Estimation of Radiation Hazards from Imported Zirconium Materials used in Ceramic Tiles Industries in Bangladesh

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Abstract

The purpose of the present study was to determine the natural radioactivity contained in fourteen ceramic materials (from zirconium silicate bags) collected from Chattogram mega port in Bangladesh using a high-purity germanium detector. The range of activity level of Ra-226 and Th-232 in collected samples varied from 21.83 ± 2.67 $Bqkg^{-1}$ to 515.13 ± 10.45 $Bqkg^{-1}$ and 15.67 ± 1.57 to 131.67 ± 4.75 $Bqkg^{-1}$ respectively. Artificial radionuclides were found below the minimum detectable activity (MDA) of the counting system. Radium equivalent activity, radiological hazard index and annual effective dose rate associated with the collected samples were also calculated. Activity concentrations of collected samples were found within exemption level (moderate amount of material) set by Nuclear Safety and Radiation Control (NSRC) rules-1997 of Bangladesh and International Atomic Energy Agency (IAEA) Safety Standards- General Safety Requirements (GSR) Part-3. This study will help to create a primary database on radionuclide content in typical building materials and their components available in Bangladesh.

***Keywords**:* Natural radioactivity, ceramic materials, gamma spectrometry, radiological hazard assessment

1. Introduction

Materials such as brick, concrete, ceramics, cement, marble, sand, granite, limestone, gypsum, etc are defined as building materials those contain natural radionuclides, including uranium (^{238}U) and thorium (^{232}Th) and their decay products and the radioactive potassium (^{40}K). The decay chain of the ^{238}U series is often called the ^{226}Ra series as radium (^{226}Ra) is radiologically the most significant in this series. Radionuclides occurring naturally in the building materials contribute to radiation exposure can be separated into external and internal exposure. Direct gamma radiation is the main reason for external exposure and people are internally exposed by inhaling the radioactive inert gas radon and its decay products [1].

Ceramic titles are used as most frequent building material. Feldspars, Clay, silica, Kaolin, talc are the components of common ceramics. When it is required to make glaze, zircon sand (Zirconium Silicate $ZrSiO_4$) is used because of the shining property of the lanthanum series [2]. Typically zirconium silicate has no color, but if impurities are added, then it produces various colors. Zirconium silicate is used for industrialized refractory materials, in manufacture of ceramics, ceramic glazes and enamels. It behaves as an opacifier when it is used in enamels and glazes. Assessment of concentrations of the natural radionuclides in the building materials is very essential for the protection of the public, as people usually use up 80% of their time indoors [3].

A few data on the radioactivity of building materials in Bangladesh [4-5] are available but journal on determining radioactivity in zirconium silicate material in Bangladesh has not been published before. This study was concerned with the natural radioactivity contained in ceramic materials (zirconium silicate) bags collected from different containers at Chattogram mega port in Bangladesh. Radium equivalent activity, gamma absorbed dose rate and annual effective dose was also calculated to evaluate possible radiological hazards in these ceramic materials and was compared with the findings of related studies carried out in other countries.

2. Material and Methods

2.1 Collection and Preparation of Sample

Total fourteen samples were collected randomly from different bags in different containers containing zirconium silicate material from custom house of Chattogram mega port in Bangladesh in 2018. All samples were prepared using the standard guidelines of the IAEA [6]. Upon collection, all the samples were appropriately packed and manifested for recognition code. Then the samples were carried and stored at the sample processing laboratory of Health Physics Division in Atomic Energy Centre Dhaka, Bangladesh Atomic Energy Commission (BAEC) where the samples were filled in cylindrical plastic containers of 7.5 cm height and 6.5 cm in diameter. Using an electrical balance the samples were weighed and the net weights of the samples were recorded. The sample-filled plastic containers were marked separately with identification number, date of preparation and net weight. In order to assume secular equilibrium [4] between ^{238}U and ^{232}Th series and their daughter progenies, the cap of the sample containers were sealed air tightly and were stored for about 30 days.

