CHAPTER 3

ZIRCONIUM APPLICATIONS

[Picture by: www.zrchem.com]

3.1 INTRODUCTION

Zirconium chemicals are used in diverse applications. Of all the zirconium consumed, about 95% is in the form of zircon, zirconia and zirconium chemicals; the remainder is consumed as the metal and its alloys [1]. The major consumer of zirconia is the refractory industry with approximately 15 000 metric tons per annum, for the year 1998 [1, 13-14]. It is estimated that the consumption of zircon for zirconia in the year 2 000 could be around 37-40 000 tons [13-14]. This chapter highlights only but a few of the uses of zircon, zirconia and zirconium chemicals, with emphasis on the most popular applications.

3.2 ZIRCON

Zircon is the mineral in which zirconium silicate $ZrSiO_4$ occurs in nature [2, 6]. Zirconium silicate exhibits some resistance towards acids and cold alkali solutions, but it is readily attacked by sodium hydroxide NaOH, at approximately 600°C and even more vigorously by sodium oxide Na_2O [2, 3]. Table 3.1 below supplies the physical properties of zircon necessary for its industrial applications.

TABLE 3.1: SELECTED PROPERTIES OF ZIRCON [18-19]

Property	Value
Range of found densities, g/cm^3	3.9-4.8
Melting point, °C	2250
Coefficient of linear expansion α, between 1250-1550°C	$35\text{-}42 \times 10^{-7}$
Thermal conductivity, W/mK	4.0-5.86
Hardness, Mohs	7.5
Refractive index (n_D^{20})	1.85
Decomposition temperature, °C	1676

3.3 ZIRCONIA

Zirconia is the oxide ZrO_2 that occurs in nature as the mineral baddeleyite. Zirconia usually exhibits three phases at different temperatures: monoclinic [m-ZrO_2; C_{2h}^5 ($P2_1/c$); Z=4] below 1 000°C, tetragonal [t-ZrO_2; D_{4h}^{15} ($P4_2/nmc$); Z=2] above 1 170°C and cubic [c-ZrO_2; O_h^5 (Fm3m); Z=4] above 2 370°C until its melting point at 2 700°C [2, 5, 17]. A fourth phase orthorhombic zirconia o-ZrO_2 has also been found, but is metastable under atmospheric pressure and transforms to into m-ZrO_2 [18]. It is this polymorphism that limits the use of zirconia, because transformation from the tetragonal to the monoclinic phase is usually accompanied by a volume shrinkage of about 3-5%, enough to cause fracture [5]. The high temperature cubic phase can be stabilised by the addition of cubic oxides such as yttria Y_2O_3, magnesia MgO, calcia CaO, even rare earth oxides [2, 5].

Partially stabilised zirconia (PSZ) can be thermally cycled to produce metastable tetragonal zirconia within the grains of cubic zirconia. The PSZ materials exhibit higher toughness than fully stabilised zirconia materials due to the stress induced martensitic transformation of the tetragonal metastable grains to the monoclinic form in the stress field of a propagating crack [2, 4].

Zirconia is fairly unreactive to many fluxes, melts, molten glass, phosphates, borate, alkalis and acids but is attached by hot concentrated sulphuric acid and hydrofluoric acid.

TABLE 3.2: ESTIMATED WORLD ZIRCONIA CONSUMPTION BY DIFFERENT MARKETS [13-14]

Zirconia use	ZrO_2 derived From zircon	Baddeleyite	Total in Metric Tonnes
Refractories	5 000	10 000	15 000–15 500
Ceramic Pigment, Glazes and Opacifiers	3 000	3 000	6 000
Abrasives	1 500	2 000	3 500
Electronics	1 400-2 000		1 400 – 2 000
Oxygen Sensors	600-850		600 – 850
Glass/Gemstones	350-750		350 – 750
Advanced Ceramics/ Catalysis	2 000		2 000
Onward processing for above markets	1 900	4 000	5 900
Total	17 000	19 000	36 000

3.4 ZIRCONIUM CHEMICALS

This group of chemicals encompasses all the other zirconium chemicals except zirconia and zircon. Table 3.4 shows the diverse applications of zirconium chemicals. Surprisingly only a small amount approximately 10% (about 50-60Kt/a) of the world's produced zircon (about 900Kt/a) is used for the production of zirconium chemicals (Table 3.3) [11]. The use of these chemicals results primarily from their ability to complex with carboxyl groups to form an insoluble organic compound [18].

Zirconium basic sulphate (ZBS) can be used for the production of zirconium basic carbonate (BZC), $Zr_2O_3(OH)_2CO_2.nH_2O$ [11-12]. BZC and ZBS play central roles in the production of many zirconium chemicals. F. Farnworth et. al. (1980) [12] provides more information on the synthesis and applications of these chemicals.

