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Radiation Protection and NORM Residue Management in the Zircon and Zirconia Industries

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RADIATION PROTECTION AND
NORM RESIDUE MANAGEMENT
IN THE ZIRCON AND ZIRCONIA INDUSTRIES

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INTERNATIONAL ATOMIC ENERGY AGENCY
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FOREWORD

The Fundamental Safety Principles (IAEA Safety Standards Series No. SF-1), together with the International Basic Safety Standards for Protection against Ionizing Radiation and for the Safety of Radiation Sources (Safety Series No. 115), set out the principles and basic requirements for radiation protection and safety applicable to all activities involving radiation exposure, including exposure to natural sources of radiation. The Safety Guides on Occupational Radiation Protection in the Mining and Processing of Raw Materials (IAEA Safety Standards Series No. RS-G-1.6) and Management of Radioactive Waste from the Mining and Milling of Ores (IAEA Safety Standards Series No. WS-G-1.2) provide guidance on the control of exposure of workers and members of the public to naturally occurring radioactive material (NORM) in industrial activities involving the exploitation of minerals. This guidance applies irrespective of whether the minerals are exploited for their radioactivity content. The zircon and zirconia industries constitute one of several industry sectors for which the radioactivity content of the minerals and raw materials involved is too small to be of commercial value but is large enough to warrant consideration by the regulatory body concerning the possible need to control exposures of workers and members of the public.

This Safety Report has been developed as part of the IAEA's programme to provide for the application of its safety standards in the field of radiation, transport and waste safety. It is a compilation of detailed information on the processes and materials involved in the zircon and zirconia industries and on the radiological considerations that need to be taken into account by the regulatory body when determining the nature and extent of radiation protection measures to be taken. This is consistent with the graded approach to regulation, in terms of which the application of the requirements of the safety standards is commensurate with the characteristics of the practice or source, and with the magnitude and likelihood of the exposures.

CONTENTS

1. INTRODUCTION

1.1. BACKGROUND

The mineral zircon (zirconium silicate) occurs in nature as a constituent of so-called heavy mineral sands and has a wide range of industrial applications accounting for an annual worldwide consumption of well over a million tonnes. It has economic importance as a raw material in its own right and also as a feedstock for the manufacture of zirconia (zirconium dioxide), zirconium chemicals and zirconium metal. Limited quantities of naturally occurring zirconia in the form of the mineral baddeleyite are also used in some industrial applications.

The geological processes that formed zircon and baddeleyite led to the incorporation of radionuclides of natural origin (i.e. those of the uranium and thorium decay series) into the crystal structure. The presence of these radionuclides is not significant enough to be of any commercial value, but creates a possible need to control exposures of workers and members of the public in accordance with the Fundamental Safety Principles [1], the requirements of the International Basic Safety Standards for Protection against Ionizing Radiation and for the Safety of Radiation Sources (the BSS) [2] and the guidance in the relevant Safety Guides [3, 4]. In particular, the activity concentrations of the ^{238}U decay series radionuclides in zircon and zirconia are such that, in terms of the Safety Guide on Application of the Concepts of Exclusion, Exemption and Clearance [5], these materials would be among those recommended for inclusion within the scope of regulation and thus within the definition of naturally occurring radioactive material (NORM).

The Safety Report on Assessing the Need for Radiation Protection Measures in Work Involving Minerals and Raw Materials [6] confirms that the zircon and zirconia industries constitute one of several minerals related industry sectors likely to warrant radiation protection measures through a system of regulatory control. That Safety Report emphasizes the particular relevance of the graded approach to regulation to ensure that any radiation protection measures applied to the industrial processes involved and to the management of NORM residues arising from those processes are commensurate with the characteristics of the operation and with the magnitude and likelihood of the exposures. This implies the need for a thorough understanding of all the processes, the process materials, the associated radiological risks to workers and members of the public and the practicalities of any protective measures that might need to be considered.

1.2. OBJECTIVE

The objective of this Safety Report is to provide detailed information that will assist regulatory bodies in implementing a graded regulatory approach to the protection of workers and members of the public against exposures associated with the industrial applications of zircon and zirconia. This information will also serve as the basis for creating a common understanding between regulatory bodies and other stakeholders such as operators, workers and their representatives, as well as health, safety and environmental professionals, of the radiological aspects of the various processes involved and the ways in which these aspects can be addressed appropriately and effectively.

1.3. SCOPE

This report provides detailed information on all the major industrial applications of zircon and zirconia, the processes involved, the management of NORM residues arising from such processes, the radiological characteristics of the process materials (feedstocks, intermediate products, final products, by-products and residues), exposure pathways to workers and members of the public, exposure levels, annual effective doses and examples of good practices with respect to monitoring techniques and practical measures to reduce doses. Each process or industrial application is described in some detail to enable those less familiar with such processes or applications to gain an appreciation of the practicalities of the relevant exposure situations and of the measures for dealing with them in an appropriate manner. The available information is used as the basis for assessing the regulatory implications in terms of the standards for radiation protection and management of radioactive waste, including, where appropriate, the requirements contained in the Regulations for the Safe Transport of Radioactive Material (hereinafter referred to as the Transport Regulations) [7]. Particular attention is given to situations where existing occupational health and safety (OHS) regulation or environmental protection regulation may be effective in avoiding or minimizing the need for additional regulatory controls aimed specifically at the control of radiation exposure.

While much of the information provided in this report has been obtained from published literature, new information has been obtained from company data contributed by industry experts engaged in the drafting of the report. An attempt has been made to include all available information of relevance, but data in some areas are still lacking. In such areas, further investigations may be necessary.

The mining of heavy mineral sands and the processes by which the various heavy minerals of commercial interest, including zircon, are concentrated and separated represent a sequence of operations common to other industrial activities such as the production of titanium dioxide pigments and the extraction of thorium and rare earth elements from monazite. For this reason, such operations are not included within the scope of this report, but a brief overview is provided in Annex I. The scope of this report also does not include the remediation of areas affected by NORM residues from past activities in the zircon and zirconia industries, although the report may be of interest to those involved in such remedial actions.

1.4. STRUCTURE

Following this introductory section, Section 2 provides an overview of the zircon and zirconia industries. Section 3 summarizes the application of the standards to industrial activities involving exposure to natural sources and examines the general regulatory implications for zirconium minerals, either when handled as raw material or when contained in residues, in the absence of any physical or chemical processing. The remaining sections address specific processes and applications involving zircon and/or zirconia that introduce new or modified exposure pathways to workers and members of the public. Section 4 deals with the milling of zircon sand to smaller particle sizes. Sections 5 and 6 address the use of zircon in the ceramics and foundry industries, respectively. The next two sections deal with the manufacture of zirconia from zirconium minerals, either by high temperature fusion with carbon (Section 7) or by chemical dissolution (Section 8), with the latter leading to possible further processing to produce zirconium chemicals. The high temperature chlorination of zircon produces zirconium tetrachloride and, after further processing, zirconium metal. These processes are dealt with in Section 9. Section 10 addresses the manufacture and use of zirconium-containing refractories using zircon or fused zirconia as raw material. The final two sections cover some additional processes and applications for which the radiological implications need to be considered but are likely to be of lesser significance, namely the use of zircon as a source of zirconia in glass (Section 11) and the use of fused zirconia in applications other than refractories (Section 12). The report is supplemented by three appendices, the first providing information on the radionuclides in the ^{238}U and ^{232}Th decay series, the second documenting the available data on radionuclide concentrations in zirconium minerals and the third summarizing the results of dose assessments for the transport of zirconium minerals. Finally, some additional information is provided in two

annexes, one summarizing the mining and processing of heavy mineral sands and the other providing an example of monitoring methods for assessing occupational exposure in zircon milling plants.

2. OVERVIEW OF THE ZIRCON AND ZIRCONIA INDUSTRIES

2.1. INTRODUCTION

Zirconium is the 18th most abundant element on Earth — three times more abundant than copper. It occurs in nature as the free oxide ZrO_2 (baddeleyite), but most commonly as zircon, a compound oxide with silica having the chemical formula $ZrO_2 \cdot SiO_2$ or $ZrSiO_4$ (zirconium silicate). Zirconium in ores is associated with small amounts of the chemically similar element hafnium, with the relative hafnium content being 1–3% (typically 2%).

Information on zirconium minerals resources is presented in Table 1, and details of worldwide mining output (in the form of zircon unless otherwise stated) are given in Table 2. Most commercial zirconium minerals originate from Australia, South Africa and the United States of America. Zircon is by far the largest source of zirconium minerals used in industrial applications. Baddeleyite is an alternative source of zirconium mineral, but occurs in a very

TABLE 1. WORLD RESOURCES OF ZIRCONIUM MINERALS [8]

	Reserves (t ZrO_2)	Contribution to total (%)
South Africa	14 000 000	37.3
Australia	9 100 000	24.3
Ukraine	4 000 000	10.7
USA	3 400 000	9.1
India	3 400 000	9.1
Brazil	2 200 000	5.9
China	500 000	1.3
Other countries	900 000	2.4
Total (rounded)	38 000 000	100

TABLE 2. WORLDWIDE PRODUCTION OF ZIRCONIUM MINERALS (ANNUAL PRODUCTION, AS REPORTED FROM TWO DATA SOURCES)

	Data source: United Kingdom[a]		Data source: USA[b]	
	Production (t)	Contribution (%)	Production (t)	Contribution (%)
Australia	439 000	37.0	450 000	39.1
South Africa	379 000[c]	31.9	305 000	26.5
USA	172 000	14.5	W[d]	W
Vietnam	60 000[e]	5.1		
Ukraine	35 000[c]	2.9	35 000	3.0
Brazil[f]	34 855	2.9	35 000	3.0
India	22 000	1.9	20 000	1.7
China	20 000[c]	1.7	15 000	1.3
Gambia	12 000[c]	1.0		
Malaysia	6 686	0.6		
Russian Federation[g]	6 500[c]	0.5	6 500[h]	0.6
Indonesia	200[c]	0.02		
Total (rounded)	1 187 000	100	1 150 000[c, h]	100

[a] Production in 2004 [9].
[b] Estimated 2005 production (rounded), from Ref. [8] unless otherwise stated. Country data do not add to the total shown.
[c] Reported in Ref. [9] as being an estimate.
[d] W: reported in Ref. [8] as having been withheld to avoid disclosing company proprietary data.
[e] Reported in Ref. [9] as being a conservative estimate, based on exports.
[f] Including caldasite.
[g] Production in the form of baddeleyite concentrate averaging 98% ZrO_2.
[h] Production in 2004 [10].

limited number of geological environments and is currently produced only in the Kovdor region of the Russian Federation. Caldasite, a mixture of baddeleyite and zircon, is also a source of zirconium minerals through its occurrence in Brazil.

A simplified, schematic representation of the various processes and products associated with the industrial applications of zircon and zirconia is given in Fig. 1.
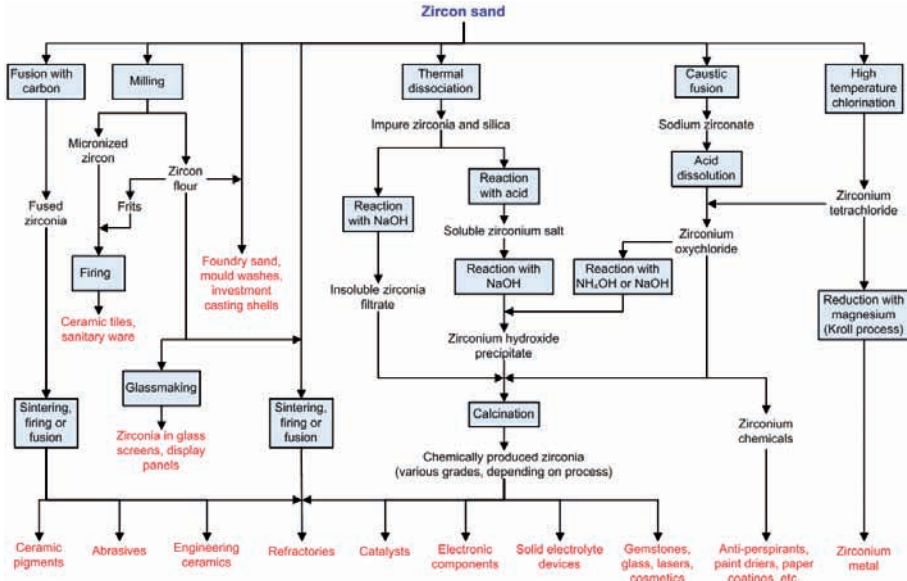
FIG. 1. Processes and products associated with zircon and zirconia.

2.2. ZIRCON

2.2.1. Sources

Zircon occurs naturally as a common accessory mineral in igneous environments such as granitic pegmatites and syenite, and also in metamorphic environments such as schists and gneiss. It occurs in the form of square, prismatic crystals or grains, which are usually small and widely distributed within the host rock. In this form (rarely exceeding 1 wt% concentration), zircon is not generally amenable to commercial exploitation. However, weathering processes, together with the tendency for zircon to naturally separate from ordinary silica sand due to its high density,[1] have led to the formation of large secondary deposits of zircon sand in river and beach placers[2]

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[1] Zircon is one of several so-called heavy minerals — these are normally defined as minerals with densities exceeding 3000 kg/m^3. The heavy minerals of major commercial importance are, in addition to zircon, the titanium bearing minerals ilmenite, leucoxene and rutile and the rare earth bearing materials monazite and xenotime.

at enhanced concentrations. The zircon in these deposits is usually associated with other heavy minerals such as ilmenite and rutile (both of which are titanium bearing minerals), monazite (a phosphate of rare earth elements and thorium), garnet, staurolite and kyanite. Zircon may also be associated with deposits containing tin or copper.

Since the 1960s, zircon has developed from a low value by-product to an important co-product of the mining and processing of heavy mineral sands for the extraction of the titanium minerals ilmenite and rutile. Heavy mineral sand deposits typically contain 1–10% heavy minerals. These are processed by gravity separation to produce a concentrate containing more than 95% heavy minerals. Zircon, along with other minerals of value, for example ilmenite, rutile and monazite, is separated from the complex mineral mix by magnetic and electrostatic separation processes. These processes can be associated with high concentrations of radionuclides due to the presence of minerals other than zircon, notably monazite, leading to a need for significant radiation protection measures. Once the zircon is separated from these minerals, the absence of these high radionuclide concentrations leads to a much lower radiological risk. In order to focus only on the risks associated with the processing and use of zircon, therefore, the processing of heavy mineral sands up to and including the separation of zircon is not included within the scope of this report. However, for completeness, a brief description of the process is given in Annex I.

Most zircon production is exported in bulk from the country of origin in seagoing bulk carriers, unpackaged. A shipment is typically 1000 t, but may be as high as 10 000 t. When transported by rail or road, zircon may be carried unpackaged in quantities of a few tens of tonnes per conveyance, or may be packaged in 1–2 t bulk bags or on pallets of typically 25 bags, each weighing 40 kg. Palletized zircon is transported as individual pallets or in containers.

2.2.2. Properties

2.2.2.1. Composition

The typical composition of premium grade commercial zircon sand is 66% ZrO_2 (and HfO_2, see Section 2.1), 32% SiO_2, 0.1% TiO_2, 0.5% Al_2O_3 and 0.05% Fe_2O_3. All zircon sand contains radionuclides of natural origin, primarily those in the uranium and thorium decay series (see Appendix I). Although the

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[2] Glacial or alluvial deposits of sand or gravel containing eroded particles of minerals of value.

concentrations of these radionuclides are low, they are significantly higher than those in normal rocks and soil.

2.2.2.2. *Physical and chemical properties*

Zircon has a density of typically 4690 kg/m^3 (range: 4200–4800 kg/m^3). It is a very tough and resistant mineral that has been unaffected by the natural, relatively low temperature processes found on the Earth's surface. Its chemical reactivity is extremely low, its melting point is well over 2000ºC, its refractive index is very high (1.80–1.98) and its hardness is 7–7.5 on the Mohs scale, making it harder than quartz (with a Mohs hardness of 7) but softer than corundum and diamond (with Mohs hardnesses of 9 and 10, respectively).

2.2.2.3. *Particle size*

Commercial zircon sand is reported to have a median diameter of 110–130 μm and a relatively narrow size range, with little material smaller than 75 μm or larger than 250 μm [11]. The typical range of particle diameters is 100–200 μm. For many applications, the particle size of zircon sand needs to be reduced by milling to create intermediate products known as zircon flour and micronized zircon. Since the 1980s, the amount of zircon sand being processed into smaller particle sizes before use has increased significantly, boosted by the strong demand for zircon in this form by the ceramic industry, and more than 70% of all zircon sand is now processed in this way.

2.2.3. Commercial uses

The relative consumption of zircon in different regions of the world is shown in Table 3 [12] and the main uses of zircon are shown in Table 4 [13].

2.2.3.1. *Ceramics*

The use of micronized zircon and zircon flour in ceramic products accounts for almost half of the worldwide consumption of zircon. It is a common opacifying constituent of glazes applied to ceramic tiles and sanitary ware and is also used as an opacifier in porcelain tiles by incorporation directly into the mixture used for forming the body of the tile.

TABLE 3. RELATIVE ZIRCON CONSUMPTION, BY REGION

	Relative consumption (%)
Europe	36
China	20
North America	14
Asia–Pacific	14
Japan	7
Rest of the world	9

2.2.3.2. Foundry sand and mould washes

Zircon sand is finding increasing use in the metal casting industry because of its good refractory properties, chemical stability, low thermal expansion, excellent bonding properties, high thermal conductivity and resistance to metal penetration. Zircon flour is used extensively in refractory mould washes, where the small grain size contributes to the achievement of a high quality casting finish, and in investment casting. However, the high cost of zircon compared with that of silica discourages its use in applications other than those where casting definition and finish are critical and post-casting machining needs to be minimized.

2.2.3.3. Refractories

Refractories are materials designed to maintain strength, dimensional stability and chemical inertness over a wide range of temperatures and are used

TABLE 4. COMMERCIAL APPLICATIONS OF ZIRCON

	Proportion of total (%)
Ceramics	49
Foundry sands and mould washes	17
Refractories	16
Feedstock for production of zirconia and other zirconium compounds	9
Cathode ray tubes	8
Other	1

9

in high temperature industrial applications such as the handling and containment of molten metals and glass. They may be produced in the form of manufactured articles such as bricks, blocks, fibres, nozzles, slide gates and valves or in the form of grouts or slurries. Zircon has good refractory properties because of its resistance to high temperatures and chemical inertness. It is used in refractories either alone or in combination with other material — for example, in some applications zircon–mullite[3] may provide refractory performance comparable with that of zircon, but at a lower cost. Furnace linings and melt ladles made of zircon or zircon blends have longer service lives than those made of more traditional materials. Zircon 'grog', a plastic material comprising zircon sand or flour mixed with a binder, is widely used as an interstitial material in assembling refractory articles or for making repairs.

Notwithstanding these good refractory properties, the use of zircon as a refractory material in its own right, as distinct from its use as a source of zirconia in refractories, is becoming superseded in the more demanding applications by the use of other materials, and its use in manufactured refractory articles is now largely limited to the manufacture of certain types of refractory brick. Zircon refractories used in molten metal flow control applications have largely been replaced by alumina refractories or, in the case of items such as flow control nozzles and slide gates, by fused zirconia refractories. The use of a zircon–pyrophyllite[4] mixture (containing typically 40% ZrO_2) to make refractory bricks for ladle linings has largely been superseded by the use of alumina refractories, due to their better thermal and mechanical properties.

Approximately 50% of the zircon consumed in refractory applications is used in the production of refractories for the glass industry. The solubility of zirconium in molten silicates and silica is very small, making these refractories suitable for use in the hot zones of glass furnaces. Glass industry refractories manufactured using zircon as a raw material include sintered zircon, sintered zircon–mullite and fused cast alumina–zirconia–silica (AZS).

AZS accounts for about 80% of the refractory material used in the glass making industry. Owing to its high alkali corrosion resistance, it is widely used both in glass contact and in non-glass-contact areas. AZS is also used in furnaces in the iron and steel industry. It is suitable for furnace temperatures of up to 1600ºC and has low porosity and excellent resistance to chemical attack by molten glass. It is reported in Ref. [14] that the crystalline phases consist of

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[3] Mullite is an aluminosilicate material ($3Al_2O_3 \cdot SiO_2$), which is generally formed by the high temperature interaction of silica and alumina bearing minerals.

[4] Pyrophyllite is a mineral consisting of aluminium silicate hydroxide ($AlSi_2O_5OH$).

corundum crystals (alpha alumina) and embedded fine baddeleyite, with just under 20 wt% glass matrix filling the space between the crystals. As the ZrO_2 content increases, free zirconia crystals (either in long chains or medium sized nodular shapes) are generated. Two standard grades are used:

(a) One grade, used for glass furnace linings and for monolithic pipe liners resistant to heat and wear, has the composition 49–52 wt% Al_2O_3, 30–33 wt% ZrO_2 and 13–17 wt% SiO_2 [15].

(b) The 'high ZrO_2' grade, typically containing 45–48 wt% Al_2O_3, 39–41% ZrO_2 and 10–13 wt% SiO_2, has a 20–30% higher corrosion resistance and is used for furnace components subject to very severe conditions [14].

2.2.3.4. Production of zirconia and other zirconium compounds

Various processes are used to convert zircon into zirconia and other zirconium compounds:

(a) Fusion of zircon in an electric arc furnace at 2800ºC with coke as a reductant[5] generates, in essentially one process step, a commercial form of zirconia known as fused zirconia.

(b) Higher purity zirconia may be produced by dissociation of zircon into its components zirconia and silica at a temperature of 1800ºC or more, followed by chemical purification of the separated zirconia component.

(c) Reaction of zircon with sodium hydroxide at 700ºC (caustic fusion) followed by dissolution in hydrochloric acid forms zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$), alternatively known as zirconium oxychloride (ZOC), an important water soluble intermediate product used in significant quantities for the manufacture of high purity zirconia and other zirconium chemicals as well being an industrial chemical product in its own right.

(d) Chlorination of zircon at 1200ºC in the presence of carbon produces zirconium tetrachloride, an intermediate product used in significant quantities for the manufacture of zirconium metal by reduction with magnesium. Zirconium tetrachloride is also used for the manufacture of other zirconium chemicals and as an industrial chemical product in its own right.

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[5] A reductant is a substance capable of bringing about the reduction of another substance as it itself is oxidized.

2.2.3.5. Cathode ray tubes and other glass products

Cathode ray tubes (CRTs) are made from alkali–alumina–silicate glass with a typical thickness of at least 5 mm and until recently were incorporated into all colour televisions and computer monitors. In order to absorb X rays, zirconia derived from the addition of zircon to the glass mixture is included as a constituent of the glass that forms the faceplate portion of the CRT, with the projection tube portion being free of zirconia. The worldwide consumption of zircon for CRT manufacture grew from 70 000 t/a in 1997 to 80 000 t/a in 2001 and is expected to reach 100 000 t/a by 2010 [16].

Zircon is also used in the glass substrates of flat panel displays such as liquid crystal displays and plasma display panels. These were developed initially for the thin, light screens needed for notebook computers and other mobile electronic equipment, but are now finding increasing use in computer monitors and flat screen televisions as the technology develops, as production costs decrease and as the demand for large television screens increases (especially with the introduction of digital format television).

Zircon is also used to produce special glasses with high refractive indices and is used as an additive in the production of lead free crystal glassware and optical fibres.

2.3. ZIRCONIA

2.3.1. Sources

Baddeleyite, the only significant natural form of zirconia, occurs in a very limited number of geological environments. Its occurrence in carbonatite rocks in South Africa and the Russian Federation has led to commercial production in these countries. However, production in South Africa ceased in 2002, leaving the Russian Federation as the sole source of supply.

South African baddeleyite, when still in production, was mined in two operations situated near one another. In one operation, baddeleyite was recovered as a by-product of a large opencast copper mine. It was beneficiated by gravity separation of heavy minerals followed by acid leaching and magnetic separation to produce three commercial grades containing 96–99.5% ZrO_2 (and HfO_2). The HfO_2 content was typically 1.5–1.7%. In the other operation, high grade baddeleyite was recovered from commercially exploited phosphate deposits.

Russian baddeleyite from the Kovdor district of the Kola Peninsula is a by-product of iron ore mining. The geology is composed of fosterite, apatite

and magnetite ores with baddeleyite dispersed through magnetite bearing and apatite bearing zones at 0.15% ZrO_2. The product is similar in purity to the highest commercial grade formerly produced in South Africa, but has a lower radioactivity content.

With commercial sources of natural zirconia being very limited, 80–90% of the zirconia used for industrial applications is nowadays manufactured from zircon using the methods outlined in Section 2.2.3.4.

2.3.2.   Properties

Zirconia is characterized by several properties that are important for industrial applications, including high strength, high fracture toughness, excellent wear resistance, high hardness, excellent chemical resistance, good oxygen conductivity and very good refractory properties. Zirconia also possesses properties that are important for the formulation of ceramics with piezoelectric, pyroelectric and dielectric properties in advanced technology applications in the electronics industry.

Zirconia exhibits three well defined crystal structures: the monoclinic, tetragonal and cubic phases. The monoclinic phase is stable up to about 1200ºC, at which point it transforms to the tetragonal phase. The tetragonal phase is stable up to about 2300ºC, at which point a further transformation takes place to the cubic phase. The cubic phase exists up to the melting point of 2680ºC. The monoclinic to tetragonal phase change is accompanied by a rapid volume change of 8%, which reverses on cooling and which limits the usefulness of pure zirconia in dense refractory applications because of the likelihood of structural failure. Due to these phase changes, zirconia in its pure form is known as unstabilized zirconia. A typical composition of unstabilized zirconia used in special ceramic applications demanding high purity is 99% ZrO_2, 0.05% SiO_2, 0.15% TiO_2, 0.01% Fe_2O_3 and 0.02% SO_3 [17].

This disruptive volume change can be avoided by the addition of cubic oxides — normally magnesium, calcium or yttrium oxides — to monoclinic zirconia during manufacture. This produces stabilized zirconia whose structure is a cubic solid solution that has no phase transformation from room temperature up to the melting point. It has a uniform thermal expansion curve and offers good refractory properties. Generally, the addition of more than 16 mol% (8 wt%) CaO, 16 mol% (6 wt%) MgO or 8 mol% (14 wt%) Y_2O_3 into the zirconia structure is needed to form a fully stabilized zirconia.

If the stabilizing oxide is added at a concentration lower than that required for complete stabilization in the cubic phase, a transformation toughened material known as partially stabilized zirconia (PSZ) is formed. This smaller addition of stabilizer to the pure zirconia causes its structure to become

a combination of cubic and tetragonal and/or monoclinic phases at temperatures below 1000ºC (with the tetragonal phase being the dominant one) and pure tetragonal phase above 1000ºC. For this reason, PSZ is also called tetragonal zirconia polycrystal (TZP) or tetragonally stabilized zirconia. Usually, PSZ comprises a minimum of 8 mol% (3 wt%) MgO, 8 mol% (4 wt%) CaO or 3–4 mol% (5–7 wt%) Y_2O_3.

Zirconia is produced in a variety of forms, depending on the type of application [18]:

(a)   High purity unstabilized zirconia in powder form;
(b)   Stabilized grades in powder or 'spray dried ready to press' form, with or without a binder;
(c)   Stabilized grades combined with a polymer;
(d)   Coloured varieties in powder or 'spray dried ready to press' form;
(e)   Granulated.

2.3.3.   Commercial uses

The total annual consumption of zirconia worldwide is about 40 000 t. A breakdown of commercial zirconia applications is shown in Table 5. A variety of production techniques, such as those shown in Table 6, is used for the more specialized applications [18].

TABLE 5. COMMERCIAL APPLICATIONS OF ZIRCONIA [19]

	Proportion of total (%)
Refractories	41.7
Ceramic pigments	22.2
Abrasives	9.7
Electronics	5.6
Advanced ceramics, catalysts	5.6
Oxygen sensors	2.4
Glass and gemstones	2.1
Onward processing for the above market applications	10.8

TABLE 6. MANUFACTURING TECHNIQUES USED IN SOME SPECIALIZED APPLICATIONS OF ZIRCONIA [18]

	Application example
Blending with other material	Glass
Die pressing	Blades
Tape casting	Substrates, filters
Cold isostatic pressing	Cutting tools
Slip casting	Laboratory ware
Ceramic painting	Complex shapes made by physical deposition using gel
Injection moulding	Thread guides, complex shapes
Extrusion	Tubes

2.3.3.1. Refractories

The manufacture of refractories is the largest single industrial application of zirconia. Baddeleyite has been the traditional source of raw material in this application, but with the diminishing production of this mineral fused zirconia derived from zircon has now become the primary source of supply. Zirconia has refractory properties similar to those of zircon, but because of its higher melting point can be used in refractories for which the high temperature performance requirements are beyond the capabilities of zircon. Fused zirconia is also added to other refractories to increase their thermal shock resistance or slag resistance. The low thermal conductivity ensures low heat losses and the high melting point permits continuous or intermittent use at temperatures of 2200ºC or more in neutral or oxidizing atmospheres.

