Radioprotection, vol. **44**, n° 5 (2009) 445–451

DOI: 10.1051/radiopro/20095083

Radon exhalation rates from zircon sands and ceramic tiles in Italy

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Abstract. Naturally occurring radionuclides in building materials are sources of external and internal exposure in dwellings. External radiation exposure is caused by the gamma radiation originating from members of uranium and thorium decay chain and from ^{40}K. Internal radiation exposure, mainly affecting the respiratory tract, is due to the short-lived daughter products of radon which are exhaled from building materials into room air. The objective of this study is to measure the radon exhalation rates from zircon materials, flours and sands, used as raw materials in the porous fired tiles body and from the final products (porcelain tiles usually commercialized in Italy). The radon exhalation rates for the zircon flours and sands ranged from 0.17 to 1.9 Bq kg^{-1} h^{-1}, and from 0.090 to 0.20 Bq kg^{-1} h^{-1}; ^{222}Rn exhalation rates for most of the porcelain stoneware tiles are near or below the minimum detectable limit (LLD) of 0.0004 Bq kg^{-1} h^{-1}.

1. INTRODUCTION

Zircon (zirconium silicate, ZrSiO4) is a mineral that occurs in small quantities in a wide range of igneous, sedimentary, and metamorphic rocks. High purity zircon can be found in deposits close to the American, Australian and South African coasts. Zircon is also a by-product of the mining and processing of heavy-minerals sands for titanium (ilmenite, rutile) or tin minerals. One of the most important use of zircon is within the ceramic industry for the production of ceramic tiles and sanitary ware. The use of micronized zircon and zircon flour in ceramic products accounts for almost half of the worldwide consumption of zircon (Table 1). Zircon is characterized by several properties that are important for ceramic applications, including high strength, high fracture toughness, excellent wear resistance, high hardness, excellent chemical resistance, and very good refractory properties.

In porous fired tiles and sanitary ware, ceramic has a two-piece body made up of a clay-based ceramic body covered with a glaze to provide waterproofing, durability and decoration. Zircon, in the form of sand and/or flour, is added to the glaze as opacifier and whitening agent (15–20%). In contrast, porcelain stoneware tiles have a one-piece ceramic body composed of clays, quartz, feldspars together with zircon (1–10%). The surface of these tiles may be glazed or unglazed. All zircon materials contain uranium and thorium in the crystal lattice. As a result of the high chemical inertness of zircon, most of the uranium and thorium found is that which was present during the crystallization of the mineral from the molten host rock (although some may also occur within other minerals present as inclusions in the zircon sand grains, for example monazite). The uranium and thorium atoms and their decay products are bound within the zircon crystal structure, substituting for a small number of zirconium atoms. In most other uranium-containing minerals, including uranium ores, the uranium atoms are not bound within the crystalline matrix but form part of the cementing material between the grains. The nature of the zircon crystal is such that the removal of uranium and thorium is not easily accomplished without destruction of the crystal lattice.

Article published by EDP Sciences and available at http://www.radioprotection.org
or http://dx.doi.org/10.1051/radiopro/20095083

Basically two radiation exposure pathways are associated with ceramic tiles and other building materials: external exposure due to gamma-decay of naturally-occurring radionuclides, and internal exposure through inhalation of radon gas and its short-lived decay products. This study reports activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K, radon exhalation rates and radon emanation coefficient from zircon materials, such as zircon sands and zircon flours, and Italian commercial porcelain stoneware tiles.

Table 1. Relative zircon consumption by region [1].

	Relative consumption (%)
Europe	36
China	20
North America	14
Asia-Pacific	14
Japan	7
Rest of the world	9

2. MATERIALS AND METHODS

2.1 Sampling procedure

The most commonly raw materials of concern used in the Italian ceramic industry (zircon flours and sands), and different types of porcelain stoneware tiles were analyzed for naturally-occurring radionuclides and radon exhalation rates. Material types and grain-size characteristics are listed in Table 2. In order to determine the radon specific exhalation rate, an amount of about 50 g of zircon flour, and about 100 g of zircon sand was used for each measurement. For the same purpose, tile samples have been cut into smaller pieces with an average dimension of about 5 × 5 cm, and a mass of 30–60 g.

