CHAPTER 9

THE OPTIMISATION OF ZIRCON DECOMPOSITION WITH SODIUM HYDROXIDE

9.1 INTRODUCTION

Decomposition of zircon with alkali hydroxides is a well-known procedure [1, 6]. Zircon is very stable, due to the high coordination of the bisdisphenoid ZrO_8 in the tetragonal structure with the low coordinated SiO_4 tetrahedra [7-8]. Thus zircon requires aggressive reactions for decomposition [1, 4, 6].

Decomposition of milled zircon, $d_{50} \approx 9\mu m$, with sodium hydroxide pearls was carried out in open reaction vessels at temperatures between 650°C and 850°C for about two hours, without the intermediate milling step. Mole increments of sodium hydroxide increased the yield significantly. For a reaction at 850°C the use of 6.0 moles of sodium hydroxide for a mole of zircon was optimal for almost complete decomposition. For a reaction at 650°C the use of 2 moles sodium hydroxide for a mole of zircon was enough for approximately 45% zirconia yield. This chapter provides zirconia, silica and residue yields for the various reaction conditions. These should provide an indication of the extent of decomposition and allow the optimisation of reaction conditions with respect to reagent use. The results given here are sub-optimal because they were obtained before the introduction of the intermediate milling step during fusion. Results after the introduction of the intermediate milling step are also provided.

From the characterisation of zircon decomposition (Chapter 8), the following products can be expected to be the most likely to form. The following reactions are not necessarily balanced.

For the fusion of a mole of zircon with one or two moles of sodium hydroxide at 650 or 850°C, under favourable conditions the following reactions can be expected:

$$3ZrSiO_4 + 4NaOH \xrightarrow{850^{\circ}C} Na_4Zr_2Si_3O_{12} + ZrO_2 + 2H_2O \tag{9.1A}$$

$$ZrSiO_4 + 2NaOH \xrightarrow{850^{\circ}C} Na_2ZrSiO_5 \tag{9.1.B}$$

$$ZrSiO_4 + 2NaOH \xrightarrow{650^{\circ}C} Na_2SiO_3 + ZrO_2 + H_2O \tag{9.1C}$$

SCHEME 9.1: A representation of a possible reaction when fusing a mole of zircon with two moles of sodium hydroxide at 650°C and 850°C. Reaction 9.1A and 9.1B predominate when fusing with one or two moles of NaOH at 850°C respectively. Reaction 9.1C predominates at 650oC when fusing with one or two moles of NaOH.

When fusing a mole of zircon with four or six moles of sodium hydroxide at 650 or 850°C, under favourable conditions the following reaction products can be expected:

$$ZrSiO_4 + 4NaOH \xrightarrow{650^{\circ}C} Na_2SiO_3 + Na_2ZrO_3 + 2H_2O \tag{9.2A}$$

$$ZrSiO_4 + 6NaOH \xrightarrow{650^{\circ}C} Na_4SiO_4 + Na_2ZrO_3 + 2H_2O \tag{9.2B}$$

$$ZrSiO_4 + 4NaOH \xrightarrow{850^{\circ}C} 2Na_2ZrSiO_5 + 2H_2O \tag{9.2C}$$

$$ZrSiO_4 + 4NaOH \xrightarrow{850^{\circ}C} Na_2SiO_3 + Na_2ZrO_3 + Na_2O + 2H_2O \tag{9.2D}$$

SCHEME 9.2: A representation of the possible reactions when fusing a mole of zircon with four or six moles of sodium hydroxide at 650 or 850°C. The conditions under which each reaction dominates are given in the reaction Scheme 9.2.

Now that the reactions, which take place during the decomposition of zircon, are known the theoretical limit can be defined. For this purpose a fraction defined with the aid of reaction 9.1A should give the theoretical limit. Reaction 9.1A consumes the least amount of NaOH when liberating the zirconia form the zircon lattice. Reaction 9.1A consumes four moles of NaOH while liberating three moles of zirconia, thus the fraction has a magnitude of 1.33 NaOH (mol) / ZrO_2 (mol).

9.2 RESULTS

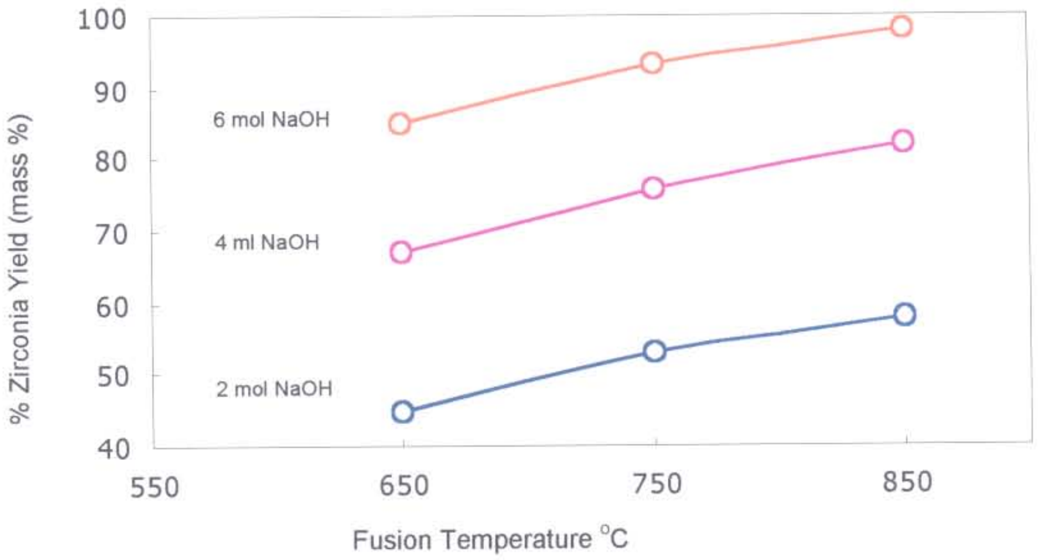

FIGURE 9.1: Influence of Fusion temperature on the yield of zirconia. Fusion time was two hours for the $d_{50} \approx 9\mu m$ zircon sand (no intermediate milling).

