

# The industrial uses of zircon and zirconia, and the radiological consequences of these uses<sup>1</sup>

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**Abstract.** This paper reviews the industrial uses of the natural mineral zircon and the zirconia derived from it. Brief reference is made to the natural mineral baddeleyite, but since it is a minor source of zirconium it is not discussed at length. The annual world market for zircon is around 1 million t and its main uses are in ceramics, refractories, foundry materials, chemicals and abrasives. More specialized uses are in glass, electronics, pigments and catalysts and for the production of zirconium metal. The paper reviews the processes used in these industry sectors, and the products made from each of them. In each case the radiation exposures to workers and the public from these industrial processes are considered. The potential exposure to workers and the public from the products of each of these industrial sectors is discussed, together with a positioning of this exposure in terms of international regulatory standards. In order to do this, a review of the current status of international standards, as applicable to zircon and zirconia, is included. The paper also covers the more generic issues such as milling, transportation and waste disposal, as applied to these industries. The paper shows that 23% of zircon and zirconia users should be outside the scope of regulation and that the radiological impact associated with a further 54% is sufficiently low to allow such users to be exempted from regulation. The remaining 23% of users could become subject to some level of regulatory control.

## 1. Introduction

The paper presents an overview of the zircon and zirconia industries including the raw materials and the product uses. The legislation which appears to be relevant for these industry sectors is reviewed and, for the purposes of this paper, summarized into a set of simplified guidelines. The remainder of the paper reviews the preparation of milled zircon and zirconia, an overview of the main uses of zircon and zirconia and a consideration of the transport issues around these materials. During the review of the uses, emphasis is placed on the process for manufacturing specific products, the exposure pathways and doses anticipated from those pathways, a consideration of the waste disposal issues and, using the simplified guidelines, the likely degree of regulation that may be required in each industry sector.

## 2. Overview of the industry

### 2.1. Zircon

Zircon occurs most commonly around the globe in beach placers or dune deposits. The distribution of the reserves of zircon is shown in Table 1, which shows that the known reserves have increased from 37 million t in 2002 to 54 million t in 2005. Most of these reserves are in Australia and southern Africa. Table 2 shows the global production of zircon, again comparing the years 2002 and 2005. Global production of zircon is around 1.1 million t/a, largely from Australia and South Africa. In contrast, Table 3 shows the main consumer countries of zircon and it is apparent that the bulk of the mineral is used in Europe and the Far East. Consequently transport becomes an essential element in this global resource market and is dealt with separately later in the paper. Of note is the significant increase in the Chinese consumption of zircon, a pattern which is repeated across many other commodity groups. Table 4 shows that the most important use of zircon is in the ceramics industry. Within this industry the production of ceramic tiles and sanitary ware is the main growth area. There have been changes in the usage pattern

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between 2002 and 2005 with a decrease in foundry and refractory uses and an increase in the production of zirconia, zirconium chemicals and ceramics.

TABLE 1. RESOURCES OF ZIRCON BY COUNTRY (courtesy: TZ Minerals International, 2005)

	Resources (million t)	
	2002	2005
South Africa	14	11
Australia	9.1	20
Ukraine	4	5
United States of America	3.4	6
India	3.4	3
Mozambique	—	6
Madagascar	—	3
Rest of the world	3.6	—
Total	37	54

TABLE 2. PRODUCTION OF ZIRCON BY COUNTRY (courtesy: TZ Minerals International, 2006)

	Production (kt)	
	2002	2005
Australia	438	437
South Africa	420	398
USA	70	164
Ukraine	35	32
India	18	23
Brazil	18	26
China	—	35
Rest of the world	134	70
Total	1132	1185

TABLE 3. CONSUMPTION OF ZIRCON BY REGION (courtesy: TZ Minerals International, 2006)

	Relative consumption	
	2002	2005
Europe	36%	35%
China	20%	26%
North America	14%	13%
Asia–Pacific	14%	15%
Japan	7%	5%
Rest of the world	9%	6%

TABLE 4. COMMERCIAL USES OF ZIRCON (courtesy: TZ Minerals International, 2006)

	Relative consumption	
	2002	2005
Ceramics	49%	54%
Refractories	16%	14%
Foundry sands and mould washes	17%	13%
Chemicals and zirconia	9%	12%
Television glass	8%	4%
Other	1%	3%