Table 2. Types of zircon material and porcelain tiles analysed. Grain-size measurements are reported for zircon sands and flours.

Code	**Sample**	**Grain size (μm)**	**Code**	**Sample**	**Grain size (μm)**	**Code**	**Sample**	**Original size (cm)**
01	Zircon flour	2.30 ± 1.60	15	Zircon flour	2.90 ± 2.60	28	Grey porcelain tile	33 × 33
02	Zircon flour	2.60 ± 2.20	16	Zircon flour	12.30 ± 9.00	29	Porcelain tile	45.2 × 45.2
03	Zircon flour	2.10 ± 1.40	17	Zircon flour	–	30	White porcelain tile	30 × 40
04	Zircon flour	2.30 ± 1.60	18	Zircon flour	12.00 ± 9.50	31	Porcelain tile	45 × 45
05	Zircon flour	2.40 ± 1.90	19	Zircon flour	–	32	Porcelain tile	34 × 34
06	Zircon flour	2.30 ± 1.60	20	Zircon flour	–	33	Porcelain tile	30 × 30
07	Zircon flour	5.70 ± 4.00	21	Zircon flour	–	34	White porcelain tile	32.5 × 32.5
08	Zircon flour	2.70 ± 2.10	22	Zircon sand	90 ± 50	35	Porcelain tile	45 × 45
09	Zircon flour	3.60 ± 3.00	23	Zircon sand	90 ± 40	36	Porcelain tile	60 × 15
10	Zircon flour	2.30 ± 1.60	24	Zircon sand	90 ± 30	37	Porcelain tile	30 × 30
11	Zircon flour	2.20 ± 1.50	25	Zircon sand	90 ± 40	38	Porcelain tile	11.5 × 11.5
12	Zircon flour	2.40 ± 1.90	26	Zircon sand	90 ± 30	39	Porcelain tile	30 × 60
13	Zircon flour	2.80 ± 2.10	27	Zircon sand	90 ± 40			
14	Zircon flour	2.90 ± 2.60						

2.2 Gamma-ray spectrometry measurements

Natural activity concentrations were measured by high-resolution γ-ray spectroscopy. The system consists of a coaxial high purity germanium detector of 22.6% nominal relative efficiency, and a resolution of 1.9 keV at 1.33 MeV (^{60}Co). 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'Energie 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.

Samples were dried, homogenized, packed, sealed in 450 mL Marinelli beakers, and kept for about three weeks before measurement, in order to achieve radioactive equilibrium between ^{226}Ra, ^{222}Rn and its short-lived decay products. Short-lived daughters with more easily measured gamma-ray emissions such as ^{214}Pb, ^{214}Bi, ^{228}Ac and ^{212}Pb were used for proxy determinations of the activity concentrations of their respective parents ^{226}Ra and ^{232}Th. Gamma-ray peaks of 609.32 and 1120.28 keV (^{214}Bi), 295.21 and 351.92 keV (^{214}Pb), 338.40, 911.07 and 968.90 keV (^{228}Ac), and 238.63 keV (^{212}Pb), and 1460,83 keV (^{40}K) were used.

Spectrum analysis was performed using a Gamma 2000 Silena v. 2.0 software. All sample were counted for 60,000 s, and measuring times were sufficient to ensure that the overall uncertainty was generally lower than 10% at a 95% confidence interval. The background was subtracted from each spectrum.

