7 EXPERIMENTAL

7.1 Introduction

This section describes the chemicals, apparatus and experimental procedure used.

7.2 Apparatus and Reagents

7.2.1 Reagents

Table 7.1: Reagents used

Name	**Purity**	**Supplier**	**Description**
Zircon	98.8%	Ferro Industrial Products	Powder
NaOH	Analytical grade	Bio-Zone Chemicals	Pellets
HCl	Analytical grade	Chemical Suppliers (Pty) Ltd	
H_2SO_4	Analytical grade	Bio-Zone Chemicals	
Methyl orange	Analytical grade	Riedel-de Haën	
Ammonium solution	Analytical grade	Chemical Suppliers (Pty) Ltd	

7.2.2 Apparatus

The following were used:

1. Moulinex coffee grinder.
2. Ohaus Explorer balance with a 2 100 g full-scale capacity and resolution of 0,01 g.
3. Fireclay crucibles resistant to alkalis.
4. Townson and Mercer low-temperature oven.
5. Model TPF 12/2 high-temperature oven.
6. Mortar and pestle.
7. Beckmann GPR model centrifuge with a maximum speed of around 5 000 r/min.
8. Mettler Delta model 340 pH meter.

7.3 Sample Preparation

Approximately 36.6 g of zircon from Ferro Industrial Products, with an average particle size of 9 µm, was weighed for each fusion experiment and ground in a Moulinex coffee grinder. To that a given amount of sodium hydroxide (e.g. 8, 16, 32 or 48 g) was added. The mixture was homogenised for approximately five minutes and then transferred to a previously weighed clay crucible.

The crucible with the mixture were weighed again and placed in the high-temperature oven, previously brought to the desired temperature. To prevent segregation of the sodium hydroxide, after 30 to 45 minutes the mixture was removed from the oven and ground using a mortar and pestle. After milling, the mixture was replaced in the oven.

After the required fusion time, the AFDZ (alkali fusion decomposed zircon) reaction mixture was allowed to cool at room temperature. The filled crucible was then weighed. The AFDZ was transferred to a beaker and the empty crucible was weighed to determine AFDZ losses.

7.3.1 Long fusion times

To identify the equilibrium phases, the fusion reaction must be allowed to take place over long periods of time. In the present case, the fusion reaction was run for 336 hours at four different mol ratios (1, 2, 4 and 6 mol of sodium hydroxide per mol of zircon) at 600, 650, 700, 750 and 850 °C.

A sample of the resultant AFDZ was analysed using XRD to identify the phases formed.

7.3.2 Leaching of the decomposed mixture

To the AFDZ in the beaker, 200 ml of distilled water was added and the mixture was stirred for 15 minutes. The supernatant liquid was decanted via centrifuging. The operation was repeated three times in order to maximise the removal of soluble salts and to hydrolyse the soluble silicates. To obtain optimum results, the mixture was gently heated while stirring.

7.3.3 Leaching solution

The leaching solution was collected in a beaker and titrated with standardised hydrochloric acid solution (32%). Methyl orange was used to identify the end-point of the titration. Alternatively, a pH meter was used to follow the titration, until pH ≈ 4.

To the titrated solution, an ammonia/ammonium chloride buffer solution was added to precipitate silica in hydrous form. This reaction is slow, so the mixture was left to rest for up to 12 hours to ensure complete precipitation.

The hydrous silica was separated by centrifugation at 5 000 r/min for 15 minutes. It was washed at least three times using 100 ml of distilled water. The water wash was decanted by centrifugation and purged.

The residual hydrous silica was dried in a low-temperature oven overnight, at 90 °C. The dried silica was transferred to a previously weighed alumina crucible, placed in a high-temperature oven at 900 °C and calcined overnight. The resulting calcined silica was weighed and expressed as a percentage of silica recovery.

7.3.4 Hydrolysis of zirconium salts

There are two zirconium salts that are formed as major components in this process: sodium zirconium silicate and sodium zirconate. Sodium zirconium silicate is insoluble in water, whereas sodium zirconate is soluble [12, 48]. When sodium zirconate is dissolved in water, it hydrolyses to hydrous zirconia. The excess of alkali produced by the hydrolysis reaction is eliminated by titration with standardised 32% hydrochloric acid solution.

To hydrolyse the sodium zirconium silicate, hydrochloric acid was added to the solution by titration. Standardised 32% hydrochloric acid solution was used, with methyl orange as indicator. This reaction is slow and therefore the titration was done slowly while stirring. A pH meter was used to follow the changes in pH until the desired pH of 3.8 was reached.

The residue of the supernatant liquid was separated by centrifugation for about 15 minutes and decantation. The residue was washed four to five times with distilled water, using centrifugation and decantation to eliminate the water.

7.3.5 Reaction with sulphuric acid

The residue containing mainly hydrous zirconia was reacted with sulphuric acid to produce acid zirconium sulphate tetrahydrate (AZST). A 5% stoichiometric excess of acid was used. The reaction was conducted at 150 °C with stirring. The excess sulphuric acid was removed by evaporation at 350 °C overnight in an oven.

The mixture of AZST and unreacted solids was separated by dissolution of zirconium sulphate in water. The heterogeneous mixture was separated by centrifugation and decantation. The liquid was crystallised at 90 °C and fired at 900 °C overnight to produce zirconia. The zirconia yield was expressed as mol percentage relative to the starting amount of zircon.

