

# Estimation of Occupational Exposure during Ceramic Manufacturing

Fawzia Mubarak<sup>1\*</sup>, Hesham Saleh<sup>2</sup>

1. Rad. Protection Dept., NRC, AEA, Cairo, Egypt
2. Biological Application Dept., NRC, AEA, Cairo, Egypt

## ARTICLE INFO

**Article type:**  
Original Article

### Article history:

Received: Apr 26, 2019  
Accepted: Jul 20, 2019

### Keywords:

Occupational Exposure  
External Dose  
Internal Dose  
Ceramics

## ABSTRACT

**Introduction:** The present study investigated the relatively high concentrations of natural radionuclides in raw material that used in ceramic manufacturing, and estimated the occupational exposure due to these activity concentrations.

**Material and Methods:** A high-purity Germanium detector was used to determine naturally occurring radionuclides in raw materials that used in ceramic manufacturing. Activity concentrations of these materials lead to potential radiological hazards due to gamma and alpha radiation. These hazards were evaluated in the present study.

**Results:** Maximum activity concentrations was 5844, 1065 and 41 Bq/kg for 226Ra, 232Th and 235U in powdered quartz; however, maximum activity concentration for 40K was 1868 Bq/kg in colors. These activities were observed to be exceeding the exemption limit. Pancreas received the lowest dose (i.e., 0.02 mSv/y), while skin received the highest dose (i.e., 0.044mSv/y). Internal hazard index (Hin) was reported as 53.74, which exceed the recommended value (Hin≤1). Alpha index was 42.4 which led to over exposure. Representative level index and excess lifetime cancer risk were 0.00062 and 0.641 respectively. The total annual external dose was 2.62 m Gy/y which led to 1.83 mSv/y effective dose. Radiological hazard due to radon inhalation was 1.53E-06 mSv/y.

**Conclusion:** Due to the high activity concentrations of raw materials (especially zirconium compounds) and consequently the associated high dose, specific regulations must be applied in the ceramic industry in Egypt.

► Please cite this article as:

Mubarak F, Saleh H. Estimation of Occupational Exposure during Ceramic Manufacturing. Iran J Med Phys 2020; 17: 175-182. 10.22038/ijmp.2019.39889.1539.

## Introduction

Naturally, occurring radionuclides usually measured in all building materials are derived from rock and soil. The most common radionuclides in the construction materials are U-238 and Th-232 series, as well as the radioactive isotope of potassium (K-40)[1-5]. Ceramic industrial processing can lead to high exposure due to products, by-products or waste materials [6-8]. Ceramic tiles are among the commonly used decorative building materials. Due to the polished surface and attractive colors of ceramic tiles, they are used as ornamental and constructive materials for interior and exterior purposes. Ceramic tiles are made of a mixture of naturally occurring radioactive materials (NORM). Glazes applied to tiles and sanitary ware commonly containing zircon as zirconium silicate (ZrSiO<sub>4</sub>) or zirconium (ZrO<sub>2</sub>) [9-11].

Releases of these radiocontaminants into the atmosphere cause external exposure due to gamma and internal exposure due to alpha, which is emitted by radon and its short-lived decay products. Therefore, it is very important to assess gamma radiation dose and alpha index as well as associated radiation hazards from natural sources [12-19]. In this

study, most of the measured samples showed concentrations exceeding the exemption limit. Exemption limit is a regulatory control determined if a source or practice activity involves radiation [20]. Table 1 tabulates the exemption levels of moderate amounts of materials without further consideration. Consequently, the purpose of this study was the investigation of the relatively high concentrations of natural radionuclide in these samples and radiological characterization, as well as the evaluation of occupational radiation exposure.

Table 1. Exempt activity concentrations and exempt activities of radionuclides

Radionuclide	Activity concentration (Bq/g)	Activity (Bq)
Ra-226	1×10 <sup>1</sup>	1×10 <sup>4</sup>
Th-232	1×10 <sup>1</sup>	1×10 <sup>4</sup>
K-40	1×10 <sup>2</sup>	1×10 <sup>6</sup>

## Materials and Methods

Forty samples of zirconium oxide, zircon sand, feldspar color-coated and clay were collected from different Egyptian ceramic factories. The samples were

\*Corresponding Author: Tel: +20 1118191414. E-mail: fawziamubarak@yahoo.com

dried at 60°C for 6-12 h to remove residual moisture. Then thoroughly mixed, weighted, filled in a polyethylene jar perfectly sealed to make them airtight and finally stored for more than 28 days before gamma spectroscopy to reach secular equilibrium between Ra-226 and its progenies. For gamma spectrometry, a high-purity germanium (HPGe) detector was used in this study. This detector has a relative efficiency of 30% and resolution full width at half maximum of 1.9 keV at 1.33 MeV (with associated electronics) connected to a multichannel analyzer and coupled with software program Genie 2000. It was shielded by 10 cm Pb thickness, 1 mm Cd, and 1 mm Cu. The main advantages of such detectors are high efficiency, high-energy resolution and very low background for the estimation of detection limits. Secondary standard sources (i.e., RGU-1, 400 µg/g of U-238 and RGTh-1, 800 µg/g of Th-232) produced by the International Atomic Energy Agency were used for the efficiency calibration of the system.

#### Measurements of Naturally Occurring Radioactive Materials

Determination of NORM was carried out by the measurements of different daughters that emit clear gamma peaks of high intensity. This was conducted by

measuring Ra-226 directly through the 186.1 keV (after subtracting the 185.7 keV line of U-235) and indirectly by measuring the Bi-214 (i.e., 609.3, 1120.2, and 1764.5 keV) and Pb-214 (i.e., 351.9 keV) photopeaks. Th-232 was determined through the measurements of Ac-228 (i.e., 911.2 keV and 968.9 keV), and Tl-208 (i.e., 583.1 keV and 2614 keV) photopeaks, as well as estimation of K-40 through the 1460.8 keV photopeak. The measuring time was 6 h for each sample and background in the present study.