For most applications, PSZ is the material of choice since, as explained in Section 2.3.2, the use of unstabilized zirconia is limited by the risk of structural failure (although it can be used as an additive to enhance the properties of other oxide refractories such as magnesia and alumina). As zirconia based refractories are relatively expensive, their use tends to be limited to those applications in which their special properties are most needed. The main applications of fused zirconia refractories are in the production of glass and metals:

(a) In the glass manufacturing industry, zirconia refractories — typically fused cast refractories containing about 40 wt% zirconia — are used for lining the vessels that hold the molten glass. Zircon refractories and zirconia refractories are both used in this application, the choice

depending on the performance requirements at a particular location. For example, zirconia refractories are used in the 'tank' portion of the glass oven, while zircon refractories are used for the roof of the oven.

(b) In the metals industry, zirconia refractories have been used very successfully for melting alloy steels and the noble metals. Zirconia is not wetted by many metals and is therefore an excellent crucible material when slag is absent. Fused zirconia is usually the material of choice in specialized high performance refractories such as nozzles, sliding gates and other wear resistant parts used in flow control for continuous steel casting, as well as in the ceramic filters used during the casting process. Fused zirconia is also used for crucibles and linings in the manufacture of titanium. In such applications the ZrO_2 content of the refractories may be as high as 94%. Milled fused zirconia is used in investment casting applications where precise control over the metallurgical properties and final dimensions of the cast part justify the increased costs involved. Examples of such applications include the casting of firearms components and aerofoils used in turbines.

2.3.3.2. Ceramic pigments

The incorporation of colouring cations into the crystal lattice of zirconia produces a wide range of ceramic pigments that are used in glazes and colours for the decoration of pottery, ceramic tiles and sanitary ware. For example, yellow pigments are made by the addition of the praseodymium or vanadium (V^{5+}) cation, blue pigments by the addition of the vanadium (V^{4+}) cation and pink pigments by the addition of the iron cation. The high light reflectivity of zirconia also leads to its use as an opacifier in these applications. With the growing use of ceramic products, significant quantities of zirconia are now being used in pigment applications. Baddeleyite used to be a major feedstock, but fused zirconia (usually in unstabilized form with a typical composition of 99% ZrO_2, 0.2% SiO_2, 0.15% TiO_2, 0.02% Fe_2O_3 and 0.3% SO_3 [17] is now used exclusively as the source of zirconia. Some use is made of zirconium basic carbonate as an alternative feedstock to zirconia.

2.3.3.3. Abrasives

Abrasives, typically in the form of grains of controlled size, achieve their cutting effect through close contact, pressure and differential motion between the abrasive material and the surface to be abraded. Abrasive products may take the form of:

(a) Loose grains;

(b) Grains attached to a flexible backing of cloth, paper or vulcanized fibre to form coated abrasives in various forms, including sheets, rolls, belts, discs, bands and cones;

(c) Grains bonded into preformed shapes such as grinding wheels and discs, as well as blocks, bricks and sticks for sharpening, polishing and honing (e.g. oilstones, scythe stones and cylinder hones).

Fused zirconia is used in abrasives as a component of alumina–zirconia mixtures, which are produced in three principal grades:

 (i) 75% alumina, 21–25% zirconia, used in resin bonded foundry type grinding wheels;

 (ii) 60% alumina, 40% zirconia, used for medium or heavy duties such as grinding mild, stainless and high alloy steels;

(iii) 65% alumina, 30% zirconia, 5% titanium dioxide, an exceedingly tough grain with fine crystal size used in resin bonded grinding wheels.

2.3.3.4. Electronics

Ceramics based on high purity zirconia have become a key constituent of microelectronic and semiconductor components used in applications such as filters in communications equipment, acceleration sensors, buzzer elements and ultrasonic devices. Zirconia used in electronic components has a typical composition of 98% zirconium, 0.07% SiO_2, 0.12% TiO_2, 0.01% Fe_2O_3 and 0.1% SO_3 [17]. Lead zirconate titanate (PZT) has important applications based on its combination of piezoelectric and pyroelectric properties, while lanthanum doped PZT (known as PLZT) is used in advanced electro-optic ceramics for applications such as electronically triggered optical shutters and optical switching and stereoscopic viewing devices.

2.3.3.5. Engineering ceramics

Zirconia, usually in the form of PSZ with a typical composition of 92.3% ZrO_2, 0.15% SiO_2, 0.15% TiO_2, 0.02% Fe_2O_3 and 5.3% Y_2O_3 [17], has important engineering applications where there is a requirement for a durable, chemically inert material with good thermal and mechanical properties including resistance to fracture and wear. These applications involve material with a zirconia content ranging from as low as 5% to more than 90% and include the following:

(a) Plasma spray coatings to create a thermal barrier on components such as refractory linings and components of gas turbine and automotive engines.

(b) Structural ceramics for specialized applications requiring high temperature performance, high strength and/or good wear resistance, including:

   (i)   Pump components, for example bearings, seals and valves;
   (ii) Components of advanced internal combustion engines, for example cylinder liners, piston crowns, cams, tappets and valve seats;
   (iii) Fibre optic connector components, thread guides, printer heads and a variety of other small, high strength components in industrial applications and consumer products;
   (iv) Dies for extrusion and wire drawing;
   (v)   Blades, for example knives for high speed cutting of paper and polymers, scissors and shears.

(c) Cutting tools for high speed metal machining operations, using 5–10% zirconia with either 90–95% alumina or 60–65% alumina plus 30% titanium carbide.

(d) Mill linings and grinding media, including sintered zirconia grinding beads stabilized with 5% Y_2O_3 or 20% CeO_2 for generating fine particle sizes and homogenous dispersions by microgrinding in horizontal and high energy mills — these microgrinding media have a longer life than conventional ceramic grinding media and therefore lead to less contamination of the material being ground.

(e) Bioceramics such as hip joint prostheses, bone replacement and dental ceramics.

2.3.3.6. Catalysts

Zirconia has properties that make it highly suitable for use in catalysts. In addition to its high melting point, low thermal conductivity and high resistance to corrosion, it has a high oxygen ion conductivity that is controlled by the concentration of the very mobile oxygen vacancies in the crystal lattice. Catalyst grade zirconia is typically produced by precipitation from ZOC or zirconium sulphate solution followed by calcination. Its properties depend on the conditions of the precipitation such as the pH and concentration of the precipitating solution and the nature of the precursor and of the doping cations — doping of the zirconia increases the specific surface area. Zirconia is used in many chemical processes, including the hydrogenation of CO_x, the oxidation of methane, dehydrogenation of propane, alkylation, condensation, cracking, dehydration, esterification and isomerization. It is used either as a catalyst support or as a single oxide or mixed oxide catalyst in its own right. The typical

composition of zirconia used as a mixed oxide catalyst is 91% ZrO_2, 8% Y_2O_3, 0.15% SiO_2, 0.15% TiO_2, 0.02% Fe_2O_3 and 0.1% SO_3 [17]. Mixtures of ZrO_2, CeO and other co-precipitated components provide a range of oxygen storage capacities in magnesium iron aluminium cyclosilicate (cordierite) honeycomb ceramics for exhaust catalysts.

2.3.3.7. Solid electrolytes

Yttria stabilized zirconia has properties that allow it to perform as a solid electrolyte. This leads to its use in various specialized applications as described in Ref. [20]:

(a)   The high temperature ionic conductivity of PSZ containing 8 mol% Y_2O_3 leads to the use of this material as a solid electrolyte for oxygen sensors to control the inlet fuel to air ratio in automobile engines. The sensors are constructed using platinum electrodes deposited on the inner and outer surfaces of the solid electrolyte and operate in the temperature range 800–1200ºC. PSZ is suited to this application because of its high temperature and shock resistance. Oxygen sensors of this type are also used for the control of high temperature furnaces, boiler flue gas monitoring and the control of oxygen in steel making.

(b)   Yttria stabilized zirconia is used as a solid electrolyte in fuel cells that convert chemical energy stored in fuel directly into electric energy through an electrochemical reaction. These fuel cells combine high conversion efficiency, flexibility in fuel use and cogeneration capability with very low chemical and acoustic pollution of the environment and are thus one of the most advantageous energy conversion technologies for the near future.

(c)   In what is essentially the reverse mode of the fuel cell process, yttria stabilized zirconia is used as a solid electrolyte in the high temperature electrolysis of water to generate hydrogen.

(d)   At very high temperatures, the ionic conductivity through vacancies in the oxygen sublattice of yttria stabilized zirconia is superseded by electrical conductivity, giving rise to applications such as:

(i)   Heating elements for high temperature kilns in conjunction with a gas or metallic resistance preheater;

(ii)   Electrodes for the magnetohydrodynamic generation of direct current by passing an electrically charged gas at high temperature (>1800ºC) and high speed through a magnetic field;

(iii) Cathodes for air plasma burners.

2.3.3.8. Other applications

Zirconia is used in limited quantities for the production of cubic zirconia gemstones. It is also an important constituent of certain optical and ophthalmic glasses for specialized applications, for example camera lenses, measuring instruments and glass fibres, enabling high refractive indices to be achieved without the loss of durability. The zirconia used in these applications is of high purity, with a typical composition of 99% ZrO_2, 0.2% SiO_2, 0.15% TiO_2, 0.0006% Fe_2O_3 and 0.25% SO_3 [17]. Zirconia is also used in the manufacture of medical lasers and cosmetics (e.g. antiperspirants).

2.4. ZIRCONIUM CHEMICALS

As described in Section 2.2.3.4, zircon is used as the feedstock for the manufacture of significant quantities of two important zirconium chemicals: ZOC (derived from the reaction of zircon with sodium hydroxide followed by dissolution in hydrochloric acid) and zirconium tetrachloride (derived from the high temperature chlorination of zircon). Although both have applications as chemical products in their own right, their main uses are as intermediates for further processing. ZOC is used for the production of high purity zirconia and other zirconium chemicals, while zirconium tetrachloride is used for the production of zirconium metal.

Other zirconium chemicals produced in significant quantities include zirconium basic carbonate (ZBC), acid zirconium sulphate tetrahydrate (AZST), zirconium basic sulphate (ZBS), ammonium zirconium carbonate (AZC), potassium hexafluorozirconate (KFZ) and zirconium acetate (ZRA). More specialized zirconium compounds are produced in smaller quantities. Zirconium chemicals are used in a wide variety of applications, including antiperspirants, paint driers and paper coatings. Further details, including annual production figures where available, are shown in Table 7.

2.5. ZIRCONIUM METAL

Zirconium metal is produced by the reduction of zirconium tetrachloride with magnesium. Worldwide production of zirconium metal is about 9000 t, most of which is used in the nuclear industry as a cladding for nuclear fuel rods and as a structural material in reactors because of its low absorption cross-section for thermal neutrons and high resistance to corrosion. Hafnium, on the other hand, a natural impurity in zirconium (see Section 2.1), is a strong

TABLE 7. APPLICATIONS OF SOME ZIRCONIUM CHEMICALS

Name	Formula	Annual production (kt)	Applications
Zirconyl chloride octahydrate or zirconium oxychloride (ZOC)	$ZrOCl_2 \cdot 8H_2O$	25	Intermediate (ZrO_2, other zirconium chemicals), textile dying, antiperspirants, TiO_2 pigment coatings, oil field acidizing agents, catalysis, thixotropy
Zirconium tetrachloride	$ZrCl_4$	>20	Intermediate (zirconium metal, other zirconium chemicals), catalysts
Zirconium basic carbonate (ZBC)	$Zr_2(CO_3)(OH)_2O_2$ or $ZrOCO_3 \cdot nH_2O$	15–18	Intermediate (ZrO_2, other zirconium chemicals), paint driers (siccatives), pigments, catalysts, paper sizing agents, antiperspirants, soaps
Zirconium orthophosphate or acid zirconium sulphate tetrahydrate (AZST)	$Zr(SO_4)_2 \cdot 4H_2O$ or $H_2ZrO_2(SO_4)_2$	5–6	Intermediate (other zirconium chemicals), TiO_2 pigment coatings, leather tanning reagents
Zirconium basic sulphate (ZBS)	$Zr_5O_8(SO_4)_2 \cdot nH_2O$ or $Zr_5O_7(SO_4)_3$	5–6	Intermediate (other zirconium chemicals), TiO_2 pigment coatings, leather tanning reagents, soaps
Ammonium zirconium carbonate (AZC)	$(NH_4)_2[Zr(CO_3)_2(OH)_2]$ or $(NH_4)_3 3ZrOH(CO_3)_3 \cdot 2H_2O$	4–6	Paper coatings (starch insolubilization), fungicidal treatment of textiles, paint and ink formulations, metal surface treatments, adhesives, catalysts
Zirconium acetate (ZRA)	$Zr(CH_3COO)_n$ or $H_2ZrO_2(C_2H_3O_2)_2$	1	Intermediate (other zirconium chemicals), water repellent on paper and textiles, catalyst production, cross-linking
Potassium hexafluorozirconate (KFZ)	K_2ZrF_6	1	Grain refiner for Mg–Al alloys, flameproofing of textiles

TABLE 7. APPLICATIONS OF SOME ZIRCONIUM CHEMICALS (cont.)

Chemical		Annual production (kt)	Applications
Name	Formula		
Zirconium hydroxychloride	$Zr(OH)OCl$		Antiperspirants
Potassium zirconium carbonate	$K_2[Zr(CO_3)_2(OH)_2]$		Starch insolubilization, thixotropy
Zirconium nitrate (ZON)	$ZrO(NO_3)_2$		Intermediate (other zirconium chemicals)
Zirconium propionate	$Zr(OH)_{2.6}(OOC \cdot C_2H_5)_{1.4}$		Adhesion promotion
Zirconium silica hydrogel	$ZrSiOH$		Fillers
Acid zirconium phosphate	$Zr(HPO_4)_2$		Ion exchange

absorber of neutrons. Consequently, the zirconium used in nuclear applications must be hafnium free, necessitating additional steps in the zirconium metal extraction process to remove the hafnium content.

Outside the nuclear industry, zirconium is used in chemical fluid handling equipment (e.g. piping, pumps, valves and heat exchangers) for highly corrosive applications and in various specialty alloys. Since the metals zirconium and hafnium are chemically very similar and difficult to separate, no attempt is made in the zirconium metal extraction process to remove the hafnium content, and the metal used in these applications is accordingly referred to as commercial grade zirconium.

3. GENERAL RADIATION PROTECTION CONSIDERATIONS

3.1. APPLICATION OF THE STANDARDS TO INDUSTRIAL ACTIVITIES INVOLVING EXPOSURE TO NATURAL SOURCES

3.1.1. Scope of regulation

Paragraph 2.5 of the BSS [2] states that "Exposure to natural sources shall normally be considered as a chronic exposure situation and, if necessary, shall be subject to the requirements for intervention…", meaning that in such circumstances the exposure does not fall within the scope of regulation in terms of the requirements for practices. One example addressed specifically in the BSS is exposure to radon in dwellings and in workplaces in which radon is incidental to the work, where the action levels for remedial action are defined as 200–600 Bq/m^3 for dwellings and 1000 Bq/m^3 for workplaces.[6] However, there are some industrial activities giving rise to exposure to natural sources that have the characteristics of practices and for which some form of control in accordance with the requirements for practices may be more appropriate. The following two situations are addressed in the IAEA Safety Standards:

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[6] In this report, the use of the terms 'radon' and 'thoron' is generally taken to include not only the parent radionuclides ^{222}Rn and ^{220}Rn, respectively, but also their short lived progeny. However, the term 'radon concentration' refers to the concentration in air of the parent radionuclide ^{222}Rn alone.

(a) In workplaces where radon is not incidental to the work (e.g. uranium mines) or in other workplaces where a reduction in radon concentrations to below the action level cannot reasonably be achieved, exposure to radon is treated as occupational exposure and subject to the requirements for practices [21].

(b) Paragraph 2.1 of the BSS [2] states that "The practices to which the Standards apply include… practices involving exposure to natural sources specified by the [regulatory body] as requiring control…". This includes "public exposure delivered by effluent discharges or the disposal of radioactive waste… unless the exposure is excluded or the practice or the source is exempted" (Ref. [2], para. 2.5(a)). The zircon and zirconia industries are identified in Ref. [6] as being among those industrial activities likely to require consideration by the regulatory body in this regard.

With respect to (b) above, the Safety Guide on Application of the Concepts of Exclusion, Exemption and Clearance [5] states that it is usually unnecessary to regulate material containing radionuclides of natural origin at activity concentrations below 1 Bq/g for radionuclides in the uranium and thorium decay series and below 10 Bq/g for ^{40}K. The Safety Guide adds, however, that "… there are some situations (such as the use of some building materials containing natural radionuclides) for which exposures from materials due to radionuclides with activity concentrations below [these values] would necessitate consideration by the regulatory body for some types of regulatory control". The Safety Guide states that the aforementioned values may be used in the definition of the scope of national regulations or to define radioactive material for the purpose of such regulations, as well as to determine whether material within a practice can be released from regulatory control.

3.1.2. Graded approach to regulation

Where the activity concentration values specified in Ref. [5] are exceeded, the BSS (Ref. [2], paras 2.8, 2.10–2.12 and 2.17) require that a graded approach to regulation be adopted. Guidance on the graded approach is given in Ref. [5] and a description of its application to operations involving exposure to natural sources is given in Refs [3, 6]. In summary, the main options open to the regulatory body, in ascending order of degree of control, are as follows:

(a) The regulatory body may decide that the optimum regulatory option is not to apply regulatory requirements to the legal person having responsibility for the material, even though the activity concentration values in Ref. [5] are exceeded. The mechanism for giving effect to such a decision

could take the form of an exemption. Exemption is likely to be the optimum option if the material does not give rise to an annual effective dose received by a worker exceeding about 1–2 mSv (i.e. a small fraction of the occupational dose limit [21]), bearing in mind that the dose received by a member of the public in such circumstances is likely to be lower by at least an order of magnitude [6]. Where radionuclides of natural origin are incorporated into consumer products, as is sometimes the case in the zircon and zirconia industries, such products may be automatically exempted without further consideration if the total activity of a given radionuclide present on the premises at any one time does not exceed the relevant exemption level for total activity given in Table I-I in Schedule I of the BSS [2].

(b)   Where the regulatory body has determined that some form of regulatory control is needed, the minimum requirement is for the legal person to formally submit a notification to the regulatory body of the intention to carry out the practice. As in the case of a decision to grant an exemption, this is an appropriate option when the maximum annual effective dose is a small fraction of the applicable dose limit, but it provides the added reassurance that the regulatory body remains informed of all such practices.

(c)   Where the level of exposure to natural sources is such that neither exemption nor the minimum regulatory requirement of notification is the optimum regulatory option, the regulatory body may decide that the legal person has to meet additional (but limited) obligations to ensure that exposed individuals are adequately protected. These obligations would typically involve measures to keep exposures under review and to ensure that the working conditions are such that exposures remain moderate, with little likelihood of doses approaching or exceeding the applicable dose limit.[7] The mechanism for imposing such obligations on the legal person is the granting of an authorization in the form of a registration [3].

(d)   Where an acceptable level of protection can only be ensured through the enforcement of more stringent exposure control measures, an authorization in the form of a licence may be required [3]. This is the highest level of the graded approach to regulation and its use for practices involving exposure to natural sources is likely to be limited to operations involving significant quantities of material with very high radionuclide

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[7]   For situations in which workers are exposed to gamma radiation and radionuclides in inhaled dust, Ref. [21] states: "Control, if considered necessary, would include the use of methods to suppress or contain any airborne dusts and general radiological supervision."

activity concentrations, for example operations involving the exploitation of ores for their radioactive properties.

3.1.3. Applicability of the Transport Regulations to material in transport

3.1.3.1. Basic criteria

The safety requirements for material in transport are set out in the Transport Regulations [7]. The transport of zirconium-containing material in its natural or processed state may or may not fall within the scope of the Transport Regulations, depending on the activity concentration of the material. The Transport Regulations apply only if the activity concentration of the material exceeds ten times the activity concentration for exempt material. For individual radionuclides, the activity concentrations for exempt material are shown in Table 8.

3.1.3.2. Mixtures of radionuclides

For mixtures of radionuclides, the activity concentration for exempt material is determined as follows:

$$X_m = \frac{1}{\sum_i \frac{f(i)}{X(i)}}$$

(1)

where

$f(i)$ is the fraction of activity concentration of radionuclide i in the mixture;
$X(i)$ is the activity concentration for exempt material for the radionuclide i;
X_m is the derived value of activity concentration for exempt material.

Application of the '10 times' criterion to Eq. (1) results in the mixture being subject to the Transport Regulations only if:

$$\sum_i \frac{x(i)}{X(i)} > 10$$

(2)

where $x(i)$ is the activity concentration of radionuclide i in the mixture.

TABLE 8. ACTIVITY CONCENTRATIONS FOR EXEMPT MATERIAL IN TRANSPORT

	Activity concentration (Bq/g)	Progeny included in secular equilibrium
U-238 decay series		
U_{nat} (^{238}U)	1	Th-234, Pa-234m, U-234, Th-230, Ra-226, Rn-222, Po-218, Pb-214, Bi-214, Po-214, Pb-210, Bi-210, Po-210
U-238	10	Th-234, Pa-234m
Th-234	1000	Pa-234m
U-234	10 or 100[a]	—
Th-230	1	—
Ra-226	10	Rn-222, Po-218, Pb-214, Bi-214, Po-214, Pb-210, Bi-210, Po-210
Pb-210	10	Bi-210, Po-210
Po-210	10	—
Th-232 decay series		
Th_{nat} (^{232}Th)	1	Ra-228, Ac-228, Th-228, Ra-224, Rn-220, Po-216, Pb-212, Bi-212, Tl-208 (0.36), Po-212 (0.64)
Th-232	10	—
Ra-228	10	Ac-228
Th-228	1	Ra-224, Rn-220, Po-216, Pb-212, Bi-212, Tl-208 (0.36), Po-212 (0.64)
Ra-224	10	Rn-220, Po-216, Pb-212, Bi-212, Tl-208 (0.36), Po-212 (0.64)
K-40	100	—

[a] The applicable value depends on the chemical form of the material.

3.1.3.3. *Materials with decay chains in equilibrium*

For materials in which the radionuclides in each of the uranium and thorium decay series are (or are deemed to be) in equilibrium, the values of activity concentration for exempt material for U_{nat}, Th_{nat} and ^{40}K (see Table 8) can be used to calculate the derived value of activity concentration for exempt material, with the progeny of ^{238}U and ^{232}Th automatically being taken into account. Equation (1) then becomes:

$$X_m = \cfrac{1}{\cfrac{f(U_{nat})}{X(U_{nat})} + \cfrac{f(Th_{nat})}{X(Th_{nat})} + \cfrac{f(^{40}K)}{X(^{40}K)}}$$

$$= \cfrac{1}{f(U_{nat}) + f(Th_{nat}) + 0.01\ f(^{40}K)} \qquad (3)$$

In this case, Eq. (2) becomes:

$$x(U_{nat}) + x(Th_{nat}) + 0.01\ x(^{40}K) > 10 \qquad (4)$$

3.1.3.4. Materials with decay chain segments in equilibrium

The available data on the radionuclide composition of the material may indicate that equilibrium conditions do not prevail throughout the decay chains but that it may be possible to treat the material as a mixture of decay chain segments, each of which is assumed to be in equilibrium. In such cases, however, the available data and/or the information in Table 8 may not always be sufficiently detailed to determine unequivocally whether the Transport Regulations apply, in which case a conservative estimate may have to be made by assigning the highest individual radionuclide activity concentration in each decay chain or chain segment to all radionuclides in that decay chain or chain segment. Further information on how to proceed when insufficient data are available on individual radionuclide activity concentrations is given in the Transport Regulations.

3.1.4. Exposure pathways and assessment of effective dose

The exposure pathways to workers and members of the public that are most likely to require consideration in the zircon and zirconia industries are those involving external exposure to gamma radiation emitted from bulk quantities of zirconium-containing material and internal exposure via the inhalation of radionuclides in zirconium-containing dust or in furnace fume.[8] Internal exposure via the inhalation of radon emitted from zirconium-containing material and via the ingestion of such material may also need to be considered. The assessment of the effective dose received by an individual

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[8] The term 'fume' in this context denotes the vapour and/or suspended fine dust particles released from a high temperature industrial process.

involves summing the personal dose equivalent from external exposure to gamma radiation in a specified period and the committed equivalent dose or committed effective dose, as appropriate, from intakes of radionuclides in the same period. The assessment method is described in more detail in Ref. [3].

3.2. RADIOLOGICAL ASPECTS OF ZIRCONIUM MINERALS

3.2.1. Incorporation of radionuclides in the crystal structure

As a result of the high chemical inertness of zircon, most of the uranium and thorium found within it is that which was present during the crystallization of the mineral from the molten host rock (although some may also occur within other minerals present as inclusions in the zircon sand grains, for example monazite). The uranium and thorium atoms and their decay elements are bound within the zircon crystal structure, substituting for a small number of zirconium atoms. In most other uranium-containing minerals, including uranium ores, the uranium atoms are not bound within the crystalline matrix but form part of the cementing material between the grains.

The nature of the zircon crystal is such that the removal of uranium and thorium is not easily accomplished without destruction of the crystal lattice.[9] Acid leaching tests conducted on various zircon sand samples, including milled samples, over a range of pressures, temperatures and oxidizing conditions have demonstrated that, even under the most aggressive conditions, no significant amounts of uranium or thorium are leached from the zircon material [22]. Further experiments conducted on zircon sand have shown that the amount of [210]Po released at a temperature of 1200ºC is negligible [23] — this temperature is much higher than the volatilization temperature of [210]Po (100–150ºC) and higher even than its boiling point (962ºC). It is only at much higher temperatures, typically those encountered in electric arc furnaces, that breakdown of the crystal structure occurs, leading to the possibility of volatilization of [210]Po and other radionuclides.

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[9] This highly stable crystal structure allows zircon to be used for dating of rocks and has prompted its consideration for application in high level nuclear waste disposal.

3.2.2. Radionuclide activity concentrations

Detailed data on radionuclide activity concentrations in zircon and baddeleyite are presented in Appendix II. The following conclusions can be drawn from these data:

(a) The activity concentrations of ^{238}U and ^{232}Th series radionuclides in commercial zircon fall mostly in the ranges 2–4 and 0.4–1 Bq/g, respectively. In one investigation, analysis of 23 zircon samples obtained from commercial operations worldwide revealed that in all but four samples the ^{238}U activity concentration fell within the 2–4 Bq/g range; similarly, in all but four samples the ^{232}Th activity concentration fell within the 0.4–1 Bq/g range [24].

(b) In baddeleyite, the radionuclide activity concentrations are more variable, with activity concentrations of ^{238}U and ^{232}Th series radionuclides falling within the ranges 3–13 and 0.1–26 Bq/g, respectively. Activity concentration data for ^{210}Po suggest some tendency for disequilibrium at the lower end of the uranium decay chain.

(c) For zircon there are generally only minor deviations from decay chain equilibrium, whereas for baddeleyite there is evidence of greater disruption of decay chain equilibrium.

(d) Since the activity concentrations of some radionuclides always exceed 1 Bq/g, all operations involving zircon or baddeleyite need to be considered for regulation (see Section 3.1.1).

During the manufacture of zirconia from zircon, there is a strong possibility that the decay chain equilibrium present in the zircon feedstock will be significantly disrupted. Since various processes are used, it is not possible to generalize when considering the radionuclide composition of the zirconia product. The high temperature fusion process is conducted at about 2800ºC and it is evident from the data in Table 9 that volatilization of radionuclides, particularly the isotopes of lead, polonium and radium, will occur, leading to depletion of these radionuclides in the material remaining in the furnace.

Suitable techniques for analysing samples of solid material to determine the activity concentrations of radionuclides of natural origin are discussed in Ref. [6]. This discussion is relevant to the analysis of the solid materials encountered in the zircon and zirconia industries. The choice of technique is particularly important when dealing with materials such as zirconia where equilibrium within the uranium and thorium decay chains cannot be assumed. For example, gamma spectrometry can be used to indirectly determine the activity concentrations of ^{238}U and ^{232}Th by measuring the gamma emissions

TABLE 9. PHASE CHANGE DATA FOR MATERIALS AND RADIOELEMENTS ASSOCIATED WITH THE HIGH TEMPERATURE PROCESSING OF ZIRCON AND ZIRCONIA

	Melting point (°C)	Boiling point (°C)
Zircon	>2000	
Zirconia	2680	
Zirconium	1855	4409
Silica	1710	2590
Uranium	1132	3927
Thorium	1842	4820
Radium	700	1737
Radium sulphate or carbonate	<1700	
Lead	328	1740
Polonium	254	962

from their progeny ^{226}Ra and ^{228}Ra, respectively, but such a determination would only be accurate if these progeny were in equilibrium with their parents. Consequently, the gamma spectrometry technique might be accurate for zircon sand but not for zirconia.

3.2.3. Release of radon

A study conducted on size classified zircon particles [25] found that the activity concentration of ^{226}Ra (the precursor of ^{222}Rn in the ^{238}U decay chain) varied inversely with particle size. In the particles studied, the ^{226}Ra concentration decreased with increasing particle size from about 4.5 Bq/g at a particle size of 50 μm to about 3 Bq/g at a particle size of 150 μm. This rate of decrease is less than that of the surface to volume ratio, suggesting that the distribution of ^{226}Ra in zircon particles is neither homogenous nor of a surface type, but possibly with the ^{226}Ra concentration being higher in the outer layer of the particle than in the inner core. The radon emanation coefficient (defined as the fraction of radon atoms released into the material pore space from a radium bearing grain) for this type of ^{226}Ra distribution is higher than for a homogenous distribution but lower than for a surface type distribution and depends on the depth of the surface layer enriched in ^{226}Ra. In any event, the radon emanation coefficient will be very low compared with that for other uranium-containing materials because the escape of radon is inhibited by the fact that ^{226}Ra, like its parent radionuclide ^{238}U, is bound within the crystal lattice.