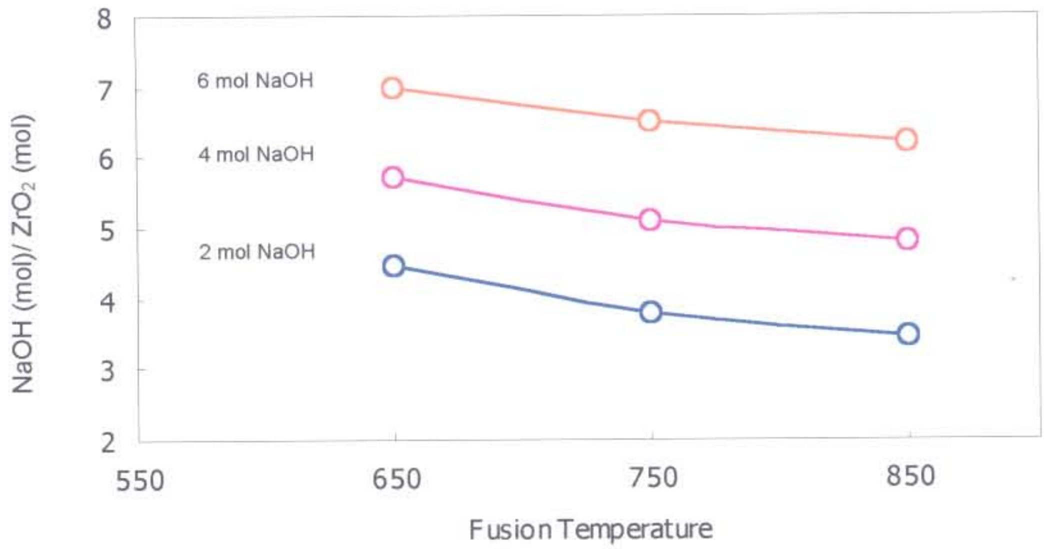

FIGURE 9.2: Influence of temperature on the efficiency of zirconia yield. Fusion time was two hours for the $d_{50} \approx 9\mu m$ zircon sand (no intermediate milling).

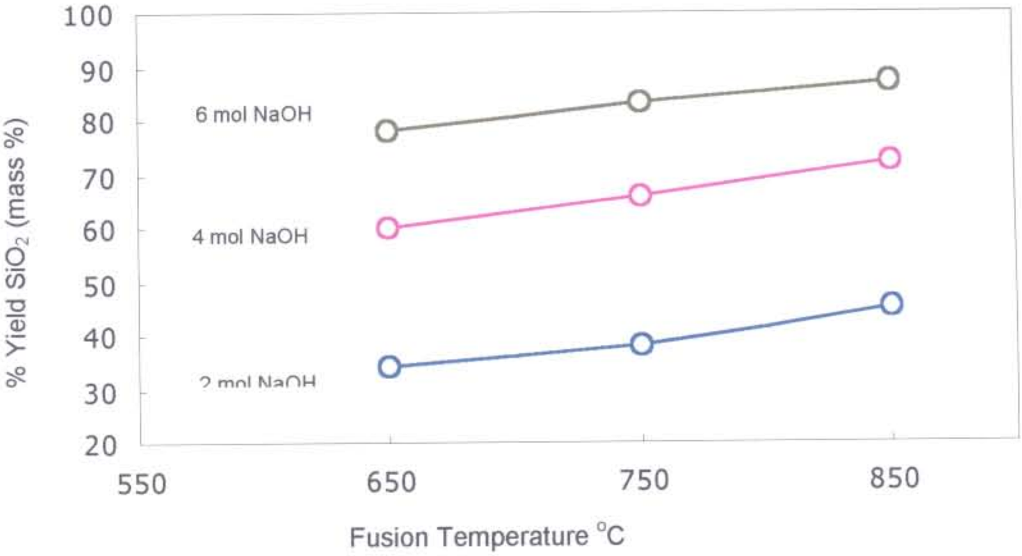

FIGURE 9.3: The influence of temperature on the yield of silica. Fusion time was two hours for the $d_{50} \approx 9\mu m$ zircon sand (no intermediate milling).

