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Radiation exposure to zircon minerals in Serbian ceramic industries

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Abstract

This paper presents the results of gamma spectrometric measurements of radioactivity levels for 41 zircon minerals samples used in the Serbian ceramic industry. The average activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K for all analyzed samples are 2532 ± 117 Bq kg^{-1}, 360 ± 16 Bq kg^{-1}, and 183 ± 12 Bq kg^{-1}, respectively. Radium equivalent activity index (Ra$_{eq}$), gamma and alpha indices (I_γ, I_α), excess lifetime cancer risk, alpha dose equivalent (H_α), and radon mass exhalation rate (E_M) are determined. Annual effective doses for workers in the ceramic industry are estimated assuming exposure to radiation for 800 h per year, and the average value is found to be 1.53 ± 0.07 mSv y^{-1}.

Keywords Gamma spectrometry · Zircon minerals · Ceramic industry · Radiation risk · Annual effective dose

Introduction

All construction materials of natural origin may contain certain concentrations of radionuclides from the series of ^{238}U and ^{232}Th as well as the primordial radionuclide ^{40}K, and such materials are classified into the Naturally Occurring Radioactive Materials (NORM) group [1–6]. Since these radionuclides are not evenly distributed in materials, knowledge of their activity concentrations is very important for assessing the impact on human health and radiation protection [7, 8]. The greatest contribution to the exposure of workers and public to the radiation from building materials has activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K whose average values for building materials in the world are 50 Bq kg^{-1}, 50 Bq kg^{-1} and 500 Bq kg^{-1}, respectively [9]. The increased content of these radionuclides can affect the exposure of workers to radiation when working with such materials (for example, in the ceramic industry), therefore it is very important to carry out tests on the level of exposure to the radiation [5]. The objective of assessing the level of exposure when working with building materials is based on the estimation of the annual effective radiation dose using the appropriate dose criterions. According to the recommendations of the European Commission in 1999 [10], dose optimization should be in the range between 0.3 mSv y^{-1} and 1 mSv y^{-1}, whereas according to the European Union Directive from 2014, this limit for public is set at 1 mSv y^{-1} while for workers is 20 mSv y^{-1} [11].

The typical annual effective dose for workers exposed to zircon minerals is 70–260 μSv y^{-1} from external exposure and 600–3000 μSv y^{-1} from inhalation of dust, giving an overall annual effective dose of 700–3100 μSv y^{-1} [12].

Serbia is one of the leading countries in southeastern Europe in the production of ceramic tiles for floors and walls with a tradition in process of production for over 50 years. Huge quantities of raw materials are imported every year for the production of ceramic tiles, and some of them are zircons (zircon minerals).

According to its composition, zircon minerals are in the form of zirconium silicate ($ZrSiO_4$), or zircon sand. For zircon crystals, various impurities can be related, as some radionuclides from the ^{238}U and ^{232}Th series, and may have an increased level of radioactivity [7, 13, 14]. Based on the measured values of the activity concentrations of ^{226}Ra in the earlier research of raw materials used in the ceramic industry, it can be concluded that the zircon is one of the most radioactive raw materials [4, 13, 15, 16]. The activity concentration of ^{226}Ra measured in some samples of zircon from North Korea reaches values up to 11,000 Bq kg^{-1} [2].

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The zircon is used in the ceramic industry in bulk, and the increased activity concentration of ^{226}Ra in zircon samples can have a significant risk of exposure to gamma radiation as well as radon (^{222}Rn) radioactive gas inhalation and its progenies [17]. In the Directive of 2014, the European Union passed the permitted limit to exposure to radon at a workplace of about 300 Bq m^{-3} [11], as recommended by the World Health Organization in the 2009 report [18].

Before use in the ceramic industry, zircon goes through the grinding process where fine particles of size ≤ 50 µm (zircon flour) are formed [13, 14]. Inhalation or ingestion of fine aerosol particles in the air, when using zircon minerals with an increased content of ^{226}Ra, poses a risk to the internal exposure of the organism (respiratory organs) to ionizing radiation, which can lead to lung cancer [12, 17, 19, 20]. Proper hygiene management in the industry is enough to minimize the impact of radiation generated by zircon flour [19].

This paper presents gamma spectrometric measurements of activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K for 41 samples of zircon mineral used in the Serbian ceramic industry. On the basis of the measured values of these radionuclides, the assessment of the radiation risk in working with these materials in terms of hazard index [radium equivalent activity index (Ra$_{eq}$), gamma index (I_γ), alpha index (I_α), annual effective dose (E), excessive lifetime cancer risk (ELCR), alpha dose equivalent (H_α) and radon mass exhalation rate (E_M)]. The obtained values are compared with the permitted values given in national and international directives, as well with the measured values for zircon minerals and other raw materials used in ceramic industries in the world.

Materials and methods

Samples of zircon minerals were collected when they were imported into the Republic of Serbia while performing a dosimetric inspection at border crossings with Croatia, Batrovci and Sid, in the period September 2018–April 2019. The gamma spectrometric measurements of all samples were carried out at the Department of Physics at the Faculty of Sciences, University of Novi Sad, Serbia. Before gamma spectrometric measurements, all samples were dried at a temperature of 105 °C for about 8 h and afterward ground (some of the samples were already in the powdery state—zircon flour) and packed in a plastic cylinder container with a diameter of 67 mm and height of 62 mm. Analysis of the radionuclides in the samples was carried out 40 days after the preparation of the samples since a secular radioactive equilibrium was established between ^{226}Ra and ^{222}Rn [21]. The mass of the prepared samples was about 400 g.

The gamma spectrometric analysis of samples was performed according to the IAEA TRS 259 standard method [22] using a low-background HPGe gamma spectrometer manufactured by Canberra, with a relative efficiency of about 36% and a resolution of 1.9 keV. The gamma spectrometry system has lead protection thickness of 12 cm and an additional 3 mm-thick copper shield, to prevent penetration of lead K-shell X-rays in the energy range of (75–85) keV.

The measurement time of the individual sample was approximately 72,000 s. The activity concentration of ^{226}Ra was estimated from gamma lines of its decay products: ^{214}Pb at 295.2 keV and 351.9 keV, and ^{214}Bi at 609.3 keV, and 1120.3 keV. The gamma lines emitted from ^{228}Ac at 338.3 and 969.0 keV, from ^{212}Pb at 238.6 keV and the gamma line of ^{208}Tl at 2614.5 keV were used to determine the activity concentration of ^{232}Th. The activity concentration of ^{40}K was determined using gamma line emitted by this radioisotope at 1460.8 keV [21, 23].

The calibration of the detector was carried out using a reference radioactive standard embedded in a silicone resin of cylindrical geometry, a volume of 250 cm^3 of the Czech Metrology Institute (Cert. No. 1035-SE-40001-17). By using the ANGLE software, correction to the effect of self-absorption was made due to the different density of the matrix of the analyzed material. This precise calibration is performed to ensure a small measurement uncertainty below 10% necessary when the activity of radioisotopes is determined in the low-energy region (below 100 keV) (e.g. for ^{234}Th, a progeny of ^{238}U) [21].

