Suid-Afrikaanse Tydskrif vir Natuurwetenskap en Tegnologie 2023; 42(1):43-63
South African Journal for Science and Technology 2023; 42(1):43-63
https://doi.org/10.36303/SATNT.2023.42.1.963E

SATNT / SAJST
ISSN: 2222-4173 EISSN: 0254-3486

REVIEW ARTICLE

Zircon as feedstock for zirconium chemicals, ceramics, the metal and alloys: A review

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South Africa is the second largest producer of zircon internationally. Local beneficiation of the mineral is minimal at present, despite the very attractive market opportunity zirconium-based products present. Several well-developed processes for the production of a range of zirconium chemicals exist. These chemicals can in their turn be used to prepare monoclinic and stabilised zirconium oxides. In the majority of cases zirconium oxychloride octahydrate – generally referred to as ZOC – is used as precursor. Zirconium-based products are generally inert and non-toxic, and may be used in several applications. These include medical implants, anti-perspirants, and even as ammonia absorbents during blood dialysis. Zirconium oxide ceramics also have many applications in medical and industrial applications due to their hardness, chemical inertness and corrosion resistance. This review provides an overview of the processing and synthesis routes between the mineral and these final products, as well as the gateway products. The local context is emphasised.

Keywords: zircon, zirconium chemistry, zirconium oxychloride octahydrate, zirconium chemicals, zirconia

Sirkoon as voerstof vir sirkoniumgebaseerde chemikalieë, keramieke, die metaal en sy legerings: ‘n Oorsigartikel: Suid-Afrika is die tweedegrootste internasionale produsent van sirkoon. Plaaslike veredeling is egter minimaal, ondanks die aantreklike markgeleentheid vir sirkoniumgebaseerde produkte. Daar is verskeie goed ontwikkelde prosesse vir die vervaardiging van ‘n reeks sirkoniumchemikalieë. Hierdie chemikalieë kan op hul beurt gebruik word om monokliniese sowel as gestabiliseerde sirkoniumoksiede te berei. In die meeste van die prosesse word sirkoniumoksichloriedoktahidraat – ook na aanleiding van die Engels bekend as ZOC – as voerstof gebruik. Sirkonium is inert en nie giftig nie, en kan daarom in verskeie toepassings gebruik word. Dit sluit in mediese implantate, antiperspirante en selfs as absorbeermiddels gedurende bloeddialise om ammoniak te absorbeer. Sirkoniumoksiedgebaseerde keramieke het ook verskeie toepassings in aggressiewe industriële prosesse as gevolg die hardheid en inerte karakter van die materiaal. Hierdie artikel gee ‘n oorsig van die prosesserings- en sinteseroetes tussen die mineraal en die finale produkte, sowel as die voerchemikalieë, met klem op die plaaslike konteks.

Trefwoorde: sirkoon, sirkoniumchemie, sirkoniumoksiechloried-oktahidraat, sirkonia, sirkooniumchemikalieë

Introduction

South Africa is richly endowed with the mineral zircon. We export, but we do not beneficiate to any significant degree, despite the fact that processing and synthesis routes are in essence non-problematic and standard – apart from the issue of radio-active contamination and the fact that meticulous attention to preparative detail is usually required. This paper provides an overview of the processing techniques, the uses of zirconium-based products, and the international markets. The zirconium-based product range include: chemically reactive zirconium chemicals; fused and chemically precipitated zirconia – stabilised and non-stabilised; inorganic zirconates; zirconia ceramics; and the metal and its alloys. The products discussed in this review are the more common ones.

Markets and Uses

Zircon mineral

Zircon is the most common and widely distributed of the commercial minerals. Originally associated with igneous deposits, a combination of weathering and natural concentration – due to its high density of 4,6 g/cm^{-3} – resulted in large secondary deposits now found in beach sand. The deposits are normally associated with the titanium minerals rutile and ilmenite as well as rare-earth deposits like monazite.

South Africa and Australia both have an abundance of zircon, also known as zirconium silicate ($ZrSiO_4$). South Africa is the second largest producer of zircon in the world after Australia (Roskill 2011a). The main producers are Australia, South Africa and the USA (UxC Consulting Services 2011). The global suppliers of zircon are presented schematically in Table I.

In South Africa, zircon is associated with heavy mineral beach sand deposits on the coasts of KwaZulu-Natal, the Eastern Cape, and at the west coast of the Western Cape. The heavy mineral sand producers in South Africa are:

- Richards Bay Minerals (RioTinto) with a capacity of about 300 000 tonnes per annum; and
- Namakwa Sands and KZN Sands, both operated by Tronox Exxaro, with a combined capacity of about 170 000 tonnes per annum.

In 2010, South Africa produced about 381 000 tonnes of zircon, which represents 29% of the total world production. Global production then amounted to 1 294 million tonnes, with a demand of more than 1 400 million tonnes. The United States Geological Survey estimates that economic exploitable reserves of zircon in South Africa amounts to 14 million tonnes, or 37% of the world total (US Geological Survey 2011).

Iluka Resources, with operations in Victoria and Western Australia, is the dominant zircon producer in Australia, with an estimated capacity of 500 000 tonnes per annum in 2010, providing for about one third of the world's zircon consumption (Roskill 2011). Iluka produces mainly premium grade zircon as an opacifier in the ceramics industry. Smaller Australian producing companies are TiWest and Bemax Resources.

Other major producing countries are the USA, with 100 000 tonnes per year (tpa) (8%) and China, with 70 000 tpa (5%) of world consumption.

An overview of the applications for zircon-derived products is given in Figure 2. Zircon's main application is as an opacifier in ceramic tiles and sanitary ware. Finely milled zircon provides high whiteness and opacity in ceramic glazes, ceramic pigments, porcelain bodies, sanitary and tableware. It is also used in refractories and friction products. There are various opacifier grades, including -10 µm, -5 µm, and -1 µm with and average d_{50} particle size distribution in the range 1–2 µm. (Snyders 2007) This is generally referred to as opacifier grade zircon.

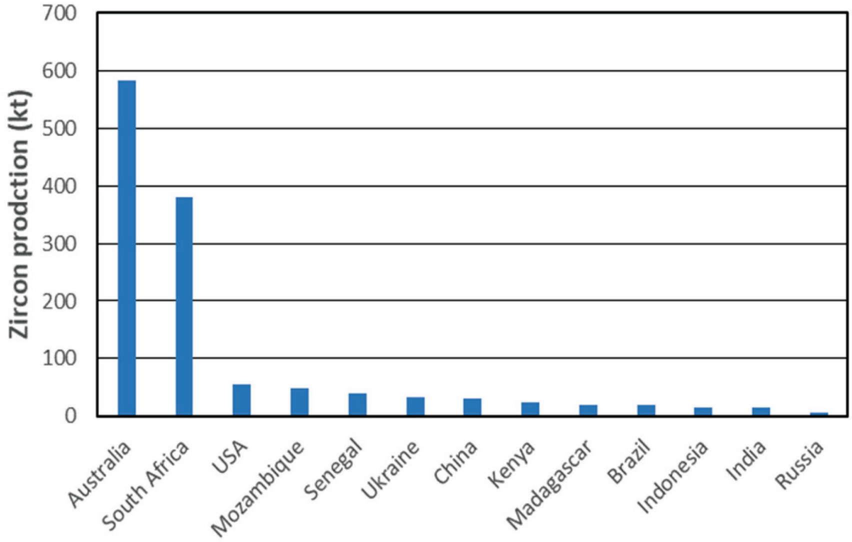


Figure 1: Global mining of zircon, 2015 (Helgi 2023)

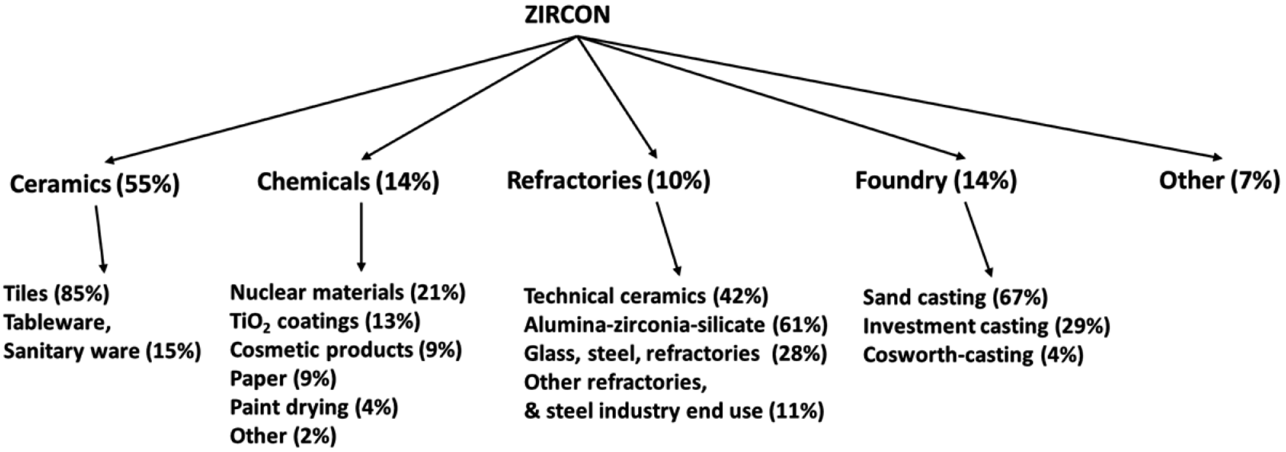


Figure 2: Zircon applications (IndustryARC, 2023)

Zircon is mined as a by-product from rutile (TiO_2), ilmenite ($FeTiO_3$), monazite and leucoxene heavy mineral beach sand deposits. Mining operations are usually done via dredging. Separation of the different minerals is conducted via gravitational and magnetic separation techniques. The zircon concentrates are normally classified as prime grade, standard grade and refractory grade. These classifications are usually done according to chemical purity and particle-size distribution. The chemical analysis of some typical zircon grades and producers are presented in Table I (Roskill 2011).

All zircon deposits contain uranium and thorium and their radio-active decay products. Zircon is therefore considered to be a Naturally Occurring Radioactive Material (NORM) and therefore has to comply with relevant regulatory standards in terms of processing and transportation. Several attempts have been made in the past to remove this radioactivity but with limited success (Hollitt et al. 1995; Levins et al. 1995).

The price of zircon concentrate has risen dramatically since 2000, the main reason being the current supply-demand imbalance. More recently the price has stabilised around the US$1 500 per metric tonne mark. Pricing of zircon over the past decade is given in Figure 3.

More than 95% of all the zircon exported from South Africa is not beneficiated. Export of un-beneficiated minerals is a serious concern for the South African government (DMR 2011). Limited local beneficiation is done by:

- Eggerdine, which has a milling operation in Richard Bay (KZN) with a capacity of about 20 000 tonnes per annum. It produces various grades of zircon flour and zircon opacifiers;
- Geratech in Krugersdorp, which was producing zirconium chemicals with a planned capacity increase 10 000 tonnes zircon sand per annum of (Lubbe, 2014). The company was, however, liquidated in 2013 due to a lack of funding; and
- Foskor in Phalaborwa in the Limpopo Province, which produces fused zirconia.

The South African Nuclear Corporation Ltd. (Necsa) developed several zircon beneficiation processes to produce zirconium chemicals, doped zircon pigments and a superior zircon opacifier from plasma dissociated zircon (Snyders 2005a; Snyders 2005b). Although some of these processes have been piloted, none have been commercialised.

Baddeleyite

Natural ZrO_2 (baddeleyite) may also be used as zirconium source; indeed, it is less problematic. However, only limited resources of baddeleyite still remain, with the exception of the deposit in Kovdor, Russia. Less than 10 000 tonnes of baddeleyite is produced from the Kovdor deposit annually, and in general the purity is around 98%. South Africa was the biggest producer of baddeleyite from the deposit at the Phalaborwa complex in Limpopo Province until 2001, when the mining of baddeleyite ceased since it was not considered to be economically profitable any more. At its peak, South Africa produced about 20 000 tonnes of baddeleyite per annum (Skidmore 2010; Roskill 2011).

