Processing and Application of Ceramics 7 [3] (2013) 123–127
DOI: 10.2298/PAC1303123J

Natural radioactivity in imported ceramic tiles used in Serbia[#]

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Received 12 June 2013; received in revised form 22 August 2013; accepted 10 September 2013

Abstract

Ceramic tiles are one of the commonly used decorative building materials. Body of ceramic tiles is a mixture of different raw materials including clays, quartz materials and feldspat, and may be glazed or left unglazed. Due to the presence of zircon in the glaze, ceramic tiles can show natural radioactivity concentration significantly higher than the average values for building materials. This study presents a summary of results obtained by a survey which was consisted of measurements of activity concentrations of natural radionuclides in imported ceramic tile samples used in Serbia using a gamma spectrometer with HPGe detector. Based on the obtained concentrations, gamma index, radium equivalent activity, the indoor absorbed dose rate and the corresponding annual effective dose were evaluated to assess the potential radiological hazard associated with these building materials.

Keywords: *clays, ceramic tiles, radioactivity, spectroscopy*

I. Introduction

All building materials contain various amounts of natural radioactive nuclides. Materials derived from rock and soil contain mainly natural radionuclides of the uranium (^{238}U) and thorium (^{232}Th) series, and the radioactive isotope of potassium (^{40}K). In the uranium series, the decay chain segment starting from radium (^{226}Ra) is radiologically the most important and, therefore, reference is often made to radium instead of uranium. The knowledge of the natural radioactivity of building materials is important for the determination of population exposure to radiations, as most of the people spend 80% of their time indoors. High levels of radioactivity in construction materials can increase external and internal indoor exposure [1].

Ceramic tiles are one of the commonly used decorative building materials: they are made of a mixture of earthly materials that has been pressed into shape and fired at high temperature. They can be glazed or left unglazed. Based on the fact that the zircon 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, ceramic tiles can show natural radioactivity concentration significantly higher than the average values for building materials [2–6].

In this study, results of the activity concentrations of ^{238}U, ^{235}U, ^{232}Th, ^{226}Ra and ^{40}K measured in 16 samples of ceramic tiles, that are commercially available, are presented. Also, radium equivalent activity, the gamma-index, the indoor gamma absorbed dose rate and the annual effective dose due to external exposure were estimated to assess the potential radiological hazards associated with these building materials.

II. Materials and methods

Samples of 16 different ceramic tiles have been collected from local store. The investigated ceramic tiles (floor and wall) were imported from Croatia, Italy, Ukraine and Spain. The samples were crushed, sieved (mesh size 2 mm) and placed into the plastic box of 100 g. All samples were left for four weeks

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[#] Paper presented at 2nd *Conference of The Serbian Ceramic Society - 2CSCS-2013, Belgrade, Serbia, 2013*

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to reach radioactive equilibrium [7] and measured after that. The samples were counted using a high purity germanium detector (HPGe) with relative efficiency of 23 % and energy resolution of 1.8 keV for the 1332 keV ^{60}Co peak. Geometric efficiency for Marinelli beaker was determined by a reference soil material (Czech Metrological Institute, Prague, 9031-OL-420/12, with total activity of 41.48 kBq on the day 31.08.2012., (^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{203}Hg, ^{88}Y, ^{113}Sn, ^{85}Sr ^{137}Cs). The spectra were analysed using the program called GENIE 2000. The activity of ^{226}Ra and ^{232}Th was determined by their decay products: ^{214}Bi (609 keV, 1120 keV and also 1764 keV), ^{214}Pb (295 keV and 352 keV) and ^{228}Ac (338 keV and 911 keV), respectively. The activities of ^{40}K were determined from its 1460 keV γ-energy. ^{235}U was determined via 186 keV corrected for ^{226}Ra. ^{238}U was determined via ^{234}Th (63 keV) or by ^{234}Pa ($t_{1/2}$ = 1.17 min, 1000 keV). Counting time interval was 60 000 s. The combined measurement uncertainty of the results was calculated at the 95% level of confidence (k = 2).

The specific activity, A, of the radionuclides in the samples was calculated using the following equation:

$$A = \frac{N}{tP_\gamma e_f m} \tag{1}$$

where N is count of the sample (imp), t - counting time [s], P_γ - probability of gamma decay [%], e_f - detector efficiency [%] and m - the mass of the sample [kg]. Minimum detectable activity was calculated by the equation:

$$MDA = \frac{LLD}{tP_\gamma e_f m} \tag{2}$$

where $LLD = 2.71 + 4.65\sqrt{B}$ is the detection limit, B is background.

