Zirconia
RS•C
Introduction

This booklet is the result of a Learning Material Workshop organised by The Royal Society of Chemistry in conjunction with The Institute of Materials and The Worshipful Company of Armourers and Brasiers. A group of chemistry teachers spent the day at MEL Chemicals, Bolton, which manufactures zirconia. The day included a presentation by the company and tour of the plant. The following day was spent brainstorming and drafting the material which is presented here in edited form.

Acknowledgement

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The material consists of:

- teacher’s background notes on zirconium and some of its compounds, including answers to the comprehension exercise;
- some suggestions for searching the internet to find out about zirconium and its compounds which could be used to begin an information and communication technology (ICT)-linked project; and
- a comprehension exercise for post-16 students.

While zirconium itself does not feature in post-16 syllabuses, the comprehension exercise uses the element and its chemistry as a vehicle to cover some familiar chemistry topics – oxidation states, coordination numbers, electron configurations etc – in an unfamiliar context.

When reading this material, one needs to take care with nomenclature:

- ‘zirconium’ refers to the metallic element;
- ‘zirconia’ refers to zirconium(IV) oxide, ZrO₂; and
- ‘zircon’ refers to zirconium(IV) silicate – this is a compound oxide (ZrO₂·SiO₂) but is often represented ZrSiO₄.
Zirconium and zirconia

The name ‘zirconium’ comes from the Persian word zargun meaning ‘gold-coloured’. Zirconium is a relatively unfamiliar metallic element, and yet its compounds (especially zirconium oxide, zirconia) have many everyday applications. Zircon (zirconium silicate, ZrSiO₄) has been known for centuries as a semi-precious stone but it was not until the 1920s that pure zirconium metal was first produced. Since then there has been a steady increase in the diversity of the uses of the metal and its compounds. One of the reasons why interest in zirconium continues to grow is that, unlike many of the other metals in common usage, zirconium has a low toxicity and is classified as being non-hazardous to the environment.

Zirconium is the 17th most abundant element on the Earth (more common than zinc, tin and mercury). It is found in igneous rocks, such as schists, gneiss, syenite and granite. In these rocks it exists in the form of baddeleyite which is zirconium oxide (zirconia, ZrO₂) which has iron, titanium and silicon oxide impurities. The most commercially important mineral is zircon (ZrSiO₄). This was originally associated with igneous deposits, but weathering and natural concentration due to its high density (4.6 g cm⁻³) has produced large secondary deposits in beach sands. These important secondary deposits are in Australia, South Africa, Asia and the East coast of the US.

The process of obtaining pure zirconium compounds from the impure zircon mineral is complex, but can be represented by the flow diagram (Fig 1).
### Zirconium data

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
<td>Zr</td>
</tr>
<tr>
<td>Atomic number</td>
<td>40</td>
</tr>
<tr>
<td>Relative atomic mass</td>
<td>91.22</td>
</tr>
<tr>
<td>Zirconium isotopes:</td>
<td></td>
</tr>
<tr>
<td>$^{90}\text{Zr}$, 51.5 per cent; $^{91}\text{Zr}$, 11.2 per cent; $^{92}\text{Zr}$, 17.1 per cent; $^{94}\text{Zr}$, 17.4 per cent; $^{96}\text{Zr}$, 2.8 per cent</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>6.5 g cm$^{-3}$</td>
</tr>
<tr>
<td>Melting point /K</td>
<td>2125</td>
</tr>
<tr>
<td>Boiling point /K</td>
<td>4650</td>
</tr>
<tr>
<td>Electronic configuration</td>
<td>[Kr] 4d$^2$5s$^2$</td>
</tr>
<tr>
<td>Ionisation energies (kJ mol$^{-1}$)</td>
<td>1st 660; 2nd 1267; 3rd 2218; 4th 3313; 5th 7860; 6th 9500; 7th 11 200; 8th 13 800</td>
</tr>
<tr>
<td>Electronegativity</td>
<td>1.4 (Pauling scale)</td>
</tr>
<tr>
<td>Metallic radius /nm</td>
<td>0.158</td>
</tr>
<tr>
<td>Covalent radius /nm</td>
<td>0.145</td>
</tr>
<tr>
<td>Ionic radius nm</td>
<td>0.072</td>
</tr>
<tr>
<td>$\Delta H_f^{\Theta} (\text{ZrO}_2) \text{kJ mol}^{-1}$</td>
<td>-1080</td>
</tr>
<tr>
<td>$\Delta G_f^{\Theta} (\text{ZrO}_2) \text{kJ mol}^{-1}$</td>
<td>-1023</td>
</tr>
<tr>
<td>$S^\Theta (\text{ZrO}_2) \text{J K}^{-1} \text{mol}^{-1}$</td>
<td>50.3</td>
</tr>
</tbody>
</table>
Zirconia crystals