Fused zirconia

Fused zirconia is produced from zircon at high temperature in an arc furnace by evaporation of SiO. Fused zirconia is another source for zirconium metal manufacturing with a purity of approximately 99%, compared to chemically precipitated zirconia at >99,5%. Both fused and chemically precipitated zirconia are associated with high manufacturing costs. In January 2012, fused zirconia was sold at US$6 000 per tonne and chemically precipitated zirconia at between US$8 000 and US$12 000 per tonne.

Zirconia-based ceramics

Zirconia-based ceramics are of both scientific and technological interest as structural and functional ceramics. Superior properties such as chemical inertness, high ionic conductivity, high reactance, low thermal conductivity with good thermal stability and resistance to thermal shock mean that zirconia

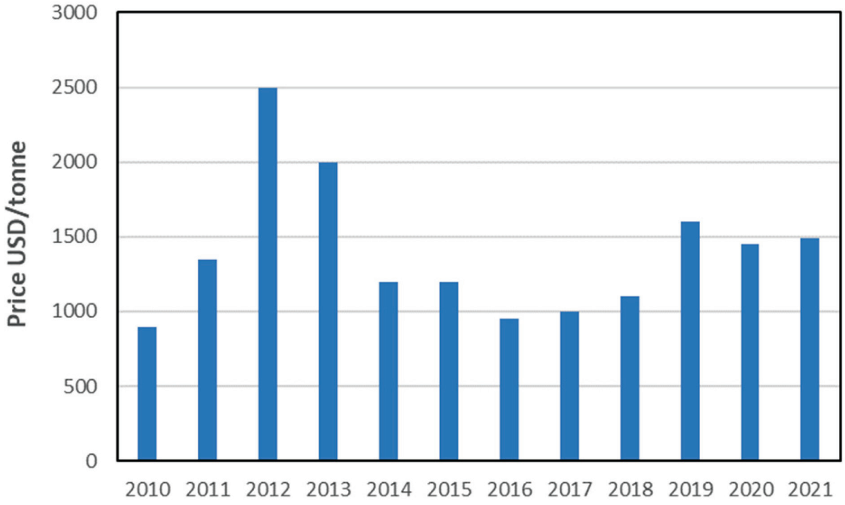


Figure 3: Zircon sand pricing (Zircomet 2023)

Table I: Typical zircon sand analyses by producer

	Grade	% ZrO_2	% TiO_2	% Fe_2O_3	% Al_2O_3	% SiO_2	ppm U + Th
Australia							
Bemax	Premium	65,8	0,12	0,06	0,0	32,5	450
	Standard	65,5	0,25	0,15	1,00	32,9	450
Iluka	Capel Premium	65,5–66,0	0,10–0,15	0,05–0,07	0,50–0,70	32,2–32,5	360–440
	Capel Coarse	66,1–66,4	0,13–0,18	0,07–0,13	0,05–0,15	32,4–32,7	400–470
	Eneabba Premium	66,5	0,13	0,07	0,35	32,5	440
Ti-west	West Coast Premium	66,4	0,13	0,06	<0,50	33,2	400
	HTZ	65,9	0,65	0,06	1,15	31,7	420
India							
IRE	OR	64,25	0,70	0,30	-	32,10	
	MK	65,80	0,25	0,10	1,20	32,50	-
	Q	65,30	0,27	0,12	-	32,80	-
South Africa							
Tronnox-Exxaro	Namakwa Sands	66,2	0,11	0.05	0,25	32,8	410
RBM	Premium	65,9	0,12	0.08	0,14	32,0	450
	Intermediate	65,5	0,25	0.12	0,25	32,5	450
USA							
DuPont	Premium	66,7	0,13	0.02	0,24	-	-
	Low Alumina	66,5	0,21	0.04	0,50	-	-
	Standard	65,9	0,27	0.04	1,15	-	-

ceramics can be used in a wide variety of applications (Guo & Chen 2004). Examples are applications in thermal barrier coatings, especially in harsh environments, and in yttria stabilised form as the solid electrolyte in solid oxide fuel cell technology (SOFC) due to its oxygen ion conductivity. SOFC cells normally operate at temperatures above 800 °C.

The coordination valence of zirconia is not always satisfied on the surface. Zirconium atoms form a Lewis acid site, and the oxygen atoms a Lewis base site. Therefore, the surface of zirconia can act both as an acid or a base with oxidising and reducing properties (Shiaw-Tseh Chiang 2015a; Chuah et al. 1996), for example by the adsorption of CO_2 and NH_3 on the surface. A SiO_2-Al_2O_3 surface can also adsorb basic NH_3, but not the acidic CO_2, whereas a MgO surface can adsorb CO_2 and not NH_3. ZrO_2 surfaces can adsorb both due to acidic and basic (amphoteric) properties (Yamaguchi 1994).

Zirconia is also a highly active catalyst for C-H bond cleavage of methyl groups. It is highly selective for the synthesis of α-olefins from secondary alcohols. Results have suggested that such reactions proceed via an acid-base bifunctional catalysis reaction and that the orientation of acid-base pair sites plays an important role in the catalytic action (Tanabe 1985).

Due to zirconia's high refraction index, applications were developed in optical devices as filler for producing nano-composites with a high refraction index, such as brightness enhancement films for LCD displays, the encapsulation of LED holographic grating, as well as in dentistry. However, a large refractive index difference between the zirconia and the resin can cause excessive optical scattering. To maintain transparency, the particles must be less than 10 nm and non-agglomerated.

Large surface area or nano-zirconia can be produced with phase stabilisation when zirconia is partially substituted in the crystal lattice with other oxides of lanthanum, magnesium, calcium and yttrium. Such substitutions lead to tetragonal phase stabilised zirconia. During zirconia ceramic production, a martensitic transformation of the tetragonal to the monoclinic phase results in the stress field as a propagating crack. This phase transformation is accompanied by a volume increase, which then results in closing of the crack. Therefore, stabilised zirconia is commercially used due to its high strength and toughness (Chuah et al. 1996).

In high temperature turbine engines, a stabilized zirconia coating plays an important role in improving the performance and lifetime by creating a large temperature gradient, in the range of 100–300 °C, between the surface and the turbine alloy components. A consequence is that the gas temperature around the engine can be increased and so improve the efficiency without changing the super-alloy components (Wang et al. 2007). Co-doping of yttria stabilised zirconia with rare-earth elements can reduce the thermal conductivity of thermal barrier coating by as much as 30% of current levels.

Zirconium chemicals

Zirconium chemicals and oxides are produced using zircon as primary feedstock. Zircon is inert towards mineral acid dissolution and is fluxed in strong basic fluxes like NaOH or Na_2CO_3 at high temperature. Carbo-chlorination, done at 1 200 °C using carbon and chlorine gas, is used as a beneficiation route to eliminate the reactive zirconium-oxygen reaction during the production of zirconium metal. The different processing methods are discussed in more detail later.

By breaking the zircon crystal structure via alkaline fluxing, zirconium is extracted by dissolution in hydrochloric acid. The most common compound to be precipitated from this solution is zirconium oxychloride octahydrate, $ZrOCl_2{\cdot}8H_2O$. Due to the zirconyl structure, it is also known as zirconyl chloride, commonly abbreviated as ZOC.

The estimated world consumption of zirconium chemicals, excluding zirconia, was more than 325 million tonnes per annum in 2011, with more than 60% of the capacity allocated to the production of ZOC. About 90% of zirconium oxychloride production is in China at an estimated capacity of 250 000 tonnes per annum. Other ZOC producing countries are France, India, Japan, Russia, UK and USA (Roskill 2011).

Zirconium metal

Zirconium alloys find application as a cladding material for nuclear fuel in power plants. Globally there are 431 operating nuclear reactors, with another 139 being built or planned to be built by 2030 (UxC Consulting Services 2011; Snyder et al. 2011). Although Eskom is in the doldrums, South Africa had plans to build six new 1 200 MW reactors by 2030 to alleviate the electricity crisis (MBM 2007). This would contribute an additional 9 600 MW of nuclear power to the electrical energy grid. A typical 1 200 MW nuclear reactor requires 27 tonnes of zirconium metal for the initial load, and thereafter is replenished with about 10 tonnes per year. More than 85% of all zirconium metal produced is used in the nuclear industry. The remainder is used in specialised alloys mainly in industries where alloys that exhibit high corrosion resistance in high temperature applications are required. Examples are immersion heaters, heat exchangers, chemical reactors and tank linings, mixers, pumps and valves (Miller 1957b). We summarise the process steps in Figure 4.

Zircon processing

Zircon is chemically inert and not soluble in any of the mineral acids, not even hydrofluoric acid. It can be dissolved by fusion in alkaline fluxes. Lubbe et al. (2012) give an overview of the zircon beneficiation processes for the production of various zirconium chemicals and oxides.

Typical alkaline fluxes include NaOH, Na_2CO_3, CaO, and MgO (Nel et al. 2011; Biswas et al. 2012; Biswas et al. 2010b; Stevens 1986). Fluxing temperature varies between 600 °C and 1 400 °C, depending on the type of flux being used. The most common industrial beneficiation method is by fluxing with NaOH at 600 °C to form a so-called frit. The stoichiometric dissociation reaction is:

$$ZrSiO_4 + 4NaOH \rightarrow Na_2ZrO_3 + Na_2SiO_3 + 2H_2O\uparrow \qquad (1)$$

Industrially an excess NaOH is used with the benefit of a softer and more workable frit:

$$ZrSiO_4 + 6NaOH \rightarrow Na_2ZrO_3 + Na_4SiO_4 + 3H_2O\uparrow \qquad (2)$$

Sodium silicate is water soluble whereas sodium zirconate is only acid soluble. In principle separating the zirconate from the excess silica in the frit can thus be done by thorough washing with water. This often requires several steps. The sodium zirconate is then dissolved in hydrochloric acid and ZOC is precipitated by evaporation.

China ranks first in zircon beneficiation to ZOC and produced more than 200 000 tonnes ZOC in 2011 (Liu et al. 2014). China exclusively uses the NaOH route for beneficiation. Alkaline fusion of zircon presents good versatility, is fairly simple, and requires both low capital and operational costs since expensive equipment and reagents are not required.

A number of academic publications have appeared, addressing the fusion of zircon. El Barawy et al. (2000) studied the kinetics of zircon dissociation with both NaOH and Na_2CO_3. They concluded that and excess of 2 mole NaOH leads to 100% decomposition of the zircon at 700 °C. They calculated the NaOH apparent activation energy to be 62,11 kJ mol^{-1}, compared to the 250 kJ mol^{-1} required to flux zircon with Na_2CO_3. With a 0,2 molar excess Na_2CO_3 to dissociate zircon according to the reaction

$$ZrSiO_4 + Na_2CO_3 \rightarrow Na_2ZrSiO_5 + CO_2\uparrow \qquad (3)$$

the optimum fusion temperature was 1 100 °C, with a 91% ZrO_2 recovery.

Biswas et al. (2010b) repeated El Barawy's work and concluded that a higher concentration of NaOH is needed for complete dissociation of zircon at 700 ºC. They determined the activation energy of the NaOH fusion to be 125 kJ mol^{-1}, indicating a chemical controlled process. The zircon particle size distribution used was between 44 and 53 µm. They also concluded that a roasting time of 1 hour with equimolar Na_2CO_3 at 1 000 ºC was sufficient to dissolve only 86% of zircon. They warned, however, that for industrial-scale operations, separation of gelatinous H_2SiO_3 and unreacted zircon from the $ZrOCl_2$ solution may be problematic.

Abdelkader et al. (2008) used equimolar ratios of NaOH and KOH to decompose Egyptian zircon sand with a mean particle size of

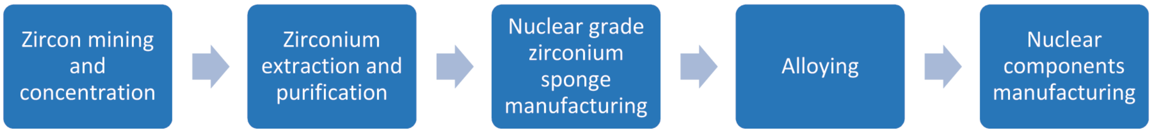


Figure 4: The main steps involved in the production of zirconium nuclear components from zircon concentrate

63 µm. They found that the dissociation efficiency increased by approximately 7% with an increase from 100% to 150% of the stoichiometric quantity of alkali required. They concluded that an excess of only 20% alkali mixture reaches the optimum dissociation efficiency at 550 °C within 60 minutes. Under these conditions, 96% of the zircon is dissociated, compared to 100% dissociation reported by El Barawy & co-workers.

