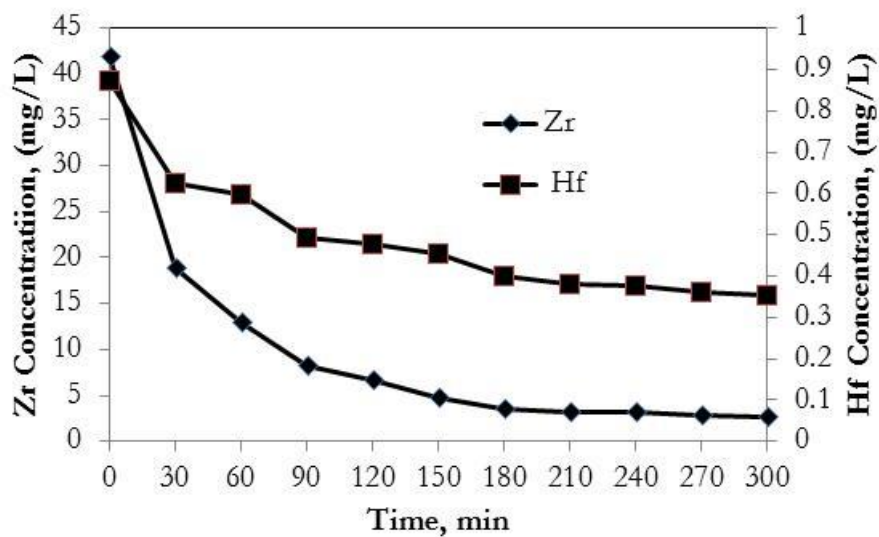
Figure 5-40: Effect of contact time on the extraction of Zr and Hf
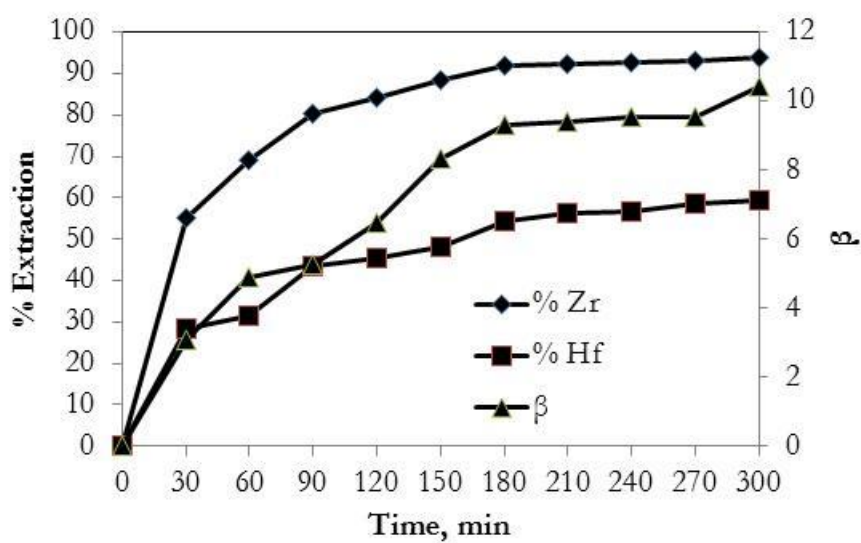
Figure 5-41: Effect of contact time on the separation of Zr and Hf

5.2.2 Effect of flow rate

The extraction and separation was investigated with the effect of changing the flow rate of the organic phase whereas the flow rate of the aqueous phase was kept constant at 200 mL/h.

The aim of this study was to investigate the possibility of operating the column under a higher flow rate condition in order to decrease the operating time.

The column was filled with the continuous aqueous phase. The pumps were started and the flow rate of both phases adjusted. Then both phase were fed into the column at a specified throughput, between 200 mL/h and 1400 mL/h for the organic phase and 200 mL/h for the aqueous phase. After a set period of time, depending on the flow rate to ensure that the hydrodynamic conditions were reached, the aqueous phase samples were taken for analysis.

