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Radiological characterization and evaluation of high volume bauxite residue alkali activated concretes

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ABSTRACT

Bauxite residue, also known as red mud, can be used as an aggregate in concrete products. The study involves the radiological characterization of different types of concretes containing bauxite residue from Ukraine. The activity concentrations of radionuclides from the ^{238}U, ^{232}Th decay series and ^{40}K were determined for concrete mixture samples incorporating 30, 40, 50, 60, 75, 85 and 90% (by mass) of bauxite residue using gamma-ray spectrometry with a HPGe detector. The studied bauxite residue can, from a radiological point of view using activity concentration indexes developed by Markkanen, be used in concrete for building materials and in road construction, even in percentages reaching 90% (by mass). However, when also occupational exposure is considered it is recommended to incorporate less than 75% (by mass) of Ukrainian bauxite residue during the construction of buildings in order to keep the dose to workers below the dose criterion used by Radiation Protection (RP) 122 (0.3 mSv/a). Considering RP122 for evaluation of the total effective dose to workers no restrictions are required for the use of the Ukrainian bauxite residue in road construction.

1. Introduction

Bauxite residue, also known as red mud, is a major byproduct that is produced during the refining of the aluminum ore by means of the Bayer process. For every ton of alumina produced, 1–1.5 t of bauxite residue is generated. It is estimated that about 120 Mt of bauxite residue was produced worldwide in 2007 [Power et al., 2011]. In China alone, about 30 Mt of bauxite residue was generated in 2009, of which only 4% was utilized [Power et al., 2009]. The disposal-costs may add up to 5% of the alumina production cost. [Kumar et al., 2006] Furthermore, improper storage of bauxite residue can lead to harmful contamination of water, land and air in the surrounding area because of its high alkalinity. Strong environmental concerns are linked to the disposal of bauxite residue. The treatment and utilization of bauxite residue is both of environmental and economic significance.

In recent years, many studies have investigated different application possibilities for bauxite residue. Several studies focus on the reuse of bauxite residue as an additive for construction materials and among other on the use in ceramics cements. [Sglavo et al., 2000a, 2000b; Pontikes et al., 2007; Tsakiridis et al., 2004; Pascual et al., 2009; Pan et al., 2002, 2003; Ke et al., 2014] However, due to the low chemical activity of bauxite residue its application in membranes is limited [Sglavo et al., 2000a, 2000b] and in several cases, an energy intensive preliminary pre-treatment is required.

Early studies already reported that the use of alkaline activation can allow for a considerable increase in bauxite residue incorporation rates for cements and concretes without reducing their physio-mechanical characteristics [Patent Krivenko et al., 1996; Rostovskaya, 1994; Glukhovsky, 1989]. The properties of alkaline activated cements and concretes are highly competitive to traditional cement concretes.

To make the reuse practices economically viable a sufficiently high fraction of bauxite residue needs to be incorporated in the concrete. In the current work it is demonstrated that it becomes possible to formulate high volume bauxite residue alkali activated

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cements and concretes with incorporation rates of bauxite residue in the concretes reaching 90% (by mass).

An important aspect that needs to be dealt with when incorporating larger percentages of bauxite residue in concrete, concerns the radiological properties. The UNSCEAR report (2000) reported activity concentrations for the bauxite ore of 0.4–0.6 kBq kg^{-1} for individual radionuclides from the ^{238}U-series and 0.3–0.4 kBq kg^{-1} for individual radionuclides from ^{232}Th-series. For Hungarian bauxite ore activity concentrations up to 0.8 kBq kg^{-1} ^{226}Ra and up to 0.5 kBq kg^{-1} ^{232}Th were published [Somlai et al., 2008]. The average activity concentrations of bauxite residues produced in several European and non-European countries were reported by Nuccetelli et al. (2015b). For the considered bauxite residues an overall average activity concentration of 0.34 kBq kg^{-1} ^{226}Ra, 0.48 kBq kg^{-1} ^{232}Th and 0.21 kBq kg^{-1} ^{40}K was obtained. For Ukrainian bauxite residue activity concentration of 0.16 kBq kg^{-1} ^{226}Ra, 0.33 kBq kg^{-1} ^{232}Th and 0.053 kBq kg^{-1} ^{40}K were reported. [U.D.C. 691.5] In general most authors consider the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K for the radiological evaluation of bauxite residue and construction materials based on the bauxite residue. [Nuccetelli et al., 2015b; Turhan et al., 2011, 2014; Viruthagiri et al., 2013; Kovacs et al., 2012, 2013; Somlai et al., 2008] Other radionuclides in the decay chains are rarely evaluated to assess the secular equilibrium in the decay chains. Since for NORM containing construction materials in general the secular equilibrium will be disturbed this aspect will be dealt with in this study in detail by analyzing a broad selection of radionuclides using gamma spectrometric analysis.

For the synthesized concretes based on bauxite residue aggregates the current work aims to investigate the radiological properties in order to control and prevent radiological problems upon large scale application. Therefore, this study will verify if the reuse meets the requirements of the new Euratom Basic Safety Standards (EU-BSS) and occurs according to the principles set by the Construction Products Regulations. [CE, 2014, CPR 305/2011] The EU-BSS covers the issue of NORM (naturally occurring radioactive materials) in industrial applications and the reuse of by-products from NORM processing industries in building materials. The EU-BSS uses an index developed by Markkanen [Markkanen, 1995] for the screening and evaluation of the public exposure from building materials that are permanently incorporated in buildings. The CPR lays down essential requirements for construction works in general. According to the CPR the construction works must be designed and built in such a way that the emission of dangerous radiation will not be a threat to the health of the occupant or neighbours. Methodology for dose assessment and classification of construction materials in view of their gamma emitting properties, linked to the implementation of the CPR, is still under development. Markkanen (1995) proposed another index specifically to evaluate the exposure to the public caused by "materials used for constructing streets and playgrounds". Both indexes, developed by Markkanen and part of the Finnish legislation [STUK, 2010] on natural radiation, are used to assess the public exposure and will be used in the current study. For the evaluation of the occupational exposure this study will follow the approach proposed by Radiation Protection (RP) 122 part II [European Commission, 2001].