The radon flux density at the surface of a porous mass of semi-infinite material depends linearly on the ^{226}Ra concentration in the material and on the radon emanation coefficient; it also depends on other properties of the material such as the density of the grains, the porosity of the material and the pore diffusion coefficient [26]. For zircon, a low radon flux density per unit ^{226}Ra activity concentration can be expected, due to the low emanation coefficient.

The results of measurements of radon emanation coefficient and radon flux density are presented in Table 10, together with values for typical rocks and soil, uranium mine tailings and gold mine tailings for comparison. The

TABLE 10. RADON RELEASE DATA FOR ZIRCON

	Radon emanation coefficient	Radon flux density (Bq·m^{-2}·s^{-1})	
		Absolute value	Value per unit activity concentration (in Bq/g) of Ra-226
Zircon sand			
USA: four samples [28]	0.0013–0.0019 Average 0.0016		
USA, large stockpile [27]		0.074	0.022
South Africa: calcined and uncalcined [29]	0.0065		
South Africa [11]	0.006		
Zircon flour (USA) [28]			
Two samples	0.008, 0.009		
Five samples of foundry waste containing zircon flour exposed to strong alkaline solutions	0.010–0.020 Average 0.014		
Other minerals, for comparison			
Typical rocks and soil	0.05–0.7 [30]	0.016 [31]	0.46[a]
Uranium mine tailings	0.1–0.4 Typical 0.2–0.3 [32]	0.1–43 [33]	≈1 [33]
Gold mine tailings	0.13–0.39 [34]		

[a] Calculated assuming the median value of Ra-226 activity concentration (0.035 Bq/g) quoted in Ref. [26].

radon emanation coefficients for zircon sand lie in the range 0.0013–0.0065. The values for zircon flour are higher, in the range 0.008–0.020, as would be expected from the greater surface to volume ratio. In a study conducted in the USA [27], the radon flux density above a 4 m high pile of zircon sand with a ^{226}Ra concentration of 3.3 Bq/g was found to be 0.074 Bq·m^{-2}·s^{-1}, resulting in a flux density per unit ^{226}Ra activity concentration of 0.022 Bq·m^{-2}·s^{-1} per Bq/g. As would be expected, both the radon emanation coefficient and the radon flux density per unit ^{226}Ra activity concentration are far below the values for typical rocks and soil and even further below the values for mine tailings.

3.2.4. Gamma radiation dose rates

Many applications of zircon involve the need to store the material in bulk quantities (see Fig. 2). This can give rise to gamma radiation exposure of workers stationed close to such stockpiles. Gamma dose rates can be readily measured using a gamma dose rate meter as shown in Fig. 3. Various measurements of gamma radiation dose rates near accumulations of zircon have been reported and the results are summarized in Table 11. The values in the table were obtained after subtraction of the local background gamma dose rates, which varied from 0.09 to 0.15 µSv/h. For large stockpiles of zircon, the measured values are in the range 1.0–1.4 µSv/h at a distance of 1 m. For a typical ^{238}U activity concentration of about 3 Bq/g, this gives a gamma dose rate of about 0.3–0.5 µSv/h per unit ^{238}U activity concentration (in Bq/g). In Ref. [6], a theoretical value of 0.43 µSv/h per unit ^{238}U activity concentration was

FIG. 2. Bulk storage of zircon (courtesy UK Health Protection Agency: Centre for Radiation, Chemical and Environmental Hazards, Radiation Protection Division).

FIG. 3. Measurement of gamma dose rates near bulk quantities of zircon (courtesy UK Health Protection Agency: Centre for Radiation, Chemical and Environmental Hazards, Radiation Protection Division).

reported for a stockpile of 1000 t, which is in good agreement with the measured values.

Considerably higher gamma dose rates have been measured near accumulations of zircon recovered as a by-product of tin mining in south-east Asia. This zircon contained unusually high concentrations of uranium and thorium series radionuclides that are not representative of current commercial zircon production (see Appendix II). The range of absorbed dose rates was reported to be 4–15 μGy/h, with typical values falling within the range 5–7 μGy/h [39].

3.2.5. Airborne dust particle characteristics

Handling of zircon can generate airborne dust (see Fig. 4), leading to the possibility of inhalation of zircon particles by workers involved in such operations. It may be necessary, therefore, to monitor airborne dust levels (see Fig. 5). Investigations at five industrial facilities in the United Kingdom carrying out various processes using zircon as the raw material concluded, on the basis of inertial impactor measurements, that an appropriate particle size (expressed in terms of the activity median aerodynamic diameter (AMAD)) for use in any assessment of the dose received by a worker would in most cases be one falling within the range 2.5–10 μm [40]. This finding supports the

TABLE 11. INCREMENTAL GAMMA RADIATION DOSE RATES MEASURED NEAR ACCUMULATIONS OF ZIRCON

	Gamma dose rate after subtraction of background (µSv/h)			Ref.
	5 m distance	1 m distance	On contact	
Small quantities				
Single 40 kg bag		0.06[a]	1.6[a]	[27]
Single 50 kg bag		0.07	0.7	[35]
Moderate quantities				
Large bag, 3.4 Bq/g U-238		0.8	2	[36]
Large bag, 4.1 Bq/g U-238		1	3.5	[36]
Stack of 40 kg bags, 1.2 m cube		0.7[a]	2.9[a]	[27]
0.5 t stack of bags, 3.0 Bq/g U-238		0.15	1.4	[37]
0.5 t stack of bags, 3.4 Bq/g U-238			1.9	[37]
20 t stack of bags, 3.0 Bq/g U-238	0.1	0.7	1.7	[37]
Sacks of zircon from two sources, 5.8 and 14.7 Bq/g U-238			5.8–25 Average 11[b]	[38]
Large quantities				
2000 t pile		1.0–1.1[a]	1.5–1.7[a]	[27]
Pile, 23 m × 15 m × 6 m high		1.2–1.4[a]	Average 1.6 Maximum 1.9[a]	[27]

[a] These dose rates have been deduced from reported exposure rates measured in röntgen per hour assuming that 1 µR/h is approximately equivalent to a dose rate of 0.01 µSv/h.

[b] These dose rates have been deduced from reported absorbed dose rates measured at 5 cm from the surface of the sacks assuming that 1 µGy/h = 1 µSv/h.

recommendation in Ref. [41] to use a default AMAD of 5 µm if the particle size distribution for a particular process is unknown. For operations involving zircon flour without any mechanical processing such as abrasion or crushing, it was found in the study from the United Kingdom that comparisons could be drawn between the particle size distribution supplied with the zircon product and the airborne particle size distribution. For processes in which zircon was subject to mechanical processing, it was found that the particle size distribution tended to be broader, extending to values below 2.5 µm, with the largest fraction in some instances being in the range 1–2.5 µm. A dust sample collected

FIG. 4. Handling of zircon sand and the potential for airborne dust generation (courtesy UK Health Protection Agency: Centre for Radiation, Chemical and Environmental Hazards, Radiation Protection Division).

near a high temperature process exhibited a particle size distribution extending up to 10 μm but with about 40% being in the <1 μm range.

Airborne particle size distributions were investigated in an Italian plant producing zirconium-containing refractories [42]. The operation involved high temperature processing using zircon sand as a feedstock. The results of the

FIG. 5. Measurement of dust levels with a real time dust monitor (courtesy UK Health Protection Agency: Centre for Radiation, Chemical and Environmental Hazards, Radiation Protection Division).

investigation suggested that the AMAD of the dust particles varied over a wide range, from sub-micron sizes to more than 10 μm.

The chemical properties of zircon (see Section 2.2.2.2) and in particular its extreme resistance to leaching of uranium and thorium and their decay progeny bound within the crystal structure (see Section 3.2.1) suggests very strongly that the most appropriate lung absorption class for this material is class S.[10] This has been confirmed by in vitro solubility tests conducted on the respirable fractions of samples of material from zircon processing operations [40]. Dose coefficients (i.e. values of committed effective dose per unit intake of activity) for inhalation of radionuclides by workers and members of the public are specified in a database compiled by the International Commission on Radiological Protection (ICRP) [43]. The values are based on the model for the respiratory tract described in Ref. [44]. The dose coefficients for workers quoted in Ref. [43] cover a wide range of AMADs. Some of the values for AMADs of 1 and 5 μm appear also in Table II-III in Schedule II of the BSS [2]. The dose coefficients for members of the public are specified in Ref. [43] for a default AMAD of 1 μm and appear also in Table II-VII in Schedule II of the BSS [2].

Table 12 sets out the inhalation dose coefficients applicable to workers in industrial operations involving airborne dust particles containing zircon or zirconia. The coefficients relate to lung absorption class S to the extent possible and cover all radionuclides with significant dose contributions. In the few instances where a value for class S is not available, the value given is that corresponding to the next fastest lung absorption class for which information is available.[11] Most of the values in Table 12 are taken from Ref. [43]. In some cases (denoted by figures in italics), values for lung absorption class S are not available from this source and data are quoted instead from the results of other calculations [45, 46] based similarly on the ICRP respiratory tract model described in Ref. [44].

Many of the assessments of worker doses reported for the zircon and zirconia industries are based on the inhalation dose coefficients quoted in Table II-III in Schedule II of the BSS [2] for AMADs of 1 or 5 μm. Although the

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[10] Class S materials are defined in Ref. [44] as "Deposited materials that are relatively insoluble in the respiratory tract. (Slow solubilization.)". The other lung absorption classes defined in Ref. [44] are class M: "Deposited materials that have intermediate rates of absorption into the blood from the respiratory tract. (Moderate rate of solubilization.)" and class F: "Deposited materials that are readily absorbed into blood from the respiratory tract. (Fast solubilization.)".

[11] The use of dose coefficients for lung absorption classes other than class S in these few instances may lead to some underestimation of the dose.

TABLE 12. INHALATION DOSE COEFFICIENTS FOR WORKERS IN INDUSTRIAL OPERATIONS INVOLVING ZIRCON AND ZIRCONIA

	Dose coefficient for specified AMAD (µSv/Bq)			
	0.3 µm	1 µm	5 µm	10 µm
Uranium decay series				
U-238	10	7.3	5.7	3.5
U-234	12	8.5	6.8	4.1
Th-230	18	13	7.2	5.2
Ra-226	4.4 (M)	*8.7*	*6.9*	*4.2*
Pb-210	0.76 (F)	*5.2*	*4.3*	*2.7*
Po-210	3.9 (M)	*3.9*	*2.7*	*1.7*
Ac-227 (from U-235 series)	88	66	47	27
Thorium decay series				
Th-232	32	23	12	8.1
Ra-228	3.3 (M)	*15*	*11*	*7.1*
Th-228	45	37	25	18
Ra-224	3.3 (M)	2.9 (M)	*2.8*	1.3 (M)

Note: The dose coefficients quoted are those corresponding to lung absorption class S, except where specified in parentheses as M or F. Values shown in italics are taken from Ref. [46] (rounded to two significant figures) or, in the case of ^{224}Ra, Ref. [45]. All other values are taken from Ref. [43].

slowest lung absorption class is usually selected, dose coefficients for the radionuclides ^{226}Ra, ^{210}Pb, ^{210}Po, ^{228}Ra and ^{224}Ra are quoted in the BSS only for lung absorption classes M and/or F. Should the most appropriate lung absorption class for dust in workplaces involving zircon and zirconia be indeed class S, the use of the BSS dose coefficients would result in an underestimation of the dose contributions from the aforementioned radionuclides. For the default AMAD of 5 µm, the degree of underestimation would be 68% for ^{226}Ra, 74% for ^{210}Pb, 19% for ^{210}Po, 85% for ^{228}Ra and 14% for ^{224}Ra. For zircon particles with typical ^{238}U and ^{232}Th activity concentrations of 3 and 0.7 Bq/g, respectively, and with decay progeny in equilibrium, the total inhalation dose would be underestimated by 25%. Considering the many uncertainties associated with any dose assessment of this nature, this degree of underestimation is probably not serious.

The derivation of the dose coefficients for ^{226}Ra (lung absorption class M) quoted in Table II-III in Schedule II of the BSS [2] is based on the assumption

that [222]Rn produced in the respiratory tract does not have the same biokinetic behaviour as its parent [226]Ra, but rather is removed to the environment with a removal rate of 100 d^{-1} (see Annex B of Ref. [47]). The derivation in Ref. [46] of the corresponding [226]Ra dose coefficients for lung absorption class S quoted in Table 12 is based on this same assumption. However, it is pointed out in Ref. [46] that if the radon emanation fraction is very low — as is the case for zircon (see Section 3.2.3) — and remains low when the particle is inhaled, the dose to the respiratory tract due to inhalation of [226]Ra could be significantly underestimated for lung absorption classes S and M. Alternative dose coefficients for [226]Ra in these lung absorption classes, based on the extreme (and possibly unrealistic) situation of zero radon emanation from the inhaled particle, are reported in Ref. [46]. The values corresponding to lung absorption class S (rounded to two significant figures) are shown in Table 13. Comparing these values with the corresponding values in Table 12 suggests that the dose contribution from [226]Ra could be underestimated by as much as 80% for AMADs of 1–10 μm. For 5 μm AMAD zircon particles with decay progeny in equilibrium and with typical [238]U and [232]Th activity concentrations of 3 and 0.7 Bq/g, respectively, the total inhalation dose could be underestimated by up to 39%.

3.2.6. Occupational exposure during the handling of zircon

Exposure to gamma radiation emitted from bulk zircon and inhalation of radionuclides in airborne dust are generally the only occupational exposure pathways that need to be considered. In an investigation at a plant in the United Kingdom, the annual effective dose estimated to be received by a worker from ingestion of dust was found to be trivial, at 10 μSv [46], while other studies [42, 48] have confirmed that neither the ingestion of dust nor the

TABLE 13. DOSE COEFFICIENTS FOR INHALATION OF RADIUM-226 BY WORKERS, ASSUMING ZERO RADON EMANATION

AMAD (μm)	Dose coefficient (μSv/Bq)
1	44
5	38
10	23

inhalation of radon are significant pathways — in the latter case, because of the very limited release of radon from zircon sand (see Section 3.2.3).

Various investigations of the handling of zircon by workers have been carried out to determine the effective doses from gamma radiation and inhalation of radionuclides in dust. The results are shown in Table 14. The results of the facility specific investigations indicate that the annual effective dose received by a worker is likely to vary from very low levels up to about 0.4 mSv, depending on the work situation. As would be expected, the doses predicted by generic modelling are slightly higher.

TABLE 14. ANNUAL EFFECTIVE DOSES RECEIVED BY WORKERS HANDLING ZIRCON

	Annual effective dose (mSv)		
	Gamma radiation	Dust inhalation	Total
Zircon milling [49]			
Warehouse: mill operators and maintenance personnel	0.238	0.046	0.284
Warehouse: general workers	0.210	0.040	0.250
Foundries			
Sand casting [35]	0.08	0.045	0.125
Sand casting [50]	0.15		
Casting [51]	0.001	0.050	0.051
Mould wash preparation [52]	0.17	0.25	0.42
Investment casting [53]	Up to 0.02	Negligible	Up to 0.02
Chemical processing of zircon using NaOH[a]			<1
Generic modelling assessments			
Exposure to large stockpile of zircon, 3 Bq/g U-238 [6]	0.52	0.19	0.71
Opening bags of zircon and feeding into process line, 5 μm AMAD [54]	0.45	0.19	0.64

[a] Unpublished company data.

3.2.7. Transport of zirconium minerals

Using Eqs (1) or (3) in Section 3.1.3 and the radionuclide activity concentration data in Appendix II, the activity concentration for exempt material can be determined, as well as the factor by which this concentration is exceeded. Comparison of this factor with a value of 10 establishes whether the material is subject to the Transport Regulations (see Section 3.1.3). The data for ^{40}K are sparse, but indicate that the activity concentration of this radionuclide is much lower than those of the uranium and thorium series radionuclides. In addition, the exempt activity concentration of ^{40}K is 100 times that of U_{nat} and Th_{nat} (see Section 3.1.3). Therefore, the lack of data for ^{40}K is of no consequence when using Eqs (1) or (3) to determine whether the material is subject to the Transport Regulations.

For zircon, since there are only minor deviations from equilibrium in the uranium and thorium decay chains (see Section 3.2.2), the activity concentration for exempt material can be derived from Eq. (3) in Section 3.1.3. For baddeleyite, there are indications of greater departures from equilibrium in the uranium and thorium decay chains, requiring the use of Eq. (1) rather than Eq. (3) to determine the exempt activity concentration. However, the use of Eq. (1) necessitates knowledge of the radionuclide composition. The composition data in Appendix II are not always sufficient to determine conclusively whether the Transport Regulations apply. In such cases, a conservative assessment can be made by taking the highest radionuclide activity concentration reported within a given decay chain or decay chain segment and assuming this to be the equilibrium value for the whole chain or chain segment.

The results of the above mentioned assessments based on the data in Appendix II are shown in Table 15. It can be concluded that:

(a) Zircon originating from Australia, India, South Africa and the USA, representing about 80% of worldwide commercial zircon production, is unlikely to be subject to the Transport Regulations.

(b) The small quantities of zircon originating from China and from Malaysian tin mining residues (amang) exhibit significantly higher activity concentrations, resulting in them falling within the scope of the Transport Regulations.

(c) Some of the baddeleyite formerly produced in South Africa would have been subject to the Transport Regulations. Current baddeleyite production, originating only from the Russian Federation, is generally regarded as having lower activity concentrations and the available data based on an analysis of one sample suggest that it falls well outside of the

TABLE 15. APPLICABILITY OF THE TRANSPORT REGULATIONS TO ZIRCON AND BADDELEYITE

	Origin	Number of data points	Factor by which activity concentration for exempt material is exceeded	
			Range	Proportion not exceeding a factor of 10
Zircon	China, Malaysia (amang)	10	15–109	None
Zircon	Australia, India, South Africa, USA	39	1.6–8.4	100%
Zircon	Unspecified	64	1.5–15.9	97%
Baddeleyite	Russian Federation	1	3.8	100%
Baddeleyite	South Africa	14	1.8–50	57%
Baddeleyite	Unspecified	8	3.3–17	75%

scope of the Transport Regulations. More data would be required to confirm this.

Some dose modelling assessments of the transport of zircon and baddeleyite have been conducted. The results, summarized in Appendix III, confirm that, even with the use of conservative assumptions, the doses received by workers and members of the public are small enough not to be of concern from a regulatory or health point of view.

3.2.8. Management of zircon-containing residues

Used zircon tends to be mixed with other, unwanted material. It is sometimes feasible to purify this zircon for reuse, but most of it is disposed of as waste in municipal landfill facilities. The quantities disposed of are moderate, especially because plant operators usually try to minimize the loss of material to reduce costs. The radiological impact of the disposal of zircon sand is greatly mitigated by the insolubility and low radon emanation rate of zircon, and the main issue is external exposure to gamma radiation. Measurements at a landfill facility in the USA for disposal of zircon-containing foundry sand indicated an average gamma dose rate, after subtraction of background, of about 0.1 μSv/h and a maximum of about 1.3 μSv/h. In a more recent study at a similar landfill

facility in the USA, the external gamma radiation dose rates were found to be much lower: 0.014–0.024 µSv/h before closure (average 0.018 µSv/h) and 0.003 µSv/h after closure [27].[12]

Various dose assessments for the disposal of zircon in landfill facilities, based on modelling of exposure scenarios, have been reported. Brief descriptions of five studies are given as follows:

(a) The annual effective doses received by waste disposal workers and an off-site resident during the landfill operation were estimated in Ref. [55], assuming that about 60 t of zircon sand was disposed of annually in a single landfill site. The annual effective dose received by a future on-site resident, taking into account indoor exposure to ^{222}Rn and its short lived progeny, was also estimated.

(b) Disposal scenarios for various zircon quantities, dilution factors and cover thicknesses were examined in Ref. [56] and the calculated doses were compared with an annual effective dose criterion of 250 µSv.[13] A residential scenario was found to be the most limiting.

(c) An assessment reported in Ref. [57] related to the landfill disposal of large quantities of diluted zircon sand and flour (3600 t per year for 20 years).

(d) An assessment reported in Ref. [50] was based on measurements of gamma dose rate, airborne dust, radon and groundwater at a foundry sand landfill disposal facility and considered the doses received during the operation of the facility as well as after closure with a 0.6 m thick cover applied in accordance with local regulatory requirements.

(e) A hypothetical exposure scenario was examined in Ref. [58], in which zircon flour was mixed with cement at a ratio of four parts flour to one part cement and formed into blocks before being buried in a landfill disposal facility. The annual effective dose received by the most exposed individual (a future resident) was estimated.

The results of the above mentioned studies are summarized in Table 16. All of the results indicate that the doses received by workers and members of the public are likely to be insignificant, especially given the conservatism

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[12] The dose rates quoted from both studies have been deduced from reported exposure rates measured in röntgen per hour, assuming that 1 µR/h is approximately equivalent to a dose rate of 0.01 µSv/h.

[13] This criterion was a public dose constraint applied by the regulatory body in the country concerned.

TABLE 16. ESTIMATED DOSES ARISING FROM THE DISPOSAL OF ZIRCON IN A LANDFILL FACILITY

| | Annual effective dose (µSv) | | | | |
| | Gamma radiation | Inhalation | | Ingestion | Total |
		Dust	Radon		
Undiluted zircon sand, 60 t/a [55]					
Waste collector					50
Landfill operator					20
Off-site resident, pre-closure	n.a.[a]	0.4	n.a.	0.2	0.6
On-site resident, post-closure					100
Zircon sand, residential scenario [56]					
100 t, no dilution or cover					≤250[b]
1000 t, no dilution, 3 m cover					≤250[b]
1000 t, fivefold dilution, no cover					≤250[b]
Diluted zircon sand, 3600 t/a [57]					
Truck driver	20	n.a.	n.a.	n.a.	20
Bulldozer operator	50	10	n.a.	n.a.	60
Inadvertent intruder[c]	93	0.6	25[d]	16	130
Spent foundry sand [50]					
Pre-closure	7–13	Negligible	Negligible	Negligible	7–13
Post-closure	2	n.a.	Negligible	Negligible	2
Zircon flour cemented into blocks, on-site resident, post-closure [58]					50

[a] n.a.: not applicable.
[b] More than 90% due to external gamma exposure.
[c] Low probability scenario (i.e. conservatively high estimate of impact) in which post-closure institutional control is lost and an individual lives, extracts groundwater (at the maximum contamination level 1000 years after closure) and grows food on the site.
[d] The indoor radon concentration is quoted in Ref. [57] as 0.04 pCi/L (1.48 Bq/m^3); the dose was derived using the conversions 1.56 mJ·h·m^{-3} per Bq/m^3 and 1.1 mSv per mJ·h·m^{-3} as specified for a member of the public in Table II–II in Schedule II of the BSS [2], assuming an annual occupancy of 7000 h, giving an overall conversion of 17 µSv per Bq/m^3.

inherent in such assessments. In view of this and of the limited quantities of zircon residues generated, the possibility of recycling of such residues, for example by incorporation into construction material, is unlikely to be an option of any practical interest. However, the indications are that, if so desired, used zircon could be incorporated into aggregates used for the concrete foundations of buildings (even residential buildings) without significantly increasing the doses received by the inhabitants. The modelling of two hypothetical exposure scenarios for the recycling of zircon flour is reported in Ref. [58]. In the first scenario, it was assumed that the flour was incorporated at 10 wt% into the concrete aggregate used in the casting of building foundations. The effective dose received by the most exposed individual (a resident) was estimated to be a few tens of microsieverts per year. In the second scenario, it was assumed that the same aggregate was used in the manufacture of outdoor paving blocks. The effective dose received by the most exposed individual (a security guard stationed on the site) was estimated to be about 300 µSv/a.

Some zircon is released into liquid effluents, although the quantities are likely to be limited because of (non-radiological) controls normally imposed on the quality of industrial effluents. The radiological impact of such releases is likely to be inconsequential because of the small quantities involved and the extremely low solubility of zircon.

3.3. REGULATORY CONSIDERATIONS IN THE HANDLING AND DISPOSAL OF ZIRCONIUM MINERALS

Since the uranium series activity concentrations in zircon and baddeleyite exceed 1 Bq/g, the handling of these minerals, as well as their disposal when not sufficiently diluted with non-radioactive material as a result of their use, necessitates regulatory consideration. However, it is evident from Section 3.2.6 that the annual effective dose received by a worker who handles zircon sand but is not directly involved in any mechanical or thermal processing operations is unlikely to exceed 0.4 mSv. Furthermore, from Section 3.2.8, it would appear that the dose received by a member of the public from the disposal of zircon sand as industrial waste in a landfill facility is unlikely to exceed 250 µSv. In such situations, therefore, the regulator could decide not to impose any radiation protection requirements other than perhaps the requirement for notification. Nevertheless, it is good practice in terms of OHS and environmental protection to identify and implement any simple measures, for example limitation of occupancy periods near accumulations of material and minimization of airborne dust, that may be effective in reducing the radiological impact on workers and members of the public.

The transport of zircon is unlikely to be subject to the Transport Regulations except for the transport of zircon originating from China and from Malaysian tin mining residues (amang). It appears that the transport of currently produced baddeleyite, which is sourced only from the Russian Federation, is not subject to the Transport Regulations, but this needs to be confirmed by further radionuclide composition analyses.

4. MILLING OF ZIRCON SAND

4.1. PARTICLE SIZE

Most of the zircon sand used in industrial applications has to be first milled to smaller particle sizes because the natural particle size of 100–200 μm is too large. Some commercial users purchase zircon in sand form and mill it using their own equipment, while others purchase zircon that has already been milled. The required particle size will depend on the application. The milled zircon product is categorized on the basis of particle size into two basic types — zircon flour and micronized zircon:

(a)   Zircon flour is produced in various grades, reflecting different particle size distributions. The grade is specified according to the screen mesh size through which most of the material (approximately 95% of the mass) is able to pass. Most commercial grades of zircon flour are specified in terms of mesh sizes ranging from –40 to –600 (the minus sign indicating passage of the material through the specified mesh screen). Products with mesh size specifications of –200 and –325 are the most common, corresponding to nominal maximum particle sizes of 74 and 44 μm, respectively. The mass median diameters quoted for these zircon grades differ according to the product specification, but are of the order of 20 and 10 μm, respectively.
(b)   Micronized zircon has a median particle size of 1–2 μm, with typically 95% of the material having a particle size less than 5 μm.

The particle size distribution of airborne dust in a milling operation can be expected to be different from that of the zircon product, as the finer dust is more likely to become airborne. However, the aerodynamic diameter will be greater than the physical diameter by the square root of the density of zircon

(i.e. by a factor of about two). Taking these two factors into consideration, an AMAD of 5 μm has been suggested as a reasonable but conservative estimate where direct particle size measurements are not available [48]. This suggestion is supported by measurements conducted in plants in the United Kingdom [46] and South Africa [59], which indicated dust AMADs of close to 10 and 5 μm, respectively.

4.2. PROCESS DESCRIPTION

Zircon sand is delivered to the milling plants either in bulk shipments or in woven plastic bulk bags (typically 1 or 2 t) and off-loaded into a storage area.

4.2.1. Production of zircon flour

In the production of zircon flour, the particle size reduction is achieved by ball milling, roller milling or autogenous milling. As zircon is hard and abrasive, the milling process can lead to the components of the mill wearing and contaminating the product. The design of the plant therefore depends on, among other things, the level of contamination that can be tolerated in the final product. Most zircon flour production is carried out in dry, air swept ball mills. These are normally lined with a refractory material and use refractory grinding balls, typically sintered alumina, to avoid contamination of the milled product with iron. In autogenous mills, compressed air causes the grains to impact one another, avoiding wearing parts and thus eliminating potential contamination. The milled particles are flushed out of the mill by a strong current of air and separated using a classifier. Particles with sizes exceeding the specification are returned to the mill for further processing. Particles conforming to the specification are discharged from the classifier and stored in sealed silos in preparation for bagging.

Dust is controlled by enclosures and local ventilation equipment, as shown in Fig. 6, to improve efficiency, to prevent loss of products and to maintain a clean operating environment. The degree of containment varies, depending on the age of the plant (some plants may be more than 25 years old). Modern operations are fully enclosed to maintain a high standard of dust containment. However, total containment of the dust is never possible. The abrasiveness of the material causes wear and failure of plant components that can lead to leakage from dust containment systems. All air extracted from the process is passed through a bag filter before release. This helps to control airborne dust levels and enables valuable product material to be recovered.

FIG. 6. Dust extraction system in a zircon milling plant (courtesy UK Health Protection Agency: Centre for Radiation, Chemical and Environmental Hazards, Radiation Protection Division).

Cleaning within the plant is generally carried out on a regular basis using machinery (see Fig. 7), brushes and shovels. Manual cleaning of floors usually involves the spreading of damp sand and sweeping up fine particles of zircon along with the sand. More rigorous cleaning may be undertaken periodically. Owing to the abrasiveness of the material, plant inspection, repair, refurbishment and replacement needs to be carried out on a more or less continuous basis by small maintenance teams. Major plant refurbishment or replacement, taking several weeks to complete, is also necessary from time to time. Entry into containment systems is often necessary, and the work typically involves exposure to significant amounts of airborne dust.

