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

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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 Na_2ZrSiO_5, $Na_4Zr_2Si_3O_{12}$ 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 Na_2ZrSiO_5, Na_2ZrO_3 and Na_2SiO_3. The phase Na_2ZrSiO_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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Sidudla mgane wam ndiyakuthanda.

Kutheni izolo ubungekho?

Ndiyakutshela udlala ngam!

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ABBREVIATION LIST

AFDZ	Alkali fused decomposed zircon
AZST	Acid zirconium sulphate trihydrate
BZC	Basic zirconium carbonate
BZS	Basic zirconium sulphate
Ca-PSZ	Calcia partially stabilised zirconia
Ca-CSZ	Calcia 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	Magnesia cubic-stabilised zirconia
Mg-PSZ	Magnesia 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