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Abstract: The present paper reports the results of a study on different types of fly ash from Serbian coal burning power plants and their potential use as a binder in alkali-activated concrete (AAC) depending on their radiological and mechanical properties. Five AAC mixtures with different types of coal burning fly ash and one type of blast furnace slag were designed. Measurements of the activity concentrations of 40K, 226Ra and 232Th were done both on concrete constituents (fly ash, blast furnace slag and aggregate) and on the five solid AAC samples. Experimental results were compared by using the activity concentration assessment tool for building materials - the activity concentration index I, as introduced by the EU Basic Safety Standards (CE, 2014). All five designed alkali-activated concretes comply with EU BSS screening requirements for indoor building materials. Finally, index I values were compared with the results of the application of a more accurate index - I(□d), which accounts for thickness and density of building materials (Nuccetelli et al., 2015a). Considering the actual density and thickness of each concrete sample index - I(□d) values are lower than index I values.
As an appendix, a synthesis of main results concerning mechanical and chemical properties is provided.

ALKALI-ACTIVATED CONCRETE WITH SERBIAN FLY ASH AND ITS RADIOLOGICAL IMPACT

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Highlights

- Fly ash from the five Serbian power plants comply with EU BSS requirements for building materials
- The radioactivity contribution of aggregates has to be taken into account
- Estimate the index I of final product from the activity concentration of its constituents is a reliable procedure
- Analysed AAFASC concretes can be safely used from the radiological point of view

ALKALI-ACTIVATED CONCRETE WITH SERBIAN FLY ASH AND ITS RADIOLOGICAL IMPACT

Abstract

The present paper reports the results of a study on different types of fly ash from Serbian coal burning power plants and their potential use as a binder in alkali-activated concrete (AAC) depending on their radiological and mechanical properties. Five AAC mixtures with different types of coal burning fly ash and one type of blast furnace slag were designed. Measurements of the activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th were done both on concrete constituents (fly ash, blast furnace slag and aggregate) and on the five solid AAC samples. Experimental results were compared by using the activity concentration assessment tool for building materials - the activity concentration index I, as introduced by the EU Basic Safety Standards (CE, 2014). All five designed alkali-activated concretes comply with EU BSS screening requirements for indoor building materials. Finally, index I values were compared with the results of the application of a more accurate index - I(ρd), which accounts for thickness and density of building materials (Nuccetelli et al., 2015a). Considering the actual density and thickness of each concrete sample index - I(ρd) values are lower than index I values.

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Keywords

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1. Introduction

The construction industry is facing great challenges in directing its activities towards sustainable development. Environmental protection, use of waste and recycled materials and reducing the use of non-renewable resources have become the focus of current research in the field of building materials. However, the European Commission with the 2013/59/EURATOM directive (CE, 2014) considered building materials emitting gamma radiation as within the scope of the directive: so, it introduced a reference level for indoor gamma radiation emitted from building materials and requirements on the recycling of residues from industries processing naturally-occurring radioactive materials into building materials. In particular, a reference level of 1 mSv per year, as an effective dose from indoor external exposure to gamma radiation has been fixed. At this scope, for building materials being of concern from a radiation protection point of view (see the indicative list in the Annex XIII of the directive) (CE, 2014), the activity concentration of natural radionuclides (^{40}K, ^{226}Ra and ^{232}Th) has to be determined, as required in Article 75(2). Moreover, to identify "materials that may cause the reference level laid down in Article 75(1) to be exceeded", the activity concentration index I -as conservative screening tool- has been introduced. The activity concentration index I is given by the following formula:

$$I = \frac{C_{226Ra}}{300} + \frac{C_{232Th}}{200} + \frac{C_{40K}}{3000} \qquad (1)$$

where C_{226Ra}, C_{232Th} and C_{40K} are the activity concentrations in Bq/kg of natural radionuclides in building material.

It has to be noted that building materials, being of concern from a radiation protection point of view, should be also regarded as "construction products" as defined in Regulation (EU) No 305/2011 (CE, 2011). Indeed, building materials - among several basic requirements - have not to be a threat for inhabitants and construction workers concerning "the emission of dangerous radiation". Therefore, it is important to account for the provisions of both two legislations when the building materials are placed on the market. Largely used bulk building materials - as concrete – can be made of many constituents, so the activity concentrations of natural radionuclides in the final building material derive from the contribution -in terms of radioactivity- of each constituent.

Furthermore, about materials incorporating residues from industries processing naturally-occurring radioactive materials (NORM), the radiological contribution of NORM residues (in terms of the activity concentration of natural radionuclides) could be assessed separately or in the final building material considering appropriate partitioning factors.

There is a big effort to develop tailor made building materials -as concrete- which takes into account environmental protection and reducing the use of non-renewable resources with health protection issues. This global aim can be reached with the development of inorganic alumino-silicate polymers synthesized starting from by-product materials rich in silicon and aluminium, which can be used instead of cement for concrete production. There are several NORM residues that have potentials to fulfill these requirements such as fly ash (FA), different types of industrial slag, red mud etc.: some of them are already utilized for such purposes (Payá et al., 2015; Shi et al., 2006).

