## CHAPTER 11

# CONCLUSIONS AND RECOMMENDATIONS

### 11.1 INTRODUCTION

There are two industrial sources of zirconia: zircon and baddeleyite [1-5]. The baddeleyite reserves in Phalaborwa (the world's major baddeleyite source) are expected to be depleted by the year 2 005 [1-3]. This leaves the Russian Baddeleyite (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 found concentrated with, especially radioactive impurities (Uranium and Thorium) [2-3]. Acid leaching of zircon does not remove these impurities [4-5]. 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 stable) habitat for these impurities [7].

Processes for the recovery of zirconia and zirconium chemicals rely heavily on precipitation or crystallisation techniques for purification [8-16]. Precipitation techniques need to be repeated to obtain the required purity. The purity of products from such methods is still suspect, as there still remains a high radioactivity content after purification [2]. The long process time is another disadvantage of these precipitation processes. These factors together are the reason for the high cost of zirconia and zirconium chemicals.

Zirconium and its compounds are regarded to be of low toxicity [1-6]. This implies that they have a great potential of replacing numerous high toxic chemicals. Prominent examples are seen in leather tanning and paints. In leather tanning chromium chemicals can be replaced. In paints lead driers and chromium chemicals for corrosion resistance can be replaced.

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. Attention was also paid to reducing the total number of process steps. The products produced at each step were analysed. Particular attention was given to the fate of the radioactive impurities.

## 11.2 ZIRCON DECOMPOSITION

The decomposition of zircon was carried out in open reaction vessels. A mole of zircon was decomposed using from one to six moles of sodium hydroxide and fusion temperatures of 650, 750 and 850°C. When the fusion time is limited to two hours non-equilibrium phases form and the products formed depend on reaction kinetics. For prolonged fusion times (e.g. 336 hours) the reaction products tend towards the expected equilibrium phases. These are the two factors that determine phase formation.

The tetragonal structure of zircon is stabilised by the bisdisphenoids linkages. The silicate phases that are formed can be polymerised to silicates low in sodium (e.g. $Na_2SiO_3$ or $Na_2Si_2O_5$). This allows the sodium to be released for further decomposition reactions. At 850°C and long fusion times the phases observed are thermodynamically stable one to those reported for higher temperatures by D'Ans and Loeffler (1930) [24, 25]. However, the phase diagram observed at 650°C differs from that obtained by them: The phases $Na_2ZrSiO_5$ and $Na_4Zr_2Si_3O_{12}$ were not observed.

### 11.2.1 DECOMPOSITION AT 650°C

Prolonged fusion at 650°C with $NaOH/ZrSiO_4 \leq 2$ mole ratio leads to the formation of sodium metasilicate and zirconia (Scheme 8.2). The XRD reveals the presence of metasilicate and zirconia in trace- or in minor amounts. The low level of detection of these compounds could be due to an amorphous state of the samples (Figure 8.24). The IR bands at 710 and 600 $cm^{-1}$ support the presence of polymerised silicates (e.g. the sodium metasilicate).

Prolonged fusion (336 hours) at 650°C with $4 \leq$ NaOH moles $\leq 6$ leads to the formation of sodium silicates high in sodium and the polymerisation (Scheme 8.1) of the orthosilicate monomers to metasilicate chains. The IR supports this conclusion showing the presence of the δ(Si-O-Si) band at 686 $cm^{-1}$ (for the fusion done in two hours). The split in the band at 686 to ones at 710 and 600 $cm^{-1}$ is indicative of the presence of highly polymerised silicates. The band at 600 $cm^{-1}$indicates the presents of silicates with rings with more than six members [19-23].

When fusing for two hours, increasing the amount of sodium hydroxide leads to the formation of silicates high in sodium (e.g. $Na_4SiO_4$) and zirconia. Zirconia, in its reduced state, is formed rather than sodium zirconate. This is a consequence of the stability of the $ZrO_8$ bisdisphenoids and the instability of the $SiO_4$ tetrahedra linkages at this temperature.

For prolonged fusion with $NaOH/ZrSiO_4 \leq 2$ mole ratio, most of the sodium followed the silicates. This suggests that the zirconium compound in the AFDZ was low in sodium or hydrolysed easily [17].

### 11.2.2 DECOMPOSITION AT 850°C

When zircon is decomposed with sodium hydroxide at higher temperatures e.g. 850°C, the formation of sodium silicates and sodium zirconates is observed. This is an indication that at this temperature the $ZrO_8$ bisphenoid linkages are not resistant to $Na_2O$ attack.

Prolonged fusion (e.g. 336 hours) at 850°C with $NaOH/ZrSiO_4 < 2$ mole ratio leads to the formation of the phase $Na_4Zr_2Si_3O_{12}$ and $ZrO_2$ (Scheme 8.4).