2. Materials and methods

2.1. Description of the studied concrete samples and their constituents

Cylindrical concrete specimens (d = typically 50 mm for P-series samples and typically 46 mm for C-series samples; h = typically 30 mm for P-series and typically 37 mm for C-series) with various incorporation rates of bauxite residue were prepared. Bauxite residue, in its state as it was produced as part of fine aggregate to produce alkali activated concrete, was incorporated directly in the specimen. In both casted (C-series) and semi-pressed (P-series) concrete specimens the aluminosilicate component was represented by a granulated blast-furnace slag with basicity modulus of 1 and content of glassy phase of 80. The compositions of concrete mixtures produced by the semi-dry pressing technique (P1–P5) and by the high slump casting technique (C1–C4) are given in Table 1. The pressing technique allows production of prefabricated products like tiles, bricks and etc. The casting technique allows production of pre-casted and on-site casted construction materials and is often applied for concrete structures on the basis of Portland cement and concrete. The different types of samples are representative for the most common ways that concretes are produced and applied. Two different samples with the same red mud bauxite concentration (P5 and C3 contain both 40% red mud by mass; P4 and C2 contain both 50% red mud by mass) were characterized by gamma-ray spectrometry to demonstrate that the impact of the production (casting or pressing) method is negligible from a radiological point of view.

A cement of the following composition (by mass) was chosen: 87% slag (Ground-granulated blast-furnace slag), 5% OPC (Ordinary Portland Cement), 4% Na_2CO_3 and 4% $Na_2O \cdot SiO_2 \cdot 5H_2O$. All cement constituents were milled until a Blaine fineness of 350–450 m^2/kg (specific surface) was obtained.

Bauxite residue from Ukraine was used in the experiments. It has the following mineralogical composition (by mass): 25–27% hematite, 25–28% goethite, 4.5–6.5% rutile and anatase, 15–17% hydrogarnets, 6–7% sodium aluminosilicate hydrate and 2.5–3.0% calcite.

Local river sand with maximum grain size of 1.2 mm and bauxite residue with particle sizes varying from 50 to 1000 μm were used as aggregates.

2.2. Radiological analysis

Bauxite residue samples for gamma-ray spectrometry were transferred to radon tight Teflon containers and stored for at least 21 days for secular equilibrium to be established between ^{226}Ra and its daughters. The sample mass ranged from 111 to 136 g (dry mass). The sample density ranged from 1.9 to 2.2 g/cm^3. The sample containers were positioned on a holder 11.4 mm on top of a HPGe-detector. This detector is located in the above ground Radionuclide Metrology Laboratory at the European Commission's Joint Research Centre in Geel, Belgium. The HPGe detector was a coaxial detector with a relative efficiency of 46% (FWHM: 1.41 at 662 keV and 1.86 at 1332 keV) with a shield composed of 1 mm Cu and 10 cm low-activity Pb. The measured percent dead time ranged from 0.02% to 0.04% for all samples. The samples were measured for a period ranging from 3 to 8 days.

Data acquisition and spectrum analysis were performed using Canberra's Genie 2000 software. The full energy peak efficiencies, ε, were calculated using Monte Carlo simulations with the EGSnrc Monte Carlo code [Kawrakow et al., 2011]. The computer model of the detector has been validated through participation proficiency testing exercises. The model uses measured dimensions of the sample, composition of the sample and the detector as input. The simulations assume that the gamma-ray emissions are isotropic and uncorrelated. All calculations assume that the radionuclides are homogeneously distributed in the sample and that the sample material is homogeneously distributed in the sample container. The use of Monte Carlo calculations has the additional benefit that the correction for coincidence summing which occurs in decays with cascading gamma-rays is obtained in the same calculation as the FEP efficiency.

Table 1
Concrete mixture design for semi-dry pressing (P = 30 MPa) and slump casting.

Sample	Concrete mixture design, % (by mass); (100% corresponds to dry mass)				Compressive strength MPa
	Cement	Bauxite Red mud	Sand	H_2O	
P1	10	90	–	17	6.78
P2	15	85	–	17	5.45
P3	25	75	–	16	5.05
P4	25	50	25	14	10.0
P5	25	40	35	12	14.0
C1	25	60	15	32.5	15.0
C2	25	50	25	25.5	17.5
C3	25	40	35	23.5	23.5
C4	25	30	45	11.25	25.0

Gamma-rays emitted by the radionuclides occurring in natural decay series of ^{238}U and ^{232}Th as well as ^{235}U and ^{40}K were investigated. An overview of the investigated emission lines is given in Table 2. For each radionuclide with multiple gamma-rays, a weighted mean of the activity was calculated taking into account the activity of the different gamma-rays. The nuclear decay data was taken from the Decay Data Evaluation Project (DDEP) tables. [DDEP website] The ^{208}Tl activity has been divided with the branching factor (0.3594).

The 186 keV peak is a doublet with contributions from ^{235}U and ^{226}Ra. The activity of ^{235}U is calculated after subtracting the contribution from ^{226}Ra to the 186 keV peak. The ^{226}Ra activity was determined by its daughters, ^{214}Pb and ^{214}Bi. The activity concentration (in this paper meaning the activity per unit mass) was determined by dividing the final activity determined for each radionuclide (the mother radionuclide in cases with short-lived daughters) by the measured dry mass of the sample.

The uncertainties of the obtained activity concentrations are the combined standard uncertainties calculated according to the GUM (Guide to the expression of uncertainty in measurement). [JCGM WG1, 2008] When combining several gamma-rays to one radionuclide and several daughters to one mother radionuclide using weighted means, the correlated parameters were added separately in quadrature in order not to obtain unrealistic and far too low final uncertainties.