In Serbia, about 70% of total electric energy is produced by five coal burning power plants. Consequently, 6 million tons of fly ash, or approxilately 1 ton per capita, are produced per year and about 200 million tons of fly ash are already landfilled (Dragaš et al., 2014). At the moment, only 2.7% of the total fly ash production in Serbia is utilized by the construction industry (Dragaš et al., 2016). The characterization of fly ash and its products will open the possibility for a wide use both outdoors and indoors, as soil stabilization, road sub-base construction and as binder in alkali-activated concrete.

Alkali-activated fly ash concrete (AAFAC) has attracted much interest in academic and commercial spheres over the past decade. Many studies have shown a great potential for use of AAFAC in the construction industry (Shi et al., 2006; van Deventer et al., 2012) and that physical and mechanical characteristics of AAFAC are influenced by many factors: fly ash particle size and chemical composition, fly ash loss on ignition (LOI), type and concentration of alkali activators (Na_2O concentration and SiO_2/Na_2O ratio), temperature and duration of curing (Fernandez-Jimenez et al., 2005; Criado et al., 2005; Kovalchuk et al., 2007; Criado et al., 2010).

Furthermore the utilization of FA in AAFAC has to be carefully studied from a radiation protection point of view because of the enhanced content of natural radionuclides compared to Portland cement. Considering the data about the average content of radionuclides - ^{226}Ra, ^{232}Th and ^{40}K - in raw and final building materials used in the European Union (i.e. cement, fly ash and concrete) (Trevisi et al., 2012; Nuccetelli et al., 2015b), a large scatter of published values is observed. Radioactivity content in FA varies a lot not only between different regions and countries but even within the same power plant during time. Obviousy, it is highly dependent on the type and features of the raw material (coal) from which FA originates. This leads to the conclusion that a detailed radiological characterization of residues, concrete costituents and concrete itself is necessary to assure that these materials are not of radiological concern. Although there is a variety of methods for screening building materials from the radiological point of view (Trevisi et al., 2013), the activity concentration index I has been widely accepted and adopted as a screening tool in the EU legislation, the 2013/59/EURATOM directive (CE, 2014).

The aim of this paper is to describe the results of the radiological characterization of FA from five Serbian coal burning power plants, concrete costituents and AAFAC in order to assess their possible application as construction materials. Moreover, about the potential classification of alkali-activated fly ash concrete (as indoor-structural e.g., slabs, beams, walls, columns) or non-structural (partitions), many parameters in terms of basic physical and mechanical properties have been considered: details about chemical, physical and mechanical properties are given in Appendix.

2. Materials and methods

2.1. Materials and preparation of Alkali-activated fly ash paste mixtures (AAFAP)

Fly ash was obtained from five coal burning power plants in Serbia, namely, “Kolubara”, "Nikola Tesla - B", “Kostolac”, “Morava” and "Nikola Tesla - A”. FA samples were marked with numbers (ID) from 1 to 5 following the above mentioned order of the power plants. These plants were chosen as they have or will have a system for direct transportation of dry fly ash to the final user. Design and preparation of the samples was performed in two steps. The first step consisted of the preparation of alkali-activated pastes with different types of fly ash and alkali activator and the testing of basic material properties. In this step several alkali-activated paste mixtures (alkali-activated fly ash paste -AAFAP) containing fly ash and blast furnace slag were also prepared. Blast furnace slag was supplied from a local steel factory (specific density 2880 kg/m^3). ID of each sample was given in the form P_FA-N or P_FA-N+S, where P stands for paste, FA-N for fly ash type and S for slag.

2.2. Alkali-activated fly ash and slag concrete mixtures (AAFASC)

Based on previous results, in the second step, alkali-activated fly ash and slag concrete was designed with the addition of other necessary components such as plasticizer and aggregate. The aggregate was a mix of natural river sand (0/4 mm) and coarse aggregate (4/8 mm and 8/16 mm) with a specific density of 2600 kg/m^3 (see Fig.1 and Table 1).

In particular, 5 AAFASC with 50% of FA and 50% of slag were designed and different mixture proportions were used. ID of each sample was given in the form C_FA-N, where C stands for concrete and FA-N for the used fly ash type.

2.3. Radiological characterization

The activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K were measured in each of the concrete solid constituents - 5 types of FA, slag, aggregates, as well as in the final products – 5 types of alkali-activated concrete made with these constituents. The measurement of radionuclides content in different AAFAC and solid constituent samples was performed by gamma spectrometry. In particular two HPGe detectors with efficiency of 30% and 70% with analysis software MAESTRO-Gammavision by ORTEC, were used. For this purpose, the dried samples of fly ash and slag as well as milled concrete samples were measured in a plastic Marinelli beaker. The ^{226}Ra activity concentration was determined by subtraction of ^{235}U contribution in the ^{226}Ra peak and the ^{232}Th activity concentration was evaluated by the ^{228}Ac activity concentration. The sample measuring time was 250.000 s for each sample.

2.4. Computation of the Activity Concentration Index (index I)

Based on the ^{226}Ra, ^{232}Th and ^{40}K activity concentration results of fly ash and slag, the index I was calculated, according to equation (1). In order to comply with requirements introduced by the EU BSS (CE, 2014), the index I must not exceed the value of 1.

Regarding index I in concrete the calculations were based on the measured activity concentrations of constituents and their mass participation in the total mass of the concrete sample (partitioning factors), as required by EU BSS (CE, 2014). Moreover the same calculation was made also by using radiological data related to concrete samples.