Assessment of radiation risk for workers

Radium equivalent activity index (Ra$_{eq}$)

Radium equivalent activity index (Ra$_{eq}$) was used to evaluate radiation hazard to the persons working with building materials (occupationally exposed individuals). Radium equivalent activity index was introduced due to the fact that the distribution of ^{226}Ra, ^{232}Th and ^{40}K in building materials is not uniform. Radium equivalent activity index was introduced with the assumption that 370 Bq kg^{-1} of ^{226}Ra, 259 Bq kg^{-1} of ^{232}Th, and 4810 Bq kg^{-1} of ^{40}K produce the same dose of gamma radiation and can be calculated using the Eq. (1) [24]:

$$\mathrm{Ra}_{\mathrm{eq}}\left(\mathrm{Bq\ kg}^{-1}\right) = C_{\mathrm{Ra}} + 1.43C_{\mathrm{Th}} + 0.077C_{\mathrm{K}} \tag{1}$$

where C_{Ra}, C_{Th}, and C_{K} are activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in Bq kg^{-1} for the given building material, respectively. Radiologically safe radiation exposure is limited to the annual effective radiation dose of 1.5 mSv y^{-1}, while the value of radium equivalent activity index must not exceed the limit of 370 Bq kg^{-1} [25, 26].

Gamma index (I_γ)

To evaluate exposure to the gamma radiation, a gamma index (I_γ) has been introduced. In this paper, the gamma index is calculated based on the Eq. (2), proposed by the European Commission in 1999 [10]:

$$I_\gamma = \frac{C_{\mathrm{Ra}}}{300\,\mathrm{Bq\,kg^{-1}}} + \frac{C_{\mathrm{Th}}}{200\,\mathrm{Bq\,kg^{-1}}} + \frac{C_{\mathrm{K}}}{3000\,\mathrm{Bq\,kg^{-1}}} \leq 1 \tag{2}$$

where C_{Ra}, C_{Th}, and C_{K} are activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in Bq kg^{-1} for the given building material, respectively. In the 2014 directive, the European Union introduced a gamma index for screening building materials where the values of the gamma index $I_\gamma \leq 1$ correspond to the annual effective dose of less than 1 mSv y^{-1} [11], which is also the recommended value by the United Nations Scientific Committee on the Effects of Atomic Radiation [26].

Alpha index (I_α)

An alpha index (I_α), which can be calculated using the Eq. (3), was introduced to estimate the exposure to excess alpha radiation generated by the building material [1, 27]:

$$I_\alpha = \frac{C_{\mathrm{Ra}}}{200\,\mathrm{Bq\,kg^{-1}}} \leq 1 \tag{3}$$

where C_{Ra} is the activity concentration of ^{226}Ra in Bq kg^{-1} for the given building material. The recommended alpha index value is $I_\alpha \leq 1$, which corresponds to the activity concentration of ^{226}Ra $C_{\mathrm{Ra}} \leq 200$ Bq kg^{-1}. The activity concentration of ^{226}Ra greater than 200 Bq kg^{-1} may give a radon concentration greater than 200 Bq m^{-3}, which represents a significant exposure to alpha radiation [27].

Absorbed dose rate (D)

The absorbed dose rate (D) due to the emission of gamma radiation from natural radionuclides present in building materials (gypsum, limestone, zircon minerals, cement, and bricks) can be estimated according to the Eq. (4) [10, 27]:

$$D\left(\mathrm{nGyh^{-1}}\right) = 0.92 \cdot C_{\mathrm{Ra}} + 1.1 \cdot C_{\mathrm{Th}} + 0.080 \cdot C_{\mathrm{K}} \tag{4}$$

where C_{Ra}, C_{Th}, and C_{K} are activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in Bq kg^{-1} for the given building material, respectively. Values 0.92, 1.1 and 0.080 in the Eq. (4) represent a specific dose rate in nGy per Bq kg^{-1} [10]. The average absorbed dose rate for building materials in the world is 55 nGy h^{-1} [28].

Annual effective dose (E)

In order to assess the exposure of workers in the ceramic industry, it is useful to know the annual effective dose derived from gamma radiation from natural radionuclides and can be calculated using the Eq. (5) [10]:

$$E\left(\mathrm{mSv\,y^{-1}}\right) = D \times 800\,\mathrm{h} \times 0.7\,\mathrm{SvG\,y^{-1}} \tag{5}$$

where D is the absorbed dose rates given in mGy h^{-1}; 800 h is the annual exposure time when working with zircon minerals in the ceramic industry [5]; 0.7 Sv Gy^{-1} is the conversion factor of the dose [10]. According to the law in Serbia, the annual effective dose of 20 mSv y^{-1} is allowed for workers [29]. This policy is in line with the EU directive from 2014 [11]. The average annual effective dose from building materials in the world is 0.460 mSv y^{-1} [26].

Excess lifetime cancer risk (ELCR)

The excessive lifetime cancer risk (ELCR) can be estimated based on the obtained annual effective dose using the Eq. (6):

$$\mathrm{ELCR} = E \times \mathrm{DL} \times \mathrm{RF} \tag{6}$$

where E is the annual effective dose, DL is the average life span (70 years) and RF is a risk factor (Sv^{-1}), fatal cancer risk per Sievert. In case of stochastic effects, the usual assumption is $RF = 0.05$ [30]. The average value of excess lifetime cancer risk in world (ELCR) is 0.3×10^{-3} [26].

Alpha dose equivalent (H_α)

In a European Commission report of 1990, the use of dose criteria is recommended for a radon concentration of 1 Bq m^{-3} corresponding to an annual effective dose of 0.05 mSv y^{-1} [31]. According to this criterion, the concentration range ^{222}Rn of 100–300 Bq m^{-3} [18] corresponds to the effective dose range of 5–15 mSv y^{-1}. The alpha dose level from ^{222}Rn and its decay products from the building material can be calculated using the Eq. (7) [32]:

$$H_\alpha = 0.18 \times \varepsilon \times C_{\mathrm{Ra}} + 0.45 \tag{7}$$

where H_α is alpha dose equivalent in mSv y^{-1}; ε is the coefficient of emanation ^{222}Rn from given building material and C_{Ra} is measured activity concentration of ^{226}Ra in Bq kg^{-1}.

Radon mass exhalation rate (E_{M})

Inside of grains of building material, the ^{222}Rn is produced by the decay of ^{226}Ra, afterward, it emanates from grains into the pores of the material. The final process is exhalation

Table 1 List of samples, country of origin and activity concentration of ^{226}Ra, ^{232}Th and ^{40}K for 41 zircon mineral samples used in Serbian ceramic industry