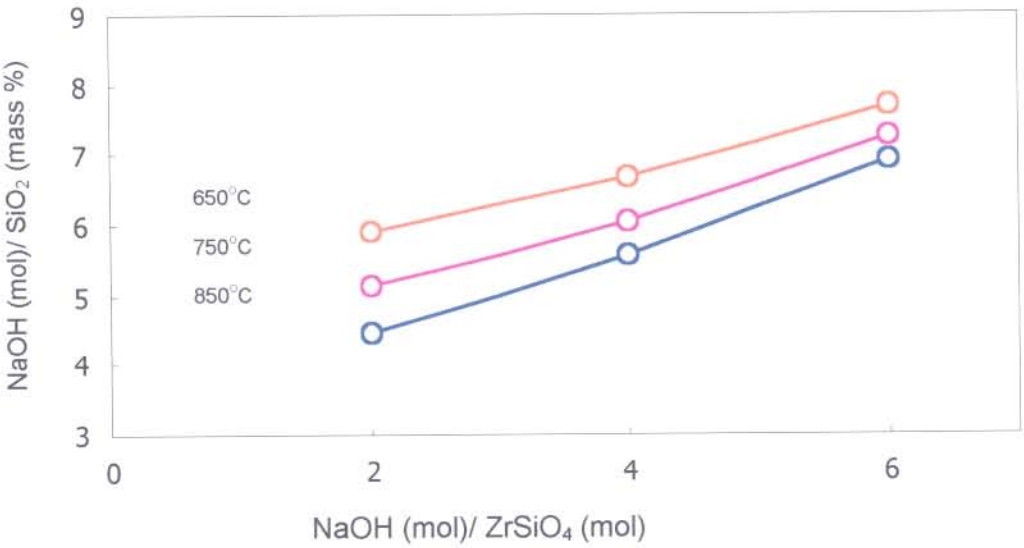

FIGURE 9.4: The influence of sodium hydroxide on the efficiency of silica yield. Fusion time was two hours for the $d_{50} \approx 9\mu m$ zircon sand.

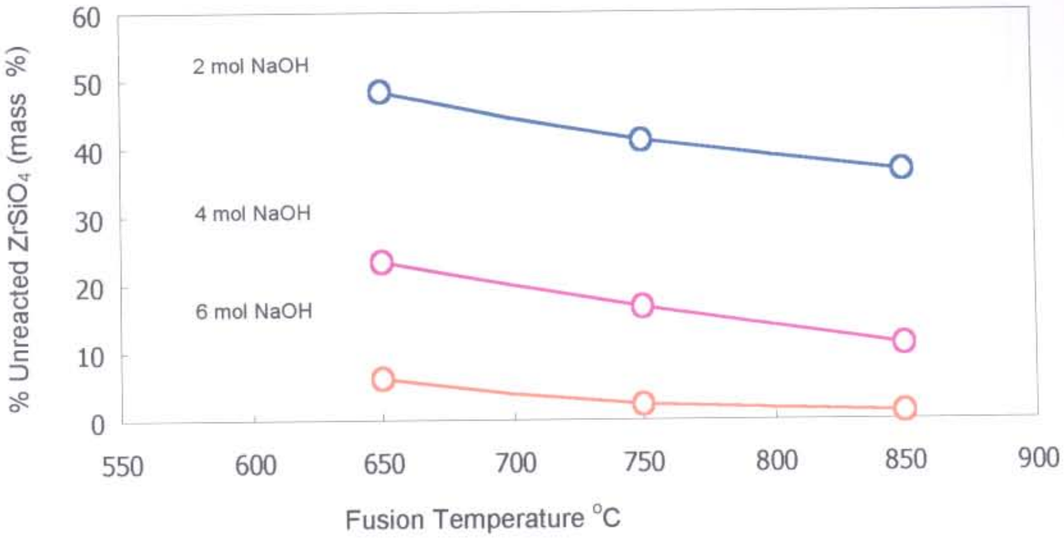

FIGURE 9.5: Influence of Temperature on the yield of Solids. Fusion time was two hours for the $d_{50} \approx 9\mu m$ zircon sand.

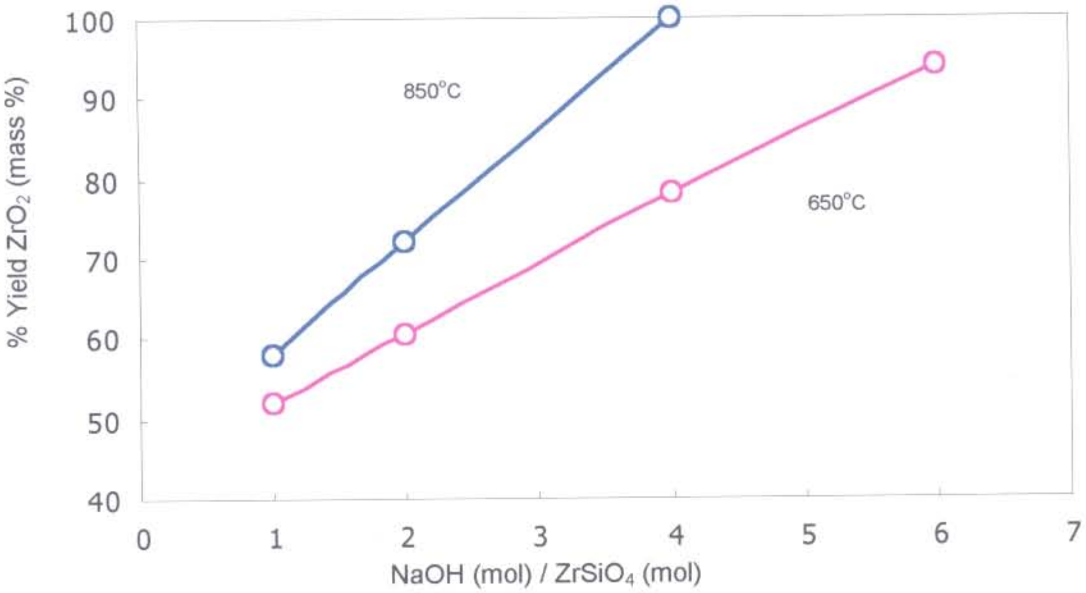

FIGURE 9.6: Influence of the moles of sodium hydroxide per mole of zircon on the yield of zirconia form zircon sand. Fusion time was 336 hours for the $d_{50} \approx 9\mu m$ zircon sand