2.5. Application of the index I(ρd) and dose calculation accounting for (ρd)

Recently, Nuccetelli et al. (2015a) published a new accurate and flexible index (namely I(ρd)), accounting for density (ρ) and thickness (d) of the building material, in order to identify building materials of radiological concern in a conservative but more accurate way as compared to the index I.

The index I(ρd) is given by the following formula with new coefficients taking into account the EU outdoor background median value of 60 nGy h^{-1} instead of 50 nGy h^{-1} considered in Radiation Protection 112 (EC 1999):

$$I(\rho d)= C_{Ra}(\rho d)^2/\{189[(\rho d)^2+268(\rho d)+5103]\} + C_{Th}(\rho d)^2/\{145[(\rho d)^2+286(\rho d)+4931]\} + C_K (\rho d)^2/\{2047[(\rho d)^2+325(\rho d)+4444]\} \qquad (2)$$

where C_{226Ra}, C_{232Th} and C_{40K} are the activity concentrations in Bq/kg of natural radionuclides ρ is the density and d is the thickness of the building material considered.

With the same approach, the calculated gamma dose rate is also expressed in terms of density and thickness. Starting from the assumptions used to elaborate $A(\rho d)_x$ and the related index I(ρd), the annual effective dose due to gamma rays from building materials can be expressed as:

$$D\ (mSv) = [B(\rho d)_{226Ra}\, C_{226Ra} + B(\rho d)_{232Th}\, C_{232Th} + B(\rho d)_{40K}\, C_{40K}] - 0.294 \qquad (3)$$

where B(ρd)'s are in mSv/(Bq kg^{-1}) with the following expression:

$$B(\rho d)_{226Ra} = \cdot(\rho d)^2/\ 170[(\rho d)^2+156\cdot(\rho d)+11477] \qquad (4)$$

$$B(\rho d)_{232Th} = \cdot(\rho d)^2/\ 130[(\rho d)^2+173\cdot(\rho d)+11226] \qquad (5)$$

$$B(\rho d)_{40K} = \cdot(\rho d)^2/\ 1870[(\rho d)^2+194\cdot(\rho d)+11610] \qquad (6)$$

and 0.294 (in mSv) is the annual outdoor background obtained by 60 nGy h^{-1} multiplied by indoor annual occupancy time (7000 h) and converted in Sv (Sv Gy^{-1}= 0.7).

As for the index I calculation, from the ^{226}Ra, ^{232}Th and ^{40}K activity concentration results of fly ash and slag and concrete samples, the index I(ρd) was computed according to equation (2), and the gamma dose (D) was estimated according to equation (3).

3. Results and discussion

3.1. Radiological characterization of fly ash, slag and aggregates

Activity concentrations of ^{232}Th, ^{226}Ra and ^{40}K in five types of fly ash and in slag are showed in Table 2. From the ^{226}Ra, ^{232}Th and ^{40}K activity concentration results of fly ashes, slags the index I was calculated according to equation (1). The results of calculations are also shown in Table 2.

Differences in activity concentrations measured with the two different efficiency HPGe detectors are within 3% which is the level of uncertainties for ^{232}Th and ^{40}K. The ^{226}Ra result uncertainties are around 5% due to the subtraction procedure of ^{235}U contribution in the ^{226}Ra peak. Measured activity concentrations of all three radionuclides for all five FA and slag samples are lower than typical values in EU as reported in the technical guidance Radiation Protection 112 (EC, 1999) with the exception of ^{232}Th in FA-2. Furthermore, ^{226}Ra and ^{40}K measured contents in all FA and slag samples are also lower than 207 Bq kg^{-1} and 546 Bq kg^{-1}respectively, the recently reported average activity concentrations of these radionuclides for EU fly ashes (Nuccetelli et al., 2015b) and slags, as elaborated in the update of the database collection (Trevisi et al., 2012) under finalization. Activity concentration of ^{232}Th measured in FA-1 and FA-2 samples are slightly higher than the average value of 80 Bq kg^{-1} found in the same database.

Owing to the small differences in the values of concentrations obtained from two detectors there were negligible differences of less than 1% in the values of the index I for each sample. The index I uncertainties, calculated from activity concentration result uncertainties, are less than 3% and 2% for single I values and average I values, respectively. Considering the indexes I of different type of fly ash and slag, three classes can be found: low value of about 0.5 (fly ash FA-3 and slag), value close to 1.0 (fly ash FA-1, FA-4 and FA- 5), and value higher than 1.0 (FA-2). As said previously, the index I is only a screening tool and the value 1.0 has to be used as a reference value for the final building material and not for raw materials or constituents. Therefore, it is not possible to conclude that FA-2 cannot be used as a constituent for alkali-activated fly ash and slag concrete, also because usually the mass portion of fly ash in the final product (AAFACS) is about 10%.

The experimental results in terms of activity concentrations of ^{232}Th, ^{226}Ra and ^{40}K and index I values for three aggregate size samples are showed in Table 3. The measurement results of aggregate mix with composition corresponding to the mix used in preparation of concrete samples are also shown. Moreover activity concentrations for aggregate mix calculated on the basis of the contribution of each aggregate fraction in the concrete mix are presented.