TABLE 3.3: THE WORLD CONSUMPTION OF ZIRCONIUM CHEMICALS (in metric tons) [13]

Product	World Production Capacity
Zirconium Oxychloride ZOC	25 000
Basic Zirconium Carbonate BZC/ZBC	15-18 000
Zirconium sulphates	5–6 000
Basic Zirconium Sulphate	5–6 000
Ammonium Zirconium Carbonate	4-6 000
Zirconium acetate	1 000
Potassium Hexafluorozirconate	1 000
Total	56 000 – 63 000

Zirconium Oxychloride (ZOC) is the largest produced zirconium chemical. ZOC can be regarded as the zirconium chemical with the most possible growth. Many other chemicals can be made from ZOC and with the effects of global warming the use in antiperspirants should increase [13].

3.5 APPLICATIONS

3.5.1 FOUNDRY

Zircon is used as foundry material. This use can be attributed to zircon's low thermal conductivity, high melting point, and chemical stability [3]. Zircon is wetted less easily by molten metal or alloy, thus it produces smooth surfaces on metal or alloy. This is one of the largest consumer of the mineral [18].

3.5.2 REFRACTORY

Zircon is used as a refractory material. This can be attributed to its high melting point of approximately 2 250°C, chemical stability and mechanical strength (hardness in Mohs, approximately 7.5). The use of zircon as a refractory has decreased significantly due to the zircon shortages in the late 1980s being substituted by less expensive refractories such as alumina spinels [2]. The glass and steel industries usually use zircon as a refractory. Fused zircon and alumina zirconia silica (AZS) refractories have a high resistance to molten glass, for this property they are used in the glass industries. The steel industries use zircon in ladles and continuous casting nozzles [2].

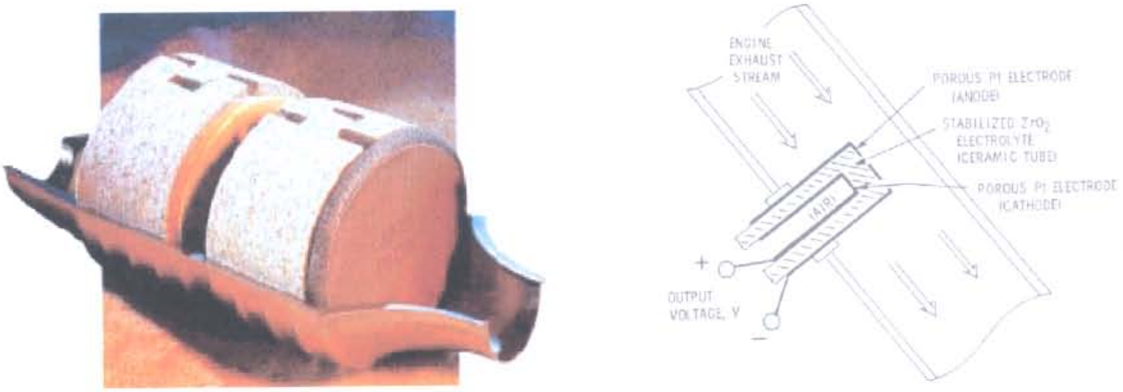
Since the early 1980s this has been an area of major growth for baddeleyite. As seen in Table 3.2 this is the major market for zirconia consumption of about 15 000 tons per annum. This area is expected to grow due to the continuous casting of steel in its production that requires high corrosion resistant refractory nozzles, sliding gates and entry tubes with high melting points [13].

3.5.3 ABRASIVES

This was one of the first major applications of zirconia. Zirconia is fused together with alumina to form alumina zirconia abrasives. The zirconia content is approximately 25–40% [2]. The zirconia consumption for this market was about 3 500 tons per annum, but this is expected to decrease due to the growing trend of near net casting which requires little use of machinery with high quality alumina zirconia abrasive grinding wheels [14-15].

3.5.4 OPACIFIER

Another major use for zircon is as an opacifier for tile glazes and porcelain enamels. This use can be attributed to zircon's high refractive index, which gives the glaze a white, opaque appearance [3]. Certain grades of paints use zirconia to coat the surfaces of Titania pigment particles. The zirconia coating acts as an ultra violet stabiliser by minimising the excitation of Titania preventing the ultra violet degradation of the paint molecules [2]. Zirconia has also been used instead of Titania as the pigment in white camouflage paints because it more closely simulates snow in the infrared and microwave spectral region [2].



(a) (b)

FIGURE 3.1: (a) A picture of a zirconia-supported palladium and zirconium couple in vehicle exhaust emission control [7]. (b) A Schematic illustration of a zirconia exhaust sensor (cross sectional view) [16].

3.5.5 OXYGEN SENSORS

Zirconia is used as oxygen sensors. This market consumes about 600-850 tons of zirconia per annum [13-14]. One example of the oxygen sensor is the exhaust gas sensor [Figure 3.1 (b)], which usually consists of a zirconia tube with porous platinum electrodes formed on both its inner and outer surfaces. The function of the sensor is to regulate the air-fuel mixture entering the engine by closed-loop process control utilising the zirconia tube as an electrochemical sensor [16].