It was noticed that at all the flow rates investigated, the extraction and separation of Zr and Hf were observed. From these results in Figure 5-42, it can been seen that the separation of Zr and Hf depends on the variation of the flow rate. To maintain a higher separation efficiency between Zr and Hf a flow rate of 600 mL/h was selected. The separation efficiency between Zr and Hf increases with the increase of the flow rate, then decreases at higher flow rate. This might be probably because of the fact that the residence time of phase is lower at a higher flow rates.
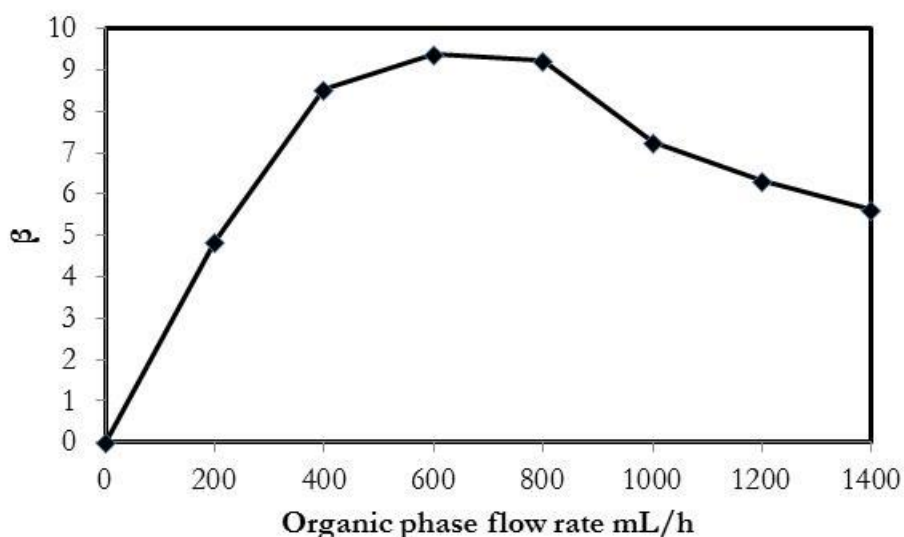
Figure 5-42: Effect of organic flow rate on the separation efficiency of Zr from Hf

5.2.3 Effect of aqueous to organic phase ratio

The study of the effect of aqueous to organic phase ratio were conducted at previous determined flow rate of 200 mL/h for the aqueous phase and 600 mL/h for the organic phase. The volume of aqueous phase was kept constant whereas the volume of the organic phase was varied from a ratio of A/O of 1:1 to 1:5. The results in Figure 5-43 indicated that increasing the phase ratio increases the extraction and separation of both metals. This result was consistent with the theory of extraction described by the Equation 3.2 which can be interpreted as to increase the amount of substance extracted, the volume of the extracting solvent can be increased. Sadigzadeh et al (2009) also find similar trends when extracting zirconium from nitric-hydrochloric acid solutions using TBP.
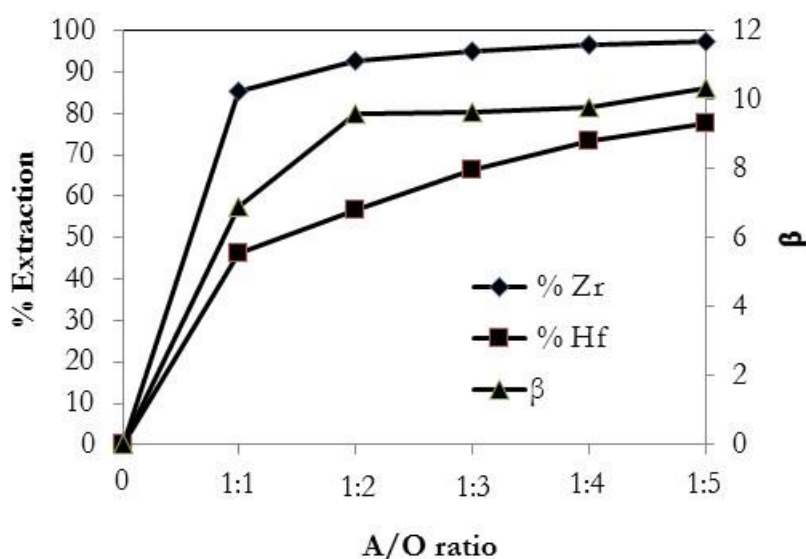
Figure 5-43: Effect of aqueous to organic phase ratio

5.2.4 Evaluation of the performance of the extraction column

The design of an extraction column that will meet the requirements of the process, necessitates knowledge of the phase equilibrium, mass transfer and hydraulic performance of an extraction column. The design of a continuous multistage contacting device, required the calculations and predictions needed for the commercial application of Zr and Hf extraction.

