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Radiological and material characterization of high volume fly ash concrete

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ABSTRACT

The main goal of research presented in this paper was the material and radiological characterization of high volume fly ash concrete (HVFAC) in terms of determination of natural radionuclide content and radon emanation and exhalation coefficients. All concrete samples were made with a fly ash content between 50% and 70% of the total amount of cementitious materials from one coal burning power plant in Serbia. Physical (fresh and hardened concrete density) and mechanical properties (compressive strength, splitting tensile strength and modulus of elasticity) of concrete were tested. The radionuclide content (^{226}Ra, ^{232}Th and ^{40}K) and radon massic exhalation of HVFAC samples were determined using gamma spectrometry. Determination of massic exhalation rates of HVFAC and its components using radon accumulation chamber techniques combined with a radon monitor was performed. The results show a beneficial effect of pozzolanic activity since the increase in fly ash content resulted in an increase in compressive strength of HVFAC by approximately 20% for the same mass of cement used in the mixtures. On the basis of the obtained radionuclide content of concrete components the I -indices of different HVFAC samples were calculated and compared with measured values (0.27–0.32), which were significantly below the recommended 1.0 index value. The prediction was relatively close to the measured values as the ratio between the calculated and measured I-index ranged between 0.89 and 1.14. Collected results of mechanical and radiological properties and performed calculations clearly prove that all 10 designed concretes with a certain type of fly ash are suitable for structural and non-structural applications both from a material and radiological point of view.

1. Introduction

1.1. Background

The building industry has one of the largest environmental impacts among all human activities: an annual consumption of 10–11 billion tons of aggregate (Meyer, 2002) and 4.18 billion tons of cement (USGS, 2015). Apart from extremely high resource and energy consumption, cement production is a significant source of CO_2 emissions, accounting for approximately 4.4% of global CO_2 emissions from industry in 2007 (Boden et al., 2010).

There are many ideas that have been proposed to make concrete "greener" and more sustainable but they are all based on two principles: reuse and reduce. Concepts based on the "reduce" principle are oriented towards decreasing cement production based on natural materials and result in a reduction in CO_2 emissions. With respect to the requirements for concrete as the world's most used man-made material, a lower production of Ordinary Portland cement must be compensated with alternative sources of binders in concrete production. There are several industrial sectors which produce significant amounts of residues such as fly ash (FA), bottom ash, red mud, steel slag, nonferrous slag, etc. which can be used for that purpose (Shi et al., 2006).

Millions of tons of FA, a by-product of coal combustion, are being generated annually worldwide (Malhotra, 2002; Coal Ash Facts). Although it has been used as a partial cement replacement for decades, there is an increased pressure to use a higher content of FA in concrete as a result of three main aspects – the economy, environmental and technical benefits. High volume fly ash concrete (HVFAC) is defined as concrete containing more than 50% FA in the total cementitious material's mass (ACI, 2014). Generally, HVFAC

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exhibits good workability, low heat of hydration, low drying shrinkage and enhanced durability related properties compared to ordinary cement concrete (Huang et al., 2013; Malhotra, 2002). However, for all replacement rates, FA generally slows down the setting time and hardening rates of concrete at early ages. However, concrete mixtures with an amount of FA that is equal or greater than the amount of cement can achieve a compressive strength equal to or comparable to concrete without FA (Bouzoubaa and Fournier, 2003; Lam et al., 1998; Poon et al., 2000; Atis, 2005).

The reuse of industrial residue streams can be beneficial from an economical and ecological point of view but mechanical properties of the final product and its effect on human health are cardinal properties to ensure safe inbuilt materials. The utilization of FA in concrete should also be considered from a radiological point of view. As a result of coal combustion the initial radionuclide content of the coal remains and thereby also accumulates in the solid residues, mainly in the bottom ash or coal slag but also in FA. This is the reason why FA belongs to the group of Naturally Occurring Radioactive Materials (NORM), materials which contain an elevated natural radionuclide content. A very large scatter of data for radionuclide content in fly ash can be found between different countries (Nuccetelli et al., 2015) and only limited data can be found for Serbian fly ash (Kisić et al., 2013). Several studies found that the natural radionuclide content in fly ash can be significantly high (Somlai et al., 1999, 2006; Petropoulos et al., 2002; Stojanovska et al., 2010). Therefore, utilization of FA as a supplementary material in cement production can cause a dose contribution to residents as a result of bulk inbuilt of concrete.

The natural radionuclide content of inbuilt building materials can have an effect on human health which can be different from the outdoor value (Sas et al., 2015a; Szabó et al., 2013; Trevisi et al., 2012, 2013). This is the reason why the reduction and limitation of exposure to building materials must meet various radiological conditions, e.g. the I-index for gamma radiation and low radon exhaling capacity (Nuccetelli et al., 2012; Kovler, 2011; Schroeyers, 2015).

