ACTA IMEKO
ISSN: 2221-870X
September 2024, Volume 13, Number 3, 1 - 5

Radiological characterization of materials used in the Italian heritage buildings

Simona Mancini[1], Serpil Aközcan Pehlivanoğlu[2], Nataša Todorovic[3], Selin Ozden[2], Michele Guida[1]

[1] *Laboratory Ambient and Radiations (AmbRa), Department of Computer Engineering, Electrical Engineering and Applied Mathematics (DIEM), University of Salerno, via Giovanni Paolo II, 134 84084 Fisciano Italy*
[2] *Kirklareli University, Faculty of Science and Literature, Department of Physics, Campus of Kayali, 39100, Kirklareli, Turkey*
[3] *Department of Physics, Faculty of Sciences, University of Novi Sad, Trg Dositeja Obradovića, 3,21000 Novi Sad, Serbia*

ABSTRACT
Building materials (BMs) can cause significant gamma dose indoors due to their natural radionuclide content. In 2013, the European Directive 59/2013/EURATOM introduced, in annex XIII, a list of types of BMs of interest for the content of gamma-emitting radionuclides among which materials or additives of natural igneous origin, such as granitoids, tuff and lava, are included. These materials have been largely employed for decorative and structural purposes in the course of centuries in the Italian heritage buildings. Aim of this study is to assess the contribute of BMs in terms of alpha exposure. Six samples of different materials, characterized in a previous study by the authors in terms of radiological content by means of a gamma spectrometry, have been analyzed in order to determine the specific exhalation rate of 222Rn, the radon emanation coefficient and excess in indoor radon concentration. Results confirm that BMs of natural igneous origin can play an important role in terms of alpha radiation dose and internal exposure due to the inhalation of the alpha particles emitted.

Section: RESEARCH PAPER

Keywords: radioactivity; building materials; dose assessment

Citation: S. Mancini, S. A. Pehlivanoglu, N. Todorovic, S. Ozden, M. Guida, Radiological characterization of materials used in the Italian heritage buildings, Acta IMEKO, vol. 13 (2024) no. 3, pp. 1-5. DOI: 10.21014/actaimeko.v13i3.1825

Section Editor: Fabio Leccese, Università Degli Studi Roma Tre, Rome, Italy

Received February 28, 2024; **In final form** June 9, 2024; **Published** September 2024

Corresponding author: Simona Mancini, e-mail: smancini@unisa.it

1. INTRODUCTION

Environmental radioactivity constitutes the main part of the external radiation dose absorbed by the world population [1], [2]. The most important source of external exposure is represented by the radioactive elements ^{238}U, ^{232}Th and their progeny, and ^{40}K, naturally present in the earth crust. Their distribution in soils and rocks is really inhomogeneous since it highly depends on the geological features of the area.

The most abundant element of the ^{238}U series that can be found in soil and rocks is ^{222}Rn (radon), a noble radioactive gas whose half-life is 3.8 days. Because of its long half-life, before decaying, it can cover long distances, escape and diffuse from the earthly rock and soil to the outdoor air by diffusion and pressure difference. When reaching closed environment, it can accumulate in the indoor air till concentrations harmful for human health. Radon inhalation constitutes the highest quota of internal exposure for population, instead. Since, as well as its progeny (^{218}Po, ^{214}Pb, ^{214}Bi and ^{214}Po) it emits alpha particles that can damage DNA, radon inhalation is associated with a high probability of lung cancer onset [3].

As people spend most of their lifetime indoors [4], the analysis of the content of radionuclides in building materials (BMs), naturally or artificially present, is crucial from a radioprotection point of view to assess and control the external and internal exposure of people, caused by direct gamma radiation and by the breathing of ^{222}Rn and its short-lived decay products.