From the equilibrium data obtained from the column experiments, the data in Table 5-9 were used to calculate different parameters.

Table 5-9: Equilibrium data obtained from the column test

Equilibrium data	Values
X_f Feed (mg/L)	4285.52
X_r raffinate (mg/L)	257.42
Y_e extract (mg/L)	4028.10
Y_s solvent (mg/L)	0
K	15.65

The height of the column was (Z_t) 1.20 m.

The experimental data obtained give a distribution coefficient (K) of 15.65. This value was introduced into the Kremser Equation (3.31) in order to determine the theoretical number of stages, which was calculated to be 2.55. The height equivalent to the theoretical number of stages could then be calculated from Equation (3.34).

HETS = 1.2/2.55 = 0.47 m.

The effect on the column performance can be calculated by changing the individual input variables. For an extraction efficiency of 99.99 % for Zr, using the same operating conditions, the theoretical number of stages required is 5.76.

There are three different ways that can be used to obtain a better theoretical number of stages.

Fistly, the height of the existing column can be increased. Therefore, using the same operating conditions, the required height of the extraction column to achieve an extraction efficiency of 99.99 % of Zr, can be calculated as follows:

$Z_t = 0.47 \times 5.76 = 2.70$ m.

Secondly a more efficient column design can be used, and thirdly, the efficiency of the exiting column can be increased.

In order to change the first two options, modification of the exiting column will be required, while the third option will necessitate extensive pilot plant studies. It seems that it is very difficult to obtain an extraction efficiency of 99.99 % Zr, unless more theoretical numbers of stages are added to the exiting column. One of the options to improve the theoretical number of stages is by changing the phase ratio between the organic and the aqueous phase. Another option is by using a more efficient column than the packed column.

5.2.5 Prediction of diffusion coefficient and calculation of mass transfer for the dispersed phase

Different equations for the calculation of the diffusion coefficient mentioned in the literature (Section 3.4.2) were used to determine the latter. According to the results obtained, the mass transfer coefficient was predicted for droplets of minimun and maximum size. Figure 5-44 shows the different sizes of the droplets of the extraction process using the column and the droplets sizes, varies between 1.5 mm - 3 mm.
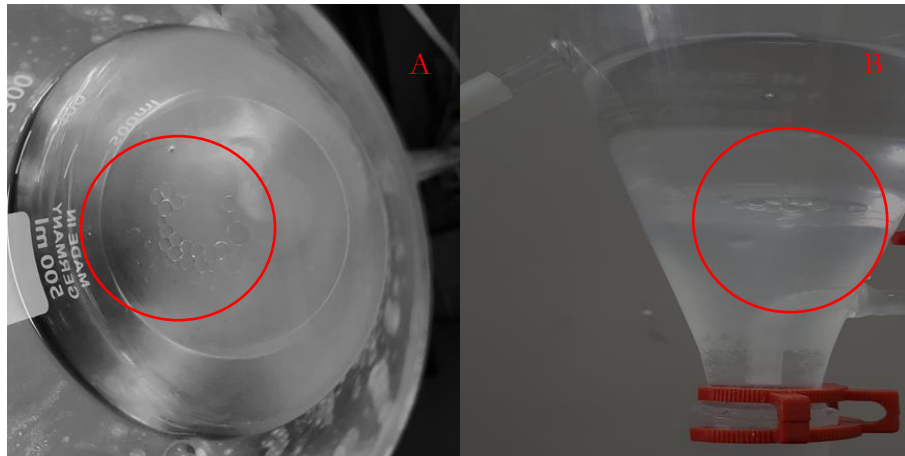
Figure 5-44: Photograph of the droplets, (A) Top view and (B) Front of the column (red circle show the droplets).

