Natural radioactivity in clay bricks and cements used in Albania

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Abstract

This study has the aim to determine the radioactivity content of clay bricks and cements used as building materials in Albania in order to characterize their potential radiological hazard to humans. Up to 60 samples are investigated in order to measure the natural activity concentrations of ^{226}Ra (^{238}U), ^{232}Th and ^{40}K. The measurements were carried out using a fully automated high-resolution gamma-ray spectrometry using two coupled HPGe detectors (MCA_Rad system). The results indicate that the activity concentration in clay bricks ranges between 490.6 ± 19.4 Bq/kg to 820.3 ± 27.0 Bq/kg for ^{40}K, between 25.8 ± 1.4 Bq/kg to 51.9 ± 1.7 Bq/kg for ^{226}Ra and between 29.2 ± 1.9 Bq/kg to 55.1 ± 2.5 Bq/kg for ^{232}Th. While for cement the radioactivity content range between 107.3 ± 6.2 Bq/kg to 250.8 ± 10.6 Bq/kg for ^{40}K, between 40.9 ± 1.2 Bq/kg to 61.4 ± 1.6 Bq/kg for ^{226}Ra and between 11.5 ± 1.0 Bq/kg to 22.9 ± 1.3 Bq/kg for ^{232}Th. The radiological hazards due to the natural radioactivity in the samples were inferred by calculation of the activity concentration index (ACI). The corresponds activity concentration index range between 0.48 ± 0.02 to 0.63 ± 0.04 for clay bricks and 0.29 ± 0.03 to 0.37 ± 0.02 for cements. These values correspond to an annual effective dose rate lower than 1mSv/y. Indeed due to the final utilization of clay bricks and cements in the dwelling the annual effective dose rate was calculated to range between 0.28 ± 0.02 mSv/y to 0.45 ± 0.04 mSv/y and 0.08 ± 0.04 mSv/y to 0.17 ± 0.02 mSv/y respectively. Therefore, these materials are classified as A1 category (according to European Commission recommendations), i.e. materials used as bulk material without restriction.

***Keywords*:** Radiological hazard; Activity concentration index; Building materials; HPGe gamma-ray spectrometer

Introduction

People are continuously exposed to natural background radiation, where an important contribution comes from the external terrestrial radiation, principally due to uranium and thorium decay chains, and by ^{40}K, which is present in the Earth's crust. According to **UNSCEAR (2008)**, this contribution corresponds to approximately 20% (ranging between 0.3-1.0 mSv/y) of the average worldwide radiation exposure (2.4 mSv/y). On the other hand, considering an indoor occupancy factor of 80%, building materials are one of the sources of direct radiation exposure for human kind. According to European recommendations (**EC, 2011**), building materials are classified as suitable for use by regulating an upper external radiation exposure limit of 1.0 mSv/y.

In this study, we measured the we measured the radioactivity levels and resulting dose rates from some building materials used Albania. Clay bricks and cements manufactured in Albania, Constitute an important proportion of the domestic construction industry, as well as being exported to several foreign countries (**INSTAT, 2011**). However, there has not been a comprehensive study on the radioactivity concentration levels in building materials in Albania. Therefore, 12 different manufacturers were investigated by measuring 60 samples using a high-resolution gamma-ray spectrometer, to characterize the concentrations of ^{40}K, ^{226}Ra and ^{232}Th in clay bricks and cements.

Material and methods

Sampling and sample preparation

The Albanian industries of clay brick and cement have become heavily developed over the last few decades, offering quality products for the European market. In this study we investigated 12 different clay brick (9) and cement (3) manufacturers located across the country. A total of 60 samples of clay bricks (45) and cements (15) were collected. The samples of clay brick were crushed and milled into fine powders with particle sizes of less than 2 mm, while the samples of cement were directly processed because they were already in powder form. To remove the moisture content, all of the samples were dried in a temperature-controlled furnace at 110 °C for at least 24 hours (or until constant weight). After cooling in a moisture-free atmosphere, each sample was transferred for measurement into a cylindrical PVC container (with dimensions of Φ 7.5 cm x H 4.5 cm and an effective volume of 180 cm^3) and was then weighted. The hermetically sealed containers were stored for at least four weeks prior to being measurement to allow ^{226}Ra and its short-lived decay products to reach the secular equilibrium.