### *Zircon and radioactivity*

All zircon contains uranium and thorium in the crystal lattice. These primordial radionuclides were added to the zircon structure during the crystallization of the zircon in molten rock. Being a very stable mineral, zircon is used as a ‘geothermometer’ and it has been shown that many commercial zircons are of great geological age — of the order of 500–1000 million years. The radionuclides added during crystallization have decayed over time to their current levels, which for most commercial zircons would be about 250–350 ppm uranium, and about 100–200 ppm thorium. Some zircons contain higher levels of thorium but these are often due to the presence of separate grains of the thorium-bearing mineral monazite. The stability of the zircon structure has been demonstrated by the low values of radon emanation fraction measured and the ability of zircon to retain  $^{210}\text{Po}$  within its structure up to temperatures of about 1200°C. The crystal structure of zircon can be destroyed by very high temperatures and chemical attack. Once the structure is destroyed the contained radionuclides are liberated and their subsequent distribution depends on the processes being used. Generally the decay chains in most zircons are in secular equilibrium.

### **2.2. Zirconia**

Naturally occurring zirconia is called baddeleyite and occurs in igneous rocks such as carbonatite. South Africa was the largest producer of baddeleyite until 2002, but these production facilities have now closed down and the only commercial source of this mineral is the Kola Peninsula region of the Russian Federation. Most of the zirconia now available is manufactured from zircon (34 000 t/a), with the natural supply from the Russian Federation being relatively small (6000 t/a). Table 5 shows the uses of zirconia — the main uses are in refractories and ceramic pigments, with the ceramic pigment sector having shown a significant increase between 2002 and 2005.

### *Zirconia and radioactivity*

In a similar manner to zircon, the baddeleyite received its content of radionuclides during crystallization from the molten rock. Unlike zircon, however, the baddeleyite may not be in secular equilibrium owing to modifications occurring in the geological environment. The activity concentrations of  $^{238}\text{U}$  and  $^{232}\text{Th}$  in baddeleyite formerly originating from South Africa were each about 9–10 Bq/g. In contrast, the activity concentration of  $^{238}\text{U}$  in baddeleyite originating from the Russian Federation is about 3 Bq/g.

### **3. Simplified guidelines for evaluating the regulatory implications for the zircon and zirconia industries**

There is a considerable degree of variability in national regulatory standards affecting NORM. This causes some confusion for the operators and traders in this industry. In order to conduct this review, national regulatory standards have not been considered, but rather the standards established by the International Atomic Energy Agency (IAEA) and the European Union (EU).

TABLE 5. COMMERCIAL USES OF ZIRCONIA (courtesy: TZ Minerals International, 2006)

	Relative consumption	
	2002	2005
Refractories	42%	39%
Ceramic pigments	22%	33%
Advanced ceramics and catalysts	6%	12%
Abrasives	10%	6%
Electronics	6%	6%
Oxygen sensors	2%	2%
Glass and gemstones	2%	1%
Other	10%	1%

The following publications were used as reference sources for the development of the simplified guidelines described below:

- The IAEA International Basic Safety Standards [1]
- The IAEA Transport Regulations [2]
- IAEA Safety Guide on Exemption, Exclusion and Clearance [3]
- EU Report Radiation Protection 122 *Practical use of the concepts of clearance and exemption* [4].

Based on these documents, the following simplified guidelines have been formulated for the purpose of establishing, later in the paper, the likely regulatory implications for the zircon and zirconia industries:

1. An occupationally exposed worker is one who receives an annual effective dose exceeding 1 mSv;
2. A supervised area is one in which a worker may receive an annual effective dose not exceeding 6 mSv;
3. A controlled area is one in which a worker may receive an annual effective dose exceeding 6 mSv;
4. The action level for radon in workplaces is 500 Bq/m<sup>3</sup>;
5. The action level for radon in homes is 200 Bq/m<sup>3</sup>;
6. The dose limit for a member of the public is 1 mSv from all sources;
7. The dose constraint for a member of the public is 0.3 mSv from a single source;
8. The regulator must be notified if the activity concentration of any material exceeds 1 Bq/g;
9. The exemption and clearance level for NORM is an annual effective dose of 0.3 mSv;
10. For NORM to be exempt from the Transport Regulations, the sum of the <sup>238</sup>U and <sup>232</sup>Th activity concentrations must be less than 10 Bq/g.