#### <sup>235</sup>U Activity Concentration Evaluation

Common types of uranium isotopes are <sup>238</sup>U (i.e., with 99.27% abundance and  $T_{1/2}=4.5$  G year) and <sup>235</sup>U (i.e., with 0.72% abundance and  $T_{1/2}=0.7$  G year). Consensus value of the <sup>238</sup>U/<sup>235</sup>U ratio is 137.88 (i.e., <sup>235</sup>U/<sup>238</sup>U=0.0072). Although the HPGe detector has a good resolution, the overlapping of some photopeaks of different radionuclides occurred due to very minor energy differences between them, such as the interference between 185.7 keV (i.e., the most predominant gamma transition to measure <sup>235</sup>U with the abundance of 57.2%) and 186.2keV (i.e., the energy line of <sup>226</sup>Ra with the abundance of 3.6%) [21-25].

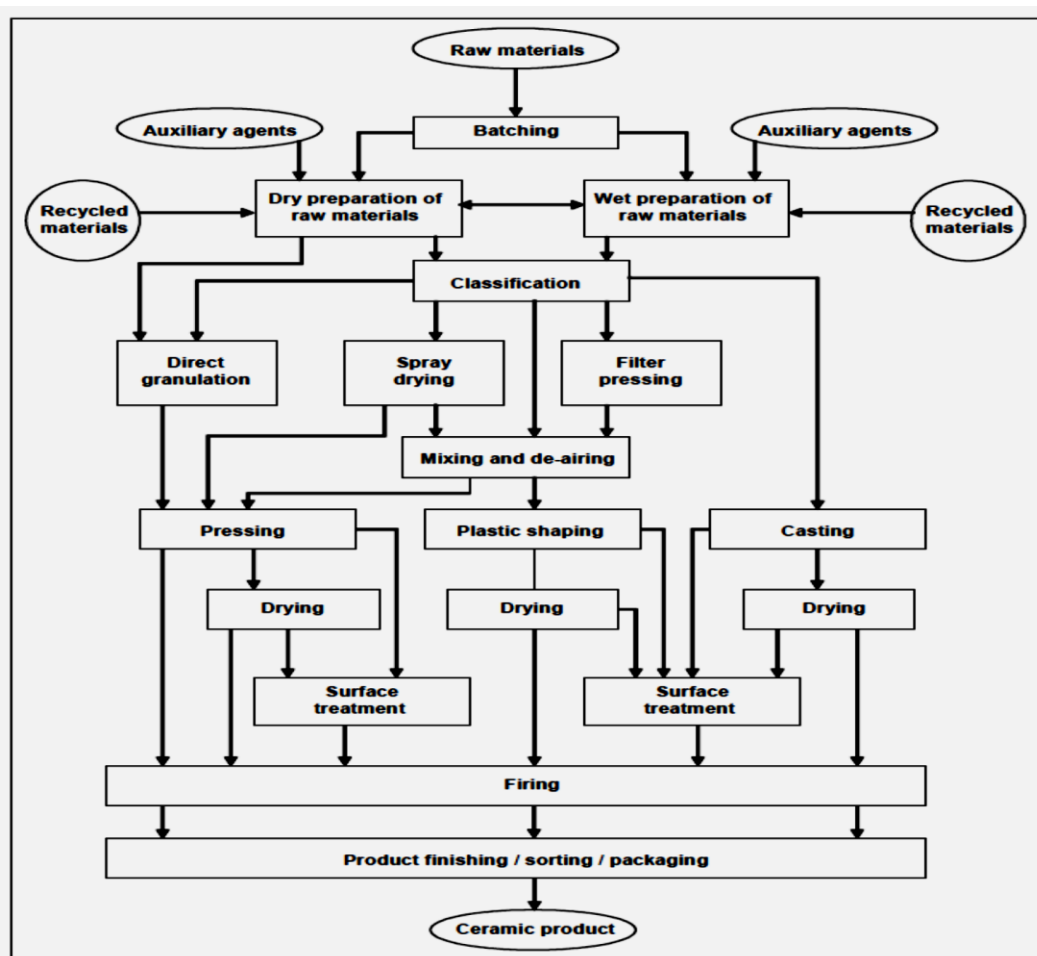


Figure 1. Schematic view of the general processing paths in ceramic manufacturing (European Commission2007)

It is more practical to calculate the activity concentration of  $^{235}\text{U}$  using 185.7 keV line due to very minor transitions of 143.76 (i.e., 10.96%), 163.33 (i.e., 5.08%), and 205.31 keV (i.e., 5.01%).  $^{235}\text{U}$  activity concentrations in different samples were mathematically evaluated using the following equation, regardless of  $^{238}\text{U}$  equilibrium status [26]:

$$\frac{C/s_{Ra}}{C/s_{U5}} = \frac{0.036A_{Ra}}{0.572A_{U5}} \quad (1)$$

Where  $C/s_{Ra}$  is counts/sec due to  $^{226}\text{Ra}$  in the 186.1 keV energy peak,  $C/s_{U5}$  is counts/sec due to  $^{235}\text{U}$  in the 185.7keV energy peak,  $A_{Ra}$  is the activity of  $^{226}\text{Ra}$  in the sample,  $A_{U5}$  is the activity of  $^{235}\text{U}$  in the sample, 0.036 is the  $^{226}\text{Ra}$  abundance, and 0.572 is the  $^{235}\text{U}$  abundance. Then, total counts at this peak can be separated as it follows:

$$C/s_{Ra} = 0.588 C/s_T \quad (2)$$

$$C/s_{U5} = 0.4117 C/s_T \quad (3)$$

$$A_{U5} = \frac{C/s_{U5}}{\varepsilon \times I_{U5} \times m} \quad (4)$$

Where  $C/s_T$  is the total counts/sec in the 186 keV energy peak,  $\varepsilon$  is its efficiency,  $I_{U5}$  is the transition of 185.7 keV energy peak (57.2%) and  $m$  is the mass of the sample (kg) [26].

