

## Determination of radon specific exhalation rate from Italian ceramic tiles

S. Righi<sup>a, b</sup>, S. Verità<sup>a, b</sup>, L. Bruzzi<sup>a, b</sup>, R. Guerra<sup>a, b</sup>, A. Albertazzi<sup>c</sup>, G. Bonvicini<sup>c</sup>

<sup>a</sup> Centro Interdipartimentale di Ricerca per le Scienze Ambientali (CIRSA)  
Università di Bologna, via S.Alberto 163, 48100 Ravenna

<sup>b</sup> Dipartimento di Fisica  
Università di Bologna, via le B.Pichat 6/2, 40127 Bologna

<sup>c</sup> Italian Ceramic Centre  
via Martelli 26, 40138 Bologna

Italy

**Abstract.** Ceramic tiles commonly used in Italy have been studied for both natural radionuclide content and radon emanation. Their body composition is made up of mixtures of clay, sand and other natural materials that are shaped into slabs and fired at high temperature up to 1250°C. From a radiological point of view, zircon sands are the most interesting raw materials used in the composition of the tiles as opacifiers in the preparation of glazes in the percentage of 10–20% and of porcelain tiles in concentrations of 1–10%. Therefore the highest natural activity concentrations are found in glazed and porcelain tiles. A high resolution gamma spectroscopy technique has been used for determining the activity concentration of <sup>226</sup>Ra and the E-PERM electret ion chamber has been employed for radon exhalation measurements.

### 1. Introduction

The study focuses on the determination of radon specific exhalation rate from Italian ceramic tiles, which are widely manufactured in Italian ceramic industries. In particular, the results obtained by experimental measurements on nine samples of porcelain tiles are reported. From a radiological point of view, glazed and porcelain tiles contain a low concentration of natural radioactivity, as low concentration of zircon sands are used as raw materials. Zircon sands have a high temperature resistance with a melting point of 2000–2500°C, acid corrosion resistance, high heat conductivity, and low thermal expansion. These properties make zircon materials particularly suitable as opacifiers in the preparation of ceramic glazes.

A previous study, focused on the determination of natural radioactivity concentrations in several zircon sands commonly used in Italian ceramic industries [1], has shown that the average activity concentrations of <sup>238</sup>U and <sup>232</sup>Th ranged between 1800 and 3150 Bq kg<sup>-1</sup>, and 360 and 1100 Bq kg<sup>-1</sup>, respectively. These concentrations are significantly higher than the world average for soils, rocks and the Earth's crust, and confirm the results obtained by other authors [2–6]; on the contrary, <sup>40</sup>K shows activity concentrations very low (30–90 Bq kg<sup>-1</sup>).

The samples analysed in this study are different kinds of Italian porcelain tiles. The main characteristics of these products are an extremely compact body, high density, low porosity and very strong intercrystalline coherence, and these properties provide the porcelain tiles with improved resistance to corrosion and erosion, high surface hardness, excellent tensile strength and abrasion, chemical and stain resistance. According to the current international standard ISO 13006, porcelain tiles are classified as a material with porosity lower than 0.5% in terms of water absorption, whereas the commercial products generally have 0.1% porosity, far lower than the ISO standards values.

The raw materials making up the porcelain tile body can be divided into two groups: the clayey materials (e.g. sedimentary clays, schistose clay, loamy clay, marl), which serve as plasticizers; and non-plastic materials including feldspar, talc and quartz used to confer a strong structure. Sometimes zircon sand is used to obtain a high white-body porcelain tile. The chemical composition of five types of porcelain tile is reported in Table 1.

The ultimate product characteristics are influenced not only by the raw materials, but also by the production processes applied (batching, grinding, pressing, drying and firing). In general, the ceramic and porcelain tile manufacturing process consists of a series of successive stages, which can be summarized as shown in Fig. 1. For many ceramic products, the body composition depends on the amount and type of raw materials, which are formulated to give the desired properties. Once the

ingredients are weighed, they are added together in a mixer (depending on the ceramic sector, mixing may range from large scale continuous operations to carefully controlled small scale batch mixing); sometimes it is necessary to add water to achieve fine grinding. If wet milling is used, the excess water is usually removed via spray drying, which involves pumping the slurry to an atomizer consisting of a rapidly rotating disc.

TABLE 1. CHEMICAL COMPOSITION OF SEVERAL TYPES OF PORCELAIN TILE [7].

