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Radioactivity Measurements of Ceramic Tiles Produced in Serbia

Predrag Kuzmanović[a,b], Sofija Forkapić[a], Igor Čeliković[c], Dušan Mrđa[a], Kristina Bikit[a], Jan Hansman[a], Jovana Knežević Radić[a,]*

a Department of Physics, Faculty of Sciences, University of Novi Sad, Trg Dositeja Obradovića 4, 21000 Novi Sad, Serbia,

b Laboratory for Physics, Department of medical and business-technological studies, Academy of applied studies Šabac, Hajduk Veljkova 10, 15000 Šabac, Serbia

c Vinča Institute of Nuclear Sciences-National Institute of the Republic of Serbia University of Belgrade, PO Box 522, 11000 Belgrade, Serbia

E-mail: predrag.kuzmanovic@df.uns.ac.rs

This paper presents the results of gamma spectrometry measurements of natural radionuclides (^{226}Ra, ^{232}Th, and ^{40}K) in some floor and wall ceramic tiles produced in Serbia and used in homes and workplaces. The level of radioactivity of some ceramic tiles produced in Serbia by two major manufacturers–Zorka Keramika and Toza Markovic was examined. The measured mean value of the activity concentration of ^{226}Ra, ^{232}Th, and ^{40}K exceeds the average values in the world for building materials with values of 67.2±6.9 Bq kg^{-1} for ^{226}Ra, 57.4±4.7 Bq kg^{-1} for ^{232}Th and 808±48 Bq kg^{-1} for ^{40}K. Based on these calculated values, the representative level index gamma index, associated with gamma radiation, whose average value is 0.78±0.06, and annual effective dose, whose average value is 0.117±0.009 mSv y^{-1} for home was obtained. Estimated values fulfill all the recommendations of the European Union for building materials, thus analyzed materials are considered not to be a health hazard for the public.

*Speaker

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1. Introduction

Materials that may contain to some extent naturally occurring radioisotopes ^{226}Ra, ^{232}Th (from uranium and thorium decay chain), and ^{40}K are often referred to as NORM (Naturally Occurring Radioactive Materials) [1, 2]. Using NORM in buildings can present a potential health risk to the population, caused by gamma radiation and indoor radon (^{222}Rn), leading to the necessary monitoring of radioactivity in used building materials [3]. Averaged values of activity concentration of ^{226}Ra, ^{232}Th, and ^{40}K in building materials worldwide are 50 Bq kg^{-1}, 50 Bq kg^{-1}and 500 Bq kg^{-1}, respectively [4]. In this paper, the level of radioactivity of some ceramic tiles produced in Serbia by two major manufacturers was examined. Ceramic tiles in Serbia are mainly used for covering floor and wall surfaces in homes, as well in workplaces.

According to the regulation in the Republic of Serbia allowed level of public exposure originating from building materials, as from other sources, is 1 mSv on an annual level [5]. Regulation in the Republic of Serbia for building materials is consistent with the one in the European Union Directive from 2014 [6].

The main goals of the paper were to measure the level of radioactivity of some ceramic tiles produced in Serbia and estimation of radiological, and apropos health risks caused by the usage of these materials in homes and workplaces.

2. Materials and methods

2.1 Sample preparation

In order to analyze samples by gamma spectrometry method, all the samples were crushed and homogenized in the ball mill (Fig. 1a) for around 45 minutes, after which they were sifted through the sieve granularity of 1.6 mm (Fig. 1b) and packed into plastic containers dimension diameter 67 mm and height 62 mm (Fig. 1c). Samples were taped with teflon tape to prevent diffusion of radon from the containers (Fig. 1d). Measurements started one month after sampling, after reaching the secular radioactive equilibrium between ^{222}Rn and ^{226}Ra. The typical weight of the prepared sample was 220 g. Before measurement, the samples were dried at 110ºC for 2 to 4 hours in order to eliminate the influence of moisture. The proportion of moisture in the samples was less than 1%.