4.2.2. Production of micronized zircon

In the production of micronized zircon, dry milling (using, for example, ceramic lined ball mills) may be employed, but it is more usual to use wet milling equipment such as vibro-energy mills (Fig. 8) or stirred ball mills. The

FIG. 7. Cleaning operations with a vacuum system (courtesy UK Health Protection Agency: Centre for Radiation, Chemical and Environmental Hazards, Radiation Protection Division).

FIG. 8. Vibro-energy mill for the production of micronized zircon.

energy required to reduce the particle size of zircon is considerable, and it is not unusual for such mills to take 10 days to produce the correct particle sizes from a recirculating batch of feed. As with dry milling, the mill components are usually made from sintered alumina or other hard refractory material. Once the wet milling operation is complete, the zircon slurry is dried using a conventional drying oven or a spray drier.

4.2.3. Packaging of the product

Following the milling operation, the zircon flour or micronized zircon is packed into bulk bags or into 25, 40 or 50 kg industrial paper packages for shipping on pallets. Bagging of the product is generally carried out with conventional automatic or semi-automatic bagging systems that weigh the product and stop the filling of the bag when a predetermined weight has been reached. The final weight may have to be adjusted manually to ensure that all bags are filled to the same weight. The bagging equipment is fitted with a dust extraction system so that the air displaced from the bag during filling is cleaned before release (see Fig. 9).

FIG. 9. Dust extraction system on bagging equipment (courtesy UK Health Protection Agency: Centre for Radiation, Chemical and Environmental Hazards, Radiation Protection Division).

4.2.4. Management of zircon-containing residues

The amount of zircon-containing residue from a zircon milling plant is likely to be small, because the high value of the product is an incentive for the operator to minimize wastage. Spilt zircon can be recycled within the process provided that it is not contaminated with other material that may adversely affect the quality of the product. Otherwise, it has to be disposed of as waste. Information from one milling company suggests that the concentration of zircon dust in the sand from floor sweepings may reach 40%, implying activity concentrations of ^{238}U and ^{232}Th series radionuclides of about 0.8–1.6 and 0.2–0.4 Bq/g, respectively.

The disposal of zircon-containing wastes from three zircon milling plants in Europe is described in Ref. [60]. At one plant, spilt zircon diluted with other substances preventing its recycling within the process is transported to a landfill disposal facility in special packages and is buried in accordance with the applicable control measures. The annual amount of this waste is about 200 t, which is reported as being "in the order of one percent of the turnover" [60]. At another plant, the unrecoverable part of the zircon is reported to be "less than 0.1% of the turnover" [60], and this is disposed of together with other (non-zircon) waste. At another plant, the waste is restricted to the loaded bags from air filters, with an estimated zircon content of 100 kg over the course of a year. From these examples, it is clear that the volume of zircon-contaminated waste can be minimized by good housekeeping. Provided that the zircon-containing waste is put into a form that prevents resuspension, the radiological implications are insignificant (see Section 3.2.8) and the material can be disposed of in a landfill facility as normal industrial waste.

4.3. OCCUPATIONAL EXPOSURE

4.3.1. Gamma dose rates

Zircon milling does not generate material with radionuclide activity concentrations exceeding those in the zircon sand feedstock. Consequently, gamma dose rates are relatively low (see Section 3.2.4). Zircon sand stores are a potential source of external gamma exposure because of the large quantities of material that may be present at any one time. However, workers tend to spend only limited periods close to the material, so the doses received from gamma radiation are likely to be low, as indicated in Section 3.2.6.

From the data presented in Section 3.2.4, it would be expected that gamma dose rates to which workers are exposed in zircon milling plants will be

of the order of 1 μSv/h or less. Measurements conducted at two South African zircon milling plants [49, 59] are in line with this expectation, as shown in Table 17. The dose rates shown in the table are based on measurements made near possible sources of exposure (at a distance of 1 m, except where indicated otherwise), from which background dose rates (0.16 μSv/h at plant A, 0.12 μSv/h at plant B) have been subtracted.

4.3.2. Airborne dust activity concentrations

In sand storage areas, airborne dust levels are likely to be low, due to the absence of sand particles small enough to become resuspended, and occupancy periods are limited. Therefore, the inhalation of radionuclides in dust is not a significant exposure pathway in such areas. However, transfer of sand from the storage area to the mills may involve manual handling, which can generate airborne dust if done in bulk form.

Dry milling operations have the potential to create airborne dust. This dust is likely to be finer than the process material (see Section 4.1), rendering it more likely to become resuspended. The inhalation pathway could therefore be

TABLE 17. INCREMENTAL GAMMA DOSE RATES MEASURED IN ZIRCON MILLING PLANTS

Plant A [59]		Plant B [49]	
Measurement location	Dose rate (μSv/h)	Measurement location	Dose rate (μSv/h)
Stack outlet floor	0.03	Next to feed hopper (mill 1)	0.28
Third floor	0.03	Next to mill 1	0.14
Second floor	0.11	Between mills	0.16
First floor	0.18	General around mills	0.13
Mill area	0.06	Stockpiles between mills, 2 m	0.53
Bagging section	0.18	Between mill 2 and stockpiles	0.28
Storage section	0.2	Between mill and stockpiles	0.32
Bulk storage area	0.95	Between mill and stockpiles	0.32
Offices, workshops	0.07	Stockpile area	0.58
Outside areas	0.04	Stockpile area, on bags	1.18
		Stockpile area, 5 m from bags	0.38
		Bagger No. 2	0.28

significant, even though the radionuclide concentrations in the dust are moderate (similar to those in the feedstock material). Air swept mills can cause significant dust generation if the equipment is not well maintained. However, there is a strong financial incentive for the operator to keep the equipment in good condition, since the generation of dust leads to a loss of valuable product. In addition, mill operators may often be required to control airborne dust levels for normal OHS reasons. In Europe, one milling company was reported to have set a maximum dust concentration in its mills of 1.3 mg/m^3, while another company set a limit of 2 mg/m^3 [60]. In wet milling operations, the inhalation pathway is insignificant, although dust could be generated if spillages and splashes are not cleaned up before they dry out. Clearly, if the operator has a choice of dry or wet milling, the latter is preferable from a radiation protection point of view. The milling operation tends to be centrally controlled and daily occupancy periods of workers in dusty areas therefore tend to be much less than the full shift [59]. In Ref. [61], it is reported that the occupancy period was less then 10 h per week, or about 500 h/a.

Handling of the milled product, especially during the filling of bags, can give rise to an inhalation hazard if the equipment used for such operations is not well maintained. In bagging operations, manual adjustment of the final bag content has been observed to generate dust [48]. Although dust levels in bagging operations may be high, the occupancy periods of workers involved in the filling of bags is reported to be only a small fraction of the total working period [48].

Workers engaged in maintenance and demolition operations may be exposed to dust levels significantly higher than those experienced during normal operations. On an annual basis, however, the exposure period to such high dust levels is likely to be only a small fraction of the total annual working period.

Some measurements of dust levels in zircon milling plants have been reported. The dust level at a US zircon milling plant was reported to be 0.8 mg/m^3 [62]. In a zircon flour production area in a plant in India, levels of 0.4–3.4 mg/m^3 (average: 1.15 mg/m^3) were reported [63]. Similar values were reported in one plant in the United Kingdom [46], where the dust concentrations during routine work activities were determined from personal air sampler (PAS) measurements to be in the range 0.4–1.5 mg/m^3 with an average value of 1.0 mg/m^3. Higher dust levels were measured in the following non-routine operations:

(a) Bag packing station (unusually high dust levels): 1.9 and 2.7 mg/m^3.
(b) Dust cascading from gantries: 3.6 mg/m^3.
(c) Dust leaking from bags: 1.9 mg/m^3.
(d) Manual loading of wet mill: 5.8 and 9.0 mg/m^3.

(e)   Maintenance inside the mill: 2.0 and 2.8 mg/m^3.

(f)   Loading sand into hoppers using a mechanical shovel: 1.9 mg/m^3.

It can be expected on the basis of these results that the dust levels to which workers are exposed in zircon milling plants will generally range up to about 2 mg/m^3, but with levels of up to about 10 mg/m^3 being possible in non-routine situations (where the use of respiratory protection would usually be required in terms of normal OHS regulations). Assuming that the maximum activity concentrations of ^{238}U and ^{232}Th series radionuclides in the dust particles are the same as those in the zircon feedstock (i.e. 4 and 1 Bq/g, respectively (see Section 3.2.2)), the maximum expected dust activity concentrations in air are as follows:

(i)   Individual ^{238}U series radionuclides: 8 mBq/m^3 (routine), 40 mBq/m^3 (non-routine).

(ii)   Individual ^{232}Th series radionuclides: 2 mBq/m^3 (routine), 10 mBq/m^3 (non-routine).

(iii) Gross long lived alpha activity: 50 mBq/m^3 (routine), 250 mBq/m^3 (non-routine).

These expectations are confirmed, in most cases, by measurements that have been conducted in various zircon milling plants, as shown in Table 18. The results also demonstrate that dust activity concentrations are likely to be higher in the bagging area than in the rest of the plant.

4.3.3.   Monitoring

In any inherently dusty industrial operation, zircon milling included, the non-radiological hazards associated with dust inhalation generally necessitate some form of routine monitoring programme for airborne dust to ensure that dust levels remain within normal OHS limits. Such a programme can be readily adapted to incorporate radiological aspects. In one plant in the United Kingdom [46], the monitoring programme comprised the following elements:

(a)   Gravimetric airborne dust monitoring;

(b)   PASs worn for periods of 8 h (or 1 h for specific operations);

(c)   PASs in static locations, deployed for typically 4 h.

Air sampling was carried out for approximately four days per month, or more frequently for specific investigations such as after changes to the plant or during certain maintenance operations. PASs were calibrated annually.

TABLE 18. AIRBORNE DUST ACTIVITY CONCENTRATIONS MEASURED IN ZIRCON MILLING PLANTS

	Activity concentration in air (mBq/m^3)		
	Individual radionuclides		Gross long lived alpha
	U-238 series	Th-232 series	
USA, ball mill [61]			
Bagger operator	48–74	5.2–19	
Area on west side of room	4.1–5.9	0.85–1.3	
Area near bagger	8.1–10	2.4–3.7	
Australia [48][a]			
New autogenous mill, dust extraction, enclosed bagging, good industrial hygiene			18.7
Old roller mill, no special dust extraction during bagging			52.5
Old ball mill, no special dust extraction			40.7
Old ball mill, semi-automatic bagging, no special dust extraction			40
Bagging operation only			184
South Africa [59]			
Stack outlet floor			2
Second floor			1
First floor			5
Bagging section			10
South Africa [49]			
Mill areas			15–25
Bagging area			21
Stockpile area			15–20
India			
Zircon flour production area [63]			20–160, average 100

[a] Except for the results for the bagging operation, the values represent the averages of dusty areas.

Monitoring for external gamma radiation may also be needed. The monitoring methods used in a survey of external gamma radiation and airborne dust in zircon milling plants in Australia [48], including a description of measurement techniques, equipment and dose calculation methods, are described in Annex II.

4.3.4. Effective dose

Various assessments of annual effective doses received by workers have been reported. The results of these assessments are summarized in Table 19, from which it would appear that in most zircon milling operations workers do not receive doses exceeding about 1 mSv/a. Except for bagging operations, this is likely to be the case even if respiratory protection is not used.

4.3.5. Measures to reduce doses

4.3.5.1. Bulk storage areas

Doses from gamma radiation depend on the distance from the source and the period of exposure and may be reduced by limiting access to bulk storage areas. In addition, experience has shown that it is possible to reduce the exposure to gamma radiation in a zircon milling plant by reducing stockpile quantities [59].

4.3.5.2. Milling areas

The most effective approach to the reduction of exposure to airborne dust in the milling area is to start by identifying the main sources of dust so that appropriate, targeted remedial action can be implemented to reduce dust levels. Where remedial action cannot reasonably achieve the necessary reductions in dust levels, the use of personal protective equipment may have to be introduced or enforced more strongly.

Dust concentrations measured at a zircon milling plant in the United Kingdom [46] (see Section 4.3.2), in addition to providing for the estimation of annual doses, indicated that:

(a) While all activities in the processing plant involved some exposure to airborne dust, certain areas or tasks were associated with consistently higher dust levels;

(b) There was some variation in the measured dust levels when different workers undertook similar tasks.

TABLE 19. DOSES RECEIVED BY WORKERS IN ZIRCON MILLING PLANTS

	Annual effective dose (mSv)		
	Gamma radiation	Dust inhalation[a]	Total
USA			
Bagger operator (respiratory protection mandatory):			
Without respiratory protection[b]	0.2	1.9	2.1
With respiratory protection [62]			<1
Australia [48]			
New autogenous mill, dust extraction, enclosed bagging, good industrial hygiene	0.4	0.27[c]	0.67
Old roller mill, no special dust extraction during bagging	0.3	0.73[c]	1.03
Old ball mill, no special dust extraction	0.1	0.56[c]	0.66
Old ball mill, semi-automatic bagging, no special dust extraction	0.4	0.56[c]	0.96
Netherlands [46]			0.8
South Africa [49]			
Mill operators (mill areas)	0.102	0.163	0.265
Mill operators and maintenance personnel (warehouse)	0.238	0.046	0.284
Maintenance personnel (mill areas)	0.067	0.042	0.109
General workers (mill areas)	0.096	0.06	0.156
General workers (warehouse)	0.210	0.04	0.250
South Africa [59][d]			
Mill attendant	0.275	0.165	0.44
Shift supervisor	0.18	0.094	0.274
Cleaner	0.2	0.134	0.33
South Africa			
Wet mill operator [64]	0.16	0	0.16

TABLE 19. DOSES RECEIVED BY WORKERS IN ZIRCON MILLING PLANTS (cont.)

	Annual effective dose (mSv)		
	Gamma radiation	Dust inhalation[a]	Total
United Kingdom [46]			
(based on dust concentrations reported in Section 4.3.2)		0.5	

[a] Except where otherwise stated, values are based on the assumption that no respiratory protection was used.

[b] These doses have been calculated from the values of gamma exposure, airborne dust activity concentration and occupancy period reported in Ref. [61] using the inhalation dose coefficients in Table 12 for an AMAD of 5 μm.

[c] The doses have been calculated using the dose coefficients reported in Ref. [45], which are similar to those in Table 12 but with the higher dose coefficient for Ra-226 as given in Table 13.

[d] The values quoted are the maximum values measured after the implementation of the following dose reduction measures: reduction of dust generation through revised engineering practices, reduction of stockpile quantities and thus of gamma exposures and reduction of surface contamination by continuous cleaning practices.

Short duration sampling (over periods as short as 1 h) proved to be of limited use in determining when and where dust levels peaked during the work. The placing of PASs at fixed locations generated more information, but it was still not possible to pinpoint specific dust sources. The use of a real time airborne dust sampler provided a significant amount of new information, enabling particular sources of high dust levels to be identified. These included a dust leak from material transfer pipes and exhaust air from the mill motor housing. It also demonstrated that both mechanized and manual sweeping of the floors resuspended significant amounts of dust. On the basis of these results, the following remedial measures to reduce dust levels were identified and implemented:

(a) Repair of dust leaks;
(b) Installation of exhaust air filtration on the mill motor;
(c) Repair of a faulty vacuum system on the mechanized floor sweeper.

As a result of these remedial actions, preliminary indications were that dust levels had fallen by 25–50%. It was found impracticable to reduce dust levels during particularly dusty operations such as manual floor sweeping and

plant maintenance, and instead greater emphasis was placed on the use of disposable dust masks during such tasks.

4.3.5.3. Bagging areas

Exposure to dust in the bagging operation can be reduced by attention to the operation itself, wearing respiratory protection and taking measures to collect dust wherever it is generated.

4.4. PUBLIC EXPOSURE

Doses from gamma radiation emitted from large stockpiles of zircon sand are principally an issue for workers, but individuals outside a zircon milling plant may also receive exposure via this pathway if they are sufficiently close to the facility. Individuals may also receive exposure from material deposited outside the plant by storm water runoff and from the inhalation of airborne dust emitted from stockpiles and openings in the plant buildings.

Discharges to air and water were estimated at a zircon milling plant in the Netherlands [65]. Discharges were assumed to consist of trans-shipment emissions (to air and water) and milling emissions (to air only). The results are shown in Table 20. The maximum annual effective dose estimated to be received by an individual outside the facility was less than 1 µSv through discharges to water and 56 µSv through air emissions. The latter figure, calculated on the basis of air dispersion modelling, related to a worker in an adjacent industrial building. In nearby population centres, the dose was found to be negligible. The maximum incremental gamma dose rate (i.e. the dose rate after subtraction of the natural background) measured in the industrial area surrounding the plant was 0.7 µSv/h. Based on this value, the annual effective dose received by a worker in a nearby industrial facility was estimated to be 320 µSv. The number of measurements made was very small and the report cautions that it was not known at the time of measurement whether the situation was representative in terms of the amount of bulk material on the site over a full year. The report also points out that the maximum total dose received by an individual was not necessarily equal to the sum of the doses from external and internal exposure.

TABLE 20.   DISCHARGES OF RADIOACTIVITY FROM A ZIRCON MILLING PLANT

	Estimated radionuclide activities discharged annually (activity concentrations of dispersed dust particles shown in parentheses) (MBq)				
	U-238 (4.8 Bq/g)	Ra-226 (3.6 Bq/g)	Pb-210 (3.6 Bq/g)	Po-210 (3.6 Bq/g)	Th-232 (0.6 Bq/g)
Emissions to air					
Trans-shipment	946	710	710	710	118
Milling	25	19	19	19	3
Emissions to water					
Trans-shipment	88	66	66	66	11

In a study carried out in the United Kingdom based on conservative modelling assumptions, the maximum annual effective dose received by a member of the public exposed to airborne dust in the vicinity of a milling plant was estimated to be 0.011 μSv [54].

Investigations were carried out at two zircon milling plants in South Africa, again based on conservative dose modelling. In the first study [66], using as input data the results of sampling and analysis of storm water sediments and airborne dust in the vicinity of the plant, the maximum annual effective dose received by a nearby resident was estimated to be 32 μSv. For an individual working in the industrial area surrounding the plant, the maximum annual effective dose was estimated to be 204 μSv. In the second study, doses received by members of the public were estimated on the basis of air dispersion modelling using local meteorological data [67]. The maximum annual effective dose received by a nearby resident was estimated to be 0.71 μSv. The maximum annual effective dose from external gamma radiation that could be received by an individual working in the surrounding industrial area, based on a single gamma dose rate measurement at the perimeter fence of the plant, was estimated to be 200 μSv.

The combined results of the investigations described above are shown in more detail in Table 21. It is unlikely on the basis of these results that zircon milling has any significant radiological impact on members of the public, especially given the conservatism inherent in the dose modelling exercises.

TABLE 21. MAXIMUM DOSES ESTIMATED TO BE RECEIVED BY MEMBERS OF THE PUBLIC IN THE VICINITY OF ZIRCON MILLING PLANTS

	Annual effective dose (µSv)			
	Gamma radiation	Dust inhalation	Ingestion	Total
Netherlands [65]				
Adjacent industrial building	320	50	6	320–376
Nearby population centre	Negligible	Negligible	Negligible	Negligible
United Kingdom [54]	Negligible	0.011	Negligible	0.011
South Africa [66]				
Site perimeter (industrial area)	Negligible	204	Negligible	204
Adult resident 1 km from plant	17	6	0.3	23
Child resident 1 km from plant	17	11	4	32
South Africa [67]				
Site perimeter (industrial area)	200	— Not determined —		
Resident	0.17	0.54	Negligible	0.71

4.5. REGULATORY CONSIDERATIONS

From the data presented in Section 4.3.3, it is evident that the annual effective dose received by a worker is likely to be always less than 1 mSv as long as respiratory protection is used in areas where airborne dust levels may be high. In most zircon milling plants, this is mandatory in terms of general OHS requirements, in which case the regulator could decide not to impose any radiation protection requirements other than perhaps the requirement for notification. Where the regulator cannot be confident that respiratory protection will be used where it is needed, this might need to be enforced by requiring the legal person to apply for an authorization in the form of a registration. From the data presented in Section 4.4, the radiological impact on members of the public is likely to be too small to warrant any specific control measures. Irrespective of whether regulatory control is deemed to be necessary, it is good OHS and environmental practice to identify and implement any simple measures, for example airborne dust minimization, that may be effective in reducing the radiological impact on workers and members of the public. In

the case of occupational exposure, there is clear evidence that such measures can be effective.

5. ZIRCON IN CERAMIC TILES AND SANITARY WARE

5.1. PROCESS DESCRIPTION

5.1.1. Introduction

A ceramic tile or sanitary ware product consists of a clay based ceramic body to which a glaze surface layer is commonly applied. The glaze is essentially a glass covering, usually a combination of complex silicates and borates, that is compounded to be compatible with the body to which it is applied. The purpose of the glaze, which is typically 0.3–0.5 mm thick, is to improve the lustre and smoothness of the surface of the ceramic product and to make it impermeable to water and resistant to mechanical damage (e.g. scratching) and to the acids and alkalis normally encountered in use. Colours may sometimes be added to the body of a ceramic product, necessitating the application of a transparent glaze to allow these colours to remain visible. Usually, however, the glaze is used as an opacifying layer that hides the colour of the ceramic body to make it suitable for the application of decorative effects or to obtain light colours or a sanitary, white appearance. Opacification results from the presence of crystallized particles, well dispersed throughout the glaze. Micronized zircon is a common opacifying constituent of glazes because its high refractive index (typically about 1.85) compared with that of the glassy phase constituents (1.5–1.6) is favourable for obtaining the necessary light scattering and reflective properties.

Where the colour of the ceramic body is dark and the glaze is light, an intermediate layer or engobe is applied. Engobes are mixtures of clays, fluxes and zircon-containing fillers that coat the substrate with a permanent, almost opaque layer. Typically the composition of the engobe lies between that of the body and the glaze. The use of an engobe reduces the opacifying requirements of the glaze, so that the final glaze does not need to be thicker than 0.5 mm.

5.1.2. Glazed tiles

In the production of glazed tiles, the first step in the manufacture of the glaze involves the preparation of a glaze slip, consisting of a finely ground mixture of raw materials such as zinc oxide, feldspar and kaolin dispersed in water. For zircon-containing glazes, micronized zircon is included in the mixture. The zircon content depends on the type of glaze being produced; it is typically about 10–15 wt% but can vary between extremes of 0.5 and 50 wt%. The slurry is sprayed onto the tile base. Several layers of different slurries may be applied, depending on the type and colour of the tile. The wet tile is then fired in a kiln at a controlled temperature of about 1200ºC for 12 h. In the traditional process, a double firing method is used — the ceramic body is fired before the slip is applied and again after application of the slip. During the second firing, the glaze materials in the slip fuse to form a glass. This double firing method is gradually being replaced by a single firing method in which the ceramic body and glaze are fired at the same time. Modern plants are highly automated, the major workload being performed by robots or machines in closed or ventilated environments. Sometimes, the glaze is sprayed manually on to items produced on a small scale. Such work tends to be performed in fume cupboards.

Many glaze ingredients, including borax, are soluble in water. If these ingredients were to be applied wet to the surface of the dry clay body of the ceramic product, they would be absorbed into the very clay on which they are meant to provide a glassy outer surface. The process of 'fritting', or fusing of the soluble glaze ingredients with silica, renders these ingredients virtually insoluble in water, allowing them to remain on the surface of the body throughout the firing process. Fritting also starts the glass formation process well before the glaze is applied to the body, significantly lowering the glaze firing temperature — glazes produced in this manner vitrify at temperatures of less than 1150ºC. The intermediate products of the fritting process, ceramic glasses known as 'frits', are usually marketed in the form of inert granular solids. A wide range of frits is available, with variations in characteristics such as colour, fusibility, viscosity, gloss and opacity. The precise composition varies and is often the proprietary technology of a specific producer. The constituents are chosen so that their crystalline components are broken down into acidic or basic oxides that combine to form a vitreous glassy base consisting of SiO_2 (50–60 wt%), fluxing elements such as Na_2O, K_2O, PbO and B_2O_3 (20–25 wt%) and stabilizing elements such as ZnO, Al_2O_3, CaO, BaO and MgO (maximum 7–9 wt%). The addition of zircon flour at a typical concentration of 12–21 wt% (8–14 wt% ZrO_2) gives rise to 'opaque frits' (sometimes referred to as 'white of zirconium'), which, in addition to having a high opacity, are glossy, viscous and of low fusibility. Occasionally, the zircon content of opaque frits may be as high as 29%.

Frits are manufactured by mixing the raw powdered components, melting the mixture at temperatures of up to 1400ºC, quenching in water and then grinding to a fine powder. The powder is mixed with water and organic additives to form a glaze slip, which is applied to the surface of the ceramic body, dried and fired. When zircon is incorporated into a frit, it enters solution during the melting process to produce a clear glass. When the frit is reheated during the firing process, recrystallization of the zircon produces particles of a more suitable size than can be obtained by adding opacifier sized zircon directly to the glaze. During the relatively short period at high temperature, some of the zircon will start to dissolve, reducing the particle size towards the ideal 0.5–0.8 μm range. The covering power for a given mass of zircon is greater if it is incorporated into a frit rather than used as a direct addition to the glaze. The manufacture of frits does not produce any significant residues — any spillage is recycled to the melting furnace.

5.1.3. Porcelain tiles

A recent development in the technology for producing tiles has led to the production of porcelain tiles. This more expensive type of tile consists of a spray dried body of selected clays, quartz and feldspar, which is shaped by dry pressing and fired at temperatures of up to 1250ºC. It is a uniform, monolithic product (although a glaze may be applied for decorative purposes) that has high water resistance and mechanical strength. Zircon is used as an opacifier where a white or near white colour is required. In this case, however, the zircon is incorporated directly into the mixture used for forming the body of the tile. The zircon concentration is typically about 1–5 wt%, or up to 15 wt% in a 'superwhite' tile. Such tiles are more resistant to wear and are thus especially suitable for flooring applications.

5.1.4. Sanitary ware

Sanitary ware is made from feldspathic flux, quartz, china clay and ball clay and is fired at a temperature of 1150–1270ºC. Fireclays are used for heavy duty applications, but these require an engobe to hide the undesirable buff body colour. Sanitary ware is usually covered with a hard, abrasion resistant, high gloss glaze in white or a range of colours. The glazes are often applied by spraying on to a 'green' (i.e. unfired) earthenware body. Sanitary ware almost always makes use of raw glazes (i.e. without the utilization of frits) consisting of feldspar or nepheline syenite opacified with zircon. Raw glazes can be used because the firing temperature and duration are greater than those used for tiles. A typical white opaque sanitary ware glaze contains about 10 wt% zircon.

5.1.5. Management of zircon-containing residues

Liquids containing zircon as a result of glaze spills enter the wastewater treatment system. At a factory consuming about 200 t of zircon per year, it was calculated that the annual spill of glaze entering the wastewater treatment system was about 175 t dry weight, corresponding to 18 t of zircon [37]. The treated water is discharged from the treatment plant, leaving water treatment residues in the form of 'ceramic sludges' containing residual zircon. To the extent possible, ceramic sludges are returned to the plant to be used in the manufacture of the tile body; otherwise they are sent for disposal in a landfill facility [68].

Broken tiles, fired or unfired, from the manufacturing process may be recycled or sent for disposal at a landfill site. Broken tiles arising from the renovation or demolition of buildings become incorporated into, and inseparable from, normal building rubble.

5.2. RADIONUCLIDE ACTIVITY CONCENTRATIONS

5.2.1. Frits

Based on the typical ranges of radionuclide activity concentrations in commercial zircon (see Section 3.2.2) and the typical zircon content of frits of about 12–21 wt% (see Section 5.1.2), the activity concentrations of ^{238}U and ^{232}Th series radionuclides in frits would be expected to be in the ranges 0.2–0.8 and 0.05–0.2 Bq/g, respectively. Measurements conducted on some zircon-containing frits [69, 70] gave radionuclide concentrations more or less in line with this expectation, as shown in Table 22.

TABLE 22. ACTIVITY CONCENTRATIONS IN ZIRCON-CONTAINING FRITS

Ref.	Zircon content (%)	Radionuclide activity concentration (%)		
		Ra-226	Th-232	K-40
[69]	15	0.5		
[70]	12	0.69	0.12	0.10
[70]	19	0.96	0.15	0.28

5.2.2. Glazes

Based on the typical ranges of radionuclide activity concentrations in commercial zircon (see Section 3.2.2) and the range of zircon content of glazes of 0.5–50 wt% (see Section 5.1.2), the activity concentrations of ^{238}U and ^{232}Th series radionuclides in zircon-containing glazes would be expected to be in the ranges 0.01–2.0 and 0.002–0.5 Bq/g, respectively.

In an Italian study [71], samples of ceramic sludges coming from the wastewater treatment systems of ceramic wall and floor tile production, and in particular those derived from the glazing operation, were analysed. Such sludges consisted of mixtures of the residues of the various types of glaze used on different production lines. For this reason, the chemical composition of the sludges, averaged over a statistically significant time, was taken to be representative of the chemical composition of the glazes employed. The samples were chosen to be representative of the main types of ceramic wall and floor tile produced in Italy. The activity concentrations of the samples were measured using gamma spectrometry. Additional measurements are reported in Ref. [68]. Direct gamma spectrometry measurements on glaze samples are reported in Refs [72, 73].

