CONCENTRATIONS OF NATURAL RADIONUCLIDES IN IMPORTED ZIRCONIUM MINERALS

by

Marija M. JANKOVIĆ** and **Dragana J. TODOROVIĆ

Radiation and Environmental Protection Department, Vinča Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia

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The natural radioactivity in imported zircon samples used as glaze for ceramic tiles in the ceramics industry has been presented in this paper. The measurements were made by gamma spectrometry with a high purity germanium detector. The average activity concentrations of ^{238}U and ^{232}Th determined in the measured samples (3250 Bq/kg, and 556 Bq/kg, respectively) are much higher than the concentrations found in the Earth's crust. The activity concentration of ^{226}Ra is also high in all analyzed samples, while ^{40}K was not detected. The gamma index, I, the external hazard index, H_{ex}, the internal hazard index, H_{in}, and the radium equivalent activity, Ra_{eq}, were calculated. Due to relatively high activity concentration level of uranium in imported zircon samples, specific regulations are necessary for zircon compound used in ceramic industry. It can be concluded that the investigated samples can be used as the component of ceramic glaze in the concentrations not above 3%.

Key words: zircon, ceramics, radioactivity, gamma spectrometry

INTRODUCTION

Many materials that are usually found in the Earth's crust contain small but measurable amount of naturally occurring radioactivity (NORM). Some particular ores contain natural radionuclides at levels much higher than those usually present in the Earth's crust, and are also subject to radioisotope enrichment, during technological process, known as technologically enhanced natural radioactivity (TENORM). The term TENORM was proposed to distinguish the NORM from that enhanced by technological process [1, 2]. Typical concentrations of ^{238}U and ^{232}Th in the Earth's crust and in various natural materials are presented in tab. 1.

Zirconium is the 18th most abundant element on Earth – three times more abundant than copper. It occurs in nature as free oxide ZrO_2 (baddeleyite), but most commonly as zircon, a compound oxide with silica having the chemical formula $ZrO_2 \times SiO_2$ 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% [6]. The investigation of zirconium ores as sources of TENORM began in the late 1970s and early 1980s [7, 8]. These works highlighted the relatively high concentrations of natural radionuclides in zirconium ores. At present, the largest exporters of zirconium minerals are Australia, South Africa, Ukraine, India, China, Brazil, and Sri Lanka [8].

Table 1. Activity of U and Th in the Earth's crust, ores, and mineral sands

Material	Activity [$Bqkg^{-1}$]		References
	^{238}U	^{232}Th	
Earth's crust	33	34	NCRP (1988) [3]
Bauxite ore	250	200	UNSCEAR (1988) [4]
Copper ore	30-80	23-100	UNSCEAR (1988) [4]
Phosphate rock	1300-2300		UNSCEAR (1982) [5]
Zircon sand	>500	>500	UNSCEAR (1988) [4]

The relative consumption of zircon in ceramics industry in different regions of the world is shown in tab. 2 and the main uses of zircon are shown in tab. 3. The use of micronized zircon and zircon flour in ceramic products accounts for almost half of the worldwide use 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 [6].

The aim of this study was to measure the radioactivity in imported zircon samples used as raw mate-

* Corresponding author; e-mail: marijam@vinca.rs

Table 2. Relative zircon use by region [6]

	Relative use [%]
Europe	36
China	20
North America	14
Asia-Pacific	14
Japan	7
Rest of the world	9

Table 3. Commercial applications of zircon [6]

	Proportion [%]
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

rial in ceramics industry for production of ceramic colors, glazes, tiles, and sanitary ware and to estimate the radiological hazards. This material is tested continuously in the Radiation and Environmental Protection Department of the Vinča Institute, Belgrade, as part of the regular inspection of imported goods from the customs.

EXPERIMENTAL

The samples of zircon imported from Italy, Great Britain, Slovenia, Sweden, Spain, Slovakia, and Germany were investigated. Before measurements, the samples were crushed, sieved, and placed in the plastic 500 cm^3 Marinelli beakers. Considering that the zircon samples are part of the regular control of imported goods from the border crossing, they were measured immediately after preparation and were not left for four weeks to reach radioactive equilibrium. Counting time interval was 3000 seconds. The activity was determined by a high purity germanium detector (HPGe) with relative efficiency of 23% and energy resolution of 1.8 keV for the 1332 keV ^{60}Co energy [9]. Gamma energies for gamma spectrometry determination are presented in tab. 4.