2.3 Measuring the rate of radon exhalation from zircon sands, zircon flours and ceramic tiles

The radon exhalation rate was measured with the standard commercially available E-Perm system, which consisted in a E-PERM® electret ion chamber measuring the ^{222}Rn activity concentration accumulated in a glass jar. The E-Perm procedure has been extensively described by Kotrappa et al. [2, 3]. Briefly, measurements consisted in sealing the sample with one of these monitors within an exposure container, and determining the average equilibrium of ^{222}Rn gas concentration during the exposure time period. The accumulation time was set at 20 days for ceramic tiles, 10 days for zircon sands, and 3 days for zircon flours (Figure 1). Triplicate measurements were carried out for each sample to take into account the natural variability of radon emanation. Equation (1) gives the ^{222}Rn activity concentration growth, C_{Rn} (Bq/m^3):

$$C_{Rn} = \frac{E\left(1 - e^{-\lambda_{Rn} t}\right)}{V\lambda_{Rn} m} + C^0_{Rn} e^{-\lambda_{Rn} t} \tag{1}$$

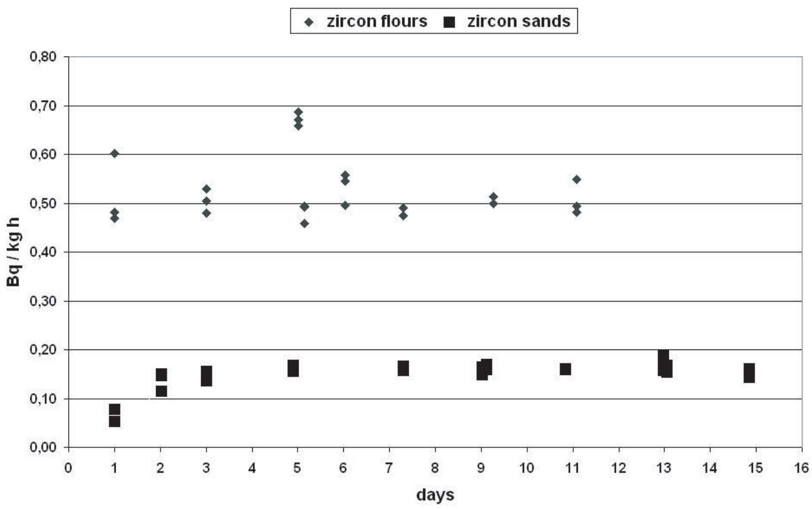

Figure 1. Accumulation time for zircon sands and zircon flours.

where E is the specific exhalation rate (Bq kg^{-1} h^{-1}) from the sample, λ_{Rn} is the ^{222}Rn decay constant (h^{-1}), V is the volume of the accumulation vessel (m^3), m is the mass of the sample (kg), and C^0_{Rn} (Bq m^{-3}) is the ^{222}Rn activity concentration in the accumulation vessel at the start of an accumulation time ($t = 0$).

3. RESULTS AND DISCUSSION

3.1 Radioactivity concentration in zircon materials and ceramic tiles

Table 3 shows the average values and ranges for activity concentrations of naturally occurring radionuclides ^{226}Ra, ^{232}Th and ^{40}K. The activity concentrations in zircon materials ranged from 1,660 to 3,600 Bq kg^{-1} for ^{226}Ra, from 270 to 500 Bq kg^{-1} for ^{232}Th and from 13 to 40 Bq kg^{-1} for ^{40}K, and these values are significantly higher than the values of ^{238}U (35 Bq kg^{-1}) and ^{232}Th (30 Bq kg^{-}1) found in the Earth's crust [4].

On the contrary, ceramic tiles show lower activity concentrations, but still little above the average Earth's crust values.

Table 3. Activity concentrations of naturally-occurring radionuclides in zircon materials and ceramic tiles.

Material	n samples	Radioactivity concentrations (Bq kg^{-1})			
		n samples	^{226}Ra	^{232}Th	^{40}K
Zircon materials	27	Mean	2640 ± 650	1100 ± 160	90 ± 15
		Range	1660–3600	270–500	13–40
Ceramic tiles	12	Mean	90 ± 60	50 ± 10	600 ± 90
		Range	30–200	40–80	370–660

3.2 Rate of radon exhalation from zircon materials and ceramic tiles

The radon exhalation rates for the zircon flours and sands ranged from 0.17 to 1.9, and from 0.090 to 0.20, with average values of 0.6 ± 0.3 and 0.15 ± 0.04 Bq kg^{-1} h^{-1}, respectively (Figure 2). The radon