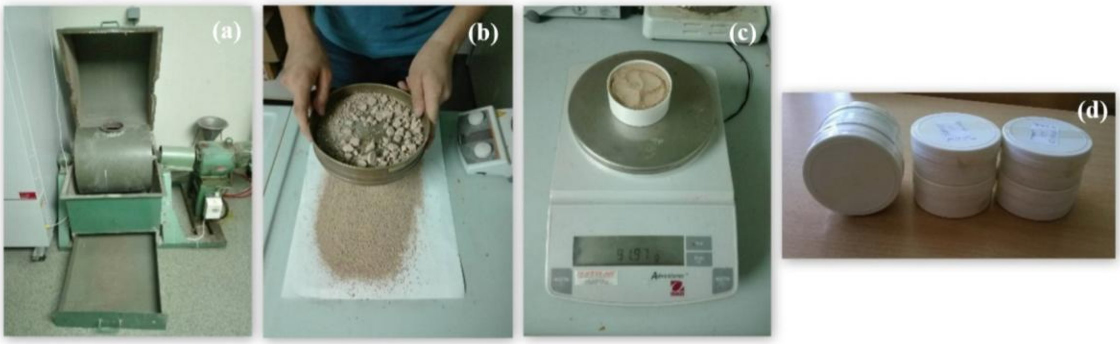

Figure 1: Grinding of the sample of ceramic tile with a ball mill for gamma spectrometry measurements of radioactivity **(a, and b)**, measuring the mass of dried sample**(c)** and packing sample in cylindrical geometry **(d).**

2.2 Radioactivity measurements

Activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K were determined using a method of low-level gamma spectrometry. Sampling and analysis of ceramic tiles were done using IAEA TRS 295 method [7]. The typical measurement time of samples was 72000 s.

Activity concentration of ^{226}Ra was determined from the gamma line of ^{214}Bi at 609.3 keV and ^{214}Pb at 351.9 keV, while for activity concentration of ^{232}Th gamma lines of ^{228}Ac at 911.2 and 969.1 keV and of ^{212}Pb at 238.6 keV was used. For determination of activity concentration of ^{40}K gamma line at 1460.8 keV was used. All the concentrations were measured by low-background HPGe ORTEC GMX gamma spectrometer (Fig. 2), with relative efficiency of 32% and an energy resolution of 1.9 keV. HPGe detector was surrounded with a 12-cm thick Pb shield. Acquisition and analysis of spectra were performed using the Canberra Genie 2000 program, which calculates activity concentration values for a given radioisotope, taking into account all significant gamma lines, after subtracting the part of the spectrum originating from background radiation. Measurement uncertainties were given with a confidence level of 95% [8]. Gamma spectrometric measurements were performed at the accredited Laboratory for radioactivity and dose measurement of ionizing rays, Department of Physics, Faculty of Sciences, University of Novi Sad, Serbia. The laboratory is accredited by the Accreditation Body of Serbia for this type of measurement.

Figure 2: ORTEC gamma spectrometry system for measuring radioactivity in an accredited laboratory for testing the dose of ionizing and non-ionizing radiation at the Department of Physics of the Faculty of Sciences in Novi Sad.

2.3 Radiation risk assessment

For the radiological characterization of building material, the gamma index has been introduced and may be calculated using Eq. (1) [6, 9, 10]:

$$I_{\gamma} = \frac{C_{\mathrm{Ra}}}{300\ \mathrm{Bq\ kg^{-1}}} + \frac{C_{\mathrm{Th}}}{200\ \mathrm{Bq\ kg^{-1}}} + \frac{C_{\mathrm{K}}}{3000\ \mathrm{Bq\ kg^{-1}}} \quad (1)$$

where C_{Ra}, C_{Th} and C_{K} represent activity concentration of ^{226}Ra, ^{232}Th and ^{40}K, in Bq kg^{-1}, respectively.According to the European Union Directive from 2014, gamma doses originating from building materials should be less than 1 mSv per year, which is ensured with a gamma index value below 1 [6].

