CHAPTER 5
ZIRCONIA EXTRACTION PROCESSES

[Picture by: Chemical & Engineering news, march 13 2000]

5.1 INTRODUCTION

Many processes exist for the extraction of zirconia, especially from zircon. The main differences, besides starting with different reagents, are in the number of extraction steps, the purity and yield of the resultant zirconia. Some processes also put some emphasis on the recovery of by-products and their methods of disposal. The hunt is for processes with the highest yield and purity at minimal costs ideally with a minimal number of process steps. This chapter takes a detailed look at some of the extraction processes of zirconia from zircon, with emphasis given to the alkali fusion method, for it is this method that was investigated.

Zircon is a refractory mineral that exhibits some resistance towards acids and cold alkali solutions, but it is readily attacked by sodium hydroxide NaOH, above 600°C and even more vigorously by sodium oxide, Na_2O [1-2]. The stability of zircon suggests that aggressive reaction conditions and reagents have to be used to decompose the zircon crystal lattice or dissociate the zircon into silica and zirconia. Thermal methods like the Plasma arc furnace are capable of dissociating the zircon and chemical methods like the alkali fusion are capable of decomposing the zircon lattice into reactive species like Na_2ZrO_3, Na_2SiO_3. Dissociation in this case refers to the breaking down of the lattice into the units MO_2 (where M is ideally Zr or Si); and decomposition, the formation of complex metal zirconates and silicates.

Processes for the recovery of zirconium compounds have three fundamental steps in common [3]. Firstly, the decomposition or dissociation of zircon either by chemical or thermal methods. Secondly, the treatment of the decomposition products, usually by making soluble and insoluble compounds. Thirdly, the isolation of zirconium compounds, usually from residual silica, rare earth's and other impurities. For zirconia recovery a fourth step exists, where the zirconium compounds are calcined to produce zirconia.

5.2 THERMAL DISSOCIATION (Figure 5.1)

METHOD 1

This reaction occurs in plasma arc furnace [3-5] or an advanced electric reactor. The zircon sand is heated in the presence of carbon at approximately 2 000°C. The zircon is dissociated to zirconia and silica at temperatures above 1 750°C [3]. The silica is reduced to the volatile monoxide at temperatures higher than 2 400°C, which re-oxidises outside the furnace to silica (fumed silica).

