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Natural Radioactivity in Ceramic Materials

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ABSTRACT

Ceramics are one of the most important types of the industrial building materials. The raw materials of the ceramic are made of a mixture of clay, feldspar, silica, talc kaolin minerals together with zirconium silicates (ZrSiO4).The ceramic raw materials and the final products contain naturally occurring radionuclide mainly U-238 and, Th-232 series, and the radioactive isotope of potassium K-40. Six raw ceramic samples were obtained from the Aracemco Company at Egypt together with a floor tile sample (final product) for measuring radioactive concentration levels. , The activity of the naturally U-238, Th-232, and K-40 were determined as (Bq/kg) using gamma spectroscopy (Hyperactive pure germanium detector). Concentration of U and Th were determined in (ppm) using spectrophotometer technique by Arzenazo 111 and Piridy l-Azo -Resercinol (PAR) indicators. Sequential extraction tests were carried out in order to determine the quantity of the radionuclide associated with various fractions as exchangeable, carbonate, acid soluble and in the residue. The results evaluated were compared to the associated activity indices (AI) that were defined by former USSR and West Germany.

Key Words: Ceramics, natural occurring radionuclide, sequential extraction,

INTRODUCTION

All building materials contain various amounts of natural radioactive nuclides. Materials derived from rock, and soil contain mainly natural radionuclide of the uranium (U-238), thorium (Th-232) series, and the radioactive isotope of potassium (K-40). Ceramics are one of the most important types of the building (decorative) materials. Materials commonly used in the chemical industry containing a remarkable content of naturally occurring radio nuclides are found in the earth crust .They have been widely discussed in a variety of reports and papers[1,2] . Survey of the natural radioactivity content in building materials has been widely discussed in several countries [3, 4].

Soils containing naturally occurring radioactive material such as UO2, ThO2, and ZrO2 are used in the manufacturing of the glass and ceramic products [5]. Common ceramics are made from a mixture of clay, feldspars, silica, talc, and kaolin. Zircon sand (ZrSiO4) is added to materials used to make glaze, due to the lanthanum series shine property [4] .Uranium is easier to be penetrated and trapped in the Lattice of zircon crystal. Ceramic products are covered with a glassy coating called glaze to prevent the components of ceramics from absorbing liquids, and makes it smoother and easier to clean .The general radiation level was higher in an area lined with glazed ceramic tile than in other areas in ceramic components [6].

The manufacture of different kinds of the ceramic tiles causes a potential radiation risk due to the radiation exposure of the workers to the naturally occurring radioactive materials such as thorium and uranium, which are present in the raw materials of the ceramics [7, 8]. Concentrations of the natural radionuclide mainly, U-232 and Th-232 series and K-40 radioactive isotope in the building materials are very important to measure the safety of the public. Leaching of the radioactive and stable elements

from the ceramic components is principally governed by the presence of various physical-chemical forms of the radionuclide and the stable elements at the ceramic fraction materials [9, 10].

In practice, a different radiological consideration seams to apply to the use of natural materials and by products as building materials[11].Controls on the radioactivity of the building materials can be based on within the European Union (EU), the radiation protection point of view should take into account the doses exceeding $1mSva^{-1}$ and the controls should base on a dose range of ($0.3\text{-}1.0\ mSva^{-1}$). High individual doses exceeding one $mSv\ a^{-1}$ should be restricted.

This study was concerned with the natural radioactivity contained in different raw ceramic materials beside the final product (ceramic tile), and how to limit the radiation exposure of both the workers and the inhabitants of dwellings built with such materials. It should be as low as reasonably achievable.

EXPERIMENTAL METHODS

Seven samples were obtained from the ARACEMCO Company in Egypt. Five samples are raw ceramic materials used for the manufacture of common ceramic, including, zirconium silicates, clay, and feldspar, kaolin, and talc minerals. The sixth sample is a mixture of the above raw minerals after several chemical treatments at the industrial processes (glaze paste). The seventh sample is a ceramic tile material (final product).

The radioactivity measurements were performed by a high-resolution gamma spectroscopic system employing a high purity germanium crystal (HPGe) coupled with multichannel analyzer (TENNELEC); it is a p-type co-axial detector. Samples were ground to obtain a powder with an average particle size. Plastic gars (300ml) were utilized in order to obtain standard volume and geometry for all samples. After filled by soil, each jar was perfectly sealed and left for four weeks to allow secular equilibrium to be reached between both Ra-226 and Th-232 and their progeny .Radioactivity concentration of each sample was measured for about 20 hours .The background activity was also measured. Sample preparation and both of energy and efficiency calibration were mentioned in other recent publications [12].

Natural Ra-226 , Th-232 radioactive series, and the radioactive isotope K-40 concentration levels have been determined .Among members of each of the natural radioactive chains , an isotope which emit clear peaks of high intensity has been selected .The activity of Bi-214 at (609 kev) was assumed to represent the Ra-226 series. While the activity of Ac-228 at (911 kev) was assumed to represent Th-232 series .K-40 has only one clear peak at (1460 kev).