As for FA, in the three aggregate sizes, differences between values of activity concentrations measured by means of the two 30% and 70% HPGe gamma detectors are generally lower than measurement uncertainties. Moreover, differences between activity concentrations of different aggregate sizes are very small: indeed, ranges of values of all measurement results were 9.7-12.3, 9.1-11.4, 191-247 Bq/kg for ^{232}Th, ^{226}Ra and ^{40}K activity concentrations, respectively.

The same phenomenon is for index I values. The difference between index I values from measured and calculated data is about 3 %, accounting for the significant digits used (see last two rows in Table 3).

Notwithstanding the low values of the index I of aggregate, the 0.16 value cannot be considered as negligible. It means that the activity concentration of aggregate should be included in the assessment of the concrete radiological characteristics like fly ash and slag by using the appropriate partitioning factors.

3.2. Radiological characterization of alkali-activated fly ash and slag concrete

Measured activity concentrations of ^{232}Th, ^{226}Ra and ^{40}K for five AAFASC samples are shown in Table 4: reported values are the average of measurement results obtained by the two 30% and 70% HPGe detectors. Since mean differences between the two measurement results for each sample are below 2% the good reliability of measured values is confirmed. In concrete samples, the substitution of cement with fly ash and slag should have led to activity concentrations in concrete higher than typical, however, measured values for all three radionuclides were lower than values for ordinary concrete- 30, 40 and 400 Bq kg^{-1} for ^{232}Th, ^{226}Ra and ^{40}K, respectively, as reported in the Radiation Protection 112 (EC, 1999). The values of indexes I for all five AAFASC types are well below 1 and in the narrow range of 0.20 - 0.26. This means that all 5 concrete types have indexes complying with the European Union reference level of 1mSv per year for gamma radiation from building materials (CE, 2014). Moreover, the application of the I(ρd), as reported in equation (2) considering a concrete thickness of 0.2 m, provided values lower than relevant index I values and in the narrow range of 0.18-0.24. These results are due to the fact that the actual densities of all the concrete samples (see Table A.4 in Annex) are lower than the density of 2350 kg m^{-3} hypothesized in the index I model (EC 1999). Finally, the estimation of gamma doses indoors, determined by the AAFAC concretes analysed and exceeding the outdoor background, gave negative values in three cases, since doses calculated by equation (3) were below the outdoor background value of 0.294 mSv per year.

3.3. Comparison between index I values from measured and calculated activity concentrations

The calculation of activity concentrations for each type of concrete starting from the activity concentrations of all solid constituents (see Tables 2 and 3) and their contribution by mass (see Table 1) in each concrete was also carried out. The ratios between the measured and calculated activity concentrations for the five AAFASC are within 11%, as shown in Table 5. Indeed, values lower than 1.0 mean that calculated values are on the conservative side compared to measured values. Only one type of concrete (C_FA-1) showed measured activity concentrations of all three radionuclides and the corresponding index I value higher than those calculated, not accounting for uncertainties.

Results of this calculation confirm that it is possible to obtain reliable index I values based on measured activity concentrations of concrete constituents by applying appropriate partitioning factors, following an approach similar to the one used by Dose et al. (2016) in the analysis of the role of constituents in Swedish concrete. Relatively small differences -up to 5%- between index I values from measured activity concentrations and calculated activity concentrations, starting from component activity concentrations reported in tables 3 and 4, can be explained by the uncertainty of mass percentage adopted for each component in the total mass of hardened concrete. Namely, unit mass quantities of components refer to unit volume of fresh concrete. During the process of curing, a portion of the liquid part of the concrete mixture evaporates which changes the volume and the mass of the concrete sample. Another reason of these differences between measured and calculated values could be the heterogeneity of concrete. Although great attention was paid during sample preparation in order to achieve sample homogeneity during the period of mixing, vibrating and casting in moulds, it is possible that the designed mass ratio between components did not match the real one in 10x10x10 cm^3 concrete specimen used for sampling.

The good agreement between index I values from calculated and measured concentrations would enable assessment of radionuclide potentials in the early phase of concrete design and tailor made concrete design according to this safety requests. The comparison would also give insight to the contribution of each constituent to the activity concentrations of the final product.

4. Conclusions

Five types of fly ash from different Serbian power plants, blast furnace slag and aggregates were tested in order to investigate possible application in alkali-activated concrete production both from a material and radiological point of view. Based on the presented analysis and measurements, the following conclusions can be drawn:

1. Fly ash from the five Serbian power plants as well as blast furnace slag from the local steel factory can be used as a base material for producing alkali-activated pastes and concretes, since – with few exceptions measured activity concentrations of all three radionuclides for all five FA and slag samples are lower than typical values in EU;
2. Replacement of 50% of FA with blast furnace slag leads to a positive effect on compressive strength of alkali-activated concrete, without prejudice from a radiation protection point of view (see Appendix);
3. All five designed alkali-activated concretes comply with EU BSS screening requirements for indoor building materials, since all index I values are well below 1;
4. From an experimental point of view, HPGe detectors with both 30% and 70% efficiency can be used for activity concentrations measurements as they showed negligible differences in results on all AAFACS components as well as concrete itself; indeed differences are within the 3%;
5. The influence of aggregate on the activity concentrations of radionuclides in AAFAC sample is not negligible and must be taken into account;
6. The index I values of the "calculated" concretes are in good agreement with the index I values of the measured concrete samples. Starting from the activity concentration of constituents to elaborate the final building material index I confirms to be a reliable procedure.
7. The application of the index I(ρd) to the concrete samples provided values lower than relevant index I values, due to the lower actual density of samples compared with the density of concrete used to elaborate I (EC 1999), and in the narrow range of 0.18-0.24, confirming the index I(ρd) as a reliable and accurate tool.
8. Finally, the annual dose, calculated with an accurate formula accounting for actual density and thickness of the AAFAC concrete samples, resulted negative in three cases and less than 2.3E-02 mSv, with uncertainties, in the other two cases. This demonstrates that AAFAC concretes analysed can be safely used from the radiological point of view, when satisfying structural requirements.