Table 4. Gamma energies for gamma spectrometry determination

Radionuclide	Notes	Energy [keV]	Yield [%]
^{238}U	via ^{234}Th	63	3.28
	via ^{234}Pa	1000	0.89
^{232}Th	via ^{228}Ac	338.32	12.4
	via ^{228}Ac	911.07	29
^{226}Ra	via ^{214}Bi	609.31	46.1
	via ^{214}Bi	1120.29	15
	via ^{214}Bi	1764.5	15.9
	via ^{214}Pb	295.21	19.2
	via ^{214}Pb	351.92	37.1
^{235}U		143	10.5
		163	4.7
^{40}K		1460.83	10.67

RESULTS AND DISCUSSION

The measured specific activities of ^{226}Ra, ^{232}Th, ^{235}U, and ^{238}U are presented in tab. 5. The combined uncertainty of the results was estimated to range from 10% to 20%. The average concentration of ^{238}U (3250 Bq/kg) was higher than the average concentration of ^{232}Th (556 Bq/kg), ^{226}Ra (3157 Bq/kg), and ^{235}U (175 Bq/kg). These values are in agreement with other recently published works (tab. 6). Considering that more than 80% of production comes from Australia, South Africa, and USA, it is evident from the data that most zircon currently produced contains ^{238}U series radionuclides at activity concentrations of about 1000-4400 Bq/kg, and ^{232}Th series radionuclides at activity concentrations of about 500-1000 Bq/kg. The worldwide average concentrations of natural radionuclides in the soil and in building materials are ^{226}Ra (32 Bq/kg), ^{232}Th (45 Bq/kg), and ^{40}K (420 Bq/kg), and in building materials: ^{226}Ra (50 Bq/kg), ^{232}Th (50 Bq/kg), and ^{40}K (500 Bq/kg) [15]. The obtained concentrations of ^{226}Ra and ^{232}Th in zirconium samples are significantly high, but these samples are used only as one component in the recipe for the production of ceramics for building materials. On the other hand, by comparison, the concentration of ^{226}Ra and ^{232}Th in zircon samples are higher than the concentrations of given radionuclides in soil samples [16, 17]. The specific activities of ^{238}U and ^{232}Th are up to two orders of magnitude and up to one order of magnitude higher, recpectively, than the activity concentrations in the Earth's crust (tab. 1).

The high level of radioactivity can be explained on the basis of the following considerations: uranium and thorium atoms are easily incorporated in the crystalline structure of the zircon; furthermore, zircon ores undergo an enrichment during sand processing which produces almost pure zirconium silicate. For these reasons zircon minerals, used in cermic industry, are ussualy included in the category of sources of technologically enhanced natural radioactivity [1].

Activity ratio ^{238}U/^{226}Ra was approximatelly 1, and can be assumed that these two radionuclides are in the radioactive equilibrium.

Good correlation (r = 0.81) was observed between the concentrations of ^{238}U and ^{226}Ra as shown in fig. 1. The obtained value is statistically significantly different from zero and statistically insignificantly different from 0.90 [18].

Table 5. Activity concentrations of radionuclides in zircon and appropriate gamma index

No.	Imported	Activity concentrations of radionuclides [Bqkg^{-1}]				I
		^{226}Ra	^{232}Th	^{235}U	^{238}U	
1	Italy	2312 347	367 73	194 58	2236 894	0.38
2		2969 297	816 106	78 33	3540 1133	0.53
3		4147 415	665 80	266 27	4522 588	0.69
4		3967 397	509 61	230 44	3855 694	0.65
5		4350 434	885 88	178 53	3853 462	0.75
6		3201 320	643 64	191 34	3948 592	0.54
7		2732 137	526 68	164 16	2425 1336	0.46
8		3031 303	630 94	198 20	3055 611	0.52
9		3993 399	555 72	203 32	3517 914	0.66
10		3661 366	658 79	279 28	3410 682	0.62
11		2961 296	570 74	214 21	2630 736	0.50
12	Great Britain	2021 202	396 59	55 26	1867 672	0.35
13		3511 351	454 54	162 41	2958 740	0.57
14		3778 378	584 64	215 54	4037 1009	0.63
15	Slovenia	2603 234	460 60	42 24	2266 748	0.44
16		2106 210	428 51	54 19	2687 564	0.36
17		814 163	187 47	71 14	672 138	0.14
18	Sweden	2941 294	565 85	225 56	2859 715	0.50
19	Spain	3008 301	596 89	206 21	3808 762	0.51
20	Slovakia	4090 1227	550 165	193 58	6524 1174	0.67
21	Germany	4092 409	624 69	258 52	3570 714	0.68