Chemical Analyses:

The major elements (Si, Al, and Fe) were determined as oxides using a spectrophotometer. 0.05g of the air-dried solid samples was fused in 5ml (30%) NaOH aqueous solution at 500^0 C for 10 minutes. The residue was dissolved in 10 ml 1:1 HCl, then the solution completed to 100ml with distilled water. Concentrations of the dissolved silicon, aluminum, and iron in aqueous solution were chemically analyzed using spectrophotometer instrument. SiO2 concentration was determined using molybdate method (13); Al_2O_3 was determined using ferron indicator [13], while Fe_2O_3 was determined using 2, 2' dipyridyl indicator [13]. Another 0.05 g of the solid sample was digested with 0.5 ml perchloric and 5ml hydrofluoric acids on sand bath. The residue was dissolved in 10 ml of 1:1 HCl aqueous solution then the solution was completed to 100 ml by distilled water .In this concern the concentrations of the dissolved uranium and thorium were measured using both Pyridyl-azo-resorcinol (PAR), and Arsenazo III indicators respectively [14] .

Sequential extraction consists of a multistep treatment of the samples under investigation using chemicals of increasing potential for dissolving certain mineral groups. The approach assumes that the chemical reactions proceed with a high selectivity and without re-distribution of the dissolved species

[15] .In the present study both of the zirconium silicate **(sample 1),** and the ceramic floor tile **(sample 7)** were selected for this treatment. Zr –silicate is the most important constituent of the glaze paste that is coating all the final ceramic products. In addition, this material has a higher radiation level than other ceramic materials and causes an external radiation exposure for the workers in such factories.

Four sequential leaching steps were carried out twice using solid to liquid ratio 1: 10 g/ml, where 10gm of the sample were mixed with 100 ml of the four reagents that are used in the sequential extraction tests. From each step of analysis U and Th, percentages released were determined [9, 10, and 16]. The sequential steps are shown in **table 1.**

TABLE 1: Summary of the Sequential Leaching Tests

Phase	**Reagents**	**Time (hours)**
1. exchangeable	$H_2O/MgCl_2$ 0.4 mol/L, pH 4.5	1
2. Carbonates	Ammonium acetate 1.0 mol / L, 25% Acetic acid, pH 4.	2
3. Oxides (Fe/Mn) & acid soluble	Hydroxylamine hydrochloride 0.04mol/L, Acetic acid 25%, pH 2.	4
4. Residue	HNO_3 / HCl/HF/$HClO_4$ + NaOH fusion at 400^{o}C.	0.25

RESULTS AND DISCUSSIONS

Table 2 shows the specific gamma activities in (Bq/Kg) of Ra-226 series, and Th-232 series and the radioactive isotope of potassium (K-40), for the samples of raw ceramic materials and the final product of the ceramic (floor tile). It is clear that zirconium silicate ($ZrSiO_4$) sample has the highest concentrations: 4336 Bq/kg for U-238, 787 Bq/kg for Th-232, while it is free from K-40. This is in a good agreement with that reported by Ibrahim et al (17) .They found that $ZrSiO_4$ samples have the highest concentrations for Ra-226 (2169-3389) and for Th-232 (429-625) Bq/kg, and it was free from K-40. It is obvious that the radioactivity present in ceramic tiles is mostly from zircon used in glaze, which varies due to different purity and formula recipe.

All other samples showed a considerable natural radioactivity concentrations, Ra-226 concentrations were 178, 112, 91, 70, 42, 9 Bq/kg, for the glaze-paste material, kaolonite, clay, ceramic floor tile, feldspar, and talc minerals respectively; while Th-232 concentrations were125, 102, 80, 60, 38, and 9 Bq/kg for the kaolonite, clay, ceramic floor tile, glaze paste, feldspar, and talc. The K-40 concentrations were 1017, 707, 580, 475 and 447 Bq/kg for the feldspar, clay, kaolinite, glaze paste, ceramic floor tile, kaolonite, and glaze paste respectively. These results were related to the average concentrations of Ra-226, Th-232 series and the K-40 that observed by rocks, and soils at the earth crust from which the building materials were derived [8].

In this work, the level of natural radioactivity in ceramic tiles, as well as in ceramic raw materials were in the same range of the values reported for most commonly used building materials in Italy [18].

The radioactivity concentrations of Ra-226, Th-232, and K-40 in Bq/kg were converted into their corresponding concentrations in g/kg by theoretical calculations [18] .Then the concentrations resulted from the chemical analysis in (g/kg) were compared by those resulted from theoretical calculations .The results shown in **table 3** are found in a good agreement with each other.

