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Natural radioactivity levels and radiation hazards for gypsum materials used in Egypt

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ABSTRACT

Radionuclides naturally occurring in building materials may significantly contribute to the annual doses to the public. For instance, familiar building materials such as the concrete and gypsum board have been reported to produce a dose of about 0.04 mSv per year for a typical person (NCRP 1987c). External as well as internal exposures are two pathways of radiation dose imparted to human beings from the building materials. As information on the radioactivity of such materials is lacking, the study of gypsum materials used in Egypt was carried out in order to estimate the annual dose to the Egyptian population due to natural radionuclides in building materials. During the study, 18 samples of commonly used gypsum raw materials were collected and measured. The activity concentrations were determined by gamma ray spectrometry. Their mean values were in the ranges of 499.29 ± 11.53 Bq·kg^{-1} for ^{40}K, 91.97 ± 2.61 Bq·kg^{-1} for ^{226}Ra, 37.62 ± 1.67 Bq·kg^{-1} for ^{238}U and 42.27 ± 2.22 Bq·kg^{-1} for ^{232}Th. The activity indexed Iγ for 18, different gypsum samples varied from 0.31 ± 0.03 to 2.3 ± 0.19 and the radium equivalent activity (R_{aeq}), from 38.81 ± 1.68 to 324.7 ± 9.42. These values are lower than the limit of 370 Bq·kg^{-1} adopted by the Organization for Economic Cooperation and Development (OECD). The average indoor annual effective gamma dose rate (DE) in (mSv/y) for the people, caused by the building materials of dwellings, was assessed for most commonly gypsum materials. It was estimated to be in the range from 0.10 ± 0.003 mSv/y to 0.74 ± 0.08 mSv/y. The internal and external hazard indices (H_{in}, H_{ex}) and the absorbed dose rate in air D in each sample were evaluated to assess the radiation hazard for people living in dwelling made of the studied materials. The absorbed dose rate of indoor air in samples G1, G2, G11, G17 and G18 is less than the international recommended value which is 55 nGyh^{-1}. While the absorbed dose rate for samples G3, G4, G5, G6, G7, G8, G9, G10, G12, G13, G14, G15 and G16 is higher than 55 nGyh^{-1}, these samples are not acceptable for use as building materials.

KEYWORDS

Gypsum; Gamma Spectrometer; Hazard Indices; NORM; Building Materials

1. INTRODUCTION

Gypsum is a naturally occurring mineral made up of calcium sulfate and water ($CaSO_4 \cdot 2H_2O$) which is sometimes called hydrous calcium sulfate. It is the mineral calcium sulfate with two water molecules attached. By weight, it is 79% calcium sulfate and 21% water. Gypsum has 23% calcium and 18% sulfur, and its solubility is 150 times than that of limestone, so it is a natural source of plant nutrients. Gypsum naturally occurs in sedimentary deposits from ancient sea beds. Gypsum is mined and made into many products like drywall used in construction, agriculture and industry. It is also a by-product of many industrial processes. Gypsum is also used as a generic name for many types of sheet products made of a non-combustible core with a paper surfacing that adds strength. These include drywall, ceiling tiles, partitions, etc., whose strength is directly related to its

thickness and a few trace materials. Gypsum has been known for centuries as a building material. The earliest known use of gypsum as a building material was in Anatolia around 6000 B.C.

Gypsum has been found in the interiors of the great pyramids in Egypt, which were erected in about 3700 B.C. Gypsum is found in every continent in the world and is one of the most widely used minerals. Synthetic gypsum is generated as a byproduct in flue-gas desulfurization (FGD) systems used to reduce sulfur dioxide emissions from coal-fired electric power plants. These (FGD) systems not only keep the air clean, but also provide a sustainable, ecologically sound source of very pure gypsum. Synthetic gypsum is also generated by various other acid-neutralizing processes [1,2]. Worldwide gypsum is used in Portland cement, which is used in concrete for bridges, buildings, highways, and many other structures that are parts of our daily life. Gypsum is also extensively used as a soil conditioner on large tracts of land in suburban areas and in agricultural regions. There are several types of naturally occurring gypsum, and many industrial processes also produce gypsum as a by-product of their systems such as phosphoric acid and citric acid manufacture. Mined gypsum is found in various locations around the world. Chemically raw mined gypsum is primarily calcium sulfate hydrated with water molecules in its chemical structure. Other materials and chemicals in mined gypsum may be small amounts of sand or clay particles and a few trace elements. The trace elements may be boron, iron, arsenic and lead and with different concentration. Primarily mined gypsum is very safe to use and is a great amendment for many soils.