The natural isotopes found in building materials can significantly contribute to radiation exposure in two ways, from external and internal exposure. Gamma radiation (extremely high electromagnetic radiation, that ionizes its surroundings and is thus biologically hazardous) released from building materials is responsible for external exposure owing to the presence of terrestrial radioisotopes. In the recently published 2013/59/Euratom Directive (CE, 2014) and in many other national standards regulating the radioactivity of building materials, classification is based on the activity concentration index (I-index), taking into account the total effect of three main natural radionuclides usually present in building materials – ^{226}Ra, ^{232}Th and ^{40}K.

The main contributor to the internal exposure of human beings is radon (^{222}Rn), a radioactive noble gas that originates from the alpha decay of ^{226}Ra. Inhaled radon and its progenies significantly augment the risk of the evolution of pulmonary cancer and it is recognized as the second most relevant risk after smoking (WHO, 2009). It can increase in poorly ventilated areas, such as mines or even in buildings. Generally the underlying soil is the most dominant indoor radon enhancing factor (Szabó et al., 2014) in the case of lower floors or single storey buildings except in extreme cases when the building materials may be the main source (Somlai et al., 1999, 2006). Despite of the elevated level of ^{226}Ra FA has a relatively low emanation coefficient which can be beneficial for HVFAC from a radon exhalation point of view (Kovler et al., 2005).

The reuse of FA from coal burning power plants as part of concrete production will result in a reduction in the environmental impact of concrete by decreasing the amount of deposits in landfills and using waste instead of natural resources for concrete production. It will also enable the management of NORM residues in a more sustainable manner providing respectable physical and mechanical properties of the final product – concrete. However, the relatively high potential gamma exposure and indoor air quality, originating from the enhanced radionuclide content, may increase the risk in the case of human health. For the sustainable utilization of FA in building materials such as concrete, both external and internal radiation exposure should be as low as possible.

1.2. Objectives

The main objective of this study is to provide reliable data regarding the utilization of HVFAC in the building sector both from a material and natural radiation point of view. The global aim of this research is the promotion of HVFAC as a sustainable solution for the construction industry. In order to achieve this aim, the following procedures, measurements and analyses were performed:

1. Design and preparation of concrete mixtures with a FA content between 50% and 70% by mass of the total amount of cementitious materials (the sum of cement and fly ash masses)
2. Measurement of basic physical and mechanical properties of fresh and hardened concrete
3. Determination of the radionuclide content (^{226}Ra, ^{232}Th and ^{40}K) in all solid components of concrete (FA, cement and aggregate) and also in the final product (HVFAC) using gamma spectrometry
4. Determination of massic exhalation rates of HVFAC and its components using radon accumulation chamber techniques combined with a radon monitor
5. Analysis of all investigated materials by means of the I-index as a widely accepted screening tool
6. Analysis of the effect of the amount of FA on radioactivity concentration, radon emanation and exhalation properties of HVFAC

2. Experimental program – description

2.1. Materials and sample preparation

FA used for concrete preparation was obtained from the power plant “Nikola Tesla B” in Obrenovac, Serbia. Its chemical and physical composition fulfills the requirements of EN 450-1:2012 (CEN, 2012), and according to ASTM C618-15 (ASTM, 2015) provisions this fly ash can be classified as Class F type. Two types of commonly used sand and coarse river aggregate with a nominal maximum size of 16 mm were used in this research. The cement used was a commercially available Portland-composite cement CEM II/A-M (S-L) 42.5R supplied from Lafarge. Cement additions with a mass of up to 20% of the total cement mass were grinded slag and limestone. A polycarboxylate ether polymer based superplasticizer was used in some mixtures to enable proper workability. The specific densities of applied materials are presented in Table 1.

Altogether 10 different concrete mixtures were designed and organized into two groups with two different quantities of cement - 200 kg/m^3 and 150 kg/m^3. FA mass varied from 200 kg/m^3 to 400 kg/m^3 in the first group and from 150 kg/m^3 to 350 kg/m^3 in the second group, Table 2. The mass of FA in all mixtures was chosen to be between 50% and 70% of the total mass of cementitious materials. The ID of each sample was given in the form CN_FM_W, where C means cement, N means the mass of cement, F means fly ash, M means the mass of FA and W means the water-to-binder ratio. Concrete was cast in moulds and the standard curing procedure was conducted. In all mixtures, the FA content was equal to or greater than the mass of cement, thus this type of concrete can

Table 1
Specific density for concretes components.

Material	Water	Aggregate			Cement	Superplasticizer	FA
		Sand [0/4]	Coarse [4/8]	Coarse [8/16]			
Specific density [kg/m^3]	1000.0	2573.0	2548.0	2591.0	3040.0	1070.0	2075.0

Table 2
Mixture proportions of all designed concrete mixtures.

