

ALKALI-FUSION PROCESSES FOR THE
RECOVERY OF ZIRCONIA AND ZIRCONIUM
**ALKALI-FUSION PROCESSES FOR THE
RECOVERY OF ZIRCONIA AND ZIRCONIUM
CHEMICALS FROM ZIRCON SAND**

Zola Kwela

ALKALI-FUSION PROCESSES FOR THE RECOVERY OF ZIRCONIA AND ZIRCONIUM CHEMICALS FROM ZIRCON SAND

A dissertation submitted by

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In partial fulfilment of the requirements of the degree of

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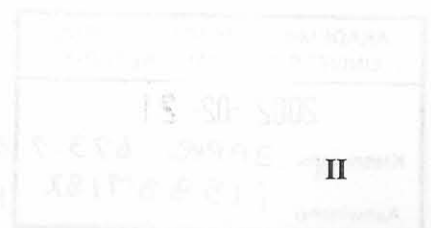
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ABSTRACT

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 zirconium extraction 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 mole 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.

Characterisation of the decomposition step, showed that within the zircon tetragonal structure, the SiO_4 tetrahedra linkages are less stable than the ZrO_8 bisdisphenoids linkages. This was shown by the preference of sodium for the SiO_4 tetrahedra.

Fusion for 336 hours with periodic intermediate milling proved the preference of sodium for attacking the SiO_4 tetrahedra linkages. This selectivity was clearly demonstrated when decomposing zircon in sodium poor (< 4 moles NaOH per mol of zircon) and low temperature (e.g. 650°C) reaction conditions. The advantage of fusing at 650°C with a mole (or even two moles) of sodium hydroxide is that it leads to minimal (< 5% m/m Na_2O) sodium in the insoluble solids after the removal of soluble silicates. This is a solution to alkali fusion processes, as high amounts of water are usually required to wash out the neutralised sodium salt e.g. 50g of NaCl usually requires a litre of distilled water to reach levels below 600 ppm Na_2O . This reaction condition can be employed when synthesising products where low amounts of sodium are required in the final products e.g. when synthesising zirconia for the ceramic industry.

When fusing for two hours without the intermediate milling step the following results were observed. The reaction at 850°C when fusing a mole of zircon with two moles of sodium hydroxide, was the most efficient in consuming sodium hydroxide. Near complete zircon decomposition was at 850°C when fusing a mole of zircon with six moles of sodium hydroxide. Characterisation with XRD, Raman and IR spectroscopy was misleading as complex spectra were measured, indicating many different phases present. The inconsistency was partly attributed to non-homogeneity in the samples due to NaOH migration.

When fusing for 336 hours with the intermediate milling step the following results were observed. The reaction at 850°C when fusing a mole of zircon with a mole of sodium hydroxide was the most efficient in consuming sodium hydroxide. This reaction condition was able to liberate 0.58 moles of zirconia per mole of sodium hydroxide. The highly improved efficiency was attributed to the formation of phases $\text{Na}_2\text{ZrSiO}_5$, $\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}$ and ZrO_2 . The process is pseudo-catalytic as it liberates zirconium while showing minimal sodium consumption. Decomposition at 650°C also showed improved efficiency but not as efficient as the 850°C sub-stoichiometric fusion. The improved decomposition was attributed to the polymerisation of the orthosilicate monomers Na_4SiO_4 to the metasilicate chains Na_2SiO_3 .

Complete decomposition of zircon was observed at 850°C when fusing a mole of zircon with four moles of sodium hydroxide. The improved efficiency of this reaction condition was attributed to the formation of the phases $\text{Na}_2\text{ZrSiO}_5$, Na_2ZrO_3 and Na_2SiO_3 . The phase $\text{Na}_2\text{ZrSiO}_5$ minimises sodium consumption.

The intermediate milling step was not introduced in these processes. It was moved from milling after to milling during fusion. Besides the improved zircon decomposition, there is no need for further milling after fusion as the powder has a small particle size ready for water dissolution.

