MANAGEMENT OF NORM – WITH PARTICULAR REFERENCE TO ZIRCON MINERALS

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1 ABSTRACT

The recent changes to legislation in Europe have focussed the field of radiation protection on areas other than nuclear power. This change has been a result of the ever decreasing limits for radiation exposure both in the work place and for members of the public. Limits introduced by the ICRP in 1990 and subsequently the IAEA and the E.U. have led to a focus on the radiation risk posed by the use of many naturally occurring materials. Many such materials have been in use for hundreds of years and have not been considered by the public to be of any concern. However due to decreasing exposure limits largely driven by increases in safety requirements in the nuclear industry, the exposures resulting from natural materials now require positive management.

This paper focuses on the management of radiation risks from the handling and use of the naturally occurring zirconium silicate, zircon. Zircon is recovered from heavy mineral sands and is used largely for its thermal properties in the fields of ceramics refractories and foundry uses. The various market sectors are discussed and the radiation risks associated with the production and use of zircon are presented. The area warranting the greatest degree of control is the dry milling of zircon into a finer grained flour and associated handling of such fine particulates. By implication the inhalation pathway for such materials becomes the highest potential risk, although storage of large quantities can also produce low levels of worker exposure.

The greatest proportion of zircon sand is used in ceramics and the impact of this use on the exposure of the public is discussed.

Waste disposal of zircon sand and flours does require some focus and the results of various studies are presented. The transportation of radioactive materials is governed by IAEA Safety Series TST-1. There is currently some debate of the application of this standard to NORM. The results of a current study on the transportation of zircon are presented, and support the wording used by the IAEA in TST-1 that NORM materials less than 10 Bq/gm U^{238} or 10 Bq/gm Th^{232} need not be regulated as radioactive materials. This principle is also seen from other uses of zircon where normal good handling practices are sufficient to ensure low radiation related risks.

The harmonization efforts recently conducted by the EU in the field of radiation related legislation has produced confusion amongst users largely as a result of the incorrect use of data in official EU publications. Methods of preventing such problems are discussed and proposals made which can be extended to the management of other NORM materials.

2 INTRODUCTION

The radioactive elements, uranium and thorium occur widely in naturally occurring substances and at widely varying concentrations. With half lives of the order of 10^9 years much of the uranium and thorium present at the time of formation of the universe, is still in existence. These elements are distributed throughout the body of the planet but do become preferentially concentrated in certain types of solid minerals and hence rocks. Due to their atomic size such elements do not easily fit into many crystal lattices during crystallisation from molten magmas. As a result during the cooling processes of molten magmas, elements such as uranium / thorium tend to be concentrated in the crystal phases which solidify towards the end of these cooling processes. There are two exceptions to this:

1. Where stable phases are formed of elements with large atomic size, which will accommodate uranium and thorium in their lattice structure, eg, zircon and baddyelite. The zirconium atom having a large size and the mineral zircon having a high melting point tends to encourage the migration of U and Th from the melt into the early crystalling zircon or baddyelite structures.

2. The other exception to the late crystalling phase principle is where the concentration of the uranium and thorium reach sufficient levels to form minerals in their own right, eg thorite (ThO_2) and uranite (U_3O_8)

In addition to the distribution of these radioactive elements in crystalline igneous rocks they may also distribute themselves widely by their varying solubility in water. Uranium and thorium taken into solution during natural erosion processes may precipitate with other secondary mineral phases based on their differing stabilities under oxiding conditions. Thorium is extremely unstable under atmospheric conditions and precipitates readily into stream sediments. Uranium whilst also of limited stability will be stable for a longer period and therefore migrate further before precipitating.

The net result of these natural geological and chemical processes is that U and Th are widely distributed in natural minerals, some of which may contain higher concentrations than others.

The exploitation of minerals for commercial and domestic use will therefore bring these radioactive elements into the sphere of life occupied by workers and members of the public. The most commonly exploited heavy minerals are ilmenite, rutile and zircon, and the occurrences of radionuclides in these minerals varies in both concentration and mode of origin. Zircon containing the highest levels of radionuclides is the subject of this paper.

3 ZIRCON

Zircon is a very tough durable and resistant mineral and is not affected by low temperature processes found on the earths surface. Consequently the uranium and thorium in zircon is that given it during crystallisation from the melt. The nature of the zircon crystal inhibits the removal of uranium and thorium and is one of the properties that allows this mineral to be used for dating of rocks. The U and Th atoms are firmly locked in the zircon lattice and the strength of this bond is reflected in the fact that the decay products, eg polonium remains within the zircon crystal even up to temperatures of 1200^{o}C (ref. 5). Only when melting or destruction of the lattice occurs do the decay products of U / Th have the opportunity to mobilise.