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List of Tables

List of Figures

Appendix

A1. Details about fly ash and the preparation of paste sample

Fly ash was obtained from five coal burning power plants in Serbia, namely, “Kolubara”, "Nikola Tesla - B", “Kostolac”, “Morava” and "Nikola Tesla - A”. FA samples were marked with numbers from 1 to 5 following the mentioned order of the power plants. The chemical composition and physical properties – in terms of density and loss on ignition (LOI) - of different FA are reported in Table A.1. All samples satisfy the ASTM-C618 criteria (ASTM, 2012) for class F fly ash, with the exception of FA_1 in terms of SO_3 content.

Particle size distribution of five FA is presented in Fig. A.1. Initially, fly ash samples FA-3, FA-4 and FA-5 didn't meet the fineness requirement for category N (CEN, 2012) so they were sieved through a sieve size of 0.08 mm in order to meet this criterion.

The preparation of concrete consisted of two stages. The first stage was the preparation of alkali-activated pastes with the different type of fly ash and alkali activator (AA) and the testing of basic material properties. In this stage several alkali-activated paste mixtures with a combination of fly ash and blast furnace slag were also prepared. Based on the results, in the second stage, alkali-activated fly ash and slag concrete was designed with the addition of other necessary components such as aggregate and plasticizer (see Fig.1). In particular natural river sand and coarse aggregate, and a commercially available liquid superplasticizer (Producer: BASF, Germany) were used as other components. Finally a mix of sodium silicate (Na_2SiO_3) and sodium hydroxide solution (NaOH) as an activator solution was used in all concrete mixtures. Sodium silicate solution was obtained from Galenika-Magmasil, Serbia, and its chemical composition was Na2O=14.7%, SiO2=28.08% and water 57.22% by mass. Sodium silicate solution Na2O·n·SiO2 had a module of n=1.91 and a specific gravity of 1514 kg/m3. The NaOH used in the study was technical grade with 98% purity, in pellets, and obtained from Superlab, Serbia. NaOH solution was prepared by first dissolving the NaOH pellets (400g of pellets for one liter of NaOH solution) in distilled water (879g of water for one liter of NaOH solution) in order to make 10 molar NaOH solution (10M NaOH). Specific gravity of 10M NaOH is 1279 kg/m3. After allowing the NaOH solution to cool down it was mixed with Na2SiO3 solution. For all paste and concrete mixtures alkali activator was made with mass ratio of Na2SiO3 / NaOH = 10. The solutions were left at room temperature (20±2ºC) in a capped plastic bottle for 24h before paste and concrete mixing. A description of the composition of paste samples is shown in Table A.2.

A2. More details about Alkali-Activated Fly Ash and Slag Concrete mixtures (AAFASC)

Details concerning the composition of 5 AAFASC with 50% of FA and 50% of slag have been given Table 1. The same amounts of FA, slag and activator were kept in order to analyse the influence of fly ash type on the physical, mechanical and radiological properties of concrete. The small differences in the amounts of aggregate were due to the different specific densities of different FA and the different amounts of added water following the total volume method in the design of concrete. One of the most important ratios for alkali-activated concrete - the ratio between the amount of activator and the total amount of fly ash and slag - was set to 0.6. This value was chosen based on the preliminary tests with one type of fly ash (from power plant Nikola Tesla B-sample 2) in order to find the best alkali activator solution and optimal AA/FA ratio (Dragaš et al, 2014; Marinković et al., 2015). Ratio AA/FA+S is relatively high (0.6) but it can also be found in other research (Nuaklong et al., 2016, Chindaprasirt P. and Chalee W., 2014, Shi et al., 2012). Workability of concrete was evaluated with the standard slump test (CEN, 2009b). Fresh concrete samples were subjected to an increased temperature regime which was set up to 80° C for 18 hours. After de-moulding, samples were stored at standard laboratory conditions, 20 ± 2°C and approximately 50% relative humidity, until compressive strength testing.

Fresh and hardened density (CEN, 2009a), workability determined by slump test (CEN, 2009b), compressive strength (CEN, 2009c) and splitting tensile strength (CEN, 2009d) of the concrete samples were tested: the results are summarised in Table A.3.

