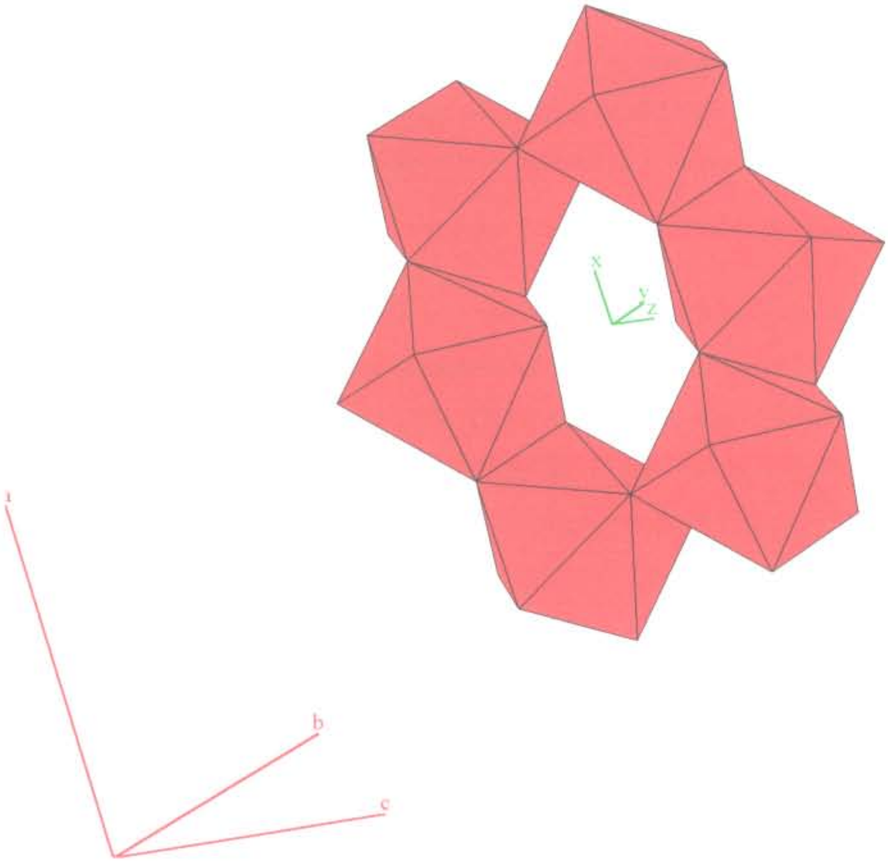
CHAPTER 6

THE STRUCTURE OF ZIRCON



Six ZrO_8 bisdisphenoids edge cell connected Ring.

6.1 INTRODUCTION

This chapter tries to explain the structure of zircon because this could serve as bases to explaining the decomposition of zircon by alkali-metal hydroxides. The structure of zircon was originally reported [1] as having the rutile-type structure, although this was later corrected [2]. Bragg and Claringbull (1965) [3] referred zircon to the rutile group because of similarities in cell dimension, which was later dismissed by X-ray data [4]. Nyman et. al. (1984) [4] showed that zircon actually was related to the rutile-type structure, which it was originally confused with, by simply relating the two structures by replacing the Ti atoms with the Zr and Si atoms in the rutile structure. The structures ABX_4 and MX_2 are actually very similar so it is easy to understand the reason for the confusion.

6.2 ZIRCON STRUCTURE

Clarification on the structure of zircon was suggested by Nyman et. al. (1984) [4] who related a number of structure types, especially those of ABX_4 compounds with a large size difference between A and B atoms. These structures were observed to consist of AX_8 bisdisphenoids or dodecadeltahedron and BX_4 tetrahedra.

The bisdisphenoid can be resolved into two penetrating tetrahedra, one elongated and the other squat with common $\bar{4}$ axis. The bisdisphenoids can also be described as consisting of two interpenetrating, concentric tetrahedra. One tetrahedra being elongated and the other being compressed along the common $\bar{4}$ axis. When the zircon structure is projected on (110), rods of alternating edge-shared tetrahedra and bisdisphenoids in zircon replace the rods of edge-shared octahedra in rutile.

The zircon structure has been related to the rutile structure by Hyde and Andersson (1989) [6], suggesting that the titanium atoms in the chains of edge-sharing rutile octahedra can be replaced by alternating larger Zr and Si atoms. The larger cations have a longer bond length to oxygen thus the higher coordination number in the bisdisphenoid ZrO_8 and lower coordination in the SiO_4 tetrahedra. In zircon the bisdisphenoids share edges in both (100) and (010) layers thus all shifts are parallel throughout the tetragonal structure.

The zircon structure can be shown as two bounded projections (Figure 6.1). Structures with AX_8 and BX_4 coordination, like zircon, are very closely related to structures MX_2, with MX_6 octahedra. In zircon the corresponding octahedral structure is that of rutile, derived by substituting alternately large Zr and small Si atoms for Ti atoms in the chains of edge sharing TiO_6 octahedra in the rutile type.