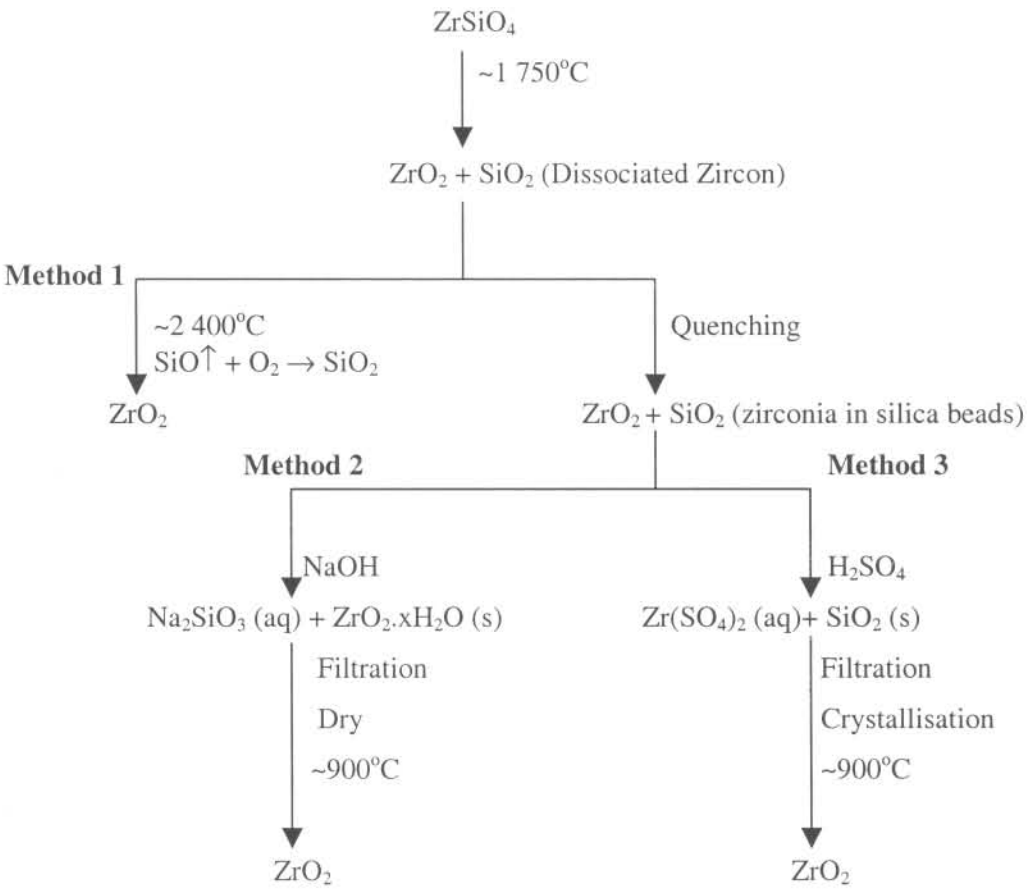

FIGURE 5.1 A Diagrammatic Representation of the Thermal Decomposition of zircon

METHOD 2

The dissociated zircon can be quenched to produce intimately mixed crystals of zirconia in a bead of amorphous silica. The crystallites can be very small, usually less than 0.1μm in diameter. The agglomerates can range in size from 2 to 20 μm depending on how the crystallites are joined [4]. The amorphous silica can be dissolved by a solution of boiling sodium hydroxide NaOH, to yield a soluble sodium silicate and an insoluble zirconium oxide residue [4-5, 13].

METHOD 3

The zirconia can be leached with sulphuric acid to yield a soluble zirconium sulphate, usually AZST and insoluble silica gel [4-5]. Heating the zircon to 2 100-2 300°C can vary the size of the agglomerates, where the silica is liquid and the zirconia is solid. The zirconia is produced as compact clusters of crystallites with a size range of 0.01-0.1μm, sufficient to allow rapid leaching out of zirconia by sulphuric acid [4]. Temperature and acid concentration have also been shown to affect the extraction of zirconia from dissociated zircon [9].

When the particle size is approximately 75 μm (obtained after milling) about 3-4 hours are required to extract approximately 90% of the zirconia. If the dissociated zircon is not ground, then only 64% of zirconia is obtained over the same period. Thus the zirconia has to be ground below 75μm to achieve good results [9].

Separation of products by filtration is followed by the production of AZST crystals by either evaporative crystallisation or salting out. Calcination of the zirconium sulphate between 900°C-1 000°C is usually how the zirconia is produced [3-5].

Evaporative crystallisation refers to water removal usually between 121-123°C. When the desired temperature is reached heating is stopped the solution is then cooled to room temperature. The crystals are filtered and washed with H_2SO_4 [9]. Salting out refers to the exploitation of a minimum in ZrO_2 solubility in the system ZrO_2-SO_3-H_2O between 45-55% (m/m) SO_3 were the zirconium crystallises out as $Zr(SO_4)_2.4H_2O$ [1, 9]. Comparison of the AZST formed from salting out showed a lower impurity level than the evaporative technique, but longer calcination times are required to lower the SO_3 content in the final material zirconia [9].

5.3 CHLORINATION (Figure 5.2)

The milled zircon sand is pelletised with coke to obtain an intimate mixture. It is directly chlorinated with chlorine gas, in a fluidised bed or shaft furnace at 800-1 200°C [3-5], producing zirconium and silicon tetrachloride. Since the reaction is endothermic, supplemental energy is supplied usually by heating the interior graphite walls of the chlorinator.

The zirconium tetrachloride is distilled and collected in a condenser at about 150-180°C [3-4] or 200°C [5] and the silicon tetrachloride at –10°C [3-4] or –20°C [5] in a secondary condenser.

METHOD 1

The zirconium tetrachloride can simply be calcined to zirconia and the silicon tetrachloride to silica [1-2].

METHOD 2

The zirconium tetrachloride can be hydrolysed with water to form zirconium oxychloride [1-2, 8]. Cooling the saturated solution from 65 to 20°C can cause crystallisation of zirconium oxychloride. This step is carried out to separate the major impurities such as titanium, aluminium, iron and silicon chlorides [1-2, 4]. The crystals can then be dried at approximately 85°C and calcined to zirconia [4].

METHOD 3

Adding ammonia solution to a solution of zirconium oxychloride leads to the precipitation of hydrous zirconia [4]. The precipitate can be calcined to produce zirconia powder agglomerates consisting of randomly oriented fine crystallites.