A3. More details about tests on fresh and hardened pastes and concretes

Concerning mechanical properties, in terms of workability and compressive strength (f_c) at the maturity of 24 hours of alkali-activated pastes, main results are shown in Table A.3. The influence of the usage of different types of fly ash on both fresh properties and compressive strength was significant. Three out of four mixtures prepared with FA showed low workability and stiff consistency. Only one mixture (P_FA-2) had promising compressive strength, two of them (P_FA-3, P_FA-5) possessed relatively low strength while one (P_FA-1) didn’t have an acceptable compressive strength. A significant increase both in workability and compressive strength of AAFAP was achieved by replacing 50% of FA with slag, see

Table 8. These conclusions are in accordance with findings of other research done in this field (Kumar et al., 2010). According to previous experience (Marinkovic et al., 2015) a decrease in compressive strength of AAFA concrete compared to the AAFA pastes prepared with the similar mixture proportions was expected. In order to gain improved mechanical properties and reach acceptable compressive strengths of AAFAC samples for structural and non-structural application, 50% of FA in each concrete mixture was replaced with slag.

Results of AAFASC testing of workability (slump test), hardened concrete density (CEN, 2009a), compressive strength ($f_{ck,cube,100}$) and splitting tensile strength ($f_{ct,sp}$) are shown in Table A.4. In order to be classified in certain classes according to CEN (2004) provisions, transformation of measured values of compressive strength obtained on 10 cm cube sample to the 15 cm sample ($f_{ck,cube,150}$) was necessary. Similarly, splitting tensile strengths were transformed to axial tensile strengths (f_{ct}) by multiplying measured values with a factor of 0.9 (CEN, 2004), Table A.4. Large differences were observed in workability and both strengths. The density of hardened concrete was similar within the whole group and was above 2100 kg/m^3 which means that all five concretes can be classified as normal-weight concrete. Two out of five concretes had a liquid consistency (C_FA-2, C_FA-4), while the other three showed very low workability measured by the slump method. Concrete prepared with fly ash type 2 and 3 (C_FA-2 and C_FA-3) resulted in compressive strengths of over 15 MPa (150 mm cube), the commonly used limit for structural application. The influence of different types of fly ash on splitting tensile strength of designed AAFASC is significant and results are in a wide range between 1.3 MPa and 2.7 MPa. The ranking of tested AAFASC according to measured tensile and compressive strengths is not the same. Deriving conclusion only on compressive strength, concrete C_FA-2 can be classified as class C25/30 according to CEN (2004) provisions, which is a widely used class of concrete in structural applications. Including the tensile strength into consideration leads to the decrease in class to C20/25 as C_FA-2 did not achieve the required 2.6 MPa for class C25/30 (CEN, 2004). According to both compressive and tensile strength concrete C_FA-3 belongs to the class C12/15 and also can be used for structural applications. The other three concretes showed significantly lower compressive strength in the narrow range between 9.7 MPa and 11.3 MPa, Table A.4. Although a small increase in compressive strength can be expected with higher maturity of samples and although C_FA-4 resulted in respectable tensile strength (Table A.4), it is more than obvious that these three concretes (C_FA-1, C_FA-4, C_FA-5) can be used only for non-structural purposes. It must be emphasized that the obtained compressive strengths probably are not maximal for the fly ash types used in this investigation. Higher compressive strength could be reached by applying different activators, i.e. higher Na_2O/FA ratios (Marinkovic et al., 2015).