The remaining solids were dried at 90 °C and calcined overnight at 900 °C. The resulting residue was collected, weighed and expressed as a percentage of unreacted zircon.

7.3.6 Effect of fusion time on zirconia yield

The effect of fusion time on conversion was studied at 750 and 850 °C. Fusions were conducted with 2 and 4 mol of sodium hydroxide per mol of zircon for 1, 2, 4, 24 and 336 hours.

7.3.7 Effect of fusion temperature on zirconia yield

The effect of fusion temperature on the equilibrium product spectrum was evaluated from the 336-hour fusion data. Five fusion temperatures were chosen, namely 600, 650, 700, 750 and 850 °C. During these fusions, the samples were intermittently milled using a mortar and pestle to homogenise the reaction mixture.

7.4 Direct Synthesis of Zirconia from Zircon

It has been reported that sodium zirconate hydrolyses completely [2,12,15] to hydrous zirconia in water. Hydrous zirconia can be fired directly to zirconia. A brief literature review showed that there have been no attempts to optimise this potential route of zirconia production. An attempt was therefore made to produce zirconia directly using this route, as described below.

7.5 Experimental Procedure

Sample preparation was done as before. Fusions were conducted with 4 and 6 mol of sodium hydroxide. The water-leaching procedure was as described above. The residue was titrated and washed as before. The remaining residue was calcined and the product was expressed as zirconia yield.

7.5.1 Purity test

To test the purity of the zirconia produced in this way, a sample of leached and titrated decomposed zircon was divided into two portions. One was calcined directly, following the previously described procedure. The final product was weighed as zirconia. Sulphuric acid was added to the product, following the procedure described in Section 7.3.5.

The second portion was treated directly with sulphuric acid, as described in Section 7.3.5, and fired to zirconia. The results were then compared.

7.5.2 Work solutions

Standardisation of hydrochloric acid solution

To standardise the hydrochloric acid solution used in titrations, a certain quantity of sodium hydroxide was accurately weighed (approximately 2 g) to a beaker and dissolved in water. This solution was titrated with hydrochloric acid, using methyl orange as indicator.

Methyl orange solution

A 0.01% methyl orange indicator was used, prepared by direct dissolution of methyl orange powder in distilled water. This solution changes colour from red to yellow in the pH interval from 3.2 to 4.4.

7.6 Analysis

7.6.1 X-ray powder diffraction (XRD)

For phase identification, X-ray diffraction was performed with a Siemens D-501 automated instrument. The working line was Cu-Kα (1.542 Å). Measurements were taken between 0.8 and 10°. The receiving slit was placed at 0.04°. The counting area was from 4° to 70° on a 2θ-scale. The step time (counting time) was 15 seconds.

7.6.2 X-ray fluorescence (XRF)

Elemental analysis was done in an ARL9400+ wavelength-dispersive instrument. The samples were ground to a particle size of less than 75 µm in a tungsten carbide milling vessel. The ground samples were then roasted at 1 000 °C to determine the loss on ignition (LOI) value. To 1 g of the sample, 9 g of lithium tetraborate was added and the mixture was fused into a glass bead. All the possible elements present in the sample were then analysed.

7.6.3 Scanning electron microscopy (SEM)

The particle morphology was examined by scanning electron microscope using a JEOL JSM-840 instrument. The current was 3×10^{-11} amperes and the acceleration voltage was kept constant at 5.0 kV.

Process step	Notes
$ZrO_2.SiO_2$ + x NaOH	
1 ↓ 650 °C – 850 °C	1. Fusion (Choose reaction conditions to maximise yield of sodium silicates and avoid formation of sodium zirconium silicates.)
Na_2ZrO_3 + Na_2SiO_3 + Na_2ZrSiO_5	
2 ↓ water leach	2. Cool down and mill. Remove sodium silicates and unreacted NaOH using a water leach.
$Zr(OH)_4.xH_2O$ + Na_2ZrSiO_5	
3 ↓ HCl to pH = 3.8	3. Neutralise to hydrolyse sodium salts.
4 ↓ leach	4. Remove remnant sodium as NaCl using a water leach.
$Zr(OH)_4.xH_2O$	
5 ↓ H_2SO_4 (stoichiometric)	5. *In situ* formation of basic sulphate at 120 °C. It is insoluble in water and very stable towards dilute HCl.
$Zr_5O_7(SO_3)_3.nH_2O + SiO_2 + ZrSiO_4$	
6 ↓ dilute HCl wash	6. Purification: Remove impurities including iron and radioactive elements.
$Zr_5O_7(SO_3)_3.nH_2O$ + solid residue	
7 ↓ H_2SO_4 (excess)	7. AZST formation. The acid sulphate is soluble in water.
8 ↓ roast @ 350°C	8. Evaporate excess sulphuric acid.
9 ↓ add water	9. Dissolve acid sulphate.
10 ↓ filtration	10. Remove silica from AZST solution.
$Zr(SO_4)_{2\ (aq)}$	
11 ↓ crystallisation, 90 °C	11. Crystallisation.
$Zr(SO_4)_2.4H_2O$ [high purity]	
12 ↓ calcination, 900 °C	12. Calcination.
ZrO_2 [high purity]	

Scheme 7.1: Outline of the De Wet alkali fusion process for acid zirconium sulphate