ASSESSMENT OF NATURAL RADIOACTIVITY LEVELS AND RADON EXHALATION RATE POTENTIAL FROM VARIOUS BUILDING MATERIALS

by

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Various imported building materials commonly used in construction and industry in Serbia were analyzed using gamma spectrometry. Based on the activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in the investigated samples, radium equivalent activity, Ra_{eq}, absorbed dose rate, D, annual effective dose, D_E, and the external hazard index, H_{ex}, were calculated to assess the radiation hazard for people. The Ra_{eq} for most of the analyzed samples (416 in total) was lower than the maximum admissible value of 370 Bqkg^{-1} set in the UNSCEAR report. The absorbed gamma dose rate in air was found to vary from 0.030 Gyh^{-1} to 1.328 Gyh^{-1} which in some cases exceeded indoor dose rates in Europe. The obtained values for annual effective dose exceed the limits of 0.41 mSv given in literature for about 5 % of measured samples, while values of H_{ex} were higher than unity for three samples of cement, eight samples of granite, and one sand sample.

As a possible source of elevated effective dose, the radon exhalation from building materials was estimated using the parameters given in literature. The internal dose due to ^{222}Rn exhaled from the building material was found to be up to nine times higher than external dose due to ^{226}Ra content in some cases.

Key words: natural radioactivity, radon exhalation rate, radiation hazard indice, building material

INTRODUCTION

Naturally occurring radionuclides are found to be present in significant amounts in soil, building materials and recycled industrial waste products [1]. All building materials, since they are mainly derived from rock and soil, contain various amounts of naturally occurring 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 content instead of uranium.

External exposure, caused by direct gamma radiation emitted from these radionuclides, is confined not only to the outdoor environment but can also occur in houses, offices and other working places [2]. The internal exposure is caused by inhalation of the radioactive inert gas radon, ^{222}Rn, and its short-lived decay products. Radon is a part of the radioactive decay series of uranium, which is present in building materials. Because radon is an inert gas, it can move rather freely through porous media such as building materials, although usually only a fraction of what was produced in the material reaches the surface and enters the indoor air, where it could be inhaled, contributing to the internal dose of inhabitants.

Building materials are derived from both natural sources (*e. g.* rock and soil) and waste products (*e. g.* phosphogypsum, alum shale, coal fly ash, oil shale ash, *etc*.), and also from industry by-products (*e. g.* power plants, phosphate fertilizer and oil industry) [3].

The concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in building materials vary depending on the local geological and geographical conditions, as well as geochemical characteristics of these materials [4]. Therefore, it is important to measure the concentration of radionuclides in all building materials collected from

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different places and to estimate the radiological hazards to human health. During the last decades, there has been an increasing interest in the study of radioactivity in various building materials [5-21], and some results of measured radionuclide content in these materials available in the literature are summarized in tab. 1.

The world-wide average concentrations of radium, thorium, and potassium in the concrete, for example, are about 40 Bqkg^{-1}, 30 Bqkg^{-1}, and 400 Bqkg^{-1}, respectively. For soil, the worldwide average concentrations of naturally occurring radionuclides are 32 Bqkg^{-1}, 45 Bqkg^{-1}, and 412 Bqkg^{-1} for ^{226}Ra, ^{232}Th, and ^{40}K, respectively [1].

Building materials and their additives contain radioactive isotopes, which can increase both external and internal radioactive exposures of humans. Knowledge of the level of natural radioactivity in building materials and radon exhalation is therefore important to assess the possible radiological hazards to human health and to develop standards and guidelines for the use and management of these materials.

The aim of this study was to measure the natural radioactivity in bentonite, cement granite, marble and sand used as construction, as well as raw material, and to estimate the potential radiological hazards. If the materials investigated in this paper are used as raw materials, their fraction in the final product which is used as construction material should be taken into the consideration.

Additionally, since nearly half of the radiation dose received by the general population originates from radon [1], although Harrison and Marsh [22] suggested that the contribution of radon might even be much higher, dose due to exhaled radon was calculated via estimated radon exhalation rate from the investigated building materials. The obtained results are presented in this paper.