Prolonged fusion at 850°C with $NaOH/ZrSiO_4 = 2$ mole ratio leads to the formation of the phase $Na_2ZrSiO_5$ (Scheme 8.4). The formation of these phases ($Na_4Zr_2Si_3O_{12}$ and $Na_2ZrSiO_5$) was not detected at 650°C.

### 11.3.1 THE IN-SITU ZBS PURIFICATION STEP

The impurities are removed from ZBS with mineral acid washes at 90°C; the concentration was varied from 0.25M to 1M HCl. The mineral acid leads to zirconia losses; these are due to both incomplete conversion and increased molarity of acid. The in-situ ZBS showed losses up to 10% m/m of zirconia for HCl of one molar. Washing ZBS with solutions of molarity greater than 0.5M HCl removes Uranium and Thorium to levels below parts per million.

A way to minimise the zirconia losses for the in-situ ZBS route is to wash it with water to dissolve AZST. The AZST can then be re-circulated to the sodium removal step or precipitated with ammonia to hydrous zirconia.

The hydrous zirconia can be reacted with stoichiometric amounts of sulphuric acid to form ZBS. The ZBS can then be washed with mineral acid to remove impurities.

### 11.3.2 THE REF. ZBS PURIFICATION ROUTE

The Ref. ZBS route has minimal zirconia losses but a longer process time; ZBS precipitates out of solution after long periods. For example when heating a 20.0 g of zirconyl chloride solution between 90 and 100°C, with stoichiometric amounts of sulphuric acid, a fine grain ZBS precipitated (about 9.0g $ZrO_2$) after 30 minutes.

This ZBS is much more stable than the in-situ ZBS (prepared from hydrous zirconia at approximately 120°C with stoichiometric amounts of sulphuric acid), this stability is attributed to a series of olation reactions and the formation of sulphate bridges through a slow ordered precipitation reaction. This route could be have been adopted by De Wet; it has minimal zirconia losses (about 2% m/m when washed with 1M HCl at 90°C).

### 11.4 THE ALKALI SILICATE BY-PRODUCT

The by-product contains sodium metasilicate as well as sodium carbonate. The presence of the latter is attributed to the reaction of atmospheric carbon dioxide with excess sodium during crystallisation. The observed $Na_2O/SiO_2$ mol ratio, in the sodium silicate stream, exceeded three for all reagent ratios for a 2 hour fusion time.

### 11.5 THE AZST PRODUCT

The zirconium sulphate tetrahydrate (AZST) prepared in this study consists of many phases owing to the nature of the crystallisation process. Similar observations were made by Bear and Mumme (1971) [19]. Appendix K confirms that a product of very high purity can be obtained.

### 11.6 THE ZIRCONIA PRODUCT

The zirconia prepared in this study is predominantly monoclinic. It consisted of oblong, spherical particles with a dimension of about 90 nm. The zirconia obtained was also of high purity as shown in Appendix K.

### 11.7 THE RESIDUE AND RE-CIRCULATION

The residue (the solids remaining after the removal of AZST) constitutes free silica and unreacted zircon. The silica can be separated from the zircon by physical means. This is due the large density difference between silica and zircon. For example when using a centrifuge (5 000 r.p.m) it was possible to separate the two. The unreacted zircon can then be re-circulated for further decomposition.

### 11.8 THE DE WET PROCESS

Finally, the De Wet's zirconium extraction process is rapid when compared to precipitation processes. The in-situ ZBS is very stable and can be washed with mineral acids to remove impurities. The in-situ ZBS is not as stable as Ref. ZBS prepared from a single precipitation route.

The products and by-product synthesised by the De Wet process are of very high purity, better than any commercial products; washing Ref. ZBS with mineral acids can attain similar purity.

The only disadvantage of this process is how it synthesises ZBS. To synthesise ZBS from hydrous zirconia with stoichiometric amounts of sulphuric acid, is difficult. Any excess or insufficient acid can lead to zirconia loses as AZST or ZOC respectively. Maintaining the ZBS as a paste during the synthesis at approximately 150°C is another complication since crosslinking of the hydroxyl groups is possible if the paste is dried. The ZBS may crosslink at the terminal hydroxyl groups including the impurities within the polymer matrix; removal of impurities from the crosslinked ZBS remains a scope for further research.

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# APPENDIX A

## A TABULATION OF THE VALUES USED IN THE OPTIMISATION OF THE DECOMPOSITION OF ZIRCON WITH SODIUM HYDROXIDE AFTER TWO HOURS OF FUSION WITH OUT INTERMEDIATE MILLING