The results of the above mentioned investigations are summarized in Table 23 and are generally in line with what would be expected from the activity concentrations in zircon and the zircon content of glazes. Some of the glaze samples analysed in Refs [72, 73] used zircon sourced from Malaysia and China, respectively, which is known to have unusually high activity concentrations that are not representative of current world production (see

TABLE 23. ACTIVITY CONCENTRATIONS IN CERAMIC TILE GLAZES

Ref.	Number of samples	Radionuclide activity concentration (Bq/g)		
		U-238 series	Th-232 series	K-40
[71]	6	0.068–0.354	0.030–0.119	0.266–0.427
[68]	2	0.116–0.193	0.045–0.062	0.320–0.330
[72]	6	0.215–5.079	0.103–0.733	≤1.202
[73]	Mean of 10	0.158	0.092	0.474
[73]	Mean of 8	0.566	0.218	0.957
[73]	Mean of 9	0.615	0.188	1.031
[73]	Mean of 6	1.088	1.218	0.736
[73]	Mean of 4	0.316	0.125	0.557

TABLE 24. ACTIVITY CONCENTRATIONS IN CERAMIC TILES

Type of tile	Ref.	Number of samples	Radionuclide activity concentration (Bq/g)[a]		
			U-238 series	Th-232 series	K-40
Unglazed	[69]	1	0.04		
	[71]	3	0.03–0.06	0.04–0.07	0.68–0.98
	[72]	Mean of 8	0.07	0.06	0.39
	[72]	Mean of 5	0.08	0.07	0.57
Glazed	[68]	2	0.06–0.08	0.05–0.07	0.83–0.89
	[69]	3	0.03–0.09		
	[71]	9	0.03–0.09	0.04–0.07	0.54–0.98
	[72]	60	0.04–0.32	0.02–0.20	
	[74]	2	0.07–0.08	0.06	0.06–0.07
	[73]	Mean of 10	0.13	0.10	0.67
	[73]	Mean of 7	0.13	0.10	0.72
	[73]	Mean of 14	0.13	0.11	0.56
	[73]	Mean of 6	0.10	0.09	0.87
	[73]	Mean of 7	0.06	0.06	0.75
Porcelain	[68]	1	0.05	0.06	0.52
White porcelain	[71]	5	0.18–0.25	0.04–0.09	0.53–1.00
Coloured porcelain	[71]	4	0.04–0.05	0.04–0.07	0.63–1.00

[a] Some values have been rounded.

Appendix II). This could account for some of the measured activity concentrations being above the expected range.

5.2.3. Tiles and sanitary ware

Radionuclide activity concentrations in various types of ceramic tile have been determined in several investigations using gamma spectrometry [68, 69, 71–74]. The results, summarized in Table 24, cover a wide range, reflecting the differences in quantities of zircon incorporated into the various types of product. There are some indications that glazed tiles have higher activity concentrations than non-glazed tiles, as would be expected from the use of zircon in the glaze layer. This effect is more pronounced in the values reported

TABLE 25.   URANIUM DECAY CHAIN EQUILIBRIUM IN GLAZED
CERAMIC TILES

Type of tile	Radionuclide activity concentration (Bq/g)			
	Gamma spectrometry		Alpha spectrometry	
	U-238 (from Th-234)	Ra-226 (from Pb-214, Bi-214)	U-238	U-234
Glazed wall tile	0.0801	0.0816	0.0675	0.0652
Glazed floor tile	0.0725	0.0773	0.0685	0.0633

in Ref. [73] — in this particular study, some of the tiles contained zircon sourced from China, which is known to have radionuclide activity concentrations significantly higher than normal (see Appendix II). Relatively high activity concentrations are also indicated for white porcelain tiles, reflecting the greater percentage of zircon used in that type of product (see Section 5.1.3). The activity concentrations in sanitary ware are much lower than those in tiles, since sanitary ware contains far less glaze per unit mass.

The data reported in Ref. [74] also give some information on the degree of equilibrium within the ^{238}U decay chain and provide a comparison of measured activity concentrations using gamma and alpha spectrometry. The results, shown in Table 25, indicate that in the upper part of the uranium decay chain, at least, there is a high degree of equilibrium. The values determined using alpha spectrometry were slightly lower than those determined using gamma spectrometry.

5.2.4.   Zircon-containing residues

Ceramic sludges have radionuclide activity concentrations similar to those in glazes [71]. Where ceramic sludges are disposed of in landfill facilities, further dilution of the radioactivity content will occur. Similarly, the disposal of broken tiles will result in dilution of the radioactivity content.

5.3.   OCCUPATIONAL EXPOSURE

5.3.1.   Manufacture of frits

During the manufacture of frits, the main exposure pathway is through gamma radiation emitted by stockpiles of zircon flour, with lesser pathways

resulting from the handling of the flour while preparing the mixture for the furnace (gamma radiation and inhalation of radionuclides in dust) and grinding of the product (inhalation of radionuclides in dust). The exposure situations associated with the storage of zircon flour and its handling prior to transfer to the furnace are discussed in Sections 3.2.4–3.2.6, where it is concluded that the annual effective dose received by a worker engaged in these operations is likely to be less than 0.4 mSv. Grinding of the product gives rise to exposure through inhalation of radionuclides in dust, but since the product material contains only 12–21 wt% of zircon (see Section 5.2.1) the exposure levels associated with this operation are likely to be lower than those associated with the milling of pure zircon by a factor of at least five. Reference to Table 19 suggests, therefore, that the annual dose received by a worker in the grinding area is likely to be no more than about 0.2–0.4 mSv.

5.3.2. Manufacture of tiles and sanitary ware

In a tile or sanitary ware manufacturing plant, stockpiles of zircon may give rise to concerns about exposure to gamma radiation. At three factories in Sweden, the amount of zircon used annually is about 50–200 t per factory and the maximum amount stockpiled at any one time is about 20 t [37]. Gamma dose rates measured in two of these plants are reported in Table 11. Workers may also be exposed to gamma radiation in glaze production areas and final product manufacture and packing areas. However, once the glaze slurry has been prepared, the zircon becomes considerably diluted with other, non-radioactive, components. Gamma radiation exposure is then not normally an issue because the activity concentrations of uranium and thorium series radionuclides in the process material are reduced to below 1 Bq/g, except in isolated circumstances where zircon with uncharacteristically high activity concentrations is used (see Sections 5.2.2 and 5.2.3).[14]

The dry mixing of the components of the glaze material (including zircon flour) can generate airborne dust, and this might give rise to some concern for internal exposure, particularly in older plants where the operation is carried out manually. Normal OHS controls, including the monitoring of airborne dust

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[14] In an investigation carried out in China, elevated gamma dose rates were measured on the surfaces of stacks of glazed tiles [38]. Some of the zircon incorporated into the glaze was obtained from local sources with a mean ^{238}U activity concentration of 14.7 Bq/g. Absorbed dose rates of 0.148–0.216 µGy/h (average 0.174 µGy/h) were measured, compared with 0.105–0.143 µGy/h (average 0.125 µGy/h) for stacks of unglazed tiles.

levels, are generally required for such operations and these will provide sufficient control over any associated radiological hazards. Once the slurry is prepared for application to the tile, the dust inhalation pathway becomes insignificant because the operation is wet.

As explained in Section 3.2.1, the zircon structure is extremely stable and retains the ^{238}U and ^{232}Th decay series radionuclides within its crystal lattice, even for volatile radionuclides such as ^{210}Po at glaze firing temperatures of up to 1200ºC [23]. Furthermore, it has been demonstrated that if the crystal lattice is destroyed by melting in a sufficiently reactive flux, the decay products become stabilized in the melt, even when the temperature is above their melting points [75]. The reactivity of the species in the melt is sufficient to form stable compounds with decay elements such as polonium and lead and therefore the enrichment of such radionuclides in furnace dusts does not occur. As a result, the inhalation of furnace fume and stack filter dust is not a significant exposure pathway.

A summary of the results of various investigations of occupational exposures in ceramic plants using zircon is shown in Table 26.

5.4. PUBLIC EXPOSURE

The manufacturing process does not give rise to any significant exposure pathways to members of the public. The products of the process — ceramic tiles and sanitary ware — have activity concentrations far below 1 Bq/g (see Section 5.2.3) and would not normally be regarded as giving rise to exposures of concern. However, since these products are essentially building materials, some consideration of their radiological impact on members of the public is warranted [5]. The potential exposure pathways are through gamma radiation and inhalation of radon released from the product.

5.4.1. Glazed tiles

Most tiles produced by the ceramic industry are glazed. They are used extensively in a wide range of building types, from public facilities to domestic dwellings, and for both floor and wall coverings. The quantity of glazed tiles used in a building tends to be greater in warm climates than in cool climates. The following assessments for members of the public exposed to glazed tiles in dwellings have been reported:

(a)   In China [38], gamma dose rates were measured in 47 randomly selected dwellings. In each dwelling, measurements were made in one or two

TABLE 26. OCCUPATIONAL EXPOSURE TO ZIRCON IN CERAMIC PLANTS

Work activity	Gamma radiation			Inhalation of radionuclides in dust			Total annual effective dose (mSv)
	Dose rate (μSv/h)[a]	Annual exposure period (h)[a]	Annual effective dose (mSv)	Concentration (mg/m^3)	Annual exposure period (h)	Annual effective dose (mSv)	
Sanitary ware plant using zircon with activity concentration 3 Bq/g U-238, 0.5 Bq/g Th-232; maximum zircon stockpile size 20 t [37]							
Glaze production	0.7 (1 m) 0.1 (5 m)	100 (1 m) 20 (5 m)	0.08	0.1–0.3	2000	0.003–0.006	0.083–0.086
Manual glazing	0.7	0	0	0.1–1.5	2000	0.004–0.04	0.004–0.04
Ceramic tile plant using zircon with activity concentration 3.4 Bq/g U-238, 0.7 Bq/g Th-232; maximum zircon stockpile size 0.5 t [37]							
Glaze production	0.15	200	0.03	0.4–0.7[b]	800	0.005–0.009	0.035–0.039
Automated glazing	0.15	0	0	0.4–0.7[b]	800	0.005–0.009	0.005–0.009
Ceramic tile plant [64]							
Store			0.012			0	0.012
Glaze production (manual)			0.04			0.44	0.48
Tile line			0.2			0	0.2
Tile packing			0.2			0	0.2

[a] Exposure to the zircon storage pile at a distance of 1 m except where stated otherwise.
[b] Derived from reported values of airborne zircon concentration and zircon content of dust (12%).

rooms in which floors and/or walls were decorated with glazed tiles and also in a room without glazed tiles for comparison. The zircon used in the glaze was of Chinese origin, with radionuclide activity concentrations several times higher than those of normal commercial zircon (see Appendix II). No increase in gamma dose rate attributable to the use of glazed tiles was found (although an increase in the beta dose rate was noted). Radon flux densities at the surfaces of glazed floor tiles in ten dwellings were also measured and no increase in radon flux density attributable to the use of glazed tiles was found.

(b)　In Australia [69], the annual effective dose attributable to gamma radiation from glazed tiles in homes was estimated to be 7.5–10 μSv. The maximum radon flux density for glazed tiles was estimated to be about 0.00072 Bq·m^{-2}·s^{-1}. It was shown that such a low flux density had minimal implications for radon levels in homes — typically, for a ventilation rate of 1 h^{-1}, the increase in indoor radon concentration was about 5 Bq/m^3 (with no allowance being made for the dilution effect of untiled rooms in a typical dwelling). Using a dose conversion of 17 μSv per Bq/m^3, based on an annual occupancy of 7000 h (see footnote d of Table 16), this corresponds to an increase in annual effective dose of about 85 μSv. A more realistic scenario might be to consider only the occupancy of the tiled rooms, in which case an annual occupancy of 1000 h might be appropriate. This would suggest a dose conversion of 2.4 μSv per Bq/m^3, giving an increase in annual effective dose of 12 μSv.

(c)　In South Africa [76], the annual effective dose attributable to gamma radiation from the glaze layer on tiles was estimated, using conservative assumptions, to be 13–57 μSv. Radon flux densities from the front surfaces of several tile samples were measured and the average value was found to be 0.00328 Bq·m^{-2}·s^{-1}. Based on conservative modelling assumptions, the annual effective dose attributable to the release of radon and thoron from the glaze layer was estimated to be 57 μSv for an air exchange rate of 0.1 h^{-1} and 6 μSv for an air exchange rate of 1 h^{-1}. The dose contributions from radon and thoron were found to be approximately equal.

(d)　In Egypt, using a simplified room model [74], the gamma dose rate at the centre of the room attributable to the use of glazed tiles on all four walls was calculated to be 0.009–0.018 μSv/h, whereas the gamma dose rate attributable to the construction materials (without tiles) varied from about 0.007 to 0.041 μSv/h, depending on the type of material used. If a room occupancy of 1000 h/a is assumed, the corresponding annual effective dose attributable to gamma radiation from glazed wall tiles would be 9–18 μSv.

(e)　In a more recent study conducted in China [72], the maximum gamma dose rate attributable to the use of floor tiles in a living room was calculated to be 0.002–0.006 μSv/h, which was reported to correspond to an annual effective dose of 12–45 μSv (implying an assumed room occupancy of about 7000 h). The maximum gamma dose rate attributable to the use of floor and wall tiles in a bathroom was calculated to be 0.009–0.033 μSv/h, which was reported to correspond to an annual effective dose of 13–48 μSv (implying an assumed room occupancy of about 1400 h).

TABLE 27. DOSES ATTRIBUTABLE TO THE USE OF GLAZED TILES
IN DWELLINGS

Ref.	Annual effective dose (μSv)		
	Gamma radiation	Inhalation of radon	Total
[69]	7–10	12[a]	19–22
[72]	12–48		
[74]	9–18[b]		
[76]	13–57	6–57[c]	19–113

[a] Derived from the reported value of incremental radon concentration (5 Bq/m^3) using
a dose conversion of 2.4 μSv per Bq/m^3 (corresponding to an annual room occupancy
of 1000 h).
[b] Derived from the reported range of incremental gamma dose rates (0.009–0.018 μSv/h)
assuming an annual room occupancy of 1000 h.
[c] Includes a contribution from thoron.

Doses attributable to the use of glazed tiles in dwellings, as determined
from these studies, are summarized in Table 27. The modelling scenarios and
assumptions vary considerably from one study to another, but in all cases the
predicted radiological impact on members of the public is very low.

5.4.2. Porcelain tiles

White or near-white porcelain tiles have a higher zircon content than
glazed tiles (see Section 5.2.3) and would therefore be expected to give rise to
correspondingly higher doses. For a residential scenario, the maximum annual
effective dose arising from exposure to gamma radiation and radon attrib-
utable to the use of porcelain tiles containing about 13% zircon was estimated
to be 120 μSv [77].

5.4.3. Sanitary ware

The zircon content of glazes applied to sanitary ware is similar to that of
glazes applied to ceramic tiles (see Section 5.1), but the surface area of glaze is
far smaller in a typical home. This leads to the conclusion that the radiological
impact of zircon used in the glazes applied to sanitary ware is very small
compared with that of ceramic tiles.

5.5. REGULATORY CONSIDERATIONS

The activity concentrations of zircon-containing frits, of the ceramic tile and sanitary ware products and of the residues from the manufacturing process (ceramic sludges and broken tiles) are all below 1 Bq/g for uranium and thorium series radionuclides and 10 Bq/g for ^{40}K. In addition, from the data presented in Section 5.2.4, it is evident that the annual effective dose received by a worker in the production of ceramic tiles and sanitary ware is likely to be always less than 1 mSv. Consequently, the production of zircon-containing ceramic tiles and sanitary ware is a candidate for exemption by the regulatory body.

Ceramic tiles and sanitary ware could be regarded as construction material, even though they constitute a very small part of the total amount of construction material used in a typical building. However, it is evident from Section 5.4 that the annual effective dose received by a building occupant attributable to the use of zircon-containing tiles and sanitary ware is unlikely to exceed about 100 μSv, implying that no regulatory action is necessary.

6. ZIRCON IN FOUNDRIES

6.1. PROCESS DESCRIPTION

6.1.1. Sand casting

Zircon sand mixed with a resin binder is used in ferrous and ferro-alloy casting operations as a mould core or as a lining for the mould cavity. To minimize costs, it is usual for zircon to be used only for the metal contact surfaces of the mould, with the remainder of the structure typically comprising silica sand and binder. After molten metal has been poured and solidified, the mould is broken apart by mechanical means such as tumbling or shaking to free the cast part. The cast part is cleaned of residual mould material, typically by shot blasting or abrasive sand blasting, prior to mechanical finishing to its final dimensions. The zircon content of the spent foundry sand is similar to that of the mould assembly (i.e. about 10%).

Mould washes are aqueous suspensions of zircon flour, alone or with a binding agent, that are applied to the metal contact surfaces of a silica sand mould to reduce penetration of metal into the mould structure. After application of the mould wash, the mould structure is dried and cured in

readiness for the casting operation. The zircon content of mould washes is typically 60–70%. Mould wash mixtures may be prepared by the foundry, but more typically are commercial products prepared by specialist manufacturers.

6.1.2. Investment casting

Zircon flour is used in investment (or 'lost wax') casting of complex shapes where smoothness and high dimensional accuracy are requirements for the production of small, detailed, ferrous and non-ferrous alloy castings. An exact replica of the shape to be cast is first made from wax. The wax replica is then coated with a slurry containing alumina, zircon and other, proprietary, components. A typical investment casting slurry formulation may comprise 30–50% zircon. Successive dipping and drying actions result in the gradual buildup of a multi-layer coating on the wax replica, called the shell. Depending on the casting process, slurries of varying composition may be used to create different layers of the shell. Heating the assembly dries the shell and liquefies the wax replica. The removal of the wax creates a hollow cavity having the same configuration of the part to be cast. After the wax has been removed, the shell may need to be retouched to rectify any small defects that may have been introduced during the wax melting process. It is then cured at a high temperature into a hard ceramic-like structure. In preparation for casting, the shell may be arranged in a matrix of other shells for mutual support, bedded in silica sand or simply left unsupported. Molten metal is introduced into the shell and allowed to solidify. Cast parts are separated from the brittle shell by mechanical means (e.g. tumbling, vibrating) and the part is cleaned of residual shell material. The broken shell material is placed in a container for disposal as waste.

6.1.3. Management of zircon-containing residues

Zircon used as a mould lining or mould wash in the casting process becomes mixed with the silica sand during mechanical treatment to separate the casting from the mould. The zircon content of spent foundry material varies widely, occasionally up to 30% but usually not more than 10%. Most of such materials are disposed of as waste in landfill facilities. However, foundries are increasingly seeking alternatives to disposal, such as reuse within the foundry or in asphalt or cement manufacturing. The zircon itself is unaffected by the casting process and reclamation of some zircon for reuse within the foundry is possible by screening, scrubbing and magnetic separation of spent foundry sand. Reclaimed zircon that is too fine for reuse within the foundry may be sold to other zircon users. Although the reuse of foundry sand in the casting process is

increasing in some countries, this trend is not universal. In most foundries in the USA, for example, zircon sand is not separated from other foundry materials and ends up being disposed of as waste. In Oregon, it is reported that the average amount of zircon disposed of per foundry is about 300 t in a year [27].

Spent investment casting shells have the appearance and consistency of broken crockery. Their zircon content depends on the amounts of zircon used in the slurry to create the shell. The overall percentage of zircon may be moderated by the use of zircon free materials to build up the outer layers of the the shell material. A zircon content of 30% might be regarded as typical. The mixing of zircon with other components in the shell formulation precludes the reuse of the shell material in the investment casting process because of strict controls over the shell composition. Although efforts have been made to recycle spent shells into alternative refractory products, most spent shells are disposed of as waste in landfill facilities.

Some zircon sand becomes incorporated into liquid effluents as a result of casting washdown and from the disposal of spent zircon slurries. It has been estimated that, in Oregon, the average amount of zircon discharged in a year is about 6 t per foundry [27].

6.2. OCCUPATIONAL EXPOSURE

6.2.1. Gamma radiation

As with any other operation involving the use of zircon, workers stationed close to zircon stockpiles are exposed to gamma radiation emitted from the material. Typical dose rates are reported in Section 3.2.4. In an investment casting plant, it was reported that the minimum stockpile required was about 200 bags, each weighing 50 kg [53]. Exposure to gamma radiation may also need to be considered in other areas where significant quantities of zircon are encountered, such as mould wash preparation areas and core storage areas. In a radiological survey at a US foundry conducted with thermoluminescent detectors at fixed locations and survey meters [50], the average gamma dose rate, after subtraction of background, was found to be about 0.07 μSv/h, with a maximum of about 0.8 μSv/h occurring in core storage areas where workers spent very little time.[15] Experience in the United Kingdom indicates that foundry workers are exposed

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[15] These dose rates have been deduced from reported exposure rates measured in röntgen per hour, assuming that 1 μR/h is approximately equivalent to a dose rate of 0.01 μSv/h.

to gamma dose rates of about 0.6 µSv/h for brief periods during the casting process [51].

6.2.2. Inhalation of radionuclides in dust

There is a potential for workers directly handling zircon during the preparation of the mould mixture to inhale airborne dust containing zircon. Investigations have revealed the following:

(a) Air monitoring in a high use area within a large carbon steel casting plant in the USA, at the breathing zone level of five workers involved in preparing the mould mixture, indicated that significant airborne contamination existed only in the breathing zone of one worker who had hand dumped eight bags, each weighing 50 kg, of zircon flour into a chute that fed the mixing equipment [27].
(b) In an investigation in a German foundry [35], dust monitoring stations near a mixer gave average airborne activity concentrations of 14 and 5 mBq/m^3 for ^{238}U and ^{232}Th series radionuclides, respectively. The annual exposure period was determined to be 60 h.

Dusty conditions can also exist during the removal by abrasive techniques of surface deposits on the casting.

6.2.3. Inhalation of radon

Owing to the very low radon emanation coefficient of zircon (see Section 3.2.3), exposure to radon in foundries, as in any facility involving the use of zircon, is not likely to be of concern. This has been confirmed by measurements at two foundries, which showed that radon levels were far below the 1000 Bq/m^3 radon action level for workplaces (see Section 3.1.1):

(a) At a German foundry, the radon concentration was measured in a room in which zircon sand was mixed [35]. The concentration was found to be 80 Bq/m^3 with the door to the room open and 140 Bq/m^3 with the door closed.
(b) In a study at a foundry in the USA [50], radon concentrations were monitored over three periods, each of four months duration, at 12 locations in the plant. The concentrations did not exceed about 70 Bq/m^3.

TABLE 28. DOSES RECEIVED BY WORKERS EXPOSED TO ZIRCON IN FOUNDRIES

	Annual effective dose (mSv)		
	Gamma radiation	Dust inhalation	Total
Average, German foundry [35]	0.08	0.054[a]	0.134
Average, US foundry [50]	0.15		
Average, typical UK foundry [51]	0.001	0.05	0.051
Mould wash workers, UK foundry [52]	0.17	0.25	0.42
Investment casting plant, Spain [53]			
Store	0.003	No pathway	0.003
Shell building area	0.02	Negligible	0.02
Foundry area	<0.01	No pathway	<0.01
Shell breaking area	0.0003	No pathway	0.0003
Finishing area	0.003	No pathway	0.003
Transport of waste shells to landfill	0.034	No pathway	0.034

[a]   Recalculated from raw data using the dose coefficients in Table 12 for an AMAD of 5 µm.

6.2.4.   Effective dose

Several assessments of the effective doses received by workers in foundries have been reported. The results are summarized in Table 28.

6.3. PUBLIC EXPOSURE

The activity concentrations of uranium and thorium series radionuclides in spent foundry sands or waste investment casting shells are likely to be of the order of 1 Bq/g or less because of the dilution of zircon with other constituents. Based on the data reported in Table 16 and taking into account the conservatism inherent in the dose modelling assessments involved, it can be expected that an annual effective dose of the order of 100 µSv is the maximum that could be received by a member of the public as a result of the disposal of these materials in landfill facilities.

6.4. REGULATORY CONSIDERATIONS

From the data presented in Sections 6.2.4 and 6.3, it is evident that:

(a) The annual effective dose received by a foundry worker is likely to be always less than 1 mSv;

(b) The annual effective dose received by a member of the public as a result of the disposal of spent foundry sand or investment casting shells in a landfill facility is unlikely to exceed about 100 μSv.

Consequently, the use of zircon in foundries is a candidate for exemption by the regulatory body.

7. MANUFACTURE OF ZIRCONIA BY FUSION OF ZIRCONIUM MINERALS

7.1. PROCESS DESCRIPTION

7.1.1. Fusion of zircon

Zircon sand is melted with coke in an electric arc furnace at a temperature of 2800ºC. The zircon dissociates into ZrO_2 and SiO_2 at about 1800°C and the coke reacts with the SiO_2 to produce SiO and CO_2. On contact with air, the SiO forms SiO_2 fume, which is removed from the furnace by a fume collection system, passed through scrubbers and collected as a very fine grained solid in a baghouse. The ZrO_2 remaining in the furnace is tapped and either cast into 'fused cast zirconia' ingots or cooled rapidly to form a granular material, generally less than 10 mm in size. The granular material is fed into skips for quality testing, screened and, depending on product requirements, either bagged directly or further screened and crushed to a product size of typically 0.5 mm. The coarser grain material is usually used in applications involving further fusion, such as the manufacture of fused cast refractories and stabilized zirconia. Material with a finer, more consistent grain size is used directly in the manufacture of specialized products such as ceramic pigments and engineering ceramics. The granular material is packaged for shipping, usually in 1 t bags.

The composition of the fused zirconia product is dependent on the purity of the zircon and any other raw material used, as there is no slag phase to remove impurities. Through the addition of certain oxides to the arc furnace during fusion (calcium oxide, magnesium oxide or yttrium oxide, depending on the proposed application), the crystalline structure of the zirconia product can be controlled, producing partially or fully stabilized zirconia (see Section 2.3.2).

7.1.2. Fusion of baddeleyite

The production of zirconia by fusion of baddeleyite has become less common because of diminishing supplies of raw material. Baddeleyite is procured in drums or bulk bags and stored until required for production. Batches of raw material are mixed with any necessary additives and then fused at high temperatures in an electric arc furnace. This alters its crystalline structure to form fused zirconia. During the process, furnace fume containing fine dust particles is released and collected by an extraction system. The extraction system transports the fume to a filter house, where a solid material comprising a mixture of the fine dust particles and condensate is separated from the vapour stream — this material is sometimes referred to as furnace dust collector fines or furnace DCF and is collected and packaged in drums. The zirconia is tapped from the furnace and cast into 1 t ingots that, after cooling, are progressively crushed and milled until the required range of particle sizes is achieved. The products are bagged and placed in storage, ready for onward distribution.

7.1.3. Management of residues

The fine grained silica produced in the zircon fusion process is usually sold as a by-product for use as an additive to cement, in brick making and in low cement castable refractories. In one report, however, it is stated that the material is treated as a waste for disposal in a landfill facility [54].

In a plant in the United Kingdom which produces 2080 t of zirconia per year by the fusion of baddeleyite, the following waste streams are reported [78]:

(a) Floor washings containing spilt feedstock material are discharged as liquid effluent.

(b) Fume containing volatile radionuclides is discharged to the atmosphere from 20 m high stacks. Annual discharge rates are estimated to be 150 MBq of ^{210}Po and 50 MBq of ^{210}Pb.

(c) Solid waste in the form of furnace DCF is collected in the filters. The annual quantity is estimated to be about 20 t. On the basis of an environ-

mental assessment, the preferred option identified for this material is for it to be disposed of as industrial waste in a landfill facility, although, at the time of reporting, this option had yet to be implemented pending the securing of an agreement with a suitable landfill facility [79].

Scrap metal arising from maintenance and decommissioning operations can exhibit significant surface contamination levels due to the mobilization of radionuclides at the high process temperatures involved. One operator reported that this contamination can be removed by high pressure water jetting or, in extreme cases, by grit blasting.

7.2. RADIONUCLIDE ACTIVITY CONCENTRATIONS

7.2.1. Fusion of zircon

The fusion process liberates the radionuclides contained in the zircon, which then end up either in the zirconia product or the silica dust, depending on the reduction potential of the elements and their boiling points (see Table 9). Various measurements of radionuclide activity concentrations have been made on the materials involved in this process and the results are shown in Table 29. There is a tendency for ^{238}U and ^{232}Th to end up in the zirconia product (at activity concentrations comparable with or higher than those in the original zircon sand) and for ^{226}Ra to end up in the silica. The zirconia product is therefore depleted in ^{226}Ra. Low activity concentrations of ^{210}Po and ^{210}Pb were measured in the zirconia — this is consistent with the expectation that both of these radionuclides will volatilize at the high furnace temperatures into the silica fume, where they will condense and attach to dust particles in the off-gas collection systems and bag filters. Indeed, one operator has reported a relatively high PbO content of 170 ppm in silica fume, and some evidence of elevated activity concentrations of ^{210}Pb and ^{210}Po in material accumulating in the filter and extraction systems is apparent from the results in Table 29.