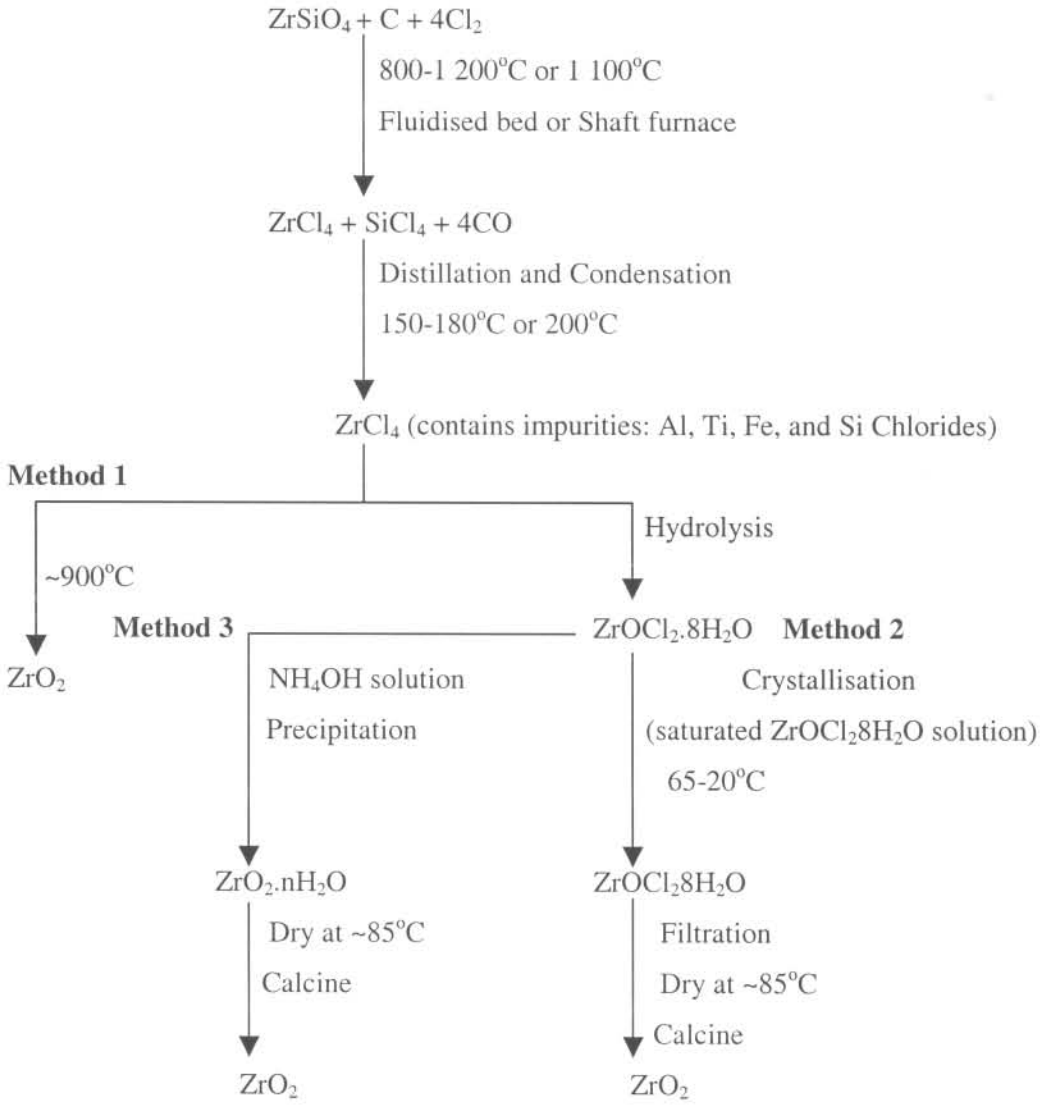

FIGURE 5.2 A Diagrammatic representation of the Different Chlorination processes

5.4 LIME FUSION (Figure 4.3)

Lime or dolomite can be reacted with zircon to produce calcium zirconylsilicate, calcium zirconate and calcium silicate even mixtures of zirconia and calcium or magnesium silicate [1-5, 11-12]. The thermodynamic parameters (at atmospheric pressure) for the existence of these various phases are: temperature, mole ratio of the zircon to the lime.