### Radiological Risk Calculations

There are different techniques in ceramic manufacturing. Figure (1) shows the general production process description [27] through which workers were exposed to naturally occurring radionuclides. Most of the raw materials are in powder shape; therefore, radiological risk was due to external and internal exposure. The potential exposure pathways were through external gamma radiation and inhalation of released radon that distributed with huge quantities. In this study, external exposure was calculated using Dose Factor EXternal (DFEXT) code after converting activity concentrations from Bq/kg to Bq/m<sup>3</sup> according to the density of each material.

### Organ Doses Assessment

The DFEXT code [28] was used for the calculation of effective organ doses of  $E_T$  (Sv) from external irradiation using the equivalent dose in tissue  $T$  per unit integrated exposure,  $h_t$  (i.e., Svm<sup>3</sup>/sec Bq), activity concentration of raw material,  $A$ (Bq/m<sup>3</sup>), and  $T$  (8 hr/d × 5 d/week × 50 week/year) as the exposure time.

$$E_T = A \times T \times 3600 \text{ (sec/hr)} \times h_t \text{ (Sv)} \quad (5)$$

Weighting factors, according to ICRP-1990 recommendations used to calculate the committed dose equivalent for each organ. For the remainder tissues, 0.2 weighting factor used to calculate committed dose equivalent, i.e.  $h_{rem} = 1/5 \sum h_t$  [29]. Exposure to airborne of raw materials in ceramic factories is controlled in the workplace by the implementation of general recommendations for safety and health protection of workers during the working time recommended by the National Institute for Occupational Safety and Health [30].

Workers exposed to high radon concentrations due to that raw materials are working in closed rooms with poor ventilation. Many workers spend much of their time inside these buildings, which may result in high internal exposure to radon [19-31]. Almayahi et al. in 2014 measured the concentration of radon activity in Egyptian ceramic factories reported as 411.45 Bq/m<sup>3</sup> [32]. In another study carried out by Shoeib and Thabayneh in 2014, the mass exhalation rate was measured and obtained at 28.7 mBq/kg [33]. The annual effective dose to different organs due to radon exposure was calculated according to the forementioned concentrations.

### Internal and External Hazards Indices

A wide range of raw materials was used in the manufacturing of wall and floor tiles, as well as household ceramics sanitary ware. These raw materials pass through many processes, such as multiple stage firing process, then, mixed, cast, and finally, pressed or shaped [27]. Internal radiological risks for workers were assessed through key quantities, including internal hazard index ( $H_{in}$ ), alpha index ( $I_\alpha$ ), representative level index (RLI), indoor absorbed gamma dose rate ( $D_{in}$ ), annual effective dose ( $E_{in}$ ), and excess lifetime cancer risk (ELCR<sub>in</sub>)[9].

### Internal Hazard Indices

The internal hazard index used to calculate the exposure to naturally occurring radionuclides should be lower than unity and is obtained according to the following equation:

$$H_{in} = \frac{A_{Ra}}{185} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \quad (6)$$

Where  $A_{Ra}$ ,  $A_{Th}$ , and  $A_K$  are the activity concentrations of Ra-226, Th-232, and K-40 in Bq/kg respectively.

### Alpha Index

Alpha radiation is very dangerous and more carcinogenic than gamma radiation; therefore, it is necessary to study alpha activity in ceramic factories [34,35]. The recommended limit is 200 Bq/kg, and then, there is overexposure to radon at levels higher than this limit. Excess of alpha radiation from the radon inhalation was calculated using the following equation [36]:

$$I_\alpha = \frac{A_{Ra}}{200} \quad (7)$$

### Representative Level Index

The RLI is a hazard indicator of gamma radiation due to NORM its value should be  $\leq 1$  and it is written as follows [6]:

$$RLI = \frac{1}{150A_{Ra}} + \frac{1}{100A_{Th}} + \frac{1}{1500A_K} \quad (8)$$

### Indoor Absorbed Gamma Dose Rate

Indoor absorbed dose rate for ceramics, marble, roofing tile, and granite can be calculated according to Monte Carlo simulation with a standard room model of

4 m × 5 m × 2.8 m, thickness of the walls, floor, and ceiling, structure density of 20 cm, and density of 2350 kg/m<sup>3</sup>[18]. It can be written as it follows [1]:

$$D_{in}(\text{nGy/h}) = 0.12 A_{Ra} + 0.14 A_{Th} + 0.0096 A_K \quad (9)$$

**Annual Effective Dose**

The annual effective dose due to 2000 h annual working is calculated by multiplying the indoor absorbed dose rate by a factor of 0.7 SvGy<sup>-1</sup> as it follows [37]:

$$E_{in}(\text{mSv/y}) = 0.7 (\text{Sv/Gy}) \times 2000 (\text{h/y}) \times D_{in}(\text{nGy/h}) \times 10^{-6} \quad (10)$$

**Excess Lifetime Cancer Risk**

Excess Life time Cancer is a stochastic effect and can be calculated according to annual internal effective dose using the life expectancy (LE: i.e. standard all life time for a person with world average of 70 years), and the fatal risk factor per Sv(RF) which is equal to 0.05 for stochastic effects [14, 29] as follows:

$$ELCR_{in} = E_{in} \times LE \times RF \quad (11)$$

**Results**

Table 2 tabulates that the activity concentrations of zirconium were within the ranges of 1460-3466, 10-24, and

382-773 Bq/kg for Ra-226, U-235, and Th-232, respectively, in comparison to the world average values reported as 3000 and 600 Bq/kg for Ra-226 and Th-232 for zircon, respectively. However, for zirconia, the activity concentrations were 7000 and 300 Bq/kg for Ra-226 and Th-232 respectively [18] It can be concluded that some samples in the results of the present study had higher Th-232 concentrations. Activity concentrations of different types of clays were within the ranges of 31-626, 0.2-4.4, 32-725 and 144-507 Bq/kg for Ra-226, U-235, Th-232 and K-40 respectively.