III. Results and discussion

Activity concentration of radionuclides detected in investigated ceramic tiles samples by gamma spectrometry is presented in Table 1. The activity concentration of ^{226}Ra has been found to be varying from 61 to 150 Bq/kg in floor ceramic tiles, while in wall tiles the activity concentration of ^{226}Ra varies from 70 to 135 Bq/kg. The activity concentration of ^{232}Th ranges from 53 Bq/kg to 72 Bq/kg and 50 Bq/kg to 101 Bq/kg in floor and wall tiles, respectively. The activity concentration of ^{40}K lies between 560 and 1030 Bq/kg for floor tiles and between 590 and 1070 Bq/kg for wall tiles. ^{235}U has concentrations between 2.8 and 4.0 Bq/kg (floor tiles) and between 2.8 and 6.4 Bq/kg (wall tiles). For ^{238}U detected concentrations were in range from 43 to 114 Bq/kg (for floor tiles) and in range from 43 to 143 Bq/kg (for wall tiles). As it is shown in this Table 1, the radioactivity in the examined samples varies greatly depending on their region of origin. The worldwide average specific activity in the building materials is given as follows: ^{226}Ra (50 Bq/kg), ^{232}Th (50 Bq/kg) and ^{40}K (500 Bq/kg) [8].

The higher natural activity concentrations found in ceramic tiles can be explained through the amount of zircon added. For example 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 usually included in the category of sources of technologically enhanced natural radioactivity [9]. Keeping in mind that the zircon is one component in the recipe for the production of ceramics it can be concluded that there are no legal restrictions in terms of radioactivity in circulation and use of the investigated materials only if 3% of the zircon is used [10]. Table 2 presents comparison with literature.

Table 1. Activity concentrations of radionuclides in ceramic tiles in Bq/kg

Country of origin	Commercial name	Type of tile	^{226}Ra	^{232}Th	^{40}K	^{235}U	^{238}U
Spain	Ala plapa blue	floor	76 ± 5	68 ± 6	1000 ± 70	3.6 ± 0.4	58 ± 18
	Ava puana verde		79 ± 5	60 ± 5	960 ± 60	4.0 ± 0.4	67 ± 16
Croatia	Teravod	floor	61 ± 4	60 ± 5	810 ± 60	3.2 ± 0.3	66 ± 17
	Joylila		95 ± 7	62 ± 6	720 ± 50	3.7 ± 0.4	114 ± 22
	Dante negro		95 ± 6	65 ± 6	800 ± 50	3.6 ± 0.4	80 ± 22
	Teradisijena		70 ± 5	66 ± 6	780 ± 50	2.8 ± 0.3	43 ± 17
	Petra		66 ± 5	53 ± 5	560 ± 40	3.3 ± 0.3	67 ± 16
Italy	Rupe river	floor	150 ± 10	70 ± 6	930 ± 60	3.5 ± 0.3	105 ± 20
	Tody		85 ± 6	69 ± 6	1030 ± 70	4.0 ± 0.4	85 ± 18
	Piazza		115 ± 8	72 ± 6	940 ± 60	3.6 ± 0.3	96 ± 21
Spain	Ava plana roso	wall	100 ± 7	60 ± 6	1040 ± 70	3.5 ± 0.3	93 ± 20
	Navarti		70 ± 5	66 ± 6	780 ± 50	2.8 ± 0.3	43 ± 17
	Ava plana blue		91 ± 7	66 ± 7	1070 ± 80	6.0 ± 0.6	111 ± 14
Croatia	Melodi marpel	wall	135 ± 9	101 ± 9	710 ± 50	6.4 ± 0.5	143 ± 36
Italy	Star gres	wall	79 ± 6	60 ± 5	590 ± 40	4.5 ± 0.4	86 ± 17
Ukraine	/	wall	115 ± 8	50 ± 5	740 ± 50	5.3 ± 0.5	115 ± 22

Table 2. Activity concentrations of radionuclides in Bq/kg - comparison with literature

Country of origin	^{226}Ra	^{232}Th	^{40}K
Italy [1]	36–87	38–86	411–996
Greek [11]	58	46	409
Egypt [12]	126	72	300
India [13]	28	64	24
China[5]	73	62	480
Turkey[3]	70	62	477
Serbia[14]	72–122	59–79	723–1013
World [8]	50	50	500

For all investigated samples gamma index, *I*, was calculated using the following equation [15]:

$$I = \frac{C_{Ra}}{Max(Ra)} + \frac{C_{Th}}{Max(Th)} + \frac{C_K}{Max(K)} \tag{3}$$

where *Max(Ra), Max(Th)* and *Max(K)* present maximum limit of radionuclide content of ^{226}Ra, ^{232}Th and ^{40}K in Bq/kg in the appropriate application (values are given in Table 3). Gamma index must be less than 1. If the values obtained for the gamma index recalculated through the equation (3) meet the requirements for interior, then the material can be used for exterior and low construction. Calculated values for gamma index are presented in Table 4. As it can be seen from Table 4, for three floor tiles from Italy this value exceed 1 for interior (values are 1.29, 1.00 and 1.13), but for exterior these values are 0.79, 0.65 and 0.72, so these tiles can be used for exterior and low construction. Also for two wall tiles from Spain and one wall tile from Croatia gamma indexes for interior are 1.05, 1.03 and 1.25, while for exterior they are 0.66, 0.66 and 0.82. Gamma index in these samples are higher than 1 because of higher concentration of ^{226}Ra. For the rest 10 samples gamma index for interior is less than 1.