Table 1. An overview of ^{226}Ra, ^{232}Th, and ^{40}K activity concentrations and Ra_{eq} in materials used in industry and construction in different countries

Material	Country	Average activity concentrations of radionuclides [Bqkg^{-1}]			Ra$_{eq}$ [Bqkg^{-1}]	Reference
		^{226}Ra	^{232}Th	^{40}K		
Mansehra granite	Pakistan	27.32	50.07	953.10	37.24-230.90 (171.91)	[12]
Cement sand	China	68.3	51.7	173.8	162.8	[7]
		40.7	21.5	302.6	96.4	
Cement	Algiers	41	27	422	112	[16]
Marble chips		23	18	310	73	
Sand		12	7	74	28	
Portland cement	Yemen	40.39	24.57	428.48	108.5	[11]
Sand		20.78	27.68	1118.36	164.5	
Hapach hard rock		68.6	95.08	2636.68		
White cement	Egypt	105	45	300	192	[17]
Portland cement		134	88	416	292	
Granite		187	118	852	421	
Marble		205	115	865	436	
Cement	Turkey	50.2	25.4	444.5	98.3	[4]
Granite	Iran	/	36.6	1299.4		[21]
Sand	Lebanon	13	6.2	4.7	22.9	[10]
Gray cement		73.2	9.0	79.7	92.2	
White cement		76.3	13.2	4.6	95.5	
Gravel		27.5	0.40	4.6	28.4	
Portland cement	Greece	14.6-139.6	8.1-45.6	141-390		[19]
Concretes		8.2-53.8	7.9-25.1	140-583		
Sand		10.6-26.8	7.5-31.8	167-656		
Granites		1.6-170	mdc-354	49-1592		
Sand	Cameroon	^{238}U 6.69-14.86	7.62-31.81	201.3-598.29		[20]
Portland cement		^{238}U 27	15	277		
Gravel		^{238}U 19.02-26.37	24.1-147.2	294-1226		
Marble		^{238}U 2.01	5	430		
Granite	Nigeria	^{238}U 27.79	19.83	132.76	66.33	[6]
Cement		^{238}U 30.65	20.65	201.45	75.65	
Sand		^{238}U 28.08	22.73	276.42	81.82	
Concrete		^{238}U 27.87	16.69	175.85	65.24	
Brick	EU (23 countries)	47(2-148)	48(2-164)	598(12-1169)		[13]
Concret		60(1-1300)	35(1-152)	392(7-1450)		
Cement		45(4-422)	31(3-266)	216(4-846)		

The investigated materials are continuously tested for several years at Institute "Vinča", Radiation and Environmental Protection Department in Belgrade, Serbia, as a part of the regular inspection of imported goods from Serbian border crossings.

MATERALS AND METHODS

The investigated materials were 416 samples of building materials:

- bentonite – 47 samples,
- cement – 60 samples,
- granite – 205 samples,
- marble – 85 samples, and
- sand – 19 samples.

Types of samples were chosen as they represent the most common types of building materials that are analyzed in the Laboratory. The number of samples in each type depended only on the availability.

Bentonite is a type of absorbent clay that is usually refined from volcanic ash. It is an absorbent aluminum phyllosilicate, essentially impure clay consisting mostly of montmorillonite. There are different types of bentonite, each named after the respective dominant element, such as potassium K, sodium Na, calcium Ca, and aluminum Al. Bentonite can be used in cement, adhesives and ceramic bodies. Also, it is used as a binding agent in the manufacture of taconite pellets as used in the steelmaking industry. In small percentages, bentonite is used as an ingredient in commercially designed clay bodies and ceramic glazes.

Cement is, in general, a binder, a substance that sets and hardens independently, and can bind other materials together. Thus, if present, the cement is always a part of a composite material, which should be considered regarding the radiological constraints of building materials. Three types of cement were investigated in this manuscript: Portland, white and aluminized cement.

Granite is one of the most popular building materials. Granite could be used both as interior and exterior building material and, regarding the radiological constraint it is treated accordingly.

Marble, similar to granite, could be used as interior and exterior building material, however, in principle it is radiologically less hazardous than granite.

Sand is a naturally occurring granular material composed of finely grinded rock and mineral particles. The composition of sand varies, depending on the local rock sources and conditions, but the most common constituent of sand in inland continental settings and non-tropical coastal settings is silica (silicon dioxide, or SiO_2), usually in the form of quartz.

Gamma spectrometry

Gamma spectrometric measurements were performed by using HPGe (Canberra) detectors with relative efficiencies of 18 %, 20 %, and 50 %. Energy and efficiency calibration of the detectors was performed by using the silicone resin matrix in geometry of the plastic Marinelli beaker of 500 ml, spiked with a common mix of radionuclides (^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{203}Hg, ^{88}Y, ^{113}Sn, ^{85}Sr, and ^{137}Cs), purchased from Czech Metrological Institute and traceable to Bureau International des Poids et Mesures.

