
Natural radioactivity in Italian ceramic tiles

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Abstract. Zircon is the mostly widely occurring zirconium-containing mineral mined commercially. Thorium and uranium may substitute for zirconium in the zircon crystal lattice. The radioactivity levels in zircon lies typically within the ranges 500–1000 Bq kg⁻¹ for ²³²Th and 1000–5000 Bq kg⁻¹ for ²³⁸U [1]. One of the most important use of zircon is as opacifier for ceramic tiles. Body of ceramic tiles is a mixture of different raw materials, including: clays, quartz materials and feldspathic materials. The body may be glazed or left unglazed. Due to the presence of zircon in the glaze or in the body, ceramic tiles can show natural activity concentration significantly higher than the average values of Earth's crust. This study contains a summary of results obtained by a survey on Italian ceramic tiles collected over three years (2005–2007). About one hundred ceramic tiles were analysed. The survey consisted of measurement of ²²⁶Ra, ²³²Th and ⁴⁰K activity concentrations and of the gamma-index [2] and radium-equivalent [3, 4] calculation. The activity concentrations of ²²⁶Ra, ²³²Th and ⁴⁰K result in the order of 100, 50 and 500 Bq kg⁻¹, respectively. Gamma index and radium equivalent activity have been found well below the acceptable limit in most of the samples.

1. INTRODUCTION

All building materials contain various amounts of natural radioactive nuclides. Materials derived from rock and soil contain mainly natural radionuclides of the uranium (²³⁸U) and thorium (²³²Th) series, and the radioactive isotope of potassium (⁴⁰K). In the uranium series, the decay chain segment starting from radium (²²⁶Ra) is radiologically the most important and, therefore, reference is often made to radium instead of uranium [3]. The knowledge of the natural radioactivity of building materials is important for the determination of population exposure to radiations, as most of the people spend ~80% of their time indoors [5]. High levels of radioactivity in construction materials can increase external and internal indoor exposure. Currently, a worldwide effort is underway to measure the activity concentrations in building materials.

Ceramic tiles are one of the commonly used decorative building materials: they are made of a mixture of earthly materials that has been pressed into shape and fired at high temperature. The body of ceramic tiles may than be glazed or left unglazed. Dust-pressed ceramic tiles with water absorption levels <0.5%, and high mechanical and chemical characteristics are known as 'Fully Vitrified Stoneware' or 'Porcelain Stoneware'. Due to the addition of zircon, as opacifier or whitening, ceramic tiles can show natural activity concentration significantly higher than the average values of Earth's crust.

Zircon is used in a wide variety of applications, either as zircon sand directly from the mine, as zircon flour, as opacifier grade zircon or chemically processed or fused to produce synthetic zirconia and zirconium chemicals. There are three main markets for zircon – ceramics, refractories, foundries – of which the ceramics industry is the largest by volume (53% of the total market). Typically, a zircon concentrate will have a ZrO₂ + HfO₂ content of 65–66%, a TiO₂ content of 0.10% and an Fe₂O₃ content of 0.05–0.12% [6].

This report contains a summary of results obtained on ceramic tiles collected over three years (2005–2007) from several Italian manufacturing firms. Sixteen samples of porous fired tiles and seventy samples of porcelain stoneware tiles were analysed. The survey consisted of measurement of ^{226}Ra , ^{232}Th and ^{40}K activity concentrations by HPGe gamma-spectroscopy and of the gamma-index and radium-equivalent calculation. The results of this investigation are compared with the findings of similar studies carried out in other countries.

2. MATERIALS AND METHODS

2.1 Gamma spectrometry measurements

Radionuclide activities were assayed by γ -ray spectrometry, using a hyperpure n-type germanium coaxial detector (22.6% efficiency, 1.9 keV resolution) coupled to a multichannel analyser. Commercial software Gamma Silena2000 was used for data analysis. Samples were dried, homogenized, packed, and sealed in 450 ml Marinelli beakers. Samples were sealed for at least 21 days prior to analysis to allow for equilibrium between ^{226}Ra and ^{222}Rn . Count times were typically in the range 10,000 to 60,000 s, giving a measurement precision of between ca. $\pm 5\%$ and $\pm 10\%$ at the 95% level of confidence. The background was subtracted from each spectrum.

