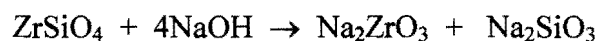


9 DISCUSSION

9.1 Long Fusion Times: Equilibrium Phases

Long fusion times were investigated to determine which equilibrium phases would form as a function of temperature and composition. Fusion experiments were conducted for 336 hours, at different temperatures and various NaOH:ZrSiO₄ mol ratios. The conclusions drawn below are based on the interpretations of the XRD spectra listed in Appendix A and tabulated in Table 8.2.

When 1 mol of zircon is fused with 2 mol of sodium hydroxide, zircon and Na₂ZrO₃ are the main reaction products at 600 °C and 650°C. The XRD spectra also reveal the presence of minor amounts of crystalline sodium metasilicate. The observed product spectrum for these temperatures is consistent with the reaction shown in Scheme 9.1 below.



Scheme 9.1: Reaction observed at 600 and 650°C when 2 mol of sodium hydroxide were fused with 1 mol of zircon for 336 hours

The XRD peaks for Na₂ZrO₃ are more intense for the 650°C fusion than the 600°C reaction. This implies improved conversion of zircon to sodium metazirconate at the higher reaction temperature. At a fusion temperature of 700 °C, Na₂ZrSiO₅ appears as a new phase in the XRD spectrum. This suggests the occurrence of an additional reaction, as shown in Scheme 9.2.

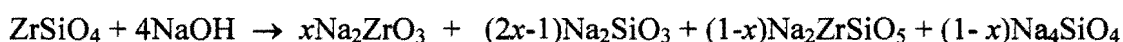


Scheme 9.2: Reaction observed above 700 °C when 2 mol of sodium hydroxide were fused with 1 mol of zircon for 336 hours

Above 750 °C, ZrSiO₄, Na₂ZrO₃ and Na₂ZrSiO₅ are the major equilibrium phases. Although sodium zirconate appears as a major phase at 750 °C and a 2:1 stoichiometry, its peak intensities are clearly reduced compared with those at the 700°C fusion temperature. This indicates that the formation of sodium zirconium silicate is favoured over sodium zirconate at low mol ratios and high temperatures.

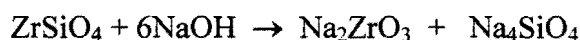
At 850 °C, the XRD spectrum of the AFDZ produced by fusion of 2 mol of sodium hydroxide with 1 mol of zircon for 336 hours shows that Na₂ZrSiO₅ is virtually the sole equilibrium phase formed. Only traces of Na₂ZrO₃ and zircon remain.

As expected, increasing the ratio of sodium hydroxide to zircon increases the sodium zirconate yield. The apparent presence of ZrO₂ (as reported on Spectrum 10 in Appendix A) may be an artefact of sodium carbonate as the XRD peaks of these two compounds show considerable overlap (see Spectrum 12 in Appendix A). The phases observed at 850 °C using the 4:1 stoichiometry indicate that the products may be explained by reactions 9.1 and 9.2 occurring simultaneously. The overall reaction is shown in Scheme 9.3.



Scheme 9.3: Reaction observed at 850 °C when 4 mol of sodium hydroxide were fused with 1 mol of zircon for 336 hours

The formation of sodium orthosilicate (Na₄SiO₄) can be explained by the reaction shown in Scheme 9.4.



Scheme 9.4: Reaction explaining the formation of sodium orthosilicate

A key observation is that sodium zirconium silicate does not form when fusing below 700 °C. This implies that sodium zirconate is the equilibrium phase at low temperatures.

9.1.1 Phase diagrams

Figures 9.1 and 9.2 show simplified phase diagrams previously reported by Manhique *et al.* [3]. They were constructed from the phases observed in the XRD spectra for 336-hour fusions. The vertical dotted line in these figures shows the locus of increasing the reactant ratio of NaOH to zircon used in the current experiments. Note that the phase Na₄Zr₂Si₃O₁₂, reported by D'Ans *et al.* [62] was not observed in this study. However, it was observed by Kwela [16] when fusing 4 mol of NaOH with 3 mol of zircon at 850 °C.

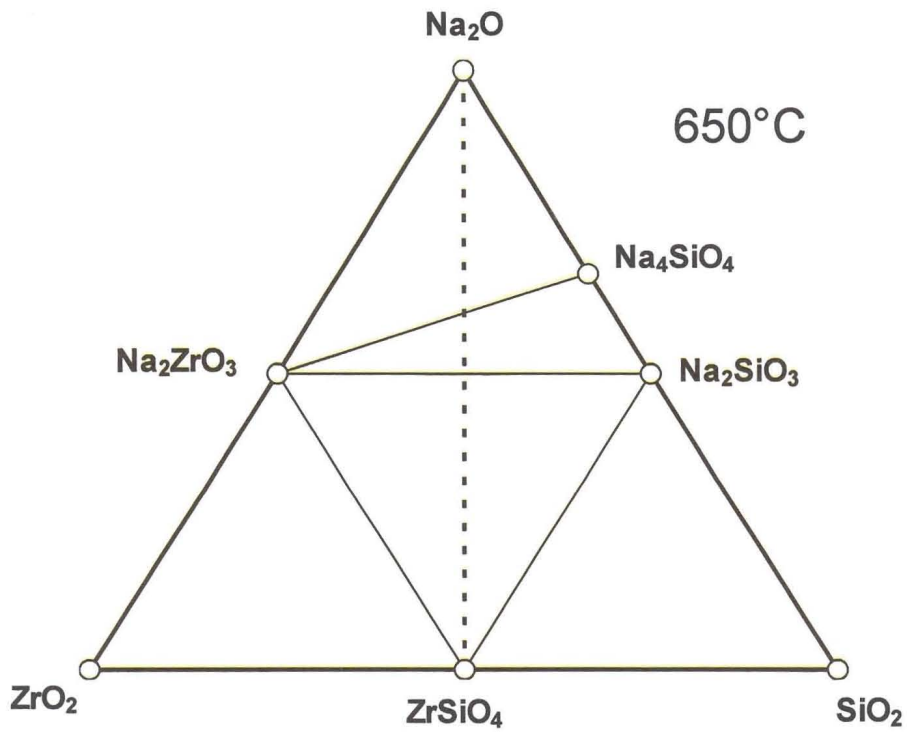


Figure 9.1: Simplified phase diagram for alkali decomposition of zircon at 650 °C