All the spectra were recorded and analyzed using the program GENIE 2000. The activity of ^{226}Ra and ^{232}Th was determined by their decay products: ^{214}Bi (609 keV, 1120 keV, and 1764 keV), ^{214}Pb (295 keV and 352 keV), and ^{228}Ac (338 keV and 911 keV), respectively. The ^{235}U was determined either via 186 keV corrected for ^{226}Ra contribution, or via its 143 keV γ-energy peak. The ^{238}U was determined via ^{234}Th (63 keV) or by ^{234m}Pa (1001 keV). The activities of ^{40}K, ^{137}Cs, and ^{210}Pb were determined through their 1460 keV, 661 keV, and 46 keV γ-energy peaks, respectively. Net count rates were corrected for background, dead time and coincidence summing effects. The background spectrum was recorded regularly before the sample counting, with an empty 500 ml plastic Marinelli beaker.

The activity concentration of a specific radionuclide in the sample, A_x given in Bqkg^{-1}, was calculated using

$$A_x \quad \frac{N/t}{P_\gamma \varepsilon m} \tag{1}$$

where *N*/*t* [E] is net count rate of the peak at energy, corrected for the background, *t* [s] – the counting time, P [E] – the fluorescent yield at energy, ε – the detection efficiency, and *m* [kg] – the mass of the sample, respectively.

Minimum detectable concentration (MDC) was calculated by

$$MDC \quad \frac{LLD}{tP_\gamma \varepsilon m} \tag{2}$$

where *LLD* is the detection limit at a given energy, $LLD \quad 2.71 \quad 4.65\sqrt{B}$, and *B* is the peak area of background radiation at the same energy. The MDC has units of Bqkg^{-1}.

The budget of combined standard uncertainties included the efficiency calibration uncertainty, the statistical uncertainties of the recorded peaks and uncertainty in mass measurement. The combined measurement uncertainties were calculated by error propagation calculation, and are given at the 95 % level of confidence ($k = 2$)

$$u(A_x) \quad \sqrt{(\delta\varepsilon)^2 \quad (\delta N)^2 \quad (\delta M)^2 \quad (\delta C)^2} \tag{3}$$

where $\delta\varepsilon$ is the relative uncertainty of the detection efficiency (2-3 %), δN – the relative statistical uncertainty of the net count, and δM includes all other contributions to the uncertainty such as measurement of the reference material mass, the uncertainty of the positioning of the sample on the detector, measurement time uncertainty, and radioactive decay during measurement *etc*., which are estimated to be 2 %. Finally, is the uncertainty of the coincidence correction factors (1.2 %).

In accordance with international recommendations [23] all the samples were mechanically prepared for measurements. Samples were crushed, minced and sieved (mesh size 2 mm) and placed in the Marinelli beakers. All samples were measured immediately after preparation in order to determine, for the shortest possible time, whether the materials are in accordance with relevant legislation. Measurement times were 3000 seconds.

Dose calculation

Radium equivalent activity, Ra_{eq}, the absorbed dose rate in indoor air, D, the annual effective dose, D_{E} and the external hazard index, H_{ex} were calculated by using the well-known equations as defined in [1, 18]

$$Ra_{\mathrm{eq}} = A_{\mathrm{Ra}} + 1.43A_{\mathrm{Th}} + 0.077A_{\mathrm{K}} \tag{4}$$

$$D = 0.92A_{\mathrm{Ra}} + 1.1A_{\mathrm{Th}} + 0.08A_{\mathrm{K}} \tag{5}$$

$$D_{\mathrm{E}} = 0.7 \quad 700\,hD \tag{6}$$

$$H_{\mathrm{ex}} = A_{\mathrm{Ra}}/370 + A_{\mathrm{Th}}/259 + A_{\mathrm{K}}/4810 \tag{7}$$

where A_{Ra}, A_{Th}, and A_{K} are the activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in Bqkg^{-1}, respectively.

Gamma indices for construction materials

Gamma indices reflect a radiological risk which is closely associated with materials used in the construction industry. Values of calculated gamma indices should be less than unity in order to meet recommendation given by the national legislation. If the construction material is going to be used for interior, it should meet more stringent criteria, than the one for exterior. Gamma indices were calculated using the following equations (Official Gazette RS 97/13, 2013), which are the same as those given in [2]

$$\begin{aligned} I_{\mathrm{int}} &= \frac{A_{\mathrm{Ra}}}{300} + \frac{A_{\mathrm{Th}}}{200} + \frac{A_{\mathrm{K}}}{3000} \\ I_{\mathrm{ext,\,high}} &= \frac{A_{\mathrm{Ra}}}{400} + \frac{A_{\mathrm{Th}}}{300} + \frac{A_{\mathrm{K}}}{5000} \\ I_{\mathrm{ext,low}} &= \frac{A_{\mathrm{Ra}}}{700} + \frac{A_{\mathrm{Th}}}{500} + \frac{A_{\mathrm{K}}}{8000} \end{aligned} \tag{8}$$

where A_{Ra}, A_{Th}, and A_{K} are the activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in Bqkg^{-1} in the building material, respectively. If the values obtained for the gamma index recalculated through the eqs. (8) meet the requirements for the interior, then the material can be used for the exterior in high and low construction as well.