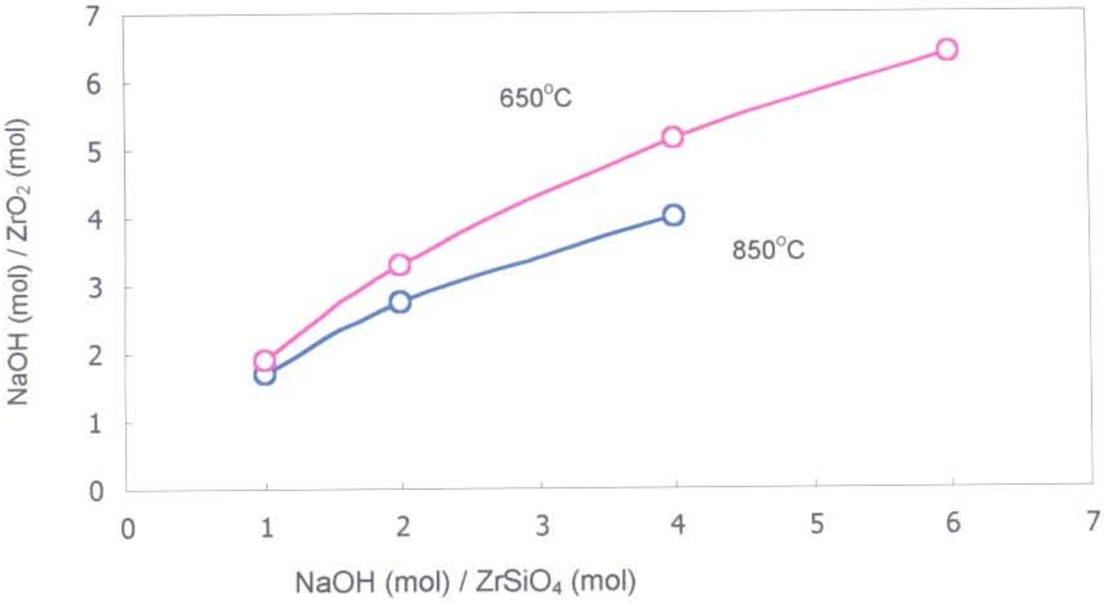

FIGURE 9.7: The influence of sodium hydroxide to zircon mole ratio on the efficiency of zirconia yield. Fusion time was 336 hours for the $d_{50} \approx 9$ µm zircon sand

9.3 RESULTS AND DISCUSSIONS

9.3.1 FUSION FOR TWO HOURS

Figure 9.2 shows the effect that the fusion temperature had on yield of zirconia. For the sub-stoichiometric fusion the yield of zirconia increases from approximately 45% at 650°C to about 58% at 850°C.With increase is sodium hydroxide the yield was observed to increase as the moles of sodium hydroxide and temperature increased (Figure 9.2). The results confirm that the yield of zirconia increases from a minimum of approximately 45% at 650°C when fusing with $NaOH/ZrSiO_4 = 2$, to near complete decomposition at 850°C when fusing with $NaOH/ZrSiO_4 = 6$

To determine the most efficient reaction, the fraction NaOH (mol)/ ZrO_2 (mol) was defined. The fraction indicates the number of moles of sodium hydroxide required to liberate a mole of zirconia from the zircon lattice. The theoretical limit, determined from reaction 9.1A (Scheme 9.1), is where the fraction has a magnitude of 1.33. The reaction at 850°C fusion with two moles of sodium hydroxide has the closest value to the theoretical limit (Figure 9.2). Thus this reaction condition is the most efficient.

Figure 9.3 shows the effect that sodium hydroxide had on the yield of silica. The yield was observed to increase as the moles of sodium hydroxide increased. The results confirm that the yield of silica increases from a minimum of approximately 35% when at 650°C with $NaOH/ZrSiO_4 = 2$, to about 90% at 850°C for $NaOH/ZrSiO_4 = 6$. In comparison to the zirconia yields the silica yields were observed to be lower, at times about 10% lower. This could be attributed to the insolubility of many complex alkali zirconium silicates [14]. This effect is further supported by the high silica composition of the residue collected after the removal of zirconium sulphate tetrahydrate, as seen in the XRF and ICP elemental analysis in Table 9.1. Never the less the silica yields remain a *rough* indicator of the extent of decomposition. Figure 9.3 have similar suggestion about efficiency and yield as the zirconia plots of such variables.

Figure 9.5 shows the effect that sodium hydroxide and temperature had on the amount of undecomposed zircon. The unreacted zircon was observed to decrease as the amount of sodium hydroxide and temperature were increased.