Radium eqiuvalent index, representing the total exposure to radiation from naturally occurring radionuclides and defined as [8]:

$$Ra_{eq}(Bq\ kg^{-1}) = C_{Ra} + 1.43C_{Th} + 0.077C_K \qquad (2)$$

The total absorbed gamma dose rate (*D*) corresponding to the model of a room dimension 4m × 5m × 2.8 m due to the emission of gamma radiation for the room built from marble, granite, or ceramic can be estimated using Eq. (3) [9, 11]:

$$D(\text{nGyh}^{-1}) = 0.12 \cdot C_{\text{Ra}} + 0.14 \cdot C_{\text{Th}} + 0.0096 \cdot C_{\text{K}} \qquad (3)$$

Values 0.12, 0.14, and 0.0096 in Eq. (3) represent specific dose rates in nGy per Bq kg^{-1}[9, 12, 13]. The average absorbed gamma dose rate for building materials worldwide is 55 nGy h^{-1} [14].

Total annual effective dose (D_e) estimated for the individual for the room with floor and walls covered with ceramic tiles, assuming the individual was spending 80% of the time in the room (home) can be estimated from Eq. (4).

$$D_e(\text{mSv y}^{-1}) = 0.7\ \text{SvGy}^{-1} \times 7000\ \text{h} \times D \qquad (4)$$

where *D* is the absorbed dose rate given in mGy h^{-1}, 0.7 Sv Gy^{-1} is the conversion factor, 7000 h is the exposure time of the individual during a period of one year (80% of the total time of the individual in closed space at home).

3. Results and discussion

Results of low-level gamma spectrometry analysis for 5 samples of ceramic tiles produced in Serbia, with types and dimensions of used samples, are given in Table 1.

The activity concentration of ^{226}Ra was in the range of 52.3±0.6 Bq kg^{-1} to 96.9±1.6 Bq kg^{-1} (sample numbers 5 and 4, respectively). The average value of activity concentration of ^{226}Ra was 67.2±6.9 Bq kg^{-1} (mean value ± standard deviation). Activity concentration ^{232}Th was in the interval from 43.6±1.5 Bq $kg^{-1}$to 69.8±1.9 Bq kg^{-1} (sample numbers 3 and 4, respectively). The average value of activity concentration of ^{232}Th was found to be 57.4±4.7 Bq kg^{-1} (mean value ± standard deviation). Activity concentration of ^{40}K was from 710±30 Bq kg^{-1} to 1020±40 Bq kg^{-1} (sample numbers 2 and 4, respectively). The average value of activity concentration of ^{40}K was 808±48 Bq kg^{-1} (mean value ± standard deviation). Obtained values of activity concentration of ^{226}Ra and ^{232}Th in four out of five samples show average activity concentrations for building materials worldwide (sample No. 4 have somewhat higher values), while activity concentration of ^{40}K in all samples is above worldwide value for this radionuclide in building materials given in Ref. [4]. The largest deviation of the average value was recorded for the activity concentration of ^{40}K, because the average value obtained was 1.6 times (or 60%) higher than the average value of 500 Bq kg^{-1} [4]. These values are comparable with values from the previous studies of the radioactivity of ceramic tiles in Serbia [15, 16], given in Table 2.

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Sample No.	**Type**	**Producer**	**Color**	**Sample size (cm)**	**Activity concentration (Bq kg^{-1})**		
					^{226}Ra	^{232}Th	^{40}K
1	Floor	Zorka Keramika	Green	33 x 33	64.6±0.8	57.0±1.8	780±30
2	Floor	Zorka Keramika	Blue	33 x 33	65.3±1.0	69.1±1.9	710±30
3	Wall	Zorka Keramika	Beige	40 x 25	56.8±0.8	43.6±1.5	790±40
4	Floor	Zorka Keramika	Dark orange	33 x 33	96.9±1.6	69.8±1.9	1020±40
5	Wall	Toza Marković	Orange	33 x 25	52.3±0.6	47.5±1.6	740±30
				Mean values ± SD	67.2±6.9	57.4±4.7	808±48
				Average values in the world	50[1]	50[1]	500[1]

Table 1: Type, manufacturer, color and activity concentration of ^{226}Ra, ^{232}Th and ^{40}K for ceramic tiles produced in Serbia.
[1]given in Ref. [4].