In order to review the possible regulatory impacts of the different zircon and zirconia uses, the concept of the graded approach regulation, as established in the IAEA standards, was used as the basis for formulating the following simplified guidelines on levels of regulation:

1. Notification is required if the activity concentration of any <sup>238</sup>U or <sup>232</sup>Th series radionuclide in material is above 1 Bq/g.
2. Exemption may be granted if the annual effective dose is less than 1 mSv for workers and 0.3 mSv for members of the public.

3. Registration of a work activity is required if the annual effective dose received by a worker exceeds 1 mSv.
4. Licensing of a work activity is required if the annual effective dose received by a worker exceeds 6 mSv.

The development of these simplified guidelines allows the uses of zircon and zirconia to be reviewed against a consistent benchmark. The actual situation may vary depending on regulatory preferences etc.

## **4. Processing of materials**

### **4.1. Milling of zircon**

This processing step is used by more than 70% of zircon users, which means that more than 700 000 t of zircon is milled each year in preparation for other processing steps. There are 3 forms of milled zircon in common use, each defined by the particle size. Zircon flour occurs as a 95% ‘minus 75µm’ product or a 95% ‘minus 45 µm’ product. Micronized zircon is generally a 95% ‘minus 5 µm’ product. The flour products are commonly prepared by the use of air swept ball mills fitted with classifiers and baghouses for dust collection. In contrast, micronized zircon is made by a wet milling process using vibro-energy or stirred ball mills. The main exposure pathways from this process are external exposures from storage of raw materials and products, inhalation exposures from plant leaks, bagging operations and process cleanups. Radon exposure is not generally significant as long as storage areas are well ventilated. Typical annual effective doses received by workers in milling plants are approximately 300 µSv from external radiation and 500 µSv from dust inhalation, giving a total of less than 1 mSv. This is dependent however on good operation of the facility to ensure that dust control is maintained. Waste disposal issues are minimized by the high value of the product which encourages recycling. Any waste that cannot be recycled is mixed with damp sand or concrete prior to disposal in a landfill facility. The annual effective dose received by a member of the public from milling operations is unlikely to exceed about 250 µSv if dust control is responsibly managed.

The regulatory implications of zircon milling, therefore, would be the submission of a notification to the regulatory body. Well managed operations could be exempted, but because of the possibility of poor management, registration may be appropriate.

### **4.2. Manufacture of zirconia**

Zirconia has three crystal structures with different temperature stability ranges. The monoclinic phase is stable up to 1200°C, at which point it changes to the tetragonal phase and then at 2300°C to the cubic phase. Dissociation occurs at 2680°C. This change in phase causes volume changes which diminish the usefulness of zirconia in high temperature applications. However the crystal structure can be stabilized by the addition of oxides of elements such as magnesium, calcium or yttrium. The degree of stabilization can also be varied to produce partially or fully stabilized zirconia. There are two process routes to make zirconia — the thermal process and the chemical process.

#### *4.2.1. Thermal process*

In this process zircon is melted with coke at 2800°C in an electric arc furnace. The carbon reduces the zircon to zirconia and silicon monoxide. Silicon monoxide, being unstable, is rapidly oxidized to silica which comes off the process as a silica fume. Stabilizing elements are added to the melt to produce the desired composition. The molten product is tapped from the furnace, cast into blocks and crushed to the desired particle size range.

Typical radionuclide activity concentrations in this process are 3–4.5 Bq/g for <sup>238</sup>U in the raw zircon, 4.5–6.8 Bq/g for <sup>238</sup>U in the zirconia and about 6 Bq/g for <sup>226</sup>Ra in the silica fume. The high temperatures used in this process destroy the crystal structure and allow the more volatile elements to be partially removed into the silica fume. Consequently the fume may be enriched in <sup>226</sup>Ra, <sup>210</sup>Po and <sup>210</sup>Pb. The zirconia phase

retains the high boiling-point elements such as uranium and thorium. Exposure pathways in this process are therefore (a) external radiation from the raw material, from product storage and from maintenance of the silica fume collector systems and (b) inhalation exposure from silica fume and zirconia dust during the milling and bagging operations. Radon exposure is usually insignificant with well ventilated storage. Typical annual effective doses received by workers in a thermal zirconia plant are 70–260  $\mu\text{Sv}$  from external exposure and 600–3000  $\mu\text{Sv}$  from dust inhalation, giving a total annual effective dose of 700–3100  $\mu\text{Sv}$ .