The reaction condition at 850°C $NaOH/ZrSiO_4 = 6$ for was observed as the point with the minimum amount of solids. The majority of the solids were actually silica. This further emphasised the extent of zircon decomposition. The reaction condition at 650°C and two moles of sodium hydroxide for the same particle size was observed as the point with the highest amount of solids. The elemental analysis (XRF and ICP) suggests that the solids constitute zircon in majority and free silica in minority.

9.3.2 FUSION FOR 336 HOURS

Figure 9.6 shows the improved decomposition obtained from decomposing the zircon sand over a period of two weeks with periodic milling. The reaction at 850°C when fusing with $NaOH/ZrSiO_4 = 4$ showed near complete decomposition. This is a point that was suggested by the characterisation with XRD, Raman and infra red spectroscopy. The reaction at 850°C fusion with one mole of NaOH per mole of zircon almost showed a 60% zirconia yield. This amount is comparable to that attained at the same temperature but at twice the amount of caustic soda without the intermediate milling step.

Figure 9.7 shows the plot of the fraction NaOH (mol) /ZrO_2 (mol) that was defined to determine the most efficient reaction condition. When fusing with NaOH (mol) /ZrO_2 (mol) =1 were observed to have the most efficient caustic soda consumption.

The increased efficiency at 650°C can be attributed to the polymerisation of the Na_4SiO_4 monomers (high in sodium content) to the metasilicate Na_2SiO_3 (low in sodium) chains. The more increased efficiency at 850°C when fusing with $NaOH/ZrSiO_4 < 2$ can be attributed to the formation of the phases Na_2ZrSiO_5, $Na_4Zr_2Si_3O_{12}$ and ZrO_2. The phases liberate high amounts of zirconium while consuming low amounts of sodium.

9.4 CONCLUSIONS

9.4.1 FUSION FOR TWO HOURS

Increments of sodium hydroxide and temperature are desirable for complete zircon decomposition.

Near complete decomposition at 850°C was observed when fusing with $NaOH/ZrSiO_4 = 6$. The other advantage associated with this is the minimal amounts of solids that constitute silica in majority. In the case of re-circulation the silica in the solids poses a problem (if it is not separated) in the consumption of raw materials, thus complicating reactor design, since the decomposition would be affected. The free silica can be separated by physical means from the undecomposed zircon due to the large density difference between the two. Centrifugation (5 000 r.p.m.) was also observed to separate zircon from the free hydrated silica.

The most efficient reaction condition was observed at 850°C when fusing a mole of zircon with two moles of sodium hydroxide. This was the reaction condition that had the closest value to the theoretical limit.

9.4.2 FUSION FOR 336 HOURS WITH INTERMEDIATE MILLING

The reaction at 850°C fusion with four moles of caustic showed near complete decomposition. This is a point that was first suggested by the characterisation with XRD, Raman and IR spectroscopy. The reaction at 850°C fusion with one mole of NaOH per mole of zircon almost showed a 60% zirconia yield. This amount is comparable to that attained at the same temperature but at twice the amount of caustic soda without the intermediate milling step.

Figure 9.7 shows the influence of the moles of sodium hydroxide on the efficiency. The reactions at sub-stoichiometric fusion were observed to have the most efficient caustic soda consumption. The increased efficiency at 650°C can be attributed to the polymerisation of the Na_4SiO_4 monomers to the metasilicate Na_2SiO_3 chains (low in sodium). The more increased efficiency at 850°C $NaOH/ZrSiO_4 < 2$ can be attributed to the synthesis of reactive phases Na_2ZrSiO_5, $Na_4Zr_2Si_3O_{12}$ and ZrO_2. The phases liberate high amounts of zirconium while consuming low amounts of sodium.

TABLE 9.1: ELEMENTAL ANALYSIS OF THE CALCINED PRODUCTS (concentration in mass percent)

Product	ZrO_2+ HfO_2	SiO_2	Na_2O	Trace
Zirconia 1 : 6 @ 850	98. 4 %	470 ppm	570 ppm	1. 49 %
Zirconia 1 : 4 @ 850	98. 5 %	480 ppm	560 ppm	1. 39 %
Zirconia 1 : 2 @ 850	98. 4 %	320 ppm	450 ppm	1. 46 %
Silica 1 : 6 @ 850	1. 03 %	98. 80 %	430 ppm	0. 17 %
Silica 1 : 4 @ 850	0. 09 %	99. 10 %	690 ppm	0. 80 %
Silica 1 : 2 @ 850	0. 40 %	99. 20 %	560 ppm	0. 42 %
Residue 1 : 6 @ 850	22. 9 %	76. 18 %	480 ppm	0. 93 %
Residue 1 : 4 @ 850	52. 4 %	46. 54 %	320 ppm	1. 05 %
Residue 1 : 2 @ 850	56. 2 %	41. 21 %	540 ppm	1. 30 %
Zirconia 1 : 6 @ 750	98. 3 %	460 ppm	540 ppm	1. 46 %
Zirconia 1 : 4 @ 750	98. 4 %	470 ppm	560 ppm	1. 52 %
Zirconia 1 : 2 @ 750	98. 2 %	420 ppm	350 ppm	1. 38 %
Silica 1 : 6 @ 750	1. 02 %	97. 80 %	830 ppm	0. 27 %
Silica 1 : 4 @ 750	0. 62 %	98. 20 %	490 ppm	1. 30 %
Silica 1 : 2 @ 750	0. 53 %	98. 30 %	260 ppm	1. 43 %
Residue 1 : 6 @ 750	22. 7 %	73. 18 %	780 ppm	1. 94 %
Residue 1 : 4 @ 750	50. 3 %	47. 74 %	420 ppm	1. 52 %
Residue 1 : 2 @ 750	54. 2 %	44. 09 %	520 ppm	1. 80 %
Zirconia 1 : 6 @ 750	98. 1 %	370 ppm	560 ppm	1. 51 %
Zirconia 1 : 4 @ 650	98. 2 %	580 ppm	570 ppm	1. 29 %
Zirconia 1 : 2 @ 650	98. 3 %	350 ppm	540 ppm	1. 62 %
Silica 1 : 6 @ 650	1. 05 %	98. 60 %	340 ppm	1. 18 %
Silica 1 : 4 @ 650	0. 07 %	98. 20 %	690 ppm	1. 90 %
Silica 1 : 2 @ 650	0. 60 %	98. 50 %	460 ppm	1. 52 %
Residue 1 : 6 @ 650	27. 9 %	70. 80 %	580 ppm	1. 20 %
Residue 1 : 4 @ 650	50. 4 %	48. 74 %	620 ppm	1. 05 %
Residue 1 : 2 @ 650	48. 7 %	37. 69 %	340 ppm	2. 30 %