The detector was calibrated using a mixed radionuclide solution, containing ^{241}Am , ^{109}Cd , ^{57}Co , ^{139}Ce , ^{60}Co , ^{113}Sn , ^{85}Sr , ^{137}Cs and ^{88}Y , certified by the Commissariat à l'Énergie Atomique (CEA), covering an energy range of approximately 60–1800 keV. Quality assurance of the measurements were assessed through the analysis of Standard Reference Material IAEA soil-375. Thorium-232 is not measurable directly because it does not emit any penetrating γ -rays. That's why the measurement relied on detecting emissions from their progeny. Thorium-232 activities were measured by taking the mean activity of photopeaks of the daughter nuclides ^{228}Ac (338.40, 911.07 and 968.90 keV) and ^{212}Pb (238.63 keV). Similarly, ^{226}Ra activities were calculated from the activity of its short-lived daughters ^{214}Pb at 295.2 and 351.9 keV, and ^{214}Bi at 609.3 keV. Activities of ^{40}K were determined directly from its γ -emission at 1460.83 keV.

The activity levels for radionuclides in the measured samples are computed using the following equation:

$$A = \frac{cps}{\varepsilon\gamma m} \quad (1)$$

where A is the activity concentration of a certain radionuclide expressed in Bq kg^{-1} dry weight, cps is the net counting rate of sample subtracted from background (counts per seconds), ε is the counting efficiency of the used detector, γ is the absolute transition probability of γ -decay and m is the dried sample weight expressed in kg.

2.2 Radium equivalent activity calculation

Radium equivalent activity (Ra_{eq}) is a very common index used to represent the specific activity of ^{226}Ra , ^{232}Th and ^{40}K by a single quantity which takes into account the radiation hazards associated with them. Ra_{eq} is a weighted sum of activities of the above three radionuclides based on the estimation that 370 Bq kg^{-1} of ^{226}Ra , 259 Bq kg^{-1} of ^{232}Th or 4810 Bq kg^{-1} of ^{40}K produce the same gamma ray dose. It is defined as [3, 4]:

$$Ra_{eq} = C_{Ra} + 1.43C_{Th} + 0.077C_K \quad (2)$$

where C_{Ra} , C_{Th} and C_K are the activity concentration of ^{226}Ra , ^{232}Th and ^{40}K (Bq kg^{-1}) respectively.

The maximum value of Ra_{eq} in building materials must be less than 370 Bq kg^{-1} for safe use, i.e. to keep the external dose below 1.5 mGy per year.

2.3 Activity concentration index calculation

A number of indexes dealing with the assessment of the excess gamma radiation originating from building materials have been proposed [7–11]. In this study, the gamma-index was calculated as proposed by the European Commission [2]. The Commission suggests that building materials should be exempted from all restrictions concerning their radioactivity if the excess gamma radiation originating from them increases the annual effective dose of a member of the public by 0.3 mSv at the most. On the contrary, doses higher than 1 mSv should be accepted only in some very exceptional cases where materials are used locally. The European Commission recommends that controls should be based on a dose in the range 0.3–1 mSv y⁻¹. This is the excess gamma dose to that received outdoors. The European Commission has proposed the following activity concentration index (*I*) for identifying whether a dose criterion is met:

$$I = \frac{C_{Ra}}{300 \text{ Bq kg}^{-1}} + \frac{C_{Th}}{200 \text{ Bq kg}^{-1}} + \frac{C_K}{3000 \text{ Bq kg}^{-1}} \quad (3)$$

where C_{Ra} , C_{Th} and C_K are the activity concentration of ²²⁶Ra, ²³²Th and ⁴⁰K (Bq kg⁻¹) respectively, in the building material. The activity concentration index shall not exceed the values shown in Table 1. Note that the activity concentration index should be used only as a screening tool for identifying materials which might be of concern. Any actual decision on restricting the use of a material should be based on a separate dose assessment. Such assessment should be based on scenarios where the material is used in a typical way for the type of material in question.

Table 1. Maximum recommended values of activity concentration index depending on the dose criterion, and the way and the amount the material is used in a building.