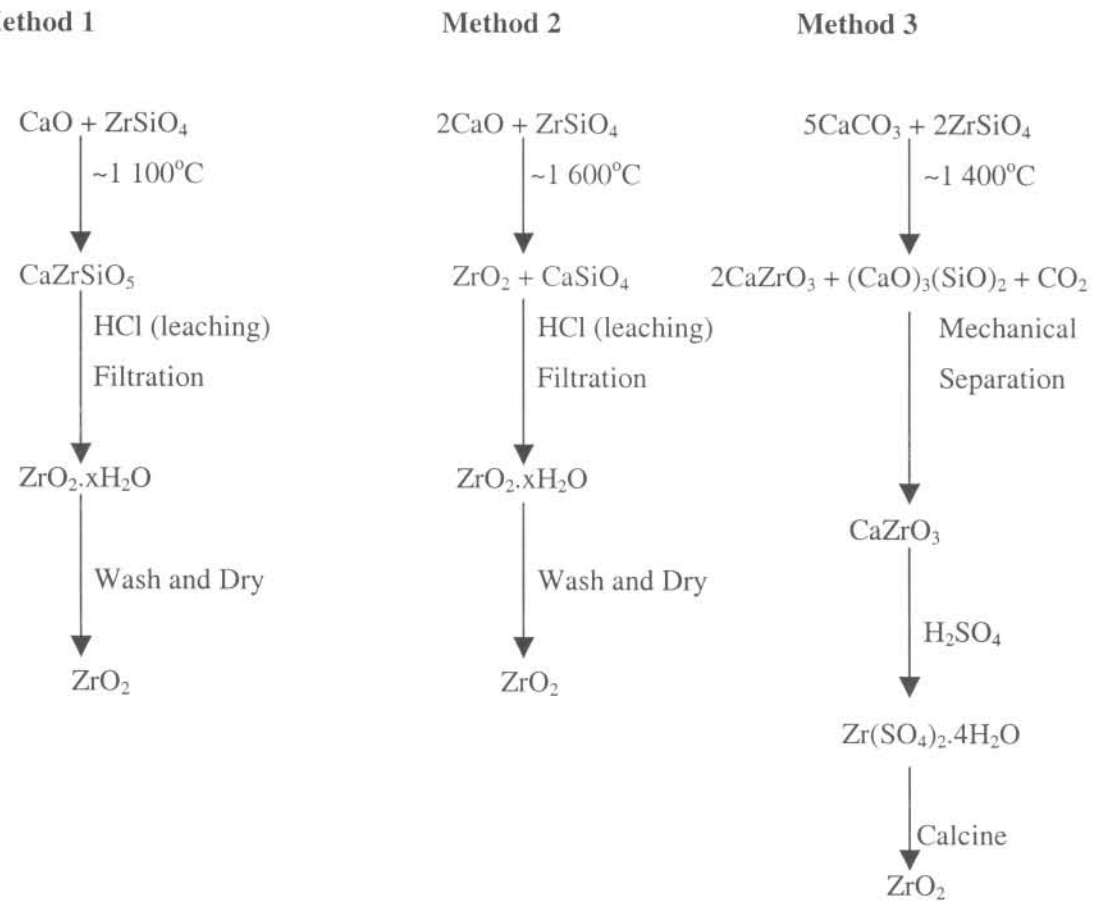

FIGURE 5.3 A diagrammatic representation of the various Lime Fusion processes

METHOD 1AND 2

The calcium and silica can be removed by leaching the fusion product with hydrochloric acid. The remaining hydrous zirconia is then washed and dried [3-4].

METHOD 3

The fused product disintegrates into very fine calcium silicate powder and coarse calcium zirconate crystals. Mechanical means can be employed to recover the calcium zirconate coarse crystals [5, 12]. Calcium zirconate crystals of a large size (30-50μm), for easy separation, are developed at a temperature region of 1 700-2 000°C [12]. The calcium zirconate is acid soluble and can easily be converted into zirconium salts such as AZST or the oxide.

4.5 CARBIDING (Figure 5.4)

The zircon is converted into carbide in an open top electric arc furnace at approximately 2 500°C. An intimate mixture of zircon and coke is continuously fed into the furnace. Insufficient carbon is used so that silicon monoxide is vaporised [5].

When the furnace is full it is cooled and the contents separated, the unreacted surface shell from the reacted. The block is broken and crushed to a diameter size less than 75 mm [5]. The ingot can be chlorinated immediately from the furnace to increase its purity [1-5]. If not, oxidation in a furnace leads to zirconia with approximately 5% of silica [5].