3.5.6 CATALYSIS

Zirconia is used in catalysis. As seen in Table 3.2 this market consumes approximately 2 000 tons of zirconia per annum. There has been a significant amount of work done in this area and possibly an area of huge industrial growth. Zirconia is used in automobile exhaust systems as catalytic converters, were zirconia forms part of a *wash-coat* in converting poisonous gases into environmentally safe gases [Figure 3.1 (a)] [7]. Zirconia is capable of catalysing a number of reactions, typical examples are as follow: hydrogenation, oxidation, electro-catalysis, esterification, polymerisation and etc. [7]. Zirconium chemicals e.g. Ammonium basic zirconium carbonate (BZC-NH_4) is also used as a reagent to produce catalysts [12].

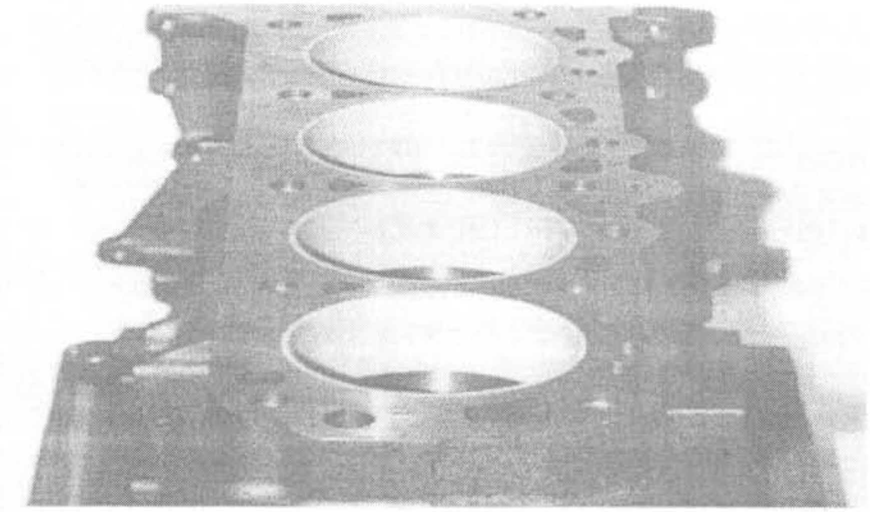


FIGURE 3.2: A picture of partially stabilised zirconia cylinder liners [10]

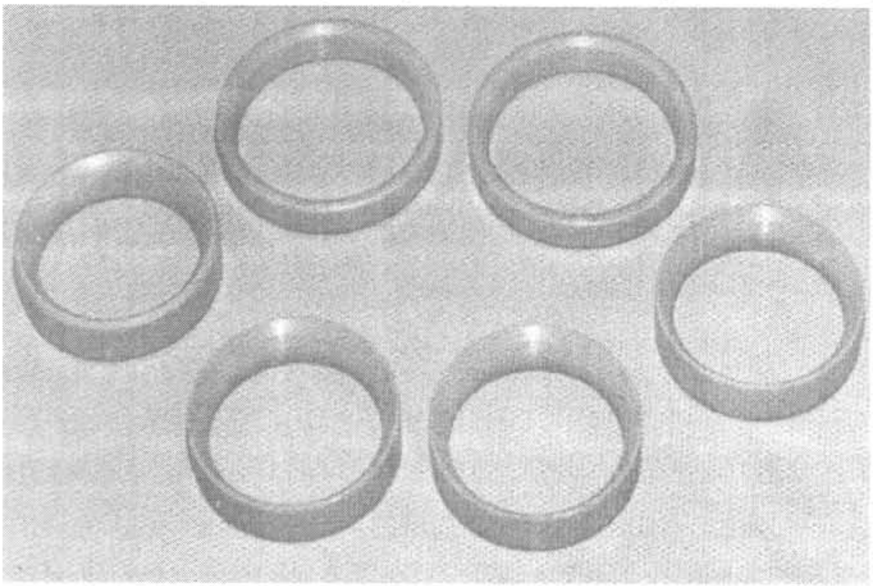


FIGURE 3.3: A picture of a partially stabilised zirconia valve seats [10]

3.5.7 ADVANCED CERAMICS

Partially stabilised zirconia ceramics, PSZ-ceramics, have been commercialised since 1970 [10]. PSZ-ceramics with varying amounts of stabilising cubic oxides show different properties in response to stress at different loading conditions [5, 8, 10]. Dworak et. al. (1983) [10] shows how PSZ-ceramics can be applied to wire drawing technology, thermal shock conditions, combustion engines (cylinder liners, valve seats, bypass valve guides), etc. (Figures 3.2-3.3). PSZ-ceramics can be applied for insulation to these adverse reaction conditions due to their low thermal conductivity, high fracture toughness and high strength.

FIGURE 3.4: A picture of water based paints containing zirconium chemicals [7]

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3.5.8 PAINT DRYERS

Zirconium chemicals e.g. BZC, ZBS, ZOC and BZC-NH_4, are used in solvent-based alkyds paints as dryers in place of toxic lead dryers and in water-based paints as thixotropes [7]. Zirconium compounds are also used in metal treatment where zirconium fluorides improve the adhesion of coatings on aluminium metals.

3.5.9 PIGMENTS

Zirconia is used in the formation of ceramic pigments. As seen in Table 3.2 approximately 6 000 tonnes of zirconia is consumed by this market. Zirconia can be used together with silica SiO_2 to form zircon based pigments, where the colour is due to the lattice distortion caused by a dopant, like vanadium [9].

