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The characterization of naturally occurring radionuclides in concrete incorporating fly ash as partial cement replacement

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ABSTRACT

Kosovo thermal power plants (TPP) produce annually more than 1 million tons of fly ash as a byproduct of lignite combustion. The focus of this study was the characterization of activity concentration of natural radionuclides of hardened concrete specimens. The measurements were done with Hyper Pure Germanium gamma-ray spectrometry (HPGe). Concrete mixtures with different content of fly ash as cement replacement were prepared. Four concrete mixes with 15, 20, 25 and 30% fly ash replacing the respective content of cement were tested for activity concentration of ^{40}K, ^{226}Ra and ^{232}Th, activity concentration index, indoor specific and annual absorption dose rate. The obtained results were compared to reference concrete mixtures without fly ash-standard concrete. The results of measurements in six concrete mixtures showed that the activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th were very low in all concrete specimens.

Keywords:

Exposure, Concrete, Fly Ash, NORMs, HPGe Gamma Ray Spectrometry, Radiation Doses, Kosovo

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1. INTRODUCTION

Concrete after the water is the most used material [1]. Generally, it is a mixture of coarse and fine aggregates, cement, water and/or admixtures. In Republic of Kosovo, a country situated in the western part of Balkan Peninsula with a population of 1.8 million inhabitants, the annual concrete production is around 3 million m^3, i.e. 1.6 m^3 per capita. The annual consumption of cement for this concrete production is around 1 Mt, i.e. 0.5 ton per capita.

97% of electrical energy is generated by Thermal Power Plants (TPP) of Kosovo Energy Corporation (KEC) with lignite as fossil fuel. The estimated exploitable lignite resources are around 14 Bt [2]. The annual electrical energy generation of around 6 GWh consumes more than 8 Mt lignite [3]. The combustion of lignite generates, apart other coal combustion byproducts (CCBP), more than 1.5 Mt of particulate matter in the form of ash. After combustion, around 80% of this ash flies with flue gases. Before getting out from the stack, it is captured by electrostatic precipitators (ESP) from where it is conveyed to silos. This ash is called fly ash (FA). Fly ash is pulverized grey-in-brown colored material with cementitious and pozzolanic properties. According to EN 450-1 European standard for Fly ash in concrete, fly ash is "Fine powder of manly spherical, glassy particles derived from burning of pulverized coal, with or without co-combustion materials, which has pozzolanic properties and consists essentially of SiO_2 and Al_2O_3 [4]. The chemical and mineralogical composition of Kosovo fly ash was analyzed with XRF spectrometry and results showed that fly ash samples taken from TTP Kosovo B unit of KEC had same mineralogical content as cement and belongs to class C fly ash (calcareous fly ash). In this regard, i.e. for utilization in concrete as partial cement replacement, six concrete mixtures, two reference mixes with ordinary Portland cement (OPC), and four with Portland cement plus different percentage of fly ash were prepared, cured and analyzed with the aim of testing some basic mechanical and physical properties. Based on the fact that all concrete ingredients are raw materials extracted from earth's crust in which there are still found radioactively active nuclides, the concretes built with fly ash, ordinary cement and crushed aggregates were investigated for activity concentration of ^{40}K, ^{226}Ra and ^{232}Th. The objective of this research, in addition to other physical and mechanical properties of concrete investigated previously, was to study the radiological properties of concrete built with fly ash as cement replacement [5]. As the other physical and mechanical properties of these concretes with fly ash favored its use in construction industry, the activity concentrations of radionuclides in specimens of concrete were examined. The essence of this gamma ray spectrometry with HPGe was to show the radiological safety of fly ash utilization as partial cement replacement in concrete and construction industry in general.

2. MATERIALS AND METHOD

2.1 Sampling

As presented above, the chemical and mineralogical composition of fly ash enables its pozzolanic and cementitious properties; in presence of water undergoes the process of hydration with the same result of forming the binder-calcium silicate hydrate (CSH) [6,7]. That was the reason for incorporating it in concrete as construction material partially replacing ordinary Portland cement (OPC). The guidance of sampling and use of fly ash in concrete, concrete production and testing were in conformity with ASTM C311: Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete, ASTM C618: Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete [8] , European standard for fly ash EN 450-1:2012 [4], The European standard for concrete, EN 206-1 [9].