2.2 Calibration and measurements by gamma ray spectrometry

The samples were analyzed using a high-purity germanium (HPGe) detector of coaxial geometry of relative efficiency 19.6% coupled with a DSPEC jr 2.0 - digital signal processing gamma ray spectrometer. The used HPGe detector has effective volume 83.469 cm^3 and energy resolution of the 1.33 MeV energy peak for ^{60}Co was found

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as 1.69 keV at full width half maximum (FWHM) with a relative efficiency of 19.6%. ^{137}Cs (mono energetic gamma source 661.66 keV), ^{60}Co (1173 & 1332 keV) and ^{40}K (1460 keV) were selected for energy calibration owing to a wide range of gamma-ray energies emitted over the whole energy range of consideration. Counting time for the samples and background was 50000 seconds.

In order to determine the counting efficiency, a standard source was prepared by adding Eu^{152} of known activity with Al_2O_3 matrix. Using this standard source, the efficiency graph (Fig. 1) of the HPGe detector was drawn using the following equation:

$$\text{Efficiency} = \frac{\text{CPS}}{\text{DPS} \times I_\gamma} \quad (1)$$

Where, CPS = counts per second for the radionuclide present in the standard sample,
DPS = disintegration per second and
$I_\gamma = \gamma$ -ray emission probability

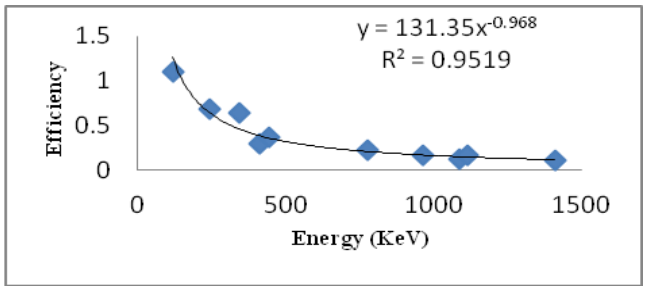

Fig. 1: Efficiency graph of HPGe Detector for solid samples

2. Radioactivity measurement

The Activity concentration of ^{226}Ra, ^{232}Th has been calculated from their daughter nuclides which consist of daughter nuclides [^{214}Pb (295.21 keV), ^{214}Pb (351.92 keV), ^{214}Bi (609.31 keV), ^{214}Bi (1120.29 keV), ^{214}Bi (1764.49 keV)] for ^{226}Ra and [^{212}Pb (238.63 keV), ^{208}Tl (583 keV), ^{228}Ac (911.07 keV), ^{228}Ac (969.11 keV)] for ^{232}Th respectively [6].

The activity of individual radionuclides in samples is calculated by the following equation:

$$A = \frac{N \times 100 \times 1000}{P_\gamma \times \varepsilon \times W} \quad (2)$$

Where

A= activity of the sample in Bqkg^{-1}

N= the net counts per second = CPS for the sample – CPS for the background value.

ε= % of the counting efficiency of the gamma energy of interest

P_γ = absolute emission probability of the gamma ray and

W= net weight of the sample (in gm).

Radioactive disintegration is a random phenomenon. Therefore, all measurement based on radiation discharged in nuclear decay is subject to modest amount of statistical variation. These fluctuations stand for an inevitable cause of uncertainty in all nuclear experiments. The errors in the counting have been articulated in terms of standard deviation (±σ) [7] where σ is expressed as:

$$\sigma = \left[{}^{N_s}/_{T_s^2} + {}^{N_b}/_{T_b^2} \right]^{1/2} \quad (3)$$

Where, N_s is the net counts measured in time T_s and N_b is the background counts measured in the T_b. The standard deviation (±σ), in cps was converted into activity in Bqkg^{-1}.

2.4 radiological hazard assessment

2.4.1 γ-ray radiation hazard indices

The radionuclides ^{226}Ra, ^{232}Th and ^{40}K are not equally disseminated in the studied samples. In order to evaluate the radiological consequence due to ^{226}Ra, ^{232}Th and ^{40}K by a distinct measurement, a general indicator named as the radium equivalent activity (Ra_{eq}) is used as follows [8]:

$$Ra_{eq} = C_{Ra} + 1.43C_{Th} + 0.777C_K \quad (4)$$

where C_{Ra}, C_{Th} and C_K are the average activity concentration in samples in Bqkg^{-1} of ^{226}Ra, ^{232}Th and ^{40}K respectively.