Washing in-situ ZBS (ZBS that was prepared from in-situ hydrous zirconia with stoichiometric amounts of sulphuric acid) once with 0.5M HCl was necessary to remove radioactive impurities to levels below parts per million.

Washing Ref. ZBS (ZBS that was prepared by precipitation from a zirconyl chloride solution with stoichiometric amounts of sulphuric acid) leads to negligible zirconia losses (< 2% m/m ZrO_2 when digesting with 1M HCl). This method offers a solution to the zirconia losses associated with washing in-situ ZBS with mineral acids. The zirconia and zirconium chemicals synthesised here are the purest obtained to date, when compared to other zirconium recovery processes. The processes used are far too rapid (in terms of time and number of steps) when compared to precipitation, crystallisation or ion-exchange techniques. The purity is attributed to the digestion of impurities in a mineral acid (e.g. HCl or HNO_3) environment. In this environment the ZBS remains insoluble.

The high amounts of silica concentrated in the unreacted zircon can be separated by physical means from the undecomposed zircon due to the large density difference between the two. This allows re-circulation of unreacted zircon.

The alkali silicate by-product contains radioactive impurities below parts per million. This is an indication that the radioactivity impurities remained insoluble during water leaching. The radioactive impurities can be collected by precipitation or crystallisation and disposed of safely.

KEYWORDS: Baddeleyite, Characterisation, Design, Efficiency, in-situ ZBS, Optimise, Process, Ref. ZBS, Sub-stoichiometric, Zircon, Zirconia and Zirconium chemicals

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In memory of my late mother Nobahle Tissang

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TABLE OF CONTENTS

| | PAGE |
|--|-------------|
| Title Page | I |
| Abstract | III |
| Acknowledgements | IX |
| Table of Contents | X |
| Nomenclature list | XV |
| | |
| CHAPTER 1 INTRODUCTION | 1 |
| 1.1 Introduction | 1 |
| 1.2 References | 3 |
| | |
| CHAPTER 2 ZIRCONIUM MINERAL SOURCES | 5 |
| 2.1 Zirconium | 5 |
| 2.2 Zircon | 8 |
| 2.3 Baddeleyite and Zirconia | 12 |
| 2.4 Conclusions | 13 |
| 2.5 References | 13 |
| | |
| CHAPTER 3 ZIRCONIUM APPLICATIONS | 15 |
| 3.1 Introduction | 15 |
| 3.2 Zircon | 16 |
| 3.3 Zirconia | 16 |
| 3.4 Zirconium chemicals | 17 |
| 3.5 Applications | 18 |
| 3.5.1 Foundry | 18 |
| 3.5.2 Refractory | 19 |
| 3.5.3 Abrasives | 19 |
| 3.5.4 Opacifier | 19 |
| 3.5.5 Sensors | 20 |

| TABLE OF CONTENTS CONTINUED... | PAGE |
|--|-------------|
| 3.5.6 Catalysts | 20 |
| 3.5.7 Advanced ceramics | 25 |
| 3.5.8 Paint dryers | 23 |
| 3.5.9 Pigments | 26 |
| 3.6 Conclusions | 28 |
| 3.7 References | 28 |
| | |
| CHAPTER 4 THE CHEMISTRY OF ZIRCONIUM | 30 |
| | |
| 4.1 Introduction | 30 |
| 4.2 The aqueous Chemistry | 31 |
| 4.2.1 The zirconyl group | 31 |
| 4.3 Tetramers | 31 |
| 4.4 Zirconium Hydroxide Chlorides | 32 |
| 4.5 Hydrolysis and polymerisation | 33 |
| 4.6 Zirconium carbonates | 34 |
| 4.7 Zirconium Sulphates | 36 |
| 4.8 Conclusions | 39 |
| 4.9 References | 40 |
| | |
| CHAPTER 5 ZIRCONIA RECOVERY PROCESSES | 41 |
| | |
| 5.1 Introduction | 41 |
| 5.2 Thermal dissociation | 42 |
| 5.3 Chlorination | 44 |
| 5.4 Lime Fusion | 46 |
| 5.5 Carbiding | 47 |
| 5.6 Fluorosilicate Fusion | 48 |
| 5.7 Caustic Fusion | 50 |
| 5.7.1 Sub-stoichiometric fusion | 50 |
| 5.7.2 Slight excess fusion | 52 |
| 5.7.3 High Stoichiometric fusion | 54 |