Dose Criterion	0.3 mSv y ⁻¹	1 mSv y ⁻¹
Materials used in bulk amounts e.g. bricks	$I \leq 0.5$	$I \leq 1$
Superficial and other materials with restricted use: tiles boards, etc	$I \leq 2$	$I \leq 6$

3. RESULTS AND DISCUSSION

Radium-226, ²³²Th, and ⁴⁰K activity concentrations measured in the tiles are presented in figures 1, 2 and 3, respectively. Tables 2 and 3 report the summary statistics of porous fired and porcelain stoneware tiles, respectively. The activity concentration of ²²⁶Ra has been found to be varying from 36 to 87 Bq kg⁻¹ (mean value 53 ± 15 Bq kg⁻¹) in porous fired tiles, while in porcelain stoneware tiles the activity concentration of ²²⁶Ra varies from 20 to 707 Bq kg⁻¹ (mean value 114 ± 118 Bq kg⁻¹). The activity concentration of ²³²Th ranges from 38 Bq kg⁻¹ to 86 Bq kg⁻¹ and 33 Bq kg⁻¹ to 145 Bq kg⁻¹ with the mean value of 53 ± 12 Bq kg⁻¹ and 55 ± 23 Bq kg⁻¹ in porous fired and porcelain stoneware tiles, respectively. Finally, the activity concentration of ⁴⁰K lies between 411 and 996 Bq kg⁻¹ and between 158 and 850 Bq kg⁻¹ in porous fired and porcelain stoneware tiles, respectively. The comparison of ²²⁶Ra, ²³²Th, and ⁴⁰K activity concentrations in porous fired tiles (table 2) and those averagely measured in soils (table 4) shows that they are completely comparable. Instead, natural activity concentrations in porcelain stoneware tiles (table 3) can be significantly higher than those averagely measured in soils, especially for ²²⁶Ra. The higher natural activity concentrations found in porcelain stoneware tiles can be explained through the larger amount of zircon added with respect to porous fired tiles as reported, for example by Bruzzi et al. [12]. Note that zircon usually contains 500–1000 Bq kg⁻¹ of ²³²Th and 1000–5000 Bq kg⁻¹ of ²³⁸U [1] and several zircon sands commonly used in Italian ceramic industries have shown the activity concentrations of ²³²Th and ²³⁸U between 360 to 1100 Bq kg⁻¹ and 1800 to 3150 Bq kg⁻¹, respectively [13].

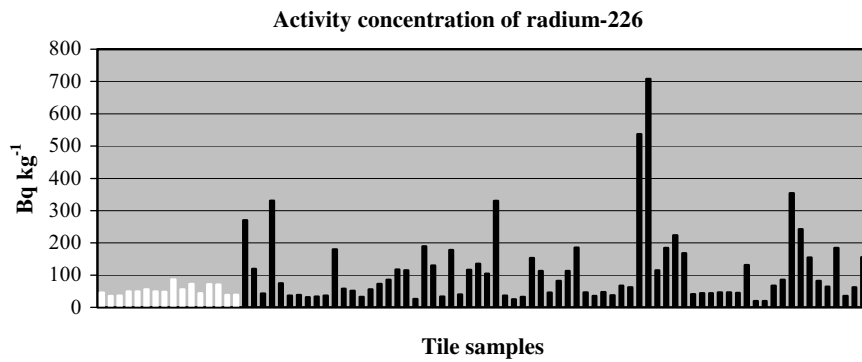


Figure 1. Radium-226 activity concentrations measured in porous fired (white bars) and porcelain stoneware (black bars) tiles.