An alternative method to extract zirconium from zircon has been proposed by Abdelkader & Daher (2008). A mixture of NaOH and KOH was used during the fritting process. After washing with water to remove the sodium- and potassium silicates, Zirconium basic sulphate was precipitated in situ by H_2SO_4 and leached from the impurities at different HCl concentrations. Neither the desired purity of zirconium oxychloride octahydrate nor of zirconium basic sulphate (ZBS) could be achieved. The ZrO_2 produced after calcination via the ZBS route was 100% tetragonal, but that produced via ZOC was a mixture of tetragonal and monoclinic phases.

Manhique et al. (2003) concluded that the patented de Wet process (De Wet 2006) for zircon beneficiation has the following advantages over other industrial methods:

- Fewer processing steps to produce acid zirconium sulphate tetrahydrate $Zr(SO_4)_2{\cdot}4H_2O$ (AZST);
- A comparatively low-cost pigment zirconia with reduced radio-active content can be produced;
- The alkali reactant can be recovered as a saleable sodium silicate product;
- Only 5% excess sulphuric acid is required to produce AZST;
- Radio-activity is leached as a solid phase. No precipitation is required;
- Fewer effluent streams with less waste are produced; and
- The disadvantage is the difficulty of producing ZOC.

Milled zircon with a mean particle size distribution of 9 µm was used in his study. Manhique concluded that the high temperature flux reaction at 700 °C is a blend of compounds:

$$ZrSiO_4 + 2Na_2O \rightarrow xNa_2ZrO_3 + (2x\text{-}1)Na_2SiO_3 + (1\text{-}x)Na_2ZrSiO_5 + (1\text{-}x)Na_4SiO_4 \quad (4)$$

The value of x is typically between 0,5 and 0,6 and has important implications for the zirconia yield and alkali recovery. Na_2ZrSiO_5 is not water soluble and prevents full alkali recovery. It must be hydrolysed with hydrochloric acid to the corresponding sodium salt waste stream and the dissolution of the zirconium. On the other hand, it facilitates high recovery of zirconia per mole of sodium hydroxide used. A lower NaOH fluxing ratio produces less waste although a higher temperature of 850 °C and a 2 h fluxing time are required for full conversion. At a temperature of 650 °C, the same results were achieved but the fluxing time of 336 hours makes the process industrially non-viable.

Da Silva et al. (2012) concluded that the optimal fusion temperature is 600 ºC for 20 minutes since higher temperatures may lead to more water insoluble compounds such as Na_2ZrSiO_5 or $Na_4Zr_2SiO_3O_{12}$. They determined the reaction rate at different temperatures and concluded that the reaction rate increases with increasing fluxing temperature with an activation energy of 130,9 kJ mol^{-1}. They recovered up to 60% of the alkali via calcium metasilicate precipitation with $Ca(OH)_2$.

Liu et al. (2014) characterised the NaOH frit with the aim of optimising hydrolysis of the produced sodium zirconate. The pH of the solution containing the sodium zirconate is lowered to a pH of 3 by acid addition to ensure complete hydrolysis the Na_2ZrSiO_5. This ensures sufficient removal of sodium ions during the precipitation and filtration of the ZOC crystals.

Welham & Walmsley (2000) and others (Puclin et al. 1995; Biswas et al. 2010a) dissolved zircon by milling in various alkaline earth oxides for 200 hours. The feed zircon had a particle size distribution between 200 µm and 300 µm. Using BaO as a flux at a 1:1 molar ratio causes 86% of zircon to be transformed into $BaZrO_3$. The HCl solubility can be further increased when higher molar ratios are used. CaO at a 3:1 ratio caused 99% dissolution and MgO at a 2:1 ratio a 97% dissolution in acid. Commercially the most viable oxide would be MgO. The mass fraction MgO is only about 31%. A slightly higher ratio may render more than 99% of the zircon soluble in an acid. Welham recommends that the best energy-effective mill be used to reduce the milling time for commercial operations.

Nel et al. (2011) used acid ammonium fluoride ($NH_4F{\cdot}1.5HF$) with the aid of microwave digestion to dissolve zircon with an average particle size distribution of 63 µm. A 5:1 excess of acid ammonium fluoride was used with each dissolution step. The undissolved fraction was recovered by filtration, washed with propanol, dried and then recycled using fresh acid ammonium fluoride. Up to 99% conversion was achieved after 285 minutes at 240 ºC. Unfortunately, Nel did not explain the processing steps of the $(NH_4)_3ZrF_7$ to produce zirconium oxide and other compounds.

Ayala et al. (1992) milled and fluxed zircon with different concentrations of Na_2CO_3 and CaO with the aim of extracting ZrO_2 powder according to reactions 5 and 6.

$$ZrSiO_4 + CaO \rightarrow CaSiO_3 + ZrO_2 \quad (5)$$

$$ZrSiO_4 + Na_2CO_3 \rightarrow Na_2SiO_3 + ZrO_2 + CO_2\uparrow \quad (6)$$

Different NaOH concentrations were used to leach the remaining silica to produce zirconium powders with a purity between 90% and 98%. True and apparent densities of the produced zirconia were lower than that of chemically precipitated zirconia. Zirconia produced via the Na_2CO_3 method exhibits a smaller and more uniform grain size distribution than that derived via the CaO route. The purity of the zircon and amount of Na_2CO_3 or CaO used for dissociation had a large influence on the quality of the resulting ZrO_2 powder.

Zirconium Oxides

Preparation

Preparation of ZrO_2 by precipitation of a zirconium salt with a base like ammonia usually leads to a mixture of the stable monoclinic ZrO_2 and the meta-stable tetragonal ZrO_2. The phase transformation between the monoclinic and the tetragonal polymorphs with increased temperature, prevents the use of zirconia directly in industry. The phase transformation can be suppressed by stabilisation of the tetragonal phase either by the appropriate cationic doping, or by tailoring the particle size to below a critical value of about 30 nm. Traditionally the tetragonal and cubic polymorphs are stabilised at room temperature through the addition of a proper amount of aliovalent cations. Stabilisation of high temperature polymorphs can also be achieved without the addition of a chemical stabiliser by simply reducing the crystallite size of the material to the nano range – so-called size-induced stabilisation (Tredici et al. 2012; Adamski et al. 2006). It is generally recognised that size-induced stabilised tetragonal zirconia is thermodynamically more stable than monoclinic zirconia at room temperature, as long as crystallite growth is prevented.

It is evident that ZOC is used as the primary starting zirconium compound for the production of zirconium oxide. During the dissolution of ZOC in water a cyclic tetrameric complex, $[Zr(OH)_2{\cdot}4H_2O]_4^{8+}$, is formed. When the pH of this solution is changed by addition of a base like ammonia, hydrolysis occurs and the tetramer releases protons from the terminal water to form $[Zr(OH)_{2+n}{\cdot}(4\text{-}n)H_2O]_4^{(8-4n)+}$ species according to reactions 12 to 14 (Adamski et al. 2006).

$$[Zr(OH)_2{\cdot}4H_2O]_4^{8+} \rightarrow [Zr(OH)_{2+n}{\cdot}(4\text{-}n)H_2O]_4^{(8-4n)+} + 4nH^+ \quad (12)$$

Subsequent polycondensation takes place by olation

$$Zr–OH + H_2O\text{-}Zr \rightarrow Zr–OH–Zr + H_2O \quad (13)$$

and oxolation,

$$Zr–OH + HO\text{-}Zr \rightarrow Zr–O–Zr + H_2O \quad (14)$$

leading to the formation of hydroxyl- and oxo-bridges between the tetramer units. The shift in equilibrium of hydrolysis according to reaction 12 can be controlled by changing the pH of the solution. Rapid addition of ammonia increases the number of the terminal hydroxyls in the tetramer in a random fashion so that polycondensation occurs rapidly and in various directions with an amorphous gel as a product. Upon crystallisation, such a gel gives rise to a mixture of monoclinic and tetragonal zirconia (Adamski et al. 2006).

Monoclinic and stabilised zirconium oxide

A characteristic feature of zirconia is the existence of three polymorphic forms, monoclinic ($P2_1/c$), tetragonal ($P4_2/nmc$) and cubic (Fm3m). They differ distinctly in bulk and surface properties. At ambient conditions for coarse grained materials, the monoclinic phase is more stable than the tetragonal phase, but in the case of fine-grained material, the tetragonal phase becomes thermodynamically more stable because of considerably lower surface energy (Jakubus et al. 2003).

Densification of green powder ceramic compacts at elevated temperatures is primarily a process to eliminate voids in the compact. During the heating cycle, shrinkage and grain growth may take place concurrently, depending on factors like sintering temperature, sintered density and the initial particle packing configuration. Grain growth is in general undesirable, because it decreases the end-point density and degrades the final properties of the product. It is important, therefore, to overcome the problem of grain growth during densification (Liu 1998). Many experimental studies have found that for nano-sized particles full densification can be achieved at sintering temperatures several hundred degrees Celsius lower than for coarse particles. Low temperature sintering effectively reduces the tendency of grain growth.

Monoclinic and stabilised zirconium oxides are normally produced via the decomposition of zirconium hydroxide. The decomposition behaviour to monoclinic zirconium oxide, produced via neutralisation of a ZOC solution, has therefore been studied by various authors.

Precipitation of zirconium hydrous oxide with an alkali

Sato et al. (1979) used potassium hexafluoro zirconate (K_2ZrF_6) as the precursor to precipitate zirconium hydroxide with ammonium hydroxide under various conditions. They concluded that the precipitate is an amorphous composition of hydrated oxyhydroxide,

$ZrO_{2-x}(OH)_{2x}{\cdot}yH_2O$. The value of x is determined by the precipitation conditions at different alkali concentrations. According to DTA analysis, adsorbed water is evaporated below 100 °C. An endothermic reaction at 140 °C arises from the dehydroxylation by the thermal decomposition of the hydroxide to amorphous zirconium oxide. A last exothermic peak, at 450 °C, is attributed to the crystallisation of the amorphous zirconium oxide to the tetragonal or monoclinic phase.

Sato (2002) followed up with dehydration studies on zirconium oxyhydroxide by precipitating ZOC solutions with sodium hydroxide and/or ammonium hydroxide under varying conditions. The results were very similar – two endothermic DTA peaks were observed at 80 and 110 °C. The first is again attributed to the release of adsorbed water and the second due to dehydroxylation during the thermal decomposition of zirconium oxyhydroxide to the amorphous oxide. The crystallisation of the amorphous oxide to the tetragonal phase is observed at 430 °C. XRD studies during heating to 800 °C as well as cooling to room temperature showed that, during heating, the oxide transformed to the tetragonal phase from 420 °C, but then only mentioned that the crystallisation progresses with a temperature increase. However, while lowering the temperature from 800 °C, mixtures of monoclinic and tetragonal phases were observed at 600 °C and 500 °C, only transforming to the monoclinic phase at 200 °C upon cooling. The thermal decomposition was proposed to proceed via the following process:

$ZrO_{2-x}(OH)_2 \cdot yH_2O \rightarrow$ amorphous $ZrO_2 \rightarrow$ metastable tetragonal $ZrO_2 \rightarrow$ monoclinic ZrO_2

where $x \leq 2$ and $1 \leq y \leq 2$, depending on the composition of the original starting material.

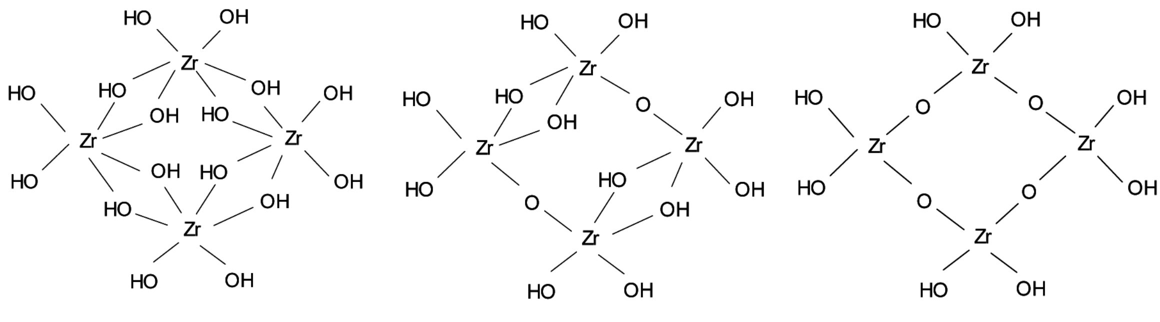
ZrO_2 can also be obtained by the calcination of the hydroxide, prepared via hydrolysis of many other zirconium salts. The crystal phase of the ZrO_2 depends on the preparation process of the hydroxide. Aging for long periods at 100 °C results in a preferred formation of the monoclinic phase while the tetragonal phase is dominant when aging is omitted. Steam treatment of the hydroxide also results in the formation of the monoclinic phase, while vacuum treatment results in the tetragonal phase (Yamaguchi 1994).