2.4.2 Internal and External radiation hazard index

The external hazard index (H_{ex}) is the radiation dose due to the external exposure to gamma radiation. On the other hand, the internal hazard index (H_{in}) occurs due to the internal exposure caused by inhaled radon and its short-lived progeny and is given by the the following formula [8]:

$$H_{ex} = \frac{A_{Ra}}{370} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \leq 1 \quad (5)$$

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

2.4.3 Outdoor and indoor absorbed dose rate

The outdoor absorbed dose rate in air at 1 meter above the ground surface owing to the presence of natural radionuclides, ^{226}Ra, ^{232}Th and ^{40}K, was anticipated by the following formula [9]:

$$D_{out} = (0.427A_{Ra} + 0.662A_{Th} + 0.0432A_K) \quad (7)$$

$$D_{in} = D_{out} \times 1.2 nGyh^{-1} \quad (8)$$

2.4.4 Outdoor and indoor annual effective dose rate

The outdoor annual effective dose rate and the indoor annual effective dose rate can be calculated using the following formula [9]:

$$E_{out} = D \times 8760 \times 0.2 \times 0.7 \times 10^{-6} (mSvy^{-1}) \quad (9)$$

$$E_{in} = D \times 8760 \times 0.8 \times 0.7 \times 10^{-6} (mSvy^{-1}) \quad (10)$$

3. Results and Discussion

The obtained activity concentration of natural radionuclides ^{226}Ra, ^{232}Th and ^{40}K in all samples are revealed in the following Table 1.

Table 1: Activity concentration of ^{226}Ra, ^{232}Th and ^{40}K in collected samples

Sample ID	Activity Concentration (Bqkg-^{1})		
	^{226}Ra	^{232}Th	^{40}K
1	217.57 ± 8.57	22.75 ± 2.37	22.22 ± 7.19
2	322.29 ± 6.29	29.25 ± 1.57	55.87 ± 6.56
3	198.13 ± 6.63	32.75 ± 2.45	21.41 ± 7.37
4	407.25 ± 6.65	48.61 ± 8.57	53.7 ± 6.29
5	371.89 ± 9.31	75.77 ± 4.63	46.72 ± 10.62
6	21.83 ± 2.67	15.67 ± 1.57	12.07 ± 7.70
7	217.75 ± 6.75	33.59 ± 3.57	13.63 ± 7.41
8	360.89 ± 9.38	70.87 ± 3.43	16.43 ± 9.1
9	192.13 ± 8.57	45.05 ± 2.67	45.31 ± 7.59
10	235.13 ± 7.89	42.33 ± 3.47	31.64 ± 9.33
11	266.38 ± 7.83	47.53 ± 2.77	7.47 ± 1.79
12	236.75 ± 7.38	44.87 ± 3.41	42.45 ± 9.35
13	227.35 ± 7.47	33.77 ± 2.87	90.63 ± 10.43
14	515.13 ± 10.45	131.67 ± 4.75	23.07 ± 8.62
Average	270.75±7.56	48.18±3.44	34.48 ±7.81

The activity concentration of the ^{226}Ra in all samples ranged from 21.83 ± 2.67 Bqkg^{-1} to 515.13 ± 10.45 Bqkg^{-1} with the average value of 270.75±7.56 Bqkg^{-1}. The activity concentration of the ^{232}Th in all samples ranged from 15.67 ± 1.57 to 131.67 ± 4.75 Bqkg^{-1} with an average value of 42.99±3.13 Bqkg^{-1}. The activity concentration of the ^{40}K in all samples varied from 12.07 ± 7.70 Bqkg^{-1} to 90.63 ± 10.43 Bqkg^{-1} with an average value of 34.48 ±7.81 Bqkg^{-1}.

The exempt activity concentration of ^{226}Ra for moderate amount of materials is 10000 Bqkg^{-1} in IAEA Safety Standards: general safety requirements (GSR) part-3 [10] and 10000 Bqkg^{-1} in Nuclear Safety and Radiation Control (NSRC) rules-1997 [11] and the exempt activity concentration of ^{232}Th is 10000 Bqkg^{-1} in GSR part-3, and 1000 Bq/kg in NSRC rules-1997 of Bangladesh. The activity concentration of ^{226}Ra and ^{232}Th of the samples was compared with exempt activity concentration of ^{226}Ra & ^{232}Th in NSRC rules-1997 and GSR part-3 and it was found that the activity concentration of ^{226}Ra and ^{232}Th of all samples were much below the exempt limit which is shown in Figs. 2-3.