ZIRCON DATA TABLE 6.1 [6]

Zircon, $ZrSiO_4$

Tetragonal, space group $I4_1/amd$, No. 141; $a = 6.607$, $c = 5.982$ Å, $c/a = 0.9054$; $Z = 4$, $V = 261.13$ Å^3

Atomic Positions (1st choice of origin, at $\bar{4}m2$): all atoms at $(0,0,0;\ \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2})$–
Zr in 4(*a*): $0,0,0;\ 0,\tfrac{1}{2},\tfrac{1}{4}$
Si in 4(*b*): $0,0,\tfrac{1}{2};\ 0,\tfrac{1}{2},\tfrac{3}{4}$
O in 16(*h*): $0,x,z;\ x,0,\bar{z};\ 0,\bar{x},z;\ \bar{x},0,\bar{z};\ 0,\tfrac{1}{2}+x,\tfrac{1}{4}-z;\ x,\tfrac{1}{2},\tfrac{1}{4}+z;\ 0,\tfrac{1}{2}-x,\tfrac{1}{4}-z;\ \bar{x},\tfrac{1}{2},\tfrac{1}{4}+z;\ x = 0.8161,\ z = 0.3203$

Bond Lengths
l(Si–O) = 1.622 Å (4×)
l(Zr–O) = 2.130 Å (4×), 2.269 Å (4×)