Activity concentration (Bq kg^{-1})			**Reference**
^{226}Ra	**^{232}Th**	**^{40}K**	
43-75	49-65	556-729	[15]
93-133 (110±21)	66-83 (77±10)	883-1,053 (940±110)	[16]

Table 2: Activity concentration of ^{226}Ra, ^{232}Th, and ^{40}K from earlier studies of the level of radioactivity of ceramic tiles in Serbia.
– range, (mean values ± standard deviation).

Calculated gamma indices (I_γ) are given in Table 3 with values in the range from 0.659±0.013 to 1.012±0.017 (sample numbers 5 and 4, respectively). Average value for the gamma index was 0.78±0.13 (mean value ± standard deviation). As can be seen in Table 3, four out of five samples have values of gamma indices that are in the agreement with the recommended value of the gamma index for building materials from the European Union [6]. Only one sample (No. 4), showed a slightly higher index than recommended value of the gamma index for building materials from the European Union.

Sample No.	I_γ	Ra_{eq} **(Bq kg^{-1})**	D **(nGy h^{-1})**	D_e **(μSv y^{-1})**
1	0.760±0.014	206±4	23.2±0.4	114±2
2	0.800±0.014	219±4	24.3±0.4	119±2
3	0.671±0.016	180±4	20.5±0.5	100±2
4	1.012±0.017	275±4	31.2±0.5	153±3
5	0.659±0.013	177±3	20.0±0.4	98±2
Mean values ± SD	0.78±0.13	211±16	23.9±0.2	117±9
Average or recommended values	≤1[2]	370[3]	55[4]	1000[5]

Table 3: Gamma index (I_γ), radium equivalent activity index (Ra_{eq}), absorbed gamma dose rate (D), and annual effective dose (D_e).
[2]given in Ref. [6]; [3]given in Ref. [11, 12]; [4]given in Ref. [14]; [5] given in Ref. [5, 6].

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Obtained values of radium equivalent activity index (Ra_{eq}) are represented in Table 3 and were in the range from180±4 Bq $kg^{-1}$to 275±4 Bq kg^{-1} (sample numbers 3 and 4, respectively). The average value of the radium equivalent activity index was 211±16 Bq kg^{-1}(mean value ± standard deviation). Estimated values do not exceed the recommended value of 370 Bq kg^{-1} defined in Ref. [11].

Calculated values of absorbed gamma dose rate (*D*) are represented in Table 3 and were in the range from 20.0 ± 0.4 nGy h^{-1} to 31.2±0.5 nGy h^{-1} (sample numbers 5 and 4, respectively). The average absorbed dose rate was found to be 23.9±0.2 nGy h^{-1} (mean value ± standard deviation). Obtained values do not exceed the average value of 55 nGy h^{-1} given in Ref. [14] for building materials worldwide.

Determined annual effective doses (D_e) are presented in Table 3, with the assumption of the room covered with ceramic tiles in case of homes (80% of time individual was spending in per one year). Annual effective doses were from 98±2 μSv y^{-1} to 153±3 μSv y^{-1} (sample numbers 5 and 4, respectively). The average annual effective dose was 117±9 μSv y^{-1} (mean value ± standard deviation). The value for the average annual effective dose was found to be 34±2 μSv y^{-1} (mean value ± standard deviation). The estimated annual effective doses were not higher than the acceptable level of 1 mSv y^{-1}[5, 6].

4. Conclusion

Building materials may contain a certain level of radioisotopes from the uranium and thorium decay chain (^{226}Ra and ^{232}Th), as well as primordial radioisotope ^{40}K. In this paper, the level of radioactivity for some ceramic tiles produced in Serbia by two leading manufacturers was analyzed. Activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K were measured by low-level gamma spectrometry using an HPGe detector. Based on the obtained activity concentrations, an assessment of health risks potentially originating from the use of this kind of material for homes and workplaces was conducted.