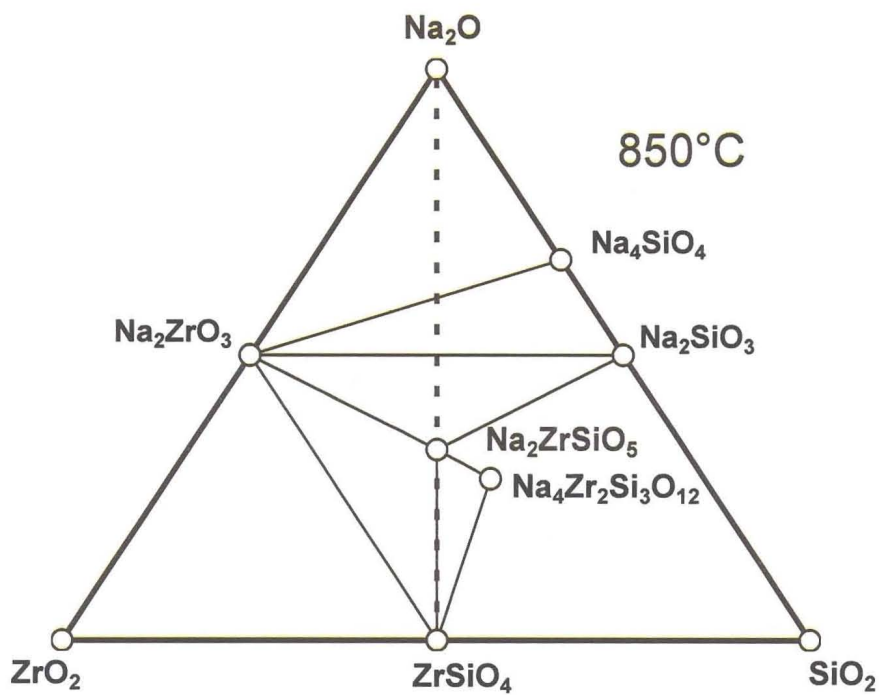


Figure 9.2: Simplified phase diagram for alkali decomposition of zircon at 850 °C

Figure 9.1 applies for fusions conducted at 650 °C, as well as at 600 °C. Figure 9.2 indicates the equilibrium product spectrum for reactions conducted at higher temperatures. The latter is similar to the phase diagram accepted in the literature for fusing zircon with sodium carbonate at temperatures above 1 000 °C [62].

9.1.2 Effect of fusion time on zirconia yield

The effect of fusion time on zirconia yield was studied. Fusions were conducted over fusion times of 1, 2, 4, 24 and 336 hours, using 2 and 4 mol of sodium hydroxide per mol of zircon in the fusion. The results are shown graphically in Figures 9.3 and 9.4.

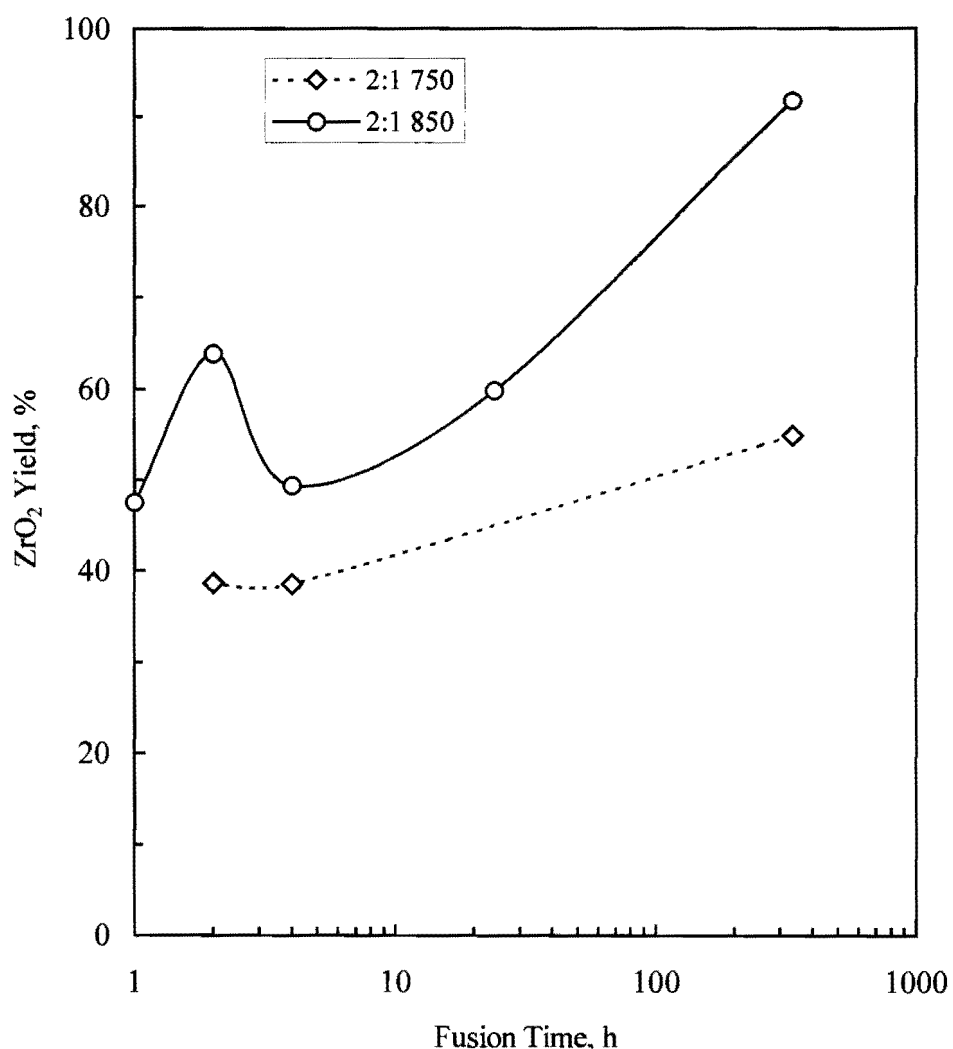


Figure 9.3: Effect of time on zirconia recovery at 750 and 850 °C, using 2 mol of sodium hydroxide per mol of zircon. A local maximum in the yield is observed at 2 hours of fusion

The zirconia yield curve at 850 °C shows an unexpected local maximum (of about 63%) at the 2-hour fusion point. Silica recovery also shows a local minimum of about 22% here. A minimum ($\approx 49\%$) in the zirconia yield is observed at 4 hours of fusion. This roughly corresponds to the maximum in the silica recovery. Similar behaviour is observed at 750 °C (Figures 9.4 and 9.5).