The radiological assessment of BMs was, for the first time, suggested by the European Commission, in 1999, with the EU Technical Guidance Radiation Protection 112 (RP112) [5] by introducing the calculation of the so called ‘gamma index (I_γ)’, as screening tool to assess the health risk due to the exposure of the radionuclides found in BMs. In 2013, the European Directive (ED) 59/2013/EURATOM [6], repealing the RP112 and the evidences of the international review studies [7], officially introduced as a requirement for some BM, listed in the Annex XIII, the radiological characterization in terms of gamma emitting radiation. The indicative list of types of building materials considered, as referred to in Article 75 of the ED, includes some materials or additives of natural igneous origin, such as granitoids (i.e. granites, syenite and orthogneiss …), porphyries, tuff, pozzolana (pozzolanic ash) and lava.

According to the European legislation the listed BMs should be controlled only in terms of gamma emissions, responsible of external exposure. But, many studies in literature have demonstrated that the characterization should include also data about the alpha emissions since BMs may constitute an important source of indoor radon and so internal exposure.

In the Italian heritage panorama, a lot of buildings including natural stones of igneous origin in decorative and structural parts may be susceptible of high indoor concentrations because of the presence of these BMs as possible source. Indeed, some regions, mainly in the central and southern part of the Italian peninsula, as Tuscany, Campania, Sicily and Lazio, boast famous quarries of tuff, pozzolana and granitoids that, since Etruscan-Roman time, provide prestigious BMs employed in the national building heritage. Particularly in these regions, all the villages and cities, reflect the complexity of the lithological types of the local territories depicting unique architectures and styles. In particular, according to the Italian complex geological features local BMs range from natural igneous stones to sand stones [8].

Different studies on the monitoring of natural local BMs in Italian historical monuments already highlighted a general high natural radioactivity content, constituting a possible issue from a radioprotection point of view, in terms of external exposure. Nevertheless, as said before, in buildings with high-radium levels, the radon exhalation from building materials may become of major importance and constitute a serious risk related to internal exposure [9].

So, this paper aims to radiologically characterize, for the first time, six samples of particular natural stones used in cultural heritage in terms of alpha emitting radiation. In particular, by means of measurements of radon activity concentration, the specific exhalation rate, emanation factor, and excess of indoor radon concentration were calculated.

The samples, already investigated in a previous work showing high level of the content of natural radionuclides [10], were selected in order to fill the gap in the characterization of particular local Italian BMs.

2. MATERIALS AND METHODS

Six samples of different building materials largely used in the Italian cultural heritage, for structural and decorative use, were selected from quarries of different Italian regions (Figure 1 and Table 1).

The samples, characterized in terms of contents of the natural radionuclides ^{226}Ra, ^{232}Th, ^{40}K in a previous work [10] were considered for further investigations since they showed significant values and so, high gamma radiation doses. In particular the attention has been focused on the possible contribute to the internal exposure due to the alpha particles emitted. In this context the main characterizing parameters are: the radium activity concentration C_{Ra} (Bq kg^{-1}), the radon emanation coefficient, ε (rel), and the radon surface exhalation rate, E_{S} (Bq m^{-2} s^{-1}) or the radon mass exhalation rate, E_{M} (Bq kg^{1} s^{-1}). [11]

Table 1. Samples data and codes.

Sample name	Type	Use	Origin area	Mass in g
Grey tuff	volcanic	structural	Campania	57
Basalt	volcanic	ornamental	Lazio	167
Peperino	magmatic	ornamental	Lazio	180
santa fiora	sandstone	ornamental	Tuscany	176
travertine	sedimentary	ornamental	Campania	179
lava stone	volcanic	ornamental	Sicily	211

The radon exhalation rate was calculated by measuring the radon concentration with an electret ion chamber (EIC) [12], in a sealed accumulator. The integrated average radon concentration at the end of the accumulation time is measured. Theoretical equations for the calculation of the radon concentration accumulated over the time in the enclosed volume are given by the manufacturer [12], [13] and are function of the days of exposure, the environmental background gamma radiation and some factors correcting errors connected with the altitude and the configuration of the system. The set up is shown in Figure 2. In particular, it consists of the following components: (1) an electrostatically charged Teflon® disk which collects ions (electret); (2) an ion chamber made of conductive plastic into which the electret is loaded, (3) a calibrate reader to read the surface potential (voltage) of the electret, (4) an 4L sealable glass jar (accumulator) where the building material sample is put and (5) a numbering computing platform for calculation of radon concentrations. The electret can be chosen according to the duration of the measurement (short or long). The ion chamber can be chosen, according to the purpose, in its