7.2.2. Fusion of baddeleyite

Investigations of zirconia production from baddeleyite in the United Kingdom were reported during the period 1994–1998 [51, 78, 79, 82]. The activity concentrations in the various process materials analysed in these investigations are shown in Table 30. The activity concentrations in the zirconia product are similar to those in the baddeleyite feedstock and consequently are higher than in zirconia obtained by fusion of zircon sand. Significant

TABLE 29. ACTIVITY CONCENTRATIONS IN PROCESS MATERIALS IN THE MANUFACTURE OF FUSED ZIRCONIA FROM ZIRCON

Ref.	Process material	Radionuclide activity concentration (Bq/g)							
		U-238 series				Th-232 series			K-40
		U-238	Ra-226	Pb-210	Po-210	Th-232	Ra-228	Th-228	
[80]	Zirconia product	3.37	2.20	0.15	0.16	0.57	0.47	0.47	
[81][a]	Zircon sand feedstock	3.9	3.8			0.6	0.54	0.54	
[81]	Zirconia product	3.89	1.78	0		0.73	0.27	0.54	0.3
[81]	Zirconia product	2.1	2.44	0.3	0.3	0.72	0.40	0.48	0.4
[81]	Zirconia product	3.71	2.45	0		0.57	0.31	0.61	0.2
[81]	Silica by-product	0.95	5.76	0		0.07	0.87	0.22	
—[b]	Zirconia product	2.6–3.3	2.2–2.9			1.0–1.2	0.6–0.8	0.9	
—	Zirconia product	3.3	0.5						
—	Zirconia product	3.6	0.6						
—	Zirconia product	4.5	1.4						
—	Zirconia product	3.0	0.6						
—	Zirconia product	3.1	0.4						
—	Zirconia product	1.9	1.6						
—	Zirconia product	3.2	1.2						
—	Silica by-product	1.2–2.0				0.01–0.1			
[36]	Zircon sand feedstock	4.1	4.1	4.1	4.1	0.61	0.61	0.61	
[36]	Zircon sand feedstock	3.4	3.4	3.4	3.4	0.56	0.56	0.56	
[36]	Zirconia product (unstabilized)	5.2				0.89			
[36]	Zirconia product (CaO stabilized)	4.8				0.81			
[36]	Zirconia product (CaO stabilized, granulated)	4.9				0.83			
[54]	Silica waste	1.5	1.5	10	10	0.6	0.6	0.6	

[a] Supplemented by unpublished company data.
[b] —: Unpublished company data.

TABLE 30. ACTIVITY CONCENTRATIONS IN PROCESS MATERIALS IN THE MANUFACTURE OF FUSED ZIRCONIA FROM BADDELEYITE

Ref.	Process material	Radionuclide activity concentration (Bq/g)							
		U-238 series					Th-232 series		
		U-238	Th-230	Ra-226	Pb-210	Po-210	Th-232	Ra-228	Th-228
[51, 78, 82]	Baddeleyite feedstock	7		7	7	7	0.3	6	2
	Zirconia product	7		7	7	7	0.3	6	2
[51, 78, 82]	Furnace DCF	3		3	200	600	0.5	8	3
[79]	Baddeleyite feedstock	9.5	1.3	10	10	3.7	0.3	2	0.4
[79]	Zirconia product	8	1	10	10	3.0	0.3	2	0.5
[79]	Furnace DCF	16	2.5	30	200	600	1.8	11	3.6

enrichment of the volatile radionuclides ^{210}Pb and ^{210}Po in the furnace DCF is evident, although there is little indication of a corresponding depletion of these radionuclides in the zirconia product.

7.3. OCCUPATIONAL EXPOSURE

7.3.1. Exposure pathways

As with any other type of operation involving zirconium-containing minerals and products, workers are exposed to gamma radiation when working close to large quantities of feedstocks and zirconia product. The transfer of feedstock to the furnace and the milling and packaging of the product are inherently dusty operations that could give rise to significant occupational exposure through the inhalation of radionuclides in the dust. Also, spills of material are not infrequent, the removal of which also involves the generation of dust. Local ventilation systems are usually installed and in many zirconia plants the use of respiratory protection is mandatory for the more dusty operations for general OHS reasons.

Entry into off-gas filtration systems is mostly limited to minor maintenance operations, and annual exposure periods are short. Major maintenance or demolition has the potential for more significant exposures.

TABLE 31. EXPOSURE LEVELS IN A ZIRCON FUSION PLANT

	Average gamma dose rate at 1 m (μSv/h)	Gross long lived alpha activity concentration (mBq/m^3)	
		Range	Average
Production areas			
Smelter area	0.66	62–63	
Grinding area	0.51	275–2990	1235
Overall	0.64	62–2990	1021
Workshops	0.40	45–58	

The disposal of furnace dust in landfill facilities gives rise to potentially significant exposure of landfill workers.

7.3.2.   Exposure levels

In a zircon fusion plant in South Africa [36, 83], gamma dose rates, after subtracting the contribution of 0.15 μSv/h from natural background, were found to vary from 0.1 to 0.85 μSv/h at a distance of 1 m from possible sources of exposure. Long lived alpha activity concentrations in airborne dust were also measured. The results are shown in Table 31. Measurements in the grinding area, the area with the highest airborne dust concentrations, were obtained from both area monitoring and personal monitoring devices, with comparable results. The gravimetric airborne dust levels corresponding to these airborne activity concentration measurements (taking into account the activity concentrations in the product quoted from Ref. [36] in Table 29) are 1.6–2.3 mg/m^3 in the smelter and workshop areas but very much higher, and more variable, in the product grinding areas (average 45 mg/m^3, range 10–100 mg/m^3), where the use of respiratory protection in the form of half-face masks was compulsory. An AMAD of 5 μm was established as being a representative value for the airborne dust.

In investigations in the baddeleyite fusion plants in the United Kingdom [51, 78, 79, 82], dust activity concentrations were determined using PASs worn by each of the operators. Respiratory protection in the form of face masks was used in the more dusty operations and sometimes in less dusty operations. Typical exposure parameters determined in these investigations are shown in Table 32.

TABLE 32. TYPICAL OCCUPATIONAL EXPOSURE PARAMETERS IN THE PRODUCTION OF ZIRCONIA FROM BADDELEYITE

Source of exposure	Exposure period			Gamma dose rate (μSv/h)	Airborne dust characteristics	
	h/d	d/a	h/a		Concentration (mg/m^3)	AMAD (μm)
Bulk ZrO$_2$	1	200	200	2.7	n.a.[a]	n.a.
ZrO$_2$ dust	7	200	1400	0	5	5
Furnace DCF	2	50	100	3.7	10	5

[a] n.a.: not applicable.

7.3.3. Effective dose

The results of dose assessments based on measurements in zircon fusion plants in South Africa are shown in Table 33. Most of the dose arises from the inhalation of radionuclides in airborne dust, reflecting the inherently dusty nature of this type of operation despite the provision of local ventilation.

Workers involved in the disposal of furnace silica dust from the zircon fusion process (where this dust was not used as a by-product) were estimated to receive an annual effective dose of 15 μSv, almost all of which (98%) was due to external gamma exposure [54]. This result was based on the assumption that the waste was sent to the landfill in a form that could readily expose workers, which was reported to be not the case for most of the waste sent to landfill from this industry — for most disposals, therefore, the annual effective dose would have been less than 15 μSv.

Typical values of annual effective dose received by workers involved in the fusion of baddeleyite can be estimated from the exposure parameters for plants in the United Kingdom given in Table 32 and the radionuclide activity concentrations in process materials given in Table 30. The results, calculated using the dose coefficients listed in Table 12, are shown in Table 34. It is assumed that respiratory protection with a protection factor of 5 is used by workers when exposed to furnace DCF, but not when exposed to ZrO$_2$ dust. The table also includes unpublished company data on the gamma radiation dose received by workers in a South African baddeleyite fusion plant. As with the zircon fusion process, the results show that most of the dose arises from the inhalation of radionuclides in airborne dust.

The inhalation doses in Tables 33 and 34 have been calculated using a dose coefficient for ^{226}Ra corresponding to a lung absorption class of either S or M, but based in either case on a ^{222}Rn removal rate of 100 d^{-1} (see Section 3.2.5). If the

TABLE 33. DOSES RECEIVED BY WORKERS IN THE PRODUCTION OF ZIRCONIA BY FUSION OF ZIRCON

Ref.	Type of worker	Annual effective dose (mSv)		
		Gamma radiation	Dust inhalation	Total (rounded to two significant figures)
	Production areas			
[81][a]	Smelter operator	0.08	0.66	0.74
[81]	Smelter supervisor			0.9
[81]	Powder operator	0.13	0.87	1.0
[81]	Powder supervisor			1.1
[81]	Annealing operator	0.26	0.74	1.0
[81]	Logistics operator			1.6
	Non-production areas			
[81]	Workshop artisan	0.07	3.0	3.1
[81]	Laboratory sampler	0.19	2.5	2.7
[81]	Laboratory analyst			2.5
—[b]	Multi-skilled plant operator practising job rotation	0.1	0.15	0.25
	Production areas			
[36, 83]	Smelter operator	1.03	1.21[c]	2.2
[36, 83]	Grinding operator	0.72	4.78[c]	5.5
[36, 83]	Workshop personnel[d]	0.60	1.59[c]	2.2

[a] Supplemented by unpublished company data. The doses were assessed using random personal monitoring within specified worker categories identified on the basis of spatial factors (such as location and building layout) and work characteristics (such as job specification and exposure period) over a four year period. The use of respiratory protection was mandatory in the smelter, powder and logistics sections, and a protection factor of 5 was assumed.

[b] —: Unpublished company data.

[c] These doses have been recalculated from the airborne activity concentrations reported in Table 31 using the dose coefficients listed in Table 12. The use of respiratory protection was compulsory in the grinding area, and a protection factor of 5 is assumed.

[d] These workers were assumed to spend 80% of their time in the workshops and 20% in production areas.

TABLE 34. DOSES RECEIVED BY WORKERS IN THE PRODUCTION OF ZIRCONIA BY FUSION OF BADDELEYITE

	Annual effective dose (mSv)		
	Gamma radiation	Dust inhalation	Total (rounded to two significant figures)
UK plants (typical)			
Bulk ZrO$_2$	0.54	n.a.[a]	0.54
ZrO$_2$ dust	0	2.48–3.15	2.5–3.2
Furnace DCF	0.37	0.66–0.76	1.0–1.1
Total	0.91	3.14–3.91	4.0–4.8
South African plant			
Average	0.3		
Maximum	2.8		

[a] n.a.: not applicable.

removal rate were to be less than 100 d^{-1}, the inhalation doses would be underestimated. In a worst case situation of zero radon emanation and lung absorption class S for ^{226}Ra (see Table 13), the degree of underestimation would be about 25–35%.

7.3.4. Measures to reduce doses

In Ref. [79], it was reported that dose levels similar to those in Table 34 were achieved in plants in the United Kingdom only after the implementation of dose reduction measures. Prior to this, the average annual dose received by workers was estimated to be more than 10 mSv. The dose reduction measures comprised the following:

(a) Engineering controls:
   (i) Some batch transfer operations (usually done by hoppers) were replaced with enclosed systems such as screw feeds;
  (ii) Separate pieces of plant were combined or replaced with a single new plant with reduced dust generation;
 (iii) The dust extraction system was upgraded and extended;
 (iv) The bag filling operation was redesigned to reduce dust generation;

(v) The furnace DCF drum collection point was enclosed to prevent dust dispersion.
(b) Working procedures:
  (i) Employees were provided with written local rules that stressed the importance of dust control;
  (ii) Routine dose rate and contamination surveys were introduced;
  (iii) Training sessions were provided for employees.
(c) Respiratory protection:
  (i) Dust masks were made compulsory for work in furnace DCF areas and for cleaning and maintenance procedures;
  (ii) The use of dust masks was encouraged for all other work.

Although it was not possible to determine the effect of specific measures, it was considered likely that the engineering controls contributed most to dose reduction. Outside the areas in which the wearing of dust masks was compulsory, they were worn voluntarily for certain tasks but were not regarded as a practical option for routine work. It was reported that, despite the provision of local rules and training, it proved difficult to maintain the right level of safety awareness among employees. Consequently, poor working practices (e.g. not cleaning up spills, using hand brushes instead of vacuum equipment and leaving inspection hatches open) still occurred.

7.4. PUBLIC EXPOSURE

The main exposure pathways to members of the public are discharges of radionuclides in liquid effluent (floor washings) and stack emissions and migration of radionuclides from the landfill disposal of furnace dust. In an investigation of the zircon fusion process [54], modelling of pathways to the public using conservative assumptions predicted the following maximum values of annual effective dose:

(a) The dose received by a nearby resident from the release of radionuclides in liquid effluents was negligible;
(b) The dose received by a nearby resident as a result of plume inhalation and fallout from stack emissions was 37 μSv, of which more than 35 μSv was due to dust inhalation;
(c) The dose received by a future site user after closure of a landfill facility containing 50 t of furnace silica dust (excluding the dose from indoor radon, for which no realistic estimate was made) was 4.5 μSv, of which 3.8 μSv was due to external gamma exposure.

In an investigation of the baddeleyite fusion process [78], the highest dose received by a member of the public due to exposure to liquid effluent and stack emissions was estimated to be a few microsieverts per year.

7.5. REGULATORY CONSIDERATIONS

7.5.1. Scope of regulation

The uranium series radionuclide activity concentrations in all the main process materials (i.e. zircon and baddeleyite feedstocks, zirconia product, silica by-product or waste, furnace DCF waste) exceed 1 Bq/g. Therefore, the production of fused zirconia (including the disposal of solid residues) and the use of the silica by-product both necessitate regulatory consideration.

In the manufacture of fused zirconia from zircon, reference to Eq. (1) (or Eq. (3) where appropriate) and to the radionuclide activity concentrations in Table 29 indicates that neither the zirconia product nor the silica by-product or waste are subject to the Transport Regulations as long as the activity concentration of the zircon feedstock is within the normal commercial range (see Section 3.2.2). In the manufacture of fused zirconia from baddeleyite, the data in Table 30 suggest that both the feedstock and the zirconia product may be subject to the Transport Regulations, although these data are not necessarily representative of current baddeleyite production from the Russian Federation (see Appendix II), implying the need for a prior radionuclide composition analysis. The furnace DCF is likely to be always subject to the Transport Regulations because of the high activity concentrations of ^{210}Pb and [210]Po.

7.5.2. Zirconia production

The annual effective dose received by a worker in a fusion plant is likely to range from less than 1 mSv up to about 5 mSv, assuming the use of respiratory protection in the dustiest operations (which is generally an OHS requirement). There is some historical evidence to suggest that the dose could be much higher if attention is not given to specific control measures for airborne dust. On the other hand, the effective doses attributable to stack emissions, aqueous discharges and disposal of solid residues in industrial landfill facilities are very low and it seems unlikely that such waste management activities would necessitate any specific measures to control radiation exposure. In view of this, the appropriate regulatory option might be a requirement for authorization in the form of a registration, in terms of which certain measures such as dust monitoring and control become mandatory

within the fusion plant (in addition to respiratory protection in the dustiest operations where this is not already mandatory in terms of general OHS requirements).

7.5.3. Use of silica by-product

The exposure implications of incorporating the silica by-product into a construction material or refractory product do not appear to have been investigated in detail and would need to be considered by the regulatory body in order to identify the most appropriate regulatory option for this type of practice (including consideration of the option of exemption). An important factor to be taken into account is the considerable dilution with non-radioactive material that is likely to occur as part of the process.

8. MANUFACTURE OF ZIRCONIUM COMPOUNDS BY CHEMICAL DISSOLUTION OF ZIRCONIUM MINERALS

Zircon and, to a much lesser extent, baddeleyite are used as feedstocks for the manufacture of zirconia and other zirconium compounds by chemical dissolution. The purity of zirconia produced in this way tends to be higher than that of zirconia produced by fusion (see Section 7), but the complexity of the process is greater. Consequently, the market for zirconia produced by chemical dissolution is usually restricted to specialized, low volume applications (i.e. catalysts, electronic components, solid electrolyte devices, bioceramics, gemstones, special glasses, medical lasers and antiperspirants), where the quality of the product is critical and cost is less of an issue.

8.1. PROCESS DESCRIPTION

Various methods involving chemical dissolution are used for the manufacture of pure zirconia and other zirconium compounds, the details of which are often proprietary to particular manufacturers. The most common method, often referred to as the caustic fusion method, involves the breakdown of zircon (or baddeleyite) through reaction with sodium hydroxide (caustic soda). At temperatures above 600ºC, sodium hydroxide and zircon react to form insoluble sodium zirconate (Na_2ZrO_3), sodium zirconate silicate and

water soluble sodium metasilicate ($Na_2SiO_3 \cdot nH_2O$). Careful control of the zircon to sodium hydroxide ratio, temperature (typically at about 700ºC) and reaction conditions (particularly the atmosphere) can produce nearly complete conversion.[16] The sodium zirconate is washed in water and filtered to remove silica and unreacted sodium hydroxide as an aqueous alkaline waste stream. The sodium zirconate is then dissolved in hydrochloric acid to produce a solution of ZOC (see Section 2.4), which is recovered by crystallization. ZOC is marketed in solid form as an industrial product or as a water soluble intermediate for the production of many other high purity zirconium compounds, including zirconia powder, zirconium sulphates (AZST, ZBS), zirconium carbonates and zirconium acetate.

Various methods are used to convert ZOC into zirconia powder. Simple calcination followed by ball milling is a low cost production method, but it is difficult to produce zirconia powder with high purity and fine particle size. Higher purity levels and finer, more uniform particle sizes (down to less than 1 μm) can be achieved by the reaction of ZOC solution with ammonium hydroxide or sodium hydroxide to precipitate zirconium hydroxide, which is then washed, filtered, freeze dried and calcined to zirconia powder. The physical characteristics and purity of the zirconia powder can be influenced by control of the precipitation and calcination conditions.

High purity zirconia may also be produced directly from zircon by dissociation into zirconia and silica at a temperature exceeding 1800ºC and then using one of two chemical dissolution methods to purify the zirconia [84]:

(a)   Reacting with sodium hydroxide to dissolve the residual silica and then filtering and washing to remove residual sodium hydroxide and sodium metasilicate;

(b)   Reacting with acid to form a soluble zirconium salt together with residual silica, dissolving in water, removing the insoluble silica by filtration and then reacting the zirconium salt with sodium hydroxide to precipitate zirconium hydroxide, which is recovered by filtration.

The products from either process are then calcined at temperatures of up to 650ºC and blended to produce different grades of high purity zirconia.

Stabilized zirconia powders with a high degree of chemical uniformity can be produced by introducing the stabilizing oxide, for example Y_2O_3, before the precipitation of zirconium hydroxide. For example, the stabilizing oxide may be

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[16]   Zircon may also be reacted with sodium carbonate (soda ash). This reaction requires a higher temperature and depends on the sodium carbonate to zircon ratio.

mixed with ZOC and hydrochloric acid to form a solution, whereupon the addition of sodium hydroxide results in the co-precipitation of the hydroxides of zirconium ($Zr(OH)_4$) and the stabilizer (e.g. $Y(OH)_3$). During the remainder of the process, the stabilizer hydroxide remains with the zirconium hydroxide and, on conversion to the respective oxides during calcination, a stabilized zirconia powder is formed.

One copper mining operation, prior to ceasing co-production of baddeleyite in 2002, manufactured AZST by reaction of baddeleyite with sulphuric acid (a by-product of copper smelting) followed by chemical purification [18].

Acidic and alkaline waste streams are used to neutralize each other where possible. This neutralization process precipitates solids containing silica, which are separated by flocculation, settling and centrifuging and sent for landfill disposal. The clarified liquid is discharged as industrial effluent. As in any chemical treatment process, there is a possibility of scale formation in pipes, pumps and other fluid handling equipment. These scales are removed during maintenance and decommissioning and are disposed of as waste.

8.2. RADIONUCLIDE ACTIVITY CONCENTRATIONS

Since the calcining processes are conducted at temperatures well below 1200ºC, the zircon crystal lattice is not destroyed and volatilization of radionuclides is unlikely to occur. However, chemical dissolution of the zirconium-containing component of the feedstock destroys the zircon crystal structure, releasing the associated radionuclides into solution. The degree of mobilization of these radionuclides depends on the exact chemical process used. They tend to become concentrated in precipitates, pipe scales and acidic liquid effluents, leaving the zirconium-containing products relatively free of radioactivity.

Data on radionuclide activity concentrations in various materials associated with chemical dissolution processes are shown in Table 35. The activity concentrations in materials associated with zircon processing are reported to be significantly lower than those in the feedstock. In a plant in India involved in the chemical processing of zircon by dissolution in sodium hydroxide, the activity concentrations in the intermediate product zirconium hydroxide are reported to be 1.8 Bq/g for [238]U and 0.35 Bq/g for [232]Th [63]. Analyses of waste streams conducted at that same plant gave gross alpha activities of 0.003–0.01 Bq/L (mean 0.006 Bq/L) in the liquid effluent and 0.30–1.70 Bq/g (mean 0.93 Bq/g) in the solid waste sludge. AZST produced by reacting baddeleyite with sulphuric acid was reported in Ref. [18] to have a very low uranium concentration of 0.1–1.5 ppm (typically 0.5 ppm), implying a [238]U

TABLE 35. ACTIVITY CONCENTRATIONS IN MATERIALS ASSOCIATED WITH THE CHEMICAL DISSOLUTION OF ZIRCONIUM MINERALS

	Radionuclide activity concentration (Bq/g)							
	U-238 series				Th-232 series			
	U-238	Ra-226	Pb-214	Bi-214	Th-232	Ac-228	Pb-212	Bi-212
Manufacture of zirconia from zircon[a]								
Zircon sand feedstock	3.8	3.9		4.2	0.69	0.61		0.58
ZOC	<0.08	<0.04		<0.005		<0.01		<0.04
Basic intermediate				1.6		0.34		
Acidic intermediate	<0.05	0.01		0.01		0.01		<0.03
Zirconia product		0.003	0.001	0.001		0.004	0.0003	
Zirconia product		0.005	0.0005	0.0004		0.0006	0.0005	
Zirconia product[b]	<0.05	≈1		≈1	<0.02	0.16		0.13
Waste stream	1.5	1.0		0.72	0.22	0.18		0.25
Manufacture of zirconium hydroxide from zircon [63]								
Zircon sand feedstock	3.4				0.51			
Zirconium hydroxide intermediate product	1.8				0.35			
Manufacture of AZST from baddeleyite [18]								
AZST product	0.001–0.02							
Manufacture of high purity chemicals from zircon [85]								
Effluent treatment acid tank deposit		>5000						

[a]   Unpublished company data.
[b]   This zirconia product was made using an older process with less refining steps.

activity concentration of 0.001–0.02 Bq/g (typically 0.01 Bq/g). In the manufacture of high purity zirconium chemicals from zircon in the United Kingdom, it is reported that the radionuclide concentrations in the liquid chemical effluent are usually quite low [85]. However, treatment of this

effluent in an ion exchange plant was found to give rise to considerable concentration effects within the pipes and vessels of the plant. A sample from the bottom of a large acid tank had a [226]Ra concentration of over 5000 Bq/g. The implications of this for occupational exposure are discussed in Section 8.3.

8.3. OCCUPATIONAL EXPOSURE

As with any process in which zirconium-containing minerals are used as feedstocks, exposures of workers to gamma radiation and to radionuclides in inhaled dust could be significant during the storage and handling of such materials, especially if baddeleyite, with its higher radioactivity content, is used as the feedstock. Exposure of workers to solid residues may also need to be considered, particularly residues in the form of scales within fluid handling equipment. In the ion exchange effluent treatment plant mentioned in Section 8.2, a maximum dose rate of 400 µSv/h was measured around the large acid tank containing a radium rich deposit, and a dose rate of 30 µSv/h was measured in a nearby workshop [85]. Internal exposure was not considered to be an issue at the time of operation because the material was effectively sealed within the column. With the subsequent termination of operations at that effluent treatment plant, decommissioning and disposal of the decommissioning waste became the main issues of concern.

Radon gas concentrations were measured in a plant that produced zirconium hydroxide by dissolution of zircon sand in sodium hydroxide [63]. The mean radon concentration was found to be 13 Bq/m^3. This level is well within the normal indoor range, confirming that inhalation of radon was not a significant occupational exposure pathway.

Unpublished company data indicate that, for the chemical processing of zircon, the annual effective dose received by a worker is less than 1 mSv for the sodium hydroxide dissolution process, 0.6 mSv for the zirconia production process and less than 0.3 mSv for effluent treatment. Higher doses — up to about 3 mSv/a — are received in operations in which the feedstock is baddeleyite. The effective doses received by workers engaged in the disposal of 20 000 t of wet residue from the chemical processing of zircon sand have been estimated to be trivial (15 µSv/a in a worst case exposure situation) [54].

8.4. PUBLIC EXPOSURE

The main potential exposure pathways to members of the public are those associated with effluent discharges (particularly acidic effluents) and the

landfill disposal of pipe scales and silica-containing residues. The release of scrap piping and other fluid handling equipment can also give rise to exposure of members of the public if such equipment is not sufficiently decontaminated. Reference [54] reports on the doses estimated to be received by members of the public attributable to the discharge or landfill disposal of residues from the chemical processing of zircon sand, based on the results of modelling using conservative assumptions. Discharge of liquid washings into a river was found to give a negligible dose to members of the public. A future resident living on a landfill site after closure, into which had been disposed 20 000 t of solid residue, was estimated to receive a dose of 750 μSv/a, mostly from external gamma radiation.

8.5. REGULATORY CONSIDERATIONS

Generally, the annual effective dose received by a worker is unlikely to exceed 1 mSv. However, a higher dose might be received when working with baddeleyite as a feedstock (owing to the possibility of higher activity concentrations than those in zircon) or when exposure to radium rich scales is involved during maintenance or decommissioning. In such cases, dose reduction measures might be warranted. In addition, the presence of radium rich scales might necessitate control measures to ensure that pipes and other fluid handling equipment are adequately decontaminated before disposal or recycling and that the scales are disposed of safely. The regulatory body would have to examine the circumstances at particular operations before deciding on the most appropriate regulatory option. In some situations, an authorization in the form of a registration might be needed to ensure that certain basic control measures are implemented and maintained.

Due to the nature of the chemical dissolution process, the radioactivity in the feedstock tends to end up in the process residues rather than in the zirconium compounds produced by the process. These zirconium compounds, including chemically produced zirconia for special applications (see Sections 2.3.3.4–2.3.3.8), can therefore be regarded as free of radioactivity and not subject to further regulation.

9. CHLORINATION OF ZIRCON AND PRODUCTION OF ZIRCONIUM METAL

9.1. PROCESS DESCRIPTION

9.1.1. Manufacture of zirconium tetrachloride and other zirconium compounds

Zircon sand is dried, mixed with coke and ground to a fine consistency in a ball mill. The coke–zircon mixture is then introduced continuously to the top of a fluidized bed chlorination reaction chamber operating at a temperature of 1200°C. The chlorine gas reacts with the mixture to form zirconium tetrachloride and silicon tetrachloride. The primary reaction is:

$$ZrO_2 \cdot SiO_2 + 2C + 4Cl_2 \rightarrow ZrCl_4 + SiCl_4 + 2CO_2$$
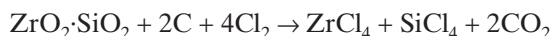
The 'crude' zirconium tetrachloride produced from this reaction contains hafnium tetrachloride as an impurity and is condensed from the off-gases along with silicon tetrachloride, from which it is separated by distillation. Unless the zirconium tetrachloride is being used for the manufacture of hafnium free zirconium metal for nuclear applications, it is unnecessary to remove the small hafnium content. Hydrolysis of the zirconium tetrachloride with water and filtration of the resulting solution to remove suspended solids results in the formation of ZOC, which can then be used as the basis for producing high purity zirconia and other zirconium compounds (see Section 8.1). The reaction is as follows:

$$ZrCl_4 + H_2O \rightarrow ZrOCl_2 + 2HCl$$
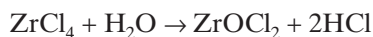
The chlorination process produces 'crude chlorinator residue'. It also generates water from various air scrubbing systems. The quantity of this water needing to be discharged as waste is minimized by recycling.

9.1.2. Manufacture of zirconium metal

The standard process for converting zircon into zirconium metal is known as the Kroll process. Although there are several variants of this process, it essentially involves the production of zirconium tetrachloride by direct chlorination of zircon as described in Section 9.1.1, purification by sublimation in an inert atmosphere in a furnace (mainly to remove residual zirconia) followed by

reduction of the purified zirconium tetrachloride (which still contains hafnium tetrachloride) to zirconium (and hafnium) in a batch process using magnesium. The zirconium tetrachloride is converted to zirconium and magnesium chloride according to the following reaction:

$$ZrCl_4 + 2Mg \rightarrow Zr + 2MgCl_2$$
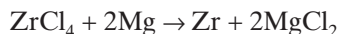
The reaction takes place in a retort furnace at a temperature of typically 875ºC. At this temperature, both the magnesium and the magnesium chloride are in the molten state. A crude zirconium metal regulus[17] is formed in the furnace along with the molten magnesium chloride. The magnesium chloride is separated from the zirconium regulus to produce zirconium sponge. Residual magnesium chloride and magnesium are removed from the zirconium sponge by vacuum distillation or by leaching with hydrochloric acid.