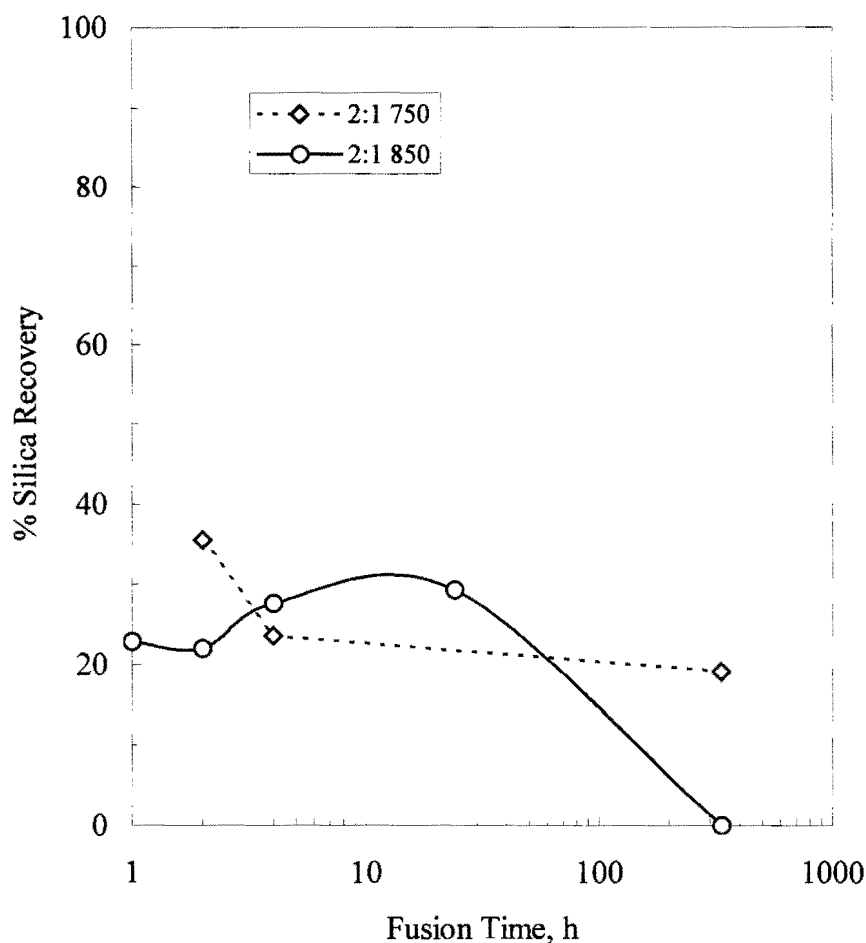


Figure 9.4: Silica recovery at 750 and 850 °C using 2 mol of sodium hydroxide per mol of zircon sand

Silica recovery reaches a minimum at 850 °C for 336 hours for the 2 mol stoichiometric ratio. This is consistent with the formation of $\text{Na}_2\text{ZrSiO}_5$, which is stable with respect to water, i.e. the compound does not hydrolyse in pure water. Consequently, sodium cannot be leached with water washing. The XRD results confirmed the formation of this phase (see Spectrum 9 in Appendix A). For the fusion at 750 °C, the silica recovery at 336 hours is still as high as 19% (Figure 9.4). This suggests the presence of soluble sodium silicates in the product

spectrum and therefore, by implication, also Na_2ZrO_3 . This is confirmed by Spectrum 7 in Appendix A. Note that the sodium silicates do not crystallise easily and it is easier to infer their presence by indirect means in the XRD.

For 4 mol, similar behaviour is observed, i.e. at 2 hours and 850 °C there is a local maximum in the zirconia yield of ca. 76% (Figure 9.5). Figure 9.6 shows the silica recovery using 4 mol of sodium hydroxide per mol of zircon.