The dispersed phase mass transfer coefficient was calculated from Equation 3.11 for a minimum and maximum droplet size using the stagnant droplet mechanism. The diffusion coefficient needed for this calculation was predicted by the three correlations of Wilke-Chang, Stokes-Einstein and Polson. The physical properties of the solvent used are T = 25 ℃ , μ = 6.2 x 10^{-2} kg/m.s, V_a = 1.58 x 10^{-4} m³/kmol and M_B = 130.23 kg/kmol. The results obtained are summarised in the Table 5-10.

Table 5-10: Prediction of diffusion coefficient

Predicted by correlation	Wilke-Chang	Stokes-Einstein	Polson
D_d [m²/s]	1.40 x 10^{-8}	8.86 x10^{-11}	8.36 x 10^{-10}
K_d [m/s] for d_{min}	1.38 x.10^{-10}	8.73 x 10^{-13}	8.24 x 10^{-12}
K_d [m/s] for d_{max}	2.76 x 10^{-10}	1.75 x 10^{-12}	1.65 x 10^{-11}

The results obtained indicate that an increase in droplet size resulted in an increase in the mass transfer coefficient. It was also observed that the value obtained using the Stokes-Einstein and Polson correlations are lower than those calculated by the Wilke-Chang correlation.

5.2.6 Calculation of mass transfer coefficient for the continuous phase

The calculation of the mass transfer coefficient for the continuous phase required some assumptions, such as that the molecular weight of the continuous solution would have the same molecular weight as pure water. The other physical properties required for the calculation of mass transfer was measured in the solution. Prior to the calculation of the overall mass transfer coefficient for the continuous phase, it is necessary to determine some dimensionless numbers such as the Schmild (Sc), Reynolds (Re) and Sherwoord (Sh) numbers. These numbers were calculated using the differents equations given in the Section 3.4.2.2. The physical properties of the mixture required for the calculation of mass transfer are shown in the Table 5-11.

Table 5-11: Physical properties of the mixture of aqueous and organic phase

Physical properties	value
ρ (kg/m^3)	1923
μ (kg/ms)	14 x 10^{-3}
U(m/s)	11.89 x 10^{-2}

The Reynolds number (Re) was calculated to be 245 using the data from Table 5-11. The results obtained from the calculation are summarised in Table 5-12.

The results for the overall mass transfer coefficient for the continuous phase indicated that increase in droplet size resulted in a decrease in the overall mass transfer coefficient. The values

obtained using Wilke-Chang correlation are higher compared to the values obtained using the Stokes-Einstein and Polson correlations.

Table 5-12: Calculation of overall mass transfer

Predicted by correlation	Wilke-Chang	Stokes-Einstein	Polson
D_c [m²/s]x 10^{-9}	1.28	0.10	1.10
Sc_c	4464.28	48840	5194.81
Sh_{oc}	168.13	372	176.79
K_{oc} [m/s] for d_{min} x 10^{-4}	1.44	0.29	1.30
K_{oc} [m/s] for d_{max} x 10^{-5}	7.17	1.45	6.48

By comparing the two methods used in this investigation, the mixer-steller present greater advantage compare to packed column as the process required only few minutes for the extraction and separation of the two metals. In terms of of extraction and separation between the two metals, the packed column gives a slightly better results compared to the mixer-settler. This may be due to the effect long residence time in a mixer-settler which in return causes solvent degradation as a results of radiolysis and hydrolysis.

The first option to improve the extraction and separation using a packed column is to increase the height of the column. In order to reduce the latter, other packing columns such as trays or perforated plates maybe used, as the mechanical energy applied to force the dispersed phase into smaller droplets, will therefore improve the mass transfer resulting in a great extraction and separation of zirconium and hafnium. Therefore a pulsed column maybe the best option in this investigation as it present a clear advantage especially when processing corrosive or radioactive solutions since the pulsing unit can be remote from the column (Asadollahzadeh et al., 2011).

Chapter 6: SUMMARY AND RECOMMENDATION

6.1 Summary

The use of liquid-liquid extraction for the separation of zirconium from hafnium was demonstrated in this study. Zirconium and hafnium have drawn considerable attention in various applications, expecially in the nuclear industry where zirconium is used as a cladding material for nuclear rods and as a structural component for reactor cores, whereas hafnium is used as a material for reactor control rods and for protective screens in reactors. About 90 % of the total amount of zirconium and hafnium produced worldwide is consumed in the nuclear industry and it is the only application that required a hafnium-free zirconium component. However, zirconium and hafnium tend to come in a mixture form. Therefore, there has been great interest in trying to separate them in order to produce pure zirconium and hafnium metals that can be used in the nuclear industy.

