Chapter 1

INTRODUCTION

There are two industrial sources of zirconia- zircon and baddeleyite [1-5]. South Africa has the largest reserves of zircon sand [1-3], with the completion of phase two in Namakwa, the production of zircon is to be increased by about 133 000 tons per annum [2]. This is sure to put South Africa as the leading producer of this mineral in the near coming future. The baddeleyite reserves in Phalaborwa are expected to be depleted by the year 2 005 [1-3]. This leaves the Russian baddeleyite (mined in the Kola Peninsula) and zircon as the only industrial sources of zirconia.

The major drawback to zircon use is the large amounts of impurities it is usually found concentrated with, especially radioactive impurities (Uranium and Thorium) [2-3]. Acid leaching of zircon does not remove impurities to acceptable levels [4-5, 18]. The impurities are usually included in the zircon lattice. The tetragonal structure of zircon with the high coordinated bisdisphenoids ZrO_8 and low coordinated tetrahedra SiO_4 create a safe (inaccessible and safe) habitat for these impurities [7, 18].

The production of high purity zirconia and zirconium chemicals from zircon sand by current means also does not remove these impurities to acceptable low levels [4-6, 8-15, 18]. The radioactivity level is still suspect. This can simply be blamed on the purification methods: magnetic separation, mechanical separation and predominantly precipitation. A disadvantage of the precipitation method is the slow nature requiring long process times. Precipitation is a process that needs to be repeated to achieve the required levels.

In 1914, Herzfield [16] patented the process of crystallising zirconyl chloride from saturated solutions of hydrochloric acid. Another purification process that has been exploited throughout the years is the formation of sulphate compounds. Zirconium sulphate tetrahydrate can be crystallised from saturated solutions. Zirconium basic sulphate can be precipitated from a zirconyl chloride solution with stoichiometric amounts of sulphuric acid [4-6]. Most processes proposed throughout the years have been exploiting this basic purification method [8-15]. The methods have been exploiting, repeated crystallisation or even combinations of both chlorine and sulphate systems [8]. These methods are time consuming and have effluents (chlorine or sulphate) associated with them. Solvent extraction and ion exchange methods have also been investigated [17-18]. The purity of the products is still suspect.

Recently, De Wet [19] patented a process were he prepared in-situ ZBS and digested the impurities with a mineral acid (e.g. HCl, HNO_3 or HCl/HNO_3). The method is very rapid because it does not precipitate the ZBS but prepares it from a hydrated zirconia source e.g. $ZrO_2.nH_2O$. ZBS is stable to mineral acid washes, even digestion with 1.0 M HCl at 90°C leads to negligible zirconia losses (~10 % m/m). De Wet exploits the ZBS stability to synthesise the purest zirconium compounds to date rapidly.

The objective of this study was to characterise and optimise the De Wet's alkali fusion processes for the beneficiation of zircon sand into high purity zirconia and zirconium chemicals. However, at each process step some factors were varied e.g. fusion temperature, reactant ratios and composition of leach solutions. Reducing the number of process steps was also explored. The products produced at each step were analysed. Particular attention was given to the fate of the radioactive impurities.

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Chapter 2
ZIRCONIUM MINERAL SOURCES

2.1 ZIRCONIUM

Zirconium, chemical symbol Zr and electron configuration [Kr]$4d^2 5s^2$, is a ductile, lustrous, heavy metallic element with a high melting point of approximately 1 852^{0}C. Like titanium, zirconium metal is hard and corrosion resistant, resembling stainless steel in appearance [1-3]. Zirconium belongs to the titanium subgroup IVB of the periodic table with a normal valency of four, whilst its coordination number can reach eight [2-3]. Its atomic number is 40 and that of Hafnium is 72. It mainly forms colourless compounds, which are regarded to be of low toxicity [3].

TABLE 2.1: MINERALS CONTAINING ZIRCONIUM [4] (Concentration in mass percent)

