RADIOACTIVITY MEASUREMENTS CAMPAIGN ON CERAMIC INDUSTRIES: RESULTS AND COMMENTS*

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Abstract. As part of the NORM evaluation programme launched by the Spanish Nuclear Safety Council, a radiological study of the ceramic industry was carried out by the Environmental Radioactivity Laboratory of the Universidad Politécnica de Valencia. The study included three types of industries: zirconium sands milling, frit ceramic factories and ceramic tiles industries. Zircon (zirconium silicate) is used in all of them. The presence of ^{238}U and to a lesser extent ^{232}Th, together with their progeny, explains the radiological interest of these kinds of industries in accordance with European Directive 96/29/Euratom. In this paper the methodology used to perform this study is presented. As a first step, information on materials and processes used in different types of factories was obtained. A radiological characterization of materials, including dust from the indoor environment, was performed. Gamma spectrometry analysis was carried out using a Ge(HP) detector. As a second step, areas where radioactive materials are present were identified, as well as the presence of workers in them. Direct measurements with a portable radiation monitor and thermoluminescent dosimeters were performed and different areas of the factory were radiologically characterized. Finally, external and internal radiation doses received by workers were estimated, based on the aforementioned measurements.

1. Introduction

The use of naturally occurring radioactive material (NORM) is well known, but it has not been under regulation in Spain until the publication of *Real Decreto* 783/2001 [1]. This Decree approves a new 'Regulation on Sanitary Protection against Ionizing Radiations', as a result of the implementation of the European Council Directive 96/29 Euratom [2]. The Regulation introduces in Title VII 'Natural Sources of Radiation', Article 62, the need to study those activities in which significant increases of the exposure of workers or members of the public could take place.

Some of these industrial activities are those that use zircon (zirconium silicate) sand as a raw material [3]. This sand is milled for use directly by the ceramic industry or as an intermediate step for producing frits to be used, after milling, also in ceramic industry (see Fig. 1).

FIG. 1. Manufacturing processes using zircon sand

Zircon occurs in nature associated with quartz and other minerals such as rutile (TiO_2), ilmenite ($FeTiO_3$) and monazite (phosphate of rare earth elements). The presence of ^{238}U and to a lesser extent ^{232}Th, together with their progeny, in the crystalline structure of zircon explains the radiological interest of these kinds of industry. In this paper the methodology used to perform a radiological study of these kinds of industry is presented, along with the measurements performed to radiologically characterize the workplaces involved. Finally, a dose estimation for workers is presented, with conclusions and comments.

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2. Materials and methods

2.1. Milling of zircon

The plant studied has two milling lines: a dry milling process and a wet milling process. The dry milling process consists of a ball mill (silex or alumina balls) and a dynamic system of classification, which feeds back the largest particles and produces ‘zircon flour’. The wet milling process consists again of a ball mill followed by a dynamic size classifier and a dryer at the end of the process which produces ‘micronized zircon’. Fig. 2 shows a schematic representation of the processes. The following zones were identified in the plant for study: raw material store, dry milling, wet milling, decantation tanks, micronized bagging area and end product store.

