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Natural radioactivity concentration in raw materials used for manufacturing refractory products

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Background: Some Particular areas contain natural radionuclide at levels much higher than those usually present in earth's crust. The radiological impact of the use of zirconium ore in zirconium industry is due to internal exposure of the lung by alpha particles and external exposure of the body by the gamma rays. The result of gamma spectrometry measurement of the concentrations of the natural radionuclide in zirconium industry is described. ***Materials and Methods:*** Gamma spectrometry system with a shielded high pure germanium (HPGe) detector connected to multi channel analyzer (MCA) was used to determine concentrations of natural radionuclide in about 45 samples of imported zirconium minerals, tiles, stone ware and waste sludge's of Iranian ceramic industry. ***Results:*** The ^{238}U concentration in the samples, ranging from 3000 to 10000 Bq Kg^{-1}, is higher than the concentration of both ^{232}Th (500-1800 Bq Kg^{-1}), and ^{40}K (50-800 Bq Kg^{-1}). The measured specific activities in the mineral showed that specific activity of baddeleyite is higher than that of zircon. The results of ceramic tiles show that the tiles usually contain small amount of zirconium compound. ***Conclusion:*** Due to relatively high concentration level of uranium in imported zirconium samples, specific regulations is necessary for zirconium compound used in ceramic industry. **Iran. J. Radiat. Res., 2007; 4 (4): 201-204**

Keywords: *Natural radioactivity, ceramic industry, gamma spectrometry, zirconium mineral.*

INTRODUCTION

Many materials that are usually found in the earth's crust contain small but measurable amount of naturally occurring radioactivity (NORM). Some particular ores contain natural radionuclide at levels much higher those usually present in earth's crust; and are also subject to radioisotope enrichment, during technological process, known as technologically enhanced natural radioactivity (TENORM). The term TENORM was proposed to distinguish the NORM from that enhanced by technological process. Typical concentrations of ^{238}U and ^{232}Th in the earth's crust and in various natural materials are compared in table 1 [1-3].

The investigations of zirconium ores as sources of TENORM began in the late 1970s, and early 1980s [4, 5]. These works highlighted the relatively high concentrations of natural radionuclide in zircon ores. Zirconium silicate ($ZrSiO_4$) is the most important compounds obtained from zircon sand; baddeleyite is a natural form of zirconium (ZrO_2). The most important applications of zircon sands are as refractories, foundry sands and ceramic opacifiers. At present, South Africa, Ukraine, India, Brazil and China are the largest exporters of zirconium materials [6].

In Iran, zirconium minerals are widely used in ceramic industry. This sector absorbed about 700 tons (1999-2001) of zircon, principally for opacifier. Iran imports zirconium sands from South Africa, Italy, Ukraine, and to lesser extent, from Germany and Belgium. Radiation dose limits for exposure of Iranian workers is 100 mSv in a period of 5 consecutive years, with a maximum dose of 20 mSv in one year. For the population, the dose limit is 1 mSv y^{-1} [7].

The internal exposure, through inhalation, and external exposure are the main radiological concern about zirconium applications. Gamma radiation dose rate close to bulk quantities of zirconium sands

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Table 1. Radioactivity in the earth's crust, ores and mineral sands.

Material	Activity (Bq kg^{-1})		
	^{238}U	^{232}Th	
Earth's crust	33	34	NCRP (1988) [1]
Bauxite ore	250	200	UNSCEAR (1988) [2]
Copper ore	30-80	23-110	UNSCEAR (1988)
Phosphate rock	1300-2300		UNSCEAR (1982) [3]
Zircon sand	>500	>500	UNSCEAR (1988)

are 1-2 μSvh^{-1} and simple precautions are generally sufficient to minimize the external radiation exposure. Proper industrial hygiene rules sufficient to avoid internal contamination resulting from zircon powders.

Threshold levels indicated in the Euratom 1996 legislation stipulate minimum activity concentration and total quantity of radioactivity, as shown in table 2 [8].

Table 2. Radioactivity threshold levels for natural radionuclides; Euratom 1996 [8].

Radionuclide	Activity (Bq)	Concentration (Bq kg^{-1})
^{40}K	10^6	10^5
^{238}U	10^3	10^3
^{235}U	10^4	10^4
^{232}Th	10^3	10^3

The aim of this study was to investigate the specific activity of imported zirconium samples, samples of ceramic tiles and sludge's resulting from ceramic tile production. The result has been examined in the light of the existing Iranian limit for the combined concentrations. Of ^{238}U, ^{232}Th and ^{40}K which are 1800 Bq kg^{-1} 900 Bq kg^{-1} and 11000 Bq kg^{-1}, respectively [9].

MATERIALS AND METHODS

The samples selected for this work include zirconium minerals, final products (wall and floor tiles), and sludge's resulting from the production cycle. The zirconium minerals are used in the ceramic industry for production of ceramic colors, glazes, tiles, sanitary and table ware. Concerning the final products, the samples chosen were representative of the main types of ceramic tiles produced in Iran. Ceramic sludge's were the solid wastes produced by the waste water treatment plant of the ceramic factory.