Figure 1

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Figure A.1_rev

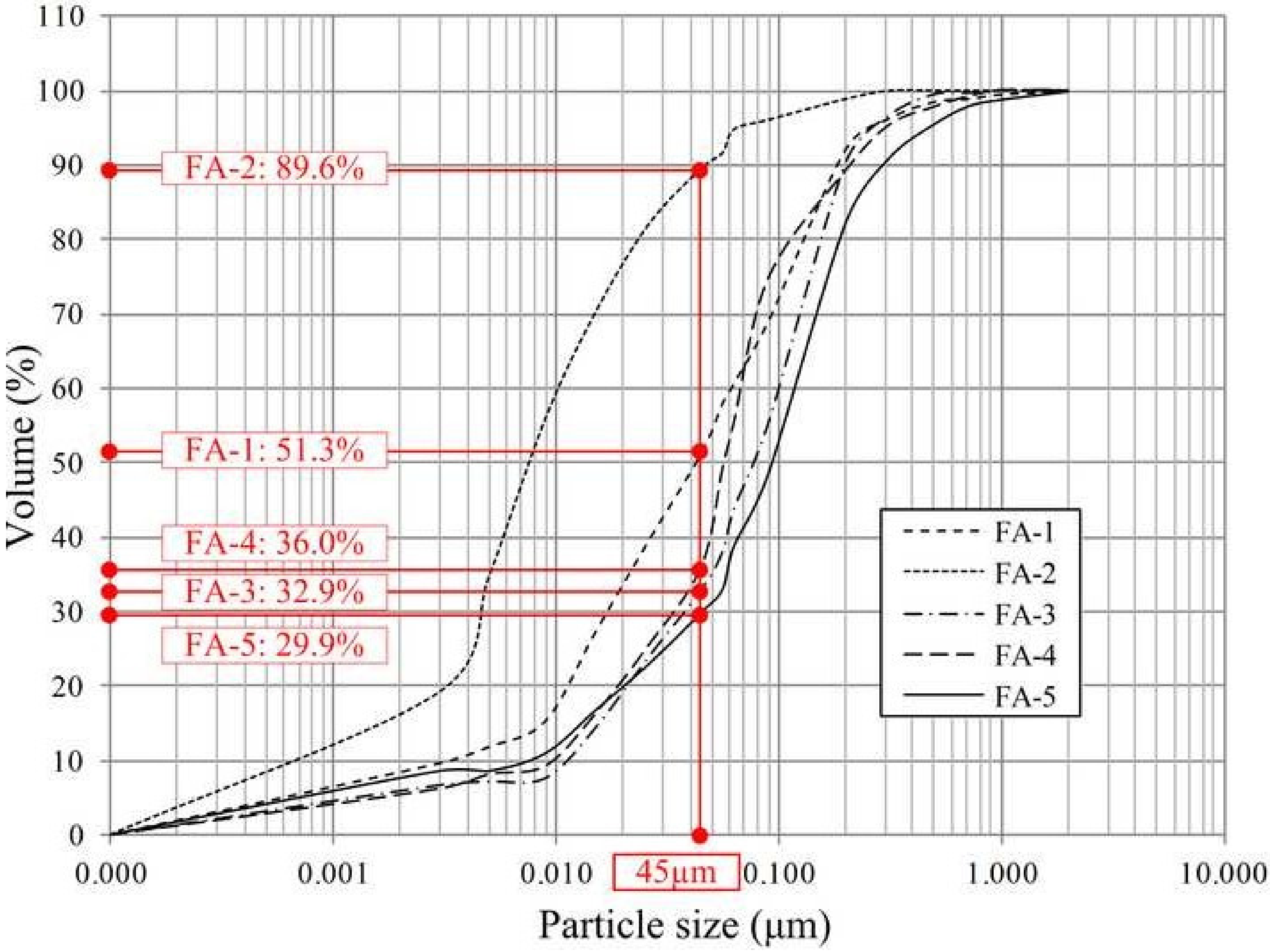

Table 1

Mixture proportions of AAFASC samples.

ID of sample	Fly ash	Slag	Alkali activator solution		Water	Plast.	Aggregate			LQ[1]/ (FA+S)[2]
			NaOH (10M)	Na_2SiO_3 (n=1.91)			0/4 mm	4/8 mm	8/16 mm	
	(kg m^{-3})	(kg m^{-3})	(kg m^{-3})	(kg m^{-3})	(kg m^{-3})	(kg m^{-3})	(kg m^{-3})	(kg m^{-3})	(kg m^{-3})	(-)
C_FA-1	200	200	21.8	218	80.0	8.0	764	459	306	0.80
C_FA-2	200	200	21.8	218	0.0	8.0	865	519	346	0.60
C_FA-3	200	200	21.8	218	33.3	8.0	830	498	332	0.68
C_FA-4	200	200	21.8	218	66.7	8.0	790	474	316	0.77
C_FA-5	200	200	21.8	218	73.3	8.0	777	466	311	0.78

[1] LQ: NaOH + Na_2SiO_3 + Water

[2] FA + S: Fly ash + Slag

Table 2

Natural radionuclide activity concentrations in Serbian FA and blast furnace slag samples.

		^{232}Th	^{226}Ra	^{40}K	index I	
	HP Ge		(Bq kg^{-1})			avg
FA-1	30%	90.0±2.4	123±6	436±10	1.0	1.01
	70%	91.8±2.4	122±7	454±10	1.02	
FA-2	30%	110±3	164±7	407±9	1.23	1.24
	70%	113±3	163±7	426±9	1.25	
FA-3	30%	42.1±1.1	56.8±3.1	198±5	0.47	0.47
	70%	43.2±1.1	55.7±2.9	200±4	0.47	
FA-4	30%	65.6±1.8	151±7	386±9	0.96	0.96
	70%	66.4±1.7	150±7	400±9	0.97	
FA-5	30%	78.1±2.1	155±7	366±8	1.03	1.02
	70%	78.5±2.1	149±6	371±8	1.01	
SLAG	30%	26.0±0.7	109±5	119±3	0.53	0.54
	70%	27.1±0.7	108±5	125±3	0.54	
Fly ash from RP112 (EC,1999)		100	180	650		
Fly ash (Nuccetelli et al., 2015b)		80	207	546		
Slag from RP112 (EC,1999)		70	270	240		
Slag*		63	147	246		

*Based on a new elaboration of the national values given in European database

Table 3

Natural radionuclide activity concentrations in aggregate samples.

		^{232}Th	^{226}Ra	^{40}K	index I	
	HP Ge	(Bq kg^{-1})				avg
(0/4mm)	30%	10.2±0.3	9.2±0.8	228±5	0.16	0.16
	70%	10.4±0.3	9.2±1.0	240±5	0.16	
(4/8mm)	30%	9.7±0.3	9.1±0.8	230±5	0.16	0.16
	70%	10.1±0.3	9.7±1.1	247±5	0.16	
(8/16mm)	30%	11.9±0.3	11.4±0.7	191±4	0.16	0.17
	70%	12.3±0.3	11.3±1.2	210±5	0.17	
Aggregate mix	30%	10.3±0.3	9.7±1.2	244±5	0.17	0.17
	70%	10.3±0.3	9.8±1.1	243±5	0.17	
Calculated	30%	10.4±0.3	9.6±0.5	221±3	0.16	0.16
	70%	10.7±0.3	9.8±0.6	237±3	0.16	

Table 4

Natural radionuclide activity concentrations of AAFASC samples: calculation of index I, index I(ρd) and gamma dose.