No. sample	Sample name	Country of origin	Activity concentration (Bq kg^{-1})		
			^{226}Ra	^{232}Th	^{40}K
1	Zircon	Czech Republic	2150 ± 140	368 ± 20	182 ± 15
2	Zircosil 300 M	EU	3200 ± 40	410 ± 20	268 ± 22
3	Zircon ore	France	2350 ± 140	230 ± 20	170 ± 17
4	Zircon sand	France	2000 ± 150	290 ± 30	130 ± 11
5	Zircon sand	France	3930 ± 210	440 ± 40	230 ± 20
6	Zircon fluor	Germany	1550 ± 60	297 ± 11	130 ± 10
7	Zircon	Germany	2020 ± 80	430 ± 22	150 ± 14
8	Zircobit	Italy	1570 ± 40	316 ± 9	52 ± 6
9	Zircobit	Italy	2890 ± 80	350 ± 20	170 ± 10
10	Zircobit Fu	Italy	2350 ± 70	532 ± 20	260 ± 22
11	Zircobit Fu 50	Italy	2760 ± 130	330 ± 26	188 ± 15
12	Zircobit	Italy	2670 ± 110	409 ± 17	200 ± 18
13	Zircosil 300 M	Italy	3600 ± 300	560 ± 40	190 ± 12
14	Zirconium silicate	Italy	3540 ± 100	570 ± 40	205 ± 10
15	Zircosil Five	Italy	1930 ± 50	276 ± 15	42 ± 5
16	Zircon	Italy	2250 ± 130	306 ± 20	150 ± 14
17	Zircosil	Italy	2160 ± 40	404 ± 18	450 ± 30
18	Zircobit	Italy	2860 ± 190	310 ± 20	200 ± 17
19	Zircobit Fu	Italy	3220 ± 50	470 ± 30	240 ± 22
20	Zircobit Mo/S	Italy	2450 ± 100	248 ± 21	180 ± 14
21	Zircobit Fu	Italy	2350 ± 40	445 ± 13	200 ± 12
22	Zircosil 300 M	Italy	2950 ± 70	350 ± 30	230 ± 22
23	Zeta zircon flour 325 Mesh	Netherlands	2840 ± 70	395 ± 15	50 ± 4
24	Zeta zircon flour 325 Mesh	Netherlands	3210 ± 230	459 ± 21	200 ± 15
25	Zircon fluor	Netherlands	2030 ± 25	260 ± 10	100 ± 11
26	Zircon fluor	Netherlands	2120 ± 40	264 ± 14	155 ± 12
27	Termocoat zircon	Slovenia	404 ± 24	71 ± 7	82 ± 6
28	Termocoat At—Zirkobit	Slovenia	1090 ± 24	202 ± 15	113 ± 17
29	White Zirconium—Moka 200 m	Slovenia	2500 ± 40	447 ± 25	240 ± 20
30	Zircobit	Slovenia	1410 ± 70	193 ± 10	106 ± 8
31	Zircosil Five	Spain	1980 ± 50	294 ± 24	160 ± 15
32	Zircosil 300 M	Spain	3040 ± 260	431 ± 22	195 ± 18
33	Zircosil	Spain	2540 ± 50	384 ± 15	240 ± 25
34	Zircosil	Spain	2370 ± 70	342 ± 19	190 ± 17
35	Zirconium silicate	Spain	4120 ± 40	367 ± 22	240 ± 26
36	Zircon flour	Spain	2930 ± 70	520 ± 40	210 ± 22
37	Zircon flour	Spain	3240 ± 120	350 ± 30	160 ± 16
38	Zirconium silicate	Spain	2980 ± 40	450 ± 30	356 ± 32
39	Zircon calcine premium	United Kingdom	2930 ± 170	377 ± 25	160 ± 12
40	Zircon prime flour	United Kingdom	3210 ± 150	423 ± 23	225 ± 18
41	Zircon flour	USA	2100 ± 40	255 ± 10	110 ± 10
Minimum			404 ± 24	71 ± 7	42 ± 5
Maximum			4120 ± 40	560 ± 40	356 ± 32
Mean ± standard deviation			2532 ± 117	360 ± 16	183 ± 12
Mean value in the world			50[a]	50[a]	500[a]

[a] Given in Ref. [9]

Table 2 Comparison of activity concentration of ^{226}Ra, ^{232}Th and ^{40}K in zircon samples measured in the world and in this paper

Country	Sample type	Activity concentration (Bq kg^{-1})			Number of samples	References
		^{226}Ra	^{232}Th	^{40}K		
Belgium	Zircon	3100 ± 150	570 ± 35	77 ± 9	10	[19]
Czech Republic	Zircon	19–4700 (3053 ± 255)	5.1–650 (405 ± 34)	70–490 (186 ± 20)	20	[16]
Egypt	Zircon ore	3341–3817 (3588 ± 125)	884–1063 (982 ± 47.7)	167–353 (217 ± 48.5)	30	[7]
Egypt	Zircon sand	4720–5110 (4910 ± 160)	1120–1250 (1195 ± 48)	170–210 (190 ± 25)	10	[3]
Germany	Zircon mineral	2210	470	74	60	[19]
India	Zircon	1324–1874 (1593)	197–347 (273)	64–195 (119)	4	[36]
Italy	Zircon sand and flour	2300–2800	450–540	26–33	10	[13]
Italy	Zircon	1690–6900 (3381 ± 209)	180–1050 (483 ± 40)	25–700 (204 ± 20)	124	[16]
South Africa	Zircon	(4400 ± 210)	(610 ± 35)	(60 ± 8)	60	[19]
South Korea	Zircon	2260–11,000 (4700 ± 4200)	402–1970 (921 ± 708)	< 17.7–306 (115 ± 133)	4	[2]
Spain	Zircon sand and flour	2681–3615	592–714	< 69–< 110	5	[14]
Spain	Zircon	1570–4920 (3161 ± 229)	145–770 (388 ± 27)	30–280 (173 ± 21)	42	[16]
Spain	Zircon	49–4130 (2168 ± 1961)	8.8–676 (390 ± 300)	–	5	[35]
Turkey	Zircon	1667–231 (1973 ± 187)	257–417 (354 ± 49)	57–270 (132 ± 69)	3	[4]
Serbia	Zircon minerals	404–4120 (2532 ± 117)	71–560 (360 ± 16)	42–356 (183 ± 12)	41	Present study

–, range; (mean ± standard deviation)

Table 3 Comparison of activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K for other raw materials in the ceramic industry in the world with values for zircon minerals in this paper

Country	Raw material	Activity concentration (Bq kg^{-1})			Number of samples	References
		^{226}Ra	^{232}Th	^{40}K		
China	Sand	11.6–38.2 (21.5 ± 8.3)	16.3–52.3 (32.7 ± 9.0)	609–949 (764 ± 105)	–	[8]
India	Quartz	6.7–38.3 (24.1)	9.4–43.7 (28.4)	50.3–302.4 (189.1)	9	[36]
South Korea	Feldspar	10.2–199 (47.6 ± 56.4)	6.25–111 (54.2 ± 38.9)	983–1860 (1320 ± 250)	10	[2]
South Korea	Silica sand	5.43–11.5 (7.52 ± 2.19)	10.4–18.5 (13.8 ± 2.5)	0.066.9–1030 (531 ± 374)	10	[2]
Turkey	Kaolin	17.5–130.5 (80.3 ± 9.8)	23.4–180.8 (89.2 ± 11.1)	17.1–1948.7 (494.8 ± 152.1)	17	[4]
Turkey	Dolomite	4.8–15.0 (10.2 ± 2.5)	2.0–4.7 (3.3 ± 0.6)	27.0–78.9 (51.4 ± 11.4)	4	[4]
Serbia	Zircon minerals	404–4120 (2532 ± 117)	71–560 (360 ± 16)	42–356 (183 ± 12)	41	Present study

–, range; (mean ± standard deviation)

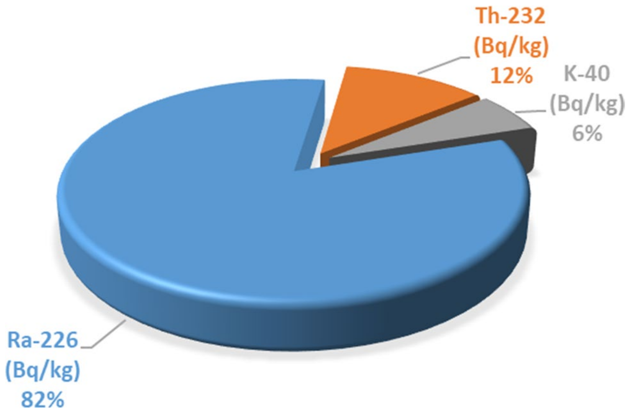

Fig. 1 Relative contribution of ^{226}Ra, ^{232}Th, and ^{40}K in 41 zircon mineral samples used in Serbian ceramic industry

of ^{222}Rn from the pores of the material to the surrounding air. Radon mass exhalation rate (E_M) can be calculated using the Eq. (8):

$$E_M = \lambda_{Rn} \times C_{Ra} \times \varepsilon \tag{8}$$

where λ_{Rn} is the radioactive decay constant of ^{222}Rn (2.1×10^{-6} s^{-1}); C_{Ra} is the activity concentration of ^{226}Ra in the sample measured after the establishment of a secular radioactive equilibrium of 1 month; ε is the coefficient of radon emanation from given building material. The radon mass exhalation rate (E_M) is given in units of Bq kg^{-1} s^{-1} [33, 34].