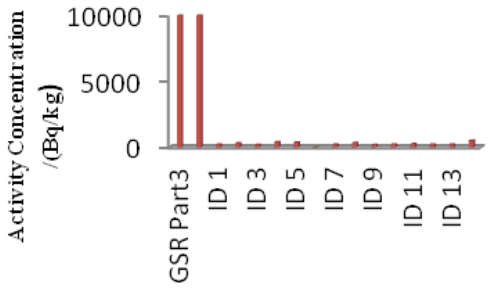

Fig. 2: Comparison of ^{226}Ra activity of the collected samples with NSRC rules-1997 and GSR part-3 guideline

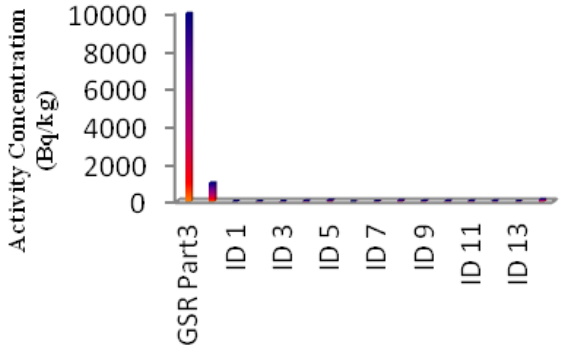

Fig. 3: Comparison of ^{232}Th activity of the collected samples with NSRC rules-1997 and GSR part-3 guideline

Table 2: Radium equivalent activity, outdoor and indoor absorbed dose rate, external and internal hazard index and effective dose rate associated with the collected samples

Sample ID	Radium Equivalent Activity (Ra_{eq}) Bqkg^{-1}	Outdoor Absorbed Dose ate (D_{out}) (nGyh^{-1})	Indoor Absorbed Dose rate (D_{in}) (nGyh^{-1})	External Hazard Index (H_{ex})	Internal Hazard Index (H_{in})	External Effective Dose rate mSvy^{-1}	Internal Effective Dose rate (E_{in}) mSvy^{-1}	Effective Dose rate (E) mSvy^{-1}
1	251.81	108.92	130.71	0.68	1.27	0.13	0.64	0.77
2	368.42	159.39	191.27	0.99	1.87	0.19	0.94	1.13
3	246.61	107.21	128.65	0.67	1.20	0.13	0.63	0.76
4	480.90	208.40	250.07	1.30	2.40	0.26	1.22	1.48
5	483.84	210.98	253.17	1.31	2.31	0.26	1.24	1.50
6	45.17	20.22	24.26	0.12	0.18	0.02	0.12	0.14
7	266.83	115.80	138.97	0.72	1.31	0.14	0.68	0.82
8	463.50	201.73	242.07	1.25	2.23	0.25	1.18	1.43
9	260.04	113.82	136.58	0.70	1.22	0.14	0.67	0.81
10	298.10	129.79	155.75	0.81	1.44	0.16	0.763	0.92
11	334.92	145.53	174.64	0.91	1.62	0.18	0.86	1.04
12	304.18	132.63	159.16	0.82	1.46	0.16	0.78	0.94
13	282.62	123.35	148.02	0.76	1.38	0.15	0.73	0.88
14	705.19	308.12	369.75	1.91	3.30	0.38	1.81	2.19

The radiological parameters such as indices of radium equivalent activity (Ra_{eq}), absorbed dose rate (D), internal hazard index (H_{in}), external hazard index (H_{ex}) and annual effective dose equivalent (D_{eff}) have been measured to estimate the radiological risk due to the presence of ^{226}Ra, ^{232}Th and ^{40}K in the samples. Table 2 depicts the values of Ra_{eq}, D, H_{in} , H_{ex} and D_{eff}.

The values of radium equivalent activity in all samples have been found to varied from 45.17 $Bqkg^{-1}$ to 705.19 $Bqkg^{-1}$. The permissible limit of radium equivalent activity is 370 $Bqkg^{-1}$ as recommended by the IAEA and four samples (Sample ID 4, 5, 8 & 14) showed more radium equivalent activity than the internationally recommended value [12].