High-resolution gamma-ray spectrometry calibration and measurements

The natural radioactivity content of the building materials was investigated using a fully automated high-resolution gamma-ray spectrometry system, called the MCA_Rad system (**Xhixha et al., 2013a**). This equipment is composed of two coaxial HPGe p-type detectors with 60% relative efficiency, having an energy resolution of 1.9 keV at 1332.5 keV (^{60}Co). The HPGe detectors are accurately shielded with 10cm thick oxygen free copper and 10cm thick lead allowing to reach an environmental background reduction of two orders of magnitude. A severe lowering of manpower cost is obtained by a fully automated system which permits to measure up to 24 samples without any human attendance. Furthermore, a user-friendly software has been developed in order to analyze a high number of spectra, possibly with automatic procedure and customized output. The absolute photopeak efficiency of the MCA_Rad system has been determined for the most intense energies of the natural isotopes contained in three reference materials certified by International Atomic Energy Agency (**IAEA, 1987**) RGU-2, RGTh-1 and RGK-1 (**Xhixha et al., 2013b**). The certified reference materials (95% confidence interval), prepared in a powder matrix (240 mesh) contain 4940±30 Bq/kg of ^{238}U (diluted uranium ore BL5), 3250±90 Bq/kg of ^{232}Th (diluted thorium ore OKA-2) in a secular equilibrium and 14000±400 Bq/kg of ^{40}K (high-purity K_2SO). Self-absorption correction, due to variations in density and composition between the samples and the reference materials, was performed, considering the approach discussed in detail by **Bolivar (1997)**. The natural activity concentration of ^{226}Ra was determined through 351.9 keV (37.1%) of ^{214}Pb and 609.3 keV (46.1%) of ^{214}Bi. The activity of ^{232}Th was estimated as ^{228}Ra by measuring the gamma-ray of 911.1 keV (30.3%) of ^{228}Ac and 583.1 keV (33.2%) of ^{208}Tl. The activity concentration of ^{40}K was determined by measuring the 1460.8 keV gamma-ray. The minimum detectable activity (MDA) concentration was calculated for each energy of interest as described by **Currie (1986)**.

Results and discussions

Activity concentrations

Measuring for 1 hour the we determined the activity concentrations of 226Ra, 232Th and 40K in 60 samples. Their distribution in clay bricks and cements are shown respectively in **Figure 1**, **Figure 2** and **Figure 3**. The average activity concentrations of ^{40}K, ^{238}U (^{226}Ra) and ^{232}Th were, respectively, 644.1 ± 64.2 Bq/kg, 33.4 ± 6.4 Bq/kg and 42.2 ± 7.6 Bq/kg in the clay brick samples and 179.7 ± 48.9 Bq/kg, 55.0 ± 5.8 Bq/kg nd 17.0 ± 3.3 Bq/kg in the cement samples. The activity concentrations of K, U, and Th in the clay bricks were found to be lower than or comparable within 1σ to the typical activity concentrations of 670 Bq/kg, 50 Bq/kg and 50 Bq/kg for ^{40}K, ^{226}Ra and ^{232}Th, respectively (**EC, 1999**).

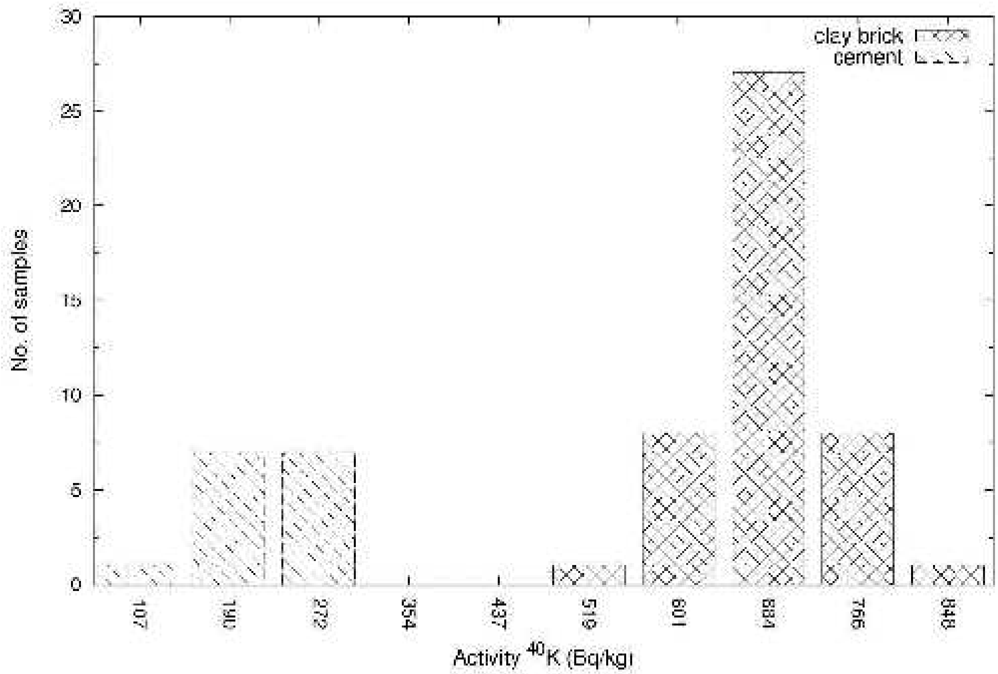

Figure 1. Distributions of activity concentration of ^{40}K (in Bq/kg) in clay bricks and cements.