The hydroxide precipitation conditions, as well as the heating programme of the hydroxide to achieve the final crystalline phase, are interpreted in terms of the change of the unit cell of the hydroxide. Three structures were identified. The α-type hydroxide is the major phase just after precipitation via hydrolysis. Aging brings about a modification to the β-type and finally the γ-type, with the loss of OH-groups. The α-type is the precursor to the tetragonal phase and the γ-type to the monoclinic phase. See Figure 5 for the model structures.

Chuah et al. (1996) prepared hydrous zirconia by precipitating a zirconium (IV) chloride solution with ammonia from a pH ≤ 1, up to pH 9. Another hydroxide was prepared by adding the acid solution directly into a concentrated ammonia solution. The pH of the ammonia solution changed from 11,8 to a final value of 9,4. After filtration and washing, the hydroxide was calcined to zirconia at temperatures from 30 °C to 100 °C and different time intervals, between 0 and 96 hours. The zirconia crystal phases and surface areas were analysed for comparison. It was observed that an increase in calcining temperature increased the surface area of the zirconia. However, it decreases above 900 °C. Calcining at up to 1 000 °C for 48 hours produces almost a 100% tetragonal zirconia. Only after calcination at 1 100 °C does it revert to the monoclinic phase. Refluxing transformed the amorphous gel particles to a crystalline product such as a hydrated oxo-hydroxide $[ZrO_x(OH)_{4-2x} \cdot yH_2O]_n$. The initial gel differs from this structure, having a much smaller value of x, therefore refluxing in the value of x. This results in the elimination of water from the double hydroxo groups to form oxo-bridges and leads to a more dehydrated oxo-hydroxide as precursor (Figure 3). Other authors did similar work and arrived at the same conclusions. (Denkewicz et al. 2011; Štefanić et al. 1997; Jakubus et al. 2003).

Guo & Chen (2004; 2005) hydrolysed ZOC at 320 °C under acidic conditions (pH 4,5) to produce nano-sized monoclinic zirconia. This temperature is about 280 °C lower than that usually required to obtain pure monoclinic zirconia via precipitation. At a crystallisation onset temperature of 310 °C, the hydrous zirconia yields a predominantly (70%) monoclinic structure co-existing with a 30% tetragonal phase. The monoclinic crystallite size was about 17 nm and the tetragonal size 28 nm. Upon heating the precipitate to 320 °C, a pure nano-crystalline monoclinic zirconia was produced with a crystallite size of 15 nm. They concluded that these data did not support the traditional view that a critical crystallite size of 30 nm is responsible for the stabilisation of the tetragonal and monoclinic phases. Acidic precipitation pH, rapid precipitation, moderate aging time and drying temperatures have a significant influence on the structure of the resulting hydrous zirconia and therefore favour the formation of the monoclinic phase rather that the tetragonal phase.

Al-Hazmi et al. (2014) continued with the work of Guo and Chen by preparing various aliphatic zirconium carboxylates and α-hydroxyl carboxylate complexes. A general trend for the initial tetragonal crystallisation of zirconia was detected between 350 °C and 450 °C. A slight increase in the average crystallite size, from 3,2 nm to 6,7 nm, was observed when the precursor was heated at 590 °C and 720 °C respectively. An average crystallite size of 18,4 nm was observed when the sample was calcined at 800 °C. At this temperature the crystal phase is predominantly monoclinic. ZrO_2 derived from aliphatic



α-type β-type γ-type

Figure 5: Model structures of zirconium polycation (Yamaguchi, 1994)

carboxylates undergo a phase transformation to the monoclinic phase at higher temperatures than the α-hydroxyl carboxylates. Furthermore, longer carboxylate ligand chains increase the surface area of the resulting zirconia (Al-Hazmi et al. 2014).

Adamski et al. (2006), like Chuah et al. (1996), precipitated hydrous zirconia by addition of ammonia to a ZOC solution, as well as by adding a ZOC solution to an ammonia solution. In both cases, the pH was maintained at 9,3. They concluded that adding a zirconium oxychloride solution to an ammonia solution, followed by prolonged aging of the precipitate at 100 °C, appears to be the best way of obtaining a pure tetragonal phase zirconia upon calcination of the hydrous zirconia gel at 600 °C for 6 hours. The concentration of the feed solution is of less importance, and ZOC solutions between 0,006 M and 0,6 M can be used. However, the more concentrated solutions favoured crystallisation of the tetragonal ZrO_2 polymorph. They explained this within the tenets of the classical nucleation and particle growth mechanism. The BET surface area for non-aged samples calcined at 600 °C for 6 hours was 23 m^2/g, and 77 m^2/g for the samples aged at 100 °C for 24 hours. An increase in the pore volume from V_p = 0,046 cm^3/g for the non-aged to 0,214 cm^3/g for the aged samples was also observed. Calcination of the non-aged ZrO_2 samples caused a pronounced increase in the crystallite size due to the rapid coalescence of the primary particles. TEM images revealed that the average diameter of the non-aged crystals calcined at 475 °C grew from 23 nm to 33 nm at 600 °C. After calcination at 1 000 °C, the crystals grew to 69 nm. On the contrary, the average diameter in the aged samples was stable in the temperature range 400–800 °C, and did not exceed the critical value of 30 nm. Sintering was only observed after the phase transformation to monoclinic, starting at 850–950 °C.

Petrunin et al. (2004) precipitated ZOC, nitrate and tetrachloride solutions with ammonia to produce zirconium hydroxide. They concluded that the nature of the starting salt as well as the heat treatment temperature have a significant effect on the phase composition and structure of the ZrO_2 crystallites. They presented a schematic diagram to explain the olation, oxolation and gelation process during neutralisation of the zirconium tetramer with a base like ammonia.

Kostrikin et al. (2010) also studied the dehydration of zirconium and hafnium hydroxides to zirconia and hafnia. The hydroxides were dried at different temperatures and the hydroxyl and oxygen elimination was identified with FTIR. The spectra consist of various bands signifying the presence of OH groups, H_2O molecules, Zr-O-H terminal groups and Zr-O(H)-Zr and Zr-O-Zr bridging groups. 1,5 mol of water is eliminated during the first drying step of $ZrO_2 \cdot 2.5H_2O$ up to 145 °C as a result of the poly-condensation of hydroxo groups. The remaining 1 mole is eliminated up to 900 °C, with the main loss below 485 °C (Kostrikin et al. 2010).

Srinivasan & Davis (1997) report a relationship between the crystal structure and the pH of the precipitation of hydrous zirconia. The pH of the solution determines the crystal phase of the calcined zirconia. Monoclinic zirconia is produces at pH range 6,5–10,4 and tetragonal zirconia in the ranges 2–4 and 13–14, although the stability to phase transformation varied widely (Figure 6).

The precipitation time of the hydrous oxide also has a huge influence of the crystal phase of the produced oxide. Srinovasan & Davis added a metal salt to NH_4OH to maintain the pH at 10,4. The precipitation time varied from rapid addition to up to 8 hours. They concluded that the volume fraction of monoclinic phase decreases with increased precipitation time (Figure 7). Should the line be extrapolated to 0% monoclinic phase, it appears as a precipitation time of approximately 10 hours should be adequate.

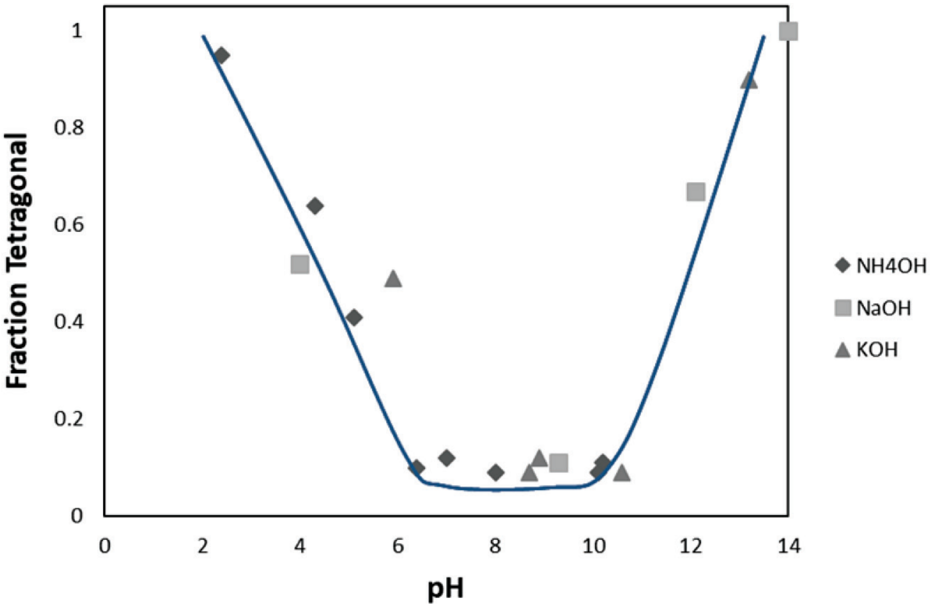


Figure 6: Relationship between pH and fraction of tetragonal phase during the precipitation of hydrous zirconia (Srinivasan and Davis, 1997)

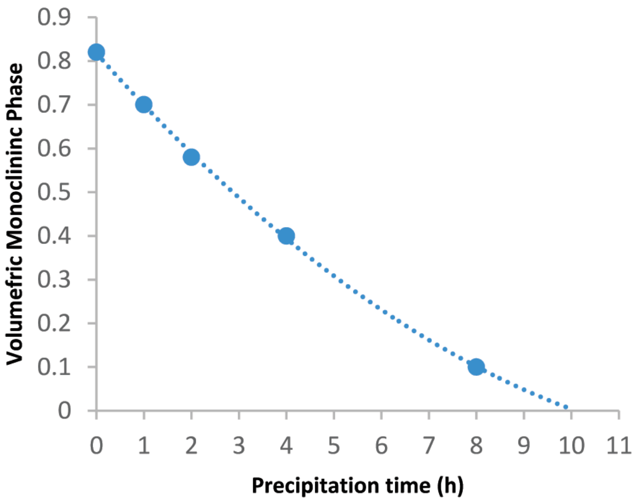


Figure 7: Volume fraction monoclinic crystal phase at pH 10.4

Sol-gel precipitation

Sol-gel (solution-gelation) precipitation is another method to produce zirconium oxides. A sol is a mixture containing solid colloidal particles dispersed in a liquid. Surface charges and Brownian motion are believed to keep a sol stable against settling. There are two procedures to use sol-gel precipitation:

- The precipitation of a colloidal suspension prepared from a metal salt;
- The preparation of a polymeric gel from the hydrolysis of the organometallic compound in a suitable organic solvent.

The primary difference is the rate of hydrolysis of the precursor and the solvent used during hydrolysis. The colloidal route involves rapid hydrolysis in water, followed by peptising and gelation. However, the hydrolysis rate is kept slow in the polymeric route using organometallic compounds (Srinivasan & Davis 1997).

Advantages of the sol-gel technique include:

- Large surface area of the dried gel;
- Chemical homogeneity;
- Manipulation of combination of materials to produce a microstructure, crystalline species and active surfaces, not easily produced by other processes;
- Convenient shaping of particles using low temperature casting methods.