The main objective of the work presented in this thesis was to develop an alternative extraction and separation method for zirconium and hafnium which will be economically viable and environmentally friendly.

Zirconium basic carbonate was dissolved using different acids, such as sulfuric acid, nitric acid, hydrofluoric acid and hydrochloric acid, at different concentrations. Potassium fluoride was added to these solutions in order to obtain the aqueous solution for the liquid-liquid extraction. The aqueous solution containing the compounds to be separated, was contacted by an organic solvent in order to separate the two metals. Analysis of the equilibrium phase allowed the calculation of the percentage extracted (% E), the distribution coefficients (D) and the separation factor (β). Modification of the aqueous phase variables, such as acidity of the feed solution, contact time and potassium fluoride concentration, usually affects the value of the percentages of zircomiun and hafnium extracted, the distribution coefficients and the separation factors. The volumetric ratio between the aqueous and organic phases also affects these values. A certain number of equilibrium stages was required in order to establish the optimum range of conditions for the extraction and separation of zirconium from hafnium. These conditions were employed in order to produce a zirconium oxide which contains very little hafnium.

In general, the percentage extracted and the separation factor obtained when extracting zirconium and hafnium from sulfuric acid, hydrofluoric acid and nitric acid media were lower than those obtained by extracting zirconium and hafnium in a hydrochloric acid medium. Consequently, hydrochloric acid was selected as the best dissolving agent in this investigation.

A feed solution containing 3573.46 mg/L of zirconium and 63.93 mg/L of hafnium was obtained by dissolving zirconium basic carbonate in 10 % hydrochloric acid. Then 1.5 M potassium fluoride was added to this solution in order to obtain a feed for liquid-liquid extraction. The latter was contacted with an immiscible organic solvent (1-octanol or 2-octanol) at different organic to aqueous ratios.

In order to make a valid interpretation of the effect of the different experimental parameters, it was necessary to ensure that equilibrium between the organic and aqueous phases was reached in all experiments. According to the results obtained, equilibrium was reached after 5 min, but a maximum value of 15 min was selected for all subsequent experiments.

The results obtained indicated that zirconium was preferentially extracted into the organic phase. Different diluents, such as toluene, kerosene and cyclohexane were tested, but these did not influence or change the extraction or separation of zirconium from hafnium.

It was observed that an increase in the concentration of hydrochloric acid decrease the mass transfer to the organic phase and increase the percentage of zirconium and hafnium extracted, and consequently the separation factor. A concentration of 10 % hydrochloric acid was considered as the optimum value. Further increase of this concentration did not change the percentage extracted or the separation factor.

An increase in the potassium fluoride used has a positive effect on the extraction and separation of the two metals. The results indicate that increasing the concentration of potassium fluoride, increases the percentage of zirconium and hafnium extracted. From further inspection of the results obtained, it was also observed that an increase in potassium fluoride decreases the distribution coefficient of hafnium, while increasing that for zirconium. Therefore, the separation factor increases. A concentration of 1.5 M potassium fluoride was considered as an optimum value. Beyond this value no further changes were observed.

The distribution coefficient and the extraction efficiency of both metals decrease with the increase in temperature. This indicates that a better extraction and separation can be only obtained at a lower temperature.

By varying the phase ratio between the organic and aqueous phases, the separation factor and the extraction efficiency of both metals increase up to a ratio A/O of 1:2, beyond this no further

advantage was observed. From this experiment an extraction percentages of 94.05 % Zr, 64.67 % Hf and 96.85 % Zr and 77.01 % Hf were obtained for respectively 1-octanol and 2-octanol, with separation factors of 8.66 and 9.20 respectively.

McCabe-Thiele diagram of zirconium extraction was constructed using the optimum conditions: 10 % HCl, 1.5 M KF, contact time 15 min, at different A/O ratio from 1:1 to 1:5. The result indicates that four equilibrium stages were necessary for the extraction of zirconium.