2.3. Activity concentration indexes as screening tools for public exposure

The activity concentration index for building materials (ACI_{BM}), proposed by Markkanen and implemented in the COUNCIL DIRECTIVE 2013/59/EURATOM (EU-BSS), is calculated using the activity concentration of ^{226}Ra, ^{232}Th and ^{40}K (Equation (1)) [CE, 2014; Markkanen, 1995]. The activity concentration index for materials used for streets and playgrounds (ACI_{SP}), as defined by Markkanen, is calculated using the activity concentration of ^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs (Equation (2)) [Markkanen, 1995]. More information on the models used for both indexes is shown in Table 3. Note that an $ACI_{BM} > 1$ indicates an effective gamma dose larger than 1 mSv/a whereas an ACI_{SP} indicates an effective gamma dose larger than 0.1 mSv/a: both indexes were designed for different dose models. To calculate the ACIs secular equilibrium is assumed between ^{232}Th and ^{228}Ra and between ^{226}Ra and its two daughters ^{214}Pb and ^{214}Bi. The used activity concentration of ^{232}Th is in reality the activity concentration of ^{228}Ac and the activity concentration of ^{226}Ra is in reality the weighted mean between the activity

Table 2
Overview of the investigated gamma lines with data obtained from DDEP. [DDEP website].

Radionuclide	Energy (keV)	Probability of emission (%)	Radionuclide	Energy (keV)	Probability of emission (%)
^{234}Th	63.3	3.75	^{228}Ac	209.248	3.97
	92.38	2.18		328.004	3.04
	92.8	2.15		409.46	2.02
^{234m}Pa	766.361	0.323		463.002	4.45
	1001.026	0.847		755.313	1.03
^{214}Pb	241.997	7.268		772.291	1.52
	295.224	18.414		794.942	4.31
	351.932	35.6		911.196	26.2
^{214}Bi	609.312	45.49		968.96	15.9
	768.356	4.892		1588.2	3.06
	806.174	1.262		1630.618	1.52
	934.061	3.1	^{224}Ra	240.986	4.12
	1120.287	14.91	^{212}Pb	238.632	43.6
	1155.19	1.635	^{212}Bi	1620.738	1.51
	1238.111	5.831	^{208}Tl	277.37	6.6
	1280.96	1.435		583.187	85
	1377.669	3.968		763.45	1.8
	1401.5	1.33		860.53	12.4
	1407.98	2.389		2614.511	99.755
	1509.228	2.128	^{235}U	143.767	10.94
	1729.595	2.844		185.72	57
	1764.494	15.31		163.356	5.08
	1847.42	2.025		205.316	5.02
	2118.55	1.158	^{40}K	1460.822	10.55
	2204.21	4.913	^{137}Cs	661.652	84.99
	2447.86	1.548			
^{210}Pb	46.539	4.252			

Table 3
Field of application and relevant parameters that define the underlying models for the activity concentration indexes and the dose assessments based on RP122.

	ACI_{BM}	ACI_{SP}	RP 122 Road construction	RP 122 Building construction
Geometry	Floor, ceiling, 4 walls	Plane	Plane	Floor, ceiling, 2 walls
Size geometry (m)	4 × 5 × 2.8 with thickness 0.2[a]	20 × 20 Thickness not specified	100 × 10 with thickness 0.4	3 × 4 × 2.5 with thickness 0.2
Density (kg/m^3)	2350	2350	2000	2300
Dilution factor	/	/	1	1
Exposure time (h)	7000	500	1800	1800
Dust concentration (mg/m3)	/	/	1	0.5
Breathing rate (m^3/h)	/	/	1.2	1.2
Direct ingestion (mg/h)	/	/	10	10
Dose criterion (mSv/a)	1	0.1	0.3	0.3
Exposure to workers/public:	Public	Public	Workers	Workers
Field of application:	Building materials	Streets, playgrounds and roads	Road construction	Building construction
Reference(s)	CE 2014; RP112 [European Commission, 1999]	Markkanen, 1995; STUK, 2010	RP 122, NIRS database	RP 122, NIRS database

[a] In Markkanen 1995 size is 12 × 7 × 2.8 m with thickness of 0.2 m.

concentrations of ^{214}Pb and ^{214}Bi. ^{40}K and ^{137}Cs were directly measured using their respective gamma emission lines at 1460.8 keV and 661.6 keV.

$$ACI_{BM} = \frac{Ac_{226Ra}}{300\,Bq/kg} + \frac{Ac_{232Th}}{200\,Bq/kg} + \frac{Ac_{40K}}{3000\,Bq/kg} \tag{1}$$

$$ACI_{SP} = \frac{Ac_{226Ra}}{700\,Bq/kg} + \frac{Ac_{232Th}}{500\,Bq/kg} + \frac{Ac_{40K}}{8000\,Bq/kg} + \frac{Ac_{137Cs}}{2000} \tag{2}$$

With Ac as activity concentration of the mentioned radionuclide expressed in Bq/kg.

The uncertainty on the activity concentration indexes (u) is calculated using Equations (3) and (4).

$$u(ACI_{BM}) = \sqrt{\left(\frac{1}{300}\right)^2 u^2\ (Ac_{226Ra}) + \left(\frac{1}{200}\right)^2 u^2\ (Ac_{232Th}) + \left(\frac{1}{3000}\right)^2 u^2\ (Ac_{40K})} \tag{3}$$

$$u(ACI_{SP}) = \sqrt{\left(\frac{1}{700}\right)^2 u^2(Ac_{226Ra}) + \left(\frac{1}{500}\right)^2 u^2(Ac_{232Th}) + \left(\frac{1}{8000}\right)^2 u^2(Ac_{40K}) + \left(\frac{1}{2000}\right)^2 u^2(Ac_{137Cs})} \tag{4}$$

where u(Ac_{226Ra}) is the uncertainty on the activity concentration of ^{226}Ra, u(Ac_{232Th}) is the uncertainty on the activity concentration of ^{232}Th, u(Ac_{40K}) is the uncertainty on the activity concentration of ^{40}K, and u(Ac_{137Cs}) is the uncertainty on the activity concentration of ^{137}Cs.