Table 3 shows that the activity concentrations of feldspar were within the ranges of 30-54 Bq/kg for Ra-226, 0.21-0.38 for U-235, 29-54 Bq/kg for Th-232, and 441-1227 Bq/kg for K-40. Table 4 presents the activity concentrations of powdered quartz and colors. Table 5 tabulates the annual effective dose to different organs of workers due to exposure to natural radionuclides in zirconium and colors. The aforementioned values represented only external exposure that was within the permissible values. Nevertheless, the internal potential radiological risk due to the inhalation of dust was still considerable.

Table 2. Activity concentrations (Bq/kg) of imported zirconium compounds and clays

Zirconium compounds				Clays				
Sample	Ra-226	U-235	Th-232	Sample	Ra-226	U-235	Th-232	K-40
Zr-1	3462	24	624	Clay-1	31	0.2	32	217
Zr-2	2020	14	720	Clay-2	31	0.2	33	144
Zr-3	1722	12	635	Clay-3	104	0.7	175	242
Zr-4	1460	10	667	Clay-4	82	0.6	172	255
Zr-5	1685	12	511	Clay-5	54	0.4	54	217
Zr-6	2870	20	662	Clay-6	44	0.3	41	208
Zr-7	3462	24	624	Clay-7	83	0.6	130	212
Zr-8	3087	22	648	Clay-8	104	0.7	207	294
Zr-9	3425	24	745	Clay-9	72	0.5	134	149
Zr-10	3466	24	773	Clay-10	100	0.7	84	156
Zr-11	2054	14	615	Clay-11	626	4.4	725	507
Zr-12	3192	22	672	Clay-12	424	3.0	558	168
Zr-13	1520	11	382	Clay-13	452	3.2	507	201
--	--	--	--	Clay-14	483	3.4	522	222
--	--	--	--	Clay-15	485	3.4	521	198
Range	1460-3466	10-24	382-773	Range	31-626	0.2-4.4	32-725	144-507
Average ≈	2571	18	637	Average ≈	212	1.5	260	226

Table 3. Activity concentrations (Bq/kg) of feldspar

Sample	Ra-226	U-235	Th-232	K-40
Fe-1	30	0.2	31	1227
Fe-2	33	0.2	29	1121
Fe-3	54	0.4	54	721
Fe-4	41	0.3	41	802
Fe-5	31	0.2	33	441
Range	30-54	0.2-0.4	29-54	441-1227
Mean± standard deviation	38±10	0.26±0.07	38±10	862±317

Table 4. Activity concentrations (Bq/kg) of powdered quartz and colors (STDEV= standard deviation)

Powdered quartz				Colors				
Sample	Ra-226	U-235	Th-232	Sample	Ra-226	U-235	Th-232	K-40
P. qu. 1	3418	24	513	Color-1	397	2.8	105	728
P. qu. 2	5694	40	872	Color-2	420	2.9	112	766
P. qu. 3	5844	41	1065	Color-3	1005	7.0	267	1868
P. qu. 4	5844	41	969	Color-4	409	2.9	109	747
P. qu. 5	4556	32	695	--	--	--	--	--
Range	3418-5844	24-41	513-1065	Range	397-1005	2.8-7.0	105-267	728-1868
Mean± STDEV	5071±1070	35±7	823±221	Mean± STDEV	558±298	3.9±2.1	148±79	1027±560

Table 5. Annual effective doses due to exposure to zirconium and colors (mSv/y)

Organ	Zirconium			Colors			
	Ra-226	U-235	Th-232	Ra-226	U-235	Th-232	K-40
<sup>1</sup> R-Marrow	1.73E-06	1.84E-04	3.99E-06	3.75E-07	3.32E-18	9.27E-07	1.32E-02
Adrenals	1.20E-06	1.59E-04	3.48E-06	2.60E-07	2.87E-18	8.08E-07	1.50E-02
<sup>2</sup> B- Surface	1.05E-05	4.86E-04	1.66E-05	2.27E-06	8.77E-18	3.87E-06	1.34E-02
Brain	1.36E-06	1.84E-04	4.05E-06	2.94E-07	3.31E-18	9.41E-07	1.32E-02
Breast	8.41E-06	2.25E-04	6.60E-06	1.83E-06	4.05E-18	1.53E-06	1.29E-02
<sup>3</sup> G-bladder	1.15E-06	1.57E-04	3.44E-06	2.50E-07	2.83E-18	7.99E-07	1.21E-02
Esophagus	8.33E-07	1.50E-04	3.05E-06	1.81E-07	2.70E-18	7.08E-07	1.42E-02
<sup>4</sup> STWall	1.55E-06	1.74E-04	4.03E-06	3.37E-07	3.13E-18	9.36E-07	1.41E-02
<sup>5</sup> SI Wall	1.06E-06	1.56E-04	3.36E-06	2.29E-07	2.81E-18	7.81E-07	1.39E-02
<sup>6</sup> ULIWall	1.19E-06	1.61E-04	3.58E-06	2.58E-07	2.91E-18	8.31E-07	1.25E-02
<sup>7</sup> LLIWall	1.13E-06	1.61E-04	3.50E-06	2.44E-07	2.91E-18	8.13E-07	1.26E-02
Heart	1.42E-06	1.71E-04	3.87E-06	3.08E-07	3.08E-18	9.00E-07	1.28E-02
Kidneys	1.84E-06	1.78E-04	4.17E-06	3.99E-07	3.20E-18	9.68E-07	1.32E-02
Liver	1.56E-06	1.78E-04	4.11E-06	3.39E-07	3.20E-18	9.54E-07	1.31E-02
Lungs	1.86E-06	1.94E-04	4.62E-06	4.03E-07	3.50E-18	1.07E-06	1.40E-02
Ovaries	1.03E-06	1.55E-04	3.24E-06	2.24E-07	2.80E-18	7.54E-07	1.25E-02
Pancreas	9.68E-07	1.54E-04	3.28E-06	2.10E-07	2.77E-18	7.63E-07	1.20E-02
Skin	2.82E-05	2.37E-04	1.09E-05	6.11E-06	4.28E-18	2.53E-06	2.59E-02
Spleen	1.19E-06	1.79E-04	4.11E-06	2.58E-07	3.22E-18	8.31E-07	1.25E-02
Testes	1.52E-06	2.16E-04	6.01E-06	3.31E-07	3.89E-18	9.54E-07	1.32E-02
Thymus	6.50E-06	1.85E-04	4.40E-06	1.41E-06	3.33E-18	1.40E-06	1.50E-02
Thyroid	1.88E-06	1.81E-04	4.42E-06	4.08E-07	3.26E-18	1.02E-06	1.34E-02
<sup>8</sup> U- Bladder	2.31E-06	1.72E-04	3.89E-06	5.01E-07	3.10E-18	1.03E-06	1.32E-02
Uterus	1.51E-06	1.53E-04	3.28E-06	3.27E-07	2.76E-18	9.04E-07	1.29E-02
Muscle	1.00E-06	1.95E-04	5.07E-06	2.17E-07	3.52E-18	7.63E-07	1.21E-02
<sup>9</sup> H_rem	4.49E-06	1.93E-04	4.95E-06	9.75E-07	3.48E-18	1.18E-06	1.42E-02
<sup>10</sup> E	4.19E-06	1.91E-04	4.76E-06	9.09E-07	3.44E-18	1.15E-06	1.41E-02