ID of concrete sample	Water [kg/m^3]	Quantity of aggregate [kg/m^3]			Cement [kg/m^3]	Superplasticizer [kg/m^3]	Fly ash [kg/m^3]	Slump/Flow [mm]	Specific density of concrete [kg/m^3]
		Sand [0/4][a]	Coarse [4/8][b]	Coarse [8/16][c]					
C200_F200_0.488	195.0	810.5	486.3	324.2	200.0	0.00	200.0	127.0	2218.0
C200_F250_0.433	195.0	748.5	486.3	324.2	200.0	1.00	250.0	148.0	2205.0
C200_F300_0.390	195.0	686.5	486.3	324.2	200.0	1.25	300.0	28.0	2193.3
C200_F350_0.355	195.0	624.5	486.3	324.2	200.0	2.24	350.0	33.0	2218.0
C200_F400_0.325	195.0	562.5	486.3	324.2	200.0	2.00	400.0	700.0[d]	2170.0
C150_F150_0.610	183.0	878.6	527.2	351.4	150.0	0.00	150.0	82.0	2240.2
C150_F200_0.523	183.0	816.6	527.2	351.4	150.0	0.00	200.0	58.0	2228.2
C150_F250_0.458	183.0	754.6	527.2	351.4	150.0	0.00	250.0	83.0	2216.2
C150_F300_0.407	183.0	692.6	527.2	351.4	150.0	0.33	300.0	40.0	2204.5
C150_F350_0.366	183.0	630.6	527.2	351.4	150.0	1.13	350.0	585.0[d]	2193.3

[a] Fine aggregate, size 0–4 mm.
[b] Coarse aggregate, size 4–8 mm.
[c] Coarse aggregate, size 8–16 mm.
[d] Flow values.

be classified as High Volume FA Concrete.

The 100 mm concrete cubes were cast for compressive strength testing. The 150 × 150 mm cylinders were cast for splitting tensile strength testing and 150 × 300 mm cylinders for testing the modulus of elasticity. Upon completion, the specimens were exposed to the standard curing procedure (CEN, 2009) which meant covering them with wet fabric and storing in a casting room at 20±2 °C for the first 24 h. Samples were demoulded and put in a water tank for 28 days after which mechanical properties were tested.

Radiological characterization was performed on all 10 concrete samples but also on their components – three fractions of aggregate, cement and fly ash. All samples were dried in an drying oven for 24 h at 105 °C to remove moisture and achieve constant weight. Concrete components and the solidified HVFAC samples were grinded and sieved through a mesh containing holes 5.0 mm in diameter. Approximately 500–700 g of sample prepared in this way was put into air-tight aluminium Marinelli beakers, weighed and enclosed for 30 days.

2.2. Determination of the radionuclide content by gamma spectrometry

To obtain the radionuclide content, a (HPGe) semiconductor detector (ORTEC GMX40-76), with an efficiency of 40% and energy resolution of 1.95 keV at 1332.5 keV was used. The data and spectra were recorded using an ORTEC DSPEC LF 8196 MCA. The ^{226}Ra concentration values were determined after 30 days (necessary to reach a secular equilibrium state between ^{226}Ra and ^{222}Rn) by measuring the gamma lines of its decay products, ^{214}Pb (295 and 352 keV) and ^{214}Bi (609 and 1120 keV) under an equilibrium state. The ^{40}K was measured using the 1461 keV gamma ray, while the ^{232}Th was measured using the 911 keV gamma ray of ^{228}Ac and ^{208}Tl using the 583 keV and 2614 keV gamma rays. To calculate the activity concentration the obtained spectra were compared with a certified reference material (IAEA-327 soil sample) (IAEA, 2003). The sample measuring time varied between 60,000 and 80,000 s.

2.3. Determination of massic exhalation and emanation rates

Radon exhalation is the radon activity that diffuses per unit of time from a material to the surrounding air, in Bq s^{-1} defined by NEN-ISO 11665-9:2016 en (NEN-ISO 11665-9:2016). The radon exhalation rate can be related either to the area of exhaling surfaces or the mass of the sample. If the exhalation is related to the surface - the areic exhalation rate (radon flux Bq m^{-2} s^{-1}) can be calculated. On the other hand, when the radon exhalation rate is related to mass - the massic exhalation rate (Bq kg^{-1} s^{-1}) is obtained. Generally, the diffusion length in the case of porous materials is greater than 40 cm (Keller et al., 2001; Mujahid et al., 2005). Owing to this fact, if the sample thickness is extremely low compared with the diffusion length of radon, all the emanated radon can exhale from the matrix. This means the geometry of the sample has no effect on the sample. Only the amount of the sample, its ^{226}Ra content and emanation factor determine its radon exhalation rate. Under those conditions the massic radon exhalation rate can be obtained (Kovler et al., 2005). Therefore, the concrete samples were prepared in the way that eliminated the problem with thickness and diffusion length, and enabled the use of massic exhalation as an acceptable method.