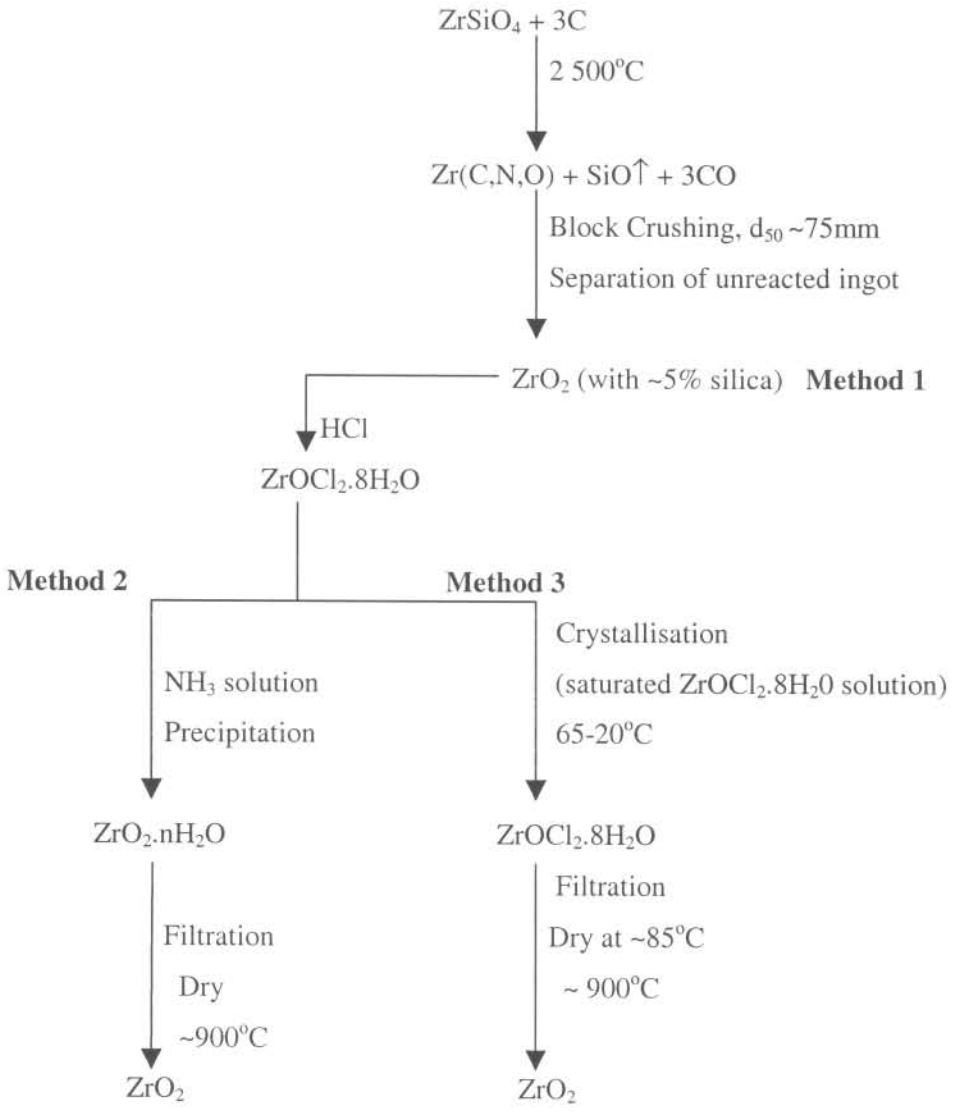

FIGURE 5.4 A diagrammatic representation of the Carbiding Processes

5.6 FLUOROSILICATE FUSION (Figure 5.5)

Zircon can be fused with potassium hexafluorosilicate at approximately 700°C to produce potassium hexafluorozirconate [5]. The fusion reaction can also be carried out in a rotary furnace at temperatures between 650-750°C [10]. The fused product is milled and leached in 1% HCl solution at ~85°C for two hours.

The saturated solution is filtered while it is still hot to remove the insoluble silica and then allowed to cool to crystallise the potassium hexafluozirconate. A zirconium hydroxide is precipitated with ammonium hydroxide from a three percent solution of potassium hexafluozirconate. The hydroxide is then filtered, washed, and then calcined to zirconia.

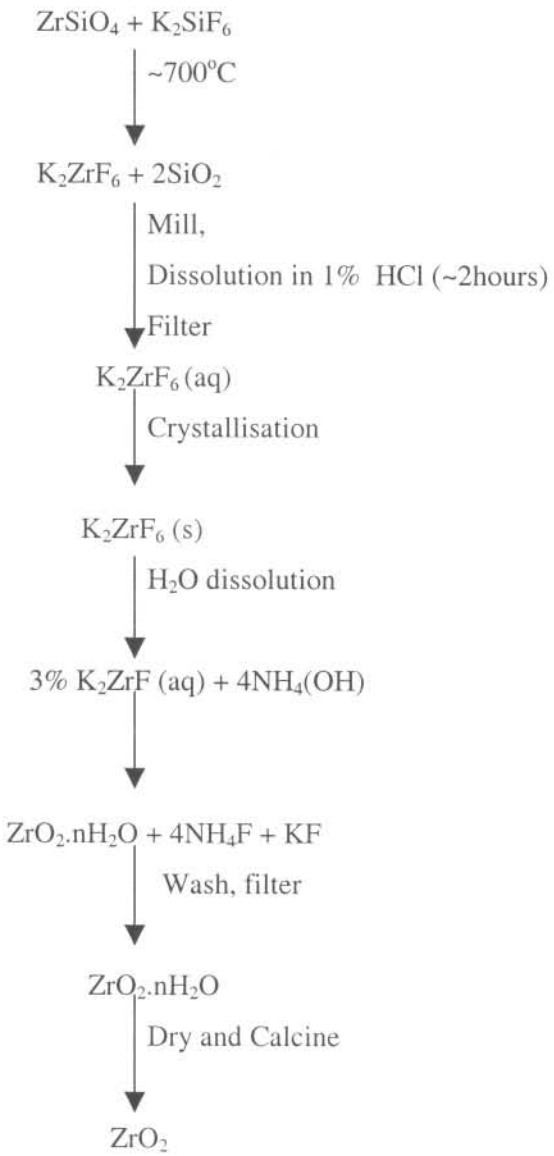

FIGURE 5.5 A diagrammatic representation of the Potassium hexafluozirconate process

5.7 CAUSTIC FUSION

This process involves the decomposition of zircon by fusion with sodium hydroxide or sodium carbonate in different mole ratios to form reactive species.