| Fusion ratio: a moles $ZrSiO_4$ to moles of NaOH | $ZrO_2$ in grams | Yield of $ZrO_2$ % (m/m) | $ZrO_2$ in moles | $ZrO_2$ g / $ZrSiO_4$ g × 100 % | Efficiency Fraction NaOH (mol) / $ZrO_2$ (mol) | $SiO_2$ in grams | Yield of $SiO_2$ % | $SiO_2$ g / $ZrSiO_4$ g × 100 % | Residue in grams (Unreacted $ZrSiO_4$ and $SiO_2$) | Residue g / Used $ZrSiO_4$ g × 100 % | Mass of AFDZ used in grams | Volume of HCl (ml) used to neutralise zirconates solids | Volume of HCl (ml) used to neutralise silicate (liquids) | $Na_2O$ % m/m in solids | $Na_2O$ % m/m in liquids |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| For the 850°C temperature region | | | | | | | | | | | | | | | |
| 1: 2 | 6.800 | 58.0 | 0.0577 | 38.850 | 3.470 | 2.700 | 45.0 | 14.75 | 5.500 | 30.05 | 23.80 | 4.00 | 15.0 | 21.0 | 79.0 |
| 1: 4 | 9.640 | 82.0 | 0.0818 | 55.110 | 4889 | 4.32 | 72.0 | 23.11 | 4.800 | 23.60 | 29.90 | 8.50 | 29.50 | 22.0 | 78.0 |
| 1: 6 | 11.530 | 98.0 | 0.0979 | 65.890 | 6.129 | 5.20 | 87.0 | 28.4 | 0.96 | 28.50 | 35.80 | 18.0 | 96.0 | 16.0 | 84.0 |
| For the 750°C Temperature region | | | | | | | | | | | | | | | |
| 1: 2 | 6.230 | 53.0 | 0.0528 | 35.600 | 3.788 | 2.28 | 38.0 | 12.45 | 9.110 | 12.46 | 23.90 | 4.50 | 15.0 | 21.0 | 79.0 |
| 1: 4 | 8.940 | 76.0 | 0.0759 | 51.090 | 5.270 | 3.960 | 66.0 | 21.66 | 4.820 | 21.48 | 29.90 | 8.00 | 29.0 | 22.0 | 78.0 |
| 1:6 | 10.950 | 93.0 | 0.0928 | 62.500 | 6.470 | 4.98 | 83.0 | 27.10 | 1.80 | 27.20 | 35.70 | 17.5 | 96.0 | 16.0 | 84.0 |
| For the 650°C Temperature region | | | | | | | | | | | | | | | |
| 1: 2 | 5.290 | 45.0 | 0.0448 | 30.240 | 4.460 | 2.05 | 34.0 | 11.20 | 10.260 | 11.12 | 23.90 | 4.50 | 15.0 | 21.0 | 79.0 |
| 1: 4 | 8.230 | 70.0 | 0.0698 | 47.029 | 5.730 | 3.6 | 60.0 | 19.67 | 5.830 | 19.70 | 29.90 | 8.50 | 29.5 | 22.0 | 78.0 |
| 1: 6 | 10.12 | 86.0 | 0.086 | 57.800 | 6.970 | 4.68 | 78.0 | 25.57 | 2.900 | 25.60 | 35.80 | 17.0 | 96.0 | 16.0 | 84.0 |

# APPENDIX B

## A TABULATION OF THE MASS BALANCE USED IN THE OPTIMISATION OF THE DECOMPOSITION OF ZIRCON AT 650°C WITH SODIUM HYDROXIDE AFTER TWO HOURS OF FUSION WITH OUT INTERMEDIATE MILLING

ASSUMPTIONS

1. Free sodium = HCl used to neutralise the sodium silicate solution
2. Ignored losses during purification
3. Ignored losses during water wash

| EXPERIMENTAL Temperature (°C) | AFDZ Theoretical | AFDZ found | AFDZ yield | NaOH (g) | Sodium silicate 32% HCl (ml) | Solid 32% HCl (ml) | $ZrO_2$ (g) | Residue: Silica&zircon (g) | Silica in SS (g) |
|---|---|---|---|---|---|---|---|---|---|
| 650 | 49.00 | 23.90 | 0.49 | 16 | 15 | 4.5 | 5.29 | 10.26 | 4.1 |
| | 61.39 | 29.90 | 0.49 | 32 | 29.5 | 8.5 | 8.23 | 5.83 | 7.2 |
| | 73.79 | 35.80 | 0.49 | 48 | 48 | 8.5 | 10.12 | 2.9 | 9.36 |

CALCULATIONS

Basis: 100 kg zircon feed

| NaOH/Zircon mol ratio | NaOH kg | Zirconia yield kg | Zircon recycle 2 kg | NaOH in SS kg | $SiO_2$ in SS kg | $SiO_2/Na_2O$ | NaOH in Solid kg | Error in NaOH % | Silica waste kg | Silica waste kg |
|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 43.72 | 29.63 | 55.92 | 34.22 | 11.20 | 0.42 | 10.27 | -1.78 | 3.24 | 1.55 |
| 4 | 87.43 | 46.17 | 31.32 | 67.41 | 19.67 | 0.38 | 19.42 | 0.68 | 2.84 | 1.39 |
| 6 | 131.15 | 56.99 | 15.22 | 110.11 | 25.57 | 0.30 | 19.50 | 1.17 | 2.21 | 1.11 |
| Theoretical: | $ZrO_2$ | 67.22 | | | | | | | | |
| | $SiO_2$ | 32.78 | | | | | | | | |