TABLE 3.4: Applications of Zirconium Chemicals, Industry and Function [11-12, 13, 18]

Zr Compound	Application	Industry	Note
BZC-NH_4 or ZrA	Waterproofing	Paper & Textiles	Replaces volatile formaldehyde resins
ZrA	Bacteriostatic &antifungicidal	Textiles	Improves wash fastness and Cu salts
BZC-NH_4	Reagent	Catalysis	Production of catalysts
K_2ZrF_6	Suppressant	Paint	Lowers organic solvent emissions
	Flame resistance	Wool	Improves wash fastness and replaces Ti and Cu salts
H_2ZrF_6 or ZrA	Grain refiner	Alloys	Grain refiner (Mg/Al alloys)
ZOC	Corrosion resistance	Paint	Replaces Cr chemicals.
ZOC	Coupling agent	Paint	Replaces silanes
ZOC, AZST	Bacteria oxidation	Antiperspirants	Captures oxygen to oxidise dead bacteria
	Tanning	Leather	Polypeptide cross-linking, (Replaces Cr chemicals)
$\propto$-$Zr(HPO_4)_2.H_2O$	Ion exchange	Medical	Kidney dialysis
AZST	U.V stability, abrasion resistance	TiO_2 Pigments	Coating of titanium pigments
ZBS	U.V stability and Starting material	TiO_2 pigment, Processing	Coating of titanium pigments, and Production of zirconium chemicals
ZBC	Starting material	Processing	Production of zirconium chemicals
BZC, ZBS, ZrO	Drier	Paint	Replaces Pb dryers and improves gloss
BZC	Rheology and Thixotropy	Cement and Paint	Replaces organic chemicals and provides a clear finish

KEY: ZrA is an abbreviation for zirconium acetate $H_2ZrO_2(C_2H_3O_2)_2$. BZC or ZBC is basic zirconium carbonate $Zr_2O_3(OH)_2CO_2.nH_2O$. ZOC is zirconium oxychloride $[Zr_4(OH)_8(H_2O)_{16}]C_{18}$ AZST is zirconium sulphate $Zr(SO_4)_{2\cdot4}H_2O$. BZC-NH_4 is ammonium zirconium carbonate $(NH_4)_3ZrOH(CO_3)_3.2H_2O$. ZrO is Zirconium Octoate.

3.6 CONCLUSIONS

1. Zircon is used in plasma spraying, as a refractory, as an opacifier and as foundry. This can be attributed to the chemical and physical properties of zircon.
2. Zirconia, its use is restricted by polymorphism. Partial or full stabilisation with cubic oxides of the cubic phase of zirconia is possible.
3. Zirconia is consumed mainly by the refractory industry. Other uses include ceramic pigments, glazes, opacifiers, electronics, Oxygen sensors, glass, gemstones, advanced ceramics and catalysis.
4. ZBC or ZBS play a central role in the production of zirconium chemicals. Approximately 10% of the produced world zircon is used in the synthesis of zirconium chemicals.

3.7 REFERENCES

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CHAPTER 4

THE CHEMISTRY OF ZIRCONIUM

[Picture by: www.zrchem.com]

4.1 INTRODUCTION

The chemistry of zirconium and hafnium is very similar than for any two known congeneric elements [1-4]. This can be attributed to the lanthanide contraction effect that causes both the atomic and ionic radii (14.5 and 8.6nm for Zr and Zr^{4+} and 14.4 and 8.5nm for Hf and Hf^{4+} respectively) to be almost identical [1-5].

The chemistry of zirconium has been pursued only along two lines, the aqueous chemistry and the non-aqueous chemistry. Both methods have their problems. In aqueous solution, zirconium compounds are hydrolysed to hydroxy species then to polymeric species [1- 5]. For the non-aqueous chemistry, solubility of reagents and the use of anhydrous reagents posses a problem of maintaining the anhydrous reaction conditions.

4.2 THE AQUEOUS CHEMISTRY

4.2.1 THE ZIRCONYL GROUP $[Zr=O]^{2+}$

Does the zirconyl group exist, or not? Solovkin and Tsvetkova concluded that this species rarely exists. They based their conclusion on stoichiometric evidence and infra red spectra being vague and bond separation being inconsistent with that expected.

Confusion about the existence of the zirconyl group came from the assumption that zirconium existed in solution as the $[Zr=O]^{2+}$ ions. Thus formulae of chlorides, sulphates, nitrates, and other salts were written as $ZrO(SO_4)$ or $ZrOCl_2.8H_2O$. Well this is not always the case, as it has it been established [11] that zirconium exists in solution predominantly as the tetramer $[Zr_4(OH)_8.16H_2O]^{8+}$.

In contrast, the zirconyl group was observed with the aid of infrared spectroscopy in thiocyanate compounds and with the aid of thermogravimetric analysis the formula $Me[ZrO(SCN)_3H_2O].H_2O$ where Me is NH_4, Rb, K or Cs containing two hydroxyl groups was suggested. Clearfield (1964) [11], opposed this deduction by saying that the sharp absorption band at 913 and 927cm^{-1}could have been due to the δ (SCN) harmonics.

