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Radioactivity content in construction materials of assets of particular historical-artistic interest

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***Abstract* – In the present paper, an investigation focused on the natural radioactivity content in construction materials widely employed for the realization of buildings of particular historical-artistic importance, was performed.**
In particular, the assessment of the activity concentration of ^{226}Ra, ^{232}Th, and ^{40}K radioisotopes in red granite and basalt aggregate samples was carried out through High Purity Germanium (HPGe) γ-ray spectrometry. Moreover, several indexes developed to evaluate the radiological risk for human beings related to radiation exposure, i.e. the radiation activity concentration index (I), the alpha index (I_α), the radium equivalent activity (Ra_{eq}), the hazard indexes (H_{in} and H_{ex}), the absorbed γ-dose rate (D) and the annual effective dose equivalent outdoor ($AEDE_{out}$) and indoor ($AEDE_{in}$), were calculated.

I. INTRODUCTION

The annual average human exposure to ionizing radiations produced by naturally occurring sources is largely dominating over the one due to artificial causes, like medical treatments, nuclear power plant accidents and nuclear weapons tests [1]. Among natural sources, the naturally occurring radioactive elements, such as ^{226}Ra, ^{232}Th and ^{40}K, contained in building materials employed for residential premises and workplaces, can provide a significant contribution to the external exposure of the occupants to gamma radiation [2].
The European Union (EU) has put in place provisions and directives since 1989 to control radiation emitted from building materials. Specifically, in 1999, the European Commission (EC) announced the ALARA (As Low As Reasonably Achievable) principle and set, as the ultimate goal of radiation control in building materials, the limitation to the radiation exposure from substances with high levels of naturally occurring radionuclides [3]. To this aim, the EC first introduced the radiation activity concentration index (I), which is generally used as a screening tool to limit gamma radiation exposure of construction materials [4]. In addition, several other indexes have been developed over the years in order to assess the radiological risk related to radiation exposure from such type of samples, including the alpha index (I_α), the radium equivalent activity (Ra_{eq}), the hazard indexes (H_{in} and H_{ex}), the absorbed gamma dose rate (D) and the annual effective dose equivalent outdoor ($AEDE_{out}$) and indoor ($AEDE_{in}$) [5]. More recently, the radiological concerns regarding the public health have been carefully considered by EU in the European Directive 2013/59 EURATOM, in Italy translated into the D.Lgs. 101/2020.
In this framework, in the present paper the High Purity Germanium (HPGe) γ-ray spectrometry was employed with the aim to evaluate the natural (^{226}Ra, ^{232}Th, ^{40}K) and artificial (^{137}Cs) radioactivity content of construction materials widely employed for the realization of buildings of particular historical-artistic interest, i.e. red granite and basalt aggregate samples. Furthermore, in order to assess any possible radiological hazard for the population, calculation of I, I_α, Ra_{eq}, H_{in} and H_{ex}, D, $AEDE_{out}$ and $AEDE_{in}$ was performed [6].

II. MATERIALS AND METHODS

A. Samples description

Red granite falls into the category of ornamental rocks, i.e. those that find use mainly in the construction-monumental-funerary field with the function of cladding and ornamentation of load-bearing structures. They are generally employed in polished slabs, but the use of only sanded or even rough slabs is also widespread [7]. In particular, the investigated red granite is characterized by a brick-red background color due to the presence of orthoclase, with a black speckling due to biotite [8].

Basalt is the most widespread magmatic or igneous effusive rock. Generally, when not greatly weathered, it has colorations ranging from dark gray to black [9]. Among the many uses in various fields [10,11], fragmented basalt aggregates, which are compact, finely grained, very dark green or black rocks produced when melted lava from the depths of the Earth's crust ascends and crystallizes, are employed as a natural resource for the manufacturing of cheap and eco-friendly construction materials with acceptable strength and durability features, particularly in line within the framework of a sustainable development [12]. In fact, the partial replacement of Portland cement with basalt aggregates in concrete, when available, could represents a more cost-efficient solution [13].

B. Methods

Five aliquots of each of the investigated samples were analyzed. In detail, each aliquot was first dried, in order to completely remove the moisture and to obtain constant mass. Then, it was inserted into a Marinelli hermetically sealed container of 250 mL capacity and left to rest for a period of 40 days, in order to reach the secular radioactive equilibrium between ^{226}Ra and its daughter products. After that, the specific activity of ^{226}Ra was quantified.

Samples were counted for 70000 s and, in order to assess the ^{226}Ra specific activity, the 295.21 keV and 351.92 keV ^{214}Pb and 1120.29 keV ^{214}Bi gamma-ray lines were used. Moreover, the ^{232}Th activity concentration was determined by using the 911.21 and 968.97 keV ^{228}Ac gamma-ray lines. Finally, regarding ^{40}K, the evaluation was performed from its γ-line at 1460.8 keV.