Table 6. Specific activites of zircon minerals

Origin	Activity concentrations of radionuclides [Bqkg^{-1}]				References	Remerks
	^{226}Ra	^{232}Th	^{238}U	^{40}K		
Australia		703	3533	49	Bruzzi *et al*., [1]	Used in Italy
Australia	2250	500			Beretka *et al*., [7]	
Belgium		570	3100	77	Fathivand *et al*., [10]	Used in Iran
China	14387	7982		2226	Wen *et al*., [11]	
Germany		590	2700	65	Fathivand *et al*., [10]	Used in Iran
India		565	2510		Haridasan *et al*., [12]	
Italy		550	3500	55	Fathivand *et al*., [2]	Used in Iran
Malaysia	16000	43000			Hu *et al*., [13]	
South Africa		610	4400	60	Fathivand *et al*., [2]	Used in Iran
Ukraine		460	2100	50	Fathivand *et al*., [2]	Used in Iran
USA		100-400	1900-4000		Armstrong *et al*., [14]	

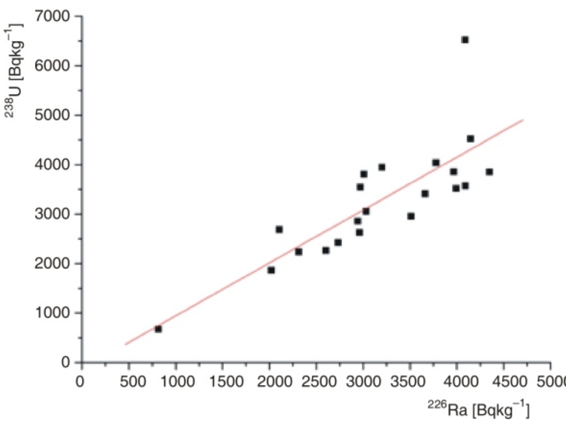

Figure 1. Correlation between concentrations of ^{238}U and ^{226}Ra in zircon samples

In order to estimate the radiological hazards, the gamma index, the external hazard index, the internal hazard index, and the radium equivalent activity, Ra_{eq} must be calculated. Due to the high activity of ^{226}Ra and ^{232}Th in the samples, the percentage of the sample that can be used in the recipe for the production of ceramics must be determined. Gamma index can be calculated using the following relation [19]

$$I \quad \frac{C_{\mathrm{Ra}}}{200} \quad \frac{C_{\mathrm{Th}}}{300} \quad \frac{C_{\mathrm{K}}}{3000} \qquad (1)$$

where C_{Ra}, C_{Th}, and C_K are the activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in Bq/kg in the building material, respectively. Gamma index must be less than 1 if the material is going to be used in high construction for interior. Gamma index for the investigated samples will be less than 1 only if 3% of the sample is used. The obtained values for gamma index for interior are presented in tab. 5. For all investigated samples $I < 1$ (in the account, 3% of the activity of ^{226}Ra, ^{232}Th, and ^{40}K was used). Hence ^{40}K was not detected in samples, 3% of the 16 Bq/kg (minimum detectable concentration) was used in all calculations. The external hazard index, H_{ex}, is defined as [7]

$$H_{ex} \quad \frac{C_{Ra}}{370} \quad \frac{C_{Th}}{259} \quad \frac{C_{K}}{4810} \tag{2}$$

where C_{Ra}, C_{Th}, and C_K have the same meaning as in eq. (2). The value of this index must be less than unity in order to keep the radiation hazard insignificant. The obtained values of H_{ex} for the zircon samples ranged from 0.09 to 0.46, as shown in fig. 2, values which are indeed less than unity (results obtained with 3% of the activity of ^{226}Ra, ^{232}Th, and ^{40}K). In addition to the external hazard, radon and its short-lived products are also hazardous to the respiratory organs. The internal exposure to radon and its decay products is quantified by the internal hazard index, H_{in}, which is given by the equation [20]

$$H_{in} \quad \frac{C_{Ra}}{185} \quad \frac{C_{Th}}{259} \quad \frac{C_{K}}{4810} \tag{3}$$

where C_{Ra}, C_{Th}, and C_K are the activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in Bq/kg in the building material, respectively. For the safe use of a material in the ceramics industry, H_{in} should be less than unity. The calculated values of H_{in} ranged from 0.15 to 0.81 as shown in fig. 2.