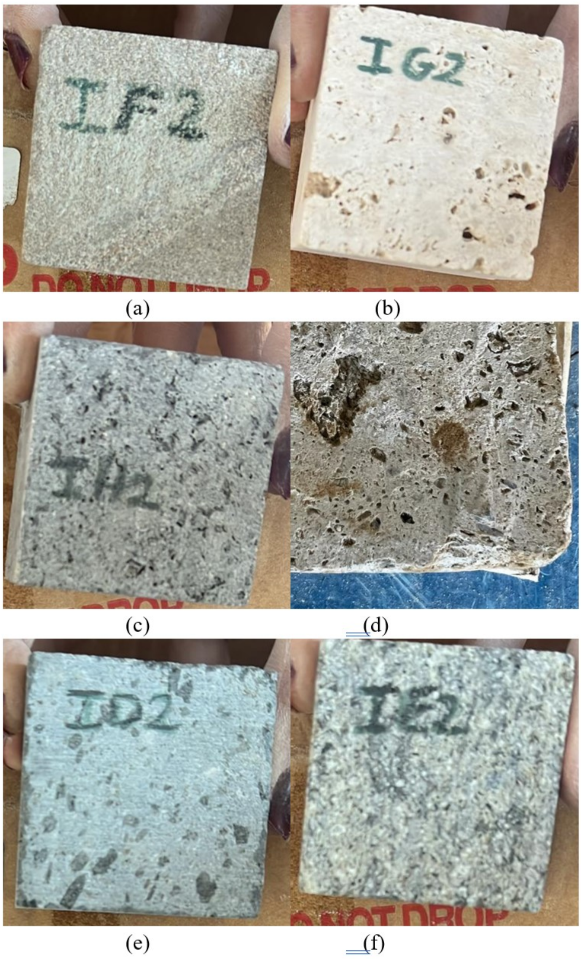

Figure 1. Building materials samples: (a) santafiora, (b)travertine, (c) lava stone, (d)grey tuff, (e) basalt (f) peperino.

Figure 2. Set up of the electret ion chamber.

standard, low or high volume. In this study an ion chamber of standard volume (S) and short-term electrets (ST) (SST measurement) were used. The exposure time was fixed in 7 days, instead.

This kind of measurement technique is not affected by humidity or temperature variations between -6 and +50 °C. During the preliminary and final operations (assembly and disassembly of the electret on the chamber) and the storage of the electrets and chambers, care has been taken to keep the lid, the electret and the inside of the chambers clean and free from dust. Dust or fibres can accelerate the charge loss of the electret or alter the surface potential reading, leading to an overestimation of the radon activity concentration measurement [14].

Accumulator methods, as the adopted one for this study, are widely used to determine the radon concentration of solid samples. The sample, placed in the sealed chamber, acts like a constant emitting source, and the sealed chamber acts as an accumulator allowing the radon growth inside. The increasing over the time of the radon concentration in the closed volume, *C*(*t*), till the equilibrium concentration, is exponential and described by the well-known theoretical equation:

$$\frac{dC(t)}{dt} = \frac{ES}{V} - \lambda_{rn} C(t) \,, \tag{1}$$

where V is the total volume of the accumulation chamber, in m^3, E is the free exhalation rate in Bq m^{-2} h^{-1}, S is the sample surface and λ_{rn} is the radon decay constant in h^{-1}.

From the theoretical curve described by eq. (1) the experimental ones could be affected by some leakages determining an underestimation of the radon concentration inside the accumulator. So, equation (1) could be written as:

$$\frac{dC(t)}{dt} = \frac{ES}{V} - \lambda C(t) \,, \tag{2}$$

where λ is the sum of the radon decay constant, the bound exhalation constant and the leakage constant.