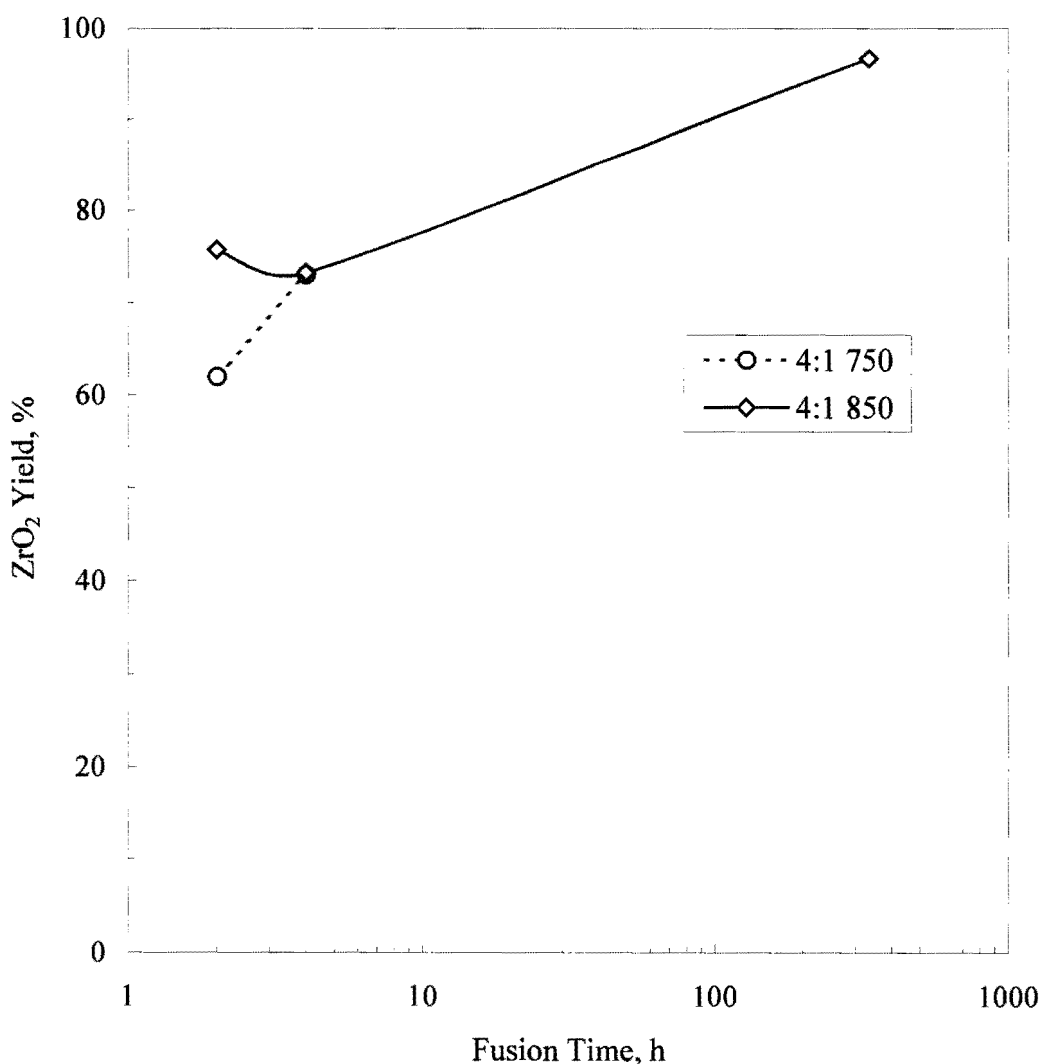


Figure 9.5: Effect of time on zirconia recovery at 750 and 850 °C using 4 mol of sodium hydroxide per mol of zircon sand

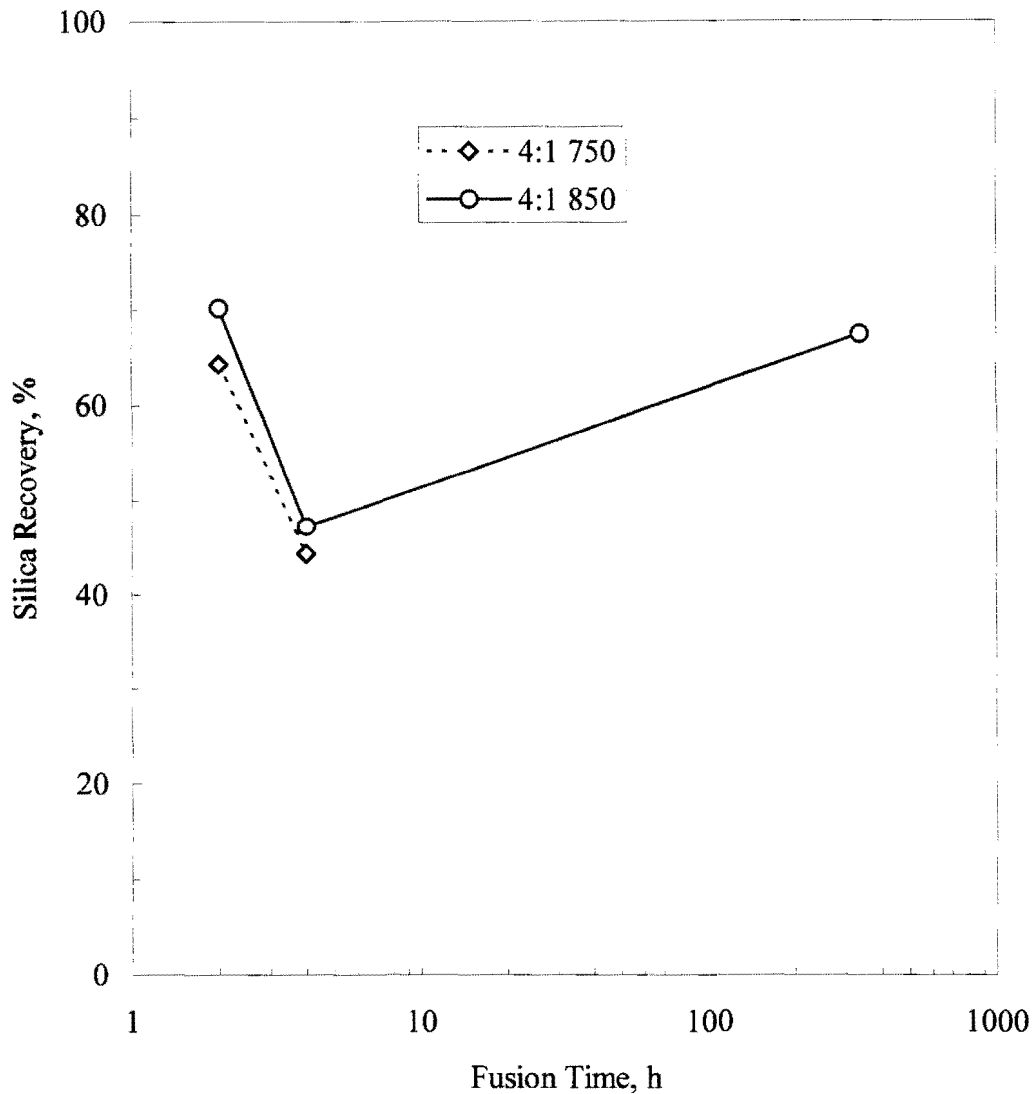


Figure 9.6: Silica recovery at 750 and 850 °C using 4 mol of sodium hydroxide per mol of zircon sand

9.2 Optimisation of Zirconia Yield at Two Hours Fusion Time

Commercially, short fusion times would be preferred. Based on this fact and the yield maximum observed with the 2-hour fusions, further experiments were limited to this fusion time. The effects of fusion temperature and stoichiometry on zirconia yield were studied and the results are presented in Figure 9.7. The zirconia yield shows a monotonic increase with temperature and mol ratio.