Radon exhalation

The radon exhalation rate is the amount of radon activity released per unit area per unit time. The radon exhalation rate depends on radium content, radon emanation factor and radon diffusion coefficient in given material, whereby the last two depend on the physical properties of building materials such as spatial distribution of radium atoms in the mineral grain, texture, humidity content, porosity, density and ambient temperature.

In many cases, the source of Rn is the soil beneath the building, rather than the building material itself and in such a case, it is not possible to find direct correlation between indoor radon concentrations and the radium content of building materials. Nevertheless, in cases where the building material can be identified as the main source of Rn (for example upper levels of a multi-story building) using measured values of radon emanation factor and radon diffusion coefficient in a given material, it is possible to estimate the radon exhalation and consequently the part of indoor radon concentration originating from the radon exhalation.

For the estimation of the exhalation rate E from the building material the following equation is used [24]

$$E = \lambda l A_{\mathrm{Rn}} \rho \varepsilon \tanh\left(\frac{L}{2l}\right) \tag{9}$$

where λ is the decay probability of radon, l – the diffusion length of radon in a given material, A_{Rn} – the radium activity in a given material, ρ – the density of the material, ε – the is radon emanation factor from grain to pore space, and L – the wall thickness.

The radon exhalation rate estimation is based on the exhalation parameters of building materials taken from the literature [23, 25-34], tab. 2.

Indoor radon concentration originating from exhalation may be estimated by

$$A_{\mathrm{Rn}} = EA/V\lambda_{v} \tag{10}$$

where E is the exhalation rate of the building material from which the house (and the rooms) are built, A – the wall area of the room, V – the volume of the room, and λ_{v} – the ventilation rate of the room. Ratio A/V is taken to be 1.6 considering a room model with dimensions (4 m × 5 m × 2.8 m) and the ventilation rate lays in the interval (0.2-2) h^{-1} [1] with the geometric mean of 0.63 h^{-1}.

Using the estimated indoor radon concentration, the indoor radon exposure could be calculated as [1]

$$H = A_{\mathrm{Rn}} \; F \; O \; DFC \tag{11}$$

Table 2. Radon exhalation parameters of building materials [24-34]

Material	Diffusion length, l [m]		Emanation factor, ε [%]		Density, ρ [kgm^{-3}]	
	Min	Max	Min	Max	Min	Max
Concrete	0.06	0.54	0.01	0.28	850	2300
Granite	0.16	0.195	0.021	0.34	2600	2800
Marble	0.207	0.207	0.012	0.164	2588	2588
Aerated concrete	0.8	0.8	0.24	0.24	0.3	1.8

Table 3. Measured specific activities of radionuclides in bentonite, cement, granite and marble in Bqkg^{-1} (range and mean value with associated standard deviation)

Sample	Number of samples	Activity concentrations [Bqkg^{-1}]			Gamma index I	
		^{226}Ra	^{232}Th	^{40}K	Interior Exterior (high) Exterior (low)	
		Min Max Mean s	Min Max Mean s	Min Max Mean s	Min	Max
Bentonite	47	8 2	30 5	43 11	0.268	0.800
		76 8	112 11	731 95		
		34 2	69 2	500 20		
Cement	60	10 3	7 2	17 6	0.117	2.224[a]
		255 51	264 40	403 36	0.080	1.550[b]
		56 7	77.3 9.8	120 20	0.048	0.912
Granite	205	7 2	7 2	28 7	0.122	5.550[c]
		311 43	887 18	2643 264	0.079	3.712[d]
		51 5	64 9	550 40	0.048	2.223[e]
Marble	85	5 2	26 5	34 10	0.237	0.861
		48 10	69 7	1353 149		
		16 2	48 12	230 100		
Sand	19	6 1	8 2	29 6	0.104	5.905[f]
		157 31	1070 107	94 14	0.071	3.978[f]
		27 13	223 212	55 10	0.042	2.376[f]

[a]6 samples > 1, [b] 3 samples > 1, [c] 16 samples >1, [d] 11 samples >1, [e] 3 samples >1, [f] 1 sample > 1

where A_{Rn} [Bqm^{-3}] is the radon concentration, F – the radon equilibrium factor (F = 0.4 EEC, where EEC stands for equilibrium equivalent concentration), O – the occupancy factor expressed as the number of hours which the inhabitant spends in the building during one year, in further calculations taken to be 7000 ha^{-1} (80 %), and DCF is dose conversion factor for radon – 9 nSvBq^{-1} m^3 EEC^{-1} h^{-1}.