The uranium contents of commercial zircon are typically about 320 ppm with thorium about 150 ppm. These produce radioactivity levels of 58 Bq/gm total uranium chain activity and 6 Bq/gm total thorium chain activity. There are zircons which contain up to several 1000 ppm of uranium / thorium however these higher levels render the zircon magnetic allowing it to be removed. Most commercial zircon operations remove the high U / Th zircons prior to final production.

3.1 The Uses Of Zircon

Zircon is primarily used for its high temperature resistance and a great resistance to chemical attack. As a result zircon uses are mainly in the ceramics and refractories industries, as shown in Table 1.

Table 1

Uses of zircon

Use	Proportion
Ceramics	40 %
Refractories	20 %
Foundry sands	10 %
Mould washes	10 %
Chemical	10 %
TV glass	5 %
Other	5 %

The size of the world market is approximately one million tons per annum, and with a price varyng from US$200 – 400 per ton puts a value of US$200 – 400 million per annum on the global market. This is a significant value for the many producers who are largely operating from Australia, South Africa, India and the USA. Additionally there are currently no products which can act as replacements for the very specific characteristics of zircon mineral.

3.2 Zircon and Radioactivity

Zircon has always had a radioactive nature due to its low content of uranium / thorium. So it is not a feature of the mineral which has changed but in the manner in which radioactivity is viewed.

Changing legislation all over the world but particularly in Europe and the USA has reduced the levels whereby a substance is classified as radioactive (ref.1,2,3,4).

This is a subjective issue as all natural substances contain some level of radioactivity so it is impossible to group substances into radioactive and non-radioactive other than by an arbitrary limit. Currently these arbitrary limits are being changed to lower levels with the consequence that many substances, which were previously not classed as being radioactive, now are being reclassified. Unfortunately the word radioactive has many negative perceptions associated with it as a result of mismanagement in the nuclear power and military sectors. Classifying a mineral as radioactive puts the same negative perceptions onto its use, as given to atomic bomb tests and Chernobyl explosions. The effect of this on the minerals market can be extremely negative and if not managed carefully has the potential to destroy the market for zircon, in much the same way has the market for uranium has been destroyed.
With this in mind it is therefore critical for the zircon industry to recognise these threats and to manage the impacts such that zircon can continue to be used in a safe and effective manner.

3.3 Zircon Uses and Radiological Impacts

The documentation of the radiological impacts of the use of zircon is a current study of the producers and users of this mineral. The uses are very diverse and the study is not yet complete. The data reported below gives some of the completed work and references to the original studies. The knowledge base is continuously being expanded by producers and users associations.

3.3.1 Zircon Production

The bulk of the worlds zircon is produced by a few relatively large operations which handle significant tonnages of zircon in one year. (10^4 – 10^5 tons per annum). It is also common for the mineral monazite to occur as a common accessory mineral with the zircon. Monazite is significantly radioactive containing over 5% ThO_2. During the separation processes, which produce zircon, the monazite is removed.

However the radiation exposure in the separation plants would be higher, due to the monazite contribution, than would be seen in a plant using only the zircon concentrate. One plant in South Africa producing in excess of 200,000 tons per annum of zircon showed the following annual worker exposures:- (ref. 16)

Process	Internal Exposure mSv/A	External Exposure mSv/A	Total Exposure mSv/A
Mining	0 – 0.12	0.15 – 0.42	0.15 – 0.54
Wet Concentration	0	0.20 – 0.40	0.2 - 0.4
Dry Concentration	1.0 – 2.1	0.70 - 1.0	1.7 - 3.0

Inspite of the presence of monazite in the zircon plant the total annual exposures do not exceed 3 mSv/A.

3.3.2 Zircon Milling

Many of the uses of zircon require the mineral in fine particle sizes. The sand as recovered from its original geological source has typically in d_{50} of 110 – 130 microns and is closely sized with little material less than 75 microns or larger than 250 microns. The most commonly used milled zircon is in two sizes a) 95% - 45 micron (zircon flour) b) 95% - 5 micron (micronised zircon).

The milling processes vary with both dry and wet processes in use. The most significant hazard in the milling of zircon is the inhalation risk so wet milling processes are inherently safer than dry processes. However a study has been done by B. Hartley is Australia and the results were published in Health Physics January 2001. (ref.10) Hartley concludes that the maximum potential doses to workers were 5.5 mSv/A with the actual measured dose being 0.66 – 1.03 mSv/A.

3.3.3 Zircon in Ceramics

The industry sector using most of the worlds zircon is the ceramic industry, with the production of glazed ceramic tiles being a significant consumer. Since such tiles are used in work and public places a study was done to research the impact on the public.