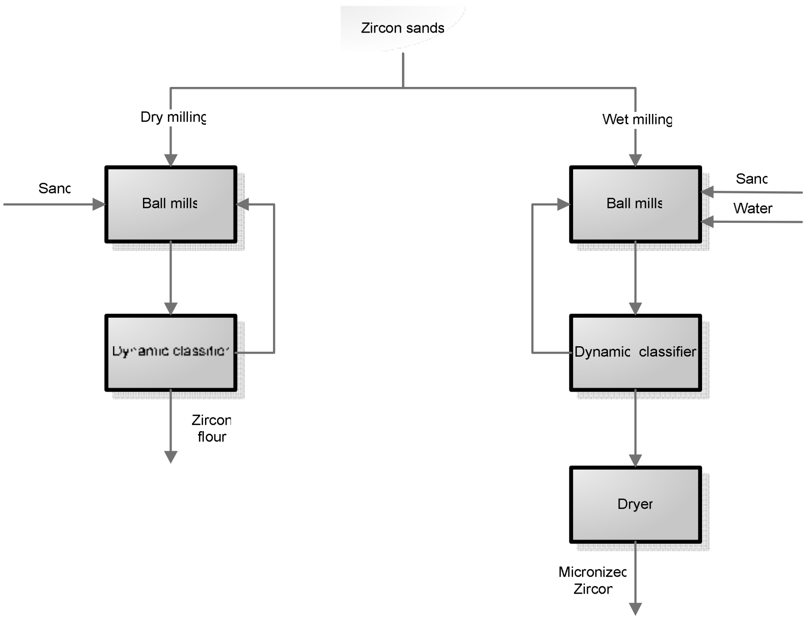

FIG. 2. Dry milling and wet milling processes

2.2. Manufacture of frits

Frits are intermediate materials for use in other factories producing end products. A wide variety of raw materials is used, of which only zircon is of radiological interest. The raw material mixes are prepared according to customer needs. Most of the formulations do not contain zircon — when they do, the ZrO_2 content rarely exceeds 18%. For this reason, these kinds of industry represent in overall terms no significant radiological risk, neither for employees nor for the environment. To perform the radiological study, the areas represented in Fig. 3 were considered.

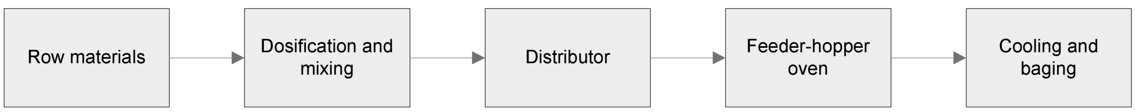

FIG. 3. Manufacturing line at a frits factory

2.3. Manufacture of ceramic tiles

This type of industry presents a great variety of processes due to the enormous amount of different manufactured end products. Nevertheless, the radiological study needed to focus only on those manufacturing lines in the factory that used zircon. Fig. 4 shows a very simplified schematic representation of one of these lines. The radiological measurements were done in places where these functions were performed.

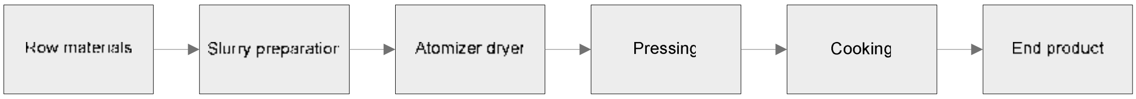

FIG. 4. Manufacturing line using zirconium compounds at a tile factory.

2.4. Experimental

The zircon milling plant operates with zircon sand having a particle diameter of 100–200 µm, obtained from Australia and South Africa. The dry milling process produces zircon flour, which has a particle size of ≤50 µm. The wet milling process produces micronized zircon, which has an even smaller particle size of ≤5 µm. Samples of zircon sand and end products were provided by the factory. The frits plant supplied three different formulations for radiological analysis, containing, respectively, 0%, 4.6% and 18% ZrO_2. From the tile factory, three samples were taken: micronized zircon as the raw material and two porcelain tiles, one of them superwhite, as the end products. All samples were dried in powder form at 100ºC to a constant weight and then sieved (0.5 mm mesh size) and placed in a 190 mL cylindrical beaker for gamma isotopic analysis.

Airborne dust sampling was conducted using a mobile low volume air sampler with an adjustable sampling gooseneck (F & J, model DF-14ME) and supplied with nitrocellulose filters with a pore size of 0.8 µm. Sample collection was made at a flow rate of approximately 30 L/min with a collection period of 3–24 h in the milling plant and 7 d in the frits and tiles factories, depending upon the dust concentration. Radon monitoring was performed, even though there was good natural ventilation in all factories. Activated charcoal type EPA canisters were placed at different points of the plant for a period of 3 d. External gamma dose rate levels were measured using a portable radiation monitor (Berthold LB 133) in different zones of the factory. Thermoluminiscent dosimeters (TLDs) of the type LiF: TLD-100 were also used to evaluate the integrated gamma dose. The TLDs were exposed for one month in zones where direct measurements were made.

All measurements of gamma ray emitting nuclides were performed with an ORTEC 919E multichannel analyser containing a type GMX Ge(HP) detector. The activity of ^{238}U was quantified by the main peaks of ^{214}Bi and ^{214}Pb. The activity of ^{232}Th was determined from the ^{228}Ac peaks. Radioactive equilibrium was assumed in both of the natural decay series [4–6]. The ^{40}K activity was determined from the 1460.75 keV photon energy peak. Radon was evaluated by measuring every canister using a type GEM Ge(HP) detector. A Harshaw 4000A reader was used to read the dosimeter cards.