Finely ground gypsum rock was used in agriculture and other industries to neutralize sodic soils, to improve soil permeability, to add nutrients, to stabilize slopes, and to provide catalytic support for maximum fertilizer benefits. Small amounts of high-purity gypsum also were used in a wide range of industrial operations, including the production of foods, glass, paper, and pharmaceuticals. Amongst the activities identified in the European, Basic Safety Standards Directives (BSS), which the standard sets the concern "with the production of residues which contain naturally occurring radionuclides causing a significant increase with the exposure of members from the public…". Such materials may include coal ash from power stations, by-product gypsum and certain slugs, which are produced in large volumes and, which may potentially be used as building materials [3]. Scientific investigations have long concluded that prolonged exposure to low-dose radiation can induce deleterious effects in humans; it was found necessary to establish levels of radioactivity in this product and associated radiation risk [4]. The aim of this paper is to investigate the radioactivity of gypsum and establish radiation levels in materials suspected to have natural radioactivity radiation risk in Egypt.

2. MATERIALS AND METHOD

18 gypsum samples were collected from natural and manufactured building materials used in Egypt. The gypsum samples were dried, pulverized and packed in 200 g by mass in the cylindrical plastic containers of radius 3 inch and height 3.5 inch, which sits on the (3 inch × 3 inches) high purity germanium (HPGe) detector with high geometry. The containers are sealed for about four weeks to ensure radioactive equilibrium between the parent radionuclides and their gaseous daughter decay products in the uranium and thorium series [5].

Each sample containing soil grain weighing about 200 g was stored in standardized polyethylene containers. The containers were sealed to avoid any possibility of out gassing of radon and kept over a period than one month to make sure the samples attained the radioactive equilibrium between ^{226}Ra with its decay products in the uranium series. It was assumed that ^{232}Th is in secular equilibrium with ^{228}Ra. For the measurement of activity concentrations of naturally occurring radionuclides of ^{226}Ra, ^{232}Th, and ^{40}K in soil samples, (HPGe) detector based gamma ray spectrometer with a relative efficiency of 30% was employed. (HPGe) Detector was coupled with a Canberra multichannel analyzer (MCA). The resolution Full width of half maximum (FWHM) of the spectrometry system was 1.8 keV at 1332 keV gamma-ray line of ^{60}Co. Spectrum of every sample was collected for 54,000 seconds (15 h). A typical spectrum is shown **Figure 1** for sample G14. Spectrum analysis was performed with computer software and activity concentrations of three natural radionuclides were determined. To reduce the background effect, the detector was shielded in a 10 cm wall lead covering lined with 2 mm copper and tow mm cadmium foils. In order to determine the background radiation distribution in the environment around the detector, an empty sealed container was counted for 10 hours [6].

3. RESULTS AND DISCUSSION

3.1. Norm in Building Materials

The determination of the presence of radionuclides and calculation of their activities were based on the following gamma-ray transitions (in keV): the ^{226}Ra activities (or ^{238}U activities for samples assumed to be in radioactive equilibrium) were estimated from ^{234}Th (92.38 keV, 5.6%), while γ-energies of ^{214}Pb (351.9 keV, 35.8%) and ^{214}Bi (609.3, 45%), (1764.5 keV, 17%) and ^{226}Ra (185.99 KeV, 3.5%) were used to estimate the concentration of ^{226}Ra. The gamma ray energies of ^{212}Pb (238.6