2.4. Dose assessment for occupational exposure

Following RP 122 (part II) dose assessments were performed that consider the impact of concrete containing bauxite residues following different scenarios for workers active in building construction and road construction. All calculations of the different scenarios were performed using the NIRS (Japanese National Institute on Radiological Sciences) database dose assessment tool. The scenarios named in part 4.2. of RP122 part II as "4.2.6. Road constructions" and "Building construction with NORM containing building materials" are listed on the NIRS website as respectively "Road construction" and "Building construction" under "Dose assessment for workers who handle NORM (including ores and building materials)". Each scenario is characterized by specific parameters listed in Table 3. In both scenarios the highest activity concentrations of all measured radionuclides from the ^{238}U decay series, from ^{232} Th day series and for ^{40}K were taken for different percentages of incorporated bauxite residue. RP 122 uses as dose criterion 0.3 mSv/year. In this case the total effective dose (external, inhalation and ingestion dose) is calculated.

Important sources of uncertainty in the dose analysis are the uncertainty on the occupation time, on the dust concentration and on the ingestion rate which are unknown. The models used for the dose assessment are simplified models that do not correspond to actual situations. The uncertainty shown in the results originates from the uncertainty on the activity concentration of the selected radionuclide with the highest activity concentration.

3. Results and discussion

Even at high incorporation rates of bauxite red mud, reaching 90% by mass, the strength of the resulting concrete remains rather high (Table 1), allowing from a mechanical point of view to manufacture such construction products as brick for various applications, tiles, plates, etc. using the technology of semi-dry pressing. Alternatively, concrete constructions can be precasted or made on site by the casting technique.

A stepwise approach is used for the radiological evaluation of the considered applications of the newly synthesized concretes that contain bauxite residues as an aggregate: (1) The activity concentrations of several radionuclides occurring in the natural

Table 4
Activity concentrations (Bq/kg, dry weight) of radionuclides from the ^{238}U decay as well as for ^{235}U (k = 2) for the nine test samples.

Series	^{238}U					^{235}U
Sample (% by mass bauxite red mud)	^{234}Th	^{234m}Pa	^{214}Pb	^{214}Bi	^{210}Pb	^{235}U
P1 (90%)	(11 ± 2)*10	(9 ± 2)*10	69 ± 8	70 ± 6	(12 ± 4)*10	3.8 ± 0.5
P2 (85%)	(10 ± 1)*10	(8 ± 2)*10	68 ± 6	68 ± 6	(12 ± 6)*10	4.3 ± 0.5
P3 (75%)	(9 ± 2)*10	(8 ± 2)*10	66 ± 6	66 ± 6	(12 ± 6)*10	3.8 ± 0.5
P4 (50%)	(7 ± 1)*10	(7 ± 1)*10	53 ± 6	52 ± 4	(7 ± 2)*10	3.3 ± 0.4
P5 (40%)	(7 ± 1)*10	(6 ± 1)*10	46 ± 4	46 ± 4	(5 ± 2)*10	2.9 ± 0.4
C1 (60%)	(8 ± 1)*10	(7 ± 1)*10	49 ± 6	48 ± 2	(8 ± 3)*10	3.5 ± 0.4
C2 (50%)	(7 ± 2)*10	(6 ± 1)*10	51 ± 5	49 ± 5	(6 ± 2)*10	2.6 ± 0.3
C3 (40%)	(6 ± 1)*10	(5 ± 1)*10	42 ± 4	40 ± 4	(4 ± 2)*10	2.5 ± 0.3
C4 (30%)	(5 ± 2)*10	(5 ± 1)*10	39 ± 4	37 ± 4	(2 ± 2)*10	1.6 ± 0.3

decay series of ^{238}U and ^{232}Th as well as ^{235}U and ^{40}K were determined using gamma-ray spectrometry while monitoring the secular equilibrium. (2) Activity concentration indexes are then used for initial screening of the public exposure regarding the use of the newly produced concretes as a building material or for constructing streets and playgrounds. (3) In addition, in order to also evaluate the occupational exposure, a dose assessment for construction workers, based on RP122 part II, is performed.

3.1. Study of the activity concentrations

As mentioned in the introduction, average activity concentrations of 165 Bq kg^{-1} ^{226}Ra, 328 Bq kg^{-1} ^{232}Th and 53 Bq kg^{-1} ^{40}K are reported in Ukrainian national studies [U.D.C. 691.5] for the Ukrainian bauxite residue. The results of the gamma spectrometric analysis of bauxite residue containing concrete mixtures produced by semi-dry pressing and casting are shown in Table 4 and Table 5.

When studying the ^{238}U decay series (Table 4) for all samples and when comparing the activity concentrations of each radionuclide to the nearest decay product measurable via gamma-ray spectrometry (^{234}Th to ^{234m}Pa; ^{234m}Pa to ^{214}Pb; ^{214}Pb to ^{214}Bi and ^{214}Bi to ^{210}Pb) secular equilibrium seems to be present in all samples when considering the measurement uncertainty. Only minor deviations from secular equilibrium can be observed in the ^{238}U decay series, for example for the sample P1, when comparing the activity concentration of ^{234}Th to the activity concentration of ^{214}Pb or ^{214}Bi. Generally speaking for the studied concrete mixtures the whole ^{238}U decay series is in equilibrium or there are only minor deviations from equilibrium. Focusing on the ^{232} Th day series (Table 5) also in this case, no disequilibrium could be observed when studying the individual samples. The uncertainty on the activity concentration of ^{212}Bi is higher in comparison with the other radionuclides of the chain. This is due to the fact that a limited number of counts is registered in the 1620.7 keV peak of ^{212}Bi, leading to limited counting statistics.

For all samples, the ^{238}U/^{235}U activity ratio shows no deviation from the expected value of 21.6 which indicates natural isotopic abundance. The measured ^{235}U activity concentrations are shown in Table 4.

In none of the samples ^{137}Cs was detected and the MDA (Minimum Detectable Activity concentration) was in all cases below 1 Bq/kg.

3.2. Public exposure

Two ACIs, as described by Markkanen, are used to verify whether the bauxite concrete mixtures are safe to use considering public exposure [Markkanen, 1995]. Fig. 1 shows the results of the ACI_{BM}, which focusses on building materials and is used by the COUNCIL DIRECTIVE 2013/59/EURATOM (EU-BSS) [CE, 2014], discussed in 3.2.1. Fig. 2 shows the results of the ACI_{SP}, which focusses on streets and playgrounds, discussed in 3.2.2.