RESULTS AND DISCUSSION

Activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K

The range of the specific activity values (maximum and minimum) of ^{226}Ra, ^{232}Th, and ^{40}K measured in the investigated building materials are shown in tab. 3. Mean concentrations of these radionuclides associated with standard deviation of mean value, s, are also given in tab. 3. Minimal detectable concentrations for ^{226}Ra, ^{232}Th, and ^{40}K in performed measurements were 3 Bqkg^{-1}, 5 Bqkg^{-1}, and 16 Bqkg^{-1}, respectively. As can be seen from tab. 3, the lowest detected value of ^{226}Ra activity concentration was (5 2) Bqkg^{-1} in marble, while the highest value was (311 43) Bqkg^{-1} measured in granite. The lowest and the highest detected value of ^{232}Th specific activity was (7 2) Bqkg^{-1} measured in cement and granite, and (887 18) Bqkg^{-1}, measured in granite sample. For ^{40}K, the lowest value for activity concentration was (17 6) Bqkg^{-1} in cement sample, while the highest value of (2643 264) Bqkg^{-1} was measured in granite sample.

Also, granite samples generally had higher activity concentrations than the other investigated samples.

Since the samples were measured immediately after preparation, in order to confirm obtained results, 10 samples of granite were sealed and measured after reaching radioactive equilibrium. Counting time intervals were 60 000 seconds and longer. The detected differences in the obtained concentrations were within the calculated uncertainties, tab. 4.

Results obtained in present investigation are comparable with data available in the literature [5-20], Measured specific activities showed that construction materials that have been used in Serbia are in the range

Table 4. Specific activities of radionuclides with associated measurement uncertainties, before and after reaching radioactive equilibrium, measured in 10 granite samples

Granite sample	Activity concentrations [Bqkg^{-1}]					
	^{226}Ra		^{232}Th		^{40}K	
	After	Before	After	Before	After	Before
1	12 2	19 6	60 6	55 11	798 80	717 86
2	5.6 1.1	9 2	18 2	24 7	594 59	662 99
3	16 2	19 4	19 2	26 7	273 27	331 46
4	2.6 0.3	< 3	1.5 0.1	< 5	66 7	67 14
5	8 0.9	< 3	< 0.2	< 5	11 0.2	< 16
6	1 0.2	< 3	2.2 0.3	< 5	72 7	78 16
7	22 2	16 3	24 3	24 5	594 53	539 139
8	34 4	38 8	48 5	56 11	1085 98	1030 103
9	20 2	18 4	28 3	28 6	400 40	320 45
10	14 2	19 4	35 4	44 9	890 80	804 96

Table 5. The calculated value ranges for radium equivalent activity, absorbed gamma dose rate, annual effective dose and external hazard index for measured samples

Sample	Ra_{eq} [Bqkg^{-1}]	$\dot{D}$ [nGyh^{-1}]	D_E [mSv]	H_{ex}
Bentonite	72.2-236	62-206	0.31-1.01	0.195-0.638
Cement	33.2-645	28-538	0.14-2.64	0.090-1.742
Granite	31.7-1566	29-1264	0.14-6.19	0.053-4.215
Marble	66.6-224	57-207	0.28-1.02	0.168-0.406
Sand	29.4-1694	25-1329	0.12-6.51	0.076-4.908

given in database for EU countries [14]. Furthermore, the obtained mean values are close to the reported lower limit for the same type of construction material.

The values of the calculated gamma indices (eq. 8) for all the samples are also presented in tab. 3. As can be seen from tab. 3, all the obtained values for gamma indices are less than 1 for all bentonite and marble samples. Calculated values for gamma indices for cement were higher than one for six samples for usage in interior and three samples for exterior for high construction. For granite samples 16, 11, and 3 samples did not meet criteria for interior, exterior high and exterior low construction, respectively. One measured sand sample did not meet any of three given criteria.