Tredici et al. (2012) synthesised nano zirconia powders via hydrolysis of alkoxides and solvothermal processes. They concluded that the powders produced via alkoxide hydrolysis showed only marginal improvements over the Pechini sol-gel method. The solvo-thermal process produced much better results. However, both structural and microstructural properties of the nano-powder were strongly affected by the solvent. Crystallite size, degree of agglomeration and the amount of tetragonal phase in the starting product play an important role to determine the quality of the sintered material. Agglomeration has a large influence on the final density but also assists in retaining the tetragonal phase during sintering. Fluffy powders are ideal for the production of uniform high density sintered samples but show a tendency towards the transition to the monoclinic phase as the crystallite size increases during the sintering cycle, whereas aggregated powders showed a retention of the tetragonal phase. They produced almost full density (r.d. 97%) samples of undoped size-stabilised zirconia with a sintering cycle of 5 minutes under uniaxial pressure of 700 MPa at temperatures as low as 900 °C. The zirconia had a crystallite size of 31 nm and a 94% purity in tetragonal phase and was thermally stable up to 900 °C.

Xu & Wang (2009) claimed to control the crystallite size in a very narrow range below 10 nm by precipitating zirconium oleate form ZOC solutions. The zirconium oleate was dissolved in oleic acid and oleylamine for 2 to 4 days in an autoclave at 200 °C. By controlling the reaction time in the autoclave, they could control the size of the zirconia crystallites. Unfortunately, there is no mention of any heat treatment of the crystals after precipitation and washing. Their results can therefore not be compared with those of other researchers because the effect of crystallite growth with increased temperatures was not investigated at all.

Sol-gel precipitation using citric acid and acrylamide was investigated by Vivekanandhan et al. (2007). They observed the tetragonal phase crystallisation peak at 575 °C. XRD identified a 50/50 ratio between tetragonal and monoclinic phases after decomposition at 600 °C. TEM analysis confirms agglomerates of <1 µm and primary ZrO_2 particles of between 10 nm and 20 nm. They prepared this ZrO_2 as precursor for dental and other biomedical applications. No mention was made regarding sintering density and bending strength.

Judes & Kamaraj (2008) used sol-gel precipitation to produce mini-spheres of ceria-stabilised zirconia. Oxalic acid was added to a ZOC solution with 13–15 mol% cerium nitrate as stabilising agent. The optimum sintering temperature for the production of a fully tetragonal phase sol-gel-derived ceria-stabilised zirconia mini-sphere was 1 500 °C.

Mini-spheres were also produced by Judes & Kamaraj (2009) via the sol-gel method. They produced a sol of ZOC, yttrium nitrate and oxalic acid with 35% polyvinyl alcohol (PVA) added to obtain the required viscosity and fluidity. The sol was dropped into a concentrated ammonia solution, and the droplets dried and sintered at temperatures up to 1500 °C. The sintered density and porosity of the produced spheres are reported in Table II.

The SOFC specifications of > 6,05 g/cm^{-3} sintered density could not be achieved by this method. A mixture of monoclinic and tetragonal phase was observed from 900 °C to 1 500 °C. Transformation toughening is directly related to the tetragonal phase, and such material should be 100% in the tetragonal phase. The authors concluded that the decrease in tetragonal phase with increased sintering temperature may indicate the sluggishness of yttria migration into the zirconia crystal structure. The tetragonal phase in the spheres is metastable and it might be due to compressive stress developed during sintering. When the tetragonal phase reverts back to the

Table II: Sol-gel sintered densities (Judes & Kamaraj 2008)

Temperature (°C)	Porosity (%)	Sintered density (g/cm^{-3})	% of theoretical density	Average crystallite size (nm)
300	67,62	n/a	n/a	n/a
500	51,35	5,01	82,13	9,87
700	33,63	5,72	93,77	17,32
900	20,36	5,89	96,56	24,17
1100	15,48	5,85	95,90	30,19
1300	2,81	5,82	95,41	49,62
1500	~0,0	5,81	95,25	54,32

monoclinic phase, the transformation results in micro-cracking, visible in the SEM photos.

A study on the effect of aging of the produced gel was done by Gavrilov & Zenkovets (2000). They precipitated ZOC with ammonia at pH 4 and pH 8 and allowed aging of both precipitates, then compared them in terms of density, surface area, micropore volume and porosity. The gel precipitated at pH 8, aged for 25 hours, gave the highest density and surface area. The relationship between these parameters was discussed and compared with a gel precipitated at pH 4.

Different methods have been proposed to produce pure monoclinic zirconia. The aqueous gelation or sol-gel route using an alkoxide of zirconium is one of the best processes to produce zirconia nano-particles (Ayral et al. 1990). George & Seena (2011) used the route to produce a gel with ZOC and sodium acetate. They observed two endothermic peaks at 110 °C and 406 °C. The first is due to the loss in adsorbed water and the latter due to dehydration of the gel. There is an overlap with the exothermic phase transformation peak between 349 °C and 460 °C. XRD studies identified only a tetragonal phase transformation at this temperature, while Raman spectroscopy identified minor monoclinic phase ZrO_2 as well. TEM analysis, however, identified cylindrically shaped nano-particles with sizes less than 25 nm.

Nano-sized zirconia powders can also be produced by other methods like mechanical milling, sol-gel precipitation, direct precipitation and vapour phase deposition processes (Ryu et al. 2010).

Other methods

Rubio et al. (2009) produced nano-sized sulfated zirconia from ammonium zirconium carbonate (AZC) solutions. Ammonia was allowed to evaporate from the AZC solution. After a week, a transparent monolith was obtained. H_2SO_4 was added at specific concentrations and the precipitate filtered and calcined at 600 °C for an hour. According to light scattering analysis, the resulting zirconia monolith had an average crystallite size of 4 nm. Sulfation produced agglomeration of the original nano-particles. Annealing of the zirconia at 600 °C showed that the tetragonal phase was stable, with no conversion to the monoclinic phase.

Ryu et al. (2010) used an argon plasma to produce nano-sized zirconia and yttria-stabilised zirconia using zirconium carbonate as precursor. The zirconium and yttrium carbonate precursors were milled to a size distribution of < 10 µm and dried at 60 °C. A mixture of monoclinic and tetragonal phased zirconia could be produced, but a decrease in tetragonal phase was observed when the plasma power was increased from 7 kW to 34 kW. The phase mixture was attributed to the fast quenching rate in the plasma reactor. Little cooling time is available to go from the cubic phase to the monoclinic phase, thus suppressing the compositional adjustment required for the formation of the monoclinic phase. Therefore, the higher the quenching rate, the lower the monoclinic phase. An increase in particle size was also observed with increase in plasma power.

Increasing the plasma gas flow was similar to increasing the plasma torch power in producing metastable zirconia, and can also be explained by the quench rate of the product. However, huge yield losses were experienced, with a recovery of only 30%. The calculated mol% yttria originally added was also not achieved during yttria stabilised zirconia production. A pure tetragonal phase was observed at 3,8 mol% yttria, while a mixture of tetragonal and cubic phases was observed at 7,7 mol% yttria. The average crystallite size was 27 nm, with a range of 10–50 nm. The authors concluded that the process has the potential for preparing nano-sized zirconia, but needs to be optimized with additional research.

Chiang identified various important factors that nano-zirconia must adhere to for opticsspecific applications. These properties are

- **Index of refraction**: The increase in refraction index is determined by the crystallinity and the zirconia nano-particle loading.
- **Viscosity**: Addition of nano-particles to an organic resin always increases the viscosity until it becomes an unworkable gel. The maximum loading capacity before gel formation depends on the aspect ratio of the particles and the association among them.
- **Transparency**: Optical transmittance of nano-zirconia composite is a function of the size of the primary particles and the degree of association among them.
- **Dispersibility:** The surface properties of nano-zirconia determine the dispersibility. The native surface of zirconia is hydrophilic and must be modified with suitable ligands to facilitate the dispersion in most organic resins (Shiaw-Tseh Chiang 2015a).

Chiang described various patented processes to prepare nano- or colloidal zirconia. He divided the different processes into four categories, namely:

- **Organic free acidic systems**: The main process employed is the forced hydrolysis of aqueous ZOC solutions.
- **Acidic aqueous systems involving organics**: Addition of chelating agents as in sol-gel precipitation. An alternative is to use an organic salt, or metal-organic compound like zirconium acetate, to produce colloidal zirconia.
- **Organic free alkaline systems**: Hydrous zirconia is prepared by precipitation with NaOH or KOH at high pH. The slurry is converted to finely divided zirconia by boiling at high temperatures.
- **Alkaline systems involving organics**: Organic compounds like alkanolamines and a carbonate salt of tetraalkyl ammonium, were used at high pH and boiling temperatures (Shiaw-Tseh Chiang 2015a).

Shiaw-Tseh Chiang (2015b) described the hydrolysis of various alkoxides, or the so-called solvo-thermal processes, together with the advantages and disadvantages of each process, of the oxide phase formed and preparation processes.

The use of zirconia as a catalyst, or as a support, is only effective when it has a large surface area and remains stable under processing conditions.

Co-doping yttria-stabilised zirconia with rare earth oxides can reduce the thermal conductivity by as much as 30%. Numerous studies on stabilised zirconia were done, mostly concentrating on the final material properties. Phase transformation studies were mainly done on the more common rare earth oxides like yttria and ceria or the alkaline earth oxides of calcium and magnesium.

Wang et al. (2007) did a comprehensive experimental and computational phase study of the system $ZrO_2 – REO_{1,5}$ (RE = La, Nd, Sm, Gd, Dy and Yb). They realised that the solubility of $REO_{1,5}$ increases as the ionic radius of RE decreases, and an approximate linear relationship can be found for solubility versus ionic radius.

Berry et al. (1999) investigated the influence of pH on the reaction mixture during zirconia production from zirconium acetate solutions. They concluded that the addition of ammonium hydroxide stabilises the tetragonal phase against conversion to the monoclinic polymorph at temperatures up to about 900 °C.

Guo & Chen (2005) produced an oxy- (or oxy-hydroxy-) acetate, by refluxing ZOC in an excess of acetic acid. Two exothermic peaks were detected with DTA analysis. The peaks at 396 °C and 545 °C can be ascribed to the decomposition of the organic complex to give rise to a mixture of cubic and tetragonal phase zirconia. At 710 °C, the produced zirconia was 61% monoclinic, 27% cubic and 12% in the tetragonal phase. The increase in decomposition temperature had a huge influence on the crystallite size as shown in Table III.

It is known that small crystallite sizes favour a tetragonal crystalline structure. With the addition of a base, hydroxyl ions are introduced in the amorphous material, which stabilises the tetragonal phase against conversion to the monoclinic polymorph (Guo & Chen 2004).

High-power ultrasound was used by Yapryntsev et al. (2012) to produce nano-crystalline zirconia. Thermogravimetric analysis (TGA) revealed huge differences between treated and untreated samples. The difference in TGA mass losses were attributed to fewer impurities adsorbed by the treated hydrous zirconia, compared to untreated samples. Xerogels, prepared at acid pH, were almost 100% tetragonal phase up to 600 °C, whereas the reference samples were mesomorphous, with about 90% tetragonal phase up to 600 °C.

Ultrasound also produced zirconia with a much larger specific surface area than the control samples at low temperatures, specifically by hydrolysis under acidic conditions. When the hydrolysis temperature was increased, the control and ultrasonic samples had similar specific surface areas from about 600 °C. It is believed that polymerisation leads to the formation of OH bridge pairs in the plane of the zirconium atoms. Acid hydrolysis normally has a higher condensation rate so that the surfaces that are formed typically have a linear structure. With increasing pH, the polycondensation rate increases relative to the hydrolysis rate. Therefore, hydrous zirconia synthesised under alkaline conditions has a branched structure with a large specific surface area.

Ultrasound treatment causes a considerable increase in specific surface area and is related to the distinctive features of gel structure formation. Under active cavitation conditions, intense local liquid microflows and shock waves lead to the formation of a gel with a looser structure and a large specific surface area. Ultrasound treatment allows precipitation of hydrous zirconia with a large surface area under acid conditions, in contrast with other techniques (Yapryntsev et al. 2012).

Table III: Crystallite size and zirconia crystal phase produced on the decomposition of zirconium oxy-hydroxy-acetate (Guo & Chen 2005)

Temperature (°C)	Crystallite size (nm)	Monoclinic phase (%)	Tetragonal phase (%)	Cubic phase (%)
396	24,3	0	34	66
545	30,4	7	41	52
710	113,1	61	12	27

From the above literature it can be seen that numerous factors can play a role in producing a pure monoclinic or tetragonal zirconia. The feed material, precipitation procedure, pH conditions and process as well as the decomposition process determine the phase and stability of the produced zirconia phase.