3.2.1. The activity concentration index for building materials

All the calculated ACI_{BM}s are below the EU-BSS threshold level of 1 and therefore from a radiological point of view the materials can be accepted for usage as building materials considering external exposure to the public. If, according to the EU-BSS, the ACI_{BM} exceeds this threshold level, the indoor external exposure to gamma radiation emitted by building materials in addition to outdoor external exposure, of 1 mSv per year needs to be verified.

When considering concrete for bulk applications in building materials, as is the case here, then the ACI is a reliable screening tool since it was designed for this type of scenario. For other types of materials next to concrete or for thin layer application it is advisable to use a density and thickness corrected index. [Nuccetelli et al., 2015a].

3.2.2. The activity concentration index for streets and playgrounds

All the calculated ACI_{SP}s are well below the threshold level of 1. This threshold level, proposed by Markkanen and used in the Finnish radiation protection regulation, corresponds to a dose

Table 5
Activity concentrations (Bq/kg, dry weight) of radionuclides from the ^{232} Th day series as well as for ^{40}K (k = 2) for the nine test samples.

Series	^{232}Th					^{40}K
Sample (% by mass bauxite red mud)	^{228}Ac	^{224}Ra	^{212}Pb	^{212}Bi	^{208}Tl	^{40}K
P1 (90%)	(12 ± 1)*10	(12 ± 1)*10	(12 ± 1)*10	(12 ± 2)*10	(12 ± 1)*10	(8 ± 2)*10
P2 (85%)	(12 ± 1)*10	(12 ± 1)*10	(12 ± 1)*10	(11 ± 2)*10	(12 ± 1)*10	(8 ± 2)*10
P3 (75%)	(10 ± 1)*10	(10 ± 1)*10	(10 ± 1)*10	(12 ± 2)*10	(11 ± 1)*10	(9 ± 2)*10
P4 (50%)	77 ± 8	80 ± 8	78 ± 8	(7 ± 1)*10	78 ± 6	(8 ± 2)*10
P5 (40%)	65 ± 6	63 ± 8	66 ± 6	(6 ± 1)*10	65 ± 6	(8 ± 2)*10
C1 (60%)	83 ± 8	(8 ± 1)*10	83 ± 8	(7 ± 2)*10	82 ± 8	(6 ± 1)*10
C2 (50%)	69 ± 7	71 ± 9	70 ± 7	(6 ± 1)*10	70 ± 7	(6 ± 1)*10
C3 (40%)	58 ± 6	56 ± 7	59 ± 6	(5 ± 1)*10	58 ± 6	(6 ± 1)*10
C4 (30%)	48 ± 5	49 ± 7	49 ± 5	(4 ± 1)*10	48 ± 5	(6 ± 1)*10

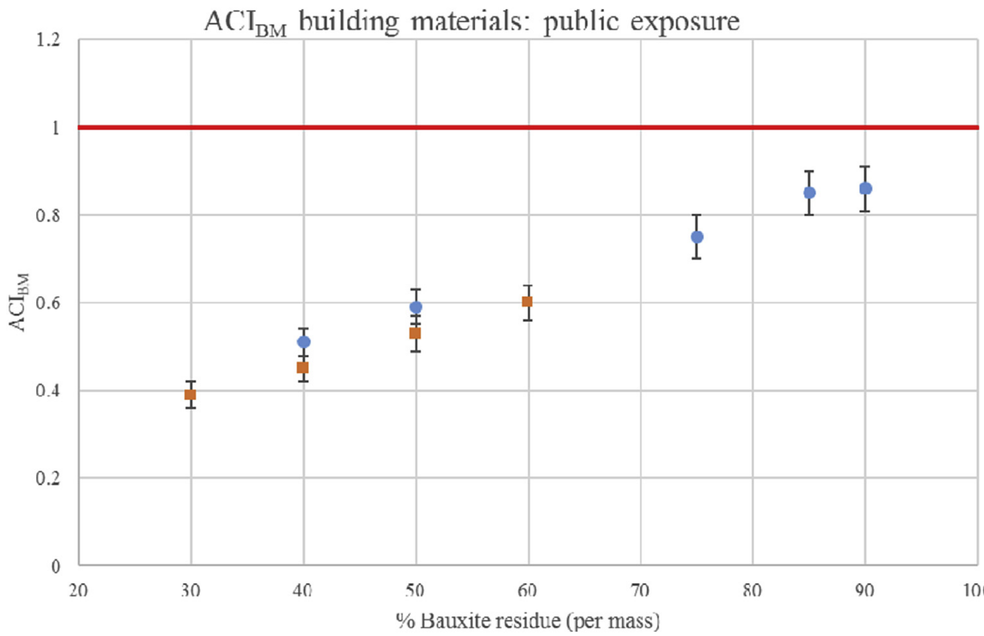

Fig. 1. Activity concentration index for building materials for different bauxite concrete mixtures with different % (by mass) of bauxite residue incorporation. Blue spheres represent the P-series, red squares represent C-series (k = 2). Red line indicates threshold value of 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