Zirconia exists in three different crystalline forms – monoclinic, tetragonal and cubic. In the monoclinic phase the Zr\(^{4+}\) ion has seven-fold coordination (ie it is surrounded by seven oxygens); in the tetragonal phase and cubic phase the Zr\(^{4+}\) ion has eight-fold coordination.

\[ \bigcirc = \text{oxygen} \quad \bullet = \text{zirconium} \]

<table>
<thead>
<tr>
<th>Phase</th>
<th>Temperature (K)</th>
<th>Density (g cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoclinic</td>
<td>1440</td>
<td>5.83</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>1440</td>
<td>6.10</td>
</tr>
<tr>
<td>Cubic</td>
<td>2640</td>
<td>6.09</td>
</tr>
</tbody>
</table>

When the tetragonal phase transforms to the monoclinic phase – on cooling – the volume actually increases by about 4 per cent and zirconia is brittle over such temperature changes.

By adding a few per cent of oxides of metals such as magnesium, calcium and yttrium, makes the cubic form of zirconia stable from zirconia’s melting point (2950 K) down to room temperature. This effect gives zirconia ceramics their unusual and highly valued properties. This is a complex effect but in simple terms, ions of the added metals take the place of some of the zirconium ions in the zirconia crystal lattice. However, these oxides are oxygen deficient compared with zirconia – the formulae are MgO, CaO and Y\(_2\)O\(_3\) respectively compared with ZrO\(_2\)). Their presence distorts the shape of the monoclinic and tetragonal lattices and has the effect of making the cubic form the most stable form down to room temperature.
Uses of zirconium and its compounds

Zirconium metal

- Zirconium is used for the cans that hold reactor fuel rods in the nuclear industry.
- It is used as pressure tubes in Canadian nuclear reactors and in the reactors of the US Navy’s nuclear submarines.
- Zirconium is used as an ingredient to increase the strength of magnesium alloys. For example, when such alloys are used in aircraft, this gives lighter weight components for the same strength. This in turn leads to more efficient use of fuel and consequent reduction of air pollution.

Zirconium oxide

Ceramics

Zirconia can be used to make ceramics, and it is this use of zirconia which has most excited scientists over the past few years.

Ceramics have been used for thousands of years for making vases, tiles etc. The first ceramic was probably discovered by accident - possibly by noticing that lumps of soft clay become extremely hard when they are left to dry and then fired. The drawback with traditional ceramics is that they are brittle, but zirconia ceramics suffer less from this disadvantage. In fact zirconia ceramics have remarkable properties of strength, hardness and wear resistance in addition to withstanding attack from molten metal, organic solvents, acids and alkalis. They can also withstand high temperatures for long periods even under severe mechanical stress.

One of the new applications is knives and scissors where the zirconia ceramic can be engineered to produce extremely fine and sharp blades which have a hardness of about 9 on the Mohs’ scale (on which diamond has a value of 10). This is significantly harder than steels, and of course, ceramics do not rust. These implements give an exceptionally good, smooth cut in even the toughest of uses – they can be used to cut through Kevlar® – as used in riot shields and bullet proof vests!

High performance scissors and knives are produced for everyday use, and these are also in great demand by deep sea divers who require sharp blades which will not corrode in marine environments. Zirconia ceramic blades flex as well as steel and are non-magnetic, anti-static, and don’t cause any metallic contamination. A new type of golf club head has been manufactured from zirconia ceramics where the extreme hardness enables a crisper and harder driving force to be delivered to the ball.

As a result of their strength, hardness and other properties, zirconia ceramics are being considered for a huge range of industrial applications which include motor engine components, high speed cutting tools, heat resistant linings in furnaces, containers for molten metals, and heat shields for space vehicles.

Some other uses of zirconia include:

- cubic zirconia gemstones (‘fake diamonds’) – the optical properties of cubic zirconia are superior to those of diamond;
catalysts: zirconia is not only used as a catalyst in its own right, but also as a support medium and enhancer for other catalysts. This enables catalysts to be used at higher temperatures or under severe conditions. Catalytic converters in vehicles contain zirconia;

- ceramic colours: made by adding compounds of other transition metals to zirconia, used in ceramic tiles and sanitary ware – baths, wash basins and toilet bowls – that can replace lead in paint. Monoclinic zirconia is used here.