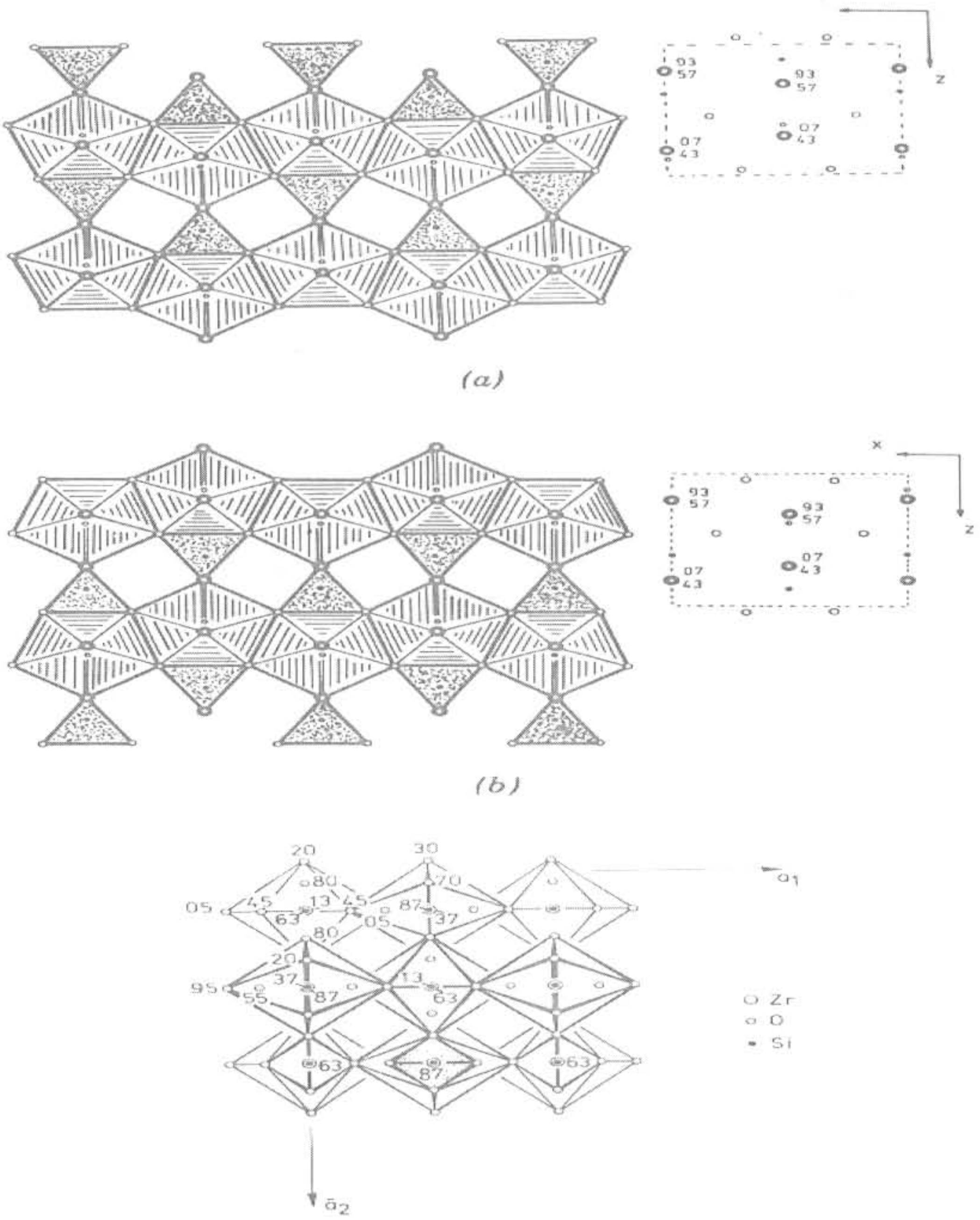


FIGURE 6.1 Bounded projections of the $ZrSiO_4$ structure projected on the (010) [≡ (100)]. [6] *(a)* $0.43 \leq y / b \leq 1.07$; (b) $0.93 \leq y / b \leq 1.57$; Cations are at heights ¾ and 1¼ respectively. The bisdisphenoids share edges in both the x and y directions. Parallel to z are infinite rods of alternating ZrO_8 bisdisphenoids and SiO_4 tetrahedra that also share the edges. (c) Is the (001) projection.

With the aid of a crystallographic programme, CaRIne crystallographie 3.0, it was also possible to construct a three dimensional projection of the zircon structure by substituting the crystallographic data in Table 6.1 in the parameters stipulated by the programme.

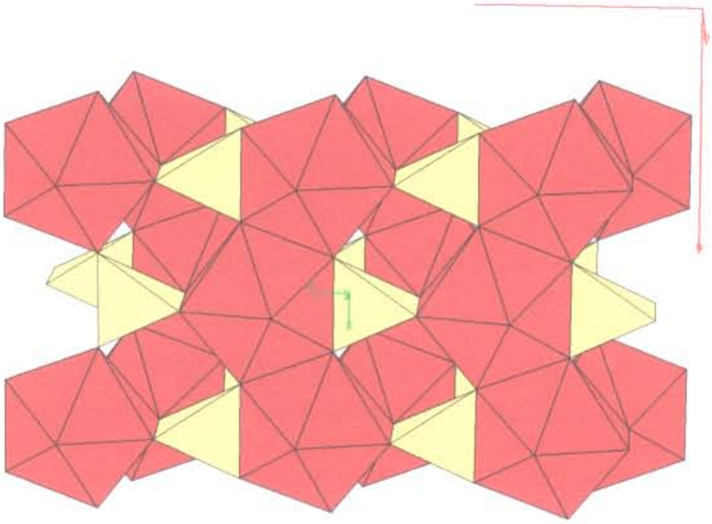


FIGURE 6.2 A three dimensional projection of the structure of zircon. The yellow regions represent the SiO_4 tetrahedra, the red ones are the ZrO_8 bisdisphenoids. The edge cell connection between the SiO_4 tetrahedra and the ZrO_8 bisdisphenoids can be seen. The SiO_4 tetrahedra are further linked to the adjacent ZrO_8 bisdisphenoids by corners.

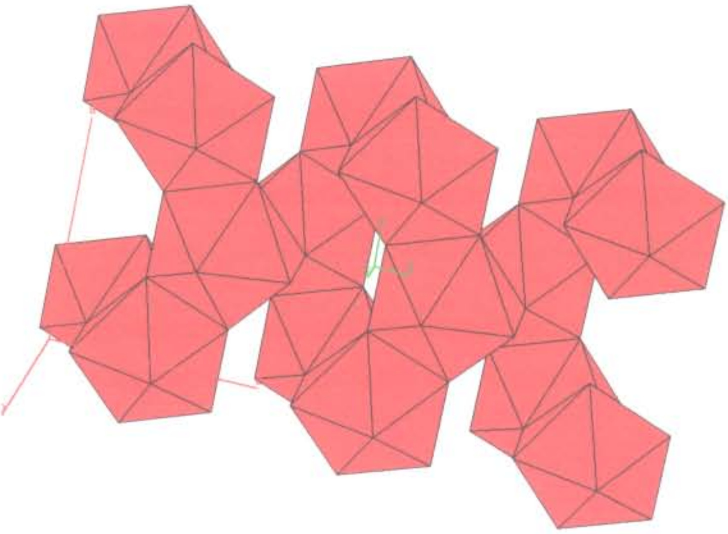


FIGURE 6.3 The edge cell connection of the bisdisphenoids results in the formation of ZrO_8 rings. A further edge cell connection joins the adjacent ZrO_8 rings. This continuous connection of the ZrO_8 explains zircon's stability and the habitat of various impurities.