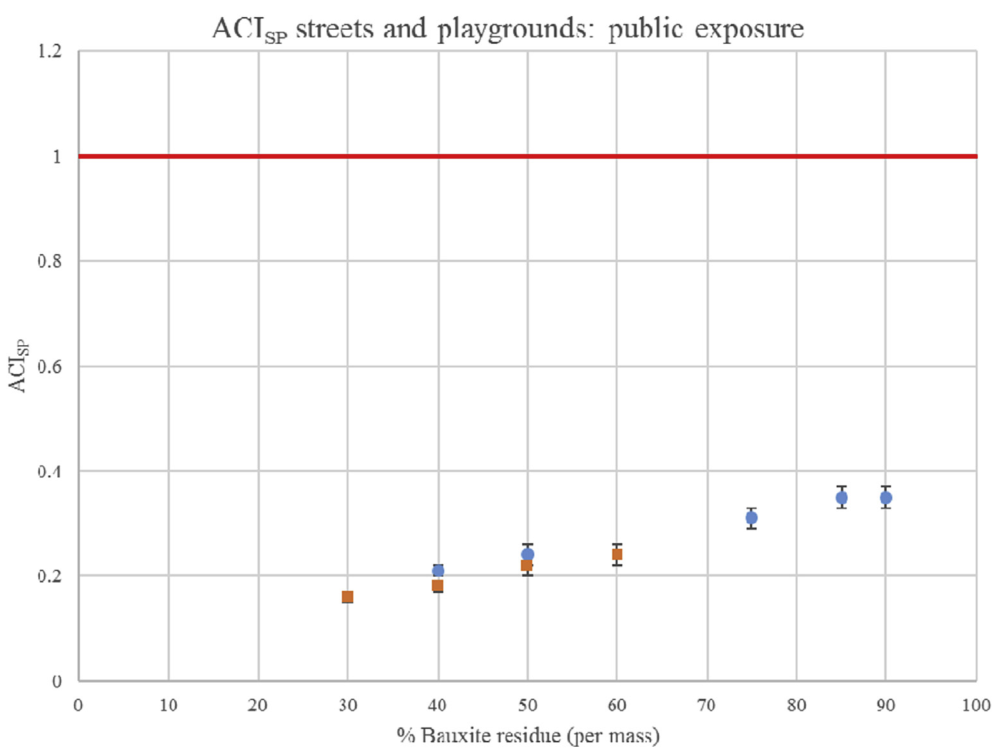

Fig. 2. Activity concentration index for streets and playgrounds for different bauxite concrete mixtures with different % (by mass) of bauxite residue incorporation. Blue spheres represent the P-series, red squares represent the C-series (k = 2). Red line indicates threshold value of 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

criterion of 0.1 mSv per year.

This implies that from a radiological point of view, the mixtures are safe for public use as road, street and playground considering external exposure [STUK, 2010; Markkanen, 1995]. The ACI$_{SP}$ developed by Markkanen involves, next to the naturally occurring radionuclides, also ^{137}Cs in the evaluation.

3.3. Occupational exposure

Following RP 122 (part II) a simplified dose assessment was made that considers the impact of concrete containing bauxite residue on building and road construction workers. The results of the simulation are shown in Figs. 3 and 4. In this case the total

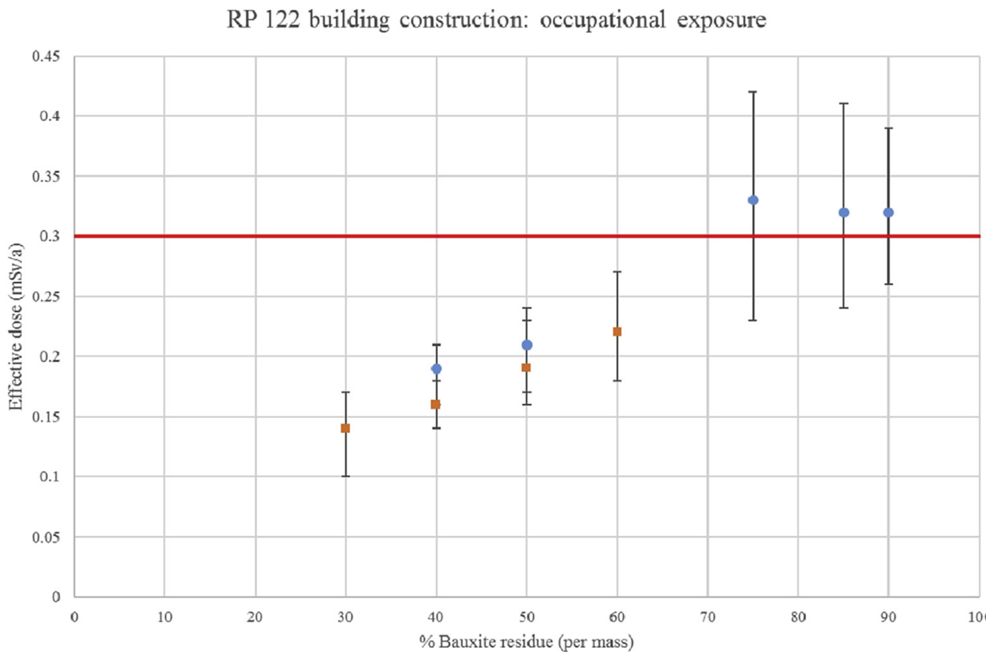

Fig. 3. Total effective dose for workers active in building construction in function of the different bauxite concrete mixtures with different % (by mass) of bauxite residue incorporation. Blue spheres represent P-series, red squares represent C-series. The red line indicates the dose criterion of 0.3 mSv/a proposed by RP122. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

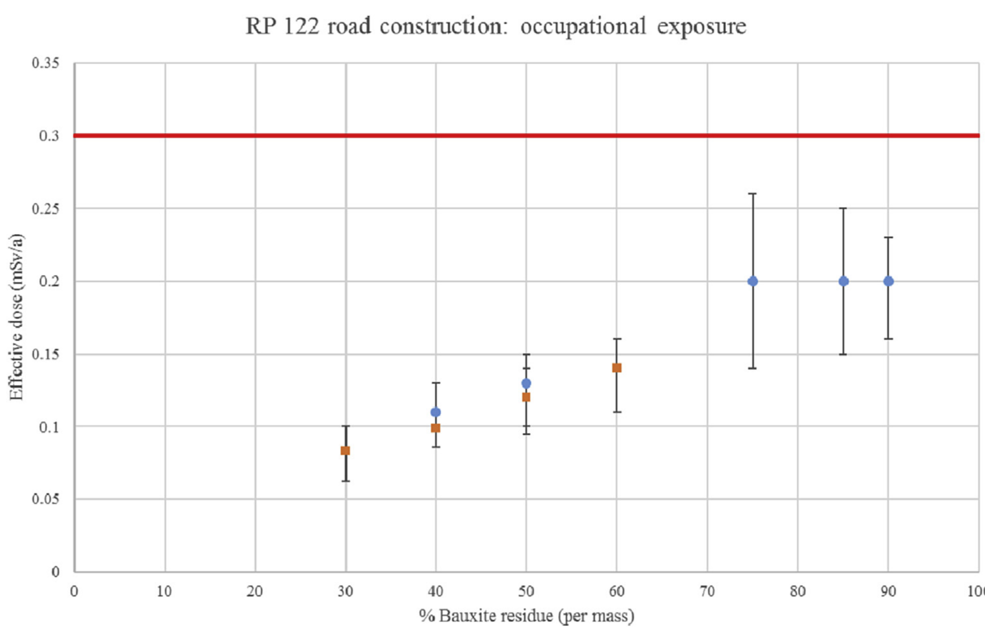

Fig. 4. Total effective dose for workers active in road construction in function of the different bauxite concrete mixtures with different % (by mass) of bauxite residue incorporation. Blue spheres represent the P-series, red squares represent the C-series. The red line indicates the dose criterion of 0.3 mSv/a proposed by RP122. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

effective dose (external, inhalation and ingestion dose) is considered. The dose criterion used by RP122 is 0.3 mSv/a.