HVFAC samples and its components were enclosed in air-tight radon accumulation chambers. Before measurements, the chambers were purged with radon-free N_2 gas prior to the accumulation to reduce the initial radon concentration to zero (Sas et al., 2015b). The accumulation time ranged between 2 and 5 days. Following that period, the radon increment in the accumulation chamber was measured by a professional Alpha GUARD PRO type radon monitor (Fig. 1). The sampling process lasted 10 min with an air flow of 1.0 dm^3 h^{-1} to ensure homogenous radon conditions in the entire sampling volume. After circulation had ceased there was also thoron (^{220}Rn) – originating from the ^{232}Th content of the samples – in the detector chamber, which cannot be distinguished by the PIC (Pulse Ionization Chamber) detector. Owing to its short half-life (55.6 s), a waiting time of 10 min is enough for the thoron to decay. The radon concentration was obtained after the atmosphere had become thoron-free in the detector chamber. The method is described in detail in a previous publication (Sas et al., 2015b). The radon exhalation rate in terms of mass can be calculated by Eq. (1) (Sas et al., 2015b):


Fig. 1. Alpha GUARD PRO type radon monitor.

$$E_{Mass} = \frac{C_t \cdot V}{m \cdot t} \cdot \frac{\lambda \cdot t}{1 - e^{-\lambda t}} \quad (1)$$

where:

- C_t = accumulated radon concentration in the measurement kit during sampling [Bq m^{-3}]
- E_{Mass} = massic exhalation rate [mBq kg^{-1} h^{-1}]
- t = accumulation time [h]
- V = volume of the accumulation kit [m^3]
- m = mass of the sample [kg]
- λ = decay constant of radon [h^{-1}]

The emanation factor (ε) is defined as the ratio of ^{222}Rn atoms that escape from the sample matrix into the pore space and total ^{222}Rn atoms that are produced in the sample matrix (Sahoo et al., 2007). The equilibrium radon activity can be calculated using the following formula:

$$A_\infty = \frac{C_t \cdot V}{1 - e^{-\lambda t}} \quad (2)$$

where:

- A_∞ = equilibrium radon activity [Bq]
- C_t = accumulated radon concentration in the measurement kit during sampling [Bq m^{-3}]
- t = accumulation time [h]
- V = volume of the accumulation kit [m^3]
- λ = decay constant of radon [h^{-1}]

3. Results and discussion

3.1. Fresh concrete properties

The investigation of the workability of concrete was conducted by a standard slump test and a flow table test for mixtures that had slump values higher than 20 cm. Lower slump values were obtained for concrete mixtures with higher amounts of FA. In the group of mixtures with 200 kg/m^3 of cement, mixtures with 300 kg/m^3 and 350 kg/m^3 of FA resulted in slump which can be categorized as of class S1 according to EN 206-1:2013 (CEN, 2013), while the mixtures with 200 kg/m^3 and 250 kg/m^3 of FA belong to the S3. In the group of mixtures with 150 kg/m^3 there was one mixture in slump category S1 (with 300 kg/m^3 of FA) and three in category S2 (with 150, 200 and 250 kg/m^3 of FA). The consistency of the two mixtures with the highest content of FA and lowest water-to-binder ratio, one from each group (C200_F400_0.33 and C150_F350_037) was quite different from the others. These mixtures were very dry during mixing but became very liquid after a superplasticizer was added in the amount of about 1% of cement mass. Apart from that, thixotropic behaviour was observed during the preparation and testing of these two mixtures. During mixing in the pan they were movable while afterwards they exhibited surface hardening. The observed behaviour is similar to the behaviour of alkali-activated fly ash concrete with dense, sticky but workable mixtures. There were only slight differences in fresh concrete densities up to 5.5% for all 10 concrete mixtures. They were all between 2230 kg/m^3 and 2355 kg/m^3, similar to the density of ordinary concrete. These results showed that it was possible to make workable HVFAC with a suitable fresh density, but in the case of very high FA content and low water-to-binder ratio, a careful choice of the amount of superplasticizer is necessary.