The leakage constant is related to lost due to the not-hermetical sealing. The bound exhalation ones related to the fact that radon atoms partly diffuse back to the sample determining a decrease of the equilibrium radon concentration inside the accumulator. Such phenomenon, called 'radon back diffusion', can be reduced if the air volume of the accumulator is more than 10 times of the sample volume. In this case, radon back diffusion effect is lower than 10 % and can be ignored [4], [15]. It is also noted by Kotrappa and Stieff that the effect of radon back diffusion increases for the measurement (analysis) periods over 5 days [11], [12]. An example of the radon accumulation process in a closed volume is reported in Figure 3. Equation (2) practically describes a balance between radon generation, produced by exhalation from the building material sample, and several radon removal processes, such as radon decay, back diffusion and possible leaks in the measurement system, considering these three processes linearly proportional to radon concentration.

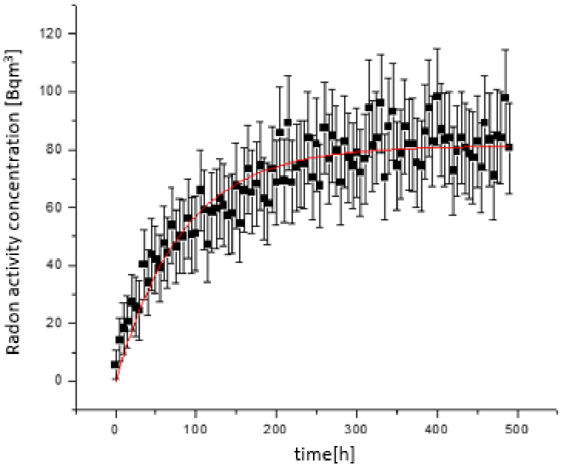

Figure 3. Radon accumulation curve: an example.

The radon specific exhalation rate E can be calculated according to the following equation, per unit mass in Bq kg^{-1} h^{-1}:

$$E = \frac{(\mathrm{C}_{rn}\,\mathrm{V}\,\lambda)/\mathrm{m}}{1-(1-\mathrm{e}^{-\lambda\mathrm{T}})/(\lambda\mathrm{T})} \,, \tag{3}$$

where C_{Rn} is the measured radon concentration in Bq m^{-3}, V is the volume of the accumulator in m^3, m is the mass of the sample in kg, λ is the radon decay constant in d^{-1} or h^{-1}, T is the time of exposure in d or h.

The radon specific exhalation rate can be calculated per surface exhalating area in Bq m^{-2} h^{-1}, similarly.

The emanation factor, ε, representing the percentage of the produced radon from the grains that finally enters at the porous system of the sample, can be calculated as following:

$$\varepsilon = \frac{E}{C_{Ra}\, m \lambda_{Rn}} \,, \tag{4}$$

where E is the calculated exhalation rate (Bq h^{-1}); C_{Ra} is the measured ^{226}Ra content (Bq kg^{-1}); λ_{Rn} is the radon decay constant (h^{-1}) and m is the mass of the sample (kg). The ^{226}Ra content was measured in a previous work as well as ^{232}Th, and ^{40}K by means of high purity germanium (HPGe) detector-based gamma spectrometry [10]. Equation (4) is applicable for all measured building materials, because the dimensions of the samples were chosen to be equal to the diffusion length of these gases for these materials (around 4 cm) [15].

3. RADON EXPOSURE

All materials containing ^{226}Ra release some radon into the surrounding air. Building materials therefore cause an excess in indoor air radon concentration.

The accumulation of radon in a closed environment, like a dwelling room, depends on factors such as the room dimension, the radon activity concentration, the subsequent radon exhalated directly from the building materials of walls, radon coming from soil (radon gain), the air exchange and the isotope radioactive decay. Therefore, building materials may cause an excess in the indoor ^{222}Rn (or ^{220}Rn) activity concentrations, which is described by the following equation [16] proposed by Markannen in 1995:

$$C_{Rn} = \frac{E_S S}{V_R \lambda_V}\ , \quad (5)$$

where C_{Rn} is the excess of indoor radon concentration (Bq m^{-3}); E_{S} is the surface exhalation rate (Bq m^{-2} h^{-1}); S is the exhalation area (m^2); V_{R} is the volume of the room (m^3) and λ_{v} is the ventilation rate of the room (h^{-1}). Generally, in buildings the ventilation rate is assumed in the range 0.2-1 h^{-1}. In our calculation ratio S/V is taken to be 2 and λ_{v} 0.5 [17]

4. RESULTS AND DISCUSSION

In Table 2, the measured radon concentration and the specific surface and mass exhalation rate are reported.