Waste disposal issues in these plants are related to the silica fume, if not used as a byproduct, and contaminated scrap from fume collection systems. Most internally generated wastes related to zircon or zirconia are recycled internally.

The operators of thermal zirconia plants should notify their regulatory bodies since both the product and the raw material are above 1 Bq/g. Since the annual effective dose received by a worker can exceed 1 mSv, the thermal zirconia process will probably require registration.

#### 4.2.2. Chemical process

There are three possible chemical process routes to zirconia. These may be subdivided into two broad groups — those that require dissociation of the zircon and those that do not. The route not requiring dissociation entails caustic soda fusion of zircon at 700°C, producing sodium zirconate. The zirconate is then dissolved in hydrochloric acid to form zirconium oxychloride, better known as ZOC. The ZOC may be converted into zirconia by calcination or by dissolution and hydroxide precipitation. Zircon dissociates into  $\text{ZrO}_2$  and  $\text{SiO}_2$  at temperatures above 1800°C. Following this step, the dissociated material may be treated with either caustic soda or acid. The alkali route dissolves the silica leaving zirconia which is then calcined, while the acid route produces a soluble zirconium salt which is later precipitated with alkali to obtain the oxide.

The chemical process also destroys the zircon crystal structure and liberates the radionuclides. The pathway followed by these radionuclides depends on which process is used, but generally the zirconia produced from these processes is greatly reduced in radioactivity. The radionuclides removed from the zircon or zirconia are contained in the process effluents which are usually neutralized and disposed of at a controlled site. The activity concentration of  $^{238}\text{U}$  is 3–4.5 Bq/g in the raw material, <0.1 Bq/g in the zirconia, 1–2 Bq/g in the process waste streams and up to 5000 Bq/g in tank residues. Since the processing is carried out in the liquid phase, the presence of radioactive scale is a risk. Exposure pathways for the process are external exposures from raw materials, pipe scales, tank residues and effluent streams. Typical annual effective doses received by workers in a chemical zirconia plant are 500–1000  $\mu\text{Sv}$ .

The main area of focus for this process route to zirconia is waste disposal, since most of the radionuclides are removed from the process in the effluents. Liquid effluents are neutralized and the precipitate is placed with any solid process wastes in a disposal dam. Authorization is needed for these disposal dams. The need for contaminated scrap to be controlled is also an issue.

The annual effective dose received by a worker in the chemical zirconia process is usually less than 1 mSv. However, because of the possibility of reaching the 1 mSv level and also because of the potential public exposure from radionuclide-containing wastes, it is likely that these plants would require registration.

## 5. Industrial uses of zircon and zirconia

### 5.1. Ceramics

The ceramics field is very diverse and includes such products as glazed tiles, porcelain tiles, sanitary ware such as baths and wash basins, frits, ceramic pigments and engineering ceramics. The main application in the ceramics field is in glazed tiles and sanitary ware. In this application the ceramic has a two-piece body — a clay based ceramic body is covered with a silicate/borate glaze to provide waterproofing, durability and decoration. Zircon is added to the glaze for opacification and to provide a white colour. The zircon

may be added in the milled form as micronized zircon or as a frit. The concentration of milled zircon in the glaze is up to 20%.

Frits are ceramic glasses containing silica and boric acid and are manufactured by melting all constituents together and then quenching in water, followed by milling. The composition of the frit is controlled to the needs of the application but the use of a frit allows a water soluble constituent to be added to the glaze and be converted into an insoluble form. Frit composition is set to control the vitrification point of the glaze. By adding the zircon in a frit form the eventual particle size of the zircon crystallites in the final glaze is controlled to the optimum for light reflection and maximum opacification. The zircon content of frits is usually 10–20%. The firing temperature for glazed ceramics is of about 1100–1270°C.

In contrast to the glazed ceramics, porcelains have a one-piece ceramic body; however they may also be glazed for decorative purposes. Porcelain ceramic tiles are more resistant to wear than the glazed variety and they are composed of clays, quartz, feldspars and nepheline syenite together with zircon. In this application the zircon is used in the milled form at concentrations of up to 15%.