Going on, the experimental setup was composed by a positive biased Ortec HPGe detector (GEM) [14], located inside lead wells to screen the environmental background radioactivity. For efficiency and energy settings, a multi-peak Marinelli γ-source (BC-4464) of 250 mL capacity, energy range 60-1836 keV, custom made to replicate the exact designs of the specimens in a water-equivalent epoxy resin matrix, was employed. The Gamma Vision (Ortec) software was used for data acquisition and analysis [15].

A photo of the experimental setup is reported in Figure 1.

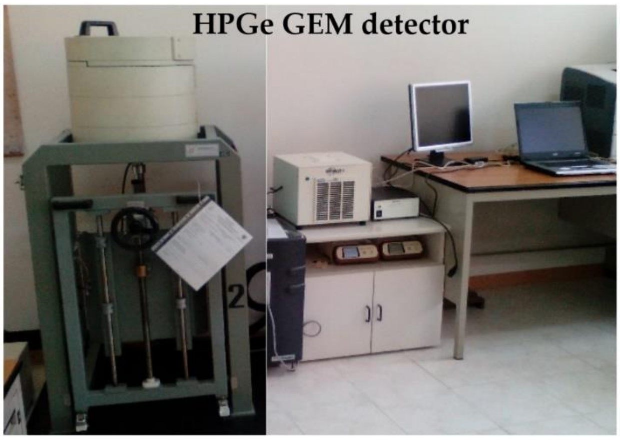

Figure 1. HPGe gamma spectrometry setup.

The activity concentration (Bq kg^{-1} dry weight, d.w.) of the investigated radioisotopes was calculated as follows [16]:

$$C = \frac{N_E}{\varepsilon_E t \gamma_d M} \quad (1)$$

where N_E is the net area of a peak at energy E, ε_E and γ_d are the efficiency and yield of the photopeak at energy E, respectively, M is the mass of the sample (kg) and t is the live time (s) [16]. The Italian Accreditation Body (ACCREDIA) certified the quality of the γ-ray spectrometry experimental results [17], thus ensuring continuous verification that the performance properties of the method are preserved.

Noteworthy, in order to estimate the radiological health risk to humans, the radiation activity concentration index, the alpha index, the radium equivalent activity, the hazard indexes, the absorbed γ-dose rate and the annual effective dose equivalent outdoor and indoor, were calculated. In particular, the radiation activity concentration index is defined by [18]:

$$I = C_{Ra}/300 + C_{Th}/200 + C_K/3000 \quad (2)$$

where C_{Ra}, C_{Th}, and C_K are the mean activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K, respectively. This index refers to the dose from γ-radiation present in a building built by means of a given construction material, in excess of the typical external exposure. It should not be more than 1 for the radiation hazard to be neglectable [18].

The alpha index was calculated with the following formula [19]:

$$I_\alpha = C_{Ra}/200 \quad (3)$$

that allows to assess the alpha radiation exposure to the indoor radon exhaled from construction materials. The activity concentration of ^{226}Ra must be lower than 200 Bq kg^{-1}, to prevent exposure to indoor radon specific activity higher than the threshold value of 200 Bq m^{-3} [20], and then I_α must be less than unity for the risk of exposure to radiation to be minimal [20].

The radium equivalent activity is instead an index that describes the specific activities of ^{226}Ra, ^{232}Th and ^{40}K in a single term [21]:

$$Ra_{eq}\ (Bq\ kg^{-1}) = C_{Ra} + 1.43C_{Th} + 0.077C_K \quad (4)$$

This index must be lower than 370 Bq kg^{-1} for the safe utilization of the investigated samples as building material [21].

Going on, the internal hazard index (H_{in}) gives the internal exposure to carcinogenic radon and its short-lived progeny [22], while the external hazard index (H_{ex}) is referred to the external exposure to γ-rays [22]:

$$H_{in} = (C_{Ra}/185 + C_{Th}/259 + C_K/4810) \leqslant 1 \quad (5)$$
$$H_{ex} = (C_{Ra}/370 + C_{Th}/259 + C_K/4810) \leqslant 1 \quad (6)$$

Both indices should not be more than 1 for the radiation hazard to be neglectable [22].

The absorbed γ-dose rate was calculated with the following formula [23]:

$$D\ (nGy\ h^{-1}) = 0.462C_{Ra} + 0.604C_{Th} + 0.0417C_K \quad (7)$$

This quantity is then employed to calculate the annual effective dose equivalent for an individual through the equations below, with occupation factors of 20% and 80% for outdoor and indoor environments, respectively [24]:

$$AEDE_{out}\ (mSv\ y^{-1}) = D\ (nGy\ h^{-1}) \times 8760\ h \times 0.7\ Sv\ Gy^{-1} \times 0.2 \times 10^{-6} \quad (8)$$
$$AEDE_{in}\ (mSv\ y^{-1}) = D\ (nGy\ h^{-1}) \times 8760\ h \times 0.7\ Sv\ Gy^{-1} \times 0.8 \times 10^{-6} \quad (9)$$

Both must be lower than 1 mSv y^{-1} for the radiological health risk to be negligible [24].