6.3 CONCLUSIONS

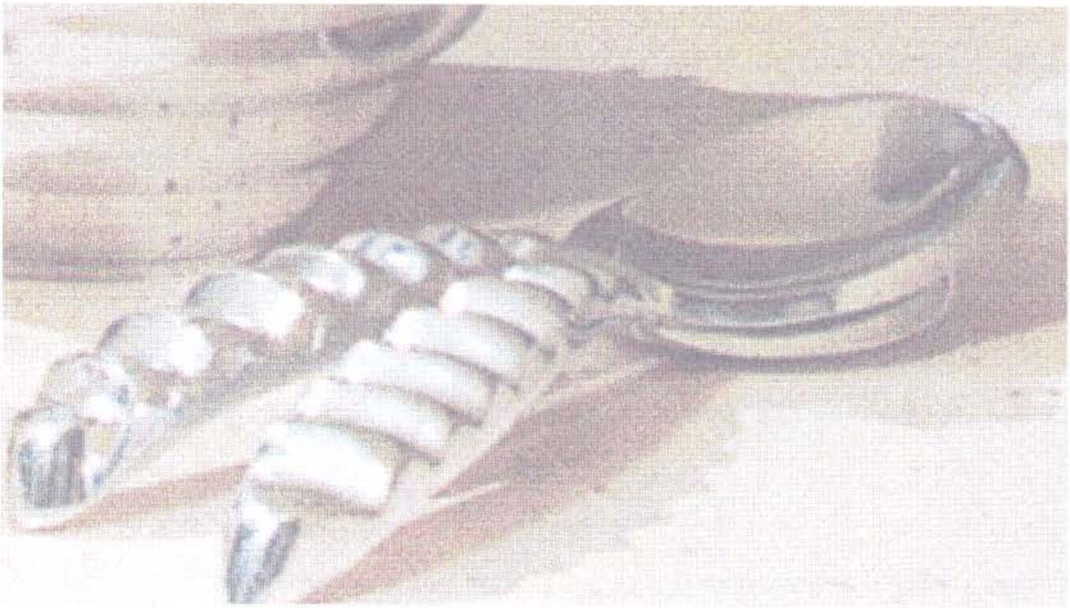
1. Zircon is of structure type ABX_4, with a large size difference between A and B, consists of AX_8 bisdisphenoids and BX_4 tetrahedra.
2. The bisdisphenoids ZrO_8 consist of two interpenetrating concentric tetrahedra. One being elongated and the other being compressed along the common $\bar{4}$ axis.
3. The smaller silicon cation is of lower coordination in the tetrahedra SiO_4.
4. The bisdisphenoids share edges in both (100) and (010) layers thus all shifts are parallel throughout the tetragonal structure.
5. The zircon tetragonal structure is of two bounded projections, with ZrO_8 and SiO_4 coordination.
6. In zircon the corresponding octahedral structure is that of rutile, derived by substituting alternately large Zr and small Si atoms in the chains of edge sharing TiO_6 octahedra in the rutile type.

6.4 REFERENCES

1. Vegard, L. (1916) Phil. Mag. Ser. 6 (32) 65
2. Vegard, L. (1926) Phil. Mag. Ser 7 (1) 1151
3. Bragg, W. L. and Claringbull G. F. (1965) Crystal structures of minerals. Bell, London.
4. Nyman, H. Hyde, B. G and Andersson, S.(1984) Acta Cryst. B (40) 441
5. Blumenthal, W.B. (1958) The Chemical Behaviour of Zirconium, Van Nostrand, N.J., U.S.A.,
6. Hyde, B. G. Andersson, S. (1989) Inorganic crystal structures, A Wiley-Interscience publication, New York.

CHAPTER 7

EXPERIMENTAL



"One table spoon of Zircon, Alumina and Soda a day is what the Doctor ordered."

7.1 INTRODUCTION

This chapter gives a description of the apparatus, planning, reagents, experimental procedures and analysis that were used to investigate the alkali fusion processes.

7.2 APPARATUS

7.2.1 PESTLE AND MORTAR

A pestle and mortar was used in the milling of zircon sand and sodium hydroxide pearls. The mortar was capable of carrying one litre of solution and the pestle was about 300mm in length with a head of diameter c.a. 100 mm.

7.2.2 FIRECLAY CRUCIBLES

Fireclay crucibles were used in the fusion of zircon with sodium hydroxide. The crucibles were capable of carrying a total of about 200 grams of zircon sand. The crucibles were resistant to sodium hydroxide. The fused product was easy to remove from the sides of the crucibles.

7.2.3 HIGH TEMPERATURE OVEN

A High temperature oven was used for calcination and fusion purposes. The oven was a TPF 12/2 model capable of reaching a maximum temperature of about 1 200°C. It was supplied and maintained by Thermopower Furnaces S. A. (Pty.) Ltd. the oven.

7.2.4 CENTRIFUGE

A centrifuge was used to separate solids from the mother liquor. A Beckmann GPR model, capable of reaching a maximum of about 5 000 revolutions per minute, was used.

7.2.5 pH METER

A pH meter, model Mettler Delta 340, was used to follow the variations in pH for the various process steps.

7.3 PLANNING

The objective of this study was to characterise and optimise the De Wet's alkali fusion zirconia extraction processes [1] from zircon sand. These processes are outlined in Figure 7.1 therefore the experiments reported here were designed around this flow diagram. However, at each process step some factors were varied e.g. fusion temperature, stoichiometric ratios, HCl washing concentration and step elimination. Figure 7.2 shows a modification (in terms of ZBS preparation) to the De Wet process.