Chemical Analysis:

Table 4 shows the total concentrations of the stable oxides of **Si, Al, Fe** and the concentrations of radioactive **Ra and Th** elements in the raw ceramic materials and the final products (floor tile) samples. The mobility of Ra and Th in the ceramic samples is greatly depending on the physico-chemical forms of the solid fractions of the samples. Chemical analysis of the raw ceramic materials

showed that **SiO_2, Al_2O_3, and Fe_2O_3** concentrations are ranging from (**45-71%), (9-15 %), (3.59-16.9 %) respectively** .These results showed that the total percentage of the measured mineral oxides is less than one hundred percent due to the lack of other minerals which are not measured . **Zr – silicate** sample has the highest percentage of Ra and Th. **The glaze -paste**, and the **ceramic floor tile** showed a considerable percentage of Ra and Th while clay, feldspar, kaolin, and talc samples showed the minimum detectable percentage of Ra, with little increase in Th percentage.

Table2: The specific radioactivity of the raw ceramic and the ceramic floor tile samples in Bq/kg

Sample	**The specific radioactivity (Bq/kg)**		
	Ra-226	**Th-232**	**K-40**
1. Zirconium silicate	4336	787	-----
2. Clay	91	102	707
3. Feldspar	42	38	1017
4. Kaolinite	112	125	475
5. Talc	9	9	-----
6. Glaze – paste	178	60	447
7. Ceramic floor tile	70	80	580

Table 3: Experimental and theoretical concentrations of U-238, Th-232, and K- 40 in the ceramic samples.

U-238	Concentrations (g/kg) × 10^{-2}				
	Ra-226		Th-232		K-40
	Exp.	Theo.	Exp.	Theo.	Theoretical
1. Zirconium Silicate	30	35	17.6	19.3	--------
2. Clay	0.52	0.73	2.0	2.5	0.27
3. Feldspar	0.22	0.34	1.02	0.93	0.39
4. Kaolinite	0.89	0.90	2.7	3.1	0.18
5. Talc	0.02	0.07	0.18	0.22	------
6. Glaze–paste	1.7	1.43	1.2	1.5	0.17
7. Ceramic floor tile	0.71	0.56	1.77	2.0	0.22

Table 4: Si, Al, Fe, U, and Th concentrations (% by weight) of all raw ceramic materials and the final product under investigation

Sample	**Concentrations (% by weight)**				
	SiO_2	**Al_2O_3**	**Fe_2O_3**	**Ra**	**Th**
1. Zirconium silicate	68.2	13	3.59	3.0	1.76
2. Clay	52	15	6.79	0.052	0.20
3. Feldspar	57	12.4	16.9	0.022	0.102
4. Kaolinite	45	9	4.23	0.089	0.27
5. Talc	67.8	8.6	----	0.02	0.018
6. Glaze – paste	58	11	----	0.17	0.12
7. Ceramic floor tile	71	12	7.96	0.071	0.177

Selective Sequential Extraction Tests:

The sequential extractions tests were carried out on the two selected samples (zirconium silicate, and ceramic floor tile), to compare between the Ra and Th, concentrations of **sample 1** and **sample7** released in the sequential extraction steps. **Table .5** shows the concentration percentages of thorium and uranium released in different sequential steps (exchangeable, carbonate, iron oxide, & acid soluble fractions).

From **table.5** it is obvious that the **Zr-silicate** sample released both of uranium and thorium in the four sequential steps .About 45% of radium was found in the residue, and 25% of Ra released in the carbonate fraction. In addition, about 66% of thorium was found in the residue, and 18% of **Th** released in the iron oxide & acid soluble fraction.

On the other hand, the **floor tile** sample also released both of **Ra** and of **Th,** in the four sequential steps. About 35% of Ra was found in the residue, and 32% released in the carbonate fraction .But, about 45% of Thorium was found in the residue and 25% released in the iron oxide & acid soluble. This is certainly, because Th is being a naturally occurring radionuclide associated to the relatively insoluble mineral phase like alumna silicates. The interpretation of the results explained that most of the radium is attached to carbonate fractions, while most of the thorium is attached to iron oxide & acid soluble .The highest concentrations of both radium and thorium are present in the residue; it is noticeable that the thorium concentrations are higher than those of the radium. These phenomena explained by that both of radium and thorium are easily penetrated and trapped inside the lattice of zircon crystal [(4)].

Table 5: Radium and Thorium % released in different sequential extraction tests

Fractions	Zr-silicate		Ceramic tile sample	
	Ra%	Th%	U%	Th%
1-Exchangeable	12	8	10	12
2-Carbonate	25	9	32	18
3-Oxide (Fe/Mn) & Acid soluble	18	17	23	25
4-Residue	45	66	35	45

CONCLUSIONS

All samples of raw ceramic materials and the final product showed considerable natural radioactivity concentrations of **Ra-226** and **Th-232** series beside the radioactive isotope **K-40. $ZrSiO_4$** sample has the highest concentrations for U-238 and for Th-232, and it was free from K-40. It is obvious that the radioactivity present in ceramic tiles is mostly from zircon used in glaze, which varies due to different purity and formula recipe. These results lead to suggest paying more attention on zircon related process. In addition, controls should be restricted at the zirconium silicate materials.

Sequential extraction analyses used in order to identify **Ra** and **Th** concentrations associated with different fractions. **Ra** was concentrated in the residue and in the carbonate fractions. **Th** was concentrated in the residue and in the iron oxide & acid soluble fractions.

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