For testing the possible radioactive hazard from use of fly ash in concrete and concrete made with OPC and crushed aggregates (99.5% calcite), six concrete mix designs were prepared. Four concrete mixes with sample ID: FA15, FA20, FA25 and FA30 were prepared with fly ash (class C) as substitution of cement content in following percentages: 15, 20, 20 and 30%, respectively. Two concrete mixes were designed and produced with cement only, i.e. without fly ash and were referred as reference concrete samples. The referent sample with identification RC was produced with OPC; the second reference sample RS with OPC and superplasticizer admixture. In all concrete mixes the cement used was Portland cement, type CEM I 52.5 N from cement factory Sharrcem, Titan Group Company, Kosovo. Standardized coarse and fine crushed aggregates were from a local quarry “Vellezerit e Bashkuar”, Shpk, Kosovo [10]. The mineralogical composition of crushed aggregates showed to be 99.5% limestone and only 0.5% impurities in form of clay etc. The designed quantities of aggregates, cement, fly ash, water and admixture were calculated for $1 m^3$ of fresh concrete. After the process of mixing, cylindrical (150 mm dia. x 300 mm ht) were filled up with fresh concrete and were weighed. The average density of fresh concrete samples was 2395 kg m^{-3} that according to EN 206-1 belongs to normal weight concrete. In Table 1 the individual quantities of materials in one cubic meter of concrete mix designs are shown.

Table 1. Composition, sample ID of concrete mix designs

Mix design composition	**Aggregate ($Kg\ m^{-3}$)**	**Cement ($Kg\ m^{-3}$)**	**Fly ash ($Kg\ m^{-3}$)**	**Water ($Kg\ m^{-3}$)**	**Admixture ($Kg\ m^{-3}$)**
Concrete Mix design ID					
RC	1888	300	0	210	0
RS	1888	300	0	190	0
FA15	1888	255	45	190	1.2
FA20	1888	240	60	190	1.2
FA25	1888	225	75	190	1.2
FA30	1888	210	90	190	1.2

The concrete specimens after releasing the moulds were placed for wet curing in a water tank for 28 days in constant temperature of 20 ($\pm$2) °C. Afterwards, the preparation of activity concentration of concrete samples followed. First, each concrete specimen with and without fly ash was crushed to grain size of about 2 cm. The process of grinding to 2 mm concrete grain size and homogenization followed. Samples for 24 hours were held at heat-controlled oven at temperature 110°C for ensuring to be moisture free. The concrete powder with volume of 180 cm^3 was placed in hermetically cylindrical PVC containers. After the weighing, the concrete samples were ready to undergo the measurement of radioactivity emission by a high-resolution gamma ray spectrometry system (HPGe).

2.2. Measurements with High-resolution gamma ray spectrometry (HPGe)

The concentrations of natural radionuclides in samples of concrete produced with fly ash, as well as concrete without fly ash (standard concrete) were measured by a fully automatic gamma ray spectrometer MCA_Rad system. The functioning and design set up of MCA_Rad are as presented in Xhixha et al. (2013) [11]. MCA_Rad system comprises two 60% relative efficiency coaxial p type HPGe detectors. The energy resolution of HPGe detectors is around 1.9 keV at 1332.5 keV (^{60}Co). These detectors are positioned opposite each other at distance of 5 cm. The shielding of detectors from background environmental gamma radiation consists of a 10 cm outer lead shield and 10 cm inner copper shield. Cylindrical polycarbonate containers containing the concrete material to be tested (specimens), labeled by a barcode, are loaded to slider which moves on under gravity pull taking the sample containers to the inner chamber, in between two HPGe detectors, by an automatic lever where the measurements take place. All the operations, i.e. sample feeding in, measurement and data record are fully automatic and controlled by a PC with adequate software for recording and analyzing the spectra. The required accuracy energy calibration for absolute photo-peak efficiency is done using certified standard point sources: ^{152}Eu and ^{56}Co. The efficiency calibration of MCA_Rad system is in the 95% interval of confidence.