Ceramic pigments are manufactured by mixing zirconia, quartz, sodium fluoride and an appropriate cation. The mixture is fired, with a controlled ramp-up of temperature to 900°C, followed by a soak time. After firing, the product is milled. The colours available vary with the cation added, with iron producing pink, vanadium 4+ producing blue and vanadium 3+ producing yellow.

There are many ‘high-tech’ uses for zirconia in the engineering field such as coatings, grinding media and cutting tools. Zirconia coatings are applied by plasma spraying, while grinding media are manufactured by high pressure forming and sintering. Zirconia contents are 60–95%. Cutting tools are made by fusion of zirconia with alumina, with a ZrO<sub>2</sub> content of 5–10%.

The exposure pathways are very similar for all of the above applications in the ceramics field. The clays and zircon contribute <sup>238</sup>U, while the feldspars and syenites contribute <sup>40</sup>K. External exposure may arise from raw material storage and materials handling, while inhalation exposure may arise from mixing and blending, or from firing of products. For occupational exposure, the manufacture of ceramics leads to an annual effective dose of 30–200 µSv from external radiation and 10–400 µSv from inhalation, with a total annual effective dose of 10–500 µSv. Public exposure pathways occur with glazed and porcelain ceramics where the dominant pathway is external exposure. Radon in homes is also a possible pathway for these applications. The typical annual effective dose received by a member of the public from glazed ceramics amounts to 7–50 µSv from external radiation, together with an increase of 3–5 Bq/m<sup>3</sup> in indoor radon concentration. In contrast, porcelain tiles give rise to an annual effective dose of 3–150 µSv from external radiation and an increase in radon concentration of 10–46 Bq/m<sup>3</sup>. Frits, ceramic pigments and engineering ceramics are used only in industrial applications, so do not result in any significant public exposure pathways.

Wastes related to raw materials are recycled internally and a typical waste from a ceramic plant has an activity concentration of about 0.6 Bq/g, while waste glaze slurry has an activity concentration of less than 2 Bq/g. There are no processes in the ceramic industries for enhancing the radionuclide levels above the natural levels in the zircon or the zirconia.

The ceramic industry could be a candidate for a generic exemption from regulation since the annual effective dose received by a worker is less than 1 mSv and that received by a member of the public from the use of the products is of the order of 100 µSv.

## **5.2. Refractories**

Refractories are materials that are designed to maintain strength, dimensional stability and chemical resistance at high temperature. They are manufactured in the form of bricks, fibres, nozzles, slide gates, valves and grouts. One of the largest uses of zircon and zirconia in refractories is in the glass industry where the linings of glass furnaces are made from a combination of zircon and zirconia bricks. The zircon bricks for glass furnaces contain typically 30–40 % zircon. Zirconia is commonly used for nozzles, slide

gates, filters, and ceramic linings, where the zirconia content approaches 94%. Refractories are typically made from alumina, magnesia, clays, binders and zircon or zirconia. There are two methods of fabrication: (a) mixing of the ingredients, pressing into the desired shapes, drying and kiln firing and (b) mixing of ingredients, melting in a furnace and casting the molten mass into the desired shapes.

The exposure pathways in such industries are external exposure from raw materials and products, inhalation exposure from mixing and blending of components and final shaping of products, especially where this is done by grinding. Inhalation exposure can also occur from furnace dusts where enrichment in polonium and lead can occur to levels of 20–30 Bq/g. The activity concentration of  $^{238}\text{U}$  in refractory products ranges from about 2.5 Bq/g for glass refractories to about 5 Bq/g for the more specialized zirconia products. This can result in external exposure pathways during the use of these products, plus a potential for inhalation exposure during the demolition of furnaces. Annual effective doses received by workers during the manufacture of refractories have been assessed to be less than 600  $\mu\text{Sv}$  from external radiation and 10–200  $\mu\text{Sv}$  from inhalation of dust, with a total annual effective dose of less than 800  $\mu\text{Sv}$ . The use of the refractory products also needs attention as dust control is needed. The type of dust control that would be required for normal occupational health protection in such work should be sufficient. The restriction of dust exposures to normal permitted levels will also keep inhalation of radionuclides under control.

