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

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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.