3.2. Hardened concrete properties

Physical and mechanical properties of hardened HVFAC are presented in Table 3. Oven-dry densities of all concretes were between 2244 kg/m^3 and 2352 kg/m^3. All designed HVFACs can be classified as normal-weight concrete as they meet EN 206-1:2013 (CEN, 2013) requirements. Obtained compressive strength values for 2 concrete mixtures prepared with 200 kg/m^3 of cement satisfy requirements for classes C30/37 while the other 3 can be classified as class C25/30. In the group of concretes made with 150 kg/m^3 of cement, 2 out of the 5 concretes can be classified as class C20/25 while the other 3 belong to class C16/20, according to EN 1992-1-1:2005 (CEN, 2005) provisions. By comparing HVFAC mixtures of the same FA content, higher compressive strengths were observed in concrete mixtures with greater cement contents of between 33% and 56%. Within the group of concretes with the same amount of cement, compressive strength increases by up to 20% as FA content increases. The correlation is not very strong but the trend is obvious. This can be explained as a consequence of a ‘filler’ effect of FA, resulting in a more compact structure of the concrete matrix.

No reliable correlation between the obtained values for splitting tensile strength and FA content in HVFAC can be found, Table 3. A relatively large scatter of results can be seen, between 2 MPa to 3.7 MPa in the first and between 2.3 MPa and 3.2 MPa in the second group of concretes. With the exception of C200_F400_0.325, the absolute values of splitting tensile strength in the group of concretes prepared with 200 kg/m^3 of cement satisfy requirements for at least class C25/30 EN 1992-1-1:2005 (CEN, 2005). A possible reason for such a low tensile splitting strength of mixture C200_F400_0.325 is its very pronounced tixotropic behaviour and hard concrete placement into moulds that could cause insufficient compacting of concrete. The group of concretes made with 150 kg/m^3 of cement meets the requirements for at least class C20/25.

There were negligible differences in the modulus of elasticity within the group of HVFACs with the same cement content. Generally, an average value of the modulus for concrete in the first group was 32.2 GPa while for the second one it was 30.2 GPa which is 6.5% lower. All concretes with higher cement content meet the requirements for concrete class C25/30, while concretes with a lower cement content can be used as class C20/25 EN 1992-1-1:2005 (CEN, 2005).

Results of testing hardened properties testing proved that it is possible to produce HVFAC with properties sufficient for structural applications, comparable and competitive with ordinary concrete.

3.3. Natural radionuclide content of samples determined by gamma spectrometry

The measured activity concentrations of concrete components and all HVFAC samples are presented in Table 4.

I-indexes of prepared HVFAC samples were calculated from the measured activity concentrations in Bq/kg of ^{226}Ra ($C_{Ra\text{-}226}$), ^{232}Th ($C_{Th\text{-}232}$) and ^{40}K ($C_{K\text{-}40}$), using Equation (3):

$$I = \frac{C_{Ra-226}}{300} + \frac{C_{Th-232}}{200} + \frac{C_{K-40}}{3000}\,[-] \quad (3)$$

The I-indices value of 1 can be used as a conservative screening tool for identifying materials that, during their use, would cause doses exceeding the reference level of 1 mSv per year for building materials laid down in Article 75(1) of the 2013/59/EURATOM council directive (CE, 2014).

The obtained results show that the ^{40}K content in aggregate samples was approximately 30% higher than in the case of other components (cement and FA), Table 4. However, it was below the value which is considered as the average activity concentration of ^{40}K for aggregate in the European Union (EU), Table 5. As expected, the potassium content of the produced concrete samples was between the values of the component material. The ^{226}Ra content was under the detection limit (DL) in the aggregate samples. Compared to the cement samples, FA had a 36% higher ^{226}Ra activity concentration. The obtained results of the current study show that the used cement has a slightly higher radionuclide content than its average value for EU countries, Table 5. The ^{40}K, ^{226}Ra and ^{232}Th content of the examined Serbian FA samples were relatively low compared to the data from a different database, Table 5. Activity concentrations of all three isotopes were below the average value for EU samples while the ^{226}Ra content was even below the lower boundary of the range for USA samples.

Regarding the final product – concrete, measured activity concentrations of all three radionuclides in all ten concrete mixtures were below the average values in the databased presented by Trevisi et al. (2012), Table 5. Radionuclide content increase in the case of 150 kg/m^3 (HVFAC_150) and 200 kg/m^3 (HVFAC_200) mixtures as FA content increased, for ^{226}Ra and ^{232}Th. The increments of ^{226}Ra and ^{232}Th activity concentrations and obtained I-indexes of different mixtures can be seen as a function of FA content in Fig. 2.

Table 4
Activity concentration and calculated I-indices of investigated samples.

ID of sample	^{40}K		^{226}Ra		^{232}Th		I-index
	Bq/kg	±	Bq/kg	±	Bq/kg	±	
Aggregate	311	41	<DL[a]	<DL[a]	24	9	
Cement	230	35	66	24	29	10	
Fly ash (FA)	240	36	90	28	66	19	
C200_F200_0.488	247	36	27	15	22	11	0.28
C200_F250_0.433	249	37	28	15	23	11	0.29
C200_F300_0.390	239	36	29	15	24	11	0.29
C200_F350_0.355	239	36	34	17	27	12	0.33
C200_F400_0.325	248	37	31	16	27	13	0.32
C150_F150_0.610	229	35	20	13	18	10	0.23
C150_F200_0.523	247	36	22	13	21	11	0.26
C150_F250_0.458	235	36	28	15	25	12	0.29
C150_F300_0.407	255	37	33	16	28	13	0.33
C150_F350_0.366	248	37	32	16	27	13	0.33

[a] Detection limit.