Most wastes arising from the manufacture of refractories are recycled internally, but waste refractories themselves are usually buried in landfill facilities. Used refractory bricks may be contaminated with non-radioactive substances such as heavy metals and the disposal of these bricks is governed more by these substances than by the radionuclide content. Depending on the furnace application, used refractory bricks may have to be sent to a hazardous waste site. Annual effective doses arising from the burial of waste refractories at landfill sites have been assessed at a few microsieverts.

Refractory manufacturers should notify their regulatory bodies as the activity concentration in their raw material is above 1 Bq/g. The annual effective dose received by a worker is generally less than 1 mSv and the dose received by a member of the public is insignificant because refractory items are for industrial use only. The refractory industry could be a case for exemption from regulation but the regulatory body would probably need to be convinced on a case by case basis.

### **5.3. Foundry uses**

Zircon is used in the preparation of moulds for the casting of metals. These moulds are generally made of quartz sand and lined with zircon sand. The refractory nature of the zircon provides temperature resistance and the ability to make more precise castings. In this application the zircon content of a sand mould would be 10–30%. A related application uses a mould wash consisting of a slurry of various minerals including zircon where the ingredients are milled prior to slurring. The sand moulds are sprayed with the mould wash to impart a refractory surface layer to the mould. In this form the content of zircon in the mould wash would be in the range 60–70%. The most precise form of metal casting is achieved by the investment casting process where a wax replica is made of the article to be cast. This wax replica is coated with a slurry containing zircon in the milled form. After several applications of the slurry with drying of each individual coat, the wax replica becomes covered with a shell of refractory material. Firing of the shell hardens the shell and removes the wax. These shells contain 30–50% zircon.

The main exposure pathways in a foundry are external exposure during handling and storage of the raw material and during handling of the used moulds, and inhalation exposure during the mixing and blending operations and during the mould removal operation. The typical annual effective dose received by a worker in a foundry operation is less than 200  $\mu\text{Sv}$  from external exposure and less than 300  $\mu\text{Sv}$  from inhalation, with a total annual effective dose of less than 500  $\mu\text{Sv}$ .

Used moulding sands are generally recycled within the foundry or reused in the construction industry. Used shells from investment casting are generally disposed of in landfill facilities. The  $^{238}\text{U}$  activity

concentration in the wastes from foundries is in the range of 0.9–1.3 Bq/g. The annual effective dose received by a member of the public from such disposal activities has been estimated to be about 100  $\mu$ Sv.

Foundry operators should notify their regulatory bodies because of the activity of the raw materials, but the foundry operations could receive a generic exemption due to the low doses received in this industry sector and the low potential exposures to the public from disposal operations.

#### **5.4. The glass industry**

Zircon is added to the glass used in the faceplates of cathode ray tubes used in televisions and computer monitors. The purpose of this addition is to absorb the X rays emitted by the electron gun in the tube and to increase the refractive index of the glass. The zircon content is in the range 3–5%. Zircon is also added to the glass used in LCD and plasma displays but at a concentration of 1–2%. The zircon is added in the flour form to the glass making ingredients.

The exposure pathways in this industry are external exposures from raw material storage and inhalation exposure from handling of zircon flour. The annual effective dose received by a worker in a CRT manufacturing facility is less than 300  $\mu$ Sv from external exposure and less than 100  $\mu$ Sv from the inhalation of dust. The increase in radon concentration is insignificant and the total annual effective dose is less than 400  $\mu$ Sv. In terms of doses received by the public from the use of such equipment, the exposure pathways would be by external exposure from the faceplates of the displays. Since the  $^{238}\text{U}$  activity concentration in a CRT face plate is less than 0.2 Bq/g, the dose received by a member of the public will be insignificant.

Recycling is common in the manufacturing part of the glass industry, but post-use recycling is not practised due to the lack of quality control that this introduces to the product. However, owing to the very low activity concentration, the product would be suitable for disposal in a landfill facility if no other route could be found. The WEEE Directive in Europe may have an influence on the disposal of such equipment.

Operators in this field should notify the regulatory body because the activity concentration in the raw material is above 1 Bq/g, but since the annual effective dose received by a worker is well below 1 mSv and since there are no significant pathways for public exposure, a generic exemption could be considered for this application.