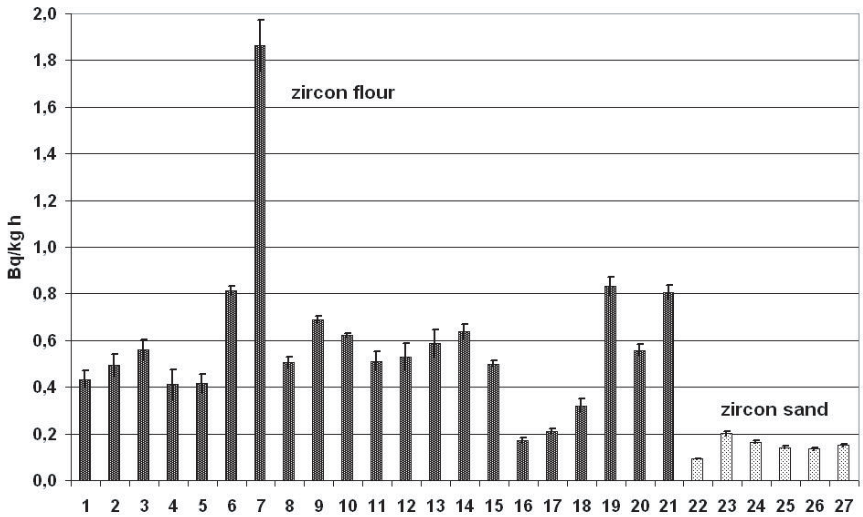

Figure 2. Radon exhalation rate from zircon materials (black bars: zircon flours; grey bars: zircon sands).

exhalation rate for zircon sands was lower than that of zircon flours, and this result is consistent with the hypothesis that the finer the grain size, the larger the exposed surface area per unit mass, and the higher the ^{222}Rn exhalation rate is.

The radon emanation coefficient (2), defined as the fraction of radon atoms released into the material pore space from a radium bearing grain, for this type of materials is very low compared to that of other uranium-containing materials, because the escape of radon is inhibited by the fact that ^{226}Ra, like its parent radionuclide ^{238}U, is bound within the crystal lattice (Table 4).

$$\eta = \frac{E}{C_{Ra}\lambda_{Rn}} \tag{2}$$

where E is the measured radon specific exhalation rate of the sample; C_{Ra} is the ^{226}Ra activity concentration and λ_{Rn} is the decay constant for ^{222}Rn.

Table 4. Radon release data for zircon.

	Radon emanation coefficient
Zircon flours (21 samples) This study	0.019–0.145 Average value (0.034 ± 0.002)
Zircon sands (6 samples) This study	0.0055–0.0147 Average value (0.0080 ± 0.0003)
USA flours (2 sample) [6]	0.008–0.009
USA flours (5 sample) [6]	0.010–0.020
USA zircon sands (4 sample)	0.0013–0.0019 [6]
South Africa [7]	0.0060
Typical rocks and soil [8]	0.05–0.7
Uranium mine tailings [1]	0.2–0.3
Gold mine tailings [1]	0.13–0.39

The results presented in Table 5 illustrate that the ^{222}Rn exhalation rates for most of the porcelain stoneware tiles are near or below the minimum detectable limit (LLD) of 0.0004 $Bq \cdot kg^{-1} \cdot h^{-1}$. The reason for that could be found in the production process (figure 3) and the characteristics of porcelain stoneware tiles. This type of tiles consists of a spray dried body of selected clays, quartz and feldspar, which is shaped by dry pressing and fired at temperatures of up to 1250 °C. It is a uniform, monolithic product (although a glaze may be applied for decorative purposes) that has high water resistance, low porosity (< 0.5%), high mechanical strength and high stain resistance. The product consists of a glassy matrix of a feldspathic nature containing disperse crystalline phases such as quartz and mullite, therefore, it is highly probable that radon produced through the decay of radium after the vitrification process remains locked up in the glass-like matrix.

Table 5. Radon exhalation from ceramic tiles.