	Composition (%)			
	Tile 1 (base body)	Tile 2 (base body)	Tile 3 (super white body)	Tile 4 (super white body)
SiO <sub>2</sub>	67	71	68	64
Al <sub>2</sub> O <sub>3</sub>	21.0	18	18	21
K <sub>2</sub> O	1.7	1.8	1.4	2.9
Na <sub>2</sub> O	4.5	4.0	3.5	3.9
CaO+MgO	0.8	0.9	0.7	0.7
Fe <sub>2</sub> O <sub>3</sub> +TiO <sub>2</sub>	0.8	0.9	0.6	0.1
ZrO <sub>2</sub>	—	—	4.4	3.1
P.F.	4.2	3.4	3.4	3.4

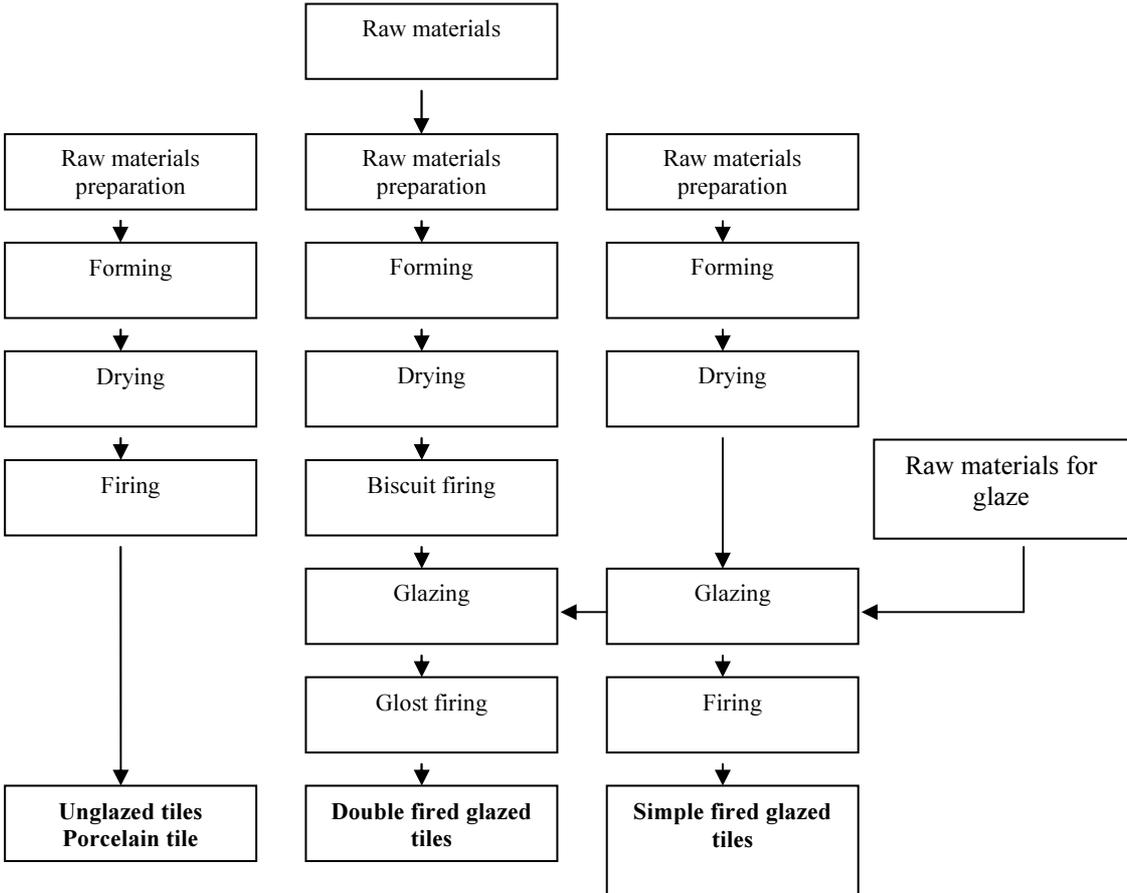


FIG.1. General production process for ceramic tiles

In this study several samples of porcelain tiles have been analyzed and experimental measurements have been conducted:  $\gamma$ -ray spectroscopy for determining the natural radioactivity concentration and E-PERM electret ion chambers [8] for determining radon exhalation rate.

## 2. Material and methods

### 2.1. Sample collection and preparation

Several porcelain tile samples have been collected from major local manufactures in Emilia-Romagna Region (Table 2). All porcelain tile samples have been cut into smaller pieces with an average dimension of about 5×5 cm, and a mass of 30–60 g (Fig. 3).