5.7.1 SUB-STOICHIOMETRIC CAUSTIC FUSION (Figure 5.6.1)

An acid soluble sodium zirconate is produced by reaction of zircon with sodium carbonate at low mole ratios. This reaction usually occurs at approximately 1 000°C as follows [1, 3-5].

$$ZrSiO_4 + Na_2CO_3 \rightarrow Na_2ZrSiO_5 + CO_2\uparrow$$

SCHEME 5.1 Reaction of zircon with sodium carbonate at sub-stoichiometric levels

METHOD 1

The fused product, usually sodiumzirconylosilicate Na_2ZrSiO_5, is milled and added to a concentrated mineral acid (e.g. HCl) to produce zirconium salts and silica gel. The zirconium salts are then separated from the silica [5]. The zirconyl chloride is then crystallised from a saturated solution or precipitated with ammonia [4].

METHOD 2

The milled fused product can be leached with water and the insoluble sodium zirconyl silicate digested with hot hydrochloric acid. The silica precipitate can simply be filtered and the zirconyl chloride treated with sulphuric acid to precipitate a zirconium basic sulphate [10, 14]. The sulphate can simply be calcined directly to zirconia. The sulphate can be converted to the hydroxide with ammonia and calcined to zirconia.

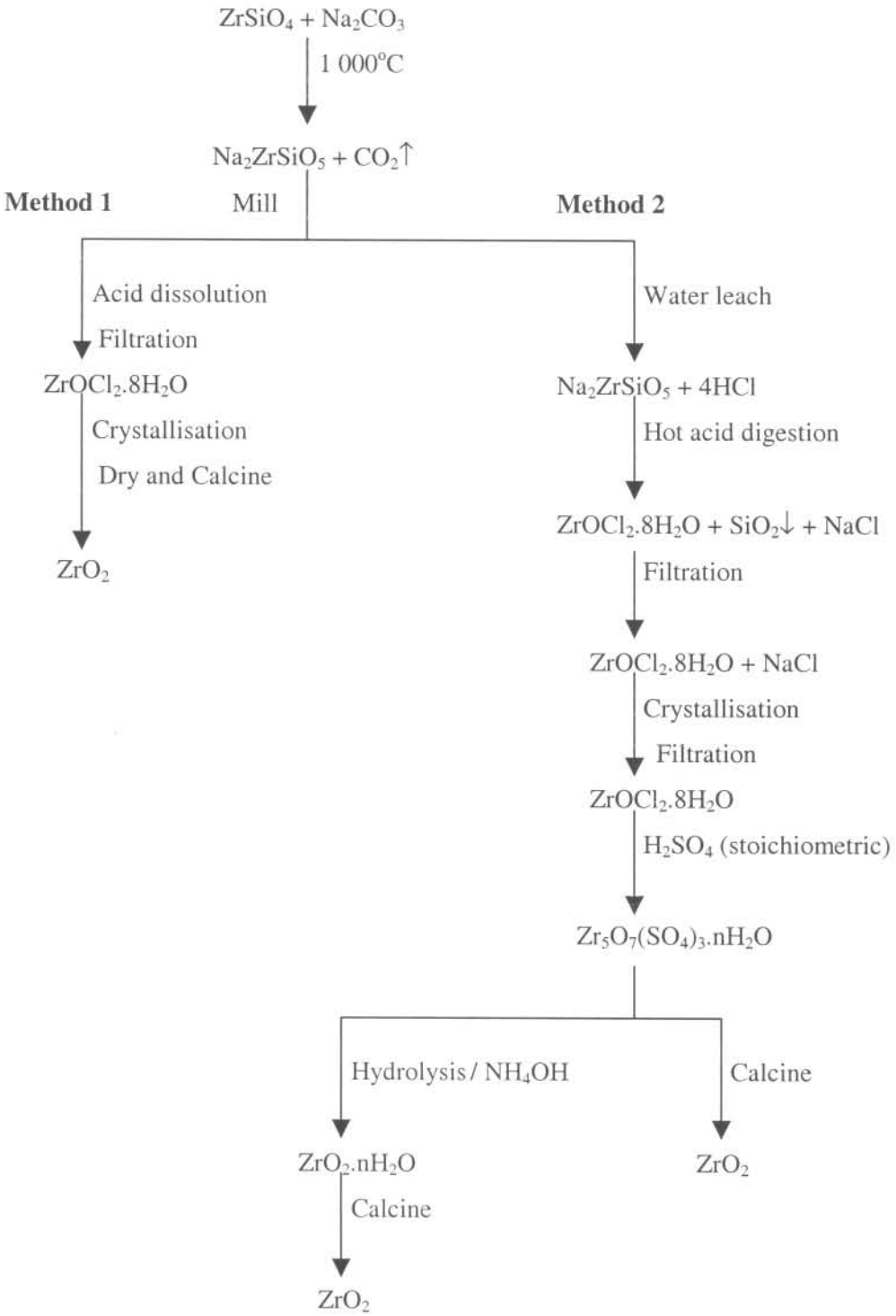

FIGURE 5.6.1 A diagrammatic representation of the Sub-stoichiometric caustic soda fusion