Table 5
Average activity concentration in concrete and concrete components.

Material	^{40}K [Bq/kg]	^{226}Ra [Bq/kg]	^{232}Th [Bq/kg]
Cement[b]	216 (4–846)[a]	45 (4–422)[a]	31 (3–266)[a]
Aggregate[b,c]	333 (3–1700)	21 (1–210)	24 (1–370)
Fly ash in the EU[d]	546 (301–1049)	207 (27–750)	80 (14–130)
Fly ash in the USA[e]	- (100–1200)	(100–600)	(30–300)
Concrete[b]	392 (7–1450)	60 (1–1300)	35 (1–152)

[a] Minimum and maximum values are given in brackets.
[b] European Union countries, Trevisi et al., 2012.
[c] Sedimentary origin.
[d] European Union countries, Nuccetelli et al., 2015.
[e] IAEA, 2003.

For that purpose, the ^{40}K, ^{226}Ra and ^{232}Th activity concentrations and I-indices of all HVFAC samples were calculated from the measured activity concentrations of the concrete components taking into account their mass portion in a concrete mass of unit volume (Table 4). An example for calculating the ^{226}Ra activity concentrations in concrete is given below:

$$C^{calc.}_{Ra-226}(C) = C^{meas.}_{Ra-226}(FA)\cdot\frac{m(FA)}{\gamma(C)} + C^{meas.}_{Ra-226}(A)\cdot\frac{m(A)}{\gamma(C)} + C^{meas.}_{Ra-226}(CM)\cdot\frac{m(CM)}{\gamma(C)} \quad (4)$$

where C, A and CM are designations for concrete, aggregate and cement, respectively, while γ is the hardened concrete density.

Afterwards, calculated values of activity concentrations and I-indices derived from these results were compared to the measured activity concentration and I-indices of the analysed HVFAC samples, Table 6.

The comparison of measured and calculated values of activity concentrations for ^{40}K and ^{232}Th leads to the conclusion that the calculated values were always 6% and 11% higher (on average), respectively, than the measured ones. Calculated values for the activity concentrations of ^{226}Ra were always 10–30% lower than measured values. However, the I-indices obtained from calculated

Table 3
Hardened physical and mechanical properties of HVFAC.

ID of concrete sample	Hardened concrete density (kg/m^3)	Compressive strength (MPa)	Splitting tensile strength (MPa)	Modulus of elasticity (GPa)
C200_F200_0.488	2303	34.2	2.9	31.3
C200_F250_0.433	2295	38.2	2.7	32.1
C200_F300_0.390	2244	36.7	2.9	31.8
C200_F350_0.355	2268	42.0	3.7	33.2
C200_F400_0.325	2255	40.2	2.0	32.7
C150_F150_0.610	2352	24.3	2.5	29.0
C150_F200_0.523	2313	25.7	2.3	31.9
C150_F250_0.458	2316	24.5	3.1	30.0
C150_F300_0.407	2291	26.8	2.9	30.1
C150_F350_0.366	2283	29.8	3.2	30.2

Table 6
Comparison of measured and theoretically calculated activity concentration of investigated samples.

ID of sample	^{40}K [Bq/kg]		Calculated/measured	^{226}Ra [Bq/kg]		Calculated/measured	^{232}Th [Bq/kg]		Calculated/measured	I - index		Calculated/measured
	Meas.	Calc.		Meas.	Calc.		Meas.	Calc.		Meas.	Calc.	
C200_F200_0.488	247	260	1.05	27	21	0.76	22	25	1.14	0.28	0.28	0.99
C200_F250_0.433	249	257	1.03	28	22	0.80	23	26	1.13	0.29	0.29	1.00
C200_F300_0.390	239	260	1.09	29	25	0.85	24	27	1.14	0.30	0.31	1.03
C200_F350_0.355	239	254	1.06	34	26	0.77	27	28	1.03	0.33	0.31	0.95
C200_F400_0.325	248	252	1.02	31	28	0.90	27	29	1.07	0.32	0.32	1.00
C150_F150_0.610	229	262	1.14	20	17	0.87	18	24	1.33	0.23	0.27	1.14
C150_F200_0.523	247	264	1.07	22	19	0.88	21	25	1.20	0.26	0.28	1.07
C150_F250_0.458	235	261	1.11	28	21	0.75	25	26	1.04	0.30	0.29	0.97
C150_F300_0.407	255	261	1.02	33	23	0.70	28	27	0.97	0.34	0.30	0.89
C150_F350_0.366	248	259	1.05	32	25	0.78	27	28	1.04	0.32	0.31	0.96
Average Calc./Meas.			1.06			0.81			1.11			1.00