#### **5.5. Zirconium chemicals and zirconium metal**

Zirconium chemicals are used mainly in paint driers, paper coatings and antiperspirants. They are also used in a diversity of other applications such as leather tanning, fungicides, grain refiners and flame proofing.

Zirconium chemical are commonly produced from the oxychloride (ZOC). This process intermediate may either be produced at the site of the chemicals manufacture or the producer may purchase the ZOC directly. The process for the manufacture of ZOC is described in Section 4.2.2.

Zirconium metal is used in the nuclear industry as the containment for nuclear fuel rods. It is produced from zircon by a carbo-chlorination process at 2000°C, where zirconium tetrachloride is produced. This material is reduced using metallic magnesium to obtain the zirconium metal. The use of zirconium in the fuel cycle also requires the removal of hafnium which is an inherent contaminant of zircon.

The exposure pathways for chemical manufacture depend on whether the operator produces ZOC on site or purchases this material. In the case of ZOC production on site, the pathways are the same as described in Section 4.2.2. If the operator has purchased the ZOC there are no significant pathways for exposure as the starting material has insignificant levels of radionuclides. The exposure pathways for metal manufacture would also be similar to those described in Section 4.2.2, but metal plants may produce radium-bearing sludges which can result in public exposure.

Operators in the ZOC production process and the metal producers would be required to notify the regulatory body owing to the activity of the raw materials, but chemical producers starting with purchased ZOC would probably not be required to notify because the activity of the raw material is less than 1 Bq/g.

### **5.6. Zirconia catalysts**

Zirconia is used as a physical support for other catalysts and as a catalyst in its own right. This application of zirconia requires ultra-pure material and the starting material is one of the zirconium chemicals. The zirconia is precipitated from a solution under carefully controlled conditions and the product is calcined. The properties of the product are controlled by the manner of preparation. Since the activity concentrations in the starting materials are less than 1 Bq/g and no enrichment takes place, the activity concentrations in the catalyst materials are also less than 1 Bq/g. Under these conditions it is unlikely that a catalyst producer would need to notify the regulatory body.

### **5.7. Electronics and solid electrolyte devices**

High purity zirconia is used for specialized electronic applications such as insulators, piezoelectrics, fibre optics and microwave systems. Owing to the purity required, this zirconia is prepared by precipitation from solutions, so is extremely low in radionuclide content and will contain well below 1 Bq/g of radionuclides. Another important use of zirconia utilizes its ability to be an electrolyte in the solid phase. This property is used in the manufacture of oxygen sensors commonly used in the control of combustion equipment, in particular the control of internal combustion engines. The zirconia used for this application is often produced using the thermal route for zirconia production and as a result may contain more than 1 Bq/g of  $^{238}\text{U}$ .

No significant exposure pathways are associated with electronics production. The manufacture of oxygen sensors will involve an external exposure pathway, but these sensors are small and may be exempted from regulatory control on the basis of the total contained activity, in accordance with the exemption levels specified in the IAEA International Basic Safety Standards [1]. These oxygen sensors may have a waste disposal issue in that they may be sufficiently active to trigger a gate monitor. However the total level of contained activity in such devices is very low and burial in a landfill facility is an appropriate method of disposal. Education of waste site operators would be required to avoid unnecessary checking.

Manufacturers of oxygen sensors may be required to notify the regulatory body but exemption should be possible for the manufacture of both the electronic and solid electrolyte devices.

### **5.8. Specialized products**

High purity zirconia is used for hip joints, bone replacements, dental ceramics, gemstones and lasers. The zirconia used in these applications is produced by the precipitation from solutions and has a  $^{238}\text{U}$  activity concentration of less 0.1 Bq/g. No enrichment processes occur in this manufacturing sector and notification should not be required.

### **5.9. Zirconia abrasives**

Zirconia is used in the manufacture of abrasives. These abrasive materials may be used in grinding wheels, sharpening stones and abrasive papers. Abrasives are made by dissolving zirconia in molten alumina. The product is solidified, crushed and sized. The zirconia content of abrasives is typically 25–40%.