3. RESULTS AND DISCUSSIONS

3.1. Activity concentration

The range and mean values from the measurements of activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in concrete specimens are shown in Table 2. The average activity concentration of ^{40}K, ^{226}Ra and ^{232}Th of reference samples (RC) were 23 ± 2, 5 ± 1, 3 ± 1 Bq kg^{-1}, respectively; from reference samples (RS) were: 17 ± 2, 5 ± 1, 3 ± 1 Bq kg^{-1}, respectively. The activity concentration, within $\pm 1\sigma$ uncertainty of data showed no difference of two concrete mix designs, i.e. the added admixture in the second mix (RS) did not cause any excess concentration of ^{40}Ra, ^{226}Ra and ^{232}Th. Then, the activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in concrete mixes with various percentage of fly ash: FA15, FA20, FA25 and FA30 were measured. In concrete with 15% cement replaced by fly ash (FA15), the average concentrations of ^{40}Ra, ^{226}Ra and ^{232}Th were 16 ± 2, 6 ± 1 and 3 ± 1 Bq kg^{-1}, respectively; in FA20 the respective average concentrations were 27 ± 3, 5 ± 1, 4 ± 1 Bq kg^{-1}; in FA25 the respective average concentrations were 18 ± 2, 5 ± 1, 2 ± 1 Bq kg^{-1}; in FA30 concentration were: 17 ± 2, 6 ± 1, 3 ± 1 Bq kg^{-1}. These results of activity concentration of ^{40}Ra, ^{226}Ra and ^{232}Th in concrete produced with fly ash showed to be very low. This indicates that the utilization/addition of fly ash in concrete as partial cement replacement did not increase the activity concentration of concrete compared to reference concrete samples. Only at the sample with 20% fly ash it was noticed a slight higher concentration of ^{40}K comparing to samples without fly ash. This is still insignificant.

The worldwide average concentrations of radium, thorium and potassium in the earth's crust are about 40 Bq kg^{-1}, 40 Bq kg^{-1} and 400 Bq kg^{-1}, respectively [12]. The typical activity concentration of radium, thorium and potassium in concrete as building material in European Union member countries are 40, 30 and 400 Bq kg^{-1} [13]. In this study the mean and average value activity concentration of ^{40}Ra, ^{226}Ra and ^{232}Th in concrete with fly ash (FA15, FA20, FA25 and FA30) and reference concrete (RC and RS) showed to be much lower than the world average in earth's crust and concrete of EU countries.

Table 2. Activity concentration, mean and range values of ordinary concrete and concrete with fly ash

Sample ID	^{40}K(Bq kg^{-1})		^{226}Ra(Bq kg^{-1})		^{232}Th(Bq kg^{-1})	
	Mean	**Range**	**Mean**	**Range**	**Mean**	**Range**
RC	23 ± 2	17.9-27.3	5 ± 1	3.8-5.3	3 ± 1	1.7-4.9
RS	17 ± 2	14.0-19.7	5 ± 1	3.9-5.4	3 ± 1	2.3-3.9
FA15	16 ± 2	13.4-18.5	6 ± 1	4.7-6.3	3 ± 1	2.1-3.3
FA20	27 ± 3	22.5-31.0	5 ± 1	4.2-6.6	4 ± 1	2.5-4.8
FA25	18 ± 2	15.1-21.7	5 ± 1	4.6-6.2	2 ± 1	1.4-3.1
FA30	17 ± 2	14.0-19.5	6 ± 1	4.9-7.2	3 ± 1	2.2-3.9

3.2. The index of activity concentration ACI

The index of activity concentration (ACI) is a key parameter in evaluating the radiological hazard caused by gamma ray radiation from building materials that contribute to the absorbed dose. In this study, the ACI of concrete was calculated using the equation (1) based on EU RPP 112 [13] and the results are presented in Table 3.

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

where, A_{40K}, A_{226Ra} and A_{232Th} are the activity concentrations in Bq kg^{-1} of potassium, radium and thorium, respectively.

Table 3. Activity concentration index (ACI) of concrete with fly ash

Sample ID	**ACI**
RC	0.04 ± 0.02
RS	0.04 ± 0.02
FA15	0.04 ± 0.02
FA20	0.04 ± 0.03
FA25	0.04 ± 0.02
FA30	0.04 ± 0.02

The RPP 112 regarding the ACI values for building material sets the criteria for their use with or without any restriction. According to RPP 112, if the ACI of any building material, based on the dose criterion of 1 mSv y^{-1}, is ≤ 1, that building material can be used in bulk quantity [13].