| TABLE OF CONTENTS CONTINUED... | PAGE |
|--|-----------|
| 5.8 Conclusions | 55 |
| 5.9 References | 56 |
| CHAPTER 6 THE STRUCTURE OF ZIRCON | 57 |
| 6.1 Introduction | 57 |
| 6.2 Zircon Structure | 58 |
| 6.3 Conclusions | 61 |
| 6.4 References | 61 |
| CHAPTER 7 EXPERIMENTAL | 62 |
| 7.1 Introduction | 62 |
| 7.2 Apparatus | 62 |
| 7.2.1 Pastel and mortar | 62 |
| 7.2.2 Clay crucibles | 62 |
| 7.2.3 High Temperature oven | 63 |
| 7.2.4 Centrifuge | 63 |
| 7.2.5 pH meter | 63 |
| 7.3 Planning | 63 |
| 7.4 Methods | 63 |
| 7.4.1 Reagents | 63 |
| 7.4.2 Zircon Fusion (Milling after fusion) | 66 |
| 7.4.3 Zircon Fusion (Intermediate milling) | 66 |
| 7.4.3.1 Leaching of AFDZ | 66 |
| 7.4.3.2 Alkali silicate | 66 |
| 7.4.3.3 Sodium and silica determination | 67 |
| 7.4.4 The alkali zirconates | 67 |
| 7.4.4 Preparation of ZBS | 67 |
| 7.4.4.1 Synthesis of in-situ ZBS | 65 |
| 7.4.4.2 Synthesis of reference ZBS | 65 |

| TABLE OF CONTENTS CONTINUED... | PAGE |
|---|-----------|
| 7.4.5 Purification and analysis of ZBS products | 68 |
| 7.4.6 Synthesis of AZST from ZBS | 66 |
| 7.4.6.2 Synthesis of AZST from hydrous zirconia | 66 |
| 7.4.7 Residue | 66 |
| 7.4.8 Zirconium chemicals | 66 |
| 7.4.8.1 Synthesis of ZBC | 66 |
| 7.4.8.2 Synthesis of ZBS | 69 |
| 7.5 Analysis | 70 |
| 7.5.1 X-ray diffractometry | 70 |
| 7.5.2 Scanning electron microscopy | 70 |
| 7.5.3 X-ray fluorescence | 70 |
| 7.5.4 Raman and infrared spectrophotometers | 70 |
| 7.6 References | 70 |
| | |
| CHAPTER 8 CHARACTERISATION | 71 |
| | |
| 8.1 Introduction | 71 |
| 8.2 Results | 72 |
| 8.3 Discussions | 112 |
| 8.3.1 Zircon decomposition (2 hours) | 112 |
| 8.3.2 Zircon decomposition (336 hours) | 116 |
| 8.4 Experimental Determination (Mass Balance) | 120 |
| 8.4.1 Sodium Determination | 120 |
| 8.4.2 Sodium recovery at 650°C | 120 |
| 8.4.3 Sodium recovery at 850°C | 121 |
| 8.5 The metasilicate | 121 |
| 8.6 Zirconium sulphate | 122 |
| 8.7 Zirconia | 122 |
| 8.8 Conclusions | 122 |
| 8.8.1 Decomposition at 650°C | 123 |
| 8.8.2 Decomposition at 850°C | 124 |
| 8.8.3 Products | 124 |