All samples have been powdered to average particle size of approximately 1mm and dried for 2h at 105 °C, accurately weighed, then placed in 300 g plastic container and sealed. Measurements have been carried out on sealed samples, after 'aging time' of about 21 days, in order to allow the re-establishment of radioactive equilibrium between ^{222}Rn and its short-lived daughter products.

The measurements of natural radioactivity level performed by gamma spectrometry, using a high purity germanium (HPGe) detector connected to a MCA (CANBERA, USA). The resolution of this type detector is particularly useful for activity measurements of the uranium and thorium chain members which present the peaks which are very close to each other.

The energy resolution (full-width at half maximum of the system) was 1.9 keV at 1332 keV for ^{60}Co with 40% relative efficiency. The detector was placed in a well consisting of layer of 10 cm thick of lead with cadmium - copper coating in the inner side. The system was equipped with software (CANBERRA SPECTR-AT V4.3) for data acquisition and analyzing. The counting time was between 10^4 and 6×10^4 seconds (2.8-16.7 h) depending on the specific activity of the samples. The calibration sources used were (RGU-1, RGTh-1 and RGK-1) for uranium, thorium and potassium from International Atomic Energy Agency. The background was measured for 6×10^4 seconds and subtracted from the sample spectra.

Assuming secular equilibrium in the uranium and thorium decay series, the ^{238}U and the ^{232}Th activities were determined indirectly via activities of their daughter

products [10].

The nuclides chosen were ^{214}Bi (609 keV), ^{214}Pb (352 keV), ^{208}Tl (583 keV) and ^{228}Ac (911 keV) for ^{238}U and ^{232}Th, respectively. The specific activity of ^{40}K was determined directly by 1461 keV photopeak.

RESULTS AND DISCUSSION

The specific activities of uranium, thorium and potassium measured in the samples, as well as corresponding standard deviations due to counting errors are presented in table 3 (zirconium minerals) and table 4 (tiles and sludge's). The ^{238}U concentration, ranging from 3000 to 10000 Bq kg^{-1}, was higher than concentration of ^{232}Th (500-1800 Bq kg^{-1}), and ^{40}K (50-800 Bq Kg^{-1}) in all samples.

The measured specific activities in the mineral showed that the specific activity of baddeleyite was higher than that of zirconium silicate and agrees with other recent works [11, 12].

The high activities in sample 1 and 6 could be explained by the origin of the mineral itself (both imported from South Africa). In fact, it is known that zirconium minerals coming from South Africa have specific activities which are generally higher than that of other countries [11]. The comparison between the specific activities of the earth's crust and the investigated zircon sands showed the specific activities of ^{238}U to be up to two orders of magnitude. The high level of radioactivity could be explain that uranium and thorium atoms were easily incorporated in crystalline structure of the zirconium; furthermore, zircon ores underwent enrichment during sand processing which produced almost pure zirconium silicate [10]. Therefore zircon minerals used in the ceramic industry, are usually included in the category of sources of technology enhanced natural radioactivity. The ^{238}U concentration in sludge's is higher than that in the end product (tiles and stoneware). The ceramic sludge's can contain appreciable concentrations of zirconium compound and slightly higher than those in earth's crust.

The result of ceramic tiles showed that tiles usually contain small amounts of zirconium compound and are not a cause of concern from the radiation protection point of

Table 3. Average specific activities of zirconium mineral samples.

Mineral	No. of samples	Imported (1999-2001)	Weight (Tons)	^{238}U (Bq kg^{-1})	^{232}Th (Bq kg^{-1})	^{40}K (Bq kg^{-1})
Zircon	4	South Africa	60	4400 ± 210	610 ± 35	60 ± 8
Zircon	8	Italy	310	3500 ± 170	550 ± 34	55 ± 7
Zircon	3	Ukraine	20	2100 ± 120	460 ± 40	50 ± 7
Zircon	3	Germany	20	2700 ± 140	590 ± 37	65 ± 8
Zircon	2	Belgium	10	3100 ± 150	570 ± 35	77 ± 9
Baddeleyite	4	South Africa	40	11500 ± 450	1800 ± 60	310 ± 20
Baddeleyite	6	Ukraine	160	4300 ± 180	425 ± 37	65 ± 8
Baddeleyite	4	Germany	60	2240 ± 110	470 ± 30	74 ± 9

Table 4. Average specific activities of ceramic tile samples and sludge.

Mineral	No. of sample	^{238}U (Bq kg^{-1})	^{232}Th (Bq kg^{-1})	^{40}K (Bq kg^{-1})
Glazed tile	6	62 ± 8	54 ± 7	810 ± 38
Stoneware	3	58 ± 6	60 ± 6	570 ± 35
Sludge	2	150 ± 17	59 ± 6	317 ± 22

view. In fact they produce negligible additional dose values. On the basis of the Iranian threshold limit for the natural concentrations in imported minerals, it appears that more specific regulations are necessary on zirconium compound used in ceramic industry.

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