# APPENDIX C

## A TABULATION OF THE MASS BALANCE USED IN THE OPTIMISATION OF THE DECOMPOSITION OF ZIRCON AT 750°C WITH SODIUM HYDROXIDE AFTER TWO HOURS OF FUSION WITH OUT INTERMEDIATE MILLING

### ASSUMPTIONS

Corrected for losses during fusion

1 Free sodium = HCl used to neutralise the sodium silicate solution

2 Ignored losses during purification

3 Ignored losses during water wash

### EXPERIMENTAL

| Temperature (°C) | AFDZ Theoretical | AFDZ found | AFDZ yield | NaOH (g) | Sodium silicate 32% HCl (ml) | Solid 32% HCl (ml) | ZrO2 (g) | Residue: Silica &zircon (g) | Silica in SS (g) |
|---|---|---|---|---|---|---|---|---|---|
| | 49.00 | 23.90 | 0.49 | 16 | 15 | 4.5 | 6.23 | 9.11 | 4.56 |
| | 61.39 | 29.90 | 0.49 | 32 | 29 | 8 | 8.94 | 4.82 | 7.92 |
| 750 | 73.79 | 35.70 | 0.48 | 48 | 48 | 8.75 | 10.95 | 1.8 | 9.96 |

### CALCULATIONS

Basis: 100 kg zircon feed

| NaOH/Zircon mol ratio | NaOH kg | Zirconia yield kg | Zircon recycle2 kg | NaOH in SS kg | $SiO_2$ in SS kg | SiO2/$Na_2O$ | NaOH in Solid kg | Error in NaOH % | Silica waste kg ($SiO_2$) | Silica wast kg (zirconium |
|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 43.72 | 34.90 | 48.09 | 34.22 | 12.46 | 0.47 | 10.27 | -1.78 | 4.55 | 2.94 |
| 4 | 87.43 | 50.15 | 25.39 | 66.27 | 21.64 | 0.42 | 18.28 | 3.29 | 2.81 | 1.65 |
| 6 | 131.15 | 61.84 | 8.01 | 110.42 | 27.21 | 0.32 | 20.13 | 0.46 | 2.94 | 2.15 |
| Theoretical: | $ZrO_2$ | 67.22 | | | | | | | | |
| | $SiO_2$ | 32.78 | | | | | | | | |

## APPENDIX D

### A TABULATION OF THE MASS BALANCE USED IN THE OPTIMISATION OF THE DECOMPOSITION OF ZIRCON AT 850°C WITH SODIUM HYDROXIDE AFTER TWO HOURS OF FUSION WITH OUT INTERMEDIATE MILLING

ASSUMPTIONS

Corrected for losses during fusion

1 Free sodium = HCl used to neutralise the sodium silicate solution
2 Ignored losses during purification
3 Ignored losses during water wash

EXPERIMENTAL

| Temperature (°C) | AFDZ Theoretical | AFDZ found | AFDZ yield | NaOH (g) | Sodium silicate 32% HCl (ml) | Solid 32% HCl (ml) | ZrO2 (g) | Residue: Silica &zircon (g) | Silica in SS (g) |
|---|---|---|---|---|---|---|---|---|---|
| 850 | 49.00 | 24.62 | 0.50 | 16 | 20 | 5 | 7.78 | 7.05 | 2.53 |
| | 61.39 | 32.00 | 0.52 | 32 | 41 | 7.9 | 9.51 | 0.772 | 3.29 |
| | 73.79 | 35.80 | 0.49 | 48 | 48 | 9 | 11.53 | 1.15 | 10.4 |

## CALCULATIONS

Basis: 100 kg zircon feed

| NaOH/Zircon Mol ratio | NaOH kg | Zirconia yield kg | Zircon recycle 2 kg | NaOH in SS kg | $SiO_2$ in SS kg | $SiO_2/Na_2O$ | NaOH in Solid kg | Error in NaOH % | Silica waste kg ($SiO_2$) | Silica waste kg (zirconium) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | 1.26 |
| | | | | | | | | | | -21.80 |
| 2 | 43.72 | 42.30 | 37.07 | 44.30 | 6.91 | 0.20 | 11.07 | -26.67 | 13.71 | 3.07 |
| 4 | 87.43 | 49.85 | 25.84 | 87.55 | 8.99 | 0.13 | 16.87 | -19.42 | 15.32 | |
| 6 | 131.15 | 64.93 | 3.41 | 110.11 | 28.42 | 0.33 | 20.65 | 0.30 | 3.24 | |
| Theoretical: | $ZrO_2$ | 67.22 | | | | | | | | |
| | $SiO_2$ | 32.78 | | | | | | | | |