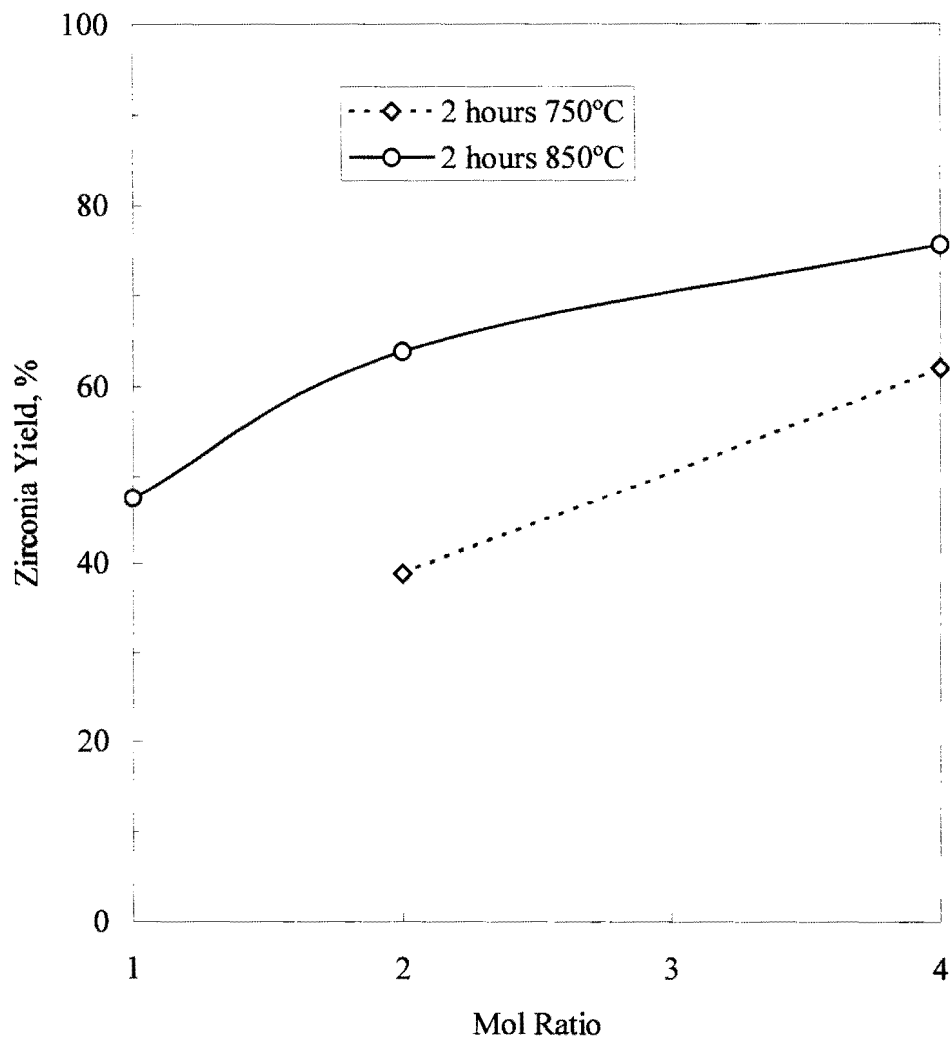


Figure 9.7: Effect of the stoichiometry of the reaction on zirconia yield after 2 hours of fusion

Silica recovery shows a minimum when 2 mol of sodium hydroxide are used at 850 °C for 2 hours. This is attributed to the formation of $\text{Na}_2\text{ZrSiO}_5$ (see Spectrum 8 in Appendix A).

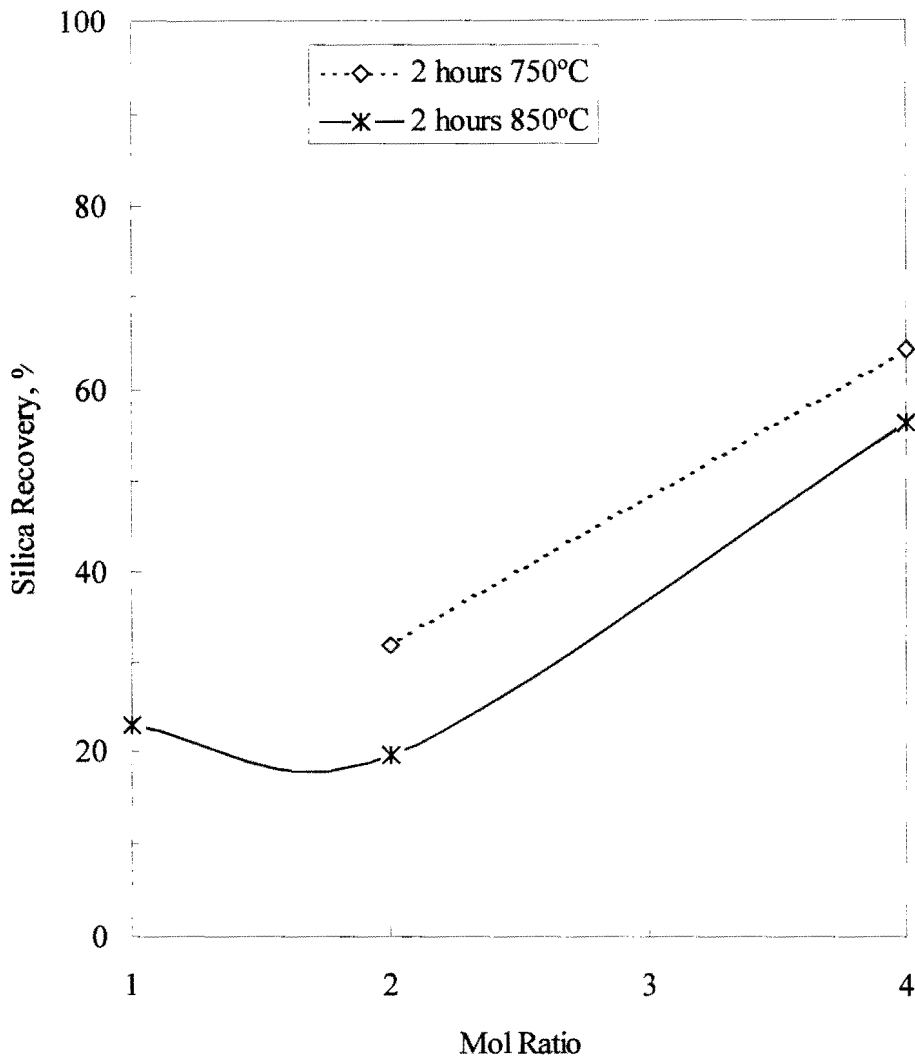


Figure 9.8: The effect of stoichiometry on silica recovery at 750 and 850 °C fusion temperatures

9.3 Efficiency of the Process

The efficiency of the process was tested by studying the zirconia yield relative to the amount of sodium hydroxide consumed (mass per mass basis), at 650, 750 and 850 °C, using 2, 4 and 6 mol at 2 hours fusion time. The results are presented in Figure 9.9. The highest reagent efficiency is attained for fusions conducted at 850 °C using 2 mol of sodium hydroxide.