III. RESULTS AND DISCUSSION

The average specific activity (the mean value of the five analyzed aliquots) of ^{226}Ra, ^{232}Th, and ^{40}K, in the investigated samples, is reported in Table 1.

Table 1. The average specific activity of ^{226}Ra, ^{232}Th, and ^{40}K in the investigated samples.

Sample	^{226}Ra (Bq kg^{-1} d.w.)	^{232}Th (Bq kg^{-1} d.w.)	^{40}K (Bq kg^{-1} d.w.)
Red granite	20.1 ± 2.8	42.8 ± 5.9	1071 ± 127
Basalt	41.3 ± 5.1	53.1 ± 6.9	157 ± 19

It is important to put in evidence that the worldwide average specific activity of ^{226}Ra, ^{232}Th, ^{40}K is 35 Bq kg^{-1}, 30 Bq kg^{-1} and 400 Bq kg^{-1}, respectively [3]. In the light of this, experimental results here reported show that, in our case, the average specific activity of ^{226}Ra is higher than the average worldwide value only for the basalt sample. Otherwise, for ^{232}Th, the average activity concentration is higher than the average worldwide value for both investigated samples. Finally, regarding to ^{40}K, its average specific activity is higher than the average worldwide value only for the red granite sample. These results are strictly correlated with the mineralogical composition of the investigated samples [25-27].

Going on, Table 2 reports the calculated values of the radiological hazard indices for the investigated samples.

Table 2. The calculated values of the radiological hazard indices for the investigated samples.

Sample	I	I_α	Ra_{eq} (Bq kg^{-1})	H_{in}	H_{ex}	D (nGy h^{-1})	$AEDE_{out}$ (μSv y^{-1})	$AEDE_{in}$ (μSv y^{-1})
Red granite	0.64	0.10	164	0.50	0.44	79.8	97.9	391
Basalt	0.46	0.21	129	0.46	0.35	57.7	70.8	283

Noteworthy, the activity concentration index, evaluated through Equation (2), was found to be less than unity in both samples, then confirming negligible radiological hazards related to γ-radiation exposure. Likewise, the alpha index, obtained by using Equation (3), was found to be less than unity in both cases, thus avoiding an exposure to the indoor radon concentration more than 200 Bq m^{-3}. The radium equivalent activity, calculated through Equation (4), was found to be lower than 370 Bq kg^{-1} for both analyzed samples, then ensuring again that they may not be harmful if employed as construction materials.

For the internal and external hazard indices, given by Equations (5) and (6), they were both achieved lower than unity in all cases, and then the radiological hazards can be regarded as neglectable.

The absorbed γ-dose rate, as obtained through Equation (7), was used to evaluate, through Equations (8) and (9), the annual effective dose equivalent outdoor and indoor due to the specific activities of ^{226}Ra, ^{232}Th, ^{40}K in the investigated samples. The obtained values were lower than the threshold value of 1 mSv y^{-1} for both samples.

Finally, in order to estimate any possible anthropic contamination, we also evaluated the average specific activity of ^{137}Cs radioisotope, by means of its gamma-ray line at 661.66 keV. For both the investigated samples, it turned out to be lower than the minimum detectable, so excluding any radiological hazard.

IV. CONCLUSIONS

The natural radioactivity content in construction materials employed for the realization of buildings of particular historical-artistic interest was analyzed through High Purity Germanium (HPGe) γ-ray spectrometry. Moreover, calculations of the radiation activity concentration index (I), the alpha index (I_α), the radium equivalent activity

(Ra_{eq}), the hazard indexes (H_{in} and H_{ex}), the absorbed γ-dose rate (D) and the annual effective dose equivalent outdoor ($AEDE_{out}$) and indoor ($AEDE_{in}$) were performed for the investigated red granite and basalt aggregate samples, in order to estimate any possible radiological hazard for the human beings related to radiation exposure. Noteworthy, the obtained values turned out to be lower than the maximum recommended ones for humans, thereby excluding any significant health impact related to exposure to ionizing radiation. Additionally, the mean specific activity of ^{137}Cs turned out to be lower than the minimum detectable activity, thus excluding an anthropogenic radioactive contamination of the investigated samples.

Data reported in this article will be implemented in the next future with an increase of the number of samples analyzed. However, the approach reported in this paper could be applied, in principle, for the evaluation of any potential radiological health risk due to the presence of radioactive elements in a large variety of construction materials, tracing a guideline for investigations focused on the monitoring of the radiological quality of these samples.

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