Radium equivalent activity can be calculated using the following equation [16]:

$$Ra_{eq} = C_{Ra} + 1.43C_{Th} + 0.077C_K \tag{4}$$

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 produces the same gamma dose rate. A radium equivalent of 370 Bq/kg in building materials will produce an exposure of about 1.5 mSv/h to the inhabitants [17]. All investigated samples presented Ra_{eq} values lower than the limit of 370 Bq/kg (Table 4), set in the Organization for Economic Cooperation and Development (OECD, 1979) report

Table 3. Maximum limit of radionuclide content in the appropriate use [15]

Max limit of radionuclide content in the appropriate use	^{226}Ra [Bq/kg]	^{232}Th [Bq/kg]	^{40}K [Bq/kg]
interior	200	300	3 000
exterior	400	300	5 000
low construction	700	500	8 000

Table 4. Radium equivalent activity, Ra_{eq}, gamma dose rate, $\dot{D}$, annual effective dose, D_E and gamma index, I in ceramic tiles

Country of origin	Commercial name	Type of tile	Ra_{eq} [Bq/kg]	$\dot{D}$ [µGy/h]	D_E [mSv]	I
Spain	Ala plapa blue	floor	251	0.23	1.11	0.94
	Ava puana verde		239	0.22	1.06	0.92
Croatia	Teravod	floor	209	0.19	0.92	0.78
	Joylila		239	0.21	1.04	0.92
	Dante negro		249	0.22	1.09	0.96
	Teradisijena		224	0.20	0.98	0.83
	Petra		185	0.16	0.80	0.69
Italy	Rupe river	floor	322	0.29	1.41	1.29
	Tody		263	0.24	1.16	1.00
	Piazza		290	0.26	1.27	1.13
Spain	Ava plana roso	wall	266	0.24	1.18	1.05
	Navarti		224	0.20	0.98	0.83
	Ava plana blue		268	0.24	1.19	1.03
Croatia	Melodi marpel	wall	334	0.29	1.43	1.25
Italy	Star gres	wall	210	0.19	0.91	0.79
Ukraine	/	wall	244	0.22	1.08	0.99

[17]. Thus, all materials would not present a significant radiological hazard when used in constructions.

The absorbed dose rate in indoor air, $\dot{D}$, was calculated using the equation (5) [18]. This equation is used to calculate the dose rate of material used in floor, ceiling and walls (all structures).

$$\dot{D}\left(nGyh^{-1}\right) = 0.92C_{Ra} + 1.1C_{Th} + 0.08C_{K} \tag{5}$$

The estimated indoor gamma dose rate values for all investigated samples are shown in Table 4. It ranges from 0.16 to 0.29 μGy/h.

To estimate the annual effective dose (D_E), one has to take into account the conversion factor from absorbed dose in air to effective dose. In the recent UNSCEAR 2010 reports [8], a value of 0.7 Sv/Gy is used as for the conversion factor to convert absorbed dose in air to effective dose received by adults. The annual exposure time used is 7000 h. The annual effective dose in units of mSv was estimated using the following equation:

$$D_E = 0.7SvGy^{-1} \times 7000h \times \dot{D} \tag{6}$$

The obtained results for annual effective dose are presented in Table 4 and show that these values, ranged from 0.80 to 1.43 mSv.

IV. Conclusions

For each sample of floor and wall ceramic tile imported from different countries investigated in this study, the specific activity of ^{226}Ra, ^{232}Th, ^{40}K, ^{235}U and ^{238}U were determined by gamma spectrometry. The radium equivalent activity, the gamma-index, the absorbed gamma dose rate in indoor air and the corresponding annual effective dose have been determined to assess the radiological hazards from these building materials commonly used in Serbia. The results show that there are considerable variations in the measured concentrations of radionuclides in ceramic tiles originating from different areas. This fact is important from the point of view of selecting suitable materials for use in building and construction. Probably, the higher natural activity concentrations found in ceramic tiles is due to the amount of zircon added for glaze. 10 samples show gamma indexes lower than the limit for interior use, while 6 samples have gamma index higher than 1 for interior use, but for exterior, these values are lower than 1.The radium equivalent activity is within the limit set by the OECD. Calculated gamma dose rate ranged from 0.16 to 0.29 μGy/h while calculated annual effective dose ranged from 0.80 to 1.43 mSv. The obtained radium equivalent activity, the absorbed gamma dose rate in indoor air and the corresponding annual effective dose calculated based on the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K given for ceramic tiles from different origin in literature cite in Table 2 (comparison with literature), was 121–290 Bq/kg for Ra_{eq}, 0.14–0.26 μGy/h for $\dot{D}$ and 0.48–1.26 for D_E. These values are in good agreement with values for ceramic tiles investigated in this paper.

From radiological point of view, the results indicate that the use of these materials in construction of dwellings could be considered safe for inhabitants.

Acknowledgements: The investigation was partially supported by The Ministry of Education and Sciences of Serbia, under Project III43009.

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