Off-gases from the furnace pass through a wet scrubber before being released. The scrubber blowdown[18] is recycled to the separation process to recover zirconium. Possible waste streams include acid leaching rinse water and spent acid leachate from zirconium sponge purification, as well as air scrubbing water from zirconium chip crushing and from magnesium recovery off-gas and ventilation air. Waste scrubber water is discharged after treatment by chemical precipitation and sedimentation.

Zirconia (in the form of baddeleyite) may also be used as a feedstock for zirconium metal production. In this process, the baddeleyite is mixed with magnesium metal powder and placed in a steel cylinder. The cylinder and its contents are then heated in a furnace. Once initiated, the reaction becomes self-sustaining. Zirconium metal sponge and magnesium oxide are produced. Zirconia can also be used to produce zirconium–nickel alloys. The process is similar to the magnesium reduction operation except that calcium hydride is used as the reducing agent in the furnace and nickel is added directly to the mixture of zirconia and calcium.

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[17] A regulus is the metallic mass that sinks to the bottom of a furnace or crucible during smelting.

[18] Blowdown in this context is defined as the minimum discharge of recirculating water for the purpose of discharging material contained in the water, the further buildup of which would cause concentration in amounts exceeding limits established by best engineering practices.

In the production of zirconium metal for nuclear applications, it is necessary to separate hafnium from the chemically similar zirconium. Details of the process and of the residue streams generated are given in Ref. [86]. The separation process is conducted at the crude zirconium tetrachloride stage after the initial high temperature chlorination step. Following the removal of iron, the crude zirconium tetrachloride solution is passed through a series of liquid–liquid extraction, stripping and scrubbing steps. Hafnium free zirconium is recovered from the aqueous zirconium stream through chemical treatment and further solvent extraction, leading to precipitation as zirconium sulphate. The addition of ammonium hydroxide converts the zirconium sulphate to zirconium hydroxide, which is then calcined to produce hafnium free zirconia. This zirconia is mixed with fine coke and subjected to a second high temperature chlorination step ('pure' chlorination) to produce hafnium free zirconium tetrachloride.

The largest volume of radioactive residue generated by the zirconium–hafnium separation process is a sludge consisting mostly of calcium fluoride, calcium sulphate and calcium hydroxide, which is sent to settling ponds. The sludge has beneficial properties as a soil conditioner (similar to those of phosphogypsum). The pure chlorination step gives rise to a residue known as 'pure chlorinator residue'. Other residues, all of which are recycled to the process where possible, include zirconium and hafnium filtrate water, iron extraction steam stripper bottoms, the ammonium thiocyanate bleed stream, calciner furnace residue and various aqueous residue streams from wet air scrubbing systems.

Blowdown from wet scrubber water recycling systems associated with the chlorination and magnesium reduction processes is treated by chemical precipitation, sedimentation and, where appropriate, dechlorination before being discharged.

9.2. RADIONUCLIDE ACTIVITY CONCENTRATIONS

Zirconia and other zirconium compounds manufactured by high temperature chlorination are generally regarded as being essentially free of radioactivity, as is the case for similar products manufactured using chemical dissolution processes (see Section 8.2), with almost all of the radioactivity in the feedstock ending up in the process residues. Similarly, zirconium metal is regarded as being free of radioactivity.

The following data on ^{226}Ra activity concentrations in process residues are reported in Ref. [27]:

(a) Crude chlorinator residue: 37–48 Bq/g.
(b) Sludge from the zirconium–hafnium separation: 0.3–7 Bq/g (dry mass).
(c) Pure chlorinator residue: 19–22 Bq/g.

It is also reported in Ref. [27] that the ^{226}Ra activity concentration in a 6500 t residue pile at a plant in the USA, accumulated during the period 1974–1978 and containing a mixture of crude and pure chlorinator residue, was 2.8–48 Bq/g. The radium was in soluble form, probably as radium chloride. Seepage water from the pile was found to contain ^{226}Ra at an activity concentration of about 800 Bq/L (filtered) and ^{222}Rn at an activity concentration of about 1500 Bq/L. The effluent released from the plant was found to contain ^{226}Ra at an activity concentration of 1.9 Bq/L, 50% of which was in soluble form.

No radiological data are available for other waste streams such as water from wet scrubbing systems, although it is reported that water from the scrubbing of air in the initial zircon sand drying process exhibits some radioactive contamination as a result of the radioactivity in the zircon sand [86].

9.3. OCCUPATIONAL EXPOSURE

No data are available on exposures of workers in the chlorination and magnesium reduction processes. The handling of feedstock material involves radiological considerations similar to those described in Section 8.3 for chemical dissolution processes, and annual effective doses received by workers can therefore be assumed to be less than 1 mSv, except where baddeleyite with higher activity concentrations is used as a feedstock.

It is reported in Ref. [27] that, at a zirconium extraction plant in the USA using zircon feedstocks: "Personnel exposure and concentrations of airborne activity have been well below permissible limits."

9.4. PUBLIC EXPOSURE

9.4.1. Sources of exposure

The nature of the sludge from the zirconium–hafnium separation process, including its radium content and large volume, gives rise to radiological issues similar to those associated with radium rich mine tailings. Consequently, sludge stockpiled in ponds and piles represents a potential source of public exposure through migration of radionuclides into the surrounding environment, particularly if there are no short term plans for using the material elsewhere, for

example as a soil conditioner. As with mine tailings, appropriate control measures involve the covering and stabilization of the residue piles [4].

Although there are obvious benefits in using sludge as a soil conditioner rather than storing it indefinitely in piles, there are radiological implications associated with the use of sludge in this manner. Sludge deposited on two agricultural fields in the USA was found to give rise to gamma dose rates at 1 m of about 0.1–1 μSv/h[19] and a radon flux density of 0.44 $Bq·m^{-2}·s^{-1}$ [27]. Assuming a typical ^{226}Ra activity concentration in the sludge of the order of about 1 Bq/g (see Section 9.2), this corresponds to a radon flux density per unit ^{226}Ra activity concentration similar to that of normal rocks and soil (see Table 10).

The seepage of radium-contaminated water from a chlorinator residue pile described in Section 8.2 suggests that such piles are a potential source of public exposure.

9.4.2. Measures to reduce doses

At the zirconium extraction facility mentioned in Section 9.2, the radiological concerns associated with the 6500 t pile of chlorinator residue from years of past operations were mitigated considerably by removal of the pile from the site to an external radioactive waste disposal facility. Residues generated on a continuous basis were also removed to an authorized disposal site. Monitoring requirements and limits were imposed on radioactive effluents and the indiscriminate use of sludge was prevented. All solid waste leaving the plant became subject to monitoring to ensure proper disposal [27].

9.5. REGULATORY CONSIDERATIONS

The chlorination of zircon and production of zirconium metal appears unlikely to give rise to any significant occupational exposure concerns. However, the elevated ^{226}Ra concentrations in sludge and chlorinator residue suggest that, in order to provide adequate protection of the public and the environment, the disposal of these residues needs to be controlled using similar measures to those used for radium rich mine tailings. Authorization in the form of a registration might be an appropriate regulatory option. The use of sludge

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[19] These dose rates have been deduced from reported exposure rates measured in röntgen per hour, assuming that 1 μR/h is approximately equivalent to a dose rate of 0.01 μSv/h.

as a soil conditioner would have to be considered by the regulatory body and the radiological implications examined in some detail.

10. ZIRCON AND FUSED ZIRCONIA IN REFRACTORIES

10.1. PROCESS DESCRIPTION

10.1.1. Zircon refractories

Zircon refractories are manufactured by mixing zircon sand or flour into a slurry with other refractory additives (e.g. alumina, calcined bauxite, magnesite) and binders (e.g. clays, lime, special additives) and forming into the required shape. The articles are then dried and fired in a kiln.

10.1.2. Zircon–mullite refractories

Zircon–mullite refractories are manufactured by heating a mixture of zircon and alumina. The following high temperature reaction takes place:

$$2ZrSiO_4 + 3Al_2O_3 \rightarrow 2ZrO_2 + 3\ Al_2O_3 \cdot 2SiO_2$$
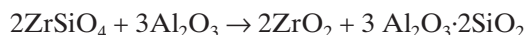
The dissociation of zircon starts at 1400ºC and at about 1600ºC the reaction is complete, forming a stable product of zirconia (18–24 wt%) and mullite.

10.1.3. AZS refractories derived from zircon

In the manufacture of AZS blocks for use in glass furnaces, zircon sand (or a semi-finished product based on zircon, for example zircon–mullite or 'scraps' from the finishing process) is mixed with alumina and sodium carbonate [42, 87]. The mixture is fused in an electric arc furnace and poured into moulds. After the elimination of sprues,[20] the blocks of AZS are left to cool for 15–20 days. They are then sandblasted, ground, polished with emery,

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[20] Sprues are the feed openings provided in injection moulding between the nozzle and cavity.

finish ground and finally cut. The resulting scraps are milled in readiness for reintroduction into the manufacturing process. As there is potential for dust generation at various steps in the process, it is usual for dust extraction systems to be installed where the mixture is produced and smelted, where sprues are eliminated and in the cooling and grinding areas. Residues are generated in the form of wastewater and sludge.

10.1.4. Fused zirconia refractories

Fused zirconia refractories are manufactured in a range of refractory shapes such as casting nozzles, rods and tubes. The addition of various materials and the use of different firing conditions generate a range of products such as AZS and magnesia–zirconia bricks suitable for different applications and chemical environments.

One manufacturing process involves pressure forming and sintering of powdered fused zirconia. As explained in Section 2.3.2, zirconia needs to be stabilized in the cubic form using a small addition of stabilizing oxide CaO, MgO or Y_2O_3 before it can be used in refractories. One method of achieving this is through a process called in situ stabilization. Before carrying out the forming process (e.g. moulding, pressing or casting), fine particles of stabilizer and unstabilized zirconia are well mixed. The mixture is then formed into the 'green' (unfired) body. The phase conversion is accomplished by firing (sintering) the doped zirconia at 1700ºC. As an alternative to in situ stabilization, chemically produced zirconia powder may be used, in which the stabilizing oxide has been introduced during the chemical process before the precipitation of sodium hydroxide (see Section 8.1). This produces stabilized zirconia with a higher degree of chemical purity and uniformity.

Fused zirconia refractories may also be manufactured by casting fused zirconia with the necessary stabilizing oxide in an electric arc furnace at a temperature exceeding 1780ºC.

10.1.5. Management of zircon and zirconia-containing residues

Residues generated on a routine basis during the manufacture of refractories are generally limited to small quantities of wastewater, sludge and airborne dust. In the United Kingdom, it has been estimated that, in the course of a year, the manufacture of 600–700 t of zircon and zirconia refractory bricks and zirconia nozzles may give rise to about 20 kg of liquid discharges from floor washings and about 5 kg of air discharges from ventilation systems [78]. In the manufacture of AZS refractories, it is reported that only the dusts produced by

sand blasting and wastewater treatment are discharged — fusion dusts and sludges are recycled within the manufacturing process [87].

There is an economic incentive for refractory manufacturers to minimize the amounts of residual refractory material, and any such material is generally limited to broken and off-specification products. This residual material may be crushed and reused within the refractories plant as an aggregate in refractory cement.

All types of refractory, including specialized zirconia flow control components and zircon and zirconia-based furnace linings used in the glass and metal industries, have a finite life and therefore require regular replacement. Glass furnaces generally have a life of about 10 years before being scrapped. In the United Kingdom, one glass factory is estimated to generate about 10 t of waste furnace bricks per year [78]. The spent refractories are broken out of their working positions and disposed of in landfill facilities. Spent refractory materials may have become contaminated with hazardous material such as heavy metals (e.g. lead, cadmium, chromium) during use, in which case their manner of disposal may be governed by the presence of such contaminants. The recycling of used refractories as feedstock material for the refractory manufacturing process is not practised on a wide scale, due to quality constraints on the composition of the feedstock. However, some consideration is being given to the use of spent refractories as aggregates in refractory cements, and one report describes the recycling of spent zircon refractories from glass furnaces by casting at 2000ºC into new refractory furnace linings and heat- and wear-resistant monolithic pipe linings [88].

10.2. RADIONUCLIDE ACTIVITY CONCENTRATIONS

Various activity concentration measurements have been reported for refractory process materials and products, and the available data are summarized in Table 36. Finished products show signs of depletion in ^{210}Pb and ^{210}Po, due to their volatilization at the high process temperatures encountered. Elevated concentrations of these radionuclides are clearly evident in the fusion furnace dust and off-gas from the AZS manufacturing process. Activity concentrations in the sludge generated by the wastewater treatment system in an AZS plant are reported to be similar to those in the product, while the wastewater itself was found to be essentially free of radioactivity [87].

TABLE 36. ACTIVITY CONCENTRATIONS IN REFRACTORY PRODUCTS AND PROCESS RESIDUES

	Radionuclide activity concentration (Bq/g)									
	U-238 series					Th-232 series				K-40
	U-238	Th-230	Ra-226	Pb-210	Po-210	Th-232	Ra-228	Th-228	Pb-212	
Zircon–pyrophyllite refractory[a]	1.9–2.6					0.2–0.5				
Zircon–alumina refractory[a]	2.9		2.3			0.4	0.6		0.4	
Zircon–alumina refractory [89]	≈3									
Zirconia-containing refractory [78]	4					0.2				
Zirconia-containing refractory [78]	1					<0.2				
Process materials [90]										
Zircon–mullite raw material			1.5			0.24				0.018
Sludge from roller cutting			0.16			0.037				0.031
Dust from ventilation system			1.0			0.17				0.036
AZS refractory [88]	1.48	1.85	1.68	0.214			0.252	0.243		0.107
AZS refractory[a]	1.5–2.6					0.2–0.5				

TABLE 36. ACTIVITY CONCENTRATIONS IN REFRACTORY PRODUCTS AND PROCESS RESIDUES (cont.)

	Radionuclide activity concentration (Bq/g)								
	U-238 series					Th-232 series			K-40
	U-238	Th-230	Ra-226	Pb-210	Po-210	Th-232	Ra-228	Th-228	Pb-212	
AZS process materials [87]:										
Furnace dust	0.36		0.15	21	35	0.02				0.01
Furnace off-gas filter					28					
Dust generated by grinding of scraps	1.2		1.0	1.0	1.3	0.2				0.3
Scraps grinding filter					6.1					
AZS refractory	1.7		1.4	0.95	1.1	0.3				0.009
AZS refractory	1.8		1.6	0.8	0.7	0.3				0
AZS refractory	1.7		1.5	1.3	1.4	0.3				0.02
Sludge	1.6		1.5	1.2	1.2	0.2				0.03

a Unpublished company data.

10.3. OCCUPATIONAL EXPOSURE

10.3.1. Manufacture of refractories

Gamma radiation and activity concentrations of airborne dust and radon were measured at various locations in a factory in Italy producing AZS blocks using zircon sand as a raw material [42]. The results of this investigation, discussed in Sections 10.3.1.1–10.3.1.3, can be regarded as indicative of the exposure situation in the manufacture of any zircon- or zirconia-containing refractory using high temperature fusion.

10.3.1.1. Gamma radiation

Gamma radiation was found to be similar to background levels except at the tops of the tanks, where workers spent only short periods of time — here, levels of about 0.2–0.8 μSv/h above background were measured.[21]

10.3.1.2. Inhalation of radionuclides in dust

The results of airborne dust measurements are shown in Table 37 and provide clear evidence of the enrichment of ^{210}Po in the furnace dust due to its volatilization in the high temperature process. The particle size distribution was bimodal, with the larger mass fraction having a mass median aerodynamic diameter (MMAD) of 6.2–10.3 μm and the smaller mass fraction — presumably the furnace dust — having an MMAD of 0.27–0.49 μm. Since activity concentration is typically proportional to mass, it is expected that these MMADs would be numerically similar to the AMADs. Dust exposure periods were not determined in the investigation, but in Ref. [91] a normal annual exposure period of 100 h was assigned to the sprue elimination area, where the highest airborne dust activity concentration was found.

The annual effective dose received by a worker from the inhalation of dust with the larger particle size (Mode II in Table 37) can be estimated from the data in Table 37 by assuming that this dust contains all of the airborne alpha activity except for the portion of the ^{210}Po activity elevated above the equilibrium value (which is more likely to be associated with the finer dust from the furnace). For the pouring area, for example, the total alpha activity

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[21] These dose rates have been deduced from reported exposure rates measured in röntgen per hour, assuming that 1 μR/h is approximately equivalent to a dose rate of 0.01 μSv/h and that the background dose rate was about 0.09 μSv/h.

TABLE 37. AIRBORNE DUST CHARACTERISTICS IN A PLANT PRODUCING AZS REFRACTORIES

| Sampling point | Alpha activity concentration (mBq/m³) | | | Dust concentration (mg/m³) | MMAD (µm) | |
| | Total, as measured[a] | Extrapolated back to time of sampling | | | | |
		Po-210	Total, other alpha emitters[b]		Mode I	Mode II
Oven operation cabin	43.7					
Pouring area	97.2	94.7	8.3			
Sprue elimination area	421.5	426.8	24.1	0.84	0.27	10.3
Cooling area central corridor	25.8					
Central oven area	29.2			0.65	0.28	9.9
Grinding area	6.8			3.13	0.27	9.0
Diamond saw area	1.9					
Pre-assembly area				0.99	0.49	6.2
Milling operator cabin	12.8					
Mill loading	158.9	122.9	52.7			

[a] Counting of total activity on filters was delayed for a sufficient time for the short lived progeny to decay and for equilibrium of the radionuclides inside the particles to be re-established.

[b] These comprised U-238, U-235 and Th-232 in equilibrium with all other alpha emitting decay progeny other than Po-210.

in the dust would be 9.3 mBq/m³ (i.e. 8.3 mBq/m³ (excluding ^{210}Po) plus 1 mBq/m³ (^{210}Po in equilibrium)). Assuming that the decay chains are in equilibrium, with the activity concentration of ^{238}U being five times that of ^{232}Th, the annual effective dose received by a worker exposed for 100 h in a year without respiratory protection would be about 0.003 mSv in the pouring area, 0.01 mSv in the sprue elimination area and 0.02 mSv in the mill loading area. These inhalation doses have been calculated using the dose coefficients in Table 12 for an AMAD of 10 µm, with the dose coefficient for ^{226}Ra being based on a ^{222}Rn removal rate of 100 d^{-1} (see Section 3.2.5). If the removal rate were to be less than 100 d^{-1}, the inhalation doses would be underestimated. In a worst case situation of zero radon emanation (see Table 13), the degree of underestimation would be 39%.

The annual effective dose received by a worker from the inhalation of furnace dust (i.e. the dust with the smaller particle size (Mode I in Table 37)) can be estimated by assuming that this dust contains the portion of the ^{210}Po alpha activity elevated above the equilibrium value plus the same amount of beta activity from ^{210}Pb. Taking again the example of the pouring area, the ^{210}Po activity would be 93.7 mBq/m^3 (i.e. 94.7 mBq/m^3 less the 1 mBq/m^3 in the dust with the larger particle size). On this basis, the annual effective dose received by a worker exposed for 100 h in a year without respiratory protection would be about 0.05 mSv in the pouring area, 0.2 mSv in the sprue elimination area and 0.07 mSv in the mill loading area.[22] Clearly, inhalation of furnace dust represents the major dust exposure pathway.

10.3.1.3. Inhalation of radon

Radon concentrations were found to be similar to normal indoor values, indicating a low emanation from zircon sand in both its original form (as would be expected) and during its conversion to zirconia in the production process.

10.3.2. Use of refractories

Manufactured refractory articles containing zircon or zirconia are potential sources of exposure for workers in industries such as glass making and metal production. However, this exposure is only likely to be significant in the case of dust inhalation by workers engaged in maintenance and demolition operations. These operations are by nature dusty operations and would be expected to be subject to OHS controls including requirements for respiratory protection where appropriate.

10.4. PUBLIC EXPOSURE

The only potentially significant source of public exposure is the burial of spent refractories at a landfill disposal site. Calculations show that the annual effective dose received by a member of the public from the disposal of furnace lining bricks and refractory nozzles in a landfill, including the dose received as a result of future, uncontrolled, residential use of the site, is likely to be no more than a few microsieverts [78].

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[22] These values have been calculated using the dose coefficients in Table 12 for an AMAD of 0.3 μm.

10.5. REGULATORY CONSIDERATIONS

The annual effective dose attributable to the manufacture of zirconium-containing refractories is likely to be a fraction of a millisievert for a worker and a few microsieverts for a member of the public. Consequently, such operations are candidates for exemption by the regulatory body. Dust control measures might need to be considered in maintenance and demolition operations involving the removal of zirconium-containing refractories from glass making and metal production facilities, if such measures are not already in place for normal OHS purposes.

Since the activity concentrations of radionuclides in the uranium and thorium decay series in refractory products are all far less than ten times the values for U_{nat} and Th_{nat} in Table 8, it can be concluded that the transport of such products is not subject to the Transport Regulations. The furnace dust generated during the manufacture of AZS refractories contains elevated activity concentrations of ^{210}Pb and ^{210}Po, but these are not sufficiently elevated to bring the material into the scope of the Transport Regulations.

11. ZIRCON AS A SOURCE OF ZIRCONIA IN GLASS

11.1. PROCESS DESCRIPTION AND RADIONUCLIDE ACTIVITY CONCENTRATIONS

11.1.1. Manufacture of cathode ray tubes

Zircon is added to the glass making ingredients as –325 or –200 mesh flour. The raw material mixture is melted in a glass making furnace at a temperature sufficiently high to cause the zircon to dissociate into zirconia and silica. The required zirconia content of the faceplate section depends on national standards. In European countries the glass must be capable of absorbing only the X rays produced during normal operation, requiring a zirconia content of 0.02%, whereas in the USA and Asia-Pacific countries it must be capable of absorbing the higher energy X rays generated when the CRT fails, requiring a zirconia content of about 2.5%. It is anticipated that the required composition will eventually become standardized at around 2–3% zirconia, implying the addition of 3–5% zircon flour to the glass making mixture.

According to Ref. [92], a typical CRT has a mass of 7.2 kg and incorporates about 55 g of zircon. On this basis, the expected activity concentrations of uranium and thorium series radionuclides would be about 0.03 and 0.005 Bq/g, respectively. However, these are average values that do not take into account the uneven distribution of radionuclides over the whole CRT surface. Gamma spectrometry measurements conducted on CRTs in colour display monitors gave activity concentrations of 0.03–0.1 Bq/g for [226]Ra (from the uranium decay series) and 0.06–0.2 Bq/g for [224]Ra (from the thorium decay series) [16].

11.1.2. Manufacture of flat panel displays

The quantities of zircon used in flat panel displays are relatively small because the thickness of the substrate is only 0.05–0.6 mm and the zirconia content is relatively low at about 1% [16]. Gamma spectrometry measurements on a flat panel monitor indicated activity concentrations below the detection limits of 0.02 Bq/g for [226]Ra and 0.002 Bq/g for [224]Ra.

11.1.3. Management of zirconia-containing residues

During the manufacture of CRTs, some glass is rejected because of flaws. Some residual glass is also generated during CRT assembly or transport, usually as a result of breakage. It is common for this glass to be returned to the CRT manufacturing process because the manufacturer has a high degree of confidence in the composition of the glass. Attempts to recycle 'post-consumer' glass (usually televisions and monitors that have reached the end of their service life) have not been successful due to large variations in glass composition — the manufacture of CRT glass is complex and necessitates precise control over the glass composition. For the time being at least, glass from disused televisions and monitors has to be disposed of as waste in a landfill facility.

One CRT producing country mentions a waste in the form of sludge containing [226]Ra at a concentration of 0.06 Bq/g and [228]Ra at a concentration of 0.15 Bq/g [93].

11.2. OCCUPATIONAL EXPOSURE

The main occupational exposure pathways are through external gamma radiation and inhalation of zircon flour during the preparation of the furnace charge. As discussed in Section 3.2.6, the annual effective dose received by a worker handling zircon in such circumstances is unlikely to exceed about 0.4 mSv.

11.3. PUBLIC EXPOSURE

There are no significant public exposure pathways.

11.4. REGULATORY CONSIDERATIONS

The use of zircon in CRTs and flat panel displays does not give rise to significant exposures and is therefore a candidate for exemption by the regulatory body.

12. FUSED ZIRCONIA IN OTHER APPLICATIONS

12.1. CERAMIC PIGMENTS

12.1.1. Process description

Fused zirconia powder is pulverized, dry, in a ball mill with ground quartz, sodium fluoride, sodium chloride and the appropriate colouring cation in oxide form. The mixture is then fired in a kiln by progressively increasing the temperature to typically 900ºC over a period of 2.5 h and maintaining this temperature for a further 1.5 h. The exact firing temperature has an influence on the colour formed. The fired product, essentially zirconium silicate, is wet milled to a particle size of about 10 μm, washed and dried. The proportion of zirconia used in the formulation is typically 55%.

The manufacturing process may occasionally result in small quantities of reject product, which is recycled within the process where possible or otherwise disposed of as industrial waste at a landfill site.

12.1.2. Radionuclide activity concentrations

The activity concentrations of ^{238}U decay series radionuclides in fused zirconia are in the range 2–5 Bq/g (see Section 7.2). During the firing process, the addition of other (non-radioactive) material reduces the activity concentration substantially. For pigments based on fused zirconia, the final activity concentration would be expected to be about 1–3 Bq/g. The results of measurements conducted on various ceramic pigments are consistent with this

expectation — yellow pigment: 0.705 Bq/g; coral pigment: 3.149 Bq/g; sky blue pigment: 1.014 Bq/g [69].

12.1.3. Occupational exposure

The main exposure pathways are likely to be through external gamma radiation during the storage and handling of the feedstock and inhalation of radionuclides in dust during the dry milling processes. The drying process may also give rise to the inhalation of radionuclides, depending on the particular process used. Considering the data presented in Sections 3.2.6 and 4.3.3 and the fact that the zirconia is diluted with non-radioactive material during the manufacturing process, it can be concluded that the annual effective dose received by a worker is unlikely to exceed 1 mSv.

12.1.4. Public exposure

Since ceramic pigments are fused materials and not leachable, the disposal of reject material at a landfill facility is not likely to lead to any significant migration of radionuclides into the surrounding environment. The incorporation of ceramic pigments into ceramic tiles and sanitary ware will not cause any appreciable increase in the overall radionuclide activity concentrations in these products.

12.2. ABRASIVES

12.2.1. Process description

An alumina–zirconia abrasive mixture is formed by dissolving fused zirconia in molten alumina. After solidification, the mixture is crushed and separated into carefully controlled particle size ranges. The grains are then bonded by one of six types of bond: ceramic, resin, rubber, shellac, sodium silicate and magnesium oxychloride.

Ceramically bonded abrasive wheels, which account for more than 50% of grinding wheel production, are formed by wet mixing the abrasive grains with feldspar and clays as bonding material. The mix is then moulded, pressed and fired. In the firing process, the wheels are brought slowly to temperatures approaching 1400ºC for periods of up to several days. This slow temperature increase fuses the clay bond mixture so that each grain is surrounded by a hard glass-like bond that has high strength and rigidity. After cooling, the wheels are machined to size. Resin bonded abrasive wheels are produced by mixing

abrasive grains with thermosetting resins and catalysts. The mixture is then moulded and hot pressed. Rubber bonded abrasive wheels are produced by kneading the abrasive grains into natural or synthetic rubber. The mix is rolled to form a sheet of the required thickness. The grinding wheels are cut out of the rolled sheet and vulcanized.

Any residual abrasive material is generally recycled within the process. Reject products may be disposed of as industrial waste at a landfill site.

12.2.2. Radionuclide activity concentrations

Fused zirconia used in the production of abrasives contains radionuclides in the ^{238}U decay chain at activity concentrations of typically 2–5 Bq/g (see Section 7.2). Given that the zirconia content varies from just over 20% to about 40%, the activity concentrations in the abrasive can be expected to be about 0.5–2 Bq/g.

12.2.3. Occupational exposure

The primary exposure pathway in the manufacture of zirconia abrasives is through inhalation of radionuclides in dust during the milling and sizing of the abrasive material. Workers involved in storage of raw material and, to a lesser extent, the final abrasive products may also be exposed to gamma radiation. Considering the data presented in Sections 3.2.6 and 4.3.3 and the fact that the zirconia is diluted with non-radioactive material during the manufacturing process, it can be concluded that the annual effective dose received by a worker is unlikely to exceed 1 mSv.

The industrial use of zirconia-containing abrasive products involves the generation of dust as a result of fracturing and/or separation of the abrasive from the substrate, leading to the possibility of inhalation of radionuclides by the workers involved.

The landfill disposal of reject abrasive products or the remnants of such products consumed during use does not give rise to any significant inhalation of radionuclides by workers on the site, since there is no mechanism for the abrasive material to be transformed into airborne dust particles.

12.2.4. Public exposure

The production process does not result in any significant discharge of radionuclides. The landfill disposal of reject abrasive products or the remnants of such products consumed during use is unlikely to result in any significant migration of radionuclides into the surrounding environment. There is no

mechanism for the material to be transformed into airborne dust and the solubility of the material is extremely low. Consequently, there are no significant exposure pathways to members of the public.