Dose assessment

Distribution uniformity of ^{226}Ra, ^{232}Th, and ^{40}K in building materials, in respect to the radiation exposure, is defined in terms of Radium equivalent activity (Ra_{eq}) in Bqkg^{-1} in order to compare the specific activity of materials containing different amounts of ^{226}Ra, ^{232}Th, and ^{40}K. The Ra_{eq} was calculated by eq. (4), and it has been assumed that 370 Bqkg^{-1} of ^{226}Ra or 259 Bqkg^{-1} of ^{232}Th or 4810 Bqkg^{-1} of ^{40}K, produce the same gamma dose rate. A 370 Bqkg^{-1} of radium equivalent activity in building materials will produce an exposure of about 1.5 mSvy^{-1} to the inhabitants [1].

Absorbed dose rate in indoor air $\dot{D}$,was calculated using the eq. (5). Dose rate originates from building material used for the floor, ceiling and walls (all structures) [33].

To estimate the annual effective dose, D_E, the conversion factor from the absorbed dose in air to the effective dose was taken into account. The D_E, was calculated by the eq. (6) using the value of 0.7 SvGy^{-1}for a conversion factor, and a value of 7000 hours for the annual exposure time [1, 34]. The $\dot{D}$ was expressed in Gyh^{-1}.

The external hazard index, H_{ex}, was calculated using the eq. (7) [18]. The value of this index must be less than unity in order to keep the radiation hazard insignificant. The maximum value of H_{ex} equal to unity corresponds to the upper limit of radium equivalent activity (370 Bqkg^{-1}).

Minimal and maximal calculated values of Ra_{eq}, $\dot{D}$, D_E, and H_{ex} are presented in tab. 5.

The lowest value of Ra_{eq} was 29.4 Bqkg^{-1}, while the highest value was 1694 Bqkg^{-1}, both obtained in the sand samples. The high Ra_{eq} values can be attributed to the high concentration of the three radionuclides ^{226}Ra, ^{232}Th, and ^{40}K in these materials as shown in tab. 3. From these results it is evident that there are considerable variations in the Ra_{eq} of the different materials and also within the same type of material originating from different areas. Three samples of cement, 17 samples of granite and one sample of sand exceed the limit of 370 Bqkg^{-1} set in the Organization for Economic Cooperation and Development report [34]. Thus, these materials would present a significant radiological hazard when used in constructions.

Through a review of the literature it can be established that Ra_{eq} varies significantly from one country to another, and that the obtained values for the measured materials are in expected ranges.

The estimated indoor gamma dose rate values for all the investigated samples, presented in tab. 5, ranged from 25 nGyh^{-1} up to 1329 nGyh^{-1}. Considering the fact that the average gamma dose rate indoors in Europe is 70 nGyh^{-1} [2], gamma dose rate calculated for bentonite, cement, granite, marble and sand samples, mostly exceeded the average value.

The obtained results for the annual effective dose, presented in tab. 5., show that these values ranged from 0.12 mSv up to 6.51 mSvy^{-1}, and exceed the limits of 0.41 mSv set in UNSCEAR report [1] for a great number of samples.

The obtained values of H_{ex} are shown tab. 5. The values of H_{ex} for building materials that had been investigated ranged from 0.053 up to 4.908. The external hazard index represents the external radiation exposure, usually associated with gamma radiation emitted by radionuclides of concern. If the external hazard index exceeds unity, we might conclude that the potential external dose(s) to exposed individual(s) will exceed the acceptable level, and some action may be required. This may mean, for example, that additional remediation of building material is necessary to reduce one or more of the contaminating radionuclides to acceptable levels. Since the values calculated for building materials which were investigated in this work exceed limits (>1)for three samples of cement, eight samples of granite, and one sand sample we can say that the radiation hazard is low.

Dose due to exhaled radon

Table 6 shows the ratio between the external exposure due to the natural radioactivity content of ^{226}Ra in building material and internal exposure from building materials exhaling ^{222}Rn. The percentage of agglomerates and matrices in composite building material is considered. In the case of concrete we accounted the approximate amount of its aggregates (25 % of cement and 75 % of sand), while in aerated concrete the amount of aggregates is (50 % of cement and 50 % of sand). Estimated maximal potential effective dose due to radon exhaled from the building materials (internal dose) is given. Corresponding effective dose due to ^{226}Ra content in building materials (external dose) is calculated using ^{226}Ra activity in building material.