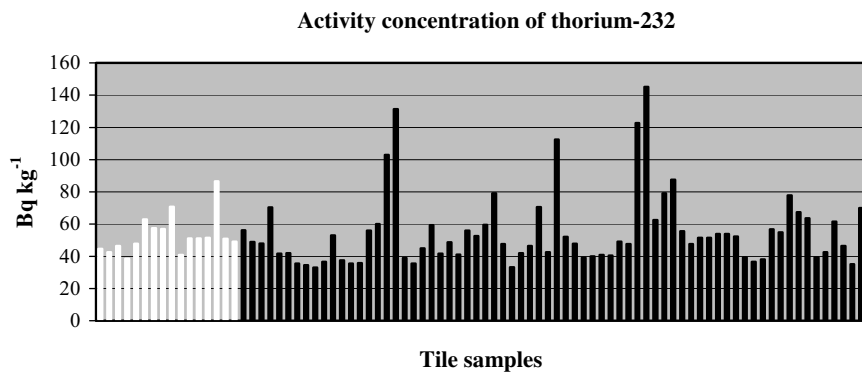


Figure 2. Thorium-232 activity concentrations measured in porous fired (white bars) and porcelain stoneware (black bars) tiles.

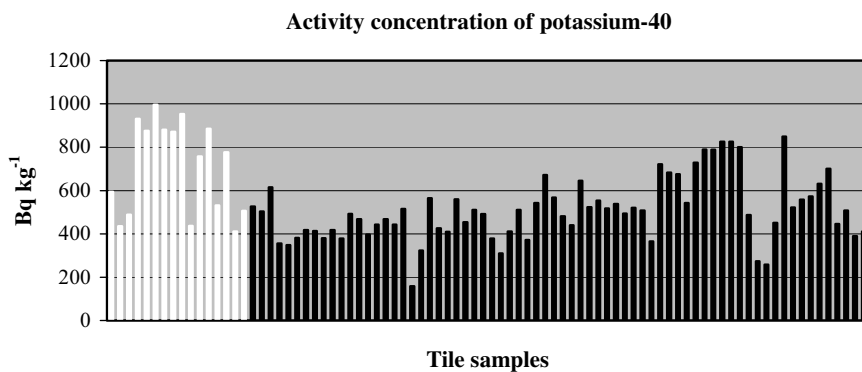


Figure 3. Potassium-40 activity concentrations measured in porous fired (white bars) and porcelain stoneware (black bars) tiles.

Summary statistics of the radium equivalent (Ra_{eq}) activities for porous fired and porcelain stoneware tiles are given in table 2 and 3 respectively. The value of Ra_{eq} of porous fired and porcelain stoneware tiles is ranging from 130 to 261 and 93 to 943 $Bq\ kg^{-1}$, respectively. The mean value of Ra_{eq} for porous fired and porcelain stoneware tiles is 183 ± 39 and $232 \pm 143\ Bq\ kg^{-1}$, respectively. From the results obtained, there's an evidence of considerable variations not only in the Ra_{eq} of the

Table 2. Summary statistics of natural radioactivity content of porous fired tiles.

	²²⁶ Ra (Bq kg ⁻¹)	²³² Th (Bq kg ⁻¹)	⁴⁰ K (Bq kg ⁻¹)	Ra _{eq} (Bq kg ⁻¹)	I
N° of samples	16	16	16	16	16
Minimum	36	38	411	130	0.48
Maximum	87	86	996	261	0.96
Mean	53	53	708	183	0.68
Standard deviation	15	12	214	39	0.15
Skewness	0.9	1.6	-0.2	0.6	0.5

Table 3. Summary statistics of natural radioactivity content of porcelain stoneware tiles.

	²²⁶ Ra (Bq kg ⁻¹)	²³² Th (Bq kg ⁻¹)	⁴⁰ K (Bq kg ⁻¹)	Ra _{eq} (Bq kg ⁻¹)	I
N° of samples	70	70	70	70	70
Minimum	20	33	158	93	0.34
Maximum	708	145	850	943	3.2
Mean	114	55	509	232	0.83
Standard deviation	118	23	144	143	0.48
Skewness	2.3	2.2	0.5	2.7	2.7

two different types of tiles, but also within the same type. Large variation in Ra_{eq} activities has been reported in many studies on natural radioactivity in building materials. For example, in 1985 Beretka and Mathew [4] calculated Ra_{eq} values ranging between 15 and 883 Bq kg⁻¹ in Australian building materials. The values obtained by Amrani and Tahtat [14] in Algerian building materials ranged from 28 to 190 Bq kg⁻¹. In Egypt, Ahmed [15] recorded the lowest values in mud and clay bricks (about 100 Bq kg⁻¹), and the highest ones in granites and marbles (about 400 Bq kg⁻¹). The recommended maximum levels of radium equivalents for building materials to be used for homes, i.e., to keep the external dose below 1.5 mGy y⁻¹, is less than 370 Bq kg⁻¹. It is worth noting that the average radium equivalent values are within the limit proposed by the OECD countries. Nevertheless, it is important to note that this recommended value is calculated for materials used in bulk amounts, and it is not appropriate for decorative building materials such as tiles.