3. Results and comments

3.1. Measurements

Table 1 shows the ^{238}U, ^{232}Th and ^{40}K activity concentrations for each sample analysed. In the zircon milling plant, concentration values for U and Th in zircon sand were similar in all cases, falling within the ranges 2681–3615 and 592–714 Bq/kg, respectively. These activity concentrations agree with values reported in the literature [5, 7]. The U and Th activity concentrations measured in the end products (zircon flour and micronized zircon) showed values similar to those of the raw material. This means that the milling process does not significantly modify the radioactivity or secular equilibrium of the natural decay chain. The activity concentration of ^{40}K was below the detection level in all these samples. The measured activity concentrations are much higher than the corresponding worldwide average values for soils, which are reported to be 35 and 30 Bq/kg for ^{238}U and ^{232}Th, respectively [8].

The ^{238}U and ^{232}Th activity concentrations measured in the samples of frits were in accordance with the ZrO_2 concentrations corresponding to the different formulations, the highest values being 901 and 230 Bq/kg respectively. Due to the presence of potassium compounds in the formulations, ^{40}K was detected in these samples. The micronized zircon coming from the tile factory showed a value in accordance with that measured in the milling plant. The values for porcelain products were much lower than those of the raw material because of their low overall zircon content.

TABLE 1. ACTIVITY CONCENTRATIONS IN RAW MATERIALS AND END PRODUCTS.

Material	^{238}U (Bq/kg)	^{232}Th (Bq/kg)	^{40}K (Bq/kg)
Zircon milling sand			
South African zircon sand	3615 ± 124	604 ± 33	<74
Australian zircon sand 1	2681 ± 93	597 ± 5	<69
Australian zircon sand 2	3159 ± 108	714 ± 37	<71
Zircon flour	3134 ± 104	592 ± 37	<110
Micronized zircon	2908 ± 101	607 ± 34	<99
Frits			
0% ZrO_2	11.6 ± 2.7	10.4 ± 7.7	1090 ± 63
4.6% ZrO_2	275 ± 12	53.6 ± 8.9	1973 ± 93
18.5% ZrO_2	901 ± 32	230 ± 17	339 ± 51
Tiles			
Micronized zircon raw material	3346 ± 111	719 ± 43	<117
Porcelain tiles	75 ± 6	68 ± 12	507 ± 58
Superwhite porcelain tiles	191 ± 11	76 ± 14	490 ± 6

The dust concentration in the air of the milling plant was found to be in the range 0.56–4.64 mg/m^3, these values corresponding to the areas designated as ‘end-product store’ and ‘dry milling 1’, respectively. The very different values found in the same area for different samples shows a variability of the dust concentration which justifies a conservative approach to dosimetric calculations. Dust concentrations in the frits factory were in the range 0.129–0.234 mg/m^3, these values corresponding to areas designated as ‘zircon silo’ and ‘mixer’, respectively. The range for the tile factory was 0.04–1.81 mg/m^3, these values corresponding to areas designated as ‘end product store’ and ‘discontinuous mill’, respectively. Filters from the milling plant were grouped and a gamma isotopic analysis was performed. The results are shown in Table 2. Gamma emitting radionuclides from the ^{238}U and ^{232}Th series were detected. Values for radon measurements were 6–34 mBq/m^3, similar to those found generally indoors for the Comunidad Valenciana.

3.2. Dose assessment

An estimation of the effective dose (E) received by workers was performed in accordance with the European Council Directive 96/29 [2]. The effective dose was obtained from the following equation:

$$E = E_{external} + \sum_j h(g)_{j,inh} \cdot J_{j,inh} \quad (1)$$

where

$E_{external}$	is the effective dose from external exposure during a year,
$\sum_j h(g)_{j,inh} \cdot J_{j,inh}$	is the committed effective dose for inhalation from intakes during a year,
$h(g)_{j,inh}$	is the committed effective dose per unit-intake for inhaled radionuclide j (Sv/Bq) by an individual in age group g,
$J_{j,inh}$	is the relevant intake via inhalation of the radionuclide j in a year (Bq).

Other intake paths were ignored.

TABLE 2. DOSE ATTRIBUTABLE TO EXTERNAL RADIATION

Area	Dose rate (µSv/h)		Annual effective dose (mSv)	
	LB 133	TLD	LB 133	TLD
Zircon milling sands				
Raw material store[a]	1.66	#	3.32	#
Dry milling 1	0.12 ± 0.04	0.16 ± 0.05	0.24 ± 0.08	0.32 ± 0.10
Dry milling 2	0.19 ± 0.06	0.14 ± 0.11	0.38 ± 0.12	0.28 ± 0.22
Wet milling	0.15 ± 0.07	0.09 ± 0.06	0.30 ± 0.14	0.18 ± 0.12
Decantation tanks	0.39 ± 0.09	0.41 ± 0.15	0.78 ± 0.18	0.82 ± 0.30
Product bagging	0.24 ± 0.11	0.22 ± 0.05	0.48 ± 0.22	0.44 ± 0.10
End product store	0.017 ± 0.015	0.20 ± 0.18	0.034 ± 0.030	0.40 ± 0.36
Frits				
Raw material store (zircon)	0.68	0.45	1.36	0.9
Tiles				
Zircon silo	0.28	0.5	0.56	1

[a]Measured at 1 m distance.
#Value not available.