In Table 3, the emanation factor calculated instead. In Table 4, the excess in the indoor radon according to (5).

Results show that the analysed materials are characterized by a not negligible potential to exhalate radon and cause an excess of radon concentration in the indoor air. The values of radium content and radon surface and mass exhalation rate and emanation factor fall in the range ‘minimum and maximum values’ reported in [10] confirming that these materials should be properly characterized and analysed in order to assure that population will be not exposed to an excess of gamma and alpha dose per year.

Table 2. Equilibrium radon activity concentration and specific mass and surface exhalation rate.

Sample	T in d	C_{rn} in Bq/m^3	E_{M} in Bq kg^{-1} h^{-1}	E_{S} in Bq m^2 h^{-1}
Grey tuff	7	200 ± 33	0.029 ± 0.002	2.25 ± 0.18
Basalt	7	880 ± 96	0.146 ± 0.008	9.81 ± 0.53
Peperino	7	474 ± 57	0.073 ± 0.004	5.29 ± 0.32
santa fiora	7	178 ± 33	0.028 ± 0.002	1.98 ± 0.18
travertine	7	133 ± 28	0.020 ± 0.002	1.48 ± 0.15
lava stone	7	299 ± 41	0.039 ± 0.002	3.33 ± 0.23

Table 3. ^{226}Ra content and calculated emanation factor.

Sample	C_{Ra226} in Bq kg^{-1}	ε
Grey tuff	85.28 ± 10.95	0.0450192
Basalt	53.29 ± 4.64	0.3627054
Peperino	126.01 ± 7.29	0.0766946
santa fiora	10.21 ± 1.10	0.3630606
travertine	< 1.3054	---
lava stone	88.47 ± 6.12	0.05836

Table 4. Excess in the indoor radon activity concentration, C.

Sample	C in Bq m^{-3}
Grey tuff	9
Basalt	39,24
Peperino	21,16
santa fiora	7,92
travertine	5,92
lava stone	13,32

5. CONCLUSIONS

In order to control the natural radiation exposure of population in indoor environment due to building materials, it is necessary to determine the natural radioactivity content, for the assessment of the external exposure, and the specific radon exhalation rate for the assessment of the radon exposure. Many studies in scientific literature revealed that construction materials, mainly of volcanic/magmatic origin can possess from medium to very high contents of natural radionuclides. These BMs have been widely used in the course of the centuries in the Italian historical cultural heritage assets and represents also unique specificity of the local architectures and styles, as tuff in the Neapolitan area, granites and marbles in Tuscany etc... Using a high-resolution gamma ray spectrometry system, the activity concentration of natural radionuclides was measured, in a previous work carried out by authors, in some samples of materials, from different Italian quarries, generally used for decorative and/or structural use in churches, monuments, etc. Since previous results revealed high content of natural radionuclides and not negligible doses related to external exposure, more investigations were carried out for better radiologically characterizing these particular samples never investigated before in their contribute to the indoor radon concentration. Measurements of radon activity concentration and calculation of the specific exhalation rate and emanation factor turns out to very important in the assessment of the radon risk in the cultural heritage in terms of radioprotection for workers and public. Measurements of radon activity concentration by using passive system technique, hermetically closing the sample in a container, were completed and the specific mass and surface exhalation rate calculated, as well as the emanation factor and the possible excess of indoor radon concentration due to the contribute of the material.

Results confirm that igneous materials can play a not negligible role as source of radon in an indoor environment. So, more studies should be carried out investigating not only the build-up curve of the activity concentration of ^{226}Ra and ^{232}Th in closed environment but also monitoring the indoor radon concentration in experimental cases for investigating the excess of indoor radon concentration due to the presence of emitting materials.