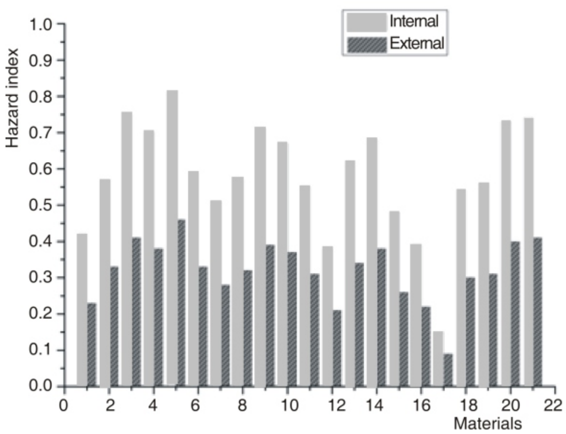

Figure 2. The calculated values of both the external and the internal hazard indices

The distribution of ^{226}Ra, ^{232}Th, and ^{40}K in building materials is not uniform [7]. Uniformity in the respect of exposure to radiation has been defined in terms of radium equivalent activity (Ra_{eq}) in Bq/kg in order to compare the specific activity of materials containing different amounts of ^{226}Ra, ^{232}Th, and ^{40}K. It is calculated using the following relation [7]

$$Ra_{eq} \quad C_{Ra} \quad 1.43\, C_{Th} \quad 0.077\, C_{K} \tag{4}$$

where C_{Ra}, C_{Th}, and C_K are the activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in Bq/kg, respectively. While defining, Ra_{eq} activity according to eq. (4), it has been assumed that 370 Bq/kg of ^{226}Ra or 259 Bq/kg of ^{232}Th or 4810 Bq/kg of ^{40}K produce the same gamma dose rate. A Ra_{eq} of 370 Bq/kg in building materials will produce an exposure of about 1.5 mSv per year to the inhabitants [15].

Figure 3 shows the Ra_{eq} values in all tested samples in increasing order of Ra_{eq} magnitude (in the account, 3% of the activity of ^{226}Ra, ^{232}Th, and ^{40}K was used). The lowest mean value of Ra_{eq} is 71 Bq/kg for samples imported from Slovenia, while the highest calculated mean value is 150 Bq/kg for samples imported from Germany. All investigated samples have shown Ra_{eq} values lower than the limit of 370 Bq/kg set in the OECD report [21], but these materials would not present a significant radiological hazard only if maximum 3% of the sample used in the recipe for the production of ceramics.

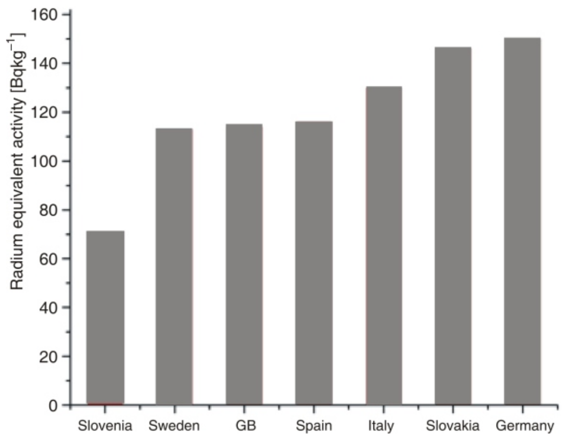

Figure 3. Radium equivalent activities calculated for zircon samples imported from different countries in ascending order of magnitude

CONCLUSION

It can be concluded that the radioactivity of imported zircon materials is lower than the limits regulated by our law [22]. As the investigated samples are used as one component in the recipe for the production of ceramics, we propose that they can be used in concentrations not above 3%.

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Марија ЈАНКОВИЋ, Драгана ТОДОРОВИЋ

КОНЦЕНТРАЦИЈА ПРИРОДНИХ РАДИОНУКЛИДА У УВЕЗЕНИМ МИНЕРАЛИМА ЦИРКОНИЈУМА

У овом раду приказани су резултати мерења природне радиоактивности у увезеним узорцима циркона који се користи у керамичкој индустрији као глазура за керамичке плочице. Мерења су извршена гама спектрометријом на германијумском детектору (HPGe). Концентрације радионуклида ^{238}U и ^{232}Th детектоване у узорцима (3250 Bq/kg и 556 Bq/kg, респективно) много су веће од концентрација датих радионуклида који се налазе у Земљиној кори. Добијене концентрације ^{226}Ra су такође високе у свим анализираним узорцима. ^{40}K није детектован у испитиваним узорцима. У раду су израчунати гама индекси, индекси радијационог ризика услед спољашњег и унутрашњег излагања. Због релативно високе концентрације уранијума у узорцима циркона потребна су одређена правила по којима се циркон меша са осталим компонентама приликом производње керамике. Испитивани узорци могу да се користе у процесу производње керамике са учешћем од само 3%.

Кључне речи: циркон, керамика, радиоактивност, гама спектрометрија