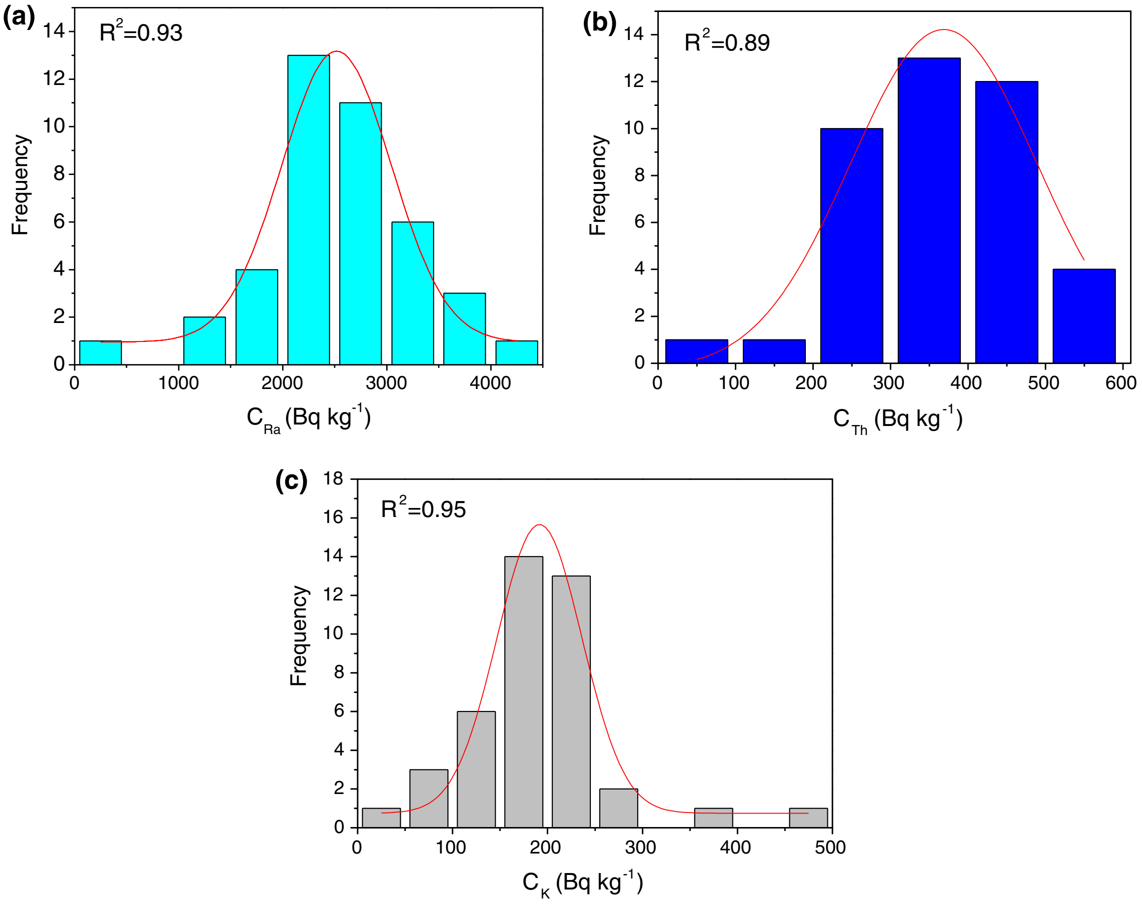

Fig. 2 Frequency distributions of **a** ^{226}Ra (Bq kg^{-1}), **b** ^{232}Th (Bq kg^{-1}) and **c** ^{40}K (Bq kg^{-1}) activity concentrations in zircon mineral samples from Table 1

Results and discussion

A list of analyzed samples of zircon minerals with countries of origin used in the Serbian ceramic industry with measured values of activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K are given in Table 1. The measured values of the activity concentration of ^{226}Ra range from 404 ± 24 Bq kg^{-1} (sample No. 27 from Slovenia) to 4120 ± 40 Bq kg^{-1} (sample No. 35 from Spain) and the average value for all 41 zircon samples is 2532 ± 117 Bq kg^{-1} (mean value ± standard deviation). The measured values of the activity concentration of ^{232}Th are in the range from 71 ± 7 Bq kg^{-1} (sample No. 27 from Slovenia) to 560 ± 40 Bq kg^{-1} (sample No. 13 from Italy) and the average value for all 41 samples of zircon samples is 360 ± 16 Bq kg^{-1}. Measured values of ^{40}K range from 42 ± 5 Bq kg^{-1} (sample No. 15 from Italy) to 356 ± 32 Bq kg^{-1} (sample No. 38 from Spain) and the average value for all 41 samples of zircon samples is 183 ± 12 Bq kg^{-1}. The measured values of ^{226}Ra and ^{232}Th for all samples are above average values for building materials in the world of 50 Bq kg^{-1}, while activity concentrations of ^{40}K are below the average value of 500 Bq kg^{-1} [9]. The measured activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K are comparable with the results reported for zircon mineral samples from Belgium, Czech Republic, Germany, Italy and Spain [4, 14, 16, 19, 35], given in Table 2. Compared to the activity concentration of ^{226}Ra, ^{232}Th and ^{40}K for other raw materials used in the ceramic industry (kaolin, quartz, feldspar, dolomite, and stone), the zircon minerals analyzed in this paper have a significantly higher level of these radionuclides, primarily ^{226}Ra and ^{232}Th (see Table 3).

The relative contribution of ^{226}Ra, ^{232}Th, and ^{40}K in 41 zircon mineral samples is 82%, 12%, and 6%, respectively (see Fig. 1).

Distribution of activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in samples of zircon minerals is presented in Fig. 2. It can be noticed that the distribution of activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K are in good agreement with Gaussian distribution, as indicated by high correlation factors (R^2): 0.93, 0.89 and 0.95, respectively.

In Fig. 3 correlations between activity concentrations of ^{232}Th and ^{226}Ra were observed with correlation factor (R^2)