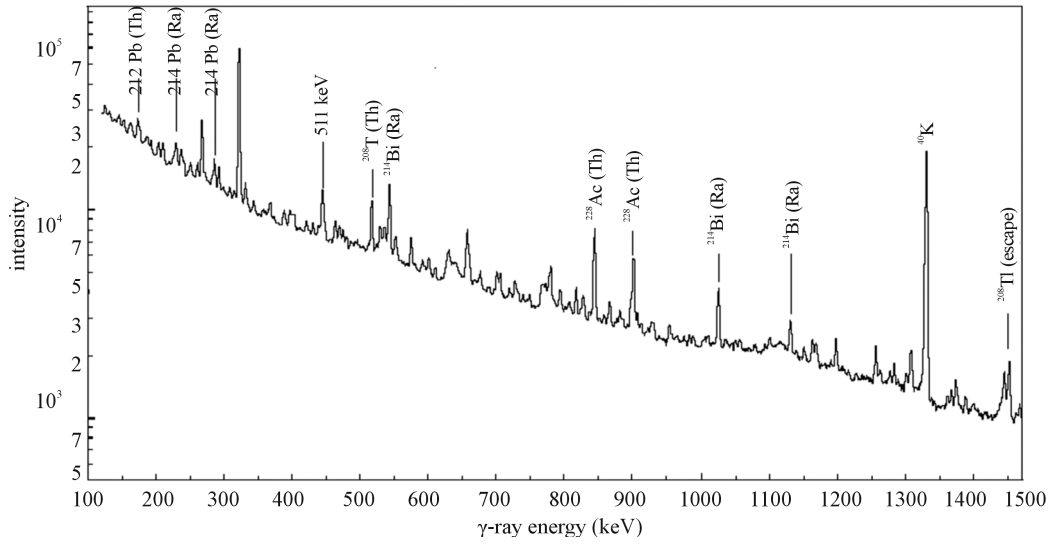

Figure 1. γ-Ray spectrum for gypsum sample G14.

keV, 45%), and ^{228}Ac (338.4 keV, 12.3%), (911.07 keV, 29%), (968.90 keV, 17%) were used to estimate the concentration of ^{232}Th. The natural abundance of ^{235}U is only 0.72% of the total uranium content and hence was not considered in the present study. The activity concentrations of ^{40}K were measured directly by its own gamma rays (1460.8 keV, 10.7%). The detector energy resolution is not sufficient to easily separate these peaks. Therefore, the concentrations of ^{235}U were calculated by subtracting the fraction of ^{226}Ra using Equation (1) [7]:

$$A_{U-235} = \left[1.75\left(CR_{T.186}\right)/\varepsilon_{186}\right] - 0.063A_{\text{Ra}-226} \quad (1)$$

where: CR_T: is the total count rate (counts·sec^{-1}) in the 186 KeV energy peak;

ε: detection efficiency; and

$A_{\text{Ra-226}}$: activity concentration of ^{226}Ra.

Determination of activity concentrations was calculated using the Equation (2) [8].

$$A = C/M\,\beta\varepsilon \quad (2)$$

where: C: is the net peak area of specific gamma ray energy (count per second).

M: is the mass of the samples (kg).

B: is the transition probability of gamma-decay. And,

ε: is the detector efficiency at the specific gamma-ray energy.

During the last three decades, there has been an increasing interest to the study of the radioactivity of different building materials. Several national surveys were conducted to establish the radioactivity concentrations in raw material, industrial by-products and building materials and their radon exhalation rate [3]. The production process and the origin of the raw materials are the most important factors that determine the radionuclide activity concentrations in the construction materials. Different types of building materials were found to contain radionuclide concentration of over two to three orders of magnitude.