Zirconium-based chemicals

Figure 10 gives a schematic overview of the production routes towards the various zirconium chemicals.

Zirconium oxychloride octahydrate ($ZrOCl_2·8H_2O$)(ZOC)

The solubility of zirconyl chloride octahydrate (ZOC) is 690 g/L at 90 °C in concentrated HCl and decreases to 8 g/L at 40 °C (Abdelkader and Daher, 2008). If contaminated zirconyl chloride crystals are dissolved at high temperature in HCl, pure crystals will precipitate once the solution is allowed to cool to room temperature. The solubility of zirconyl chloride octahydrate in water is 1 700 g/L at 20 °C. A solution of ZOC crystals in water can be used to precipitate various other zirconium chemicals (Lubbe et al., 2012).

Chou & Chou (1988) studied the solubility of ZOC in HCl. The solubility reaches a minimum value in 25% HCl. See Figure 9.

When ZOC is crystallised from supersaturated solutions, it always precipitates as needle-like crystals. The induction period for crystallisation is caused by the growth of critical nuclei to a visually detectable size and with the formation of surface nuclei as the controlling step.

Clearfield & Vaughan (1956) and Mak (1968) concluded that the zirconyl species is a complex tetramer, $[Zr_4(OH)_8·16H_2O]^{8+}$ in which the zirconium atoms are arranged in a square and are linked along each edge of the square by pairs of OH groups. There are four additional water molecules bound to each Zr atom in such a way as to produce a distorted square antiprism. The remaining water molecules and the chloride ions form a matrix that holds the zirconyl complex together. The average Zr–O distance is 2,24 Å and the average of all the radii is 2,20 Å.

Henderson & Higbie (1954) worked on increasing the overall precipitation yield by adding acetone to a saturated ZOC solution. The acetone reduces the solubility of the oxychloride in hydrochloric acid, thereby increasing the precipitation yield. They found that the optimum ratio for satisfactory recrystallisation appears to be 1 mL of a saturated zirconyl chloride solution, 5 mL acetone and 1 mL concentrated HCl. ZOC recoveries of 96–99% were obtained.

Castor & Basolo (1953) dried acetone-washed ZOC over magnesium perchlorate and sodium hydroxide, and thereby identified hydrates with 8, 7,75, 7,5, 7,25, 7, 6,5, and 6 moles of water.

Biswas et al. (2012) precipitated ZOC after seeding the solution and leaving it to precipitate overnight. The crystals were filtered,

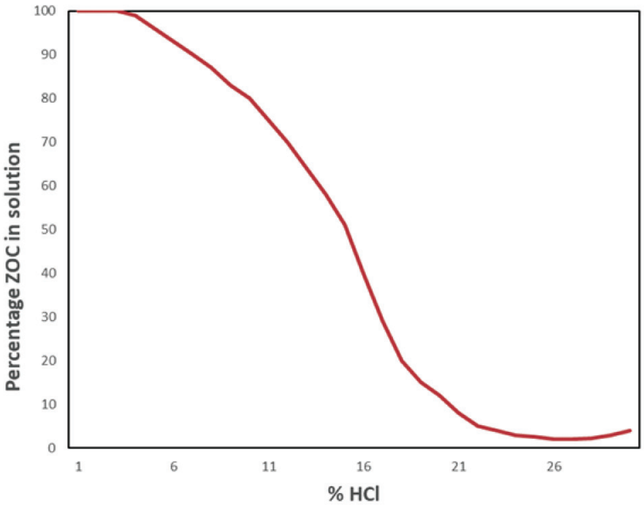


Figure 9: Solubility of ZOC in aqueous HCl (Chou & Chou 1988)

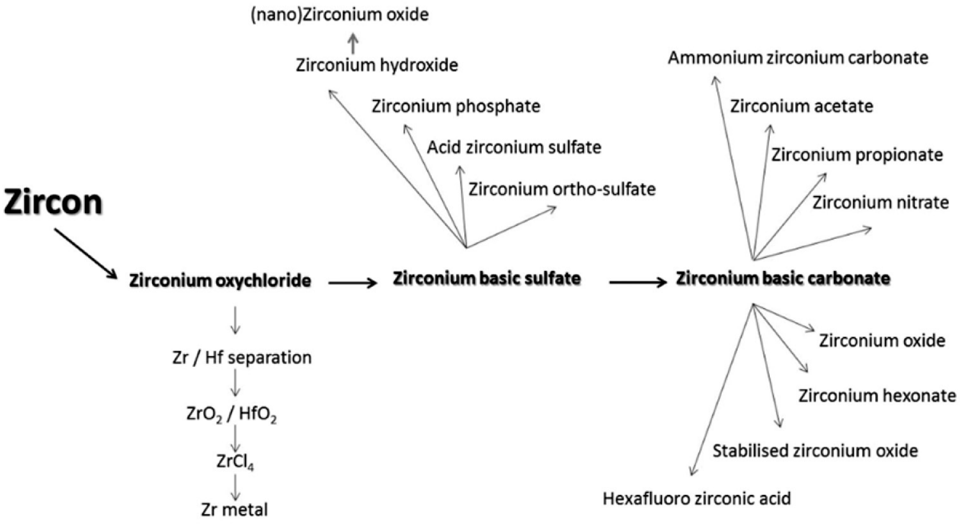


Figure 8: Zirconium chemicals production routes

washed with ethanol and dried at ambient conditions for an 85% recovery yield. The product was identified by TGA as hexahydrated zirconyl chloride. The observed 38% mass loss up to 400 °C was assigned to the removal of six molecules of water of crystallisation. The remainder of the 57% total mass loss observed up to 700 °C was ascribed to the substitution of Cl_2 by oxygen to form ZrO_2.

Beden et al. (1969) and Beden & Guillaume (1970) decomposed ZOC isothermally at low temperatures to confirm the decomposition to ZrO_2. According to their results, water is lost up to 90 °C to produce an anhydrous salt. They predicted the decomposition to ZrO_2 to be complete at about 450 °C.

$$ZrOCl_2{\cdot}4H_2O \rightarrow ZrO(OH)Cl_2{\cdot}H_2O \rightarrow Zr_2O_3Cl_2{\cdot}H_2O \rightarrow ZrO_2 \quad (7)$$

There appears to be a discrepancy regarding the decomposition temperatures of ZOC to zirconia. Barraud et al. (2006) suggest that it may be related to the uncertainties about the hydration state of the starting compound being investigated and quoted the following decomposition reactions:

80 °C tot 190 °C: $ZrCl_4 + 2H_2O \rightarrow Zr(OH)_2Cl_2 + 2HCl$ (8)

190 °C tot 220 °C: $Zr(OH)_2Cl \rightarrow ZrOCl_2 + H_2O$ (9)

220 °C tot 325 °C: $2ZrOCl_2 + ½O_2 \rightarrow Zr_2O_3Cl_2 + Cl_2$ (10)

325 °C tot 750 °C: $Zr_2O_3Cl_2 + ½O_2 \rightarrow 2ZrO_2 + Cl_2$ (11)

Atherton & Sutcliffe (1988) repeated the work by using azeotropic dehydration with toluene, benzene, hexane and pentane as solvents. Dehydration with pentane at 37 °C resulted in the loss of some interstitial water. Using hexane at 62 °C, a further loss of water was observed but some interstitial water still remained. At this temperature the first chloride loss was also observed. Dehydration with benzene at 80 °C brought about the most significant changes. The tetramer starts to ionise with the loss of protons from co-ordinated water molecules. The formation of oxo linkages follows and a polymeric structure is formed. The degree of polymerisation ultimately depends on the number of chloride ions eliminated. With dehydration at 110 °C, dehydrochlorination and olation are further extended and extensive polymerisation is expected.

The results of Powers & Gray (1973) did not agree with previously reported thermal dehydration of zirconyl chloride and proposed that dehydration basically proceeds in four steps:

- The first and second, at 46 °C and 77 °C, involve the loss of 2 equivalents of water respectively.
- The third step, at 117 °C, involves the loss of 2 equivalents of water plus 1 equivalent of hydrogen chloride. After the third step a period of slow hydrogen chloride and water loss follows, but no stoichiometric phases could be detected. They concluded that above 150 °C, most of the structural features of the feed ZOC are lost and the product can therefore be formulated as ZrO_2 contaminated with chloride and water. The sharp weight loss at 500 °C seems to be primarily attributable to halide removal.
- The fourth step at 650 °C is assigned to the dehydration to ZrO_2, with no further weight loss at higher temperatures.

Inoue et al. (1975) did their decomposition experiments in and electrical furnace. They started with $ZrOCl_2{\cdot}6.3H_2O$ and recorded a 53,25% weight loss up to 300 °C, 57,27% at 400 °C, 57,44% at 500 °C and 57,57% at 600 °C. With increasing decomposition temperatures, the physical properties like pore size distribution shift in the direction of much coarser pores. This data is also compared to the decomposition of $ZrO(NO_3)_2{\cdot}2.4H_2O$ under the same experimental conditions. The mean crystallite size increased from about 15 nm at 400 °C to about 24 nm at 800 °C. The highest sintered density achieved for ZOC at 1 600 °C was 5,34 g/cm^3, which corresponds to approximately 92% of the theoretical density.

It is evident that there is no clear correlation between different researchers regarding the decomposition route of zirconyl chloride to zirconia. Current instrumentation has better resolution and detection limits and the decomposition should be revisited to confirm the mechanism.

Zirconium basic sulphate (ZBS) and zirconium acid sulphate tetrahydrate (AZST)

Zirconium basic sulphate (ZBS) is precipitated from ZOC as a precursor. ZBS is then used to produce zirconium acid sulphate tetrahydrate (AZST) or zirconium basic carbonate (ZBC). Different grades of ZBS can be precipitated by varying the ZrO_2:H_2SO_4 molar ratio. The optimum ratios are between 1:0,45 and 1:0,85. These variations also lead to different particle size distributions as well as crystallite sizes. With tight control over conditions like heating rate of precipitation, sulphate molar ratio and starting pH, the crystallite and particle size distribution of the ZBS product can be controlled within a narrow range. Particle size distribution is important in industrial applications for the production of different zirconium chemicals with ZBS as feed. Crystallite size has a huge influence if ZBS is used to produce zirconia via decomposition at high temperature (calcination) for niche market applications.

Zirconium sulphate can be classified as anionic, neutral or basic (amphoteric). Neutral compounds have a Zr:SO_4 molar ratio of exactly 1:2, while the basic salts are deficient in SO_4^{2-}, with the balance made up by the presence of OH groups. Anionic complexes contain more than two sulphate ions per zirconium ion (Squattrito et al. 1987). The three basic structures can be written as:

- $Zr_n(OH)_{2n+2}(SO_4)_{n-1}$ (n > 1)
- $Zr_n(OH)_{2n}(SO_4)_n$ (n = 2)
- $Zr_n(OH)_{2n-2}(SO_4)_{n+1}$ (n > 2)

Dirksen (1992) investigated the precipitation of ZBS by monitoring nine crucial parameters during the precipitation step. He concluded that small processing changes cause diverse changes in the precipitated product. He listed the most important points to be controlled during ZBS precipitation as:

- A constant reaction pH;
- A change in pH gives an increase in specific surface area;
- Solubility decreases with increased precipitation temperature, i.e. increasing the zirconium yield;
- Increased reaction temperature yields larger aggregates with fast filtration rates;
- Reaction yield can be maximised by precipitating at high temperature and adding concentrated ammonia to the solution;
- A reaction pH >1,5 ensures a $Zr:SO_4$ molar ratio > 2,3. It also controls the amount of impurity rejections during precipitation;
- Increase in mixing speed increases the average particle size distribution, together with a decrease in specific surface area;
- Reactor design should prevent concentration gradients inside the reactor, thereby preventing changes in product particle size;
- Shear aggregation is the dominant growth mechanism for particles over 1 µm.

Strydom & Pretorius (1993) studied the thermal decomposition of zirconium sulphate tetrahydrate (AZST) to ZrO_2 and determined the energy required for the decomposition reaction. They analysed the starting compound to be $Zr(SO_4)_2{\cdot}5.5H_2O$ instead of $Zr(SO_4)_2{\cdot}4H_2O$. They concluded that the material is hygroscopic and that water was absorbed during handling of the sample, probably due to an excess of sulphuric acid present. However, the $Zr:SO_4$ molar ratio was not analysed to determine if any free H_2SO_4 was present to assist with water absorption. Total energy of 2 505 Jg^{-1} is needed to obtain monoclinic ZrO_2 above 900 °C and 2 306 Jg^{-1} to obtain tetragonal ZrO_2. Tetragonal ZrO_2 is obtained during low temperature decomposition and converts to monoclinic ZrO_2 at temperatures above 900 °C.