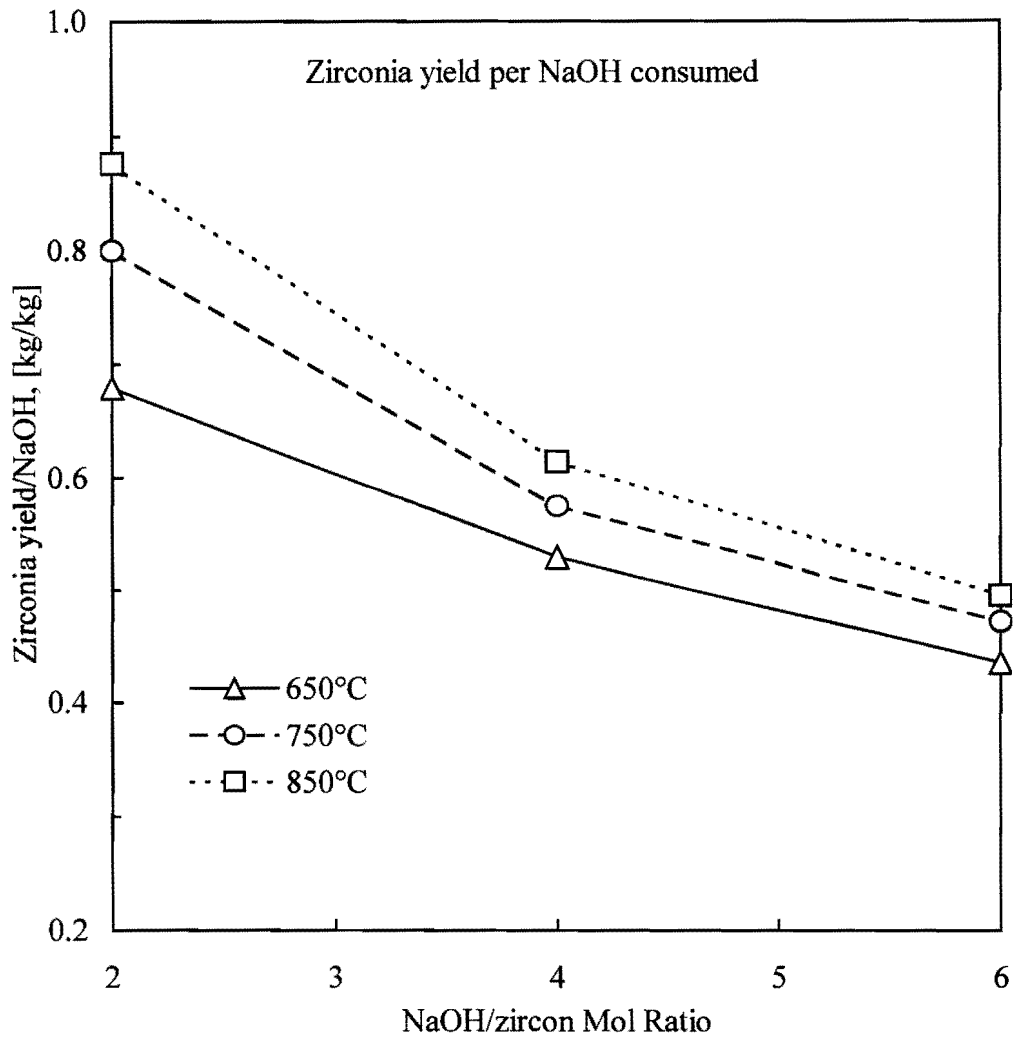


Figure 9.9: Efficiency of the process analysed for the effects of fusion temperature, stoichiometry for 2-hour fusion times

The process also allows the recovery of alkali in the form of a saleable sodium silicate product stream. The formation of $\text{Na}_2\text{ZrSiO}_5$ exacerbates the generation of waste, as it has to be hydrolysed using acid. This not only creates a salt-based waste stream, but also consumes additional acid reagent. Figure 9.10 shows that fusions conducted at 850 °C using 2 mol of sodium hydroxide also yield the lowest amount of salt waste.