<sup>1</sup>Red Marrow, <sup>2</sup>Bone Surface, <sup>3</sup>Gall Bladder, <sup>4</sup>Stomach Wall, <sup>5</sup>Small Intestine Wall, <sup>6</sup>Upper Large Intestine Wall, <sup>7</sup>Lower Large Intestine Wall, <sup>8</sup>Urinary Bladder, <sup>9</sup>H\_for reminder tissues and <sup>10</sup>Effective dose.

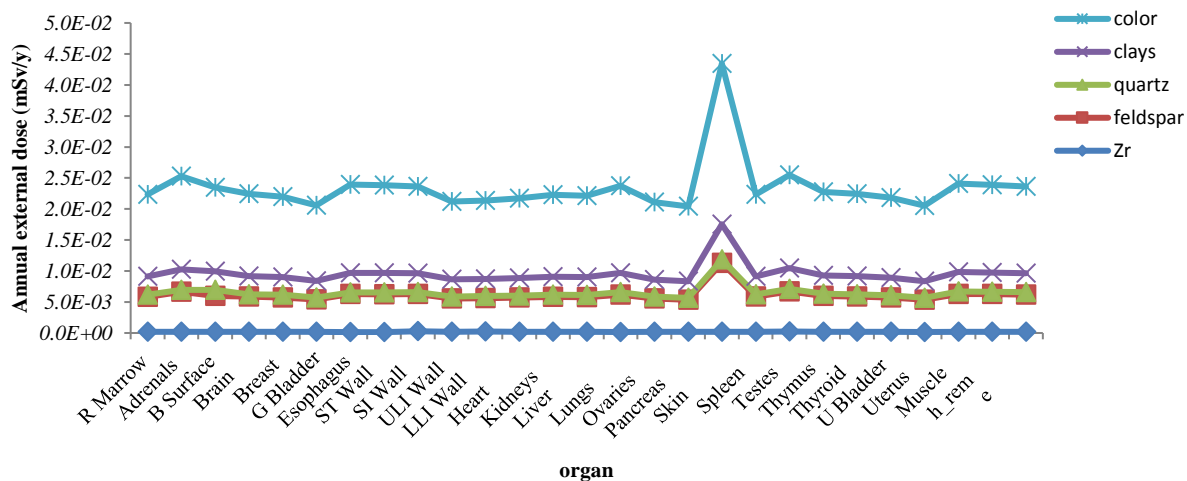


Figure 2. Total annual effective dose due to different raw materials (mSv/y)

Figure 2 depicts the total annual effective dose due to different types of raw materials in which the higher exposure is due to colors as the higher K-40 activity concentrations, which have the highest conversion dose factors. Figure 3 illustrates the summation of an external

equivalent dose to different organs due to all different raw materials. The skin appears to receive the highest external exposure (i.e., 0.044mSv/y), while pancreas receives the lowest value (i.e., 0.02mSv/y).

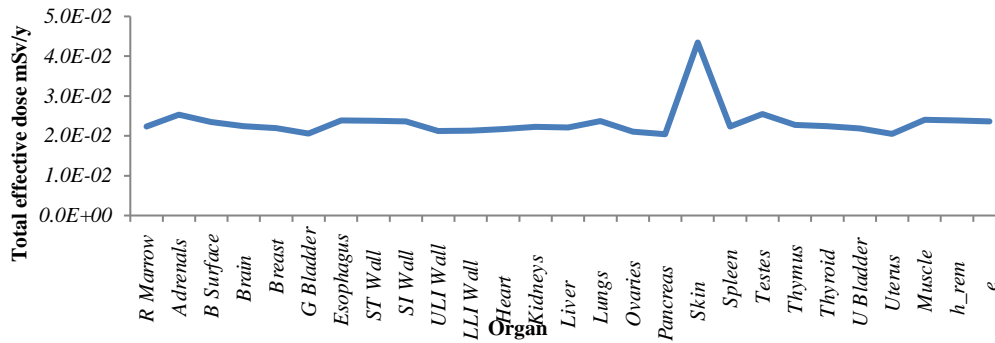


Figure 3. Summation of annual effective dose due to different raw materials (mSv/y)

Table 6. Annual effective doses due to exposure to all raw materials and radon inhalation (mSv/y)