Sulfuric acid was found to be the most effective strippint agent for the zirconium-loaded organic phases. Stripping efficiency investigations were done in terms of type of stripping agent, stripping concentration and contact time. The maximum stripping percentage of Zr from the loaded organic phase is obtained with 3.5 M H_2SO_4. The contact time was also investigated and it was found that 40 min was the best condition for 98.52 % stripped Zr. The McCabe-Thiele diagram constructed indicated that five equilibrium stages are required for the stripping of zirconium from the loaded organic solution.

The product obtained after stripping was precipitated using a solution of 28 % ammonium hydroxide. After filtration, the solution was washed with water and calcined in the oven for 3 h at 600 ℃. Using XRD and SEM-EDS analysis, the product obtained was characterised. The results indicated that the zirconium oxide obtained contained a small percentage of hafnium and potassium.

The recovery of hafnium was done by mixing the aqueous solution from the extraction and stripping of zirconium. The solution was first scrubbed using sulfuric acid then stripped for hafnium using different stripping agents. The results indicate that a mixture of oxalic acid and nitric acid was the best stripping agent for hafnium. It also indicated that three equilibrium stages were required in order to obtain 97.25 % hafnium stripped from the loaded organic solution.

The solution obtained was precipitated using a solution of 28 % ammonium hydroxide. After precipitation, the solution was washed using hot water, then calcined for 3 h at 600 ℃. XRD and SEM-EDS analysis was used to characterise the product obtained. The results indicated high presence of hafnium oxide, but the product also contained zirconium and potassium which need to be removed.

Before finalising the extraction process using the mixer-setller and zirconium basic carbonate as the feed solution, any additional difference and improvement in the extraction and separation of zirconium from hafnium with octanol by using zirconium oxychloride as the source of the aqueous feed solution, were investiageted . The results indicated no additional improvement. It was concluded that the use of zirconium basic carbonate as the feed solution gives good results compared to zirconium oxychloride.

Synergistic extraction studies of zirconium and hafnium with octanol in the presence of MIBK or TBP were carried out with a view of enhancing the extraction or separation efficiency of these two metals. When the MIBK/octanol system was used, the results indicated that there is an increase in the separation factor at lower MIBK concentration, then a decrease at higher MIBK concentration. However there is no enhancement of extraction effeciency when compared to the octanol system. This indicate that the effect of synergism was not observed. The results also indicated that there is a decrease in the extraction and separation efficiency in the octanol/TBP system, which means that this system is antagonistic.

The observation from the packed column experiment revealed that the extraction and separation efficiency of zirconium increases with the increase of both the flow rate and phase ratio respectively. The overall mass transfer coefficient for continuous pahse and dispersed phase decrease and increase repecvtively with the increase of droplet size. In order to produce a zirconium of 99.99 purity a 5.76 (6) theoretical number of stages and 2.7 m height equivalent to theoretical number of stage are required.

6.2 Recommendations and future work

- Positive results was obtained from this study, where zirconium and hafnium have been extracted and separated from a rich zirconium solution (zirconium basic carbonate) with octanol showing a high selectivity toward zirconium. Future studies could focus on using zircon, baddeleyite or others zirconium or hafnium salts as starting materials.

- It would be beneficial to obtain a more complete picture of the speciation preference of zirconium and hafnium in the solution in order to improve the extraction, separation, stripping of zirconium and recovery of hafnium. Molecular modelling may be a suitable tool to help unravel the speciation challenge.

- An economic and environmental impact assessment study would be needed to determine the economic viability especially due to the use of potassium fluoride in this process.
- The packed column should be optimised to an industrial scale pilot plant.

6.2.1 Evaluation of the study

The main focus or primary objective of this study was to develop an alternative separation and purification method for zirconium and hafnium, which will be economically viable and environmentally friendly, in order to produce pure zirconium oxide containing as little as posible hafnium, starting with a typical zirconium-rich ore or concentrate. The process selected as a result of this research consisted of the following processing steps as outlined at the beginning of this study which constituted the aims of this research :

(1) Four different acids namely sulfuric acid (H_2SO_4), hydrochloric acid (HCl), nitric acid (HNO_3), and hydrofluoric acid (HF), were investigated to determine the most suitable acid for the digestion of the ore and the extraction of zirconium and hafnium.

