8 RESULTS

The main focus of this study was on optimising the fusion step in the De Wet process for the beneficiation of zircon sand. In this chapter, the yield and XRD results obtained for the alkali-decomposed zircon are reported. All the detailed XRD spectra are contained in Appendix A.

The composition of the zircon raw material from Ferro Industrial Products was determined using X-ray fluorescence (XRF). Table 8.1 shows the results. The raw material contained in excess of 98% zircon. Appendix A shows the XRD spectrum for the zircon raw material used in this study, as well as a spectrum for pure zirconia from Aldrich Chemicals with a purity of 99% and a particle size of 9 μm. The latter is the main end product sought in this investigation. The zircon XRD pattern shows an intense peak at 27° on the 2θ scale. Other peaks are located at 20°, 35.7° and 53.5°, with media intensity. In the zirconia XRD spectrum, the intense peaks are located at 28.2° and 31.6°. There is a series of medium intensity peaks.

Table 8.1: Composition of zircon raw material

Component		ZrO_2+HfO_2	SiO_2	Ti	Fe	Ca	P	U	Th
Concentration	ppm	65.7%	33.6%	738	683	666	455	331	144

ppm: parts per million on a mass basis.

8.1 Long Fusion Times

In order to establish the equilibrium products for the zircon and sodium hydroxide reaction, 336-hour experiments were conducted. These reactions were conducted at different temperatures and different reactant ratios, with intermediate milling every 24 hours. Appendix A shows the XRD spectra of the alkali fused decomposed zircon (AFDZ). Table 8.2 shows the main phases identified from the XRD spectra at the given fusion temperatures and mol ratios. Kwela [16] has reported additional data, especially at 650 °C.

Table 8.2: Equilibrium phases identified in the XRD spectra of AFDZ produced after fusion at 336 hours, with intermediate milling after every 24 hours, at different temperatures

$NaOH:ZrSiO_4$	Temperature (°C)	Phases			
		$ZrSiO_4$	Na_2ZrO_3	Na_2ZrSiO_5	Na_2SiO_3
2:1	600	Major	Minor	-	Minor
2:1	650	Major	Major	-	Minor
2:1	700	Major	Major	Major	Minor
1:1	750	Major	Minor	Major	-
2:1	750	Major	Major	Major	Minor
4:1	750	-	Major	Trace	Minor
2:1	850	Trace	Trace	Major	-
4:1	850	-	Major	Major	-
6:1	850	-	Major	-	Minor

8.2 Effect of Fusion Time

To study the effect of fusion time on conversion, experiments were conducted over 1, 2, 4, 24 and 336 hours, at a fusion temperature of 850 °C. Table 8.3 summarises the phase data obtained from the XRD spectra listed in Appendix A.

Table 8.3: Phases identified in the XRD spectra of AFDZ produced by fusion at 850 °C using different fusion times and mol ratios

$NaOH:ZrSiO_4$	Time (hours)	Phases			
		$ZrSiO_4$	Na_2ZrO_3	Na_2ZrSiO_5	Na_2SiO_3
1:1	48	Major	-	Minor	-
2:1	1	Major	Minor	Trace	Minor
2:1	2	Major	-	Major	Minor
2:1	4	Major	Minor	Major	Minor
2:1	24	Major	-	Major	Minor
2:1	48	Major	-	Major	-
4:1	2	Minor	Major	-	-

8.3 Effect of Stoichiometry on Two-hour Fusions

Appendix A also shows the XRD spectra for the other experiments conducted at various temperatures, times and mol ratios. Table 8.4 lists the phases identified in the XRD spectra of AFDZ obtained by fusion at 850 °C.

Table 8.4: Phases identified in the XRD spectra of AFDZ produced by fusion at 850 °C for 2 hours and different mol ratios

$NaOH:ZrSiO_4$ (mol)	Phases			
	$ZrSiO_4$	Na_2ZrO_3	Na_2ZrSiO_5	Na_2SiO_3
2:1	Major	Major	Major	Minor
4:1	Minor	Major	Trace	Trace

8.4 Fusion Times at Other Temperatures

In order to understand the kinetics of reaction of the alkali fusion process, fusions were also conducted at other temperatures, i.e. at 650 and 750 °C. Table 8.5 shows the phases identified in the fused reaction products from the XRD spectra listed in Appendix A.

Table 8.5: Observed phases in the XRD spectra of samples fused at 650 and 750 °C

$NaOH:ZrSiO_4$ (mol)	Time (h)	Temperature (°C)	Phases				
			$ZrSiO_4$	Na_2ZrO_3	Na_2SiO_3	$Na_6Si_2O_7$	Na_4SiO_4
2:1	2	650	Major	Minor	Trace	-	-
2:1	4	650	Major	Minor	-	-	-
4:1	1	650	Major	Major	-	Minor	-
4:1*	2	650	Major	Major	-	Minor	-
4:1	4	650	Major	Major	-	-	Minor
4:1*	24	650	Major	Major	-	-	-
6:1	1	650	Minor	Major	-	-	Minor
6:1*	2	650	Trace	Major	-	Minor	Minor
4:1*	4	700	Major	Major	-	-	-
2:1	2	750	Major	-	Minor	-	-
4:1	2	750	Major	Major	-	-	Minor

*Sample poorly crystallised.

8.5 Direct Synthesis of Zirconia

The direct synthesis of zirconia requires the exclusive formation of sodium zirconate. Experiments were therefore conducted to maximise this phase in the fusion products. Fusions were conducted at 650 and 750 °C, using 2 to 6 mol of sodium hydroxide per mol of zircon. Fusion times were varied from 2 to 48 hours. Table 8.5 also reports on the phases identified in the XRD spectra of these decomposition products.