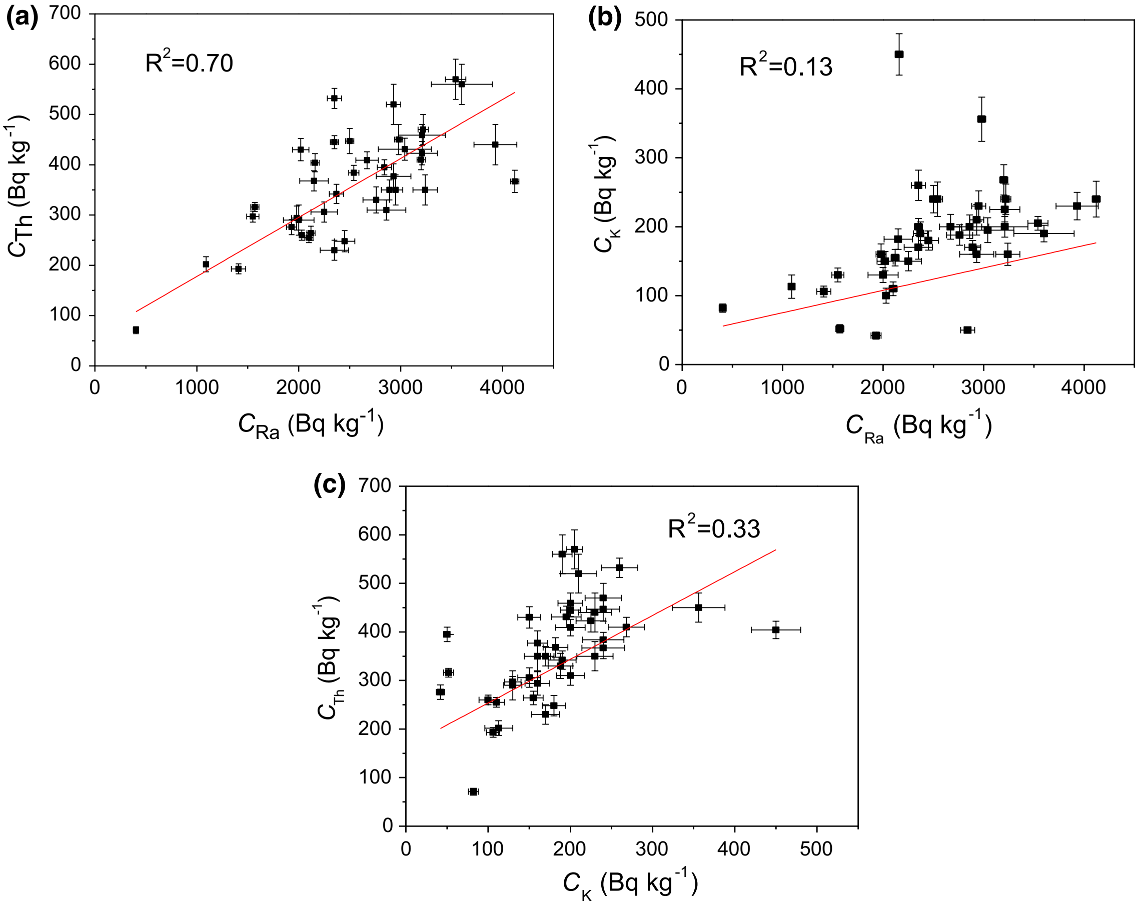

Fig. 3 Correlation between ^{232}Th and ^{226}Ra, ^{40}K and ^{226}Ra, ^{232}Th and ^{40}K activity concentration of 41 zircon samples from Table 1

of 0.70, while correlations between activity concentration of ^{40}K and ^{226}Ra and ^{232}Th and ^{40}K are not remarkable, based on the obtained correlation factors (R^2) of 0.13 and 0.33, respectively.

The obtained values of radium equivalent activity indices (Ra$_{eq}$), gamma indices (I_γ), alpha indices (I_α) and radon mass exhalation rate (E_M) are given in Table 4.

The radium equivalent activity index (Ra$_{eq}$) ranges from 512 ± 26 Bq kg^{-1} (sample No. 27 from Slovenia) to 4663 ± 51 Bq kg^{-1} (sample No. 35 from Spain). The average value of radium equivalent activity index for all 41 samples of zircon minerals is 3062 ± 135 Bq kg^{-1} (mean value ± standard deviation). The values obtained for all samples are above the recommended value of 370 Bq kg^{-1} [26].

Figure 4 shows a strong correlation between activity concentration of ^{226}Ra and Ra$_{eq}$ with a correlation factor (R^2) of 0.99, while weaker correlations were observed between Ra$_{eq}$–^{232}Th and Ra$_{eq}$–^{40}K with correlation factors (R^2) of 0.77 and 0.35, respectively.

Gamma index values (I_γ) range from 1.73 ± 0.09 (sample No. 27 from Slovenia) to 15.7 ± 0.2 (sample No. 35 from Spain). The average gamma index for all samples is 10.3 ± 0.5 (mean value ± standard deviation). Gamma index values for all samples are above the recommended value of $I_\gamma \leq 1$ [26]. The obtained values of the gamma index in this paper are comparable with the values reported in papers [16, 35].

Alpha index (I_α) range from 2.02 ± 0.12 (sample No. 27 from Slovenia) to 20.6 ± 0.2 (sample No. 35 from Spain). The average alpha index for all samples is 12.7 ± 0.56 (mean value ± standard deviation). For all samples, the alpha index is higher than the recommended value of $I_\alpha \leq 1$ [27].

Calculated values of absorbed dose rates (D), annual effective doses (E), excess lifetime cancer risks (ELCR) and alpha dose equivalents (H_α) are given in Fig. 5.

The obtained absorbed dose rates (D) range from 450 ± 30 nGy h^{-1} (sample No. 27 from Slovenia) to 4200 ± 60 nGy h^{-1} (sample No. 35 from Spain). The average value of absorbed dose rate for all samples of zircon minerals is 2730 ± 120 nGy h^{-1} (mean value ± standard deviation). The values obtained for all 41 samples of zircon minerals are above average values of 55 nGy h^{-1} for building materials worldwide [28].

Table 4 Radium equivalent activity index (Ra_{eq}), gamma index (I_γ), alpha index (I_α) and radon mass exhalation rate (E_M) for 41 zircon mineral samples used in Serbian ceramic industry