7.4 METHODS

7.4.1 REAGENTS

All reagents used were of analytical grade supplied by local fine chemical companies. These reagents were sulphuric acid, hydrochloric acid, sodium hydroxide pearls and sodium carbonate decahydrate.

Milled zircon, $d_{50} \approx 9\mu m$, 99.8% (m/m) from Richards' bay, South Africa supplied by Ferro Industrial products, was used for the purpose of these experiments. The chemical and physical analysis is supplied in Table 2.4 and 2.5 respectively.

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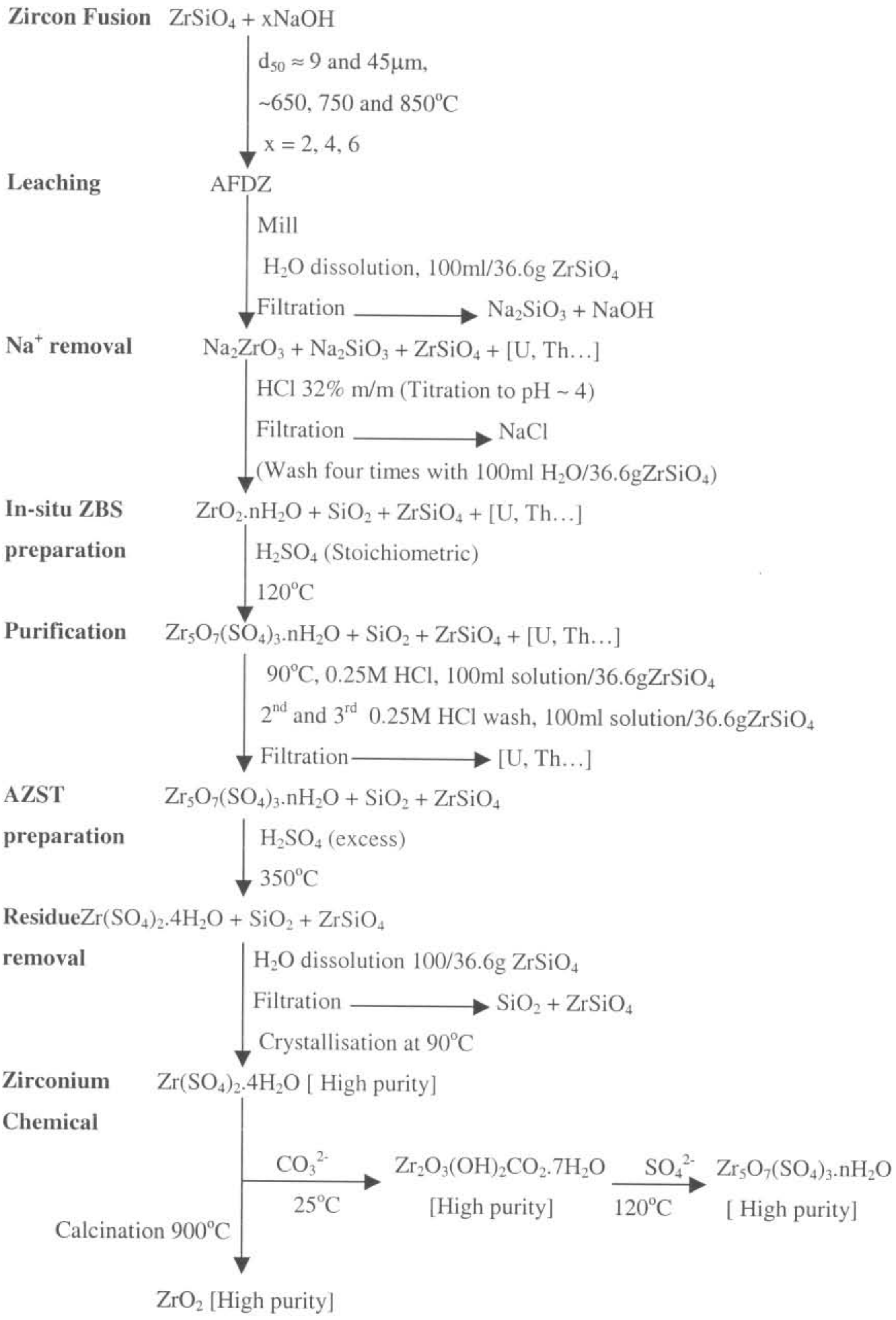

FIGURE 7.1 A diagrammatic representation of the alkali fusion processes (De Wet's process) used to synthesise high purity zirconium sulphate and zirconia