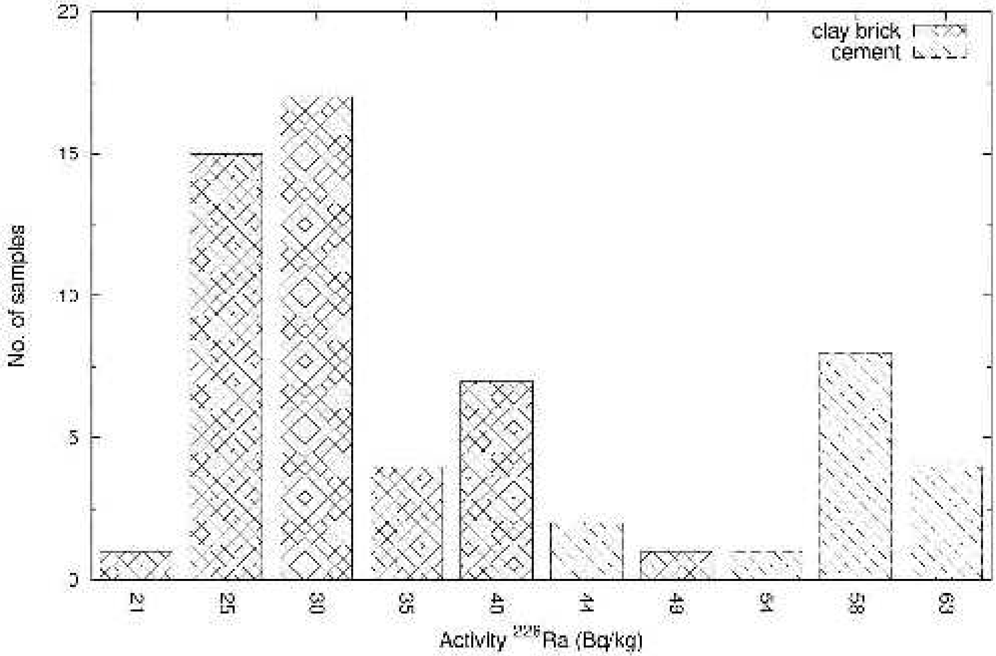

Figure 2. Distributions of activity concentration of $^{238}U(^{226}Ra)$ (in Bq/kg) in clay bricks and cements.