Code	**Specific exhalation rate ($Bq \cdot kg^{-1}h^{-1}$)**	**Radon emanation coefficient (%)**	**Code**	**Specific exhalation rate ($Bq \cdot kg^{-1}h^{-1}$)**	**Radon emanation coefficient (%)**
01	<to 0.0004	–	**07**	<to 0.0004	–
02	0.0016 ± 0.0008	0.2	**08**	0.0010 ± 0.0001	0.4
03	<to 0.0004	–	**09**	<to 0.0004	–
04	<to 0.0004	–	**10**	<to 0.0004	–
05	0.0016 ± 0.0004	0.2	**11**	0.0017 ± 0.0004	0.5
06	<to 0.0004	–	**12**	<to 0.0004	–

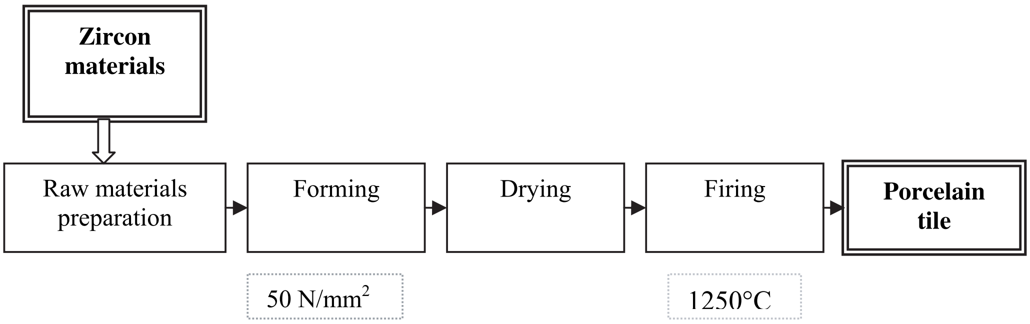

Figure 3. Porcelain tiles production process.

4. CONCLUSIONS

The geological processes that formed zircon and baddeleyite led to the incorporation of radionuclides of natural origin (i.e. those of the uranium and thorium decay series) into the crystal structure. The presence of these radionuclides creates a possible need to control exposures of workers and members of the public.

The activity concentrations of ^{238}U and ^{232}Th series radionuclides in Italian zircon sands and flours fall mostly in the ranges 1660–3600 Bq/kg and 270–500 Bq/kg, respectively.

The activity concentrations of ^{238}U and ^{232}Th series radionuclides in the porcelain stoneware tiles fall mostly in the ranges 90–200 Bq/kg and 40–80 Bq/kg, respectively.

The exposure pathways to workers and members of the public that are most likely to require consideration in the zircon and zirconia industries are those involving external exposure to gamma radiation emitted from bulk quantities of zirconium-containing material, and internal exposure via the inhalation of radionuclides in zirconium-containing dust. Internal exposure via the inhalation of radon emitted from zirconium containing material and via the ingestion of such material may also need to be considered.

This study shows that the measured ^{222}Rn exhalation rates from the porcelain stoneware tiles were at or below the minimum detectable exhalation rate; on the contrary, zircon sands and flours reported ^{222}Rn exhalation rate two order of magnitude higher. The most likely explanation for this observation is that the glassy matrix of the porcelain stoneware tile is impervious to diffusion of ^{222}Rn gas after it is released from the zircon grains.

Although high level of internal radiation exposure are potentially associated with zircon materials, low radon emanation coefficients are found in porcelain tiles. To sum up, the internal radiation exposure could be considered negligible, and the gamma radiation constitutes the major contribution to the indoor dose from ceramic tiles.

Acknowledgments

This work could not have been carried out without the collaboration with of the Health Physics Service of Ravenna Hospital and the skilful technical assistance of M. Carnevali and C. Orlandi. The authors wish to express their deep appreciation to the Institute of Advanced Studies for awarding a scholarship for Young Researchers to Dr. M. Jeyapandian to conduct a semestral activity of research at the Interdepartmental Centre for Environmental Science Research of Bologna University. The authors also are grateful to Prof. L. Bruzzi for his helpful suggestions and advice. Finally, the authors would like to thank Dr. A. Albertazzi, Dr. G. Bonvicini and E. Rastelli of Ceramic Centre of Bologna for the kind assistance in supplying and preparing the samples.

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