# APPENDIX E

## A TABULATION OF THE MASS BALANCE USED IN THE OPTIMISATION OF THE DECOMPOSITION OF ZIRCON WITH SODIUM HYDROXIDE AT 750°C AFTER 336 HOURS OF FUSION WITH OUT INTERMEDIATE MILLING

Fixed

### ASSUMPTIONS

Corrected for losses during fusion

1 Free sodium = HCl used to neutralise the sodium silicate solution

2 Ignored losses during purification

3 Ignored losses during water wash

### EXPERIMENTAL Values

| Temperature (°C) | AFDZ Theoretical | AFDZ found | AFDZ yield | NaOH (g) | Sodium silicate 32% HCl (ml) | Solid 32% HCl (ml) | $ZrO_2$ (g) | Residue: Silica &zircon (g) | Silica in SS (g) |
|---|---|---|---|---|---|---|---|---|---|
| | 21.86 | 40.74 | 1.86 | 8 | 2 | 22 | 17.49 | | |
| 750 | 49.00 | 49.58 | 1.01 | 16 | | | 21.81 | | |
| | 61.39 | | 0.00 | 32 | | | | | |
| | 73.79 | | 0.00 | 48 | | | | | |

### CALCULATIONS

Basis: 100 kg zircon feed

| NaOH/Zircon mol ratio | NaOH Kg | Zirconia yield kg | Zircon recycle2 kg | NaOH in SS kg | SiO2 in SS kg | SiO2/Na2O | NaOH in Solid kg | Error in NaOH % | Silica waste kg (SiO2) | Silica waste kg (zirconium) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 21.86 | 25.64 | 61.86 | 1.19 | 0.00 | 0.00 | 13.14 | 34.43 | 12.50 | -61.86 |
| 2 | 43.72 | 58.89 | 12.40 | 0.00 | 0.00 | #DIV/0! | 0.00 | 100.00 | 28.71 | -12.40 |
| 4 | 87.43 | #DIV/0! | #DIV/0! | #DIV/0! | 0.00 | #DIV/0! | #DIV/0! | #DIV/0! | #DIV/0! | #DIV/0! |
| 6 | 131.15 | #DIV/0! | #DIV/0! | #DIV/0! | 0.00 | #DIV/0! | #DIV/0! | #DIV/0! | #DIV/0! | #DIV/0! |
| Theoretical: | $ZrO_2$ | 67.22 | | | | | | | | |

# APPENDIX F

## A TABULATION OF THE MASS BALANCE USED IN THE OPTIMISATION OF THE DECOMPOSITION OF ZIRCON AT 650°C WITH SODIUM HYDROXIDE AFTER 336 HOURS OF FUSION WITH OUT INTERMEDIATE MILLING

### ASSUMPTIONS

Corrected for losses during fusion

1 Free sodium = HCl used to neutralise the sodium silicate solution

2 Ignored losses during purification

3 Ignored losses during water wash

### EXPERIMENTAL

| Temperature (°C) | AFDZ Theoretical | AFDZ found | AFDZ yield | NaOH (g) | Sodium silicate 32% HCl (ml) | Solid 32% HCl (ml) | $ZrO_2$ (g) |
|---|---|---|---|---|---|---|---|
| 650 | 21.86 | 39.99 | 1.83 | 8 | 17.5 | 1 | 12.29 |
| | 49.00 | 40.74 | 0.83 | 16 | 34 | 4 | 14.74 |
| | 61.39 | 57.70 | 0.94 | 32 | 51 | 24 | 19.19 |
| | 73.79 | 72.38 | 0.98 | 48 | 75 | 40 | 23.13 |

### CALCULATIONS

Basis: 100 kg zircon feed

| NaOH/Zircon mol ratio | NaOH kg | Zirconia yield kg | Zircon recycle2 kg | NaOH in SS kg | $SiO_2$ in SS kg | $SiO_2/Na_2O$ | NaOH in Solid kg | Error in NaOH % | Silica waste kg (SiO2) | **Silica waste kg (zirconium)** |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 21.86 | 18.36 | 72.69 | 10.65 | 0.00 | 0.00 | 0.61 | 48.51 | | |
| 2 | 43.72 | 48.44 | 27.94 | 45.51 | 0.00 | 0.00 | 5.35 | -16.36 | 23.62 | **-27.94** |
| 4 | 87.43 | 55.79 | 17.01 | 60.40 | 0.00 | 0.00 | 28.42 | -1.58 | 27.20 | **-17.01** |
| 6 | 131.15 | 64.43 | 4.16 | 85.10 | 0.00 | 0.00 | 45.39 | 0.50 | 31.41 | **-4.16** |
| Theoretical: | $ZrO_2$ | 67.22 | | | | | | | | |
| | $SiO_2$ | 32.78 | | | | | | | | |