Organ	Zirconium	Feldspar	Quartz	Clay	Color	Radon	Total
R- Marrow	1.7E-04	5.66E-03	3.67E-04	2.91E-03	1.32E-02	1.51E-06	2.23E-02
Adrenals	1.7E-04	6.45E-03	3.16E-04	3.31E-03	1.51E-02	1.30E-06	2.53E-02
B- Surface	1.8E-04	5.78E-03	9.88E-04	3.00E-03	1.35E-02	3.04E-06	2.35E-02
Brain	1.8E-04	5.69E-03	3.65E-04	2.92E-03	1.33E-02	1.50E-06	2.24E-02
Breast	1.8E-04	5.54E-03	4.62E-04	2.85E-03	1.29E-02	1.79E-06	2.20E-02
G- Bladder	2.0E-04	5.21E-03	3.12E-04	2.68E-03	1.22E-02	1.27E-06	2.06E-02
Esophagus	1.6E-04	6.10E-03	2.97E-04	3.13E-03	1.42E-02	1.24E-06	2.39E-02
STWall	1.6E-04	6.06E-03	3.46E-04	3.11E-03	1.41E-02	1.38E-06	2.38E-02
SI Wall	2.8E-04	5.99E-03	3.09E-04	3.07E-03	1.40E-02	1.28E-06	2.36E-02
ULIWall	1.84E-04	5.38E-03	3.21E-04	2.76E-03	1.26E-02	1.31E-06	2.12E-02
L LIWall	2.28E-04	5.40E-03	3.21E-04	2.77E-03	1.26E-02	1.32E-06	2.13E-02
Heart	1.91E-04	5.50E-03	3.40E-04	2.82E-03	1.28E-02	1.38E-06	2.17E-02
Kidneys	1.88E-04	5.65E-03	3.54E-04	2.90E-03	1.32E-02	1.43E-06	2.23E-02
Liver	1.77E-04	5.61E-03	3.54E-04	2.88E-03	1.31E-02	1.43E-06	2.21E-02
Lungs	1.57E-04	6.03E-03	3.87E-04	3.10E-03	1.41E-02	1.55E-06	2.38E-02
Ovaries	2.05E-04	5.35E-03	3.08E-04	2.74E-03	1.25E-02	1.25E-06	2.11E-02
Pancreas	2.02E-04	5.17E-03	3.05E-04	2.65E-03	1.21E-02	1.24E-06	2.04E-02
Skin	1.99E-04	1.11E-02	5.31E-04	5.70E-03	2.59E-02	1.90E-06	4.35E-02
Spleen	1.84E-04	5.66E-03	3.56E-04	2.91E-03	1.32E-02	1.42E-06	2.23E-02
Testes	2.28E-04	6.45E-03	4.40E-04	3.31E-03	1.51E-02	1.73E-06	2.55E-02
Thymus	1.91E-04	5.77E-03	3.69E-04	2.96E-03	1.35E-02	1.48E-06	2.28E-02
Thyroid	1.88E-04	5.69E-03	3.62E-04	2.92E-03	1.33E-02	1.44E-06	2.24E-02
U- Bladder	1.77E-04	5.54E-03	3.42E-04	2.84E-03	1.29E-02	1.37E-06	2.18E-02
Uterus	1.57E-04	5.21E-03	3.04E-04	2.68E-03	1.22E-02	1.25E-06	2.05E-02
Muscle	2.05E-04	6.10E-03	3.95E-04	3.13E-03	1.42E-02	1.57E-06	2.41E-02
H_rem	2.02E-04	6.06E-03	3.90E-04	3.11E-03	1.41E-02	1.55E-06	2.39E-02
E	1.99E-04	5.99E-03	3.84E-04	3.08E-03	1.40E-02	1.53E-06	2.36E-02
R- Marrow	1.7E-04	5.66E-03	3.67E-04	2.91E-03	1.32E-02	1.51E-06	2.23E-02
Adrenals	1.7E-04	6.45E-03	3.16E-04	3.31E-03	1.51E-02	1.30E-06	2.53E-02
B- Surface	1.8E-04	5.78E-03	9.88E-04	3.00E-03	1.35E-02	3.04E-06	2.35E-02
Brain	1.8E-04	5.69E-03	3.65E-04	2.92E-03	1.33E-02	1.50E-06	2.24E-02
Breast	1.8E-04	5.54E-03	4.62E-04	2.85E-03	1.29E-02	1.79E-06	2.20E-02
G- Bladder	2.0E-04	5.21E-03	3.12E-04	2.68E-03	1.22E-02	1.27E-06	2.06E-02
Esophagus	1.6E-04	6.10E-03	2.97E-04	3.13E-03	1.42E-02	1.24E-06	2.39E-02
STWall	1.6E-04	6.06E-03	3.46E-04	3.11E-03	1.41E-02	1.38E-06	2.38E-02
SI Wall	2.8E-04	5.99E-03	3.09E-04	3.07E-03	1.40E-02	1.28E-06	2.36E-02
ULIWall	1.84E-04	5.38E-03	3.21E-04	2.76E-03	1.26E-02	1.31E-06	2.12E-02
L LIWall	2.28E-04	5.40E-03	3.21E-04	2.77E-03	1.26E-02	1.32E-06	2.13E-02
Heart	1.91E-04	5.50E-03	3.40E-04	2.82E-03	1.28E-02	1.38E-06	2.17E-02
Kidneys	1.88E-04	5.65E-03	3.54E-04	2.90E-03	1.32E-02	1.43E-06	2.23E-02
Liver	1.77E-04	5.61E-03	3.54E-04	2.88E-03	1.31E-02	1.43E-06	2.21E-02
Lungs	1.57E-04	6.03E-03	3.87E-04	3.10E-03	1.41E-02	1.55E-06	2.38E-02
Ovaries	2.05E-04	5.35E-03	3.08E-04	2.74E-03	1.25E-02	1.25E-06	2.11E-02
Pancreas	2.02E-04	5.17E-03	3.05E-04	2.65E-03	1.21E-02	1.24E-06	2.04E-02
Skin	1.99E-04	1.11E-02	5.31E-04	5.70E-03	2.59E-02	1.90E-06	4.35E-02
Spleen	1.84E-04	5.66E-03	3.56E-04	2.91E-03	1.32E-02	1.42E-06	2.23E-02
Testes	2.28E-04	6.45E-03	4.40E-04	3.31E-03	1.51E-02	1.73E-06	2.55E-02
Thymus	1.91E-04	5.77E-03	3.69E-04	2.96E-03	1.35E-02	1.48E-06	2.28E-02
Thyroid	1.88E-04	5.69E-03	3.62E-04	2.92E-03	1.33E-02	1.44E-06	2.24E-02
U- Bladder	1.77E-04	5.54E-03	3.42E-04	2.84E-03	1.29E-02	1.37E-06	2.18E-02
Uterus	1.57E-04	5.21E-03	3.04E-04	2.68E-03	1.22E-02	1.25E-06	2.05E-02
Muscle	2.05E-04	6.10E-03	3.95E-04	3.13E-03	1.42E-02	1.57E-06	2.41E-02
H_rem	2.02E-04	6.06E-03	3.90E-04	3.11E-03	1.41E-02	1.55E-06	2.39E-02
E	1.99E-04	5.99E-03	3.84E-04	3.08E-03	1.40E-02	1.53E-06	2.36E-02