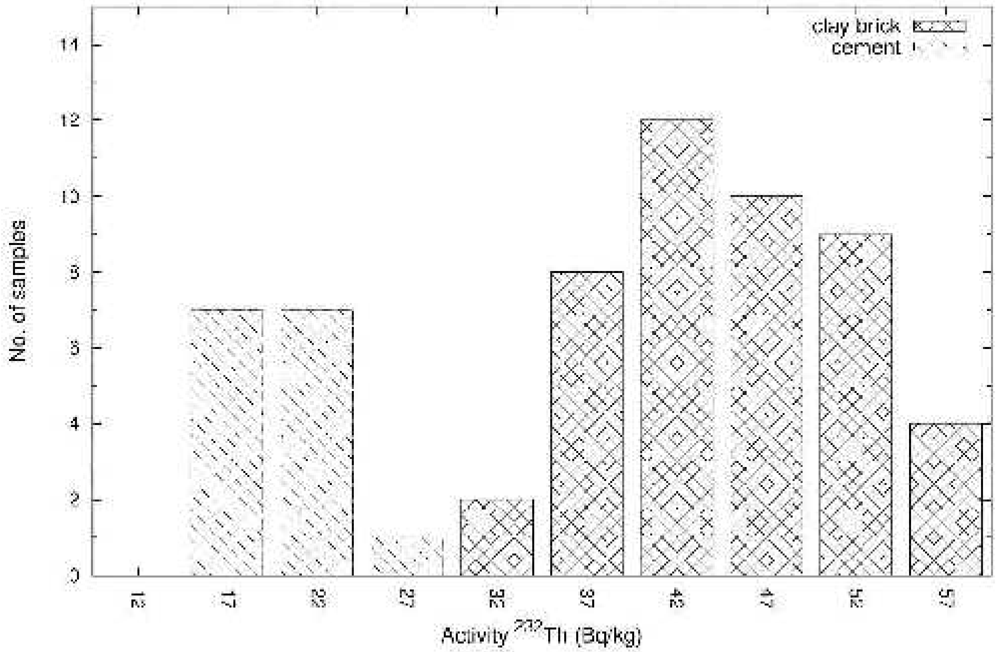

Figure 3. Distributions of activity concentration of ^{232}Th (in Bq/kg) in clay bricks and cements.

Radiological hazard characterization

The radiological hazards of the building materials were calculated by adopting the following Activity Concentration Index (ACI), which is widely used at the investigation level for practical monitoring purposes (20):

$$ACI = \frac{C_{Ra}}{300} + \frac{C_{Th}}{200} + \frac{C_K}{3000}, \qquad (1)$$

where C_{Ra}, C_{Th} and C_K are the activity concentrations in Bq/kg for radium (equivalent to uranium under secular equilibrium conditions), thorium and potassium, respectively. Following (**EC, 2011**), the radiological hazard could be classified into four classes, leading to two categories of materials used in bulk amounts and materials with superficial or restricted uses (**Table 1**). The calculated activity concentration index (ACI), varied from 0.48 ± 0.02 to 0.63 ± 0.04 in the clay brick samples and from 0.29 ± 0.03 to 0.37 ± 0.02 in the cement samples. Based on the ACI, all of the clay brick and cement samples were categorised as A1 materials. The authors can exclude (at 3σ level) any restriction of their use as bulk materials.

Table 1. The scheme for the association of the default dose, according to the Activity Concentration Index (ACI) criteria defined in European commission recommendation (**EC, 1999**).

Category (corresponding default dose)	**Type 1 Materials used in bulk amounts, e.g. concrete, bricks etc…**	**Type 2 Superficial and other materials with restricted use, e.g. tiles, boards, etc…**
A (≤ 1 mSv/y)	for ACI ≤ 1 category A1	for ACI ≤ 6 category A2
B (> 1 mSv/y)	for ACI > 1 category B1	for ACI > 6 category B2

To calculate the absorbed gamma dose rate in indoor air, D (nGy/h), the following formula is used (**EC, 1999**; **Markkanen 1995**):

$$D = 0.92C_{Ra} + 1.10C_{Th} + 0.08C_K \,. \qquad (2)$$

The absorbed dose conversion coefficients (0.92, 1.10 and 0.08 for ^{226}Ra, ^{232}Th and ^{40}K, respectively and expressed in nGy h^{-1}/Bq kg^{-1}) are determined by the Monte Carlo simulation, with a standard room model of 4 m x 5 m x 2.8 m and with thicknesses of the walls, floor and ceiling and density of the structures of 20 cm and density of 2350 kg/m^3 (concrete). The excess in external absorbed dose rates in indoor air was estimated by subtracting the "background" outdoor average absorbed dose rate of 58 nGy/h (**UNSCEAR, 2008**). The absorbed dose rates in indoor air are reported, which varied from 56.2 ± 4.6 to 92.4 ± 8.5 nGy/h in clay bricks and from 17.0 ± 8.8 to 35.3 ± 4.6 nGy/h in the cements. The listed values were lower or comparable (within 1σ) to the published world average dose rate of 84 nGy/h (**UNSCEAR, 2008**).

The annual effective dose equivalent, AEDE (mSv/y) rate is calculated as follows:

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

where where 0.8, 0.7 Sv/Gy and 8760 h are indoor occupancy factor, the dose conservation factor (the conversion coefficient from absorbed doses in the air to the effective dose received by an adult must be considered as 0.7 Sv/Gy as **UNSCEAR (2000)**) and total hours in one year, respectively. The corresponding average annual effective dose equivalents (AEDEs) values vary from 0.28 ± 0.02 to 0.45 ± 0.04 mSv/year in clay bricks and from 0.08 ± 0.04 to 0.17 ± 0.02 mSv/year in cement. Considering the average world annual effective dose equivalent (AEDE) from indoor terrestrial gamma radiation of 0.41 mSv/year (corresponding to an indoor absorbed gamma dose rate of 84 nGy/h), the estimated doses were lower or comparable within 1σ.