No. sample	Ra_{eq} (Bq kg^{-1})	I_γ	I_α	E_M (µBq kg^{-1} s^{-1})
1	2690 ± 143	9.1 ± 0.5	10.8 ± 0.7	13.5 ± 0.9
2	3800 ± 50	12.8 ± 0.2	16.0 ± 0.2	20.2 ± 0.3
3	2692 ± 143	9.0 ± 0.5	11.8 ± 0.7	14.8 ± 0.9
4	2424 ± 156	8.2 ± 0.5	10 ± 1	12.6 ± 0.9
5	4576 ± 218	15.4 ± 0.7	20 ± 1	24.8 ± 1.3
6	1984 ± 62	6.7 ± 0.2	7.8 ± 0.3	9.8 ± 0.4
7	2646 ± 86	8.9 ± 0.3	10.1 ± 0.4	12.7 ± 0.5
8	2025 ± 42	6.8 ± 0.2	7.9 ± 0.2	9.9 ± 0.3
9	3403 ± 85	11.4 ± 0.3	14.5 ± 0.4	18.2 ± 0.5
10	3130 ± 76	10.6 ± 0.3	11.8 ± 0.4	14.8 ± 0.4
11	3246 ± 135	10.9 ± 0.5	13.8 ± 0.7	17.4 ± 0.8
12	3270 ± 113	11.0 ± 0.4	13.4 ± 0.6	16.8 ± 0.7
13	4415 ± 305	15 ± 1	18 ± 2	23 ± 2
14	4370 ± 115	14.7 ± 0.4	17.7 ± 0.5	22.3 ± 0.6
15	2328 ± 54	7.8 ± 0.2	9.7 ± 0.3	12.2 ± 0.3
16	2699 ± 133	9.1 ± 0.5	11.3 ± 0.7	14.2 ± 0.8
17	2770 ± 50	9.4 ± 0.2	10.8 ± 0.2	13.6 ± 0.3
18	3320 ± 190	11.2 ± 0.6	14 ± 1	18.0 ± 1.2
19	3910 ± 66	13.2 ± 0.2	16.1 ± 0.3	20.3 ± 0.3
20	2820 ± 100	9.5 ± 0.4	12.3 ± 0.5	15.4 ± 0.6
21	3001 ± 44	10.1 ± 0.2	11.8 ± 0.2	14.8 ± 0.3
22	3468 ± 82	11.7 ± 0.3	14.8 ± 0.4	18.6 ± 0.4
23	3408 ± 73	11.5 ± 0.3	14.2 ± 0.4	17.9 ± 0.4
24	3881 ± 232	13.1 ± 0.8	16 ± 1	20.2 ± 1.4
25	2409 ± 30	8.1 ± 0.1	10.15 ± 0.13	12.8 ± 0.2
26	2509 ± 45	8.44 ± 0.15	10.6 ± 0.2	13.4 ± 0.3
27	512 ± 26	1.73 ± 0.09	2.02 ± 0.12	2.5 ± 0.2
28	1387 ± 32	4.68 ± 0.11	5.45 ± 0.12	6.9 ± 0.2
29	3157 ± 54	10.7 ± 0.2	12.5 ± 0.2	15.8 ± 0.3
30	1700 ± 70	5.7 ± 0.3	7.1 ± 0.4	8.9 ± 0.4
31	2410 ± 60	8.1 ± 0.2	9.9 ± 0.3	12.5 ± 0.3
32	3671 ± 262	12.4 ± 0.9	15 ± 1	19.2 ± 1.6
33	3107 ± 54	10.5 ± 0.2	12.7 ± 0.3	16.0 ± 0.3
34	2873 ± 75	9.7 ± 0.3	11.9 ± 0.4	14.9 ± 0.4
35	4663 ± 51	15.7 ± 0.2	20.6 ± 0.2	26.0 ± 0.3
36	3689 ± 90	12.4 ± 0.3	14.7 ± 0.4	18.5 ± 0.4
37	3752 ± 127	12.6 ± 0.4	16.2 ± 0.6	20.4 ± 0.8
38	3650 ± 59	12.3 ± 0.2	14.9 ± 0.2	18.8 ± 0.3
39	3481 ± 174	11.7 ± 0.6	14.7 ± 0.9	18.5 ± 1.1
40	3832 ± 154	12.9 ± 0.5	16.1 ± 0.8	20.2 ± 0.9
41	2473 ± 42	8.31 ± 0.14	10.5 ± 0.2	13.2 ± 0.3
Minimum	512 ± 26	1.73 ± 0.09	2.02 ± 0.12	2.5 ± 0.2
Maximum	4663 ± 51	15.7 ± 0.2	20.6 ± 0.2	26.0 ± 0.3
Mean ± SD	3062 ± 135	10.3 ± 0.5	12.7 ± 0.6	16.0 ± 0.7
Recommended value	≤ 370[a]	≤ 1[a]	≤ 1[b]	–

SD standard deviation

[a] Recommended value given in Ref. [26]

[b] Recommended values given in Ref. [27]

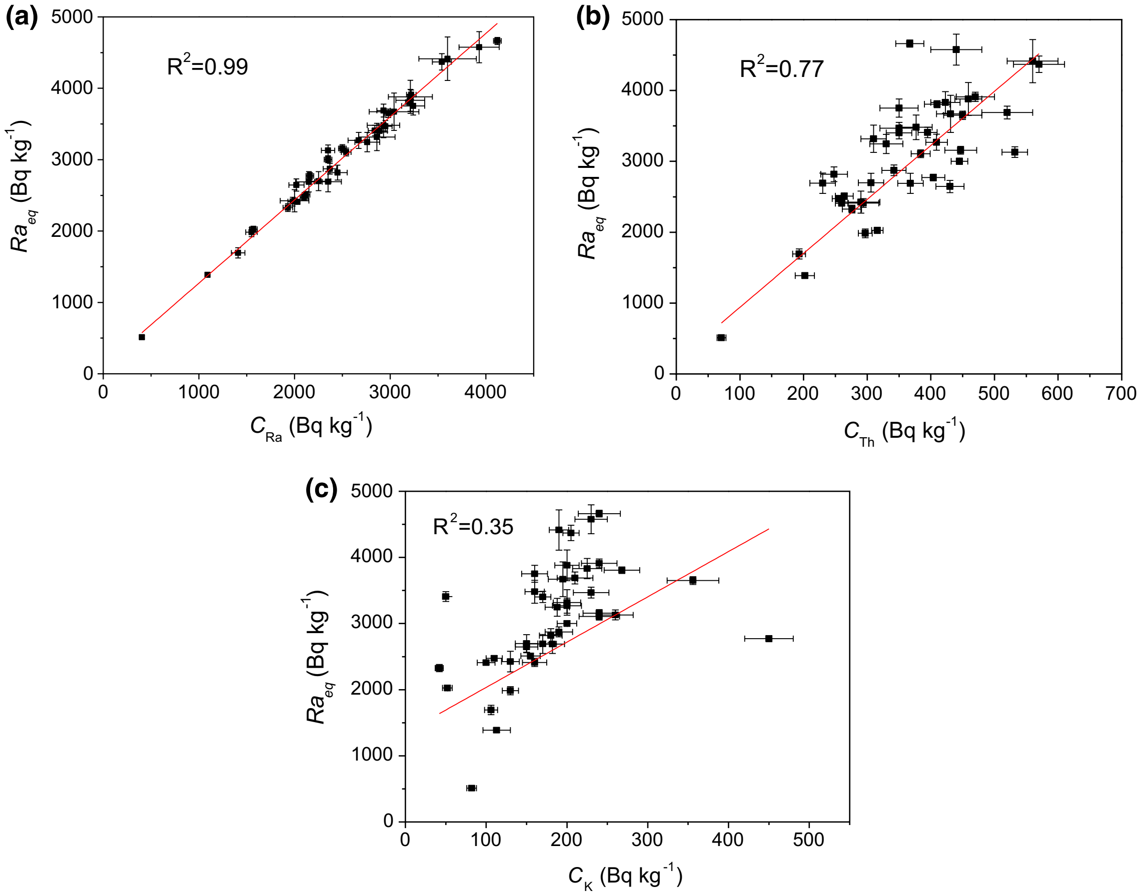

Fig. 4 Correlation between activity concentration of ^{226}Ra, ^{232}Th, ^{40}K, and Ra_{eq} for 41 zircon mineral samples from Table 1

The obtained annual effective dose (E), calculated base on the assumption that the worker in the ceramics industry spends 800 h in a year in the work with zircon minerals, ranges from 0.252 ± 0.015 mSv y^{-1} (sample No. 27 from Slovenia) to 2.35 ± 0.015 mSv y^{-1} (sample No. 35 from Spain). The average annual effective dose for all 41 samples is 1.53 ± 0.07 mSv y^{-1} (mean value ± standard deviation). All annual effective dose values are below 20 mSv y^{-1} as defined by Directive for professional exposure radiation in the Republic of Serbia and the European Union [11, 29]. All obtained values of annual effective doses exceed the average value of 0.460 mSv y^{-1} for building materials in the world [26].

Calculated values of ELCR range from $(0.88 \pm 0.05) \times 10^{-3}$ (sample No. 27 from Slovenia) to $(8.0 \pm 0.4) \times 10^{-3}$ (sample No. 35 from Spain). The average value of ELCR for all 41 samples is $(5.4 \pm 0.3) \times 10^{-3}$ (mean value ± standard deviation). All obtained values exceed the average value in the world for building materials of 0.3×10^{-3} [26].