NAME	OBSERVED ZrO_2 CONTENT
Industrially important	
Baddeleyite	Up to ~97.4 – 97.5% ZrO_2
Zircon	$ZrSiO_4$ with up to 66% ZrO_2
Metal zirconium silicates	
Anderbergite	A complex vanadium-zirconium silicate
Catapleiite	$Na_2ZrSi_6O_{15}.3H_2O$ with up to ~40% ZrO_2
Dalyite	$K_2ZrSi_6O_{15}$
Elpidite	$Na_2ZrSi_6O_{15}.3H_2O$ with up to 20% ZrO_2
Minerals containing Zirconium as Impurities	
Chalcolamprite	A zirconium niobate-silicate, ~5.7% ZrO_2
Aahrenite	Usually about 3-4% ZrO_2
Arfvedsonite	Up to ~7% ZrO_2
Astrophyllite	$(K, Na)(Fe,Mn,Al)_4(Zr, Ti, Si)_{14}(OH, F)_2$
Aurlite	Up to ~3% ZrO_2
Beckelite	Up to ~2.5% ZrO_2
Cerite	Up to ~8% ZrO_2
Columbite	Up to ~11% ZrO_2
Endeolite	Up to ~3.8% ZrO_2
Eucolite and Eudialite	$Na_{13}(Ca,Fe)_6Cl(Si, Zr)_{20}O_{52}$ with up to 17% ZrO_2
Fergusonite	Up to ~2% ZrO_2
Guarinite and Hiortdahlite	$Na_2Ca_4F_2(Si, Zr)_5O_{14}$ with up to 22% ZrO_2
Loranskite	Up to 20% ZrO_2
Lorenzenite (Ramsayite)	Up to ~11.9% ZrO_2
Polymignite	Up to ~29% ZrO_2
Uhligite	$Ca(Ti, Zr)O_5.Al_2TiO_5$, up to 33% ZrO_2
Zirkelite	$(Ca, Fe)_{0.2}(Zr, Ti, Th)O_2$ with up to 53% ZrO_2

Zirconium does not occur in nature freely as the element, but as zirconium silicates in zircon and its metamic forms, zirconium dioxide in baddeleyite, zirconium silicates with sodium, calcium, etc., zirconium carbonates with sodium, calcium etc., and others (Table 2.1) [4].

In addition zirconium is found as an impurity in many minerals such as titanates, niobanates, tantaloniobates, rare-earth silicates, etc... [4].

The number of known minerals containing zirconium exceeds thirty, but only baddeleyite and zircon are currently of industrial importance [3].

Zirconium is the eighteenth most abundant element and the ninth most abundant metal in the Earth's crust. It has an average element abundance of 160-165 parts per million (Table 2. 2) [4-5].

TABLE 2.2: ABUNDANCE OF THE ELEMENTS OF THE TITANIUM GROUP IN THE EARTH'S CRUST [8]

ELEMENT	CONCENTRATION (ppm)	RANKING
Titanium	6 320	9
Zirconium	160-165	18
Hafnium	2.8	45

Hafnium, chemical symbol Hf and electron configuration [Xe]$4f^{14}5d^{2}6s^{2}$, is an element of the zirconium subgroup that always accompanies zirconium and does not form its own minerals[1]. Usually the hafnium to zirconium ratio in different ores varies from approximately 0.01 to 0.02. This also reflects their abundance ratio in the earth's crust.

It is possible to find ores (Hafnon, hafnium orthosilicate) with a hafnium content larger than 95% (m/m) as was the case with a tantalum ore found in Mozambique [6]. Usually ores with a high hafnium content contain more radioactive elements [6].

Hafnium, like zirconium, is also highly resistant to corrosion and exhibits similar chemical properties. Zirconium is practically unaffected by water, hydrochloric, nitric, dilute sulphuric acid, alkali solutions, even on heating. Dissolution of both metals is observed in HF and mixtures of HCl with HNO_3 [1]. Upon heating, both metals readily react with oxygen or nitrogen to form metal oxides or nitrides.

FIGURE 2.1 A picture of Zircon Sand [Picture by: www. zrchem.com]

2.2 ZIRCON

Zircon, the natural form of zirconium silicate $ZrSiO_4$, is the most abundant and widely distributed zirconium commercial mineral [3]. It is found as an accessory mineral in silica rich igneous rocks such as granite, pegmatite, and nepheline syenite [3, 6]. Sedimentary and metamorphic rocks also contain zircon but in small amounts [6]. Because of its high specific gravity of 4.6-4.8, zircon is found concentrated with other heavy minerals such as rutile, ilmenite, monazite, leucoxene and garnet in river and beach sands with titanium and iron as the main constituents [6, 10].

Zircon is usually produced as a by-product in the mining and processing of heavy-mineral sands for the recovery of the titanium minerals, rutile and ilmenite; consequently there are no mines totally devoted to zircon [6]. Typical zircon chemical and physical analysis are provided in Table 2.3 and 2.4 below.