Table 4. Worldwide average natural radionuclide content in soil [16].

	²³⁸ U (Bq kg ⁻¹)	²²⁶ Ra (Bq kg ⁻¹)	²³² Th (Bq kg ⁻¹)	⁴⁰ K (Bq kg ⁻¹)
Mean	35	35	30	400
Range	16-110	17-60	11-64	140-850
Population weighted average	33	32	45	420

Gamma indexes summary statistics of the samples are shown in table 2 and 3. The gamma index (I) has been found to be varying from 0.48 to 0.96 in porous fired tiles and 0.34 to 3.2 in porcelain stoneware tiles. The European Commission [2] suggests that building materials should be exempted from all restrictions concerning their radioactivity if the excess gamma radiation originating from them increases the annual effective dose of a member of the public by 0.3 mSv at the most, corresponding to a gamma index ≤ 1 (See Table 1). On the contrary, doses higher than 1 mSv (corresponding to a gamma index > 6) should be accepted only in some very exceptional cases, when materials are used locally.

Table 5. Comparison of activity concentrations and radium equivalent activities in ceramic tiles in different areas of the world.

Country	²²⁶ Ra	²³² Th	⁴⁰ K	R _{eq}	Reference
South Korea	44-82	34-96	310-1019	124-264	Lee et al. [17]
Algeria	55	41	410	145	Amrani & Tahtat [14]
India	28	64	24	121	Kumar et al. [18]
China	64-131	55-107	561-867	200-331	Xinwei [19]
Egypt	40-230	10-130	80-600		Ahmed [15]
Egypt	61-118	55-98	730-1050	267	El Afifi et al. [20]
Greece	25-174	29-47	411-786		Krstić et al. [21]
Spain	75-191	68-76	507-490		Serradell et al. [22]
Italy (porous fired tiles)	27-88	42-69	544-977		Bruzzi et al. [23]
Italy (porcelain stoneware tiles)	39-247	40-92	528-1000		Bruzzi et al. [23]
Italy (porous fired tiles)	36-87	38-86	411-996	130-261	Present study
Italy (porcelain stoneware tiles)	20-708	33-145	158-850	93-943	Present study

All porous fired tiles show gamma indices lower than 1. Twelve porcelain stoneware tiles show gamma indices higher than 1. None of the samples show a gamma index higher than 6.

Activity concentrations and radium equivalent activities for porous fired and porcelain tiles are compared with results obtained by other authors in Table 5. As it is possible to observe, activity concentration maximum values of porcelain stoneware tiles result much higher than those reported by the other authors, and than those measured in porous fired tiles in this study. Despite employing different technologies, this difference between porous fired and porcelain stoneware tiles was also observed in a previous Italian study (see Table 5) [23].

4. CONCLUSIONS

Activity concentrations of ²²⁶Ra, ²³²Th and ⁴⁰K were measured and next radium equivalent activities and gamma indexes were calculated in a number of Italian ceramic tiles. The authors divided tile samples into two group: porous fired tiles and porcelain stoneware tiles. Results confirm that mean values measured in porous fired tiles are comparable with mean worldwide value in earth crust, instead natural activity concentrations in porcelain stoneware tiles are found slightly higher than those averagely measured in soils. Probably, the higher natural activity concentrations found in porcelain stoneware tiles is due to the larger amount of zircon added with respect to porous fired tiles. From a radiological point of view, the results indicate that the use of these materials in construction of dwellings could be considered safe for inhabitants. As matter of fact, all samples show gamma indexes much lower than the limit indicated by the European Commission and, except some porcelain stoneware tiles, in all samples the radium equivalent activity is within the limit set by the OECD.

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