# APPENDIX G

## A TABULATION OF THE VALUES USED IN THE OPTIMISATION OF THE DECOMPOSITION OF ZIRCON WITH SODIUM HYDROXIDE AFTER 336 HOURS OF FUSION WITH INTERMEDIATE MILLING

| Fusion ratio: $ZrSiO_4$ (mol) : NaOH (mol) | $ZrO_2$ (g) | Yield of $ZrO_2$ % (m/m) | $ZrO_2$ (mol) | $ZrO_2$ g / $ZrSiO_4$ g × 100 % | Efficiency Fraction NaOH (mol) / $ZrO_2$ (mol) | NaOH (g) / 18.3 (g) of $ZrSiO_4$ | NaOH (mol) | Mass of Silica | Percentage Yield of $SiO_2$ (m / m) | Mass of AFDZ (g) | Volume of HCl (ml) used to neutralise zirconates solids | Volume of HCl (ml) used to neutralise silicate (liquids) | $Na_2O$ % m/m in solids | $Na_2O$ % m/m in liquids |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| For the 850°C temperature region | | | | | | | | | | | | | | |
| 1: 1 | 7.130 | 58.0 | 0.0578 | 38.960 | 1.730 | 4.0 | 0.100 | | | 23.90 | 16.0 | 2.0 | 90.0 | 10.0 |
| 1: 2 | 8.970 | 73.0 | 0.0728 | 49.016 | 2.747 | 8.0 | 0.200 | | | 29.90 | 32.0 | 4.0 | 90.0 | 10.0 |
| 1: 4 | 12.060 | 98.0 | 0.0979 | 68.850 | 4.086 | 16.0 | 0.400 | | | 35.80 | 27.0 | 48.0 | 36.0 | 64.0 |
| For the 650°C temperature region | | | | | | | | | | | | | | |
| 1: 1 | 6.150 | 50.0 | 0.0499 | 33.60 | 2.004 | 4.0 | 0.100 | | | 21.20 | 1.0 | 16.0 | 6.0 | 94.0 |
| 1: 2 | 7.380 | 60.0 | 0.0598 | 40.33 | 3.344 | 8.0 | 0.200 | | | 23.90 | 4.0 | 32.0 | 11.0 | 89.0 |
| 1: 4 | 9.590 | 78.0 | 0.0778 | 52.40 | 5.141 | 16.0 | 0.400 | | | 29.90 | 48.0 | 27.0 | 64.0 | 36.0 |
| 1: 6 | 11.56 | 94.0 | 0.0938 | 63.17 | 6.397 | 24.0 | 0.600 | | | 35.80 | 38.0 | 76.0 | 66.0 | 34.0 |

# APPENDIX H

## CALCULATED ZIRCONIA AND SILICA YIELDS IF THE PREDOMINANT PHASES ARE THOSE SUGGESTED BY THE REACTIONS IN CHAPTER 8

| The mole ratio of zircon and NaOH | Expected Zirconia yield if $Na_2SiO_3$ and $ZrO_2$ are the predominant phases formed (% m/m) | Expected $ZrO_2$ yield if $Na_4SiO_4$ and $Na_2ZrO_3$ are the predominant phases | Expected zirconia yields if $Na_4Zr_2Si_3O_{12}$ and $ZrO_2$ are the predominant phase | Expected Zirconia yields if $Na_2ZrSiO_5$ is the predominant phases | Expected Silica yields if $Na_2SiO_3$ and $ZrO_2$ are the predominant phases formed | Expected Silica yields if $Na_4SiO_4$ and $Na_2ZrO_3$ are the predominant phases | Expected Silica yields if $Na_4Zr_2Si_3O_{12}$ and $ZrO_2$ are the predominant phase | Expected Silica yields if $Na_2ZrSiO_5$ are the predominant phases |
|---|---|---|---|---|---|---|---|---|
| For the 650°C temperature region | | | | | | | | |
| 1: 1 | 50 | 16.697 | | | 50 | 16.67 | | |
| 1: 2 | 100 | 33.394 | | | 100 | 33.33 | | |
| 1: 4 | 100 | 66.788 | | | 100 | 66.67 | | |
| 1: 6 | 100 | 100 | | | 100 | 100 | | |
| For the 750°C or 850°C Temperature region | | | | | | | | |
| 1: 1 | | | 75.137 | 50 | | | 0.0 | 0.0 |
| 1: 2 | | | 100 | 100 | | | 0.0 | 0.0 |
| 1: 4 | | | 100 | 100 | | | 0.0 | 0.0 |
| 1: 6 | | | 100 | 100 | | | 0.0 | 0.0 |

The Yields of silica are those expected for soluble silica [silica that removed after the dissolution of AFDZ after fusion (Procedure 7.4.3)].