Zircon is added to glazes to increase their durability and to enhance whiteness and opacity. The tiles used for the study contained 6.15% ZrO_2 in the glaze. The study (ref. 11) by Strydom and Selby (Heavy Minerals 99) concluded that the dose to the most exposed member of the public would not exceed 40μSv/annum in a Northern hemisphere home.

3.3.4 Disposal of Zircon Sand

Waste disposal of radioactive minerals is a subject receiving much debate particularly in Europe. It is not normal for a zircon user to dispose of large quantities of zircon sand since this would be economically unfavourable. However it is also unlikely that a user would produce no waste. Consequently a study was done to estimate the public exposure which would result from disposing of varying quantities of zircon sand in a shallow land fill.

The study by de Beer and Selby (ref 12) was published in Heavy Minerals 99, and showed that quantities of up to 100 tons of zircon sand could be disposed in a land fill with no cover or dilution. The resultant public exposure would not exceed 250μSv/annum. As the quantity of material to be disposed increased to 10,000 tons the cover thickness increased to 3 metres for European conditions to maintain exposures at less than 250μSv/A. A similar study was conducted by Bernhardt and Rogers of Rogers and Associates Engineering, Salt Lake City, USA. (ref.13) This study included TCLP leach tests to determine specific dispersion coefficients and soil to plant uptake parameters. The highest dose to a member of the public was estimated as 110μSv/annum and this was for an intruder scenario and assumed a residence was built on excavated waste. Both of the above disposal studies concluded that the public exposure from land fill disposal of zircon wastes were well below the public exposure limits in most countries.

3.3.5 Radon Emanation from Zircon

The amount of radon liberated from the zircon mineral is a critical parameter used in many dose assessments. Since zircon is an extremely stable material it may be expected that the radon would be retained largely inside the mineral grains. Two data sets are available and confirm this.

	EMANATION FRACTIONS		
Zircon Source	**Sand**	**Flour**	**Ref**
USA	0.002	0.008	15
South Africa	0.006	Currently being determined	14

It is important to note that as would be expected the emanation fraction is higher in flour i.e. smaller particle sizes. In all cases however the amount of radon emanating from zircon mineral is extremely low. This is further confirmed by equilibrium studies, which showed that the full uranium and thorium chains are in secular equilibrium. A South African study showed the following isotopic data for zircon sand:- (ref.17)

Uranium chain

$U^{238} \rightarrow$	$Ra^{226} \rightarrow$	$Pb^{214} \rightarrow$	$Bi^{214} \rightarrow$	Po^{214}
3.9	3.9	3.9	3.8	3.9

Thorium chain

$U^{232} \rightarrow$	$Ac^{228} \rightarrow$	$Pb^{212} \rightarrow$	$Bi^{212} \rightarrow$	Po^{212}
0.6	0.5	0.5	0.5	0.4

This data confirms the retention of decay products in the zircon grains.

3.3.6 Transport of Zircon

Zircon is transported around the world in sea going bulk carriers. A typical shipment may be 10^3 tons but single ships may carry 10^4 tons of the mineral in a load. In this mode of transport the mineral is unpackaged in a ships hold. Smaller quantities are conveyed by rail and road within Europe. Once milled the zircon is always conveyed in a packaged form usually in 40kg bags palletised to 1 ton, or in 2 ton bulk bags.

A study is currently in progress in South Africa to evaluate the radiation exposures throughout the transport route. This study is part of a Coordinated Research Program (CRP) being done for the IAEA. The study is due for completion at the end of 2001 but has so far shown the highest worker exposure of 200 μSv/annum and the highest public exposure of 8μSv/annum. The results so far indicate no radiological risk during the bulk transport of zircon.

3.3.7 Studies Still in Progress

The collection of knowledge on the radiological impacts of zircon usage is still in progress with the following areas under investigation:-

1. Refractories
2. Foundaries
3. Abrasives
4. T.V. Glass
5. Chemicals

4 THE LEGISLATIVE PROCESSES AFFECTING ZIRCON

4.1 Education of Legislators and Regulators

It is important for the minerals industry to make the legislative and regulatory bodies aware of their products and how they fit into the international arena. Often new legislation is formulated from an academic stand point with absolutely no knowledge of the mineral in question, the effect of trade in that mineral on the supply or the user countries GDP, the employment created by that Industry or the effect on industrial and domestic sectors in their own countries. Often legislators act conservatively because they have no information about a particular issue, so in the interest of public / worker protection they apply arbitrary factors where often these are unnecessary or overly restrictive.