- electroceramics used in piezoelectrics – gas lighters, etc. – and capacitors. (Zirconia has some rather peculiar electrical properties and can under certain circumstances become electrically conducting.); and

- solid electrolytes: used in fuel cells and in oxygen sensors used in combustion control systems in boilers and in some car engines.

Other zirconium compounds
Zirconium phosphate is used in the ion-exchange medium in kidney dialysis machines
Zirconium on the internet

Further information on zirconium chemistry in general and MEL Chemicals in particular is available on the internet.

MEL Chemicals has a web site at www.zrchem.com

This site contains further information about the company as well as more specialised detail about the uses of zirconium and zirconia.

Maniago is an Italian company which produces, amongst other things, divers’ knives made from zirconia. Their web site is www.italpro.com.

Other information about zirconia and related matters can be found by using a search engine.

An Infoseek search for information on the keyword Zirconia produces well over 1000 references, so a narrower more precise search instruction is more useful. For example, searching for ‘+zirconia +ceramics -cubic’ gives about a dozen hits. (This searches for documents which contains the words zirconia and ceramics, but omits any which contain the word cubic). A search for ‘+zirconia +cubic +jewellery’ gives information only on the uses of cubic zirconia as a gemstone and results in about ten sources.

Other search engines may work slightly differently and this could be a good teaching point. Searches like this could form the basis of a ICT exercise on using the internet to find information, and should develop ICT skills as well as turn up some interesting chemistry.
Answers

1. Fuse means to melt the two solids together.

2. Hydrolysis means reaction with water.

3. \[
\text{ZrSiO}_4 + 4\text{NaOH} \rightarrow \text{Na}_2\text{ZrO}_3 + \text{Na}_2\text{SiO}_3 + 2\text{H}_2\text{O}
\]
   \[
\text{Na}_2\text{ZrO}_3 + 3\text{H}_2\text{O} \rightarrow \text{Zr(OH)}_4 + 2\text{NaOH}
\]
   \[
\text{Zr(OH)}_4 + 2\text{HCl} + \text{ZrOCl}_2 + 3\text{H}_2\text{O}
\]

4. The sodium silicate dissolves in water.

5. + IV

6. Zr(IV) has lost the two 5d electrons and the two 6s electrons and is therefore 5d\(^0\).
   Electronic transitions between part-filled d-orbitals are what causes the colour of compounds of d-block elements. (A d\(^0\) electron arrangement is why Ti(IV) compounds are colourless and a d\(^{10}\) arrangement is why Zn(II) does not behave as a transition metal.)

7. 74 per cent

8. 72.6 kg

9. a) [Xe] 4f\(^{14}\) 5d\(^2\) 6s\(^2\)
   b) [Kr] refers to the electron configuration of the inert gas krypton
   \[
   \text{ie 1s}^2 \text{2s}^2 \text{2p}^6 \text{3s}^2 \text{3p}^6 \text{3d}^{10} \text{4s}^2 \text{4p}^6
   \]
   c) The 4f electrons shield only poorly the outer electrons from the nuclear charge because of their shape. (This is called the lanthanide contraction.)
   d) The whole outer shell of electrons has been lost in the +IV state.

10. Hf\(^{4+}\) and Zr\(^{4+}\) have almost identical ionic radii. Therefore their oxides have very similar properties making them very difficult (and therefore expensive) to separate.

11. a) At the corners of a cube of which the zirconium ions is at the centre.
    b) 6+. Each Zr is \(^{4+}\) and there are 2 OH\(^-\)
    c) 7

12. Relative atomic mass of zirconium = 91.3
Student material
Zirconium
and its compounds

Zirconium – atomic number 40 – is an element in the d-block of the Periodic Table. Its main industrial uses are as the oxide (ZrO₂) usually called zirconia. Purified zirconia is used to produce gemstones similar to diamonds but much cheaper. The other major use of the oxide is in making tough, heat resistant ceramics, used in engine components, cutting tools, knives and golf clubs. Recently zirconia has been used to improve the efficiency of catalytic converters in cars. When mixed with compounds of other d-block elements, such as iron, vanadium and cobalt, the oxide forms pigments used for colouring washbasins, baths and ceramic tiles. The colours are heat resistant and do not fade, because the added coloured ions lock permanently into the oxide lattice.