3.2. ^{226}Ra, ^{232}Th and ^{40}K Concentration in Building Materials

The activity concentrations of NORM in building materials vary according to the type and origin of the building material (**Tables 1** and **2**). It shows the typical and maximum activity concentrations in common building materials and industrial by-products used for building materials in Europe, e.g. typical and maximum activity concentrations in natural gypsum are 10, 10, 80 (Bq/kg) and 70, 100, 200 (Bq/kg) for ^{226}Ra, ^{232}Th and ^{40}K, respectively [3]. The average activity concentrations of the natural radionuclides of gypsum both as structural materials or covering layers from different countries all over the world are shown in **Table 3** for comparison. This comparison was indicated that the variations in activity concentrations of radium isotopes content in NORM samples of different origins could be due to geological considerations (**Table 4**). Comparison of radionuclide concentrations (Bq·kg^{-1}) in gypsum samples in the present work with those obtained by previous studies in Egypt.

It is clearly the mean activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K of samples in a present study are slightly lower (499.29 ± 11.53, 42.27 ± 2.22 and 91.97 ± 2.61 Bq·kg^{-1} respectively) than those reported by [15] for gypsum from Qena City, Upper Egypt. While our results proved that the mean activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K much higher than those reported by [4] in Egypt.

The total error includes the statistical uncertainty in the peak area, calibration and counting error. **Table 5**

Table 1. Typical and maximum activity concentrations in common building materials and industrial by-products used for building materials in Europe [RP-112 1999].

Material	^{40}K		^{232}Th		^{226}Ra	
	Max.	Typical	Max.	Typical	Max.	Typical
Concrete	1600	400	190	30	240	40
Aerated and light-weight concrete	1600	430	190	40	2600	60
Clay (red) bricks	2000	670	200	50	200	50
Sand-lime bricks	700	330	30	10	25	10
Natural building stones	4000	640	310	60	500	60
Natural gypsum	200	80	100	10	70	10

Table 2. Most common industrial by-products used in building materials in Europe [RP-112 1999].

Material	^{40}K		^{232}Th		^{226}Ra	
	Max.	Typical	Max.	Typical	Max.	Typical
Phospho gypsum	300	60	160	20	1100	390
Blast furnace slag	1000	240	340	70	2100	270
Coal fly ash	1500	650	300	100	1100	180

Table 3. Comparison of radionuclide concentrations (Bq·kg^{-1}) in gypsum samples with those obtained in other published data.

Country	^{40}K	^{232}Th	^{226}Ra	References
China	35	35	370	**[9,10]**
Nordic Countries	40	49	80	**[9]**
West Germany	14	18.5	259	**[11]**
Finland	37	43	1034	**[11]**
Bangladesh	88.1	68.2	256.4	**[12]**
Spain	14.1	17.39	266.77	**[13]**
Turkey	44.5	3.6	10.8	**[14]**
USSR	14.8	140.8	259	**[11]**
India	22	9.3	233	**[11]**

summaries the results for the range and mean natural activity concentrations of ^{238}U; ^{226}Ra; ^{232}Th and ^{40}K for different gypsum samples in Bq/kg. The lowest mean value of the ^{238}U concentration is 7.5 ± 0.54 (Bq/kg) in a sample G1, while the highest is 74.80 ± 3.15 (Bq/kg) in sample G14. The lowest mean value of the ^{226}Ra concentration is 10.73 ± 0.63 (Bq/kg) in sample G1, while the highest is 170.42 ± 5.04 (Bq/kg) in sample G5. It can also be seen that the highest mean value of ^{232}Th is 70.80 ± 2.75 (Bq/kg) in sample G5 and the lowest mean value is 3.10 ± 0.05 (Bq/kg) in a sample G1. The highest and lowest mean values of ^{40}K are 689.10 ± 19.07 and 301.30 ± 8.32 (Bq/kg) in samples G5 and G15, respectively.

Uncertainties are given within one standard deviation.

Table 4. Comparison of activity concentration (Bq/kg) of gypsum used in Egypt with those of previous studies.

Countries	^{226}Ra	^{232}Th	^{40}K	References
Egypt (1)	91.97	42.27	499.29	**Present work**
Egypt (3)	105	45	500	**[15]**
Egypt (4)	31.7	55	116	**[4]**

Table 5. Activity concentration range (Bq/kg) of gypsum in Egypt current works.