3.3.1. Dose assessment for building construction worker

The mass incorporation of 75% bauxite in the concrete mixtures already leads to effective doses above the dose criterion of 0.3 mSv/a (Fig. 3). From the dose calculations it can be assessed that an incorporation rate of 60% (by mass) provides an acceptable incorporation level to assure that the dose to the workers will not be higher than the dose criterion proposed by RP 122. Typically 95% of the calculated total dose could be assigned as external dose.

3.3.2. Dose assessment for road construction worker

Even when using high incorporation rates of 90% (by mass) for road construction the dose criterion of 0.3 mSv/a is not exceeded (Fig. 4). From a radiological point of view, road construction workers are able to safely use bauxite concrete mixtures with high contents of bauxite red mud. In this case typically 85% of the calculated total dose could be assigned as external dose.

As reported by Nuccetelli et al. (2015b), average activity concentrations of bauxite residue are origin and therefore country dependent. For European countries activity concentrations for bauxite residue of up to 379 ± 43 Bq/kg ^{226}Ra, 472 ± 23 Bq/kg ^{232}Th and 21 ± 11 Bq/kg ^{40}K (Greece) were found. In the world even activity concentration of 1047 Bq/kg ^{226}Ra, 350 Bq/kg ^{232}Th and 335 Bq/kg ^{40}K are reported (Jamaica). When assuming a dilution factor of 0.9 (90% (by mass) incorporation of the bauxite residue) total doses up to 0.64 mS/a (Greece) and 0.89 mS/a (Jamaica) can be calculated for road construction workers. Also in this case the external dose is the main contributing factor (0.58 mSv/a for workers in Greece; 0.8 mSv/a for workers in Jamaica) to the total dose of the workers. Therefore an adapted monitoring strategy, taking into consideration the way that variations in the origin of the incoming material occur over time, is required to ensure that the dose criteria are met.

4. Conclusion

The current study demonstrates that the studied Ukrainian bauxite residue can, based on the ACI_{BM} defined by the EU-BSS and the ACI_{SP} defined by Markkanen for streets and playgrounds, be used for building materials and for road construction, even in percentages reaching 90% (by mass) incorporation.

However when also considering occupational exposure and using the dose assessment models of RP122 (part 2) for building construction workers it becomes advisable to incorporate less than 75% (by mass) of bauxite red mud. Upon incorporating 75% (by mass) bauxite residue or more a total effective dose higher that the dose criterion proposed by RP122 (0.3 mSv/a) was found. 60% (by mass) of bauxite residue incorporation was found to be acceptable for building construction. For the case of road construction, based on the model proposed by RP122, 90% (by mass) bauxite residue incorporation can be accepted also from the perspective of occupational exposure.

Considering the large variation in the activity concentration of the bauxite ore and resulting bauxite residues and considering that the ores accepted by industries and the processing of the ores will vary over time, the authors recommend that screening of the bauxite residues should determine the possible applications.

In order to evaluate reuse options for NORM residues, the COST Action NORM4Building recommends to use a holistic approach and to consider all aspects that can determine whether a specific reuse practice becomes possible. A holistic approach can only function if chemical, radiological, physical and mechanical data is available for a specific type of residue or construction material. Therefore in addition to this paper, a detailed study of the chemical, physical and mechanical properties of the discussed concretes is in preparation. [Krivenko et al., in preparation].

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References

CE - Council of the European Union, 2014. Council Directive 2013/59/EURATOM of 5 December 2013 laying down basic safety standards for protection against the dangers arising from exposure to ionising radiation, and repealing Directives 89/618/Euratom, 90/641/Euratom, 96/29/Euratom, 97/43/Euratom and 2003/122/Euratom. Off. J. Eur. Union L 13, 1e73, 17.1.2014.

CPR 305/2011, 2011. European Parliament regulation No 305/2011 laying down harmonized conditions for the marketing of construction products.

DDEP website, Laboratoire National Henri Becquerel http://www.nucleide.org/DDEP_WG/DDEPdata_by_Z.htm, consulted in March and April of 2016.

European Commission, 1999. Radiation Protection 112 Radiological Protection Principles Concerning the Natural Radioactivity of Building Materials.

European Commission, 2001. Radiation Protection 122 Practical Use of the Concepts of Clearance and Exemption Part II Application of the Concepts of Exemption and Clearance to Natural Radiation Sources.

Glukhovsky, V.D., 1989. Durability of concrete: aspects of admixtures and industrial by-products. In: Proc. 2nd Int. Science, edit Leif Berntsson et.al., Swedish Council for Building Research, Trondheim, Norway, pp. 53–62.

JCGM WG1., 2008. Evaluation of Measurement Data – Guide to the Expression of Uncertainty in Measurement.

Kawrakow, I.I., Mainegra-Hing, E., Rogers, D.W.O., Tessier, F., Walters, B.R.B., 2011. The EGSnrcCode System: Monte Carlo Simulation of Electron and Photon Transport. Technical Report PIRS–701 (4th Printing). National Research Council of Canada, Ottawa, Canada.

Ke, X., Ye, N., Bernal, S.A., Provis, J.L., Yang, J., 2014. Preparation of one-part geopolymer from thermal alkali activated bauxite red mud. In: Proc. Second Int. Conf. On Advances in Chemically-activated Materials. June 1–3, Changshi, P.R.China, pp. 204–211.