Table 7. Radiological indices due to stockpiles of raw materials inside storage areas

Materials	D <sub>in</sub> (n Gy/hr)	D <sub>in</sub> (m Gy/y)	E <sub>in</sub> (m Sv/y)	ELCR <sub>in</sub>	H <sub>in</sub>	RLI	I <sub>α</sub>
Zirconium	397.70	0.80	0.56	0.195	16.36	1.83E-05	12.86
Feldspar	18.16	0.04	0.03	0.009	0.53	4.39E-04	0.19
P. quartz	723.74	1.45	1.01	0.355	30.59	1.35E-05	25.36
Color	71.26	0.14	0.10	0.035	3.80	6.55E-05	2.79
Clay	97.54	0.20	0.14	0.048	2.46	8.02E-05	1.21
Summation	1308.39	2.62	1.83	0.641	53.74	6.17E-04	42.40

D<sub>in</sub>: Indoor absorbed gamma dose rateELCR<sub>in</sub>: Excess lifetime cancer risk

RLI: Representative level index

E<sub>in</sub>: Annual effective doseH<sub>in</sub>: Internal hazard indexI<sub>α</sub>: Alpha index

Table 6 shows annual equivalent and effective doses due to exposure to naturally occurring radionuclides and radon inhalation (mSv/y). Table 7 tabulates the total annual external dose (i.e., 2.62 m Gy/y), effective dose (i.e., 1.83 m Sv/y), ELCR (i.e., 0.641), and alpha index (i.e., 42.4) due to all raw materials inside storage areas. Internal exposure due to dust inhalation should be carefully and specifically taken into consideration. The internal hazard index should be  $\leq 1$ , and the results of this study showed a value of 53.74, which may cause potential radiological hazards. In the present study, the RLI was reported as 0.00062.

## Discussion

Maximum activity concentrations were reported as 5844, 1065, and 41 Bq/kg for Ra-226, Th-232, and U-235 in powdered quartz, respectively. However, the highest activity concentration of K-40 was 1868 Bq/kg in color. These concentrations were observed to be exceeding the exemption limit. The skin received the highest external exposure (i.e., 0.044 mSv/y), while pancreas received the lowest value (i.e., 0.02 mSv/y). Internal hazard indices due to all raw materials and alpha index were 53.74 and 42.4, respectively. The aforementioned higher values caused higher exposure and potential radiological hazards, compared to the recommended values. For the whole body, the total annual external dose and total annual effective dose were 2.62 mGy/y and 1.83 mSv/y, respectively.

## Conclusion

High concentrations of some raw materials (especially zirconium compounds) in addition to the activities of their whole masses of shipments (multiple tons) were observed to be exceeding the allowed activity limits and then led to overdoses due to external and internal exposure. Due to the associated high doses, specific regulations are necessary to be applied in the ceramic industry in Egypt. In this study, it is recommended to limit the working time to 8 h as a daily work shift during 5 days of workweek over 50 weeks per year. These limitations help to prevent or greatly reduce the risks of eye, skin, and respiratory organs.

## References

1. European Commission. Radiological protection principles concerning the natural radioactivity of building materials. *Radiat. Prot.* 1999;112(16):6-16.
2. Xhixha G, Ahmeti A, Bezzon GP, Bitri M, Brogini C, Buso GP, et al. First characterisation of natural radioactivity in building materials manufactured in Albania. *Radiation protection dosimetry.* 2013;155(2):217-23.
3. Attia TE, Shendi EH, Shehata MA. Assessment of natural and artificial radioactivity levels and radiation hazards and their relation to heavy metals in the industrial area of Port Said City, Egypt. *Journal of Earth Science & Climatic Change.* 2014;5(4):1-11.
4. Issa SA, Alaseri SM. Determination of Natural Radioactivity and Associated Radiological Risk in Building Materials Used in Tabuk Area, Saudi Arabia. *Int. J. Sci. Adv. Technol.* 2015;82:45-62.
5. Wadi IA, Dirar M, Elhassan A, Abdalla WA. Study of Natural Radioactivity for Some Building Materials Used in Al Kharj Area. *inter. J. of Math. & Phys. Sci. Research.* 2015;3 (1), 94-104.
6. Raghu Y, Harikrishnan N, Chandrasekaran A, Ravisankar R. Assessment of natural radioactivity and associated radiation hazards in some building materials used in Kilpenathur, Tiruvannamalai Dist, Tamilnadu, India. *InAIP Conference Proceedings.* 2015; 1675(1):020047.
7. Hofmann J, Leicht R, Wingender HJ, Wörner J. Natural radionuclide concentrations in materials processed in the chemical industry and the related radiological impact. Office for Official Publications of the European Communities; 2000.
8. Lust M, Realo E. Assessment of natural radiation exposure from building materials in Estonia. *Proceedings of the Estonian Academy of Sciences.* 2012;61(2).107-12.
9. Janković MM, Rajačić M, Rakic TM, Todorović D. Natural radioactivity in imported ceramic tiles used in Serbia. *Processing and Application of Ceramics.* 2013;7(3):123-7.
10. FATHI VA, Amidi J, Hafezi S. Natural radioactivity concentration in raw materials used for manufacturing refractory products. 2007;4(4):201-4.
11. Saridag S, Tak O, Alniacik G. Basic properties and types of zirconia: An overview. *World Journal of Stomatology.* 2013;2(3):40-7.
12. Asaduzzaman K, Khandaker MU, Amin YM, Bradley DA. Natural radioactivity levels and radiological assessment of decorative building materials in Bangladesh. *Indoor and Built Environment.* 2016;25(3):541-50.