From the Table 3 it can be seen that ACI of ordinary concrete as well as concrete with fly ash is 0.04, that is much lower than threshold criterion ≤1. This is an indicator that regarding the ACI of <1 the concrete as building material and concrete built with up to 30% cement replaced with fly ash belong to A1 category of building materials, i.e. concrete with fly ash and ordinary concrete with OPC are suitable for use in bulk quantities without any restriction regarding the radioactivity. This justifies the utilization of fly ash in concrete as building material about radioactivity concerns.

3.3. Assessment of radiological hazard

The determination of radiation of ^{40}K, ^{226}Ra and ^{232}Th from concrete with and without fly ash in the indoor air, was done based on the room model according to references [13,14]. The calculation of the absorbed dose rate in the room, caused by the gamma radiation of ^{40}K, ^{226}Ra and ^{232}Th, was done by the equation (2) and results are presented in Table 4:

$$D^{indor} = 0.08C_K + 0.92C_{Ra} + 1.1C_{Th} \quad (2)$$

where, C_K, C_{Ra} and C_{Th} are respective activity concentration of potassium, radium and thorium. From the values of D^{indor} in Table 4 it can be concluded that even at the concrete samples with the highest quantity of fly ash (FA30), 90 kg m^{-3}, there is no excess radiation to the indoor absorption dose rate in the air of the room comparing to the concrete samples without fly ash. The absorbed dose rate in the indoor air from all concrete samples, with and without fly ash, is much lower than the average of outdoor absorbed dose rate value of 58 nGy h^{-1} of background radiation [15].

The determination of the rate of annual effective dose equivalent (AEDE) in mSv y^{-1}, was calculated by the Eq. (3):

$$AEDE = D^{indoor} \times 10^{-6} \times 8760 \times 0.8 \times 0.7 \quad (3)$$

The calculated average values of AEDE for four concrete samples with fly ash and two without fly ash are presented in Table 4.

Table 4. Indoor absorption dose rate D^{indoor} and annual effective dose equivalent rate AEDE

Sample ID	D^{indoor} (nGy h^{-1})	AEDE (mSv y^{-1})
RC	9.57	0.047
RS	8.99	0.044
FA15	9.31	0.046
FA20	11.0	0.054
FA25	8.96	0.044
FA30	10.17	0.050

The results of all six concrete mixes (samples) have almost the same value of AEDE varying from 0.044 mSv y^{-1} to 0.054 mSv y^{-1}. Comparing to the worldwide average of the annual effective dose of 0.41 mSv y^{-1}, these values determined from concrete are very low.

4. CONCLUSIONS

This is the first assessment of natural radionuclides in concrete in general and particularly concrete with fly ash as cement replacement in Kosovo. The activity concentration of ^{40}K, ^{232}Ra and ^{236}Th and indoor absorbed dose rate of concrete with fly ash were compared with the results from ordinary concrete samples with OPC. The range of activity concentration of reference concrete (RC, RS) and concrete with fly ash (FA15, FA20, FA25, FA30) for ^{40}K were (13.4- 31.0) Bq $kg^{-}1$; for ^{232}Ra (3.8-7.2) Bq kg^{-1}; for ^{236}Th were in the range of (1.4-4.9) Bq kg^{-1}. These values are very low comparing to average concentration of ^{40}K, ^{232}Ra and ^{236}Th (400 Bq kg^{-1}, 40 Bq kg^{-1}, and 40 Bq kg^{-1}, respectively) in the earth's. The activity concentration index ACI of all concrete mixes, reference and with fly ash showed to be around 0.04 ± 0.02, i.e. the ACI is ≤ 1. This value does not exceed the dose criterion of 1mSv y^{-1}, and the Kosovo concrete with fly ash or without fly ash is categorized as category A1, which means that without any restriction can be used as material in bulk quantities in constriction industry.

In regard to the hazardous effects of concrete, the values of external absorbed dose rates in the indoor air, and annual effective dose equivalents of concrete samples with fly ash, as well as without fly ash, were found to be very low and varied from 0.046 mSv y^{-1} to 0.054 mSv y^{-1}. These values of annual effective dose are very low in comparison to global average of the annual effective dose rate of 0.41 mSv y^{-1}.

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