Sample	A_k(Bq/Kg)	A_{Th}(Bq/Kg)	A_{Ra}(Bq/Kg)	A_U(Bq/Kg)
G1	307.5 ± 8.32	3.1 ± 0.05	10.73 ± 0.63	7.51 ± 0.54
G2	365.6 ± 9.91	11.7 ± 0.64	14.5 ± 0.76	9.7 ± 0.57
G3	681.3 ± 19.07	59.8 ± 1.81	119.3 ± 3.31	43.2 ± 1.85
G4	433.2 ± 12.09	41.4 ± 1.69	87.6 ± 2.56	23.5 ± 1.45
G5	689.1 ± 19.07	70.8 ± 2.75	170.42 ± 5.04	48.3 ± 1.91
G6	417.7 ± 11.68	39.3 ± 1.76	75.3 ± 2.45	34.6 ± 1.57
G7	528.4 ± 14.91	61.2 ± 2.31	136.2 ± 4.12	74.8 ± 2.45
G8	564.3 ± 15.75	49.1 ± 2.17	121.9 ± 3.24	37.9 ± 1.67
G9	531.3 ± 14.92	56.7 ± 2.28	138.1 ± 4.12	22.1 ± 1.43
G10	678.1 ± 18.65	67.4 ± 2.32	97.7 ± 2.81	61.9 ± 2.33
G11	349.2 ± 9.71	23.8 ± 1.46	23.6 ± 1.46	19.4 ± 1.89
G12	689.1 ± 19.05	52.9 ± 2.16	74.0 ± 2.38	49.7 ± 2.11
G13	431.9 ± 12.08	58.1 ± 1.72	121.1 ± 3.23	61.9 ± 2.33
G14	654.6 ± 18.37	63.8 ± 2.41	148.3 ± 4.16	74.8 ± 3.15
G15	301.3 ± 8.32	16.5 ± 0.86	132.5 ± 4.06	10.4 ± 0.62
G16	407.7 ± 11.27	31.3 ± 1.06	116.7 ± 3.27	27.2 ± 1.57
G17	517.4 ± 14.50	18.2 ± 1.20	39.8 ± 1.69	25.9 ± 1.51
G18	439.3 ± 10.12	35.8 ± 1.56	27.8 ± 0.48	44.62 ± 1.74
Min	**301.3 ± 8.32**	**3.1 ± 0.05**	**10.73 ± 0.63**	**7.51 ± 0.54**
Max	**689.1 ± 19.07**	**70.8 ± 2.75**	**170.42 ± 5.04**	**74.80 ± 3.15**
Mean	**499.29 ± 11.53**	**42.27 ± 2.22**	**91.97 ± 2.61**	**37.62 ± 1.67**
Standard Deviation	**131.58**	**20.3**	**48.83**	**20.7**

3.3. Radon Exhalation from in Building Materials

The radon emanation power or emanation coefficient,

denoted by ζ, is defined as the fraction of ^{222}Rn produced by the disintegration of ^{226}Ra in the grains of the material that can escape from it. The emanation power is dimensionless and ranges from 0 (no radon escapes from the material) to 1 (all radon escapes). The rate of radon exhalation is proportional to the gradient of the radon concentration in the internal pores.

$$E = -D \cdot dC/dx\big|_{x=1} \quad (3)$$

where D is the effective diffusion coefficient and dC/dx is the change from the radon concentration. The principal factors affecting the radon exhalation rate (from a building material) per unit activity concentration of ^{226}Ra are the porosity and the density as the material, the diffusion coefficient, the water content, the age and the composition as the material (as seen in Equation (4)).

For the following boundary conditions:

$C(1) = C(-1)0$ and $(dx/dC) = 0$ the radon exhalation rated *E*:

$$E = \zeta \cdot C_{Ra} \cdot \rho \cdot \sqrt{\lambda}\, D/P \cdot \tan h\left(\sqrt{\lambda}\, D/P \cdot I\right) \quad (4)$$

where ρ is the density, *l* is the half thickness as the material, *P* is the porosity of the material, λ is the decay constant of ^{222}Rn and $\zeta \cdot C_{Ra}$ is the effective radium concentration (the fraction of the total radium which contributes to radon exhalation).