# APPENDIX I

## CALCULATED AMOUNTS OF SODIUM($Na_2O$ m/m) IN THE IN SITU ZIRCONATES OR SODIUM ZIRCONIUM SILICATES, IF THE PREDOMINANT PHASES ARE THOSE SUGGESTED IN CHAPTER 8

| The mole ratio of zircon and NaOH | Expected $Na_2O$ % (m/m) in insoluble solids if $Na_2SiO_3$ and $ZrO_2$ are the predominant phases formed | Expected $Na_2O$ % (m/m) in insoluble solids if $Na_4SiO_4$ and $Na_2ZrO_3$ are the predominant phases | Expected $Na_2O$ % (m/m) in insoluble solids if $Na_4Zr_2Si_3O_{12}$ and $ZrO_2$ are the predominant phase | Expected $Na_2O$ % (m/m) in solids if $Na_2ZrSiO_5$ is the predominant phases | Expected $Na_2O$ % (m/m) in insoluble solids if $Na_2ZrO_3$ and $Na_2SiO_3$ are the predominant phases | Expected $Na_2O$ % (m/m) soluble Silicates if $Na_2SiO_3$ and $ZrO_2$ are the predominant phases formed | Expected $Na_2O$ % (m/m) in soluble Silicates if $Na_4SiO_4$ and $Na_2ZrO_3$ are the predominant phases | Expected $Na_2O$ % (m/m) in soluble silicates if $Na_4Zr_2Si_3O_{12}$ and $ZrO_2$ are the predominant phase | Expected $Na_2O$ % (m/m) in soluble silicates if $Na_2ZrSiO_5$ is the predominant phases | Expected $Na_2O$ % (m/m) in soluble silicates if $Na_2ZrO_3$ and $Na_2SiO_3$ are the predominant phase |
|---|---|---|---|---|---|---|---|---|---|---|
| For the 650°C temperature region | | | | | | | | | | |
| 1: 1 | 0.0 | 33.33 | | | 50 | 100 | 66.67 | | | 50 |
| 1: 2 | 0.0 | 33.33 | | | 50 | 100 | 66.67 | | | 50 |
| 1: 4 | 0.0 | 33.33 | | | 50 | 100 | 66.67 | | | 50 |
| 1: 6 | 0.0 | 33.33 | | | 50 | 100 | 66.67 | | | 50 |
| For the 750°C or 850°C Temperature region | | | | | | | | | | |
| 1: 1 | | | 100 | 100 | 50 | | | 0.0 | 0.0 | 50 |
| 1: 2 | | | 100 | 100 | 50 | | | 0.0 | 0.0 | 50 |
| 1: 4 | | | 100 | 100 | 50 | | | 0.0 | 0.0 | 50 |
| 1: 6 | | | 100 | 100 | 50 | | | 0.0 | 0.0 | 50 |

The above calculations do not only assume complete conversion to the phases in the table, but that the zirconates are not hydrolysed to NaOH and hydrated zirconia.

# APPENDIX J

## A TABULATION OF THE VALUES USED IN THE OPTIMISATION OF THE DECOMPOSITION OF ZIRCON WITH SODIUM HYDROXIDE AFTER 336 HOURS OF FUSION WITH INTERMEDIATE MILLING

### ASSUMPTIONS

Corrected for losses during fusion

1 Free sodium = HCl used to neutralise the sodium silicate solution
2 Ignored losses during purification
3 Ignored losses during water wash

### EXPERIMENTAL

| Temperature (°C) | AFDZ Theoretical | AFDZ found | AFDZ yield | NaOH (g) | Sodium silicate 32% HCl (ml) | Solid 32% HCl (ml) | $ZrO_2$ (g) |
|---|---|---|---|---|---|---|---|
| 850 | 21.86 | 39.64 | 1.81 | 8 | 2 | 16 | 14.26 |
|  | 49.00 | 46.87 | 0.96 | 16 | 4 | 32 | 17.96 |
|  | 61.39 | 57.38 | 0.93 | 32 | 48 | 27 | 22.99 |

### CALCULATIONS

Basis: 100 kg zircon feed

| NaOH/Zircon mol ratio | NaOH kg | Zirconia yield kg | Zircon recycle2 kg | NaOH in SS kg | $SiO_2$ in SS kg | $SiO_2/Na_2O$ | NaOH in Solid kg | Error in NaOH % | Silica waste kg (SiO2) | Silica waste kg (zirconium) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 21.86 | 21.48 | 68.05 | 1.23 | 0.00 | 0.00 | 9.82 | 49.46 |  |  |
| 2 | 43.72 | 51.30 | 23.69 | 4.65 | 0.00 | 0.00 | 37.23 | 4.19 | 25.01 | -23.69 |
| 4 | 87.43 | 67.20 | 0.03 | 57.16 | 0.00 | 0.00 | 32.15 | -2.15 | 32.77 | -0.03 |