13. AamidalddinSQ, AlzahraniJH, AamoudyZM, Fakeha AA, Al-Habeaddi HHM, Ibraheim NM. Study of Natural Radionuclides and its Radiation Hazard Index in Building Materials Used in Saudi Arabia. *Life Science Journal*. 2015;12 (2).
14. Shittu HO, Olarinoye IO, Baba-Kutigi AN, Olukotun SF, OjoEO, Egga A. Determination of the Radiological Risk Associated with Naturally Occurring Radioactive Materials (NORM) at Selected Quarry Sites in Abuja FCT, Nigeria: Using Gamma-Ray Spectroscopy. *world*. 2015;2:3.
15. Uosif MA. Estimation of radiological hazards of some Egyptian building materials due to natural radioactivity. *International Journal of u-and e-Service, Science and Technology*. 2014;7(2):63-76.
16. Salih I, Ali S, Eisa S, Idriss H. Radiation exposure of workers in storage areas for building materials. *Journal of Taibah University for Science*. 2014;8(4):394-400.
17. International Commission on Radiological Protection. Protection Against Radon-222 at Home and at Work: A Report of a Task Group of the International Commission on Radiological Protection Adopted by the Commission in September 1993. Pergamon Press; 1994.
18. United Nations Scientific Committee on the Effects of Atomic Radiation. Sources and Effects of Ionizing Radiation. 2010. United Nations, New York. Annex B: Exposures from Natural Radiation Sources and Annex D: Medical Radiation Exposures. 2010;1.
19. ICRP .Radiation Protection and Safety of Radiation Sources, International Basic Safety Standards, and General Safety Requirements ICRP, No. GSR Part 3. 2011;3:65-90.
20. ICRP. The Recommendations of the International Commission on Radiological Protection. ICRP Publication 103, Annals of the ICRP (37), Annex B. Quantities Used in Radiological Protection. 2007.
21. Condon DJ, McLean N, Noble SR, Bowring SA. Isotopic composition ( $^{238}\text{U}/^{235}\text{U}$ ) of some commonly used uranium reference materials. *Geochimica et Cosmochimica Acta*. 2010 ;74(24):7127-43.
22. Richter S, Alonso A, De Bolle W, Wellum R, Taylor PD. Isotopic "fingerprints" for natural uranium ore samples. *International Journal of Mass Spectrometry*. 1999;193(1):9-14.
23. Brennecke GA, Borg LE, Hutcheon ID, Sharp MA, Anbar AD. Natural variations in uranium isotope ratios of uranium ore concentrates: Understanding the  $^{238}\text{U}/^{235}\text{U}$  fractionation mechanism. *Earth and Planetary Science Letters*. 2010;291(1-4):228-33.
24. Mathew K, Mason P, Voeks A, Narayanan U. Uranium isotope abundance ratios in natural uranium metal certified reference material 112-A. *International Journal of Mass Spectrometry*. 2012;315:8-14.
25. Fujikawa Y, Shizuma K, Ikeda E, Baba T, Yoshimoto T, Fukui M, et al. Uranium and plutonium isotope ratio measurement as a tool for environmental monitoring-experiences in Osaka, Gifu and Hiroshima, Japan. *Journal of Nuclear Science and Technology*. 2002;39(3):564-7.
26. EbaidYY. Use of gamma-ray spectrometry for uranium isotopic analysis in environmental samples. *Rom. Journ. Phys*. 2010;55(1-2):69-74.
27. European Commission (EUC).Reference Document on Best Available Techniques in the Ceramic Manufacturing Industry. 2007.
28. Eckerman KF, Ryman JC.External Exposure to Radionuclides in Air, Water, and Soil. Federal Guidance Report No. 12, EPA Report 402-R-93-081. 1993;12.
29. International Commission on Radiological Protection. The 1990 Recommendations of the Commission. ICRP Publication 60, Annals of the ICRP, 21(1-3). 1990; (3): 295-302.
30. National Institute for Occupational Safety and Health. Occupational Exposure to Refractory Ceramic Fibers. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health; 2006.
31. International Atomic Energy Agency. Assessing the need for radiation protection measures in work involving minerals and raw materials. IAEA; 2006.
32. Almayahi BA, Alsaedi AK, Alasadi AH, Ali AS, Hussein RO,et al. Ceramic Rn222 exhalation rates from different countries .*International Journal of Scientific & Engineering Research*. 2014;5(1).
33. Shoeib MY, Thabayneh KM. Assessment of natural radiation exposure and radon exhalation rate in various samples of Egyptian building materials. *Journal of Radiation Research and Applied Sciences*. 2014;7(2):174-81.
34. Ghosh D, Deb A, Bera S, Sengupta R, Patra KK. Assessment of alpha activity of building materials commonly used in West Bengal, India. *Journal of environmental radioactivity*. 2008 ;99(2):316-21.
35. Stoulos S, Manolopoulou M, Papastefanou C. Assessment of natural radiation exposure and radon exhalation from building materials in Greece. *Journal of Environmental Radioactivity*. 2003 ;69(3):225-40.
36. Msila X, Labuschagne F, Barnard W, Billing DG. Radioactive nuclides in phosphogypsum from the lowveld region of South Africa. *South African Journal of Science*. 2016; 112(1-2):1-5.
37. Eissa MF, Mostafa RM, Shahin F, Hassan KF, Saleh ZA, Yahia A. Natural radioactivity for some Egyptian building material. 2008.