radionuclide contents were very close to the I-indices calculated from the measured activity concentrations. In the group of concretes with higher cement content, differences between calculated and measured based values of I-indices are within 5%. A larger scatter of these results is observed in the group of concretes with 150 kg/m^3 of cement and increases up to 14% on the conservative side and up to 11% on the underestimate side. These differences can be explained by the extraordinarily low radionuclide content of the used aggregates and also by the sensitivity of the detector. Another reason for disagreement between measured and calculated values most likely originates from uncertainties of the mass portion of components in the total mass of particular concrete samples.

A combination of mechanical property and natural radiation results of radiological analysis leads to the conclusion that an increase in FA content in concrete ensures increased compressive strength but at the same time higher I-indices. This means that despite the beneficial effect of FA on mechanical properties, the risk originating from the gamma dose caused by the elevated radionuclide content of FA requires a survey of concrete components especially FA. However, obtained I-indices for all concrete mixtures are significantly lower than the recommended limit value (1.0) which enables the utilization of HVFAC without any elevated gamma radiation exposure to residents.

However, the accuracy of the measured value of the ^{226}Ra activity concentration can be slightly disputable due to the extraordinarily low radionuclide content of the aggregate. It can be stated that the calculation of the radionuclide content of mixtures from the results of the component materials is suitable for predicting the radionuclide content and I-indices of the final concrete products.

According to these results, HVFACs based on the analysed type of FA in amounts up to 400 kg/m^3 can be widely used as building materials, both for indoor and outdoor applications and for structural as well as for non-structural use.

Table 7
Massic exhalation rate and emanation factor of investigated samples.

ID of sample	Massic exhalation rate		Emanation	
	mBq kg^{-1} h^{-1}	±	%	±
Aggregate	6	2	<DL[a]	<DL[a]
Cement	32	2	6	1
Fly ash (FA)	15	4	2	1
HVFAC_200_200_0.488	30	4	14	3
HVFAC_200_250_0.433	31	5	15	5
HVFAC_200_300_0.390	29	5	13	4
HVFAC_200_350_0.355	32	5	12	4
HVFAC_200_400_0.325	28	5	12	4
HVFAC_150_150_0.610	29	5	19	5
HVFAC_150_200_0.523	37	6	22	6
HVFAC_150_250_0.458	33	5	16	5
HVFAC_150_300_0.407	38	5	15	4
HVFAC_150_350_0.366	29	5	12	4

[a] Detection limit.

3.4. Exhalation measurement

The obtained massic exhalation rate of the investigated samples is listed in Table 7. The obtained massic exhalation rate was the lowest in the case of aggregate samples. Despite the relatively high ^{226}Ra content of the FA the measured exhalation rate was only 15 ± 4 mBq kg^{-1} h^{-1}. The emanation coefficient of aggregate samples could be calculated due to the very low ^{226}Ra activity concentration which was under the detection limit. In the case of FA the emanation factor was only 2%, which explains the very low massic exhalation rate of FA. This fact is not unusual since the applied heating temperature used in coal combustion power plants has a great effect on internal structural conditions since it reduces the amount of open pores in FA grains.

In spite of the relatively low ^{226}Ra content of the prepared HVFAC samples the obtained massic exhalation results were higher than in the case of concrete ingredients. This can be explained by the different microstructure of concrete samples that formed as a result of the chemical transformation of ingredients. Although the porosity features were not studied in this research previous studies have proven that a significant correlation can be found between the nanopores and radon emanation features (Sas et al., 2015b).

The obtained emanation factors for concrete were 2–3 times higher compared to the results for cement, which had the highest emanation factor as a concrete component. It can be stated that the preparation process of concrete clearly changes (increases) the massic exhalation rate of the applied ingredients. However the measured exhalation rates as a function of the FA content exhibited no significant changes (Table 7). A strong correlation was found between the content of FA and the obtained emanation features (Fig. 3). The radon emanation has a decreasing tendency with the increase of FA content for all mixtures in spite of the increasing ^{226}Ra activity concentration. This phenomenon can be explained by the increasing amount of FA which posseses a lower emanation factor compared to cement.