Table 6. gives the maximum potential dose due to ^{222}Rn exhalation and corresponding ^{226}Ra activity. The activities of ^{226}Ra which will correspond to annual dose of 1 mSv are 153 Bqkg^{-1}, 144 Bqkg^{-1}, 346 Bqkg^{-1}, and 48 Bqkg^{-1} for granite (superficial material), cement (concrete), marble and sand (concrete), respectively. Although the gamma index should prevent exposure of inhabitants to doses higher than 1 mSv according to [2] the concentration of ^{226}Ra which induce an external dose of 1 mSv is 276 Bqkg^{-1} (6 276 = 1656 Bqkg^{-1} for granite – a superficial materials). It could be concluded that the potential internal exposure due to exhaled ^{222}Rn will not be always constrained by the gamma index to values lower than 1 mSv. In fact, the results presented in the tab. 6 imply that for the superficial materials radon exhalation should be put also under constrain.

The comparison between the dose due to exposure to ^{226}Ra in building material and the dose due to the exhaling radon from the same building material was performed. If the maximum possible radon exhalation is considered, the dose due to exhaled radon can be higher than dose due to ^{226}Ra in building material for factor of 6.58, and for superficial material even higher – 9.22. For instance, in the case of one sand sample with the ^{226}Ra concentration 157 Bqkg^{-1}, the annual effective dose for inhabitants due to external exposure to ^{226}Ra is 533 Sv per year, while the maximum estimation of the internal effective dose due to exposure to exhaled ^{222}Rn from this sample is 3484 Sv per year. Gamma index is defined in such way that the effective dose of inhabitants due to exposure to radionuclides in building materials should not exceed 1 mSv per year. In the mentioned case the activity of radium of 157 Bqm^{-3} in the sand easily fit the requirement of gamma index, whereby the effective dose due to exhaled radon (direct progeny of the very same radium in the sand) may exceed 3 mSv per year, which is three times more than the gamma index allows.

The granite and the marble are used as superficial materials (wall and floor covering tiles, boards

Table 6. Comparison of external dose due to ^{226}Ra content in building material and internal dose due to ^{222}Rn exhaled from the same material

Material	Maximum potential dose due to ^{222}Rn exhalation [Sv]	Corresponding ^{226}Ra annual dose [Sv]	Corresponding ^{226}Ra activity [Bqkg^{-1}]	Ratio between ^{222}Rn and ^{226}Ra doses	
				Min	Max
Cement (in concrete)	607	93	82	0.01	6.58
Cement (in aerated concrete)	619	93	82	0.08	4.64
Sand (in concrete)	3484	533	157	0.01	6.57
Marble	148	36	48	0.03	4.14
Granite	2152	234	311	0.04	9.22

Table 7. Estimated effective dose due to radon (internal dose) exhaled from investigated granite sorted by country of origin

Country	Number of samples	Internal effective dose [Sv]	
		Median	Max
Bosnia and Herzegovina	11	104	735
Greece	37	211	2022
Croatia	6	396	650
India	4	78	78
Italy	51	331	1404
South Africa	49	117	351
China	10	156	598
Cypress	6	188	1020
Germany	5	299	585
Switzerland	6	143	201

etc.) for which the gamma index value is six for dose criterion of 1 mSv [2]. This means effectively that the concentration of ^{226}Ra of 1800 Bqkg^{-1} corresponds to 1 mSv per year in superficial materials. Useful data regarding the exhalation rates for a number of granite types used in Serbia can be found in [35]. The radon exhalation from granite is calculated for 3 cm thick tiles and the estimated effective dose due to exposure of inhabitants to radon (internal dose) exhaled from granite investigated in this study, sorted by country of origin, are presented in tab. 7. Since some of the measured samples contained lower quantities of ^{226}Ra than the minimal detectable activity, maximum and median values are presented.

CONCLUSIONS

The specific activities of ^{226}Ra, ^{232}Th, and ^{40}K were measured in bentonite, cement, granite, marble and sand samples, using gamma spectrometry. In general, the highest values were measured in granite samples and in some samples of cement. Accordingly, the greatest radiation risks were associated with these samples. Measured specific activities were comparable with those given in the literature for other countries.

The results may be important from the point of view of selecting suitable materials for building construction.

The radium equivalent activities ranged from 29.4 Bqkg^{-1} to 1694 Bqkg^{-1}, in sand and granite, respectively. For 18 samples in total, values for $R_{a\mathrm{eq}}$ exceeded the limit of 370 Bqkg^{-1} set in [1, 34].

The estimated indoor gamma dose rate in air was found to vary from 25 nGyh^{-1} up to 1329 nGyh^{-1}, which was higher than European average of 70 nGyh^{-1} for a great number of measured samples. The annual effective dose ranged from 0.12 mSv up to 6.51 mSv and exceeded limits of 0.41 mSv [1] for a significant number of samples.