KEY: The name of the product is given first, then the reaction conditions. For an example the sample "Silica 1:6 @ 850" stands for the silica product at six moles sodium hydroxide and 850°C fusion temperature.

9.5 REFERENCES

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Chapter 10

THE *in-situ* ZBS PURIFICATION STEP

10.1 INTRODUCTION

The De Wet process provides a rapid purification method when compared with other wet-chemical zirconium processes. This is due to the use of a mineral acid washing step, which is much more rapid than precipitation methods [1-3]. This step is capable of removing the concentration of Uranium and Thorium compounds to concentrations below parts per million. The key is the synthesis of a stable and insoluble zirconium basic sulphate of the formula $Zr_5O_7(SO_4)_3nH_2O$. The basic sulphate remains insoluble to mineral acid washes e.g. HCl and the radioactive compounds form soluble products thus are easily washed out.

Since this step proves to be the most crucial, the stability of this basic sulphate, with respect to zirconia losses per HCl washing step, was investigated.

10.2 RESULTS

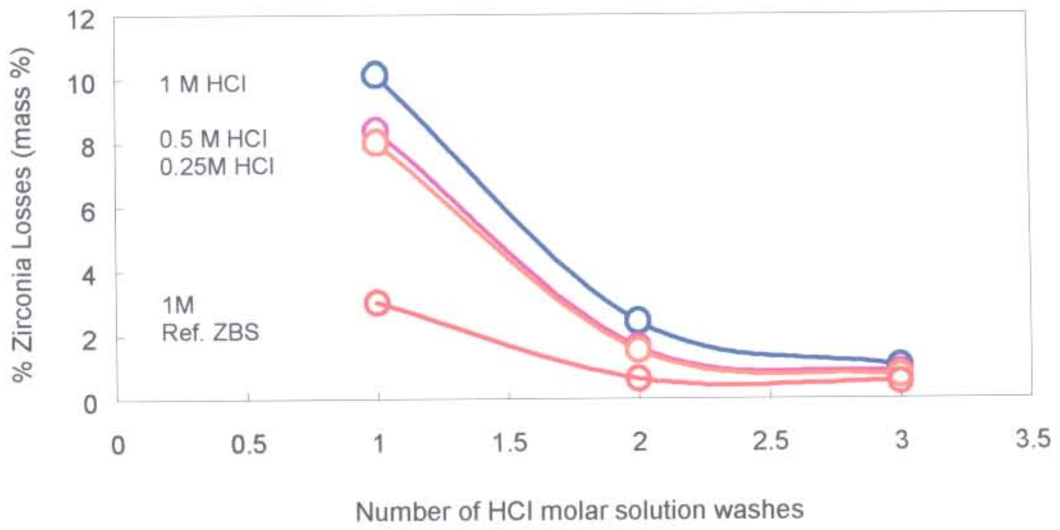

FIGURE 10.1: The influence of the number of washes on the *in-situ* ZBS solubility. In the first wash the ZBS was digested with hot (90°C) HCl molar solutions. Reference ZBS (Ref. ZBS) was washed with one molar HCl solution.