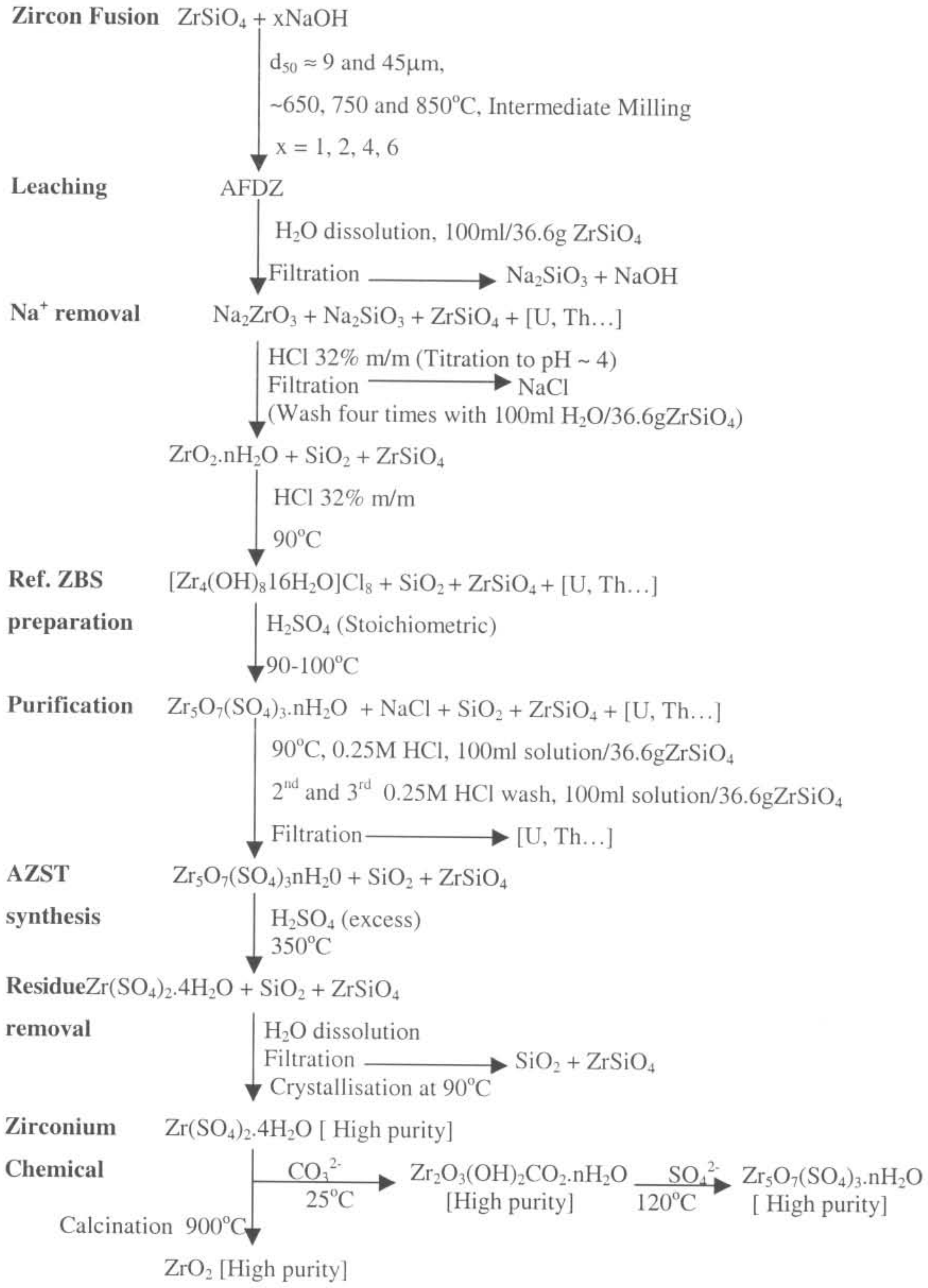

FIGURE 7.2 A diagrammatic representation of the alkali fusion processes (**modified process**) used to synthesise high purity zirconia and zirconium chemicals. The process employs a single precipitation technique to prepare ZBS. The ZBS synthesised by this method is much more stable than the ZBS synthesised from adding sulphuric acid to hydrous zirconia at 120°C (Fig. 7.1).

7.4.2 ZIRCON FUSION (MILLING AFTER FUSION)

Milled zircon, $d_{50} \approx 9\mu m$, 99.8% (m/m) from Richards' bay, South Africa supplied by Ferro Industrial products, was fused with sodium hydroxide in a high temperature oven at varying mole ratios and fusion temperatures. The moles of sodium hydroxide, per mole of zircon, were varied from two to six, at two mole increments. The fusion temperature ranged from 650 to 850°C with 100°C increments. Fusion time was about two hours. For example in one experiment, 36.6g of zircon sand was reacted with 16.0g of sodium hydroxide at 750°C. This reaction represented a mole of zircon fused with two moles of sodium hydroxide fusion at 750°C.