TABLE 2. SAMPLES ANALYSED IN THE STUDY

Code	Sample	Original size (cm)
01	Grey porcelain tile	33 × 33
02	Porcelain tile	45.2 × 45.2
03	White porcelain tile	30 × 40
04	Porcelain tile	45 × 45
05	Porcelain tile	34 × 34
06	Porcelain tile	30 × 30
07	White porcelain tile	32.5 × 32.5
08	Porcelain tile	45 × 45
09	Porcelain tile	60 × 15



FIG.3. Example of porcelain tiles analysed in the study

### 2.2. Gamma-ray spectrometry measurements

The activity concentrations of  $^{226}\text{Ra}$  have been determined by use of high resolution  $\gamma$ -ray spectroscopy. The system consists of an HPGe coaxial high purity germanium detector of 22.6% nominal relative efficiency and with a resolution of 1.9 keV at 1.33 MeV ( $^{60}\text{Co}$ ). The samples are closed in 450 mL Marinelli beakers and kept for about three weeks before measurement, in order to achieve radioactive equilibrium between  $^{226}\text{Ra}$ , radon and its short lived decay products. Short-lived daughters with more easily measured gamma-ray emissions such as  $^{234\text{m}}\text{Pa}$ ,  $^{214}\text{Pb}$ ,  $^{214}\text{Bi}$ ,  $^{228}\text{Ac}$  and  $^{212}\text{Pb}$  were used for proxy determinations of the activity concentrations of their respective parents  $^{238}\text{U}$ ,  $^{226}\text{Ra}$  and  $^{232}\text{Th}$ . Gamma-ray peaks of 1001.03 ( $^{234\text{m}}\text{Pa}$ ), 609.32 and 1120.28 keV ( $^{214}\text{Bi}$ ), 295.21 and

351.92 keV ( $^{214}\text{Pb}$ ), 338.40, 911.07 and 968.90 keV ( $^{228}\text{Ac}$ ), and 238.63 keV ( $^{212}\text{Pb}$ ) were used. The counting time is 60 000 s. Measurement times were sufficiently long to ensure that the overall uncertainty was generally less than 10% at a 95% confidence interval.

### 2.3. Radon exhalation rate measurements

The radon exhalation rate was measured by hermetically closing the sample in a container and following the radon activity as a function of time. The system involved E-PERM<sup>®</sup> electret ion chambers and consisted of determining the  $^{222}\text{Rn}$  activity accumulated in a glass jar (Fig. 4) that is a component part of the E-PERM<sup>®</sup> radon-in-water measurement test kit [8, 9]. The accumulation measurements were performed with screw-capped and gasketed glass jars, the chamber configuration was SST (chamber ‘S’, Short-Term electret), and the total accumulation volume after subtracting the excluded volume for the E-PERM<sup>®</sup> chamber is 3.6 L. The accumulation time was set at 20 d. Triplicate measurements were carried out for each sample to take into account the natural variability of radon emanation. More details are given in [10].



FIG.4. Electret ion chamber and glass jar of E-PERM<sup>®</sup> system

The radon activity growth,  $C_v$  ( $\text{Bq}/\text{m}^3$ ) is given by:

$$C_v = \frac{E(1 - e^{-\lambda t})}{V_c \lambda} + C_0 e^{-\lambda t}$$

where:

- $E$  the radon exhalation rate ( $\text{Bq h}^{-1}$ ) from sample;
- $V_c$  is the volume of the container ( $\text{m}^3$ );
- $\lambda$  is the radon decay constant ( $7.56 \cdot 10^{-3} \text{ h}^{-1}$ );
- $t$  is the accumulation time;
- $C_0$  is the  $^{222}\text{Rn}$  activity concentration ( $\text{Bq m}^{-3}$ ) in the accumulation vessel at the start of an accumulation time ( $t = 0$ ).

### 2.4. Emanation coefficient measurements

The radon emanation coefficient representing the proportion of the  $^{222}\text{Rn}$  released to the total amount of radon produced was calculated by the following equation [11]:

$$\eta = \frac{E}{C_{Ra} \lambda_{Rn}}$$

where:

$E$  is the measured exhalation rate of the sample ( $\text{Bq h}^{-1}$ );

$C_{Ra}$  is the  $^{226}\text{Ra}$  content ( $\text{Bq kg}^{-1}$ );

$\lambda_{Rn}$  is the radon decay constant ( $7.56 \times 10^{-3} \text{ h}^{-1}$ ).