To estimate the alpha dose equivalent (H_α) value using the Eq. (7), the value of the emanation coefficient (ε) obtained in earlier research was used [37], which is 0.3%. The obtained alpha dose equivalent values range from 0.668 ± 0.013 mSv y^{-1} (sample No. 27 from Slovenia) to 2.67 ± 0.02 mSv y^{-1} (sample No. 35 from Spain), see Fig. 5. The average value of the alpha dose equivalent is 1.67 ± 0.08 mSv y^{-1} (mean value ± standard deviation). The obtained alpha dose equivalent values are less than 5 mSv y^{-1} for all samples, which according to the dose criterion given in [31] and the recommended values of the World Health Organization for exposures of radon in range 100–300 Bq m^{-3} [18], indicate that workers are exposed to a radon concentration of less than 100 Bq m^{-3}. The obtained alpha dose equivalent values are significantly higher than those estimated for cement, gypsum, ceramic, granite, brick, concrete, and other building materials, given in the papers [32, 38].

The obtained values of the radon mass exhalation rate (E_M) for all samples are shown in Table 4 and are in the range from 2.5 ± 0.2 μBq kg^{-1} s^{-1} (sample No. 27 from Slovenia) to 26.0 ± 0.3 μBq kg^{-1} s^{-1} (sample No. 35 from Spain). The average value of the radon mass exhalation rate for all 41 samples of zircon samples is 16.0 ± 0.7 μBq kg^{-1} s^{-1}

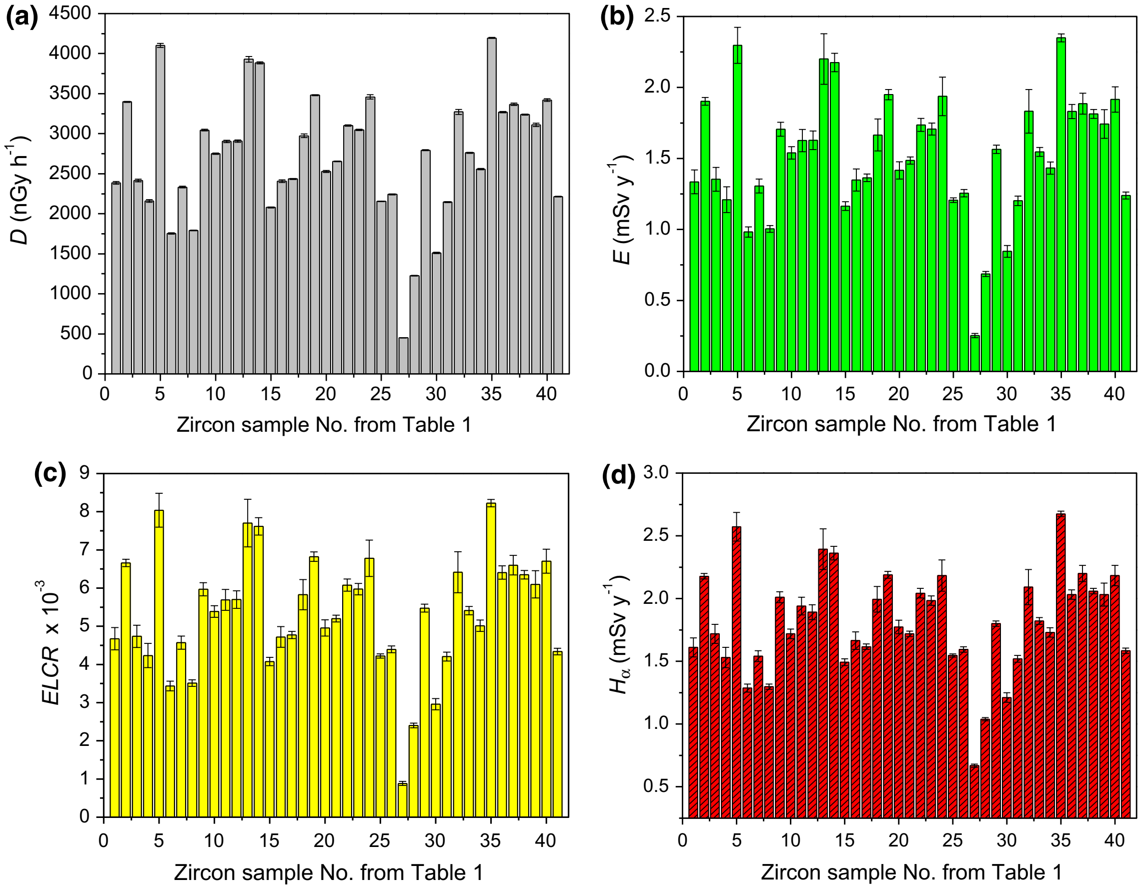

Fig. 5 Absorbed dose rates-*D* (**a**), annual effective doses-*E* (**b**), excess lifetime cancer risks—ELCR (**c**), and alpha dose equivalents-H_α (**d**) for 41 zircon mineral samples used in Serbian ceramic industry

(mean value ± standard deviation). The obtained radon mass exhalation rates are comparable with the values for granites given in the work [34] and for mortar, cement and chalk powder, which were analyzed in the paper [33]. Small values of emanation coefficient and mass exhalation rate can be attributed to the high density of zircon minerals matrix, which is about 4200–4500 kg m^{-3}. The high density of the matrix prevents the exhalation of the radon from the zircon sample compared with other building materials that usually have a lower density.

Conclusion

This paper presents the results of gamma spectrometric measurements for 41 samples of zircon minerals used in the ceramic industry in Serbia. Based on measured values of ^{226}Ra, ^{232}Th and ^{40}K, the radiation risk assessment was carried out when working with these materials in terms of hazard indices, annual effective doses, ELCRs, alpha dose equivalents, and radon mass exhalations. On the basis of the obtained values, it can be concluded that the activity concentration of ^{226}Ra is significantly high, compared to the other raw materials used in the ceramic industry. The obtained hazard indices exceed the recommended values, while the annual effective doses do not exceed the allowed limit of 20 mSv per year, for all samples. Estimated alpha dose equivalent and the radon mass exhalation rate for zircon are comparable with the values for other building materials. From this, it can be concluded that there is no particular danger to the exposure of workers in the ceramic industry to the ionizing radiation originated from zircon minerals.

Implementing a standard precaution while working with zircon minerals such as maintaining personal hygiene after the work are sufficient to reduce the level of radiation risk to an acceptable level.