On the other hand, the values of external hazard index and internal hazard index for different samples varied from 0.12 to 1.91 and 0.18 to 3.30. The value of external and internal hazard index have to be less than unity with the aim of remains the radiation hazard insignificant [12]. Almost all the samples (except one sample) showed internal hazard index greater than unity.

The measured value of annual effective dose rate for different samples have been found in the range of 0.14 $mSvy^{-1}$ to 2.19 $mSvy^{-1}$. The secure value for total (outdoor and indoor) annual effective dose rate is 1 $mSvy^{-1}$ to maintain radiation hazard insignificant [12]. Six samples (Sample ID 2, 4, 5, 8, 11 and 14) showed effective dose greater than 1 $mSvy^{-1}$.

Although some samples showed higher radium equivalent activity, internal hazard index and annual effective dose rate, it is worth mentioning that this suggested value (radium equivalent activity, hazard index, annual effective dose rate) is meant for materials used in bulk amounts, and is not intended for decorative building materials for example tiles, so these higher values of activity will not pose any significant health hazards to the users, when these are used in their buildings.

A relative assessment was also carried out for the activity concentrations and radium equivalent activities of building materials in the current work with other research performed home and aboard and is shown in the Table-3.

Table 3: Review of activity concentrations and radium equivalent activities in building materials in various regions of the world

Country of origin	Material used	Obtained Result ($Bqkg^{-1}$)			
		^{226}Ra	^{232}Th	^{40}K	Ra_{eq}
India [13]	Cement, Brick, Sand, Ceramics	3.2-151.7	14-63.7	24.3-151.7	10.36-234.21
China [14]	Glaze	158.3- 1087	91.7 - 1218	473- 1031	>370
	Ceramic tiles	63.5 -131.4	55.4-106.5	386- 866	< 370
Egypt [15]	Bricks, Cement, Gypsum, Ceramics, Marble, Limestone and Granite	116 ± 54	64 ± 34	4.8 ± 2.2	Maximum 436 ± 199
Italy [16]	Porous fired tiles	36-87	38-86	411-996	130-261
	Porcelain stoneware tiles	20-708	33-145	158-850	93-943
Algeria [17]	Building materials	12-65	7-51	36-675	<370
Turkey [18]	Clay, Kaolin and End Product (Glazed Ceramic Wall and Floor Tiles)	1.7 -5563	0.9-657	11.5 -3633	205.17± 11.5-255.07± 21.5
Australia [8]	Zircon Quartz Alumina	2249.6	503.2	325.6	<370
		3.7	25.9	1705.7	
		62.9	162.8	403.3	
Bangladesh [4]	Cement	61.1±0.8	79.9±1.2	1132.6± 17	<370
	Sand	51.3 ± 1.4	135 ± 4		
	Hollow concrete bricks	44.65± 2.7	101.35± 6	1557.5± 11	
Bangladesh [5]	Sand	12-18	5-24	138-497	29-190
	Stone	8-16	12-18	280-303	
	Cement	15-34	14-24	213-426	
	Tile	17-80	10-59	207-655	
	Marble	14-21	16-19	237-243	
Present Study (Bangladesh)	Ceramics (Zirconium Silicate)	21.83-515.13	15.67-131	12.07-90.63	45.17-705.2

From the Table 3, we see that glaze samples in China [14], Porcelain stoneware tiles in Italy [16], Zircon Quartz Alumina in Australia [8], glazed ceramic titles in Turkey [18] showed comparatively higher radium equivalent activity than other building materials which is comparable with the present high radium equivalent activity found in ceramics (Zirconium Silicate) material in Bangladesh.

4. Conclusion

Although the activity concentration of collected samples were found within exemption level set by NSRC rules 1997 of Bangladesh and GSR Part 3 of IAEA, the result of ceramic tiles material (zirconium silicate) showed higher radium equivalent activity, hazard index and annual effective dose rate. The higher level of radioactivity enlightened that uranium and thorium atoms are easily combined in crystalline formation of the zirconium; furthermore, zircon ores go through enrichment throughout sand processing which create approximately pure zirconium silicate [19]. Therefore zircon minerals utilized in the ceramic industry, are typically integrated in the group of technology enhanced natural radioactivity and will not produce any significant health effects to the end users.

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