Radon exhalation from building materials has been studied since the early 70's as one of the contributors to the indoor radon concentration. In Hong Kong and The Netherlands was found to be the major contributor to the population radon dose [16,17]. The radon exhalation rate from concrete varies according to the age of the concrete, the water content and the addition of fly ash. The exhalation increases almost linearly with the moisture content up to 50% - 60%, peaks at 70% - 80% and decreases steeply for higher moisture levels. The addition of fly ash to concrete generally increases the ^{226}Ra activity, while the radon exhalation rate slightly increases or even decreases [18-20].

Several methods for exhalation measurements have been developed, as contrary the well established gamma spectrometry procedures for the measurements of ^{226}Ra, ^{232}Th and ^{40}K. Measurements of radon from the exhaling area into a closed chamber, purge and trap of the radon, radon flux measurements from the material surface and *in-situ* measurements have been reported.

3.4. Assessment of Radiation Hazard from Egyptian Gypsum

1) Estimation of the Absorbed Dose Rate (D), Annual Indoor Effective Gamma Dose Rate (DE) and Radium Equivalent Activity (Ra_{eq}):

The absorbed dose rate (D) in air upon a height of 1.0 m above the ground from the radionuclides ^{40}K and also ^{232}Th and the ^{238}U decay series, were calculated using Equation (6), if the naturally occurring radionuclides are uniformly distributed [21,22].

$$D = 0.52813C_{Th} + 0.38919C_{Ra} + 0.03861C_{K} \quad (5)$$

where: C_{Ra}, C_{Th}, and C_K are the activity concentration of ^{226}Ra, ^{232}Th, and ^{40}K in (Bq/kg), respectively. Results of γ-radiation absorbed dose rate are shown in **Table 6**. Average values of calculated absorbed dose rates in samples under investigation are ranged between 19.69 ± 0.40 to 151.43 ± 4.13 nGyh^{-1}; it was found that an average value of 151.43 ± 4.13 nGy/h, which is higher by a factor of 2.75 than world average of 55 nGyh^{-1} [23].

Annual effective dose rates values of the absorbed dose rate were used in the calculation of annual outdoor effective dose rate considering some correction factors. A conversion factor (CF = 0.7 Sv/Gy) was applied for conversion of the absorbed dose in air to the corresponding effective dose. The outdoor occupancy factor

Table 6. Absorbed dose rate (Bq/kg) and Radium equivalent activity of gypsum in Egypt.

Sample	Ra_{eq} (Bq/Kg)	D (nGyh^{-1})	DE indoor (mSv/y)
G1	38.81 ± 1.68	19.69 ± 0.40	0.10 ± 0.003
G2	59.38 ± 2.30	29.21 ± 0.53	0.14 ± 0.003
G3	257.27 ± 7.25	120.66 ± 3.30	0.59 ± 0.07
G4	180.16 ± 5.35	84.25 ± 2.52	0.41 ± 0.04
G5	324.7 ± 9.42	151.43 ± 4.13	0.74 ± 0.08
G6	163.66 ± 4.59	76.61 ± 2.47	0.38 ± 0.04
G7	264.4 ± 7.32	122.96 ± 3.24	0.60 ± 0.08
G8	235.56 ± 6.60	110.34 ± 3.18	0.54 ± 0.07
G9	260.09 ± 7.26	121.17 ± 3.23	0.59 ± 0.08
G10	246.3 ± 6.97	115.27 ± 3.21	0.57 ± 0.07
G11	84.52 ± 2.52	40.24 ± 1.72	0.20 ± 0.02
G12	202.71 ± 6.32	95.77 ± 2.75	0.47 ± 0.05
G13	237.44 ± 6.61	110.04 ± 3.18	0.54 ± 0.06
G14	289.94 ± 8.06	135.43 ± 4.33	0.66 ± 0.08
G15	179.3 ± 4.95	84.03 ± 2.52	0.41 ± 0.04
G16	192.85 ± 5.35	90.35 ± 2.77	0.44 ± 0.04
G17	105.67 ± 3.05	51.27 ± 1.96	0.25 ± 0.02
G18	112.82 ± 3.17	53.39 ± 2.17	0.26 ± 0.02
Min	**38.81 ± 1.68**	**19.69 ± 0.40**	**0.10 ± 0.003**
Max	**324.7 ± 9.42**	**151.43 ± 4.13**	**0.74 ± 0.08**
Mean	**190.87 ± 5.34**	**89.56 ± 2.61**	**0.44 ± 0.04**