3.3. *External dose*

External exposure is caused mainly by gamma radiation from radionuclides in the ^{238}U and ^{232}Th decay series. As already mentioned, TLDs and a portable radiation monitor (LB 133) were used to detect and measure external radiation exposures in several work areas at the plant. The results of these measurements are presented in Table 2. The annual effective dose corresponding to a total of 2000 working hours (8 h/d × 250 d/a) is included in the Table.

3.4. *Internal dose*

In accordance with Eq. (1), the internal committed effective dose due to inhalation of dust particles was calculated as:

$$\sum_j h(g)_{j,inh} \cdot J_{j,inh} \qquad (2)$$

The conversion factors $h(g)_{j,inh}$ were obtained from Annex III of the European Directive, using the values for members of the public over the age of 17. The intake ($J_{j,inh}$) was calculated as the product of the dust mass inhaled and its activity concentration:

— The total dust mass inhaled by a worker was estimated from the dust concentration in air (mg/m^3), an annual exposure period of 2000 h, and an inhalation rate of 1.25 m^3/h. In order not to underestimate the dose, the inhalable fraction of the dust was set to unity.

— It was assumed that the activity concentration of each dust sample was the same as that in the materials present in the area in which the sample was collected (Table 1).

The estimated total committed effective dose from inhalation of dust particles, i.e. the internal dose contribution, is shown in Table 3.

3.5. *Total effective dose*

Finally, the total annual effective dose was calculated as a combination of the external and internal doses. The results for all the factories studied showed an annual external dose in the zircon store areas sometimes greater than 1 mSv (3.32 mSv in the milling plant) or otherwise around 1 mSv (1.36 and 1 mSv for the manufacture of frits and tiles, respectively). The annual internal dose was above 1mSv only in some areas of the zircon milling plants, i.e. the dry milling and product bagging areas, with values of 2.04 and 1.13 mSv, respectively. In the rest of the factories these values are practically zero, with an appreciable value (0.32 mSv) only occurring close to the zircon silos at the tile factory, due to the higher activity of the materials and the dust present in the area. All these values are consistent with those found elsewhere in the literature [5, 6] and with those considered by the European Commission in its publication on the establishment of reference levels for regulatory control of workplaces [9].

TABLE 3. TOTAL ANNUAL EFFECTIVE DOSE (mSv)

Area	External	Internal	Total
Zircon milling sands			
Raw material store	3.32	#	3.32
Dry milling 1 [a]	0.32	2.04	2.36
Dry milling 2	0.38	0.54	0.92
		1.00	1.38
Wet milling	0.30	0.83	1.13
		0.59	0.89
Decantation tanks	0.82	#	0.82
Product bagging	0.78	1.11	1.89
		1.13	1.91
End product store	0.40	0.25	0.65
Frits			
Raw material store (zircon)	1.36	0.05	1.41
Raw material store, (no zircon)	0	<0.01	0
Mixing	0.04	0.03	0.07
Distributor	0	0.02	0.02
Tiles			
Zircon silo	1.00	0.32	1.32
Discontinuous milling	0.06	0.08	0.14
Atomizer	0.02	0.07	0.09
End product store	0.14	<0.01	0.14

[a]Internal dose corresponding to samples taken near the area of unloading of raw material.
[#]Value not available.

It should be noted that doses have been calculated assuming an annual exposure of 2000 h for each of the areas studied. Consideration has not been given to the fact that the plant concerned has introduced rotating shift work, moving workers periodically through every working area.

4. Conclusions

The total annual effective doses show some values over the annual dose limit of 1 mSv for members of the public, mainly in the milling plants, so this type of industry need to be carefully evaluated. Some areas show quite high values for external dose, so shielding walls are recommended and the occupancy of these areas by workers must be regulated. Also, the internal dose makes an important contribution to the total dose, so it is very important to set up a highly efficient air cleaning system. Factories manufacturing frits and tiles show lower values of total effective dose — in both cases, only the zircon silo gives an effective dose exceeding 1 mSv, mainly due to external exposure. It should be borne in mind that the dose values obtained are conservative due to the fact that the occupancies assumed in the dose calculations are much higher than actual values.

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