## APPENDIX K: THE ELEMENTAL ANALYSIS OF THE ALKALI FUSION PROCESS (All percentages are given as mass percent)

| Sample | $ZrO_2$ | $HfO_2$ | $SiO_2$ | $Na_2O$ | CaO | $Y_2O_3$ | $Al_2O_3$ | $TiO_2$ | MgO | $SO_3$ | $Fe_2O_3$ | Cl | $P_2O_5$ | $U_3O_8$ | $ThO_2$ | $V_2O_5$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $ZrSiO_4$ | 66.5 | 1.64 | 28.6 | 0.220 | 0.205 | 0.180 | 1.23 | 0.382 | 0.165 | | 0.216 | | 0.151 | 470ppm | 870ppm | 79ppm |
| $Na_2ZrO_3$ | 59.0 | 1.28 | 15.6 | 22.0 | 0.16 | 0.361 | 1.03 | 660ppm | | | 520ppm | | | 480ppm | 880ppm | 86ppm |
| $Na_2ZrO_3$ | 56.0 | 1.08 | 24.6 | 32.0 | 0.20 | 0.45 | 1.35 | 0.1 | | | 660ppm | | | 760ppm | 340ppm | 87ppm |
| $Na_2ZrO_3$ | 46.0 | 1.34 | 25.9 | 28.0 | 0.14 | 0.145 | 1.24 | 0.185 | | | 870ppm | | | 340ppm | 450ppm | 45ppm |
| $ZrO_2.nH_2O$ | 62.0 | 1.08 | 12.6 | 680ppm | 0.12 | 0.231 | 1.03 | 0.16 | | | | | | 460ppm | 780ppm | |
| $ZrO_2.nH_2O$ | 58.0 | 1.18 | 23.4 | 48ppm | 0.10 | 0.782 | 1.35 | 0.15 | | | | | | 320ppm | 600ppm | |
| $ZrO_2.nH_2O$ | 28.0 | 1.32 | 27.2 | 220ppm | 0.24 | 0.122 | 1.24 | 0.185 | | | | | | 540ppm | 800ppm | |
| $Na_2SiO_3$ | 1.01 | | 7.09 | 85.9 | 120ppm | | 0.107 | 66ppm | 370ppm | | 200pm | | 390ppm | | | |
| $Na_2SiO_3$ | 0.144 | | 8.45 | 86.7 | 130ppm | | 0.230 | 54ppm | 258ppm | | 180ppm | | 380ppm | | | |
| $Na_2SiO_3$ | 0.323 | | 9.32 | 88.2 | 126ppm | | 0.142 | 87ppm | 430ppm | | 320ppm | | 420ppm | | | |
| NaCI | 0.440 | | 1.04 | 54.9 | 0.145 | | 380ppm | | | 0.980 | 99ppm | | | | | |
| NaCI | 0.132 | | 1.02 | 52.7 | 0.133 | | 240ppm | | | 0.860 | 120ppm | 42.5 | | | | |
| NaCI | 0344 | | 1.84 | 62.0 | 0.124 | | 320ppm | | | 0.670 | 86ppm | 43.8 | | | | |
| AZST | 50.4 | 1.09 | 0.420 | 0.690ppm | 360ppm | 0.115 | 0.112 | 930ppm | | 47.4 | 600ppm | 44.6 | | | | |
| AZST | 50.7 | 1.07 | 0.260 | 0.797ppm | 320ppm | 750ppm | 0.123 | 690ppm | 500ppm | 47.4 | 490ppm | | | | | |
| AZST | 62.6 | 1.08 | 0.134 | 0.633ppm | 0.259 | 0.201 | 0.106 | 0.105 | 670ppm | 34.8 | 812ppm | | | | | |
| $ZrO_2$ | 98.54 | 1.09 | 0.124 | 240ppm | 320ppm | 24ppm | 0.101 | 630 | 500ppm | 0.130 | 260ppm | | | | | |
| $ZrO_2$ | 98.62 | 1.04 | 0.234 | 234ppm | 450ppm | 750ppm | 0.120 | 690ppm | 670ppm | 0.05 | 490ppm | | | | | |
| $ZrO_2$ | 98.42 | 1.12 | 0.101 | 560ppm | 0.359ppm | 20ppm | 0.134 | 220ppm | 220ppm | 0.12 | | | | | | |
| R-AZST | 69.7 | 1.53 | 0.134 | 0.227 | 0.384 | 0.377 | 0.134 | 0.127 | | 23.0 | 940ppm | 3.50 | 0.214 | 0.204 | 0.143 | |
| R-AZST | 72.3 | 1.62 | 0.142 | 0.234 | 0.352 | 0.420 | 0.147 | 0.110 | | 19.2 | 960ppm | 2.58 | 0.310 | 0.101 | 0.098 | |

**KEY**: - $ZrSiO_4$ is zircon. - $Na_2ZrO_3$ are the zirconates or zirconium silicates before HCl titration. - $ZrO_2.nH_2O$ is the hydrous zirconia after the removal of sodium. - $Na_2SiO_3$ is the silicate by-product. - NaCl is the sodium chloride effluent. - AZST is the zirconium sulphate used as a central chemical in the synthesis of zirconium chemicals. - $ZrO_2$ is the zirconia product obtained from the calcinations of AZST. R-AZST is the AZST effluent obtained from the purification of ZBS (note the high uranium and thorium content)