AAFASC samples	^{232}Th	^{226}Ra	^{40}K	index I	I (ρd)	D(ρd) (mSv y^{-1})
		(Bq kg^{-1})				
C_FA-1	18.4±0.4	28.5±1.5	232±4	0.26±0.1	0.23±0.1	0.8E-02±1.0E-02
C_FA-2	18.6±0.4	28.8±1.3	225±4	0.26±0.1	0.24±0.1	1.4E-02±0.9E-02
C_FA-3	12.5±0.2	21.2±0.9	196±3	0.20±0.1	0.18±0.1	-6.4E-02±0.6E-02
C_FA-4	14.9±0.3	27.7±1.7	218±3	0.24±0.1	0.21±0.1	-1.6E-02±1.0E-02
C_FA-5	16.1±0.3	28.3±1.2	197±3	0.24±0.1	0.21±0.1	-1.9E-02±0.8E-02

Table 5
Ratios between measured and calculated activity concentrations and between relevant indexes I in AAFASC samples.

	Experimental/Calculated value ratios			
	^{232}Th	^{226}Ra	^{40}K	I
C_FA-1	1.01±0.02	1.01±0.05	1.06±0.02	1.02±0.09
C_FA-2	0.94±0.02	0.95±0.04	1.02±0.02	0.96±0.08
C_FA-3	0.89±0.02	0.96±0.05	0.96±0.02	0.94±0.08
C_FA-4	0.96±0.02	0.92±0.06	1.03±0.02	0.96±0.08
C_FA-5	0.94±0.02	0.91±0.04	0.92±0.02	0.92±0.08

Table A.1

Chemical composition and physical properties of FA.

	FA-1	FA-2	FA-3	FA-4	FA-5
SiO_2, %	50.21	58.24	56.38	56.78	53.59
Al_2O_3, %	23.83	20.23	17.57	20.26	21.18
Fe_2O_3, %	9.89	5.33	10.39	6.44	6.20
TiO_2, %	0.54	0.45	0.52	0.5	0.56
CaO, %	4.79	7.62	7.46	8.19	7.61
MgO, %	3.12	2.01	2.13	2.69	2.74
P_2O_5, %	0.05	0.00	0.025	0.088	0.027
SO_3, %	5.24	2.21	0.95	0.82	0.78
Na_2O, %	0.35	0.52	0.38	0.63	0.44
K_2O, %	0.44	1.51	0.57	1.37	1.22
MnO, %	0.026	0.03	0.028	0.046	0.03
LOI, %	1.84	1.64	2.94	2.19	4.91
Specific density, kg/m^3	2125	2075	2220	2280	2200

Table A.2
Mix design composition for alkali-activated pastes.

ID of specimen	Fly ash	Slag	Alkali activator solution		Water	AA[1]/ (FA+S)[2]	LQ[3]/ (FA+S)[2]
			NaOH (10M)	Na_2SiO_3 (n=1.91)			
			(g)				
P_FA-1	500	0	27.3	272.7	200	0.60	1.00
P_FA-2	500	0	27.3	272.7	0	0.60	0.60
P_FA-3	500	0	27.3	272.7	50	0.60	0.70
P_FA-5	500	0	27.3	272.7	100	0.60	0.80
P_FA-3+S	250	250	27.3	272.7	0	0.60	0.60
P_FA-4+S	250	250	27.3	272.7	25	0.60	0.65
P_FA-5+S	250	250	27.3	272.7	25	0.60	0.65

[1] AA = NaOH + Na_2SiO_3

[2] FA + S: Fly ash + Slag

[3] LQ = NaOH + Na_2SiO_3 + Water

Table A.3
Results of alkali activated paste testing of workability and compressive strength.

ID of specimen	Workability	f_c[1] - 24 h (Mpa)
P_FA-1	stiff	2.49
P_FA-2	plastic	56.77
P_FA-3	stiff	22.92
P_FA-5	stiff	17.19
P_FA-3+S	plastic	32.29
P_FA-4+S	plastic	24.87
P_FA-5+S	plastic	25.11

[1] cube, 40/40/40 mm

Table A.4

Results of alkali activated concrete testing on physical and mechanical properties.

ID of sample	Slump	Density	Measured		Calculated		Concrete classification
			$f_{ck,cube,100}$	$f_{ct,sp}$	$f_{ck,cube,150}$	f_{ct}	
	(cm)	(kg m^{-3})	(Mpa)		(Mpa)		
C_FA-1	5.5	2171	11.3	1.5	10.7	1.4	non-structural
C_FA-2	30	2319	34.6	2.7	32.8	2.4	structural
C_FA-3	4	2261	19.7	2.1	18.7	1.9	structural
C_FA-4	20	2239	9.7	2	9.2	1.8	non-structural
C_FA-5	2	2151	10.6	1.3	10.0	1.2	non-structural

$f_{ck,cube,100}$ - compressive strength, 100 mm cube; $f_{ck,cube,150}$ - compressive strength, 150 mm cube
$f_{ct,sp}$ - splitting tensile strength, cylinder Ø150x150mm; f_{ct} - axial tensile strength