The activity concentration in the raw material for this industry will be 4–6 Bq/g, as thermally derived zirconia is usually used in this application. The activity concentration in the abrasive product is 1–2 Bq/g. Exposure pathways will be external from raw material storage and handling, inhalation from the crushing and sizing operations and further inhalation pathways from the use of the grinding wheels. The annual

effective dose received by a worker in an abrasive manufacturing facility has been assessed to be less than 1 mSv.

Raw materials from manufacturing are usually recycled and other waste disposed from this industry is usually buried in a landfill facility, as the materials have low external exposure potential and no dust generating properties.

The potential for inhalation of dust during the use of such products requires good dust control systems. Since the use of this type of abrasive is usually industrial, the maintenance of normal occupational hygiene control is sufficient to keep dust exposure to low levels. However the abrasive manufacturers should notify the regulatory body, owing to the activity concentration in their raw material being above 1 Bq/g. Exemption may be possible for this sector after a risk assessment has confirmed good management practices.

## 6. Transport of zircon, zirconia and their products

The transport of radioactive materials is subject to the requirements of the IAEA Transport Regulations [2]. Materials do not fall within the scope of these regulations if they are natural materials or ores containing naturally occurring radionuclides which are not intended to be processed for the use of these radionuclides provided that the total activity concentration of  $^{238}\text{U}$  and  $^{232}\text{Th}$  (with their decay products in equilibrium) does not exceed 10 Bq/g. All zircon sands and flours are therefore exempt from the Transport Regulations. Dose assessments have been carried out to support this exempt status and the results are shown in Table 6. Most baddeleyite is also exempt, although some of this natural zirconia is above 10 Bq/g and secular equilibrium cannot be assumed. However, baddeleyite from the Russian Federation is usually exempt from the Transport Regulations.

TABLE 6. DOSES ATTRIBUTABLE TO THE TRANSPORT OF ZIRCON

	Annual effective dose ( $\mu\text{Sv}$ )	
	Worker	Member of the public
Zircon sand in bulk	150	10
Zircon flour in bags	500	110

All zircon and zirconia products contain less than 10 Bq/g total activity, but in the strict sense they are not naturally occurring materials. They are however manufactured from NORM. For the purposes of this paper it is assumed that the exemption provided for in the Transport Regulations also covers products made from NORM, and under these conditions all zircon and zirconia products are exempt. This point is not made entirely clear in the Transport Regulations and it would be useful for operators if clarity could be provided on this issue.

## 7. Conclusions

In analyzing the information collated above for all the industrial uses of zircon and zirconia, it is apparent that 77% of current operators would need to notify their regulatory bodies because the activity concentrations in their raw materials exceeds 1 Bq/g. Conversely 23% of operators would not need to notify the regulator of their activities. The 77% for whom notification is required can be further split into 54% of operators that should be eligible for exemption and 23% that will probably need to be registered. It is of note that, from the above analysis, no operator should require to be licensed.

A more in-depth look at the industry sectors requiring registration shows that they consist of the following:

1. The zircon millers who annually process some 700 000 t of zircon and whose operations involve a potential inhalation hazard to workers.

2. The zirconia producers who annually treat about 50 000 t of zircon and whose operations involve a potential external radiation and inhalation hazard to workers, as well as a potential for public exposure.
3. The zirconium metal producers who annually process about 20 000 t of zircon and whose operations involve a potential inhalation hazard to workers, as well as a potential for public exposure.

To put these industries in perspective it is useful to compare their exposures, as shown in Table 7. While the annual effective doses received by workers in these industries can exceed the threshold level of 1 mSv for treating the exposure as occupational, the amount by which the threshold is exceeded is marginal. Furthermore, the doses do not approach levels where licensing would be required.

TABLE 7. DOSES RECEIVED BY WORKERS IN INDUSTRY SECTORS THAT MAY REQUIRE REGISTRATION

	Material handled (t)	Occupational exposure: annual effective dose (mSv)	Public exposure
Zircon milling	700 000	~1	—
Thermal zirconia production	50 000 (thermal + chemical)	~3	—
Chemical zirconia production		~1	Potential from waste disposal
Zirconium metal production	20 000	~1	Potential from waste disposal

It can be concluded that, while low levels of radiation exposure are potentially associated with the zircon and zirconia industries, the high price of the materials provides a financial incentive for the operators to maintain good control. Around 80% of the industry sectors are amenable to exemption from regulatory control while the other 20%, with good management practices, should require minimal regulatory control.

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