12.3. ENGINEERING CERAMICS

The zirconia content of engineering ceramics varies widely from about 5% to more than 90% and the radionuclide activity concentrations in these products can be expected to be similarly subject to wide variation, typically 0.1–5 Bq/g. Occupational exposure to gamma radiation is of possible concern if large quantities of zirconia feedstock are involved. Occupational exposure due to the inhalation of radionuclides is unlikely to be of concern, as most processing operations involve high temperature sintering or fusion, with limited possibilities for the generation of high dust levels. Owing to the high cost of the raw materials and the opportunities for recycling within the process, the amounts of residual material disposed of as waste are likely to be insignificant. Engineering ceramic products may eventually be disposed of at landfill facilities at the end of their service life, but, as with the disposal of other zirconia products, the likelihood of migration of radionuclides into the surrounding environment is very small.

12.4. OXYGEN SENSORS FOR AUTOMOTIVE APPLICATIONS

The use of zirconia in the manufacture of solid electrolyte devices usually involves chemically derived, high purity zirconia, which is essentially free of radioactivity (see Section 8.2). In the automotive industry, however, some fused zirconia is used in the manufacture of solid electrolyte devices in the form of oxygen sensors. The radionuclides contained in the fused zirconia feedstock may give rise to some occupational exposure to gamma radiation in the manufacturing process if significant quantities of zirconia feedstock are involved. The oxygen sensors are encased in metal, and their size is such that the total activities of individual radionuclides are likely to be below the BSS exempt activity values (see Section 3.1.2). Used sensors may end up being disposed of in landfill facilities, leading to the possibility of gate monitoring devices being triggered at such facilities even though the used sensors are unlikely to pose any significant hazard.

12.5. REGULATORY CONSIDERATIONS

Applications of fused zirconia that involve the storage and handling of large quantities of zirconia feedstock (and possibly even zirconia-containing products) will give rise to occupational exposure to gamma radiation that may be significant enough to be of regulatory concern. In such cases, simple measures such as limiting the occupancy periods and quantities of material stockpiled might be appropriate. Occupational exposure to radionuclides in airborne dust during the manufacture of pigments and abrasives is unlikely to be of regulatory concern because the material is diluted with other, non-radioactive material. However, dust control measures might need to be considered for prolonged occupational exposure situations in the industrial use of zirconia-containing abrasives, if such measures are not already in place for normal OHS purposes.

Appendix I

URANIUM AND THORIUM DECAY SERIES

The ^{238}U and ^{232}Th series are the main decay series of interest. The ^{235}U decay series is less important for radiation protection purposes, except for the radionuclide ^{227}Ac, which can contribute significantly to inhalation exposure. If necessary, the presence of ^{235}U (and, by implication, its decay progeny) can be taken into account on the basis of the abundances of ^{235}U and ^{238}U in natural uranium (0.711 and 99.284 wt%, respectively) — the corresponding ^{235}U: ^{238}U activity ratio is 0.046. Details of the ^{238}U and ^{232}Th decay series, as reported in Ref. [94], are given in Tables 38 and 39.

TABLE 38. URANIUM-238 DECAY SERIES

	Half-life	Mode of decay[a]	Gamma energy (keV)[b]
U-238	4.468×10^9 a	Alpha	
Th-234	24.10 d	Beta	63.29 (4.8%), 92.38–92.8 (5.6%)
Pa-234m	1.17 min	Beta	1001.03 (0.837%)
U-234	245 700 a	Alpha	
Th-230	75 380 a	Alpha	
Ra-226	1600 a	Alpha	186.211 (3.59%)
Rn-222	3.8235 d	Alpha	
Po-218	3.10 min	Alpha	
Pb-214	26.8 min	Beta	351.932 (37.6%)
Bi-214	19.9 min	Beta	609.312 (46.1%)
Po-214	164.3 μs	Alpha	
Pb-210	22.20 a	Beta	46.539 (4.25%)
Bi-210	5.012 d	Beta	
Po-210	138.376 d	Alpha	
Pb-206	Stable		

[a] Only major modes of decay are shown.
[b] Only major gamma emissions of interest are shown.

TABLE 39. THORIUM-232 DECAY SERIES

	Half-life	Mode of decay[a]	Gamma energy (keV)[b]
Th-232	1.405×10^{10} a	Alpha	
Ra-228	5.75 a	Beta	
Ac-228	6.15 h	Beta	911.204 (25.8%)
Th-228	1.912 a	Alpha	
Ra-224	3.66 d	Alpha	240.986 (4.10%)
Rn-220	55.6 s	Alpha	
Po-216	0.145 s	Alpha	
Pb-212	10.64 h	Beta	238.632 (43.6%)
Bi-212	60.55 min	Beta: 64.06% Alpha: 35.94%	727.330 (6.67%)
Po-212	0.299 μs	Alpha	
Tl-208	3.053 min	Beta	583.191 (84.5%), 2614.533 (99.16%)
Pb-208	Stable	—	

[a]   Only major modes of decay are shown.
[b]   Only major gamma emissions of interest are shown.

Appendix II

**RADIONUCLIDE ACTIVITY CONCENTRATIONS IN
ZIRCONIUM MINERALS**

A wide range of ^{238}U and ^{232}Th activity concentrations in zirconium minerals is reported in the literature, from <1 to values of the order of 100 Bq/g [95]. The activity concentrations in commercially exploited zirconium minerals are less variable and tend to be at the lower end of this range.

II.1. ZIRCON

Activity concentrations in commercial zircon are shown in Tables 40 and 41. If, during the separation of zircon from the mineral sand concentrate, monazite is not completely removed, the residual monazite will give rise to elevated levels of thorium in the zircon product. Most current zircon production involves material containing moderate levels of radioactivity, with producers tending to avoid the higher activity material that was sometimes used in the past. Considering that more than 80% of production comes from Australia, South Africa and the USA, it is evident from the data that most zircon currently produced contains ^{238}U series radionuclides at activity concentrations of about 1–4 Bq/g and ^{232}Th series radionuclides at activity concentrations of about 0.5–1 Bq/g.

The uranium and thorium decay series radionuclides in zircon are normally regarded as being in equilibrium with their parent radionuclides and most activity concentration data are reported as values applicable to all radionuclides in the decay chain concerned. In the limited number of cases where individual radionuclide concentrations have been reported, a close approximation to decay chain equilibrium is generally demonstrated, but there are some departures from equilibrium conditions, as shown in Tables 42 and 43.

II.2. BADDELEYITE

Radionuclide activity concentrations in commercial baddeleyite are shown in Table 44. Compared with zircon, there is a lesser likelihood of decay chain equilibrium.

TABLE 40. ACTIVITY CONCENTRATIONS IN COMMERCIAL ZIRCON,
BY COUNTRY OF ORIGIN

	Radionuclide activity concentration (Bq/g)			Source of data	Remarks
	U-238 series	Th-232 series	K-40	Ref. Year	
Australia	2.8–3.4	0.7–0.8	0.07	[42] 1985	
	2.3	0.3		[96] 1985	Western Australia and New South Wales, mean of three values
	3.6–4.3	0.6–0.7		[97] 1991	Four samples
	2.1	0.9		[71] 1991	–45 µm particle size
	2.3	0.9		[71] 1991	–5 µm particle size
	1.9–3.7	0.6–1.0		[98] 1993	Typical range
	3.4	0.56		[36] 1994	Used in South Africa
	2.1–2.3	0.6–0.7		[99] 1994	Eastern Australia
	2.5–3.1	0.7–0.9		[99] 1994	Western Australia
	3–4.5			[25] 1994	
	5.8	1.9	0.7	[100]1995	Used in China
	3.5–3.9	0.6		[101]1996	
	3.3–3.9	0.7–0.8	0.05–0.06	[68] 2000	Three samples
	2.5–3.0	0.7–0.8		[102]2001	
	3.0–3.9	0.5–0.7		[37] 2002	Four samples
	1–4	0.6–1.2		[103]2003	Typical range
	4	1		[104]2004	Typical values
China	14.4	8.0	2.2	[100]1995	
	14.7	8.2	2.3	[38] 1997	
India	6.3			[93] 1998	
	2.2	0.54		[63] 2006	
	2.0	0.64		[63] 2006	
	3.4	0.51		[63] 2006	
	2.3	0.38		[63] 2006	
	1.6	0.67		[63] 2006	

TABLE 40. ACTIVITY CONCENTRATIONS IN COMMERCIAL ZIRCON, BY COUNTRY OF ORIGIN (cont.)

	Radionuclide activity concentration (Bq/g)			Source of data	Remarks
	U-238 series	Th-232 series	K-40	Ref. Year	
Malaysia	18	33		[105] 1984	By-product from tin mining residue (amang)
	16–21	2–88		[106] 1984	
	15–17	42–45		[107] 1985	
	25–50	41–57		[108] 1987	
	16–18	40		[101] 1996	
	62	10		[39] 1996	
	13	2.2		[93] 1998	
South Africa	5.2–7.8	0.9–1.1		[109] 1990	
	3.8–4.1	0.5–0.6		[110] 1993	
	4.1	0.61		[36] 1994	
	2.8–3.2	0.8		[99] 1994	
	3.4–3.7	0.7–1.0		[49] 1999	
	3.5–4.3	0.5–0.6		[111] 1999	
	3.8–3.9	0.54–0.6		[81] 2001	
	3.1–3.3	0.5–0.6		[23] 2002	
USA	2.5–3.1	0.4–0.6		[99] 1994	
	1.9–4.0	0.1–0.4		[112] 1998	From wellbore fracture studies, three samples

TABLE 41. ACTIVITY CONCENTRATIONS IN COMMERCIAL ZIRCON, ORIGIN UNSPECIFIED

Radionuclide activity concentration (Bq/g)			Source of data		Remarks
U-238 series	Th-232 series	K-40	Ref.	Year	
3.0–3.7			[27]	1980	Used in the USA
3	0.7		[113]	1983	
	8		[114]	1984	Used in the UK, typical value
3.9	0.7		[115]	1987	'Bagged zircon'
2.5–3.6	0.6–0.9		[116]	1988	Six samples
3.6–4.8	0.5		[117]	1991	
1–5	0.5–1		[118]	1993	
2.5–4.0	0.6–0.7		[35]	1993	Two samples
	0.7		[119]	1993	
4	0.6		[89]	1993	Used in the Netherlands
2.5	0.6–0.7		[35]	1993	
2.1–2.3	0.9		[120]	1993	Used in Italy
5	0.5		[121]	1994	Zircon residue
4–5	0.5		[60]	1994	Typical range
3.6–4.8	0.6		[65]	1996	
1.9–3.7	0.4–1.0		[122]	1996	
3.1	3.3	<0.05	[123]	1997	Used in Italy
2.6–3.2	0.6		[93]	1997	Used in Malaysia
1.8–9.6	0.4–5.2		[24]	1997	23 samples, 19 were within 2–4 Bq/g (^{238}U series) or 0.4–1 Bq/g (^{232}Th series)
1.3–10	0.3–2.0		[79]	1998	Used in the UK 1990–1996
3	0.6		[124]	1999	Average values
1.9–3.1	0.6–1.0		[55]	1999	
3.9	1.1		[76]	1999	Derived from tile glaze activity
	1–5		[125]	1999	
3.7–4.3	0.4–0.6		[126]	2001	Typical commercial range
	0.5–0.6		[127]	2001	

TABLE 41. ACTIVITY CONCENTRATIONS IN COMMERCIAL ZIRCON, ORIGIN UNSPECIFIED (cont.)

Radionuclide activity concentration (Bq/g)			Source of data		Remarks
U-238 series	Th-232 series	K-40	Ref.	Year	
4.0	0.5		[128]	2001	Used in the Islamic Republic of Iran, average values
13.4	1.3		[128]	2001	Used in the Islamic Republic of Iran, maximum values
	0.5–0.6		[129]	2001	
3.1–4.3	0.4–0.8		[130]	2002	Commercial range
4	0.6		[131]	2004	Typical values
3	0.7		[46]	2004	Used in one UK plant
2.3–3.4	0.4–0.7		[40]	2004	Used in five UK plants, seven samples
2.7–3.6	0.5	0	[87]	2005	Used in Italy
3	0.6		[54]	2005	Used in the UK, typical values

TABLE 42. RADIONUCLIDE COMPOSITION OF COMMERCIAL ZIRCON, URANIUM-238 DECAY SERIES

Radionuclide activity concentration (Bq/g)								Ref.	Country of origin
U-238	Th-230	Ra-226	Pb-214	Bi-214	Po-214	Pb-210	Po-210		
3.9		3.5						[101]	Australia
			15	17				[107]	Malaysia (from amang)
18		16						[101]	
5.2–6.7		6.1–7.8						[109]	South Africa
3.9		3.8	3.8	3.8	4.1			[110]	
3.43	3.43	3.43					3.7	[49]	
			3.1				3.3	[23]	
3.9		3.9	3.9	3.8	3.9			[11]	
	3.9–4.0		1.9–2.0					[112]	USA
6		7						[109]	Unspecified
4.8		3.6						[117]	
5		4						[60]	
4.8		3.6				3.6	3.6	[65]	
9.5	1.3	10				10	3.7	[79]	
3.6		3.2				2.7	2.7	[87]	

TABLE 43. RADIONUCLIDE COMPOSITION OF COMMERCIAL ZIRCON, THORIUM-232 DECAY SERIES

Radionuclide activity concentration (Bq/g)									Ref.	Country of origin
Th-232	Ra-228	Ac-228	Th-228	Ra-224	Pb-212	Bi-212	Po-212	Tl-208		
0.5			0.3						[96]	Australia
		45						42	[107]	Malaysia (from amang)
0.6		0.5	0.5		0.5	0.5	0.5		[110]	South Africa
1.0			0.7	0.7					[49]	
		0.5				0.6			[23]	
0.6		0.5			0.5	0.5	0.4		[11]	
				0.1–0.4	0.1–0.4				[112]	USA
0.3	2		0.4						[65]	Unspecified
0.6		0.5			0.6	0.6			[127]	
0.6		0.6			0.6	0.5			[129]	

TABLE 44. ACTIVITY CONCENTRATIONS IN COMMERCIAL BADDELEYITE BY COUNTRY OF ORIGIN

	Radionuclide activity concentration (Bq/g)											Ref.	Remarks
	U-238	U-234	Th-230	Ra-226	Pb-210	Po-210	Th-232	Ra-228	Th-228	Ra-224	K-40		
Russian Federation	3.4						0.4				0.03	[68]	
South Africa	8.7			10			2.1			3.8		[36]	
	31						19					[36]	
	6.3			10			0.07	2.9	0.9			[83]	
	6.6			9.3			0.1	2.5	0.7			[83]	
	8.0			12			2.0	5.2	2.2			[83]	
	7.3			13			0.7	6.4	1.7			[83]	
	9.3	9.3	6.4	8.2		16	0.2		0.2	0.6		[132]	
	9.1	9.1	14	9.2		26	0.1		0.6	0.1		[132]	
	8.2	8.2	1.9	6.2		10	0.1		0.3	0.3		[132]	
	8.5	8.5	0.1	8.6		1.2	0.3		0.7	0.7		[132]	Milled
	5.0	5.0	5.0	6.4	6.4	6.4	0.9	1.1	1.1			[80]	
	6.6	6.6	6.6	8.0	8.0	8.0	1.6	1.9	1.9			[80]	
	13						2.7				0.3	[68]	
	11						1.8				0.2	[68]	

TABLE 44. ACTIVITY CONCENTRATIONS IN COMMERCIAL BADDELEYITE BY COUNTRY OF ORIGIN (cont.)

	Radionuclide activity concentration (Bq/g)											Ref.	Remarks
	U-238	U-234	Th-230	Ra-226	Pb-210	Po-210	Th-232	Ra-228	Th-228	Ra-224	K-40		
Unspecified	7						0.9					[113]	
	7						0.3	6	2			[78]	
	8.6						8.3				<0.06	[123]	Used in Italy
	9.5		1.3	10	10	3.7	0.3	2	0.4			[79]	Used in the UK 1990–1996
	5.1						0.36					[91]	
	5.4						0.4					[91]	
	8.1			9.3			6.8					[133]	Used formerly in Romania
	3						0.3					[133]	

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Appendix III

DOSES ATTRIBUTABLE TO THE TRANSPORT OF ZIRCONIUM MINERALS AND RAW MATERIALS

III.1. ZIRCON SAND

A modelling assessment — supported to the extent possible by measurements to determine the contributions from gamma radiation, radon and dust — was carried out for the transport of bulk zircon sand from two minerals separation plants in South Africa to a customer's warehouse in Europe [130]. This involved transport by rail or road, ocean-going ship and river barge. The most highly exposed worker was determined to be a member of the barge crew who was estimated, conservatively, to receive a maximum effective dose of 24 μSv attributable to the transport operation. In theory, such a worker could have been involved with six consignments in a year, giving an estimated annual effective dose of 144 μSv. The most highly exposed member of the public was determined to be an individual next to a truck transporting a container of zircon sand from the container depot to the harbour, who was estimated, conservatively, to receive a maximum dose of less than 0.2 μSv attributable to the transport operation. In the highly unlikely event that such an individual was similarly exposed to 30 consignments in a year, the annual effective dose would have been 5 μSv.

III.2. ZIRCON FLOUR

The annual effective dose received by a truck driver as a result of external gamma exposure while transporting zircon flour was assessed by modelling [55]. The effective dose received while transporting one consignment over a period of 24 h was estimated to be 2 μSv. Assuming the same driver transported 25 consignments per year, the annual dose was estimated to be 60 μSv. In another assessment, the effective dose received by a truck driver in a year was estimated, using conservative assumptions, to be 350 μSv/a. This dose was attributable entirely to external gamma radiation [54].

III.3. BADDELEYITE

A dose modelling assessment was conducted for the transport of South African baddeleyite [132]. The assessment covered packaging into freight containers in consignments of 16–17 t, transport by road and rail to a port and loading on to seagoing vessels. The annual effective dose received by a worker was estimated to be 18–53 μSv.

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Annex I

MINING AND PROCESSING OF HEAVY MINERAL SANDS

Heavy mineral sand deposits may occur underwater or may form part of sea beaches or coastal dunes. They may also occur inland in coastal strips up to a few tens of kilometres wide. Heavy mineral sand deposits are mined by dry mining methods using conventional earthmoving equipment (e.g. front end loaders, bulldozers or scrapers) or by wet dredging from ponds. The various heavy minerals of commercial value, usually accounting for about 10% of the ore, are separated from the remaining, low value material ('gangue' minerals) using wet separation techniques that rely on differences in density. This process, referred to as the primary separation process, is often carried out at the mine site and produces a heavy mineral concentrate with a typical composition of 73% ilmenite ($FeO \cdot TiO_2$), 20% zircon ($ZrO_2 \cdot SiO_2$), 5% rutile (TiO_2), 1% leucoxene ($Fe_2O_3 \cdot TiO_2$), 1% monazite (($CeY)PO_4$) and <1% xenotime (YPO_4) [I–1]. In the next stage of the processing operation, referred to as the secondary separation process, the heavy mineral concentrate is dried and its constituent minerals extracted in a series of dry separation steps using magnetic and/or electrostatic separators. The complete extraction process typically involves the following steps:

(a) Large rocks, roots and other oversize material are removed by screening and returned to the mining void.

(b) Fine particles known as slimes, mainly clay particles less than 75 μm in size, are removed by hydrocyclones. The slimes are normally returned to the mining void, in some cases after drying in evaporation ponds, in others by mixing directly with the coarser sand tailings arising from the next separation stage. The slimes can be processed through a thickener to recover some of the associated water.

(c) The majority of the wet separation work involves the use of groups of spirals, as shown schematically in Fig. I–1. Sand-bearing water at a carefully controlled density is fed into the spirals, illustrated in Fig. I–2, from a 'constant density tank'. As the slurry flows down the spirals, the smaller and less dense minerals (essentially silica sand) are thrown to the outside while the larger and darker coloured heavy minerals are guided into offtake holes on the inside of the spirals by splitters (the yellow tabs shown in Fig. I–3) and collected as a heavy mineral concentrate. Various types of spiral group are used, with considerable recycling of the various
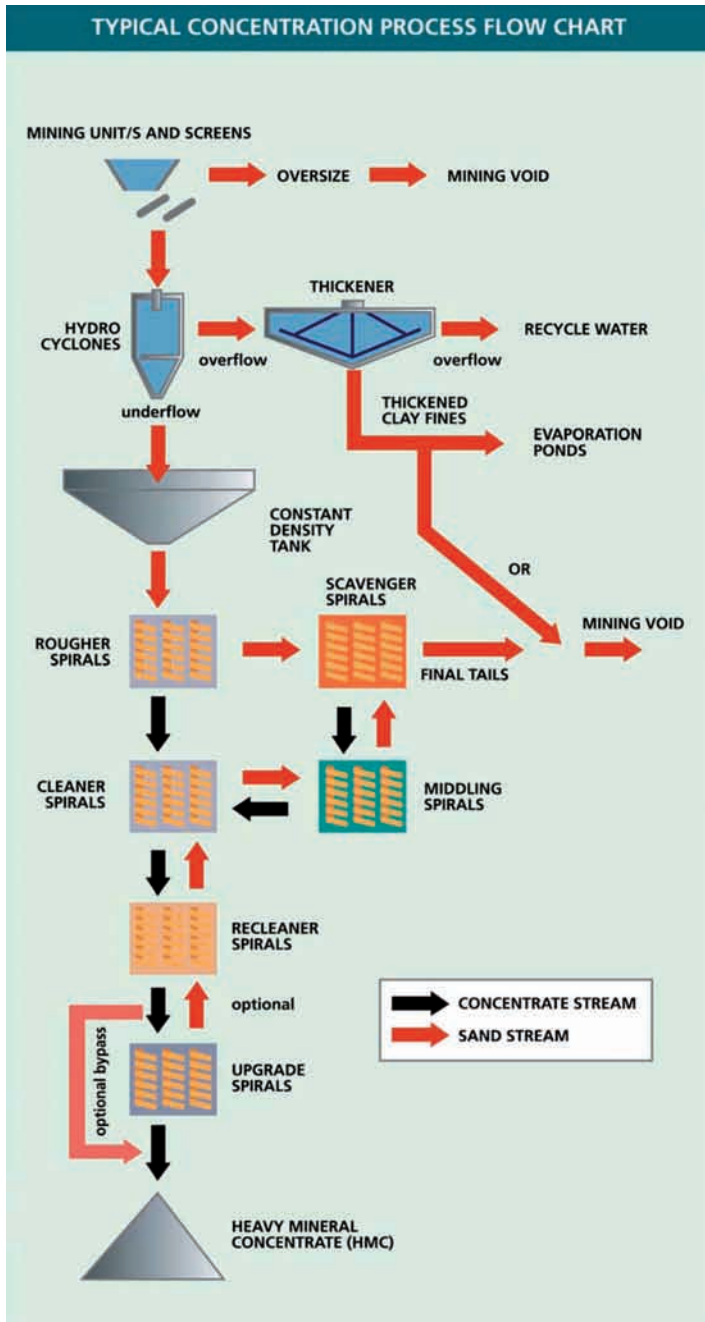
FIG. I–1. The primary separation process (courtesy Iluka Resources Limited, Australia).

FIG. I–2. Groups of spirals used in the primary separation process.

streams between the different spiral groups to maximize both the grade and recovery of the mineral products.

(d) The dry separation techniques applied to the heavy mineral concentrate involve various magnetic and electrostatic separators. A typical dry separation plant circuit is shown schematically in Fig. I–4. The higher iron content of ilmenite gives it a higher magnetic susceptibility than rutile, zircon and monazite, allowing it to be magnetically separated from these minerals early in the process. The rutile and zircon remain together after this initial magnetic separation stage and are subsequently separated

FIG. I–3. Detailed view of a spiral used in the primary separation process.

from each other electrostatically by taking advantage of the higher electrical conductivity of rutile relative to zircon. Residual magnetic minerals, such as the small amounts of ilmenite that might have been recovered with the rutile, are removed using stronger magnets than used earlier. The small quantities of quartz, kyanite and staurolite contained in the heavy mineral concentrate have similar magnetic and conductive properties to zircon and follow it when it is separated from ilmenite and rutile. Most of these particles are removed by gravity separation through more spirals. Any rutile that might have slipped through to this point is removed by further electrostatic separation and returned to the rutile circuit. Magnetic and air table separation techniques are used for final cleaning of the zircon. In some cases, traces of iron associated with the zircon particles can be removed by leaching to produce a higher quality product.

Typical concentrations of uranium and thorium in Australian heavy mineral sands and their component minerals, as reported in Ref. [I–1], are shown in Table I–1. Significant deviations from these typical values can,

FIG. I–4. The secondary separation process (courtesy Iluka Resources Limited, Australia).

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TABLE I–1. TYPICAL URANIUM AND THORIUM CONCENTRATIONS IN HEAVY MINERAL SANDS

	Uranium		Thorium	
	Mass concentration (ppm)	U-238 activity concentration (Bq/g)[a]	Mass concentration (ppm)	Th-232 activity concentration (Bq/g)[a]
Ore	$\approx$3	$\approx$0.04	5–15	0.02–0.1
Heavy mineral concentrate	<10	0.1	80–100	0.3–0.4
Ilmenite	<10–30	<0.1–0.4	50–500	0.2–2
Leucoxene	20–50	0.2–0.6	80–700	0.3–3
Rutile	<10–20	<0.1–0.2	<50–350	<0.2–1.5
Zircon	150–300	2–4	150–250	0.6–1
Monazite	1000–3000	10–40	50 000–70 000	200–300
Xenotime	4000	50	15 000	60

[a] Derived from the mass concentration assuming decay chain equilibrium.

however, be found. The main occupational exposure pathways in the separation process are through the inhalation of radionuclides in dust during the dry separation process and through external exposure to gamma radiation near stockpiles of material. Monazite exhibits particularly high radionuclide activity concentrations; thus the monazite content of the ore has a strong influence on exposure levels. Modern dry separation plants have well developed dust control and dust extraction systems, but there are likely to be many plants still in operation that do not incorporate these features. Experience suggests that, in the absence of such dust control systems, exposures of workers to inhaled dust can be significant. It is reported that typical gamma exposure levels are about 0.2 µGy/h near primary separation tailings, 1–2 µGy/h near heavy mineral concentrate stockpiles, several µGy/h near secondary separation tailings and stockpiled mineral products and over 200 µGy/h near stockpiled monazite [I–1]. Again, deviations from these typical values can be found. The doses received by workers depend on the type of plant and its layout, the presence and location of significantly radioactive material such as monazite, the time spent and tasks undertaken by workers in the plant and the existence, use and maintenance of control measures. In Ref. [I–2], doses received by workers are reported for mineral sands processing operations in India over a five year period. The average annual

effective dose at one plant was 1.1–3.2 mSv, while at another plant, in which ore with a higher monazite content was processed, the average annual effective dose was 4.3–5.1 mSv.

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Annex II

MONITORING FOR THE ASSESSMENT OF OCCUPATIONAL EXPOSURE IN ZIRCON MILLING PLANTS

The following is a description of the monitoring methods used in an assessment of the exposures of workers in Australian zircon milling plants [II–1].

II–1. GAMMA RADIATION

Gamma radiation exposure levels were measured using portable electronic radiation monitors worn by selected workers in the zircon processing and bagging areas. Background radiation levels, determined either from environmental radiation measurements or from measurements in office areas away from zircon storage or processing areas, were subtracted from the levels measured in the plant to determine the occupational exposures. The gamma monitors were calibrated by a national laboratory using a monazite reference source.

II–2. INHALATION OF RADIONUCLIDES IN DUST

Dust levels were measured with personal dust monitoring devices in which air was drawn through a 25 mm diameter PVC filter with a pore size of 5 μm. Due to impaction and electrostatic attraction, the loss by non-collection of particles smaller than 5 μm was considered to be no more than 5% of the total dust. The pump flow rate (nominally 2 L/min) was measured at the start and end of the sampling period (usually 8 h) and the average value was used for determining the dust concentration.

The radioactivity in the dust collected on the filters was determined by alpha particle counting using a solid state detector. The count was compared with standard sources, which in turn had been independently calibrated against a source verified by a national laboratory. The counts were normally made over a period of 1 h, but this period was increased to 3 h when the activity in the dust was small. The counts were corrected for background and the measured efficiency of the counting system and recorded as gross alpha activity per unit volume of air. Counting was conducted at least a month after sample collection to ensure that even in the unlikely event of the equilibrium between ^{226}Ra and radon being disturbed, equilibrium would have been re-established. Self-absorption of the alpha particles in the zircon or in overlying layers was not

considered to be an issue with the dust loadings on the samples. The uranium and thorium concentrations in the zircon feedstock were used to apportion the alpha activity between the two decay chains, assuming full equilibrium in each decay chain.

The arithmetic mean values of the gamma and dust exposures were used to estimate the dose. This could have led to an underestimation of the dose to an individual worker, due to differing work patterns. The estimation of the doses received by individual workers would have required a comprehensive monitoring programme with details of time spent in the different parts of the plant and cross-checking of time schedules. In view of the low average doses received, such a comprehensive monitoring programme was not considered to be warranted.

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This Safety Report is a compilation of detailed information on the processes and materials involved in the zircon and zirconia industries, and on the radiological considerations that need to be taken into account by the regulatory body when determining the nature and extent of radiation protection measures. It has been developed as part of the IAEA's programme on the application of its safety standards in the field of radiation, transport and waste safety. The information provided is consistent with the graded approach to regulation, in terms of which the application of the requirements of the safety standards is commensurate with the characteristics of the practice or source, and with the magnitude and likelihood of the exposures.