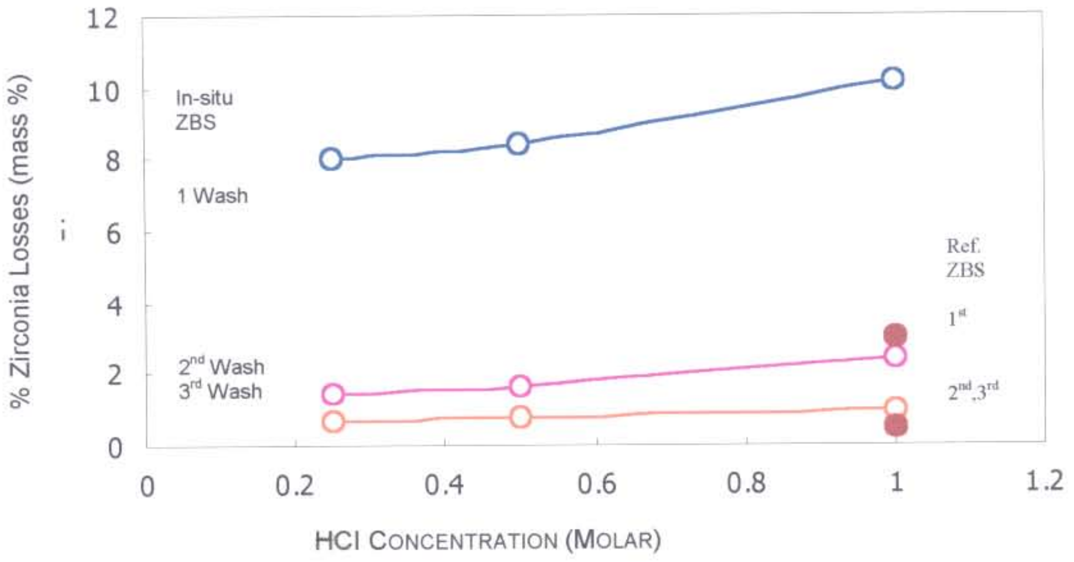

FIGURE 10.2: The influence of increasing HCl molarity on the solubility of *in-situ* and Ref. ZBS products. In the first wash, the ZBS wash digested with hot (90°C) HCl molar solutions.

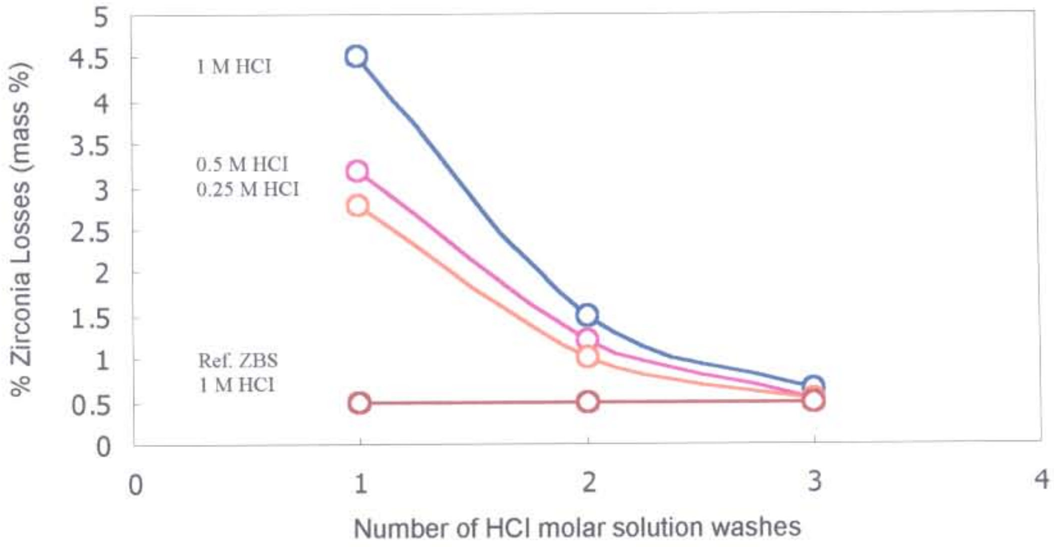

FIGURE 10.3: The influence of the number of washes on the *in-situ* and Ref. ZBS solubility. The ZBS was washed with HCl molar solutions at room temperature.

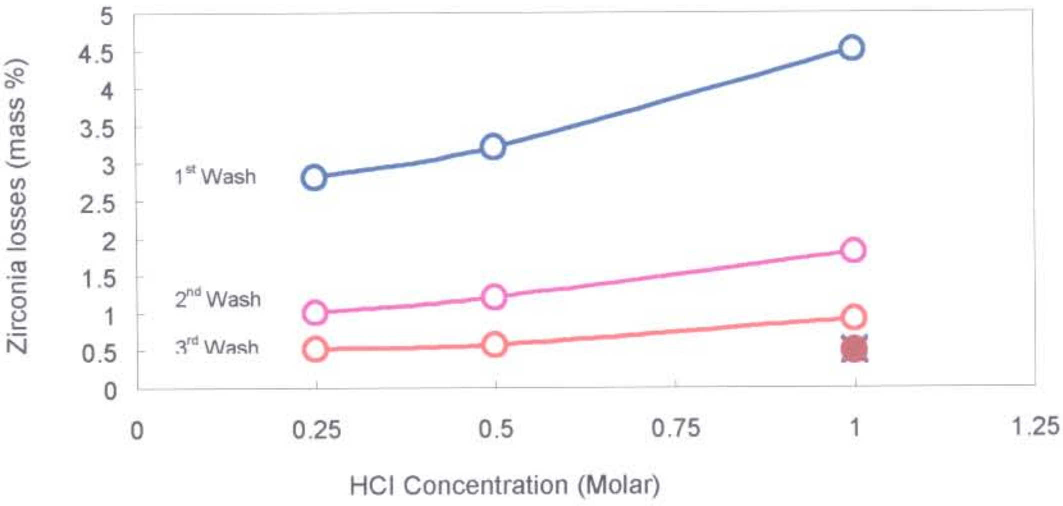

FIGURE 10.4: The influence of increasing HCl molarity on the solubility of *in-situ* and Ref. ZBS products. The ZBS was washed with HCl molar solutions at room temperature.