Solutions containing Zr^{4+} and SO_4^{2-} consist of a multiplicity of different species, rather than a single preferred structure. Such solutions almost never reach precipitation equilibrium upon standing. Small changes in conductivity and/or solids being precipitated have been observed over long periods of time (Squattrito et al. 1987). Squattrito et al. (1987) determined the crystal structure of ZBS with high Zr:sulphate molar ratios by means of an X-ray crystallographic study. They precipitated $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6}{\cdot}33H_2O$ and compared the structure to other known structures. Empirically the formula can also be written as $ZrO_2{\cdot}0.7SO_3{\cdot}3.1H_2O$. They formulated a set of rules to explain the crystal structure of various basic zirconium sulphate ratios:

- Sulphate ions prefer to bridge across zirconium atoms in conditions where neutral and basic sulphate structures form, i.e. the molar ratio is less than 1;
- At high acidity and sulphate concentrations, the sulphate ion may precipitate as bidentate chelates;
- The preferred zirconium coordination numbers in the solid phase are 7 and 8;
- Monodentate or non-bridged sulphate ions represent unstable situations, and will further polymerise by bridging or displacement of hydroxyl groups;
- Non-bridged hydroxyl groups are also unstable and will be displaced by water or sulphate, or may even precipitate in further olation with other hydroxyl-containing fragments;
- Two hydroxyl groups displace one sulphate group, followed by olation;
- Oxolation takes place between olated chains by splitting out water to produce an oxygen atom coordinated by four zirconium atoms.

Matijevic et al. (1969) determined the solubility boundaries of zirconium sulphate as a function of pH by adding solutions of lithium, potassium and magnesium sulphate at different concentrations to solutions of zirconium nitrate, rather than adding sulphuric acid to a zirconium salt. Their results are summarised in various solubility diagrams that will not be discussed in this review.

Nielsen & Govro (1956) developed a method very similar to that of Dirksen to precipitate ZBS from ZOC at a molar ratio of 1 Zr:0.4 SO_4^{2-}. The solution is heated to 90 °C, diluted with hot water and the pH adjusted with ammonia, upon which ZBS immediately precipitates. They claimed a 99% recovery rate using this process. Sufficiently pure zirconium oxide was produced with negligible loss of zirconium.

Chatterjee et al. (1989) decomposed ZBS at high temperature to produce zirconia. They precipitated ZBS at various zirconium to sulphate molar ratios for their study. They observed the loss of water below 600 °C and the decomposition of sulphate groups around 780 °C. Depending on the different zirconium to sulphate molar ratios, after decomposition at 1100 °C, the particle size distribution of the zirconia varied between 60 nm and 0,3 µm, based on TEM analysis. The ZrO_2 was dominantly monoclinic, irrespective of the ratio or precipitation conditions.

Ahmen et al. (1999) synthesised various zirconium sulphates, hydroxide sulphates and oxide sulphates. ZrO_2 was dissolved in sulphuric acid with varying concentrations between 50% and 97%. The resulting precipitates were identified as $\alpha\text{-}Zr(SO_4)_2$, $Zr(SO_4)_2{\cdot}7H_2O$ and $Zr(SO_4)_2{\cdot}4H_2O$. Upon partial thermal decomposition the corresponding oxide sulphates were obtained as intermediates. TGA and DTA analyses were performed on all products and the results are discussed in detail.

Zirconium basic carbonate (ZBC)

Zirconium basic carbonate (ZBC) is normally produced from zirconium basic sulphate and is an important feed material for the production of other zirconium chemicals. It is soluble in a variety of organic acids to produce the associated zirconium compound. During such reactions, the carbonate is decomposed, with the advantage that the organo-metallic product is not contaminated with additional anions like chlorides of sulphates. Most common industrial applications of zirconium basic carbonate are in antiperspirants, catalysts, zirconia and as feed material to produce additional zirconium chemicals.

Zirconium, like in the case of zirconium sulphate, forms a variety of carbonate complexes. When the $Zr:CO_3^{2-}$ molar ratio is 1:<0,8, the product is an amorphous solid readily soluble in acid. Once the ratio is increased to 1:>1, the zirconium carbonate starts to dissolve in its own absorbed water to a clear zirconium carbonate solution. The dissolution reaction is slow at ratios close to 1, but increases at higher ratios. Industrially, the most common zirconium carbonate solution is known as ammonium zirconium carbonate (AZC), with applications mainly in the paper industry. The viscosity of the product solution can be manipulated by varying the carbonate molar ratio in solution. The solution has a shelf life of about 1 year, after which the viscosity starts to increase with time. Limited literature is available on the polymerisation process during this increase in viscosity.

In the event that a ZOC solution is treated directly with a carbonate containing material such as sodium carbonate, a gelatinous precipitate is formed which is essentially non-filterable (Bell 1970). Pokhodenko & Tselik (1976) and Fenner (1981) patented processes to produce a readily filterable zirconium carbonate from ZOC solutions. The processes entailed the precipitation of ZBS from ZOC by addition of sulphuric acid at the boiling point. The zirconium basic sulphate is reslurried in water and a suitable carbonate reagent is added at 80 ºC. The amorphous carbonated zirconium hydrate particles prepared this way retain the original shape of the zirconium sulphate particle. A slightly modified process is used industrially to precipitate zirconium basic carbonate.

Pokhodenko et al. (1972) also produced ZBC from the ZBS, but washed the product with alcohol and dried it in air. After analysis of the various species, they concluded that the formula was $Zr_2O(OH)_4CO_3{\cdot}nH_2O$. They realised that the weight loss during heating decreases with ageing of the product and identified the different compounds on drying and ageing as:

- Fresh → $Zr_2O(OH)_4CO_3{\cdot}mH_2O$
- After 24 hours → $Zr_2O(OH)_4CO_3{\cdot}nH_2O$
- After 1 week → $Zr_2O_x(OH)_{6-2x}CO_3{\cdot}pH_2O$
- After 1 year → $Zr_2O_{2.5}(OH)CO_3{\cdot}qH_2O$

Decomposition during heat treatment of the air-dried product is described as:

- Fresh → $Zr_2(OH)_4CO_3{\cdot}nH_2O$
- 60 ºC – 170 ºC → ≈ $Zr_2O_x(OH)_{6-2x}$
- 300 ºC – 500 ºC → ≈ ZrO_2 (amorphous)
- >500 ºC → ZrO_2 (crystal)

The carbonate is decomposed at low temperature to an amorphous zirconium hydroxide and converts to zirconia at about 500 °C.

Kerina et al. (1984) did a well-planned follow-up study on Fenner's work on the formation of zirconium basic carbonate from zirconium basic sulphate. It was concluded that an excess of about 30% carbonate is needed to ensure complete removal of sulphate ions during conversion to zirconium carbonate. The excess carbonate does not react with the product and can be removed by washing. The molar ratio of carbonate in the final zirconium carbonate is equal to the molar ratio of sulphate used to precipitate the original ZBS feed.

Gimblett et al. (1988) decomposed different zirconium salts in a TGA and observed a sequence of ligand removals with increasing temperatures. The sequence is reported as: 'loosely bound' $H_2O > CO_3^{2-} \sim C_2O_4^{2-} > NO_3^- > OH^-$ or 'tightly bound $H_2O > SO_4^{2-}$. In general, the ligand removal led to the generation of cubic zirconia, which converts to monoclinic zirconia at ca. 1 000 ºC.

Ammonium zirconium carbonate (AZC) and potassium zirconium carbonate (KZC)

AZC is used commercially whenever a soluble zirconium solution in an alkaline environment is required. The solutions are prepared at ambient temperature by dissolving zirconium basic carbonate in a solution containing ammonium carbonate or a mixture of ammonium bicarbonate and ammonium hydroxide (Phillips 1977; Phillips 1978). The main application for AZC is as an insolubiliser for the starch binders in paper coating formulations. ZBC with a $Zr:CO_3^{2-}$ molar ratio of about 1:0,5 is used as the feed material. This ratio is increased to 2:1 with ammonium or potassium carbonate.

The shelf life of AZC is very dependent on the zirconium to carbonate molar ratio. Attempts were made to prepare a "dry" AZC powder but have been unsuccessful to date.

Potassium zirconium carbonate (KZC) is produced by dissolving ZBC in potassium carbonate at room temperature. KZC, compared to AZC, can be spray dried without any degradation of effectivity. The KZC powder can be dissolved in water when required.

Zirconium metal and alloys

The processing of zircon to nuclear grade zirconium sponge

All zircon concentrates contain hafnium in a ratio of roughly 50:1. The hafnium is present in the solid-state crystal structure of the zircon. The chemical properties of zirconium and hafnium are almost identical. In spite of their large difference in atomic mass, the phenomenon of lanthanide contraction makes their atomic radii almost identical, resulting in hafnium being easily accommodated in the crystal structure of all zirconium compounds.

The full process for nuclear grade zirconium sponge generally starts with the carbo-chlorination of milled zircon at temperatures in excess of 1 000 °C. This is usually done in a fluidised bed reactor under an inert gas atmosphere. The reaction is presented in Equation 15. The presence of hafnium is indicated in parentheses.

$$Zr_{1-x}(Hf)_xSiO_4(s) + 4C(s) + 4Cl_2(g) \rightarrow Zr_{1-x}(Hf)_xCl_4(s) + SiCl_4(l/g) + 4CO(g) \qquad (15)$$

The $Zr_{1-x}(Hf)_xCl_4$ and $SiCl_4$ are separated by means of fractional distillation and selective condensation – $Zr_{1-x}(Hf)_xCl_4$ having a boiling point of 123 °C and $SiCl_4$ a boiling point of 56 °C. The $SiCl_4$ is a by-product that can be purified further by multiple distillation steps to be used as precursor for producing optical, electronic or epitaxial grade $SiCl_4$.

It can also be used as a feed material to manufacture amorphous or fumed silica in a plasma or flame reactor, as presented in Equation 16.

$$SiCl_4(l) + 2H_2O\,(l) \rightarrow SiO_2(s) + 4HCl(g) \qquad (16)$$

Fumed silica is a high value product with various applications. At Necsa in South Africa, fumed silica was produced from $SiCl_4$ in a pilot scale plasma system according to Equation 17. Using oxygen rather than water allowed the recovery of chlorine as $Cl_2(g)$, rather than the more stable HCl(g). The Cl_2 is recycled back to the initial carbochlorination step, thereby improving the over-all economics.

$$SiCl_4(l) + O_2 \rightarrow SiO_2(s) + Cl_2(g)\uparrow \qquad (17)$$

$SiCl_4$, as by-product, is considered a waste stream in the nuclear industry and it is sold to the silicon industry. The alternative is to not use zircon as starting material at all, but rather purchase chemically pure zirconia (ZrO_2) for the carbo-chlorination step according to Equation 18. It is more expensive due to the increase in raw material cost, but involves fewer production steps.

$$Zr_{1-x}(Hf)_xO_2(s) + 2C + 2Cl_2(g) \rightarrow Zr(Hf)Cl_4(s) + 2CO(g)\uparrow \qquad (18)$$

The $Zr_{1-x}(Hf)_xCl_4(s)$ is converted to zirconyl oxychloride (ZOC) via hydrolysis in water as presented in Equation 19. It is a violent exothermic reaction and extremely dangerous if not well controlled. Careful control of the reaction parameters like pH, temperature, *etc.* is required in order to prevent the precipitation of $Zr_{1-x}(Hf)_x(OH)_4$.

$$Zr_{1-x}(Hf)_xCl_4(s) + 9H_2O \rightarrow Zr_{1-x}(Hf)_xOCl_2(s).8H_2O + 2HCl(aq) \qquad (19)$$

During the precipitation of zirconyl oxychloride octahydrate (ZOC), almost all the impurities stay in solution due to the high acid concentration. The precipitated ZOC is washed and filtered. It can be re-crystallised in HCl to improve the purity. ZOC is used as feed chemical for Zr and Hf separation. For normal industrial applications of zirconium metal, the presence of Hf has no detrimental effect. However, for nuclear applications, it is essential to remove the Hf due to its high neutron absorption cross section.