5.7.2 SLIGHT EXCESS CAUSTIC SODA FUSION (Figure 5.6.2)

Zircon is fused with sodium hydroxide in a one is to four mole ratio at approximately 650°C to produce sodium zirconate and sodium silicate [1, 3-5]. This reaction can also occur with sodium carbonate above 1 000°C [3-5].

$$ZrSiO_4 + 4NaOH \rightarrow Na_2ZrO_3 + Na_2SiO_3 + 2H_2O \uparrow$$

SCHEME 5.2 Reaction of zircon with sodium hydroxide in a one is to four mole ratio at 650°C

The fused product is crushed and dissolved in water. The sodium silicate is dissolved by water. The sodium zirconate is hydrolysed by water to soluble sodium hydroxide and insoluble hydrous zirconia [3-5]. The liquid phase is separated from the solids by filtration. Numerous ways exist on how to treat the hydrous zirconia to produce zirconia of different purity.

METHOD 1

The hydrous zirconia can be simply fired to zirconia [1-2, 5, 8].

METHOD 2

Another way could be by using hydrochloric acid, where the hydrous zirconia is treated with hydrochloric acid to produce zirconium oxychloride, $ZrOCl_2.8H_2O$. The separation of insoluble products and the precipitation of zirconium hydroxide with drying and calcination resulting in zirconia follow this step [3-5].

METHOD 3

A method that is capable of producing zirconia of very high purity for alkali fusion is the one that uses hydrochloric acid and sulphuric acid [9]. In this method the hydrous zirconia is initially digested with hydrochloric acid to form zirconyl chloride and soluble chlorides of the radioactive elements. The AZST is crystallised with the addition of sulphuric acid (salting out). The AZST precipitate is then washed to remove the soluble chlorides of the radioactive chlorides. The AZST is then calcined to zirconia.