The oven product, commonly called alkali fusion decomposed zircon (AFDZ), was allowed to cool to room temperature, weighed to determine water evaporation during the course of the reaction, milled and weighed again to determine any losses due to experimental error. The milled fused product (MAFDZ), was divided into two parts, this was done to establish the reproducibility of each data point.

7.4.3 ZIRCON FUSION (INTERMEDIATE MILLING)

This step was introduced for the fusion optimisation experiments. The zircon was fused with sodium hydroxide for about 45 minutes. The AFDZ was removed from the oven and allowed to cool to room temperature for 30 minutes. The AFDZ was then milled with a pastel and mortar for about 5 minutes. The AFDZ was fused again for about an hour.

7.4.3 LEACHING OF THE ALKALI FUSED DECOMPOSED ZIRCON

7.4.3.1 ALKALI SILICATE

The MAFDZ was leached in water to remove most of the sodium and soluble silicates from the insoluble zirconium containing species. The liquids were separated from the solids using centrifugation (5 000 r.p.m.). The liquids were then dried in an evaporating oven and sent for elemental analysis.

7.4.3.2 SODIUM AND SILICA DETERMINATION

The MAFDZ was leached in water to remove the soluble sodium and silicates from the insoluble zirconium containing species. The water leach was titrated while stirring with a standardised 32% (m/m) HCl solution. Bromomethyl orange was used as an indicator and a pH meter to determine the equivalence point at pH = 4. The hydrated silica was precipitated with an ammonia and ammonium chloride solution with the pH adjusted to seven. The sodium salts were then separated from the hydrated silica using centrifuge washes (5 000 r.p.m.). About 100ml of water was used for each wash. The hydrated silica was dried overnight in a drying oven at 90°C and calcined at 900°C to silica.

7.4.3.3 THE ALKALI ZIRCONATES

SODIUM REMOVAL (PREPARATION OF IN-SITU HYDROUS ZIRCONIA)

The zirconium containing solids remaining after the silica was leached out, were titrated with 32% (m/m) HCl solution to a pH = 4. The sodium containing salts e.g. NaCl were washed from the hydrous zirconia 4 to 5 times with a centrifuge using 250ml of distilled water for 36.6g $ZrSiO_4$ in each wash.

7.4.4 PREPARATION OF ZBS

7.4.4.1 PREPARATION OF in-situ ZBS FROM in-situ HYDROUS ZIRCONIA

The solids containing the hydrous zirconia were reacted with stoichiometric amounts of sulphuric acid at 150°C to form in-situ ZBS, $Zr_5O_7(SO_4)_3.nH_20$. Care was taken not to dry the paste in the oven. For example in-situ hydrous zirconia obtained from the fusion of 36.6g $ZrSiO_4$ 99.8% (m/m) with 32.0g NaOH 99.8% (m/m) (with intermediate milling at 850°C) was reacted 11.98g of standardised H_2SO_4 98% (m/m) at 90°C for about 20 min. Care was taken not to dry the paste.

7.4.4.2 PREPARATION OF REFERENCE ZBS SYNTHESIS (REF. ZBS)

For the purpose of optimising the HCl purification step, this type of ZBS had to be prepared. The sodium free solids (hydrous zirconia) were digested with HCl at 90°C to form zirconyl chloride $[Zr_4(OH)_8 16H_2O]Cl_8$.

For example in situ hydrous zirconia obtained from the fusion of 36.6g $ZrSiO_4$ 99.8 % (m/m) with 32g NaOH 99.8% (m/m) (with intermediate milling at 850°C) was reacted 61.4 g of standardised 32% (m/m) HCl at 90°C for about 20 min while stirring. The reaction continued until a clear slightly yellow solution was obtained. The ZOC solution was separated from the unreacted solids with centrifugation (5 000 r.p.m.).

The Ref. ZBS was prepared from ZOC solution by adding stoichiometric amounts of a standardised sulphuric acid solution (about 11.98g H_2SO_4 98% m/m) at 90°C while stirring for 30 minutes. The precipitated ZBS was washed 3-4 times with distilled water using a centrifuge (5 000 r.p.m.).

7.4.5 THE PURIFICATION AND ANALYSIS OF THE ZBS PRODUCTS

The impurities in the ZBS product were digested with a hydrochloric acid solution in the first wash at approximately 90°C for about 10 minutes. For the purpose of the De Wet's process, 0.25-1.0M HCl solutions were used. The second and third wash ZBS products were washed using centrifugation (5 000 r.p.m.) with about 100ml of distilled water per 36.6g $ZrSiO_4$ was employed for each washing step. The washing water was collected and evaporated at approximately 80°C in an oven overnight. The solids left from the evaporation were collected and calcined at 900°C. The calcined zirconia was weighed and sent for elemental analysis. The in-situ ZBS was collected from each washing step, converted to AZST, separated from the residue with centrifugation, calcined to zirconia then sent for elemental analysis. A similar procedure for sample collection for Ref. ZBS was used.