4.3 TETRAMERS

Zielen and Connick. (1956) [9] studied the polymeric nature of the aqueous zirconium species at metal concentration greater than 10^{-3}M and hydrogen ion concentration less than 1M, using spectrophotometric indication reactions. Johnson et al. (1956) [10] also studied this system but used ultracentrifugation. Both confirmed the existence of tetramers, $[Zr_4(OH)_8.16H_2O]^{8+}$, and trimers, $Zr_3(OH)_4^{8+}$, in solution.

Light scattering studies of zirconyl chloride in 2.80M hydrochloric and metal ion concentration of 0.02-0.04M lead to the conclusion that at this concentration range the predominant species is the trimer with a total charge of three. While at lower acid concentrations, such as 0.75M H^+, the polymer appears to be a metal hexamer with a charge less than unity.

Clearfield et al. (1956) [11] provided direct evidence for the existence of polymeric species by X-ray data on zirconyl halides. The halides react vigorously with water to form salts commonly referred to as zirconyl halides. These easily crystallised halides have a general molecular formula $ZrOX_2.8H_2O$ ($X \equiv Cl^-, Br^-, I^-$) were the zirconyl ion is possibly a tetramer, $[Zr(OH)_2.4H_2O]_4^{8+}$. The halogen ions are not bonded to the zirconium atoms but are held in the crystal by electrostatic forces and hydrogen bonds.

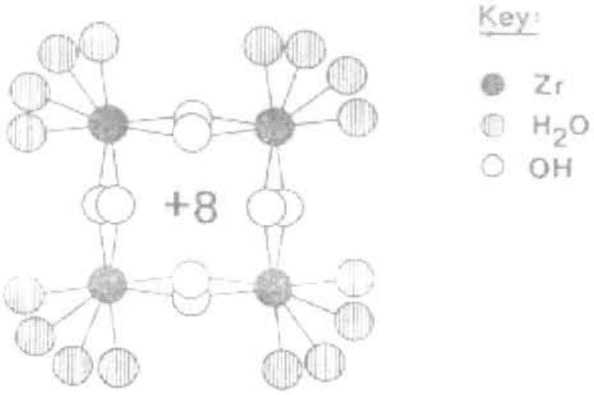

FIGURE 4.1 The structure of the $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ associated with zirconyl chloride

In the zirconyl ion, four zirconium atoms are located at the corners of a slightly distorted square and are joined by double hydroxyl bridges above and below the plane of the square.

These four oxygen atoms and four more from water molecules are situated about the zirconium at the vertices of an Archimedian antiprism [11].

Hydrolytic polymerisation of these tetramers can be readily achieved by simply ageing, heating or by reduction in acidity [1-5].

4.4 ZIRCONIUM HYDROXIDE CHLORIDES

The compound $ZrOCl_2.8H_2O$ commonly called zirconyl chloride, zirconium oxychloride, and zirconium oxide dichloride are all common names given to zirconium hydroxide dichloride. The real structure is, $[Zr_4(OH)_8.16H_2O]Cl_8.12H_2O$ [1-4, 13]. The hydroxide dichloride is prepared by dissolving hydrous zirconium oxide or zirconium carbonate in hot hydrochloric acid or by hydrolysis of zirconium tetrachloride in water [1-4, 19].

Zirconium hydroxide monochloride, $[Zr_4(OH)_{12}.16H_2O]Cl_4$ is formed in solution by reacting equimolar amounts of hydrochloric acid with hydrous zirconium oxide or zirconium basic carbonate, or by the action of hydrogen peroxide on zirconium hydroxide dichloride [13].

4.5 HYDROLYSIS AND POLYMERISATION

Zirconium and Hafnium compounds have a tendency to hydrolyse in aqueous solutions; this can be attributed to the high charge and small radius [1-4, 13]. Simple zirconium salts, such as tetrahalides react readily with water to form oxyhalides (of general formula $ZrOX_2.8H_2O$) and strongly reducing the pH. For instance, the halide $ZrCl_4$ dissolves in water to form the oxychloride $ZrOCl_2.8H_2O$ and releasing two H^+(aq) ions for oxygen thus, decreasing the pH [1-4]. At 0.05M of a solution of the respective salt the pH is as low as 1. Solovkin (1957) [4] established the following equilibrium reaction and its constants in aqueous solutions at 25°C:

$$Zr^{4+} + nH_2O \leftrightarrow Zr(OH)_n^{4-n} + nH^+$$

SCHEME 4.1 A diagrammatic representation of the reaction for the formation of the hydroxide. For n = 1, the equilibrium constant $K_1 = 0.6$; n = 2, $K_2 = 0.24$; n = 3, $K_3 = 0.09$ and for n = 4, $K_4 = 0.068$.

From the reaction above it can be seen that at low H^+(aq) ion concentration, the formation of the hydroxide increases. The degree of hydrolysis is dependent on the concentration of the initial solution as was noted with increases in dilute solution [4]. Temperature and time was also observed to have extensive effects on hydrolysis.