10.3 DISCUSSIONS

Figure 10.1 shows plots of the zirconia losses with the number of washes. Both in-situ and Ref. ZBS were digested with HCl solutions at 90°C. The curves are seen to be exponential. The initial washing step was seen to have the highest zirconia losses, the last with the least zirconia losses. This shows the increasing stability or insolubility of the ZBS paste to the HCl solutions.

Figure 10.2 shows the zirconia losses with increments in the HCl molarity. The zirconia loses were observed to increase with increasing molarity of HCl. The reference ZBS showed loses up to 3% m/m of ZrO_2 in the first wash when digested with a one molar HCl solution. While the in-situ ZBS showed losses up to 10% m/m of ZrO_2 for digestion at the similar molarity. The first wash, for all three molar concentrations, for both in-situ and reference ZBS, was observed to cause the highest zirconia losses. Two possibilities could be responsible for these high losses. Firstly the incomplete conversion of the hydrous zirconia to ZBS. Secondly the instability of the ZBS to hot 90°C HCl solutions.

To verify each possibility both types of ZBS were washed with HCl solutions at room temperature. Figures 10.3 and 10.4 show the influence that washing at room temperature had on the zirconia losses. The reference ZBS showed minimal to negligible losses (< 0.5% m/m of ZrO_2), while the in-situ ZBS showed losses less than 5% m/m of ZrO_2. This indicates the incomplete conversion of the hydrous zirconia to in-situ ZBS.

Table 10.1 shows the elemental analysis of the zirconia that was lost and the in-situ ZBS that was collected after each washing step. The ZBS was converted to the AZST to separate it from the residue. For the one molar HCl first wash, the AZST had a Uranium and Thorium concentration that was below three parts per million. A similar observation was made for the half a molar HCl solution. The quarter molar solution was observed to have a similar effect after the third wash.

10.4 CONCLUSIONS

The zirconia losses for the in-situ ZBS are due to both incomplete conversion and increased molarity of the mineral acid, e.g. HCl.

The in-situ ZBS showed losses up to 10% m/m of ZrO_2 when washed with HCl solution with molarity greater than 0.5M. For solution with molarity greater than 0.5M, digestion in the first wash is necessary to remove the Uranium and Thorium to levels below three parts per million. To minimise the zirconia losses for the in-situ ZBS route, the ZBS can be washed with water to dissolve AZST. The AZST can then be re-circulated to the sodium removal step or precipitated with ammonia to hydrous zirconia. The Ref. ZBS route has minimal loses but is process time and energy consuming. This is because the Ref. ZBS is prepared by precipitation from hot solutions while stirring.

TABLE 10.1: ELEMENTAL ANALYSIS OF THE LOST SOLIDS AND THE *in-situ* ZBS

Sample	U_3O_8	ThO_2	ZrO_2	SO_3	Al_2O_3	Fe_2O_3
ZrO_2 1M@1W	0.204 %	0.165 %	97.2 %	0.237 %	0.01 %	0.17 %
ZrO_2 1M@2W	< 3 ppm	< 3 ppm	98.1 %	0.136 %	0. 11 %	0.42 %
ZrO_2 1M@3W	< 3 ppm	< 3 ppm	97.6 %	0.242 %	0.02 %	0.23 %
AZST1M@1W	< 3 ppm	< 3 ppm	62.6 %	34.8 %	1.19 %	890 ppm
AZST1M@2W	< 3 ppm	< 3 ppm	69.7 %	23.0 %	1.16 %	730 ppm
AZST1M@3W	< 3 ppm	< 3 ppm	65.6 %	29.1 %	1.12 %	800 ppm
ZrO_2 0.5M@1W	0.46 %	0.146 %	96.7 %	0.213 %	0.05 %	0.43 %
ZrO_2 0.5M@2W	0.25 %	0.082 %	94.3 %	0.260 %	0.123 %	0.54 %
ZrO_2 0.5M@3W	< 3 ppm	< 3 ppm	97.2 %	0.134 %	0.08 %	0.91 %
AZST0.5M@1W	480 ppm	690 ppm	64.7 %	32.8 %	1. 23 %	790 ppm
AZST0.5M@2W	< 3 ppm	< 3 ppm	68. 1 %	30.7 %	0.89 %	980 ppm
AZST0.5M@3W	< 3 ppm	< 3 ppm	66.3 %	31.7 %	0.78 %	450 ppm
ZrO_2 0.25M@1W	0.173 %	0.096 %	96.6 %	0.320 %	0.23 %	0.12 %
ZrO_2 0.25M@2W	0.123 %	0.070 %	98.4 %	0.434 %	0.12 %	0.16 %
ZrO_2 0.25M@3W	0.023 %	0.033 %	98.2 %	0.323 %	0.04 %	0.17 %
AZST0.25M@1W	360 ppm	720 ppm	66.7 %	30.12 %	1.09 %	745 ppm
AZST0.25M@2W	100 ppm	320 ppm	64.4 %	33.9 %	0.98 %	950 ppm
AZST0.25M@3W	< 3 ppm	< 3 ppm	68.9 %	29.7 %	0.74 %	420 ppm

KEY: The Sample names are given first, then the concentration of the HCl solution and then number of the wash. For example, ZrO_2 0.25M@3W is the zirconia sample from the 0.25M HCl solution after the third wash.

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