For this reason it is critical for the minerals industry to communicate details of their products, the uses, the safety measures, the recommended operating and waste management procedures. It is equally important for legislators to make the effort to understand the effects of their legislation changes before blindly proceeding with such changes. All parties being affected by legislation should have the opportunity to comment on such legislation. Minerals industry members who have registered offices in various countries should lobby for the opportunity to comment on new legislation.

4.2 Compliance with legislation changes

Many mineral users will adopt the 'heads down approach' and hope they will not be singled out by their regulators. This is a shortsighted approach and users should be assisted to reach compliance with new and inevitable regulation so that they continue to use the mineral in question. Too much difficulty enforced on a user by a regulator could result in him ceasing to use the mineral, to the detriment of the industry. If the producers assist the users this risk can be overcome.

Producers can assist users in many ways such a producing simplified easy to read data sheets (ref.6). Radiation legislation / regulations are often very difficult to interpret for a user. A simplified data sheet tailored for his operation type will remove much frustration and cost.

Many countries have industry groupings or trade associations. In the zircon industry a grouping known as the ZMC – Zircon Minerals Committee (ref.8) has been established as a producers / users industry body. The aim of the ZMC is to ensure the continued safe and sensible of use of zircon by cooperation with all involved parties. The ZMC operates mainly in Europe, South Africa and Australia. A similar grouping in the USA is known as the ZEC – Zirconium Environmental Committee (ref.7). This group deals exclusively with matters inside the USA. However the two groupings ZMC and ZEC cooperate together.

Membership of these associations by producers and users will encourage dialogue and assist in calming user panic over new regulation. In order to assist the user the producers obviously need to do the necessary studies to allow them to provide informed and sensible assistance e.g. the type reported in section 2.3. These studies may take the form of a radiation hazard assessment, eg the assessment could involve measuring the exposure of workers in a particular users operation, or members of the public who purchase a users products. Such information may be used to assist a user with his compliance program. It is important for an industry grouping to have at its disposal all the scientific knowledge needed to educate a legislator, assist a user with his regulator, or defend an issue with the media. To do this a risk assessment needs to be done to identify which areas of product use or handling have the potential to cause problems in the prevailing regulatory climate. Having identified these the problem areas the study programs can be directed to provide information to resolve the problem area. For example if it is perceived that the use of zircon in a particular refractory brick may result in elevated worker exposure. The study must be directed to measuring such exposures so that the true exposure of such workers is known. This information can be provided to all refractory manufacturers worldwide so that they will be in a position to answer such a query, should it arise. In the areas of radiation protection there is no excuse for not knowing the exposure of any worker or member of the public who is involved in the normal use of the mineral, this knowledge will ensure that minerals may continue to be used safely without undue hazard.

4.3 Responsible Development of Legislation

There has been a considerable growth in the amount of guidance documentation produced by the European Union. This is in response to the Directive 96/26/EURATOM in which title VII has focussed on the natural sources of radiation. The development of such documentation is a very positive move and will greatly assist both national legislators and the regulated users. This however will only be the case if the guidance is based on accurate data and assumptions.

A specific example of inaccurate guidance is given in the document RP95 – (ref.3) “Reference levels for work places processing materials with enhanced levels of naturally occurring radionuclides: - published in 1999 by the European Commission.

In this document a worked example is included which uses zircon sand to demonstrate the determination of screening and reference levels. The example quoted activity levels for the U-238 chain members of 0.8 Bq/gm – such levels do not occur in any commercial zircons which, normally range from 3 – 4 Bq/gm. In addition radon and thoron doses are overestimated due to the use of emanation and diffusion coefficients which are too high by factors of almost 10 and 2 respectively.

RP 95 was reviewed independently by a team from the South African Atomic Energy Corporation (ref.9) and a written report was submitted to the Director – General, Environment, Nuclear Safety and Civil Protection, at the European Commission. Whilst such a review is able to highlight inaccurate data and assumptions it does not correct the confusion which can be caused amongst the regulated users by the original inaccuracies.

There is an abundant source of accurate data on the radiological properties of zircon, which resides with the producers and users. This data is available to all responsible authorities and improved communication between these parties would ensure that guidance documentation is as accurate as possible.

5 CONCLUSIONS

The mineral zircon has recently become the focus of regulatory interest due to its radioactive nature. This paper has presented the results of many studies on the uses of zircon, which show that the exposure levels of workers and the public are low. Indicating that sensible management of the NORM industry can control the radiological risks without undue complexity.

The involvement of producers and users in understanding the radiological risks is encouraged, as is the education of legislators and regulars in the understanding of the minerals industry.

Finally an appeal is made for accuracy and minimum use of assumptions in developing legislation and guidance. This will assist in avoiding over regulation and of the industry and minimise confusion caused by in accurate guidance.

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