TABLE 2.3: TYPICAL ZIRCON CHEMICAL ANALYSIS (Concentration in mass percent)

COMPOSITION	RICHARD'S BAY	NAMAKWA ZIRCON	SARM13	UTAH ZIRCON
$ZrO_2 + HfO_2$	66.2	66.2	63.31	68.45
SiO_2 (total)	32.6	32.46	32.56	
Fe_2O_3	0.05	0.05	0.187	< 0.1
TiO_2	0.11	0.11	0.295	0.03
Al_2O_3	1.2	0.24	0.61	0.07
Na_2O				
Cr_2O_3	< 0.01	< 0.01		< 0.01
CaO	< 0.05	0.05	0.14	0.02
P_2O_5	0.11	0.11		
V_2O_5	0.01	0.01		
Y_2O_3				
MgO			440 ppm	< 0.01
U		235 ppm	328 ppm	
Th		165 ppm	300 ppm	
U + Th		400 ppm	628 ppm	< 150 ppm

The grades called Superfine and microfine are prepared from the mineral zircon mined at Richard's bay in South Africa. The concentration of the radioactive compounds was not supplied, but by looking at SARM 13, the XRF standard (SABS approved, originally in 1981 and revision date not given) of zircon sand from the same place, a broad-spectrum analysis is given. The zircon grade from Utah has been found to contain the least amount of radioactivity when compared with other zircon grades [12].

The physical properties of some of the above mentioned zircon grades are given below.

TABLE 2.4: TYPICAL ZIRCON PHYSICAL ANALYSIS (COMMERCIAL GRADES)

Parameter	Superfine (5μm)	Microfine (6μm)
Mean particle size d_{50}	1.55μm	1.7μm
Melting point	2 200°C	2 200°C
Specific gravity	4.6-4.8	4.6-4.8
pH	7.1-8.8	7.1-8.8
Loss on ignition	0.15-0.35%	0.15-0.35%

TABLE 2.5: ZIRCONIUM MINERAL PRODUCTION BY COUNTRY 1/ 2/

(Production in metric tons)

COUNTRY	1993	1994	1995	1996	1997 e/
Australia	414 000	511 000 r/	518 000 r/	502 000 r/	424 000 3/
South Africa e/ 6/	243 000	226 000	250 000	300 000	360 000
Brazil 4/	13 252	17 064	16 343	17 000 r/	17 000
China e/	15 000	15 000	15 000	15 000	15 000
India e/	17 000	18 000	18 000	19 000	19 000
Indonesia e/	2 500	2 500	2 000	2 000	2 000
Malaysia	2 184	1 656	3 790	4 511 r/	2 500
Russia e/ 5/	2 500	3 000 r/	4 000 r/	4 500 r/	5 000
Sierra Leone e/	1 200	1 300	---	---	---
Sri Lanka	14 401	22 310	21 971 r/	15 863	16 000
Thailand	707	326	---	---	---
Ukraine	70 000	65 000	60 000	55 000	65 000
United States	W	W	W	W	W

KEY: e/ Estimated. r/ Revised. W/ Withheld to avoid disclosing company confidential data. 1/ World data and estimated data are rounded of to three significant figures 2/ includes data available through June 18, 1998. 3/ Reported figures. 4/ Includes production of baddeleyite-caldasite. 5/ Includes baddeleyite production. 6/ Includes production of by-product zircon from titanium sands mining and 10 000-15 000 tons per year baddeleyite from Phalaborwa Mining Co. Ltd. [5].

The world production of zirconium mineral concentrates in 1997 was estimated to be 926 000 metric tons (Table 2.5). This was a decrease of approximately 1% compared to 1996, excluding the production from the United States (U.S). Australia and South Africa supplied about 85% of all production outside the U.S. Australia is still the largest producer at approximately 400 000 metric tons per annum. South Africa produces around 300 000 metric tons mostly from Richards Bay. Namakwa sands is also expected to increase production soon with the completion of the construction of another zircon plant, Phase 2 in the year 2 000. This is expected to contribute about 133 000 metric tons per annum [12].

2.3 BADDELEYITE AND ZIRCONIA

Baddeleyite is the naturally occurring monoclinic form of zirconia. It always contains a small amount of hafnium oxide together with other impurities [3, 11]. Baddeleyite is the second most important zirconium mineral after zircon, when compared in terms of availability and price [3].