| TABLE OF CONTENTS CONTINUED... | PAGE |
|--|------------|
| 8.9 References | 125 |
| CHAPTER 9 OPTIMISATION OF ZIRCON DECOMPOSITION | 126 |
| 9.1 Introduction | 126 |
| 9.2 Results | 128 |
| 9.3 Discussions | 132 |
| 9.3.1 Fusion for two hours | 132 |
| 9.3.2 Fusion for 336 hours | 133 |
| 9.4. Conclusions | 133 |
| 9.4.1 Fusion for two hours | 133 |
| 9.4.2 Fusion for 336 hours | 134 |
| 9.5 References | 136 |
| CHAPTER 10 THE <i>in-situ</i> ZBS PURIFICATION STEP | 137 |
| 10.1 Introduction | 137 |
| 10.2 Results | 138 |
| 10.3 Discussions | 139 |
| 10.4 Conclusions | 140 |
| 10.5 References | 142 |
| CHAPTER 11 CONCLUSIONS | 143 |
| 11.1 Introduction | 143 |
| 11.1 Zircon decomposition | 144 |
| 11.2.1 Decomposition at 650°C | 145 |
| 11.2.2 Decomposition at 850°C | 145 |
| 11.3.1 The ZBS <i>in-situ</i> purification step | 146 |
| 11.3.2 The Ref. ZBS purification route | 126 |
| 11.4 The By-product | 147 |
| 11.5 The AZST product | 147 |

TABLE OF CONTENTS CONTINUED...

PAGE

| | | |
|--------------------------------|--|-----|
| | 11.6 Zirconia | 147 |
| | 11.7 The residue and re-circulation | 147 |
| APDZ | 11.8 De Wet's process | 147 |
| AZST | Ammonium zirconium sulphate trihydrate | |
| BZC | Basic zirconium carbonate | |
| ZNS | Zinc zinc sulphate | |
| C ₁ -F ₁ | Calcium partially stabilised zirconia | |
| C ₂ -F ₂ | Calcium fully stabilised zirconia | |
| C ₃ -F ₃ | Calcium zirconium zirconia polycrystalline | |
| Ca | Calcium hydroxide carbonate | |
| CaO | Calcium oxide | |
| DC | Dioxane solution | |
| DC | Dioxane solution | |
| Sp-1-7 | Magnox radial fuel element | |
| Sp-1-8 | Magnox radial fuel element | |
| niZ | Nickel zirconium | |
| FS | Partially stabilised zirconia | |
| ReAZS | Refractory zirconium oxide | |
| Ref. ZBS | Reference zirconium sulphate | |
| SEM | Scanning electron microscope | |
| TTP | Tetrapropylammonium tetrafluoroborate | |
| TZP | Tetragonal zirconia polycrystalline | |
| Y ₂ O ₃ | Yttrium oxide | |
| Y ₂ O ₃ | Yttrium oxide | |
| ZBC | Zirconium basic carbonate | |
| ZBS | Zirconium basic sulphate | |
| ZOC | Zirconium chloride | |
| ZST | Zirconium sulphate trihydrate | |

ABBREVIATION LIST

| | |
|--------------------|---|
| AFDZ | Alkali fused decomposed zircon |
| AZST | Acid zirconium sulphate trihydrate |
| BZC | Basic zirconium carbonate |
| BZS | Basic zirconium sulphate |
| Ca-PSZ | Calcium partially stabilised zirconia |
| Ca-CSZ | Calcium cubic-stabilised zirconia |
| Ce-TZP | Ceria tetragonal zirconia polycrystal |
| CSZ | Cubic stabilised zirconia |
| c-ZrO ₂ | Cubic zirconia |
| DZ | Dissociated zircon |
| DP | Decomposed product |
| Mg-CSZ | Magnesium cubic-stabilised zirconia |
| Mg-PSZ | Magnesium partially stabilised zirconia |
| m-ZrO ₂ | Monoclinic zirconia |
| PSZ | Partially stabilised zirconia |
| R-AZST | Radioactive zirconium sulphate |
| Ref. ZBS | Reference zirconium basic sulphate |
| SEM | Scanning electron microscope |
| TZP | Tetragonal Zirconia polycrystal |
| t-ZrO ₂ | Tetragonal zirconia |
| XRD | X-ray diffraction |
| XRF | X-ray fluorescence |
| ZBC | Zirconium basic carbonate |
| ZBS | Zirconium basic sulphate |
| ZOC | Zirconyl chloride |
| ZST | Zirconium sulphate tetrahydrate |