Kovacs, T., Sas, Z., Somlai, J., Jobbagy, V., Szeiler, G., 2012. Radiological investigation of the effects of red mud disaster, 2012. Radiat. Prot. Dosim. 152, 1–3, 76-79.

Kovacs, T., Sas, Z., Jobbagy, V., Csordas, A., Szeiler, G., Somlai, J., 2013. Radiological aspects of red mud disaster in Hungary. Acta Geophys. 61 (4), 1026–1037.

Krivenko, P., Petropavlovsky O, Rostovskaya, G., 1996. Patent of Ukraine UA 10286 a, C 04 B7/06, 7/06, 25.12.96, Bulletin No 4.

Krivenko, P., Kovalchuk, A., Pasko, A., Croymans-Plaghki, T., Schreurs, S., Hult, M., Lutter, G., Marissens, G., Schroeyers, W., 2016. In Preparation for Construction and Building Materials.

Kumar, S., Kumar, R., Bandopadhyay, A., 2006. Innovative methodologies for the utilization of wastes from metallurgical and allied industries. Resour., Conserv. Recy. 48, 301–314.

Markkanen, M., 1995. Radiation Dose Assessments for Materials with Elevated Natural Radioactivity, 1995. STUK-B-STO 32, Helsinki, p. 25. + app. 13 pp.

NIRS database. NIRS, NORM Database Research Center for Radiation Protection – National Institute of Radiological Sciences. consulted in March and April 2016. http://www.nirs.go.jp/db/anzendb/NORMDB/ENG/1_datasyousai.php.

Nuccetelli, C., Leonardi, F., Trevisi, R., 2015a. A new accurate and flexible index to assess the contribution of building materials to indoor gamma exposure. J. Environ. Radioact. 143, 70–75.

Nuccetelli, C., Pontikes, Y., Leonardi, F., Trevisi, R., 2015b. New perspectives and issues arising from the introduction of (NORM) residues in building materials: a critical assessment on the radiological behaviour. Constr. Build. Mater. 82, 323–331.

Pan, Z., Dongxu, L., Jian, Y., Nanru, Y., 2002. Hydration products of alkali-activated slag-bauxite red mud cementitions materials. Cem. Concr. Res. 32, 357–362.

Pan, Z., Dongxu, L., Jian, Y., Naunu, Y., 2003. Properties and microstructure of the hardened alkali-activated bauxite red mud slag cementitions material. Cem. Concr. Res. 33, 1437–1441.

Pascual, J., Corpas, F., Lopez-Beceiro, J., Benitez-Guerrero, M., Artiaga, R., 2009. Thermal characterization of a Spanish bauxite red mud. J. Therm. Analysis Calorim. 96 (2), 407–412.

Pontikes, Y., Nikolopoulos, P., Angelopoulos, G.N., 2007. Thermal behavior of clay mixtures with bauxite residue for the production of heavy clay ceramics. J. Eur. Ceram. Soc. 27, 1645–1649.

Power, G., Grafe, M., Klauber, C., 2009. Review of Current Bauxite Residue Management, Disposal and Storage: Practices, Engineering and Science, pp. 3–4. CSIRO Document DMR-3608.

Power, G., Gräfe, M., Klauber, C., 2011. Bauxite residue issues: I. Current management, disposal and storage practices. Hydrometallurgy 108, 33–45.

Rostovskaya, G.S., 1994. Alkaline binders based on bauxite residues. In: First Int. Conference on Alkaline Cements and Concretes, Kyiv, Ukraine, 1, pp. 329–346.

Sglavo, V.M., Maurina, S., Conci, A., Salviati, A., Carturan, G., Cocco, G., 2000a. Bauxite red mud in the ceramic industry Part 2: production of clay- based ceramics. J. Eur. Ceram. Soc. 20, 245–252.

Sglavo, V.M., Campostrini, R., Maurina, S., Carturan, G., Monagheddu, M., Budroni, G., Cocco, G., 2000b. Bauxite red mud in the ceramic industry. Part 1 Thermal behaviour. J. Eur. Ceram. Soc. 20, 235–244.

Somlai, J., Jobbágy, V., Kovács, J., Tarján, S., Kovács, T., 2008. Radiological aspects of the usability of red mud as building material additive. J. Hazard. Mater. 150 (11), 541–545, 3.

STUK, 2010. Guide ST 12.2, the Radioactivity of Building Materials and Ash, pp. 1–7.

Tsakiridis, P.E., Agatzini-Leonardou, S., Oustadakis, P., 2004. Bauxite red mud addition in the raw meal for the production of Portland cement clinker. J. Hazard. Mater. 116, 103–110.

Turhan, S., Arıkan, I.H., Demirel, H., Gungör, N., 2011. Radiometric analysis of raw materials and end products in the Turkish ceramics industry. Radiat. Phys. Chem. 80, 620–625.

Turhan, S., Gündüz, Y., Varinlioğl, A., 2014. Gamma, spectrometric characterization of refractory products used in Turkey. Radiat. Phys. Chem. 97, 1–5.

U.D.C. 691.5, Register # ИА 01013445Р, Krivenko, P., Petropavlovsky, O., Rostovska, G., 1992-1995. Synthesis of Analogs to Natural Minerals and Development of Technological Parameters and Selection of Equipment for Ecologically Friendly Localization of Toxic and Radioactive Wastes in Building Materials and Compounds", State Budget of Ukraine, Program 16.3.4, Ministry of Education: "Toxicological Studies. To Develop Recommendations on Rational Uses of Red Muds and Articles Thereof. To Develop Normative Documentation" (01.01.1995-31.12.1995).

UNSCEAR, United Nations, 2000. Sources and Effects of Ionizing Radiation. United nations scientific committee on the effects of atomic radiation, Report to the General Assembly, with Scientific Annexes. United Nations Scientific Committee on the Effects of Atomic Radiation, New York.

Viruthagiri, G., Rajamannan, B., Jawahar, K.S., 2013. Radioactivity and associated radiation hazards in ceramic raw materials and end products. Radiat. Prot. Dosim. 157 (3), 383–391.