

10 CONCLUSIONS

The main objective of the present work was to optimise the alkali fusion step in the De Wet process for the recovery of zirconia from zircon sand. For this purpose experiments were conducted using various fusion times, fusion temperatures and stoichiometric ratios. Fusion times from 1 to 336 hours at temperatures between 600 °C and 850°C, at stoichiometric ratios ranging from 1 mol to 6 mol of sodium hydroxide per mol of zircon, were investigated.

The equilibrium phases at each temperature were determined using 336-hour fusions with intermittent milling of the reaction mixture. At temperatures below 650 °C, sodium zirconate (Na_2ZrO_3) is the equilibrium zirconium-containing phase. Above 700 °C, both sodium zirconate and sodium zirconium silicate ($\text{Na}_2\text{ZrSiO}_5$) are formed as products. As expected, for these temperatures, the product ratio depends on the reagent stoichiometry. Sodium zirconium silicate is almost the only zircon-based product that forms when 2 mol or less of NaOH are used per mol of zircon. Above this level, the sodium zirconate content in the reaction product increases with the NaOH:zircon mol ratio.

Thus, at low fusion temperatures, the zirconium-containing product is sodium zirconate, independent of the reagent mol ratio. At high temperatures and low mol ratios, the main phase formed is sodium zirconium silicate, while above mol ratios of 4:1 it is sodium zirconate. Sodium metasilicate is the only crystalline silicate phase formed after a long period of fusion, independently of the stoichiometry of the reaction, provided it is below a ratio of 4:1 (NaOH: ZrSiO_4).

Both equilibrium products are suitable for the recovery of zirconia from zircon sands. In water, sodium zirconate hydrolyses directly to form hydrous zirconia. Sodium zirconium silicate is hydrolysed only in the presence of a dilute acid, e.g. hydrochloric acid, yielding hydrous zirconia as well as hydrous silica. The liberation of zirconia from zircon via sodium zirconate requires 4 mol NaOH per mol of zircon. In contrast, the formation of sodium zirconium silicate requires only 2 mol of NaOH per mol of zircon. However, in the sodium zirconate route, the sodium can be recovered from the wash water as saleable sodium silicate. With the sodium zirconium silicate route, the sodium is not recovered. Additional acid reagent is consumed during hydrolysis and a salt-containing waste stream results. Optimum zirconia

yields and minimum waste-stream generation are achieved when 2 mol of NaOH are fused with 1 mol of ZrSiO_4 at 850 °C for 2 hours.

In general, the fusion product contains both compounds. From a practical point of view, short fusion times are preferable. A 1-hour fusion does not produce acceptable conversion. Fusions conducted at 850 °C with a 2:1 reagent mol ratio showed a maximum zirconia yield at 2 hours. This is attributed to a high proportion of $\text{Na}_2\text{ZrSiO}_5$ in the product spectrum. The drop in zirconia yield might be caused by a disproportional reaction between $\text{Na}_2\text{ZrSiO}_5$ and Na_2SiO_3 that reconstitutes zircon.

When NaOH:zircon mol ratios exceeding 4:1 are fused, Na_2ZrO_3 is the dominant product. The silica is present as ortho- and meta-silicates and can be leached with water. In principle, exhaustive water leaching also leads to the hydrolysis of the sodium zirconate. In practice, it needs to be accelerated by adding dilute acid. After leaching, the residue should essentially consist of hydrated zirconia. This can be fired to produce zirconia directly. The best results were obtained with a 24-hour fusion and a 6:1 stoichiometric mol ratio. This reaction produced zirconia at 86,5% purity. Reducing the stoichiometry to 4:1 yielded, under similar reaction conditions, zirconia with a purity of 84%. In both cases, the impurity was zircon.

Attempts to synthesise zirconia directly from AFDZ only yielded impure product. High yields required high sodium hydroxide to zircon mol ratios. A product containing 79% zirconia was obtained by fusing for 24 hours at 650 °C using a 6:1 mol ratio. The corresponding silica recovery was always lower than the zirconia purity owing to the formation of sodium zirconium silicate.