Clearfield (1964) [12] refluxed aqueous slurries of gelatinous hydrous zirconia that were precipitated from the zirconium chloride or nitrate solutions. He also observed the large decrease in pH on dissolution of the chloride. During refluxing the anions in the hydrous oxide were displaced by hydroxyl groups. The refluxing was capable of transforming the amorphous gel particles into a crystalline product. The initial mixture contained cubic and monoclinic crystallites. After long periods of continued refluxing, the slurries were converted to colloidal, crystalline, hydrous zirconia sols (Figure 4.2).

X-ray line broadening showed that the crystallites contained 12-24 unit cells or differently 48-96 monomer units. The inter-planar spacing of the sol and gel particles were observed to be identical and very close to those in the calcined oxides. The Zr-Zr distance in the sheets is 35.6nm compared to 35.8nm in cubic zirconia. This lead to the observation that within the crystallites the composition must be close to $[ZrO_2]_n$, but the crystalline hydrous oxide particles still retained coordinated water. The crystallites were also observed to contain hydroxyl groups as indicated by their ion exchange properties [17].

The tetramer was also observed to be very stable and it remained intact under very acidic solutions. Each zirconium atom in the tetramer complex is bonded to two sets of double hydroxyl bridges, lying in planes, which are nearly at right angles to each other. Thus it would be expected that olation between any two adjacent tetramer units would occur in such a way as to place the diol bridges at right angles to those already present. But each tetramer group contains numerous olation sites; thus growth can occur can occur in many directions depending on the rate of crystallisation (Figure 4.3). If the olation process were carried indefinitely it would lead to the formation of sheets of composition $[Zr(OH)_4]_n$. Each zirconium atom, not at the edge of the sheet, is surrounded by eight hydroxyl groups in the form of a distorted cubic arrangement, thus changing the original square antiprism coordination to the coordination present in cubic zirconia.

4.6 CARBONATES

Basic zirconium carbonate (ZBC), of empirical formula $ZrO_2.CO_2.xH_2O$ [1-4]. The ratio of ZrO_2 : CO_2 has been observed to vary considerably, from 4 : 1 to 1 : 1 depending on the method of preparation [20]. Adding sodium carbonate solution to a solution of zirconium basic sulphate normally produces ZBC. Adding sodium carbonate to a solution of zirconium sulphate to a pH of approximately 6.75 has been observed to precipitate the carbonate $Zr_2O_3(OH)_2CO_2.nH_2O$ with a ZrO_2 : CO_2 ratio of 1 : 0.8 [19].

ZBC reacts with sodium or ammonium carbonate solutions to give water-soluble double carbonates e.g. $NH_4[Zr_2O(OH)_3(CO_3)_3]$. None of these carbonates combined with ammonia, confirming the absence of HCO_3^- [1-4].

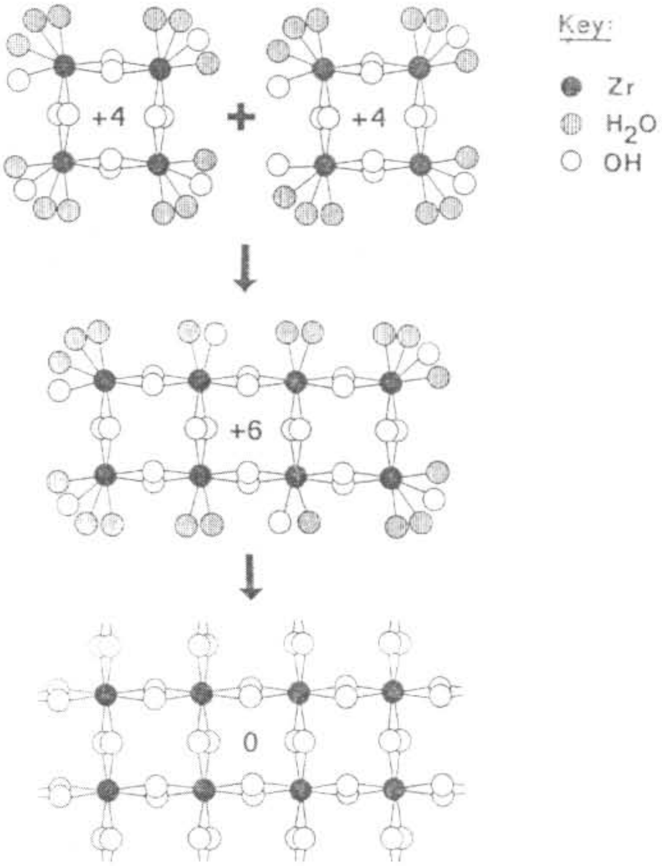

FIGURE 4.2: Schematic representation of the tetramer combination sequence. Polymerisation occurs through olation between the tetramer units. Olation describes the formation of hydro-bridges as a result of hydrolysis.