7.4.6 PREPARATION OF ZIRCONIUM SULPHATE TETRAHYDRATE

7.4.6.1 AZST PREPARATION FROM IN-SITU ZBS

The in-situ ZBS was reacted with sulphuric acid in a well-ventilated oven at 150°C to form in-situ AZST. The excess sulphuric acid was evaporated at 350°C in a well-ventilated oven. The solids were allowed to cool to room temperature. The in-situ AZST was separated from the unreacted solids by water dissolution and centrifugation (5 000 r.p.m.). The AZST was then crystallised overnight at 90°C by water evaporation

7.4.6.2 AZST PREPARATION FROM IN-SITU HYDROUS ZIRCONIA

This route of preparing AZST from hydrous zirconia was followed when the decomposition step was being optimised. This step ignores the losses experienced in the purification step. The sodium free solids (in-situ hydrous zirconia) were reacted with sulphuric acid 98% (m/m) to form zirconium sulphate tetrahydrate $Zr(SO_4)_2.4H_2O$ (AZST) in a well-ventilated oven, firstly at 150°C then at 350°C to evaporate any excess sulphuric acid.

The solids were allowed to cool to room temperature, and the AZST was dissolved in the water and separated from the unreacted residue. About 100ml of distilled water per 36.6g $ZrSiO_4$ was used. The AZST was then crystallised overnight at 90°C by water evaporation and calcined to zirconia at 900°C.

7.4.7 THE RESIDUE

The solids remaining after the AZST dissolution were dried at 90°C. The solids were also calcined at 900°C. All the calcined products: zirconia, silica and residue were collected and weighed for mass balances and elemental analysis with XRF and ICP spectroscopy

7.4.8 ZIRCONIUM CHEMICALS

7.4.8.1 SYNTHESIS OF ZIRCONIUM BASIC CARBONATE

Zirconium basic carbonate was precipitated at room temperature from solutions of AZST. The AZST, of High purity, was synthesised from the alkali fusion process shown in Figure 7.1. For example, a 0.6 M Na_2CO_3 or $(NH_4)_2CO_3$ solution was added to 100ml of 0.1M AZST solution with continuous stirring until a pH of 6.75. The ZBC precipitate was thoroughly washed with a centrifuge (5 000 r.p.m.). The ZBC was washed four times with 100ml of distilled water to remove the sodium or ammonium and sulphate ions.

7.4.8.2 SYNTHESIS OF ZIRCONIUM BASIC SULPHATE

Zirconium basic sulphate (ZBS) was prepared from ZBC by adding stoichiometric amounts of sulphuric acid. The reaction was allowed to continue at 150°C for about 30 minutes. For instance, about 5.12ml of 18.72 M H_2SO_4 solution was added to a paste of ZBC $Zr_2O_3(OH)_2CO_2.nH_2O$ prepared from 36.6g of zircon decomposed with 32.0g of NaOH.

Differently, about 5.12 ml of 18.72 M H_2SO_4 solution was added to about 34.72g of ZBC. The ZBS $Zr_5O_7(SO_4)_3.nH_2O$ product was washed four times with about 100ml of distilled water with centrifugation (5 000 r.p.m.).

7.5 ANALYSIS

7.5.1 X-RAY POWDER DIFFRACTOMETRY (XRD)

X-ray diffraction (XRD) measurements between 0.8 and 10° 2θ were obtained with Siemens D-501 automated diffractometer Cu-*K*α (15.418 nm) with the Soller slits at 2° (diffracted beam side), divergence slits at 1° and Receiving slits at 0.05°. A scintillation counter detector was used, over the range 3-65° 2θ and step width 0.02°, at the scan rate of 30s per step.

7.5.2 SCANNING ELECTRON MICROSCOPE (SEM)

The particle morphology was examined by the scanning electron microscope with a JEOL JSM-840 instrument. The probe current was 3×10^{-11} ampere and an acceleration voltage of 5.0 kV kept constant for all measurements.

7.5.3 X-RAY FLUORESCENCE (XRF)

The elemental analysis was done with an ARL 9 400 XP + wavelength dispersive XRF spectrophotometer. The samples were ground to < 75µm in a Tungsten carbide milling vessel and pressed in a powder briquette using a saturated Movial solution as binder. Analysis was executed on the samples using a wide confidence limit program i.e. analysis was carried-out for every possible element present in the samples.

7.5.4 THE RAMAN AND INFRARED SPECTROPHOTOMETER

The Raman spectra were recorded in the region 200-3 600 cm^{-1} using the microprobe on the XY Dilor Multichannel instrument. Excitation was accomplished with the 514.5 nm line of an Argon ion laser. Incident power was approximately 100 mW. Infrared spectra were recorded on the Bruker IFS 113 v FTIR spectrometer as KBr pellets in the region 400-4 000 cm^{-1}.

REFERENCE:

1. Wet, W.J. (1999) Method for treating zircon, S. A. Patent 2000/2797