Table IV represents the ASTM B349 specification for nuclear grade zirconium metal (B349/B349M-03) and Table III the absorption cross section for thermal neutrons in measured in barns (10^{24} cm^2) (see Table V) (Schemel 1977). From Tables II and III it can be seen that the elements that exhibit a high absorption cross section for thermal neutrons have very stringent specifications in terms of maximum allowable concentration (e.g. B <0,00005 wt%, Cd <0,00005 wt% and Hf <0,01wt%). Although the ASTM specification for hafnium is <0,01 wt%, the current trend in the nuclear industry is to lower the hafnium concentration even further to <0,005 wt%. This is to improve the neutron economics of a nuclear reactor and to achieve longer burn-up times in nuclear reactors.

The separation of hafnium from zirconium is a difficult and complex procedure (Kok 2009; Miller 1957a; Poriel et al. 2006), due to the fact that zirconium and hafnium have very similar chemical properties. There are several separation processes described in the literature, a number of which are patented. The companies who mastered this technology usually keep it as a closely guarded secret.

Table IV: ASTM B350 specification for primary nuclear grade zirconium metal

Element	Maximum (% by mass)	mg/kg metal
Al	0,0075	75
B	0,00005	0,5
Cd	0,00005	0,5
C	0,027	270
Cr	0,020	200
Ce	0,002	20
Cu	0,005	50
Hf	0,010	100
Fe	0,1500	1500
H	0,0025	25
O	0,1400	1400
Mg	0,002	20
Mn	0,005	50
Mo	0,005	50
Ni	0,007	70
Si	0,012	120
Ti	0,005	50
W	0,01	100
	0,00035	3.5

Table V: The absorbance cross section of thermal neutron for some elements and compounds (Schemel 1977)

Material	Thermal neutron absorption cross section (barn)*
Magnesium	0,059
Lead	0,17
Zirconium	0,18
Zircaloy 4	0,22
Aluminium	0,23
Iron	2,56
Austenitic stainless steel	3,1
Nickel	4,5
Titanium	6,1
Hafnium	115
Boron	750
Cadmium	2 520
Gadolinium	48 890

*Barn: Unit of area for measuring the cross-sections of nuclei, 1 barn equals 10^{-24} cm^2.

The following processes are described in general: solvent extraction, selective precipitation, extractive distillation, sublimation, vacuum distillation and ion exchange. The most common solvent extraction chemicals are methyl isobutyl ketone (MIBK) and tributyl phosphate (TBP) processes. Solvent extraction starts with zirconium-hafnium oxychloride as a water-soluble feed material. Selective precipitation is based on the slight difference between the solubility of K_2ZrF_6 and K_2HfF_6 (Westhuizen 2010; Branken 2009).

Sublimation is based on the differences in sublimation temperature of $ZrCl_4/HfCl_4$ or ZrF_4/HfF_4. These separations involve several consecutive steps, until the specification of <100 mg kg^{-1} Hf is achieved.

The separation of Zr and Hf is considered to be the most expensive process step during the manufacture of nuclear grade zirconium metal. Research continues to find alternative separation techniques, or improving on existing ones. The solvent extraction procedure is notorious for producing high volumes of chemical waste.

Attempts are also being made for separation by means of differences in their respective coordination chemistries (Viljoen 2007; Steyn 2007).

After separation, the hafnium-enriched stream is used to manufacture hafnium metal, more or less in the same way that zirconium metal is manufactured. The price of hafnium metal is between US$3 000 and US$5 000 per kg, and is generally in low demand, probably due to the high selling price. However, hafnium metal and hafnium chemicals do find growing applications in advanced electronics, optical systems and the aero-space industry. Due to the relatively high neutron absorption coefficient for thermal neutrons, it is also used as control rods in nuclear reactors (MBM 2007; Keller et al. 1982; SMA 2011). The control rods in certain types of nuclear reactors are manufactured from dysprosium hafnate ($Dy_2O_3 \cdot HfO_2$).

The hafnium-free zirconium stream is precipitated with ammonia to form $Zr(OH)_4$ according to Equation 20. The precipitation conditions are carefully controlled due to possible polymerisation and gel formation, which can cause very slow filtration and washing of the precipitate. All remaining trace contaminants are removed during this step.

$$ZrOCl_2.8H_2O + NH_4OH \rightarrow Zr(OH)_4(s) + NH_4Cl(aq) \qquad (20)$$

After filtration, the $Zr(OH)_4$ is calcined at high temperature to ZrO_2 according to Equation 21.

$$Zr(OH)_4(s) \rightarrow ZrO_2 + H_2O(g)\uparrow \qquad (21)$$

This ultra-pure ZrO_2 is finally carbo-chlorinated to $ZrCl_4$ to be used as feed material for zirconium metal production via the Kroll process. $ZrCl_4$ is hygroscopic and must always be handled in an inert atmosphere. The presence of H and O is detrimental in the zirconium metal manufacturing process.

Nuclear grade zirconium sponge

The Kroll process, as developed by the US Bureau of Mines, is well known and has been used for more than 50 years, especially in the manufacturing of titanium and zirconium metal (Kroll et al. 1946; Miller 1957c). The Van Arkell-Boer process (Nielsen et al. 2001) is another metal reduction process. However, the Kroll process is still the preferred method on industrial scale. Magnesium is used as reductant, but calcium can also be used. The reaction is exothermic but needs activation energy to start and is usually conducted in batch reactors between 800 °C and 1 200 °C (Equation 22).

$$ZrCl_4(l) + 2Mg(s) \rightarrow Zr(s) + 2MgCl_2(s) \qquad (22)$$

The cooled, solid ingot still contains $MgCl_2$ as a by-product and can be removed by high temperature vacuum arc melting, or in an electron-beam furnace. During this process, the $MgCl_2$ is evaporated (boiling point =1 412 °C) leaving a pure zirconium metal with a spongelike structure, the so-called zirconium sponge. This primary zirconium metal, which now conforms to nuclear specifications in terms of purity, is used for the manufacturing of zirconium alloys.

All the above-mentioned processes are performed under inert atmosphere in order to avoid C, H and O contamination. Zirconium has a great affinity for oxygen and carbon (Blumental 1958). The presence of these elements has detrimental metallurgical effects on the final metal, especially in a nuclear reactor environment. The presence of hydrogen will cause hydrogen embrittlement, which is aggravated on exposure to radiation (Kok, 2009). Oxygen levels must be controlled between 500 and 2 000 mg kg^{-1}. When zirconium is exposed to air or water at ambient temperatures, a self-protecting zirconium oxide layer immediately forms on the surface. Zirconium carbide forms at the granular interfaces and has an effect on the mechanical strength of the zirconium component.

Manufacture of zirconium alloys

Pure, unalloyed zirconium metal does not have the metallurgical properties that are required in nuclear components. Under normal conditions, zirconium metal is chemically inert and corrosion resistant due to its stable protective oxide layer. However, under the harsh conditions in a nuclear reactor, where it is exposed to water temperatures between 300 °C and 400 °C, or even superheated steam (depending on the type of reactor), it is prone to oxidation. In general, a nuclear reactor is licensed to allow a maximum zirconium oxide layer of less than 100 µm.

Zirconium and its alloys display strong anisotropic behaviour. Consequently, alloying of zirconium includes the addition of alpha and beta stabiliser elements (Davis 2008). Under radiation conditions, the corrosion rate of zirconium increases exponentially with burn-up time in the nuclear reactor. In order to improve the corrosion resistance and its mechanical and metallurgical properties, the zirconium metal is alloyed. During the past few decades, several zirconium alloys have been developed in order to comply with stringent nuclear specifications. The most well-known zirconium alloy is the Zircaloy™ series, and the Zr-2.5Nb alloy.

Zircaloy™ 1 and 2 were developed to improve mechanical and metallurgical properties by adding Sn into the alloy. It was later discovered that Sn has a detrimental effect on the corrosion resistance of zirconium alloys at higher nuclear burn-up rates and Sn was replaced by Nb – addition of Nb improves the corrosion resistance properties of zirconium alloys. Many other manufacturers followed suit and there are currently numerous zirconium alloys available. Some of these trade names are Zirlo, Ziron, HIFI, Dx, E115, etc. It has to be borne in mind that different nuclear reactor types usually require different zirconium alloys. In general, a niobium content of between 0,8% and 1,2% is specified for nuclear cladding material, although some alloys have a niobium content of up to 2,5%. The manufacturers of zirconium alloys usually keep their final composition as proprietary information.

For the alloying process, the solid zirconium sponge ingot is crushed into 10–20 mm pieces. Recovered zirconium scrap is also added. The alloying elements are added, and the material is pressed and vacuum arc melted. The melting process is repeated three to four times to ensure complete homogeneity of the alloy. This produces an ingot of up to 6 m high and 400–500 mm in diameter, weighing several tonnes, from which zirconium alloy components for the nuclear industry are manufactured.

Summary

The block diagram in Figure 10 provides a broad overview of the processing steps between zircon and the various product end products. Several variations of these processes are described in the technical and patent literature. Industrially, each of the processes usually implies a discrete chemical plant, each with several intermediate steps or separate unit operations.

There are various well-developed processes for producing a range of zirconium compounds. These chemicals in turn may be used to produce monoclinic as well as stabilised zirconium oxides. In most of the processes reviewed, ZOC is used as feed. Hydrous zirconia may be precipitated under various conditions and decomposed to zirconia. It is evident from the literature that there is no single and simple process to produce nano-zirconia. Depending on conditions like pH, temperature, concentration and aging, mixtures of monoclinic and tetragonal zirconia are produced. However, it is evident that results can vary from laboratory to laboratory, depending on the processes used.

More than 85% of all zirconium metal produced is used as nuclear components and as nuclear fuel cladding material. In order to manufacture nuclear grade zirconium metal, several chemical steps and processes are required. The initial processing step here is usually carbochlorination. Separation of Zr and Hf is the most expensive and the most complex of the processes. In the alloying and manufacturing process, strict control over various parameters is required for compliance with metallurgical and mechanical specifications for use in a nuclear reactor environment.

Although South Africa is the second-largest producer of zircon in the world, almost no local beneficiation is done.

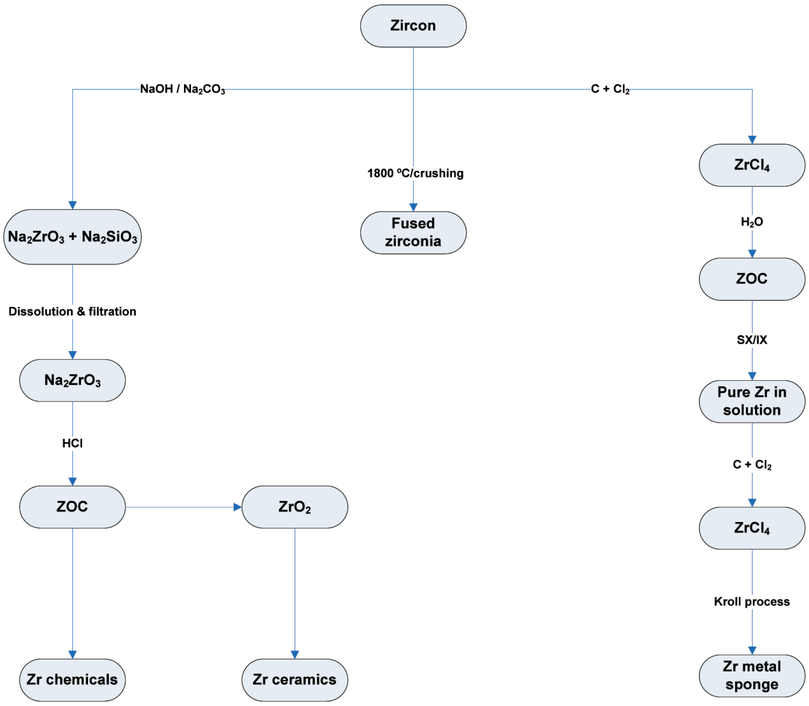


Figure 10: General processing steps for the beneficiation of zircon

Acknowledgements:

The authors thank Dr Johann Nel for technical inputs and Mr Nols Jansen for language editing.

Dates:

Received: 25/03/2023
Accepted: 27/06/2023
Published: 21/08/2023

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