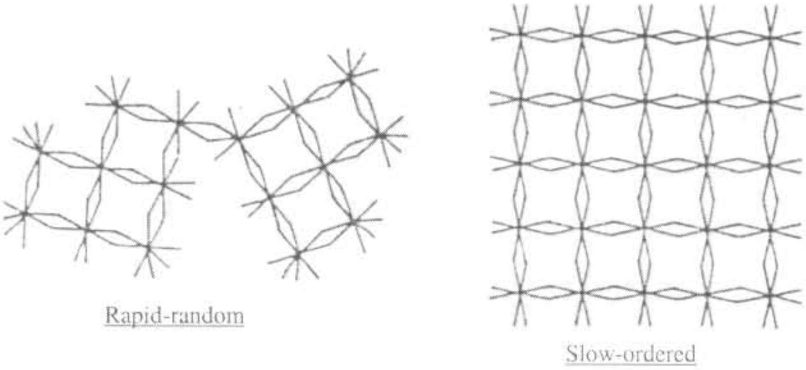

FIGURE 4.3 Schematic representation of the tetramer combination sequence of (a) rapid and (b) slow addition of base upon the structure of gelatinous hydrous zirconia

4.7 ZIRCONIUM SULPHATES

Bear et al. (1971) [15] studied the phase system $Zr(SO_4)_2$-H_2O with respect to its normal salts, where the ratio of Zr/SO_4 in the molecular formula, is one is to two. Thus distinguishing them from the basic and acidic sulphates, where the Zr/SO_4 ratio is greater and less than one is to two, respectively. They were able to establish, with the aid of XRD data, the structure and the conditions under which each sulphate exist.

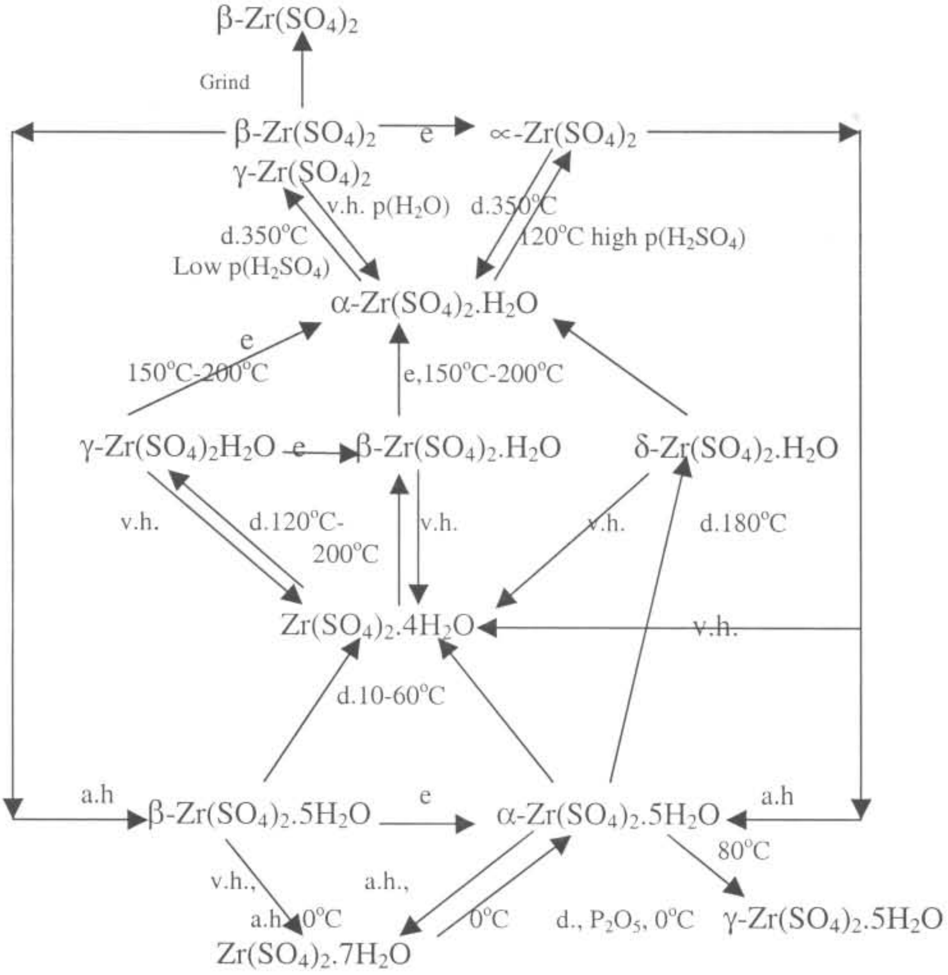

FIGURE 4.4 A diagrammatic representation of the chemical inter-relationships in the $Zr(SO_4)_2$-H_2O system [15]

KEY: a.h., aqueous hydration; v.h., vapour hydration;

e, equilibration; d, decomposition

The sulphate ion strongly complexes the zirconium atom, as is seen in the series [13]:

$$OH^{-} > CO_3^{2-} > PO_4^{3-} \sim C_2O_4^{2-} > SO_4^{2-} > NO_3^{-} > Cl^{-} > ClO_4^{-} > Br^{-} \sim I^{-}$$

SCHEME 4.2 A representation of the zirconium complex series

In comparison to the sulphate, the nitrate, chloride, and perchlorate ions are weak complexing agents and show little tendency to form bridges between zirconium atoms. The sulphate is capable of displacing the hydroxy group from a hydrolysed zirconium species to form sulphate bridges between zirconium atoms.