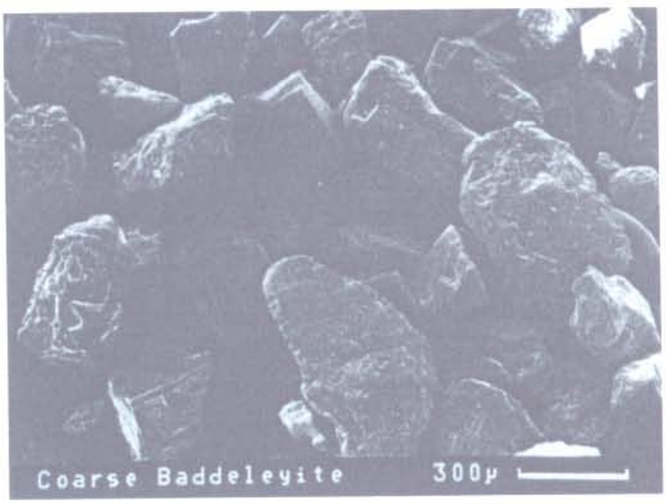

FIGURE 2.2 SEM micrograph of coarse South African Baddeleyite [9]

PMC recovers baddeleyite as a by-product of one of the world's largest open-cast copper mines, whilst Foskor recovers the mineral from phosphate deposits [11]. Beneficiation of the mineral at PMC is by gravity separation of heavy minerals, followed by acid leaching or magnet separation to produce commercial Grades **1**, **2** and **3** as shown in Table 2.6 below. The baddeleyite grades produced by Foskor, labelled **99E** in the same Table 2.6. The Baddeleyite grade, labelled Grade **R**, has the lowest radioactivity level. Kovdor Mining and Dressing Mills produce it as a by-product from iron ore mining in the Kola Peninsula.

TABLE 2.6: CHEMICAL COMPOSITION OF BADDELEYITE [11]

(Concentration in mass percent)

COMPOSITION	GRADE 1	GRADE 2	GRADE 3	GRADE 99E	GRADE R
$ZrO_2 + HfO_2$	99.0 min	99.0 min	99.0 min	> 98	97.5-98.4
SiO_2 (total)	0.25-0.5	0.25-0.4	0.25-0.35	< 1.0	0.5-0.8
TiO_2	0.20-0.30	0.20-0.25	0.20-0.25	≤ 0.3	0.15
ThO_2	0.005-0.025	0.005-0.025	0.005-0.025		
ThO_2/U_3O_8					0.03-0.05
U_3O_8	0.07-0.10	0.07-0.10	0.07-0.10		
CeO_2	0.05-0.1	0.05-0.10	0.05-0.1		
Total activity				< 500Bq/g	
Fe_2O_3	0.10-0.3	0.06-0.20	0.06-0.20	≤ 0.3	0.1-0.15
CuO	0.01-0.1	0.01-0.1	0.01-0.1	≤ 0.05	0.01 max
Al_2O_3	0.03-0.05	0.03-0.05	0.03-0.05		0.01-0.03
CaO	0.05-0.1	0.05-0.1	0.05-0.1		0.30-0.50
P_2O_5	0.10-0.20	0.05-0.10	0.05-0.10	< 0.05	0.15-0.30
SO_3					0.07-0.16

The physical properties of the above mentioned baddeleyite grades are given below in Table 2.7 below.

TABLE 2.7: PHYSICAL PROPERTIES OF BADDELEYITE ORES [11]

Property	Grade 1, 2 and 3	Grade 99E	Grade R
Colour	Grey-black sand	Black powder	Red sand-like powder
Bulk density	3.1 g/cm^3	3.05-3.15g/cm^3	
Melting point	2 700°C		
Specific gravity	5.8-6.0	± 5.76	
Crystal structure	Monoclinic	Monoclinic	

2.4 CONCLUSIONS

1. Zirconium and Hafnium are elements of the titanium subgroup (IVB). They have very similar physical and chemical properties.
2. Hafnium is usually contained within the crystal lattice of zirconium minerals.
3. Zirconium usually occurs in nature as zircon or zirconia. It is also an impurity in many compounds such as titanates, niobanates, tantaloniobanates, rare-earthsilicates, etc.
4. Zircon the most important zirconium mineral, is usually found concentrated with other heavy minerals such as rutile, ilmenite, monazite, leucoxene garnet, etc.
5. Zircon has the following physical properties: specific gravity of 4.6, melting point is approximately 2 200°C and Hardness in Mohs approximately 7.5.
6. The main producers of zirconium minerals in the world are Australia and South Africa. Together they supplied approximately 85% of a total of 926 000 metric tons in the year 1997. South Africa is expected to increase production by about 133 000 metric tons in the year 2 000 due to the completion of Phase 2 in Namakwa.
7. Baddeleyite is the naturally occurring monoclinic form of zirconia. South Africa produces baddeleyite that is virtually silica free. They are also the main producers of this mineral.
8. Grade R from Russia has the lowest radioactivity content than any other grades produced commercially.

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