REFERENCES

[1] United Nations Scientific Committee on the Effects of Atomic Radiation, Report to the General Assembly, with scientific annexes United Nations: New York. Effects of atomic radiation to the general assembly, 2000. United Nations, New York

[2] United Nations Scientific Committee on the Effects of Atomic Radiation. Report of the United Nations Scientific Committee on the effects of atomic radiation 2013. vols I and II. United Nations, New York

[3] World Health Organization, WHO Handbook on Indoor Radon: A Public Health Perspective. Geneva: World Health Organization; 2009.

[4] World Health Organization, Regional Office for Europe. WHO guidelines for indoor air quality: selected pollutants. World Health Organization. Regional Office for Europe 2010.

[5] European commission report on radiological protection principles concerning the natural radioactivity of building materials 1999 Radiat. Prot. 112.

[6] European Commission, ED2013/59/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 2013.

[7] Trevisi, S. Risica, M. D'Alessandro, D. Paradiso, C. Nuccetelli. Natural radioactivity in building materials in the European Union: a database and an estimate of radiological significance. J. Environ. Radioact., 105, 2012, pp. 11-20. DOI: 10.1016/j.jenvrad.2011.10.001

[8] G. La Verde, A. Raulo, V. D'Avino, G. Paternoster, V. Roca, M. La Commara, M. Pugliese, Pietra Leccese and Other Natural Stones in Puglia Region: A New Category of Building Materials for Radiation Protection? Int J Environ Res Public Health. 2021 Oct 26;18(21):11213. DOI: 10.3390/ijerph182111213

[9] S. Rizzo, M. Brai, S. Basile, S. Bellia, S. Hauser, Gamma activity and geochemical features of building materials: estimation of gamma dose rate and indoor radon levels in Sicily, Applied Radiation and Isotopes, Volume 55, Issue 2, 2001, pp. 259-265. DOI: 10.1016/S0969-8043(00)00384-5

[10] S. Akozcan, S. Mancini, N. Todorovic, S. Ozden, M. Guida, Assessment of the natural radioactivity content in typical building materials employed in the Italian cultural heritage. Proc. of the 2023 IMEKO TC4 Int. Conf. on metrology for archaeology and cultural heritage, Rome, Italy, 13-21 October 2023, pp. 866-870. DOI: 10.21014/tc4-ARC-2023.161

[11] Naturally Occurring Radioactive Materials in Construction Integrating Radiation Protection in Reuse (COST Action Tu1301 NORM4BUILDING) 2017. Editor: Wouter Schroeyers ISBN: 978-0-08-102009-8 .

[12] Rad Elec Inc., E-PERM. Online [Accessed 18 September 2024] https://www.radelec.com/

[13] P. Kotrappa, F. Stieff, Radon exhalation rates from building materials using electret ion chamber radon monitors in accumulators, Health Physics, 97, pp. 163-166. DOI: 10.1097/HP.0b013e3181a9ab15

[14] L. Zhang, X. Lei, Q. Guo, S. Wang, X. Ma, Z. Shi, Accurate measurement of the radon exhalation rate of building materials using the closed chamber method, J. Radiol. Prot. 32, 2012, p. 315. DOI: 10.1088/0952-4746/32/3/315

[15] C. Samuelsson, The Closed-Can Exhalation Method for Measuring Radon, Journal of Research of the National Institute of Standards and Technology, Vol. 95, pp. 167-169. DOI: 10.6028/jres.095.019

[16] M. Markannen, Radiation Dose Assessments for Materials with Elevated Natural Radioactivity. 1995 ISSN 1235-6719 Painatuskeskus Oy Helsinki 1995.

[17] S. Stoulos, M. Manolopoulou, C. Papastefanou. Assessment of natural radiation exposure and radon exhalation from building materials in Greece. Journal of Environmental Radioactivity. 2003;69(3), pp. 225–240. DOI: 10.1016/S0265-931X(03)00081-X