Further proof of the complexing ability of the sulphate ion is seen in the large number of salts that form between the zirconium ion and the sulphate ion [1]. The well-known stable normal sulphate, zirconium sulphate tetrahydrate, $Zr(SO_4)_2.4H_2O$, often called acid zirconium sulphate trihydrate (AZST), crystallises easily out of relatively strong sulphuric acid solutions [2]. Decreasing the acidity or diluting zirconium sulphate solutions, will result in the precipitation of a variety of zirconium basic sulphates (ZBS) [1-4].

Normal zirconium sulphate crystals consist of infinite sheets of zirconium atoms linked together by sulphate groups [12]. Four different sulphates are bonded to each zirconium atom while each sulphate group is bonded to two zirconium atoms. Sheets rather than chains form because no two sulphates have more than one zirconium atom in common [12]. Four water molecules can coordinate to each zirconium atom thus forming a square antiprism with the four sulphate oxygen atoms [2-3, 12].

Dissolution of zirconium sulphate sheets occurs by scission of the bonds between zirconium atoms and the sulphate groups. This usually occurs by displacement of sulphate by hydroxy groups to anionic species [12].

$$[Zr(SO_4)_2.4H_2O]_n + 2nH_2O \Leftrightarrow n[Zr(OH)_2(SO_4)_2.4H_2O]^{2-} + 2nH^+ \qquad (1)$$

$$[Zr(SO_4)_2]_n + 3nH_2O \Leftrightarrow n/2[Zr_2(OH)_3(SO_4)_4]^{3-} + 3nH^+ \qquad (2)$$

$$[Zr(SO_4)_2]_n + 4nH_2O \Leftrightarrow n/3[Zr_3(OH)_4(SO_4)_6]^{4-} + 4nH^+ \qquad (3)$$

SCHEME 4.3 Reaction (**1**) shows that two sulphate groups are displaced for each zirconium atom. Reaction (**2**) and (**3**) have similar implications but with the omission of coordinated water to the zirconium sulphate.

The anionic species would not be expected to exist for any appreciable length of time because of the unsatisfactory bonding conditions. Rather they would be expected to stabilise by olation or by formation of sulphate bridges. This serves as bases for the formation of zirconium basic sulphates form the anionic species [2, 12].

Consider the basic sulphate with the molecular formula, $ZrO_2.SO_3.H_2O$. This basic sulphate consists of species $[Zr(OH)_2]_n^{2+}$, which forms chains in which each zirconium atom is bonded to four hydroxyl groups. A series of olation reactions with displacement of sulphate groups, makes this structure possible [12]. The remaining sulphate groups form bridges between the chains. The general formula for ZBS is, $Zr_5O_{(10-x)}(SO_4)_3$ where $3.5 > x > 1.8$. The most common basic sulphate is $Zr_5O_7(SO_4)_3.nH_2O$ [13]. Basic sulphates of type $Zr_n(OH)_{2n+2}(SO_4)_{n-1}$ have also been proposed [12].

Recently, Squattrito and Clearfield (1987) [16] has provided the crystal structure and synthesis of a new complex basic zirconium sulphate $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6}.33H_2O$. This further emphasises the diversity of these basic salts with departure from those previously reported.

4.8 CONCLUSIONS

1. The chemistry of zirconium and hafnium is more similar than any other two congeneric elements. This can be attributed to the near identical atomic and ionic radii.
2. The zirconyl group rarely exists for zirconium aqueous chemistry.
3. At metal concentrations greater than 10^{-3}M and hydrogen ion greater than 1M, tetramers and trimers exists in zirconium solutions.
4. Many different zirconium normal sulphates exist at different reaction conditions
5. The sulphate strongly complexes the zirconium ion.
6. Disulphato-oxy-zirconic acid trihydrate $H_2ZrO(SO_4)_2.3H_2O$, commonly called acid zirconium sulphate trihydrate (AZST) $Zr(SO_4)_2.4H_2O$, is a stable normal sulphate.
7. AZST crystallises easily out of relatively strong sulphuric acid solutions. The crystals consist of infinite sheets of zirconium atoms linked together by sulphate groups. Four different sulphates are bonded to each zirconium atom while each sulphate is bonded to two zirconium atoms.
8. Decreasing the acidity or diluting zirconium sulphate solutions, will result in the precipitation of a variety of zirconium basic sulphates.
9. Simple zirconium salts like $ZrCl_4$ are hydrolysed in water to form zirconium hydroxide chlorides $[Zr_4(OH)_8.16H_2O]Cl_2.8H_2O$.
10. Adding sodium carbonate to a solution of zirconium sulphate to a pH of approximately 6.75 has been observed to precipitate the carbonate $Zr_2O_3(OH)_2CO_2.7H_2O$ with a $ZrO_2 : CO_2$ ratio of 1 : 0.8
11. ZBC reacts with sodium or ammonium carbonate solutions to give water-soluble double carbonates e.g. $NH_4[Zr_2O(OH)_3(CO_3)_3]$.

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