### 3. Results and discussion

Table 3 shows the activity concentrations of the naturally occurring radionuclides  $^{238}\text{U}$ ,  $^{226}\text{Ra}$  and  $^{232}\text{Th}$ , the radon exhalation rate, and the radon emanation coefficient in the ceramic tiles examined. The radon exhalation rate is given per unit mass in units of  $\text{Bq kg}^{-1} \text{ h}^{-1}$ . The activity concentrations range from 46 to 257  $\text{Bq kg}^{-1}$  for  $^{238}\text{U}$ , from 33 to 197  $\text{Bq kg}^{-1}$  for  $^{226}\text{Ra}$  and from 39 to 76  $\text{Bq kg}^{-1}$  for  $^{232}\text{Th}$ . It is seen from Table 3 that in six samples the exhalation rate was lower than the LLD of  $0.0006 \text{ Bq h}^{-1}$  for the 15–20 d exposure time and in the other three samples it was very low ( $0.0010$ – $0.0016 \text{ Bq kg}^{-1} \text{ h}^{-1}$ ). These results are consistent with the results observed in a previous study [10]. That study focused on the radon exhalation in building materials used in Italian dwellings and also analysed four samples of ceramic tiles (two glazed tiles and two porcelain tiles). All four samples showed exhalation rates below the detection limit ( $0.0015 \text{ Bq h}^{-1}$  for an exposure time of 240 h). Many authors [11–15] have reported radon exhalation rates higher than those reported for porcelain tiles in this work and in Ref. [10]), although  $^{226}\text{Ra}$  and  $^{238}\text{U}$  activity concentrations of their materials are similar or lower than those shown in Table 1. This observation is in agreement with the findings of a survey of radionuclide content and radon emanation rate in building materials used in the United States of America [15], where it was noted that the uranium content of a material alone cannot be used to predict how much radon is emanated.

TABLE 3. ACTIVITY CONCENTRATION, RADON EXHALATION RATE AND RADON EMANATION COEFFICIENT FOR PORCELAIN TILES

Code	Type of tile	Activity concentration ( $\text{Bq/kg}$ )			Specific exhalation rate ( $\text{Bq kg}^{-1} \text{ h}^{-1}$ )	Radon emanation coefficient (%)
		$^{238}\text{U}$	$^{226}\text{Ra}$	$^{232}\text{Th}$		
01	Grey porcelain	126	114	52	< to 0.0006	
02	Porcelain	130	111	55	0.0016	0.2
03	White porcelain	217	197	62	< to 0.0006	
04	Porcelain	204	153	47	< to 0.0006	
05	Porcelain	115	113	76	0.0016	0.2
06	Porcelain	257	186	48	< to 0.0006	
07	White porcelain	94	46	39	< to 0.0006	
08	Porcelain	46	33	42	0.0010	0.4
09	Porcelain	47	46	43	< to 0.0006	

As explained in Section 1, porcelain stoneware is made from mixtures of kaolin, white-firing plastic clays, feldspars, quartz sands, alumina and zircon sands. Radon exhalation from clay and clay bricks has been observed in [11, 16–20], the radon emanation coefficient in quartz sands has been determined in Ref. [21] and the radon emanation rate and emanation coefficient of mineral zircon has been measured in Refs [10, 22]. So, while porcelain tile raw materials show measurable radon exhalation rates, the exhalation rate in the end products appears to be close to the detection limit. From these considerations it seems highly probable that the manufacturing process makes it extremely difficult for radon to be released from tiles.

A possible cause for this effect is the high density and low porosity (<0.5%) obtained by the pressing process and firing, as it is well known that a dense material with low porosity do not allow radon to diffuse through it quickly [23, 24]. In fact, firing aims to achieve vitrification of the mass that depends on the reactivity of the clayey components and the synergistic vitrification action developed by the

feldspars. It is recognised that vitrification chemically binds the contaminants in a glass-like matrix that significantly reduces contaminant mobility [25]. Therefore, it is highly probable that radon present in the tile is released during vitrification, whereas the radon produced through the decay of radium after the vitrification process remains locked up in the glass-like matrix.

In summary, the dose from the inhalation of radon emanating from these building materials was found to be extremely small. Indeed, ceramic floor and wall coverings could act as a barrier that inhibits the migration of radon from structural building materials (bricks and cement) to indoor air. To confirm that radon exhalation from porcelain tiles is not a significant problem, additional measurements eventually extending the counting time up to 700–800 h (about 1 month) are needed.

#### 4. Conclusion

From this study, the natural radionuclide content, radon exhalation rate and emanation fraction of some porcelain tiles commonly manufactured in Italian ceramic industries were determined. The activity concentration ranged from 46 to 257 Bq kg<sup>-1</sup> for <sup>238</sup>U, from 33 to 197 Bq kg<sup>-1</sup> for <sup>226</sup>Ra and from 39 to 76 Bq kg<sup>-1</sup> for <sup>232</sup>Th. In six samples, the exhalation rate was lower than the LLD of 0.0006 Bq h<sup>-1</sup> for about 15–20 d exposure time and in the other three samples was very low (0.0010–0.0016 Bq kg<sup>-1</sup> h<sup>-1</sup>). It seems highly probable that the manufacturing process makes it extremely difficult for radon to be released of from tiles; in fact, the main characteristics of these products are an extremely compact body, high density, low porosity and very strong intercrystalline coherence obtained by the pressing and firing processes. It is recognized that vitrification chemically binds the contaminants in a glass-like matrix that significantly reduces contaminant mobility. Therefore, it is highly probable that the radon present in the tile is released during vitrification whereas the radon produced through the decay of radium after the vitrification process remains locked up in the glass-like matrix.

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