Natural radioactivity in Italian ceramic tiles

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INTRODUCTION

All building materials contain various amounts of natural radioactive nuclides. Materials derived from rock and soil contain mainly natural radionuclides of the uranium (^{238}U) and thorium (^{232}Th) series, and the radioactive isotope of potassium (^{40}K). In the uranium series, the decay chain segment starting from radium (^{226}Ra) is radiologically the most important and, therefore, reference is often made to radium instead of uranium (EC, 1999). 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 (UNSCEAR, 1993). 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 a high temperature. Ceramic tiles get their sanitary white appearance from zircon ($ZrSiO_4$). 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, ceramic tiles can show natural activity concentration significantly higher than the average values of Earth's crust. 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, and of gamma-index and radium-equivalent calculation. The results of this investigation are compared with the findings of similar studies carried out in other countries.

MATERIALS AND METHODS

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 and packed 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. ±5% and ±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 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.

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. As defined by OECD (1979) and Beretka and Mathew (1985):

$$Ra_{eq} = C_{Ra} + 1.43C_{Th} + 0.077C_K$$

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

Activity concentration index calculation

A number of indexes dealing with the assessment of the excess gamma radiation originating from building materials have been proposed. In this study, the gamma-index was calculated as proposed by the European Commission (EC, 1999). 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. European Commission has proposed the following activity concentration index (I) for identifying whether a dose criterion is met:

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

where C_{Ra}, C_{Th} and C_K are the activity concentration of ^{226}Ra, ^{232}Th and ^{40}K (Bq kg^{-1}) in the building materials. The activity concentration index shall not exceed the values shown in Table 1.

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	$I \leq 2$	$I \leq 6$

RESULTS AND CONCLUSIONS

The activity concentration of ^{226}Ra 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 ^{226}Ra varies from 20 to 707 Bq kg^{-1} (mean value 114±118 Bq kg^{-1}). The activity concentration of ^{232}Th 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 ^{40}K 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 ^{226}Ra, ^{232}Th, and ^{40}K activity concentrations in porous fired tiles and those averagely measured in soils shows that they are completely comparable. Instead, natural activity concentrations in porcelain stoneware tiles appear significantly higher than those averagely measured in soils, especially for ^{226}Ra. 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. (2000). 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±143 Bq kg^{-1}, respectively.

From the results obtained, there's an evidence of considerable variations not only in the Ra_{eq} of the 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 calculated Ra_{eq} values ranging between 15 and 883 Bq kg^{-1} in Australian building materials. The values obtained by Amrani and Tahtat (2001) in Algerian building materials were ranging from 28 to 190 Bq kg^{-1}. In Egypt, Ahmed (2005) 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 1.5mGy y^{-1}, is less than 370 Bq kg^{-1}. 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.

Country	**Sample name**	**^{226}Ra**	**^{232}Th**	**^{40}K**	**Ra_{eq}**	**Reference**
South Korea	Tile	44-82	34-96	310-1019	124-264	Lee *et al.*, 2001
Algeria	Ceramics	55	41	410	145	Amrani & Tahtat, 2001
India	Ceramics	28	64	24	121	Kumar *et al.*, 2003
China	Glazed tiles	64-131	55-107	561-867	200-331	Xinwei, 2004
Egypt	Ceramics	40-230	10-130	80-600		Ahmed, 2005
Egypt	Ceramics	61-118	55-98	730-1050	267	El Afifi *et al.*, 2006
Greece	Ceramics	25-174	29-47	411-786		Krstić *et al.*, 2007
Spain	Porcelain tiles	75-191	68-76	507-490		Serradell *et al.*, 2007
Italy	Porous f. tiles	36-87	38-86	411-996	130-261	Present study
Italy	Porcelain tiles	20-708	33-145	158-850	93-943	Present study

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 (EC, 1999) 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. 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 2. As it is possible to observe, activity concentrations 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.

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