(2) The extraction conditions of zirconium and hafnium from the digested mass with an organic solvent such as 1-octanol and 2-octanol were evaluated. In this step the effects of contact time, potassium fluoride (KF) and acid concentration were evaluated. The relative extraction and separation efficiencies of 1-octanol and 2-octanol were also evaluated.

(3) Separation of zirconium and hafnium batchwise processes using shake-out tests were investigated. The distribution and separation coefficients were determined. A McCabe-Thiele diagram was constructed in order to determine the number of equilibrium stages needed for complete extraction and stripping of both metals.

(4) Stripping zirconium and hafnium from their respective loaded solvent was studied. The effects of different stripping agents were investigated and a McCabe-Thiele diagram for the stripping of zirconium was constructed.

(5) Precipitation of zirconium and hafnium using ammonium hydroxide and high temperature calcination, was carried out in order to produce zirconium and hafnium oxide.

(6) Characterisation of the final product was perforrmed.

(7) Extraction and separation of zirconium form hafnium was done using a packed column system (i.e. use of counter-current column).

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This study has been succesful in achieving all the objectives as outlined in Chapter 1 Section 1.3 and as reflected by the results obtained and discussed in Chapter 5.

The zirconium-rich ore was dissolved in different acid. The complete dissolution of the zirconium-rich ore was succesfull accomplished using H_2SO_4, HF, HNO_3 and HCl. The results indicate that the extraction and separation of both metals are possible using all four acids investigated. However, low extraction and separation were observed for H_2SO_4, HF and HNO_3. Nevertheless, high extraction and separation were observed when HCl was used as the dissolution agent.

The results indicate that it is practically impossible to extract and separate zirconium from hafnium without the use of potassium fluoride as a salting agent. The addition of potassium fluoride to the process allowed the extraction and separation to take place. It was observed that increasing the potassium fluoride concentration increases the extraction and separation efficiency between zirconium and hafnium. The extraction and separation performance was higher when 2-octanol was used as the extractant compared to the 1-octanol. For this reason 2-octanol was used in all the processes.

A McCabe-thiele diagram for the extraction of zirconium was constructed and the results indicated that four equilibrium stages are required for the extraction of zirconium.

The stripping process showed that zirconium could be stripped from the loaded organic solvent using sulfuric acid. Detailed analyse of sulfuric acid concentration indicated that 3 M H_2SO_4 could be used to strip all the zirconium from the loaded organic solvent. It also indicated that five equilibrium stages were required for complete stripping of zirconium from the loaded organic solution. Based on this analysis, hafnium was stripped using a mixture of oxalic acid and nitic acid and the results indicated that three equilibrium stages were needed for the stripping of zirconium from the loaded 2-octanol.

The zirconium and hafnium solutions obtained after stripping were precipitated using a 28 % ammonium hydroxide solution in order to obtain zirconium and hafnium oxide. The products were then calcined at 600 ℃.

After calcination, the products obtained were characterised using SEM-EDS and XRD. The results confirmed that the products obtained were indeed zirconium and hafnium oxides, which contained a low concentration of impurities.

6.2.2 Advantages of the proposed process

Some points can be highlighted from the extraction and separation process for zirconium and hafnium. These are considered to be the advantages resulting from this investigation.

- It is possible to extract and separate zirconium from hafnium without the use of environmentally unfriendly chemicals like as in the MIBK-thyiocyanic process where the waste stream contains a high concentration of ammonium cyanides that leads to an environmental concerns.

- Zirconium and hafnium of high purity can be produced for use in the nuclear industry by increasing the number of equilibrium stages for the extraction and stripping of zirconium from the loaded organic solvent.

- The use of octanol as extractant presents both a direct advantage by reducing the cost of the process, and an indirect advantage by the avoidance of environmental problems. Octanol is cheaper than either MIBK or TBP and there is no third phase formation which could required the use of expensive chemicals. Octanol presents some advantages compared with MIBK and TBP, such as its low volatility, high flash point and low viscosity. The cost of potassium fluoride used in this process is lower compared to ammonium thiocyanate used in the MIBK process.

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