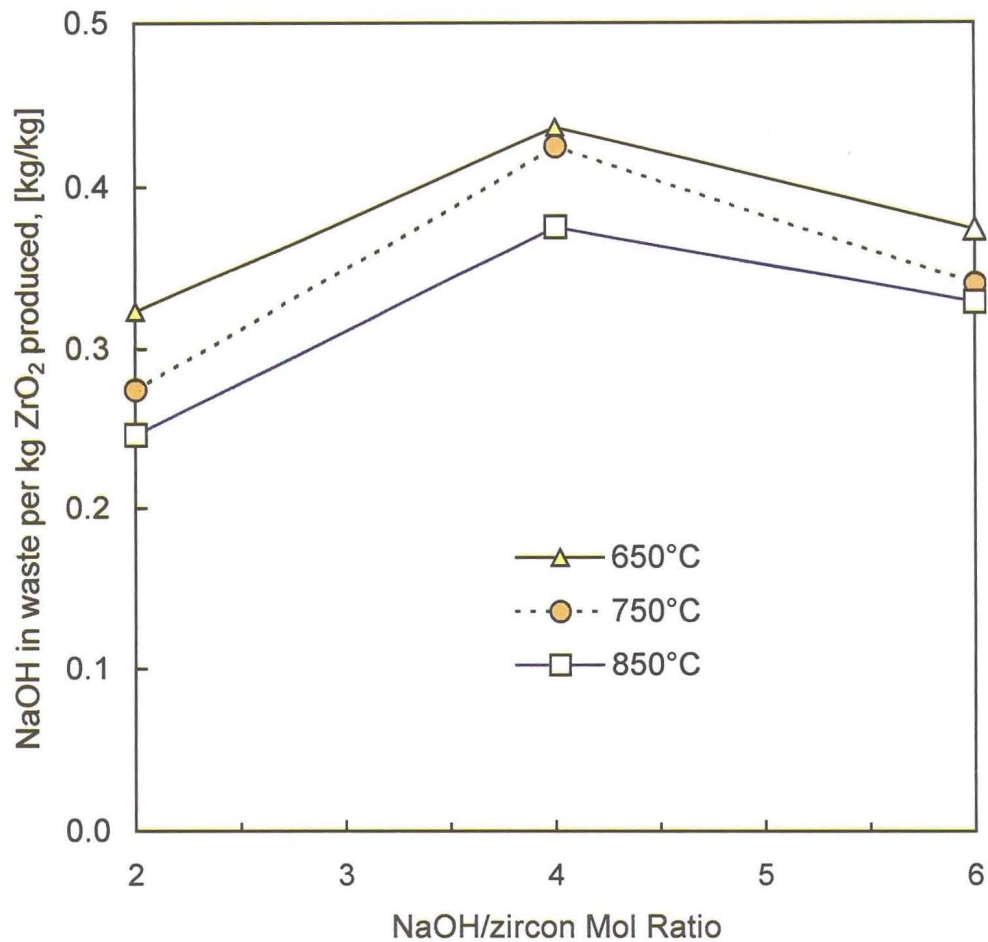


Figure 9.10: Generation of salt waste stream by the process, analysed for the effects of fusion temperature, stoichiometry for 2-hour fusion times

9.4 Possible Explanation for Na_2ZrO_3 Formation to the Detriment of $\text{Na}_2\text{ZrSiO}_5$ Formation

The 336-hour fusions at high temperatures showed that $\text{Na}_2\text{ZrSiO}_5$ is the equilibrium phase at a mol ratio of 2:1. The formation of this phase also guarantees the most efficient use of alkali for the liberation of zirconia from zircon. Thus the local yield maxima observed at a 2-hour fusion time in Figures 9.3 and 9.5 are due to the initial formation of this phase. However, as the fusion time is extended, the proportion of this phase in the product tends to decline before increasing again. This presents a paradox: How does one explain the temporary disappearance of the equilibrium phase once it has been formed? An attempt is made below to provide a rationalisation of these observations.

Zircon is a highly refractory compound with a melting point above 2 550 °C. The sodium hydroxide reagent melts at about 318 °C. Thus it is reasonable to assume that a “shrinking core” model applies to the decomposition reaction. During the fusion reaction, the liquid-like high-basicity outer layer etches away the surface of the solid zircon particle. In the process, the composition of the liquid phase changes. A progressive change in basicity is expected as the reaction proceeds to completion. With regard to the phases observed in the XRD, the progress of the reaction under ideal conditions and for 1 mol of zircon reacting with 2 mol of NaOH can be described in terms of the following product spectrum:

Initially: $\text{ZrSiO}_4 + 2\text{NaOH}$

Intermediate: $x\text{Na}_2\text{ZrO}_3 + y\text{Na}_2\text{SiO}_3 + z\text{Na}_4\text{SiO}_4 + u\text{Na}_2\text{ZrSiO}_5 + v\text{ZrSiO}_4 + w\text{NaOH}$

Complete conversion: $\text{Na}_2\text{ZrSiO}_5$

This scheme is connected to the experimental results obtained via the following additional assumptions:

1. The reaction does not proceed to completion.
2. The zirconia yield reflects the formation of Na_2ZrO_3 and $\text{Na}_2\text{ZrSiO}_5$.
3. The solid residue consists of unreacted zircon and silica only. Thus the zirconium remaining in the residue can be calculated from the zirconia yield.
4. From this, the silica content of the residue can be determined.
5. All the silica in the sodium silicate stream stems from the soluble Na_2SiO_3 and Na_4SiO_4 , accepting that the $\text{Na}_4\text{Si}_2\text{O}_7$ is a linear blend of the previous two species.
6. The total amount of silica, i.e. the silica in the sodium solution plus the silica in the residue, is equal to the amount of zirconia, on a mol basis.

From these assumptions, we can establish the following mass balance equations:

Zirconia yield:	$Zr_Y = x + u$
Zircon in the residue:	$v = 1 - x - u$
Silica in the residue:	$Si_R = u$
Silica in the sodium silicate stream:	$Si_{SS} = y + z$
Total mol of silicon equals mol of zirconium:	$y + z + u + v = x + u + v$ Therefore: $y + z = x$

From these relationships, it can be deduced that:

- the mol of $\text{Na}_2\text{ZrSiO}_5$ present (u) equals the mol of silica in the residue; and
- The quantity of Na_2ZrO_3 present equals the zirconia recovered minus the silica in the residue.

Since all these quantities were measured, the change in the product spectrum can be determined. The results are shown in Figure 9.11.