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References

1. Muntean LE, Cosma C, Moldovan DV (2014) Measurement of natural radioactivity and radiation hazards for some natural and artificial building materials available in Romania. J Radioanal Nucl Chem 299:523–532. https://doi.org/10.1007/s10967-013-2837-8
2. Chang BU, Koh SM, Kim YJ, Seo JS, Yoon YY, Row JW, Lee DM (2008) Nationwide survey on the natural radionuclides in industrial raw minerals in South Korea. J Environ Radioact 99:455–460. https://doi.org/10.1016/j.jenvrad.2007.08.020
3. El Afifi EM, Hilal MA, Khalifa SM, Aly HF (2006) Evaluation of U, Th, K and emanated radon in some NORM and TENORM samples. Radiat Meas 41:627–633. https://doi.org/10.1016/j.radmeas.2005.09.014
4. Turhan S, Arıkan IH, Demirel H, Gungor N (2011) Radiometric analysis of raw materials and end products in the Turkish ceramics industry. Radiat Phys Chem 80:620–625. https://doi.org/10.1016/j.radphyschem.2011.01.007
5. Todorovic N, Mrdja D, Hansman J, Todorovic S, Nikolov J, Krmar M (2017) Radiological impacts assessment for workers in ceramic industry in Serbia. Radiat Prot Dosim 176:411–417. https://doi.org/10.1093/rpd/ncx025
6. Xinwei L (2004) Natural radioactivity in some building materials and by-products of Shaanxi, China. J Radioanal Nucl Chem 262:775–777. https://doi.org/10.1007/s10967-004-0509-4
7. Attallah MF, Hilal MA, Moussa SI (2017) Quantification of some elements of nuclear and industrial interest from zircon mineral using neutron activation analysis and passive gamma-ray spectroscopy. Appl Radiat Isot 128:224–230. https://doi.org/10.1016/j.apradiso.2017.07.018
8. Chao S, Lu X, Zhang M, Pang L (2014) Natural radioactivity level and radiological hazard assessment of commonly used building material in Xining, China. J Radioanal Nucl Chem 300:879–888. https://doi.org/10.1007/s10967-014-3065-6
9. UNSCEAR (1993) Sources, effects and risks of ionizing radiation. United Nations Scientific Committee on the Effects of Atomic Radiation, New York
10. Commission European (1999) Radiation protection 112—radiological protection principles concerning the natural radioactivity of building materials. EC, Luxembourg
11. Council Directive 2013/59/Euratom of 5 Dec. 2013 (2014) Laying down basic safety standards for protection against the dangers arising from exposure to ionising radiation, and repealing directives 89/618/Euratom, 90/641/Euratom, 96/29/Euratom, 97/43/Euratom and 2003/122/Euratom. L13, vol 57. ISSN: 1977-0677. https://ec.europa.eu/energy/sites/ener/files/documents/CELEX-32013L0059-EN-TXT.pdf
12. Schroeyers W (2017) Naturally occurring radioactive materials in construction—integrating radiation protection in reuse (COST Action Tu1301 NORM4BUILDING). Woodhead Publishing, Cambridge. https://doi.org/10.1016/C2016-0-00665-4
13. Righi S, Andretta M, Bruzzi L (2005) Assessment of the radiological impacts of a zircon sand processing plant. J Environ Radioact 82:237–250. https://doi.org/10.1016/j.jenvrad.2005.01.010
14. Ballesteros L, Zarza I, Ortiz J, Serradell V (2008) Occupational exposure to natural radioactivity in a zircon sand milling plant. J Environ Radioact 99:1525–1529. https://doi.org/10.1016/j.jenvrad.2007.12.019
15. Crespo MT, Peyres V, Jose Ortiz M, Gomez-Mancebo MB, Sanchez M (2018) Dissolution and radioactive characterization of resistate zircon sand. J Radioanal Nucl Chem 318:1043–1105. https://doi.org/10.1007/s10967-018-6214-5
16. Todorović N, Bikit I, Krmar M, Mrđa D, Hansman J, Nikolov J, Todorović S, Forkapić S, Jovančević N, Bikit K, Janković Mandić L (2016) Assessment of radiological significance of building materials and residues. Rom J Phys 62(9–10):817
17. International Atomic Energy Agency (2007) Radiation protection and NORM residue management in the zircon and zirconia industries. Safety reports ser. no. 51, Vienna, Austria. https://www.iaea.org/publications/7673/radiation-protection-and-norm-residue-management-in-the-zircon-and-zirconia-industries
18. World Health Organization (2009) In: Zeeb H, Shannoun F (eds) Handbook on indoor radon: a public health perspective. WHO Library Cataloguing-in-Publication Data, World Health Organization, Geneva
19. Fathivand AA, Amidi J (2009) Natural radioactivity concentration in raw materials used for manufacturing refractory products. Radioprotection 44:265–268. https://doi.org/10.1051/radiopro/20095051
20. Todorovic N, Forkapic S, Bikit I, Mrdja D, Veskovic M, Todorovic S (2011) Monitoring for exposures to TENORM sources in Vojvodina region. Radiat Prot Dosim 144:655–658. https://doi.org/10.1093/rpd/ncq414
21. Kuzmanović P, Todorović N, Nikolov J, Hansman J, Vraničar A, Knežević J, Miljević B (2019) Assessment of radiation risk and radon exhalation rate for granite used in the construction industry. J Radioanal Nucl Chem 321:565–577. https://doi.org/10.1007/s10967-019-06592-9
22. International Atomic Energy Agency (1989) Measurement of radionuclides in food and the environment. Technical reports series no. 295, Vienna, Austria
23. Todorovic N, Hansman J, Mrđa D, Nikolov J, Krmar M (2017) Concentrations of ^{226}Ra, ^{232}Th and ^{40}K in industrial kaolinized granite. J Environ Radioact 168:10–14. https://doi.org/10.1016/j.jenvrad.2016.07.032
24. Beretka J, Mathew PJ (1985) Natural radioactivity of Australian building materials, industrial waste sand by-products. Health Phys 48:87–95
25. NEA-OECD (1979) Nuclear Energy Agency. Exposure to radiation from natural radioactivity in building materials. Reported by NEA group of experts. OECD, Paris
26. UNSCEAR (2000) Sources and effects of ionizing radiation. United Nations Scientific Committee on Effects of Atomic Radiation. Exposures from natural radiation sources, Annex B. United Nations Publication, New York
27. Ozdis BE, Cam NF, Canbaz OB (2017) Assessment of natural radioactivity in cements used as building materials in Turkey. J Radioanal Nucl Chem 311:307–316. https://doi.org/10.1007/s10967-016-5074-0
28. UNSCEAR (2008) Sources and effects of ionizing radiation. Report to the general assembly with scientific annexes. United Nations Scientific Committee on the Effects of Atomic Radiation, Annex A and B, United Nations, New York, USA
29. Official Gazette RS 86/2011 and 50/2018 (2018) Rulebook on limits of exposure to ionizing radiation and measurements for assessment of the exposure levels **(in Serbian)**
30. International Commission on Radiological Protection (1990) Recommendations of the international commission on radiological protection. ICRP Publication 60, Pergamon Press, Oxford
31. European Commission (1990) Commission recommendation of February 1990 on the protection of the public against indoor exposure to radon (90/143/Euroatom)

32. Bruzzi L, Mele R, Padoani F (1992) Evaluation of gamma and alpha doses due to natural radioactivity of building materials. J Radiol Prot 12:67–76. https://doi.org/10.1088/0952-4746/12/2/002
33. Chowdhury MI, Alam MN, Ahmed AKS (1998) Concentration of radionuclides in building and ceramic materials of Bangladesh and evaluation of radiation hazard. J Radioanal Nucl Chem 231:117–122. https://doi.org/10.1007/BF02388016
34. Aykamis AS, Turhan S, Aysun Ugur F, Baykan UN, Kilic AM (2013) Natural radioactivity, radon exhalation rates and indoor radon concentration of some granite samples used as construction material in Turkey. Radiat Prot Dosim 157:105–111. https://doi.org/10.1093/rpd/nct110
35. Madruga MJ, Miró C, Reis M, Silva L (2018) Radiation exposure from natural radionuclides in building materials. Radiat Prot Dosim. https://doi.org/10.1093/rpd/ncy256
36. Viruthagiri G, Rajamannan B, Suresh Jawahar K (2013) Radioactivity and associated radiation hazards in ceramic raw materials and end products. Radiat Prot Dosim 157:383–391. https://doi.org/10.1093/rpd/nct149
37. Bikit I, Mrda D, Grujic S, Kozmidis-Luburic U (2011) Granulation effects on the radon emanation rate. Radiat Prot Dosim 145:184–188. https://doi.org/10.1093/rpd/ncr055
38. Hassan NM, Mansour NA, Fayez-Hassan M (2013) Evaluation of radionuclide concentrations and associated radiological hazard indexes in building materials used in Egypt. Radiat Prot Dosim 157:214–220. https://doi.org/10.1093/rpd/nct129