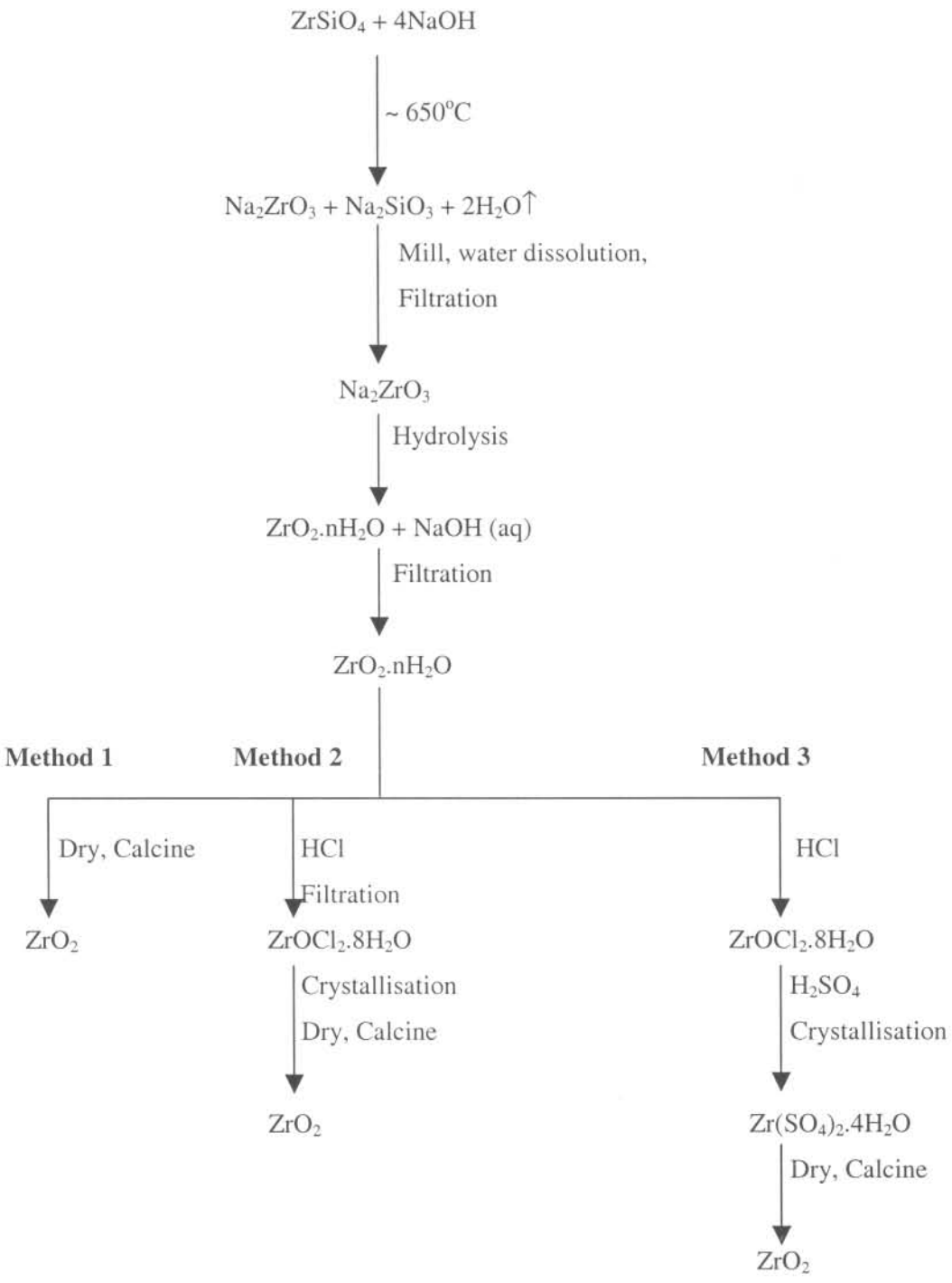

FIGURE 5.6.2 A diagrammatic representation of the various pathways of an Alkali Fusion process.

5.7.3 HIGH-STOICHIOMETRIC CAUSTIC FUSION (Figure 5.6.1-5.6.2)

By adjusting the mole ratio and reaction conditions it is possible to produce almost complete conversion. Consider the reaction at approximately 600°C of the mole ratio [3-4]:

$$ZrSiO_4 + 6NaOH \rightarrow Na_2ZrO_3 + Na_4SiO_4 + 3H_2O \uparrow$$

SCHEME 5.7.3: Reaction of zircon with six moles of caustic soda

In this particular case fusion improves dramatically with almost complete conversion of zircon to sodium zirconium silicate and sodium silicate thus leading to higher zirconia (and silica) yields. This reaction is also possible with sodium carbonate but at higher temperatures above 1 000°C.

The fused product is crushed and slurried in water. The silicate is dissolved in water and separated from the zirconate. The sodium zirconate is hydrolysed by the water to sodium hydroxide and a complex hydrated hydroxide. The sodium hydroxide is separated from the gelatinous complex zirconium hydroxide [3-4]. There are numerous methods of treating the complex hydrated hydroxide similar to those for the sub-stoichiometric and slight excess fusion.

5.8 CONCLUSIONS

1. Zircon is dissociated by thermal methods, for example plasma, at temperatures greater than 1 750°C. At temperatures greater than 2 400°C, the silica is volatilised to the monoxide and re-oxidised to the dioxide outside the oven. The silica volatilisation temperature can be lowered to 2 000°C in the presents of carbon.
2. At temperatures less than 2 400°C, further chemical processing is required, especially to obtain a product of higher purity. This processing is limited by the size of the agglomerates (2-20μm). For sufficient rapid leaching the mean particle size must be between 0.01 and 0.1μm.
3. To obtain highly pure products, precipitation methods are used. For example, the salting out method which refers to the exploitation of a minimum in ZrO_2 solubility in the system ZrO_2-SO_3-H_2O between 45-55% (m/m) SO_3 were the zirconium crystallises out as $Zr(SO_4)_2.4H_2O$.
4. The disadvantage of such methods is the time spent while stirring. For the above example there is also the need for long calcination to lower the SO_3 content. An additional step, for example $ZrO_2.nH_2O$ precipitation and $(NH_4)_2SO_4$ effluent washing can alternatively be employed.
5. Chlorination processes also exploit such precipitation methods, but use zirconyl chloride as the precipitate. The factors time, effluent and number of steps come into play.
6. Alkali fusion methods can decompose zircon into reactive species at lower temperatures when compared to thermal methods. These species can be exploited with the traditional methods of precipitation obtain pure products.
7. Zircon can be fused with potassium hexafluorosilicate at approximately 700°C to produce potassium hexafluorozirconate.
8. Zircon can be decomposed with different moles of caustic soda at approximately 600°C. The presence of the various complex metal zirconium silicates depends heavily on the fusion mole ratio. For example Na_2SiO_3 and Na_2ZrO_3, form in the presents of four moles sodium hydroxide for a mole of zircon.
9. The sodium content in zirconates can be minimised by hydrolysis to the hydroxide $ZrO_2.nH_2O$. The problem is the long process time while heating.
10. Depending on what route is taken, the traditional precipitation and crystallisation routes can be employed to obtain a pure product.

5.9 REFERENCES

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