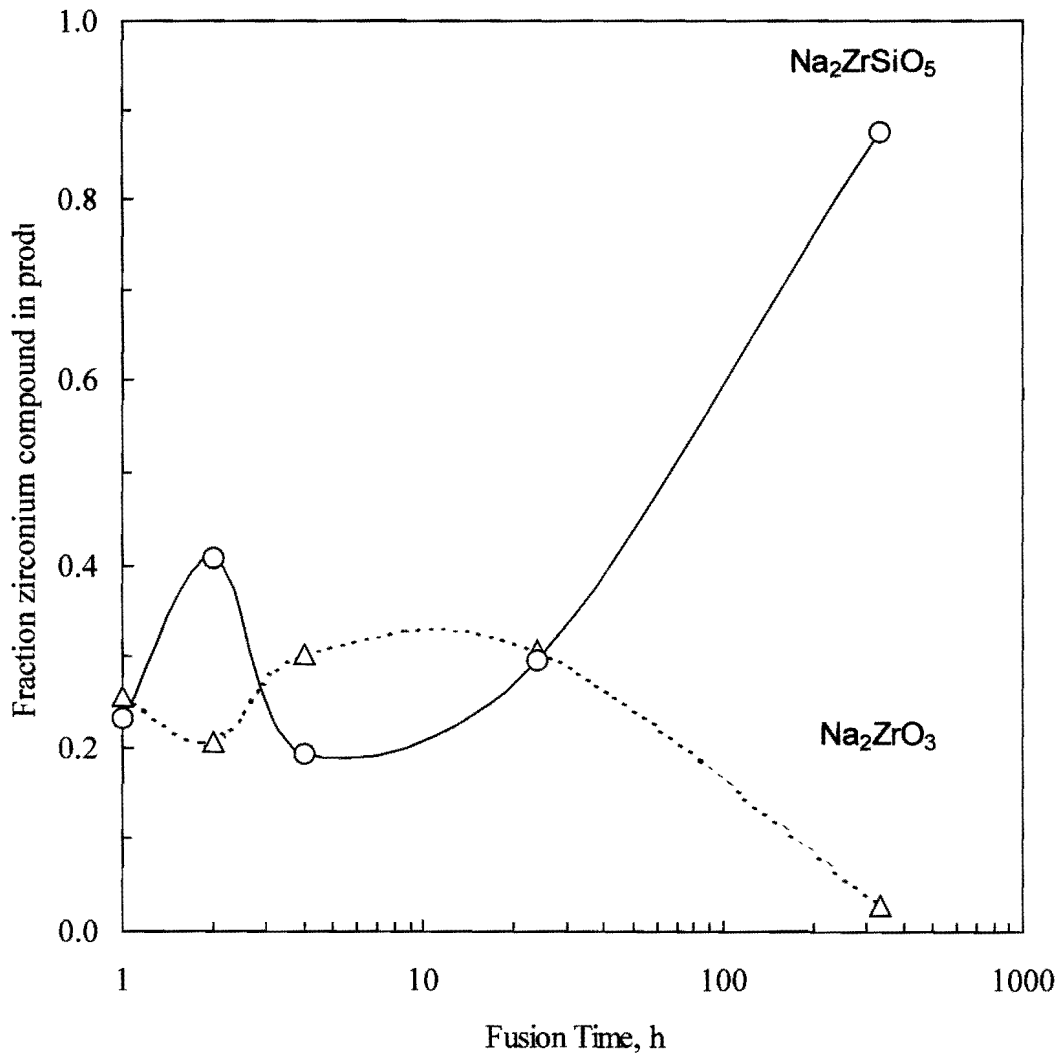


Figure 9.11: Correlation of fractions of Na_2ZrO_3 and $\text{Na}_2\text{ZrSiO}_5$, from mass balance

From the graph it can be seen that initially the phases Na_2ZrO_3 and $\text{Na}_2\text{ZrSiO}_5$ were formed in the same proportion, at the 1-hour fusion point. At 2 hours, the concentration of $\text{Na}_2\text{ZrSiO}_5$ is higher but it then falls to a minimum at about 4 hours, after which its concentration again

increases. This observed behaviour confirms the paradox: it is observed that the final equilibrium product initially forms, then wanes and then reforms. The explanation might be that the actual products in equilibrium with the melt depend on the composition of the latter.

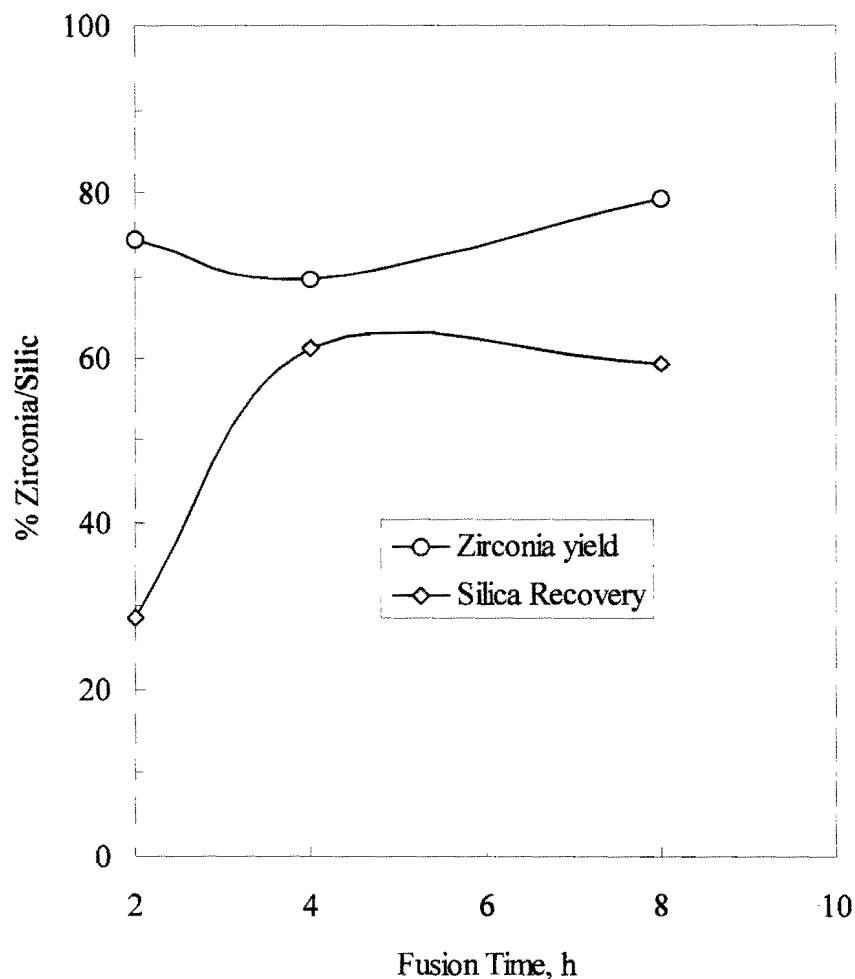
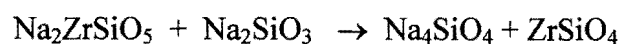


Figure 9.12: Zirconia yield and silica recovery obtained fusing a mole of zircon with four moles of sodium hydroxide at 850 °C

A reaction that may explain the concomitant decrease in zirconia yield at intermediate fusion times is presented in Scheme 9.5.



Scheme 9.5: Reaction that probably explains the drop in the zirconia yield

This reaction is consistent with the change in the product spectrum presented in Figure 9.10 and the sodium orthosilicate observed in the infrared spectra by Kwela [16]. He concluded that the sodium attacks the silica tetrahedra in preference to the zirconia.

9.5 Direct Zirconia Synthesis

Direct synthesis of zirconia from the AFDZ yielded a zirconia with purity as high as 87 %. This required fusion for 24 hours at 650 °C using 6 mol sodium hydroxide per mol of zircon. When fusing with 4 mol sodium hydroxide for 8 hours at 850 °C a yield of 79 % was obtained. A similar result was obtained using four moles of sodium hydroxide at 650 °C for 48 hours. The corresponding silica recoveries fell in a narrow range varying from a high of 65% to a low of 50%. However, 2-hours resulted in poor silica recovery. The low silica recoveries are attributed to formation of sodium zirconium silicate; it is not hydrolysed to hydrous zirconia by water alone.