Obtained values of activity concentration of ^{226}Ra and ^{232}Th in four out of five were around average values found in building materials worldwide, while activity concentrations of ^{40}K were higher than the average values defined in Ref. [4], however, they are consistent with the results from earlier studies in Serbia [15, 16]. Gamma indices and radium equivalent activity are below and around recommended values [6, 11]. Annual effective doses originating from ceramic tiles in homes were also under limited value regulated in Serbia [5], leading to the conclusion there is no health risk in the case of using analyzed ceramic tiles in building constructions, hence from the radiological standpoint they are safe and may be used without limitation.

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References

[1] E.O. Joshua *et al. Natural radionuclides and hazards of rock samples collected from Southeastern Nigeria*, Radiat. Meas. 44, 401–404 (2009).

[2] E. Alali *et al. Radioactivity measurement and radiological hazard assessment of the commonly used granite and marble in Jordan*, Radiat Prot Dosim 182, 386-393 (2018).

[3] S. Abdullahi *et al. Determination of indoor doses and excess lifetime cancer risks caused by building materials containing natural radionuclides in Malaysia*, Nucl Eng and Technol 51, 325-336 (2018).

[4] UNSCEAR, *Sources, Effects and risks of ionizing radiation*. United Nations Scientific Committee on the Effects of Atomic Radiation, United Nations, New York, USA (1993).

[5] Official Gazette RS 36/18. Regulation on limits of radionuclide content in drinking water, foodstuffs, feeding stuffs, drugs, items of general use, building materials and other goods to be placed on the market (2018).

[6] Euratom, Council Directive 2013/59/Euratom of 5 December 2013 laying down basic safety for protection against the dangers arising from exposure to ionizing radiation, and repealing Directives 89/618/Euratom, 90/641/Euratom, 96/29/Euratom, 97/43/Euratom and 2003/122/Euratom (2014). https://energy.ec.europa.eu/celex-32013l0059-en-txt_en

[7] International Atomic Energy Agency. *Measurement of Radionuclides in Food and the Environment*, Technical Reports Series No. 295, Vienna, Austria (1989).

[8] N. Todorović et al. *Monitoring for exposures to TENORM Sources in Vojvodina region*, Radiat Prot Dosim 144, 655–658 (2014).

[9] EC (European Commission). Radiation protection 112, *Radiological protection principles concerning the natural radioactivity of building materials*, Directorate—General Environment, Nuclear Safetyand Civil Protection (1999).

[10] J. Beretka, P.J. Mathew, *Natural radioactivity of Australian building materials, industrial waste sand by-products*, Health Phys 48, 87–95 (1985).

[11] NEA-OECD, Nuclear Energy Agency. *Exposure to Radiation from Natural Radioactivity in Building Materials*. Reported by NEA Group of Experts, OECD, Paris (1979).

[12] UNSCEAR (United Nations Scientific Committee on Effects of Atomic Radiation), *Sources and effects of ionizing radiation*, *Exposures from Natural Radiation Sources, Annex B*, United Nations Publication, New York, USA (2000).

[13] M. Markkanen, *Radiation dose assessments for materials with elevated natural radioactivity*, Finnish Centre for Radiation and Nuclear Safety STUK-B-STO 32, Helsinki (1995).

[14] UNSCEAR (United Nations Scientific Committee on Effects of Atomic Radiation), Sources and effects of ionizing radiation. United Nations Scientific Committee on the Effects of Atomic Radiation. United Nations Publication, New York, USA (2008).

[15] V.M. Manić *et al. The dose from radioactivity of covering construction materials in Serbia*, Nucl Technol Radiat 30(4), 287-293 (2015).

[16] G. Pantelić *et al. Measurement of radioactivity in building materials in Serbia*, J Radioanal Nucl Chem, 303(3), 2517-2522 (2014).

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