Activity concentrations and ACI values for clay bricks and cements are compared with results obtained by other authors in **Table 2**. As it is possible to observe, average activity concentration and ACI values of clay bricks and cements are within the range of values reported in other studies. In general, ACI values are 1σ below the limit value of ACI = 1, with the exception of two cases of study, in Egypt and Turkey. On the basis of this study, it is clear that the clay brick and cement industries in Albania produce building materials of low activity concentrations, as characterized according to European recommendations.

Table 2. The mean activity of ^{40}K, ^{226}Ra, ^{232}Th in Bq/kg measured in this study and compared with reported bibliographic results. The activity concentration index (ACI) is calculated based on mean activity concentation.

Author of study	Country	^{40}K (Bq/kg)	^{226}Ra (Bq/kg)	^{232}Th (Bq/kg)	ACI
Clay brick					
This study	Albania	644.1	33.4	42.2	0.54
Trevisi et al., 2012	EU	598	47	48	0.60
Amrani and Tahtat 2001	Algeria	675	65	51	0.70
Beretka and Mathew, 1985	Australia	681	40.7	88.8	0.81
Chowdhury et al., 1998	Bangladesh	292.3	29.5	52.5	0.46
Malanca et al., 1993	Brazil	747	65.3	51.7	0.73
Xinwei, 2005	China	713.9	58.6	50.4	0.69
Zhao et al., 2012	China	846	46	56	0.72
Brigido Flores et al., 2008	Cuba	857	57	12	0.54
Sharaf et al., 1999	Egypt	227	24.4	24.5	0.28
Ahmed, 2005	Egypt	511	33	37	0.47
Kumar et al. 2003	India	47.2	12.6	53.9	0.33
Faheem et al., 2008	Pakistan	431	23	35	0.40
Krstić et al., 2007	Serbia	579	34	43	0.52
Turhan et al., 2008	Turkey	775.8	31.2	37.2	0.55
Baykara et al., 2011	Turkey	201.4	15.7	3.8	0.14
Cement					
This study	Albania	179.7	55.0	17.0	0.33
Trevisi et al., 2012	EU	216	45	31	0.38
Amrani and Tahtat 2001	Algeria	422	41	27	0.41
Chowdhury et al., 1998	Bangladesh	329.0	62.3	59.4	0.61
Malanca et al., 1993	Brazil	564.0	61.7	58.8	0.69
Xinwei, 2005	China	173.8	68.3	51.7	0.54
Zhao et al., 2012	China	310	52	103	0.79
Brigido Flores et al., 2008	Cuba	467	23	11	0.29
Sharaf et al., 1999	Egypt	48.6	31.3	11.1	0.18
Ahmed, 2005	Egypt	416	134	88	1.03
Kumar et al. 2003	India	39.6	7.1	34.1	0.21
Faheem et al., 2008	Pakistan	245	25	37	0.35
Turhan et al., 2008	Turkey	316.5	39.9	26.4	0.37
Baykara et al., 2011	Turkey	2493.1	24.7	20.7	1.02

Conclusions

The radioactivity content of ^{40}K, ^{226}Ra and ^{232}Th were measured in 45 clay brick and 15 cement samples manufactured in Albania and then were compared with results from other countries. The average activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th were, respectively, 644.1 ± 64.2 Bq/kg, 33.4 ± 6.4 Bq/kg and 42.2 ± 7.6 Bq/kg in clay bricks and 179.7 ± 48.9 Bq/kg, 55.0 ± 5.8 Bq/kg and 17.0 ± 3.3 Bq/kg in cement. These activity concentrations were found to be comparable with reported results from other studies worldwide. These results were useful in the assessment of the radiological hazards due to these materials' final utilization as building materials. Adopting the “new” ACI index, these materials can be categorized within a 3σ uncertainty as A1 materials, i.e., suitable for use in bulk amounts without any restrictions. The external absorbed dose rates in indoor air, due to natural radioactivity, in such building materials was estimated to be in the range from 56.2 ± 4.6 to 92.4 ± 8.5 nGy/h in clay bricks and from 17.0 ± 8.8 to 35.3 ± 4.6 nGy/h in cement and was comparable, at close to a 1σ level, to the average world dose rate of 84 nGy/h. This level corresponds to an annual effective dose equivalent varying from 0.28 ± 0.02 to 0.45 ± 0.04 mSv/year in clay bricks and from 0.08 ± 0.04 to 0.17 ± 0.02 mSv/year in cement. These data are comparable with the average world annual effective dose equivalent (AEDE) from indoor terrestrial gamma radiation of 0.410 mSv/year. The clay bricks and cements manufactured in Albania do not pose a significant radiological hazard when used for building construction.

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