Zirconium ore comes from Australia, Asia, South Africa, and the East coast of the US. It is called ‘beach sand’, because it also contains silicon dioxide (SiO₂) and has the formula ZrO₂·SiO₂, often written as ZrSiO₄. The zirconium oxide is extracted from the ore in a series of steps. The first stage is to fuse the ore with sodium hydroxide to form sodium zirconate (Na₂ZrO₃) and sodium silicate (Na₂SiO₃). The mix is then washed with water and the zirconate hydrolyses to form complex hydrated zirconium hydroxides. Acid is added to the mix and zirconium salts form, which can be precipitated. The zirconium salts can then undergo further reaction to form zirconium oxide.

The process is summarised in the flow diagram.

Flow diagram
One of the complex zirconium hydroxides is thought to contain the ion below

\[
\text{Zirconium hydroxide complex ion}
\]

This ion can be dehydrated to give the bridged structure below.

\[
\text{Bridged structure}
\]

After purification the final powder is 98 per cent ZrO\(_2\) and 2 per cent HfO\(_2\), hafnium oxide. The hafnium oxide is not normally separated from the zirconia.

Hafnium and titanium are elements in the same group as zirconium in the d-block of the Periodic Table. Some of their properties are given in the table. The electron configuration of hafnium has been omitted.

<table>
<thead>
<tr>
<th>Property</th>
<th>Titanium</th>
<th>Zirconium</th>
<th>Hafnium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>22</td>
<td>40</td>
<td>72</td>
</tr>
<tr>
<td>Electronic configuration</td>
<td>[Ar](3d^2)(4s^2)</td>
<td>[Kr](4d^2)(5s^2)</td>
<td>[Xe]</td>
</tr>
<tr>
<td>Atomic radius (nm)</td>
<td>0.147</td>
<td>0.160</td>
<td>0.158</td>
</tr>
<tr>
<td>Radius in +IV oxidation state (nm)</td>
<td>0.061</td>
<td>0.072</td>
<td>0.071</td>
</tr>
<tr>
<td>Density (g cm(^{-3}))</td>
<td>4.5</td>
<td>6.51</td>
<td>13.28</td>
</tr>
</tbody>
</table>

Some properties of titanium zirconium and hafnium
Questions

1. What does ‘fuse the ore with sodium hydroxide” mean?

2. Explain the term ‘hydrolysis’.

3. Write balanced equations for the reactions in the flow diagram by which the ZrSiO$_4$ in beach sand is converted into ZrOCl$_2$. There are three steps.

4. Suggest how the sodium silicate is removed during the extraction process.

5. What is the oxidation state of the zirconium in sodium zirconate Na$_2$ZrO$_3$?

6. Most compounds of the d-block elements are coloured. Given that the electronic configuration of Zr is [Kr]4d$^2$5s$^2$, explain why Na$_2$ZrO$_3$ is colourless.

7. The price of ZrO$_2$ depends on the total mass of zirconium per 100 kg in the final powder. Calculate the percentage of Zr by mass in the oxide.
   \( A_s: \text{Zr} = 91.22, \text{O} = 16.0 \)

8. What mass of zirconium is there in a 100 kg batch of 98 per cent pure zirconium oxide?

9. Use the information in the table to answer the following questions.
   a) Write down the rest of the electronic configuration for Hafnium.
   b) Explain what is meant by [Kr] in the electronic structure of zirconium as given in the table.
   c) Suggest a reason for the similarity in radii between zirconium and hafnium despite the difference in atomic number.
   d) Explain why the radius of zirconium in the +IV oxidation state is so much smaller than its atomic radius.

10. Many properties of the elements are governed by the charge/size ratio. Suggest why the impurity in hafnium oxide is not removed from the zirconium oxide by the chemical manufacturer.

11. a) Suggest the geometry of the arrangement of the groups surrounding each Zr atom in the ion below.

   ![Diagram of Zr ion with surrounding groups]

   b) What is the charge on this ion?

   c) What is the coordination number of each Zr atom in the bridged structure?
12. Naturally-occurring zirconium consists of the following isotopes:

\[
\begin{align*}
\text{\(^{90}\text{Zr}\)} & \text{51.5 per cent} \\
\text{\(^{91}\text{Zr}\)} & \text{11.2 per cent} \\
\text{\(^{92}\text{Zr}\)} & \text{17.1 per cent} \\
\text{\(^{94}\text{Zr}\)} & \text{17.4 per cent} \\
\text{\(^{96}\text{Zr}\)} & \text{2.8 per cent}
\end{align*}
\]

Use these figures to calculate the relative atomic mass of zirconium to three significant figures.