A correlation was observed between the water-to-binder ratio and the emanation factor, as illustrated in Fig. 4. According to this diagram, the emanation coefficient increases as the water-to-binder ratio increases. In general, the total porosity of concrete increases with the increase of the water-to-binder ratio (Neville, 1995; Lafhaj et al., 2006, Volz et al., 2012). However, increased total porosity does not necessarily imply that radon emanation increases (Ulbak et al., 1984) as the radon emanation is mainly affected by nanoporosity of the prepared concrete (Sas et al., 2015b). The pore size distribution was not within the scope of the

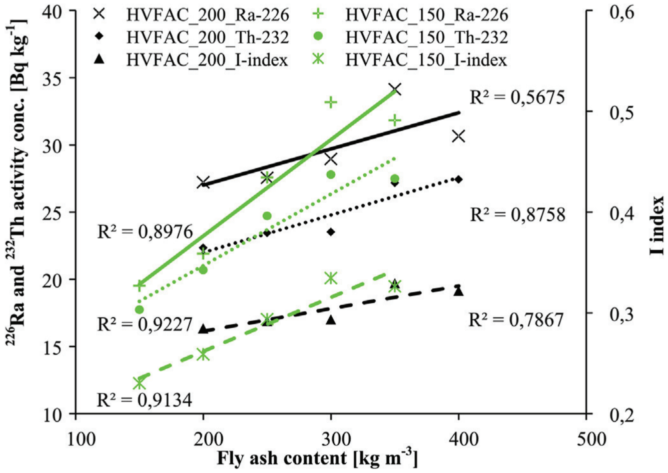

Fig. 2. Activity concentration of HVFAC as a function of the amount of used FA.

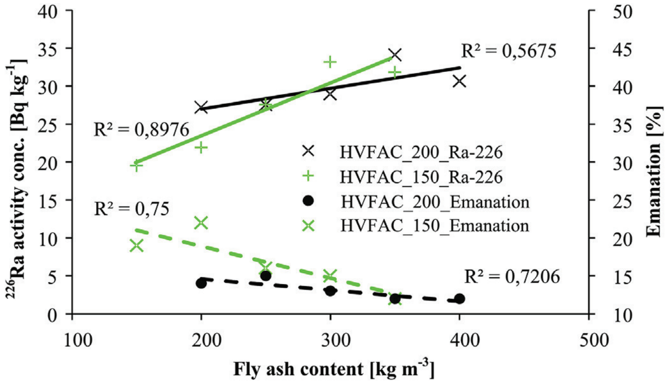

Fig.3. Massic exhalation rate of HVFAC and emanation coefficient as a function of FA content.

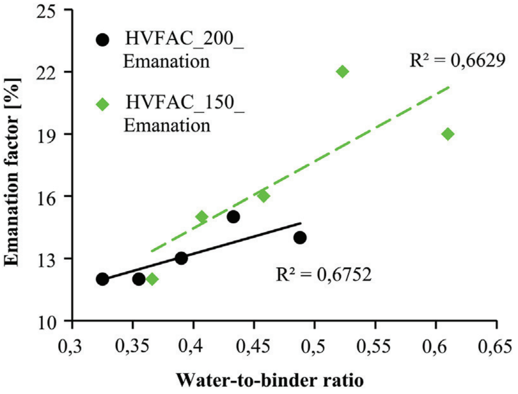

Fig.4. Emanation factor of HVFAC concretes as a function of the water-to-binder ratio.

current study and its influence on the emanation coefficient will be studied in the future work.

4. Conclusions

The objective of this work was the investigation of physical, mechanical and radiological properties of HVFAC made with different amounts of fly ash from one Serbian coal burning power plant. Based on the presented results and discussion, the following conclusions can be drawn:

- Testing of physical and mechanical properties showed that the designed HVFAC can be used both for structural and non-structural applications.
- Compressive strength of HVFAC increases by approximately 20% as the FA content increases from 50% to 70% of the mass of total cementitious materials.
- The natural radionuclide content of ^{226}Ra, ^{232}Th and ^{40}K in all solid components (aggregate, cement and FA) for all concrete samples was significantly lower than the recommended limit value for the I-index of 1.0. As a result, the investigated FA from a Serbian coal burning power plant does not require any restrictions on the amount for HVFAC production from a radiological point of view.
- The ^{226}Ra activity concentration of the investigated FA was 90 Bq/kg, which was the highest value among all investigated components. As the FA content in the HVFAC samples increased, an increase in the I-index was observed.
- Differences in the I-index for HVFAC obtained from measured activity concentrations of concrete and calculated from the activity concentrations of solid concrete components were within 5% for higher cement content mixtures and within 14% for lower cement content mixtures. Generally, the I-index of the final product (HVFAC) can be predicted from the activity concentrations of the concrete components with acceptable accuracy.
- The massic exhalation features of the studied HVFAC samples were nearly constant in spite of the increase in FA (and its ^{226}Ra) content due to the decreasing emanation factor of the final products.
- Generally, an increase of the water-to-binder ratio in concrete mixtures increased the emanation factor, but further investigation is required to explain this phenomenon.

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