The values of external hazard index, H_{ex} for building materials that had been investigated ranged from 0.053 up to 4.908, and exceed limits (>1) for three samples of cement, eight samples of granite, and one sand sample.

The present study shows that some of the measured construction materials could pose significant source of radiation hazard, considering the values of assessed doses and gamma indices. If the materials investigated in this paper are used as raw materials, it should be noted what is their fraction in the final product which is used as construction material. Also, materials with high content of radionuclides should be used in final construction material in sufficiently low percentage in order to avoid enhanced radiological hazard.

Previous consideration was related to external exposure, but the internal exposure due to radon inhaling was also taken into consideration. Influence of the radon exhaling from building materials on effective dose was estimated.

The radon exhalation was estimated using the parameters given in literature. It is implied that an internal dose due to exhaled radon can exceed the dose due to external exposure to ^{226}Ra content in building materials, especially in the case of superficial materials like granite.

Two important conclusions regarding the radon exhalation from building materials must be emphasized as follows.

The internal dose due to exposure to the exhaled radon from a building material can exceed several times the external dose from the ^{226}Ra from the same building material.

The radon exhalation estimation using the exhalation parameters from the literature is not reliable, since the estimation gives an interval spreading to two orders of magnitude.

This implies that in the cases of higher radium content in building materials, although within the allowed limits, the radon exhalation should be measured directly. The limit of the ^{226}Ra content at which the exhalation measurement should be conducted have to be determined carefully, in principle, based on a wider scale of measurements of different building materials. Furthermore, the average ventilation rate in a given country or a region should be considered.

The measured values of parameters relevant to the radon exhalation are distributed within relatively wide intervals (see tab. 2). Some parameters vary for more than order of magnitude. This suggests that use of default values of these parameters in dose estimation should be applied carefully.

Results presented in this paper give an assessment of radiological risks originated from building materials, as well as comparison between external doses due to presence of gamma emitting radionuclides in building materials and internal doses due to radon exhaled from these materials. Results show that none of these two aspects should be neglected in radiological risk assessments.

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AUTHORS' CONTRIBUTIONS

I. S. Vukanac, M. M. Janković, and J. D. Krneta Nikolić wrote the main part of the manuscript. M. M. Rajačić, D. J. Todorović, and J. D. Krneta Nikolić conducted the measurements presented in this paper. The P. N. Ujić provided the calculations necessary for the radon exhalation rate. The G. K. Pantelić and N. B. Sarap provided the proof reading of the manuscript and checked all the data and also contributed to writing of the manuscript. The J. D. Krneta Nikolić served as a corresponding coauthor.

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ПРОЦЕНА НИВОА ПРИРОДНЕ РАДИОАКТИВНОСТИ И ЈАЧИНЕ ЕКСХАЛАЦИЈЕ РАДОНА ИЗ ГРАЂЕВИНСКОГ МАТЕРИЈАЛА

Различите врсте увозног грађевинског материјала који се користи у грађевинарству и индустрији у Србији, испитивани су гама спектрометријом. На основу измерених концентрација ^{226}Ra, ^{232}Th и ^{40}K у испитиваним узорцима, одређена је радијум еквивалентна активост Ra_{eq}, јачина апсорбована дозе $\dot{D}$, годишња ефективна доза D_{E} и екстерни хазард индекс H_{ex} у циљу процене радијационог ризика за грађанство. Ra_{eq} је за већину анализираних узорака (од укупно 416) био испод максималне дозвољене границе од 370 Bqkg^{-1} дефинисане у UNSCEAR извештају. Јачина апсорбоване дозе у ваздуху је варирала од 0.030 Gyh^{-1} до 1.328 Gyh^{-1} што је у неким случајевима било изнад вредности измерених у европским земљама. У случају око 5 % мерених узорака, измерене вредности за годишњу ефективну дозу прелазе границу од 0.41 mSv дефинисану у литератури, док су вредности H_{ex} биле изнад 1 за три узорка цемента, осам узорака гранита и један узорак песка.

Ексхалација радона из грађевинског материјала, као потенцијални узрок повишене ефективне дозе, процењена је на основу параметара дефинисаних у литератури. У неким случајевима, израчунато је да је интерна доза која је последица ексхалације ^{222}Rn из грађевинског материјала, до девет пута виша од екстерне дозе која је последица садржаја ^{226}Ra у узорку.

Кључне речи: природна радиоактивност, јачина ексхалације радона, индекс радијационог ризика, грађевински материјал