(OF = 0.8) was taken into account, since the people spend most of their time (80%) in buildings. Finally, the ratio of indoor to outdoor gamma dose rates (R = 1.4) was also applied as used by other investigators [24] to calculate the annual indoor effective gamma dose rate (DE) in (Sv/y) as given to follow:

$$DE = D \times CF \times OF \times R \times t \quad (6)$$

where: D is the dose rate in (Gy/h^{-1}) and **t** is the duration of the exposure **(= 365 × 24 h)**. Results for indoor annual effective dose rates are shown in **Table 6**. It ranged from 0.10 ± 0.003 to 0.74 ± 0.08 mSv/y with an average value of 0.44 ± 0.04 mSv/y. Finally all samples gave annual effective dose lower than the world wide indoor average annual effective dose 1 mSv/y.

It is important to assess the gamma radiation hazards to persons associated with the used sand, limestone, shale and gypsum for building materials. To represent the activities due to ^{226}Ra, ^{232}Th and ^{40}K by a single quantity which takes into account the radiation hazards which may be caused a common index called the radium equivalent activity (Ra_{eq}) in $Bq \cdot kg^{-1}$ has been introduced [25-27], defined as:

$$R_{eq} = C_{Ra} + 1.43C_{Th} + 0.077C_K \quad (7)$$

where: C_{Ra}, C_{Th}, and C_K are the activity concentration of ^{226}Ra, ^{232}Th, and ^{40}K in (Bq/kg), respectively. This index (R_{eq}) is related to both internal dose due to radon and external gamma dose [20], and should have the highest value of 370 Bq/kg for safe use of the building materials. As reference, the permissible dose limit for public which is recommended by ICRP (1991) [28] are 1.5 $mSv \cdot y^{-1}$ or equivalent to 370 $Bq \cdot kg^{-1}$. The mean calculated Ra_{eq} values are shown in **Table 6** for the different gypsum types and the regions from where they were collected. The minimum (38.81 ± 168 $Bq \cdot kg^{-1}$) and the maximum (324.70 ± 9.42 $Bq \cdot kg^{-1}$) values of Ra_{eq} were found in G(1) and G(5) gypsum types, respectively. The mean Ra_{eq} values of all the measured samples were almost lower than limit value of 370 $Bq \cdot kg^{-1}$ recommended by the Organization for Economic Cooperation and Development.

2) Hazard Indices

To limit the external γ-radiation dose from building materials to 1.5 mSv/yr, the external hazard index (H_{ex}) is defined by some workers, Beretka and Mathew introduced a hazard index for the external and internal gamma radiation dose from building materials as given bellow [29].

The external hazard index is obtained from Ra_{eq} expression through the supposition that its maximum value allowed (equal to unity) corresponds to the upper limit of Ra_{eq} (370 $Bq \cdot kg^{-1}$). Then, the external hazard index can be defined as:

$$H_{ex} = \left(C_U/370 + C_{Th}/259 + C_K/4810\right) < 1 \quad (8)$$

In addition to the external hazard, radon and its short-lived products are also hazardous to the respiratory organs. The internal exposure to radon and its daughter products is quantified by the internal hazard index (H_{in}) which is given by the equation:

$$H_{in} = \left(C_U/185 + C_{Th}/259 + C_K/4810\right) < 1 \quad (9)$$

where C_U, C_{Th} and C_K are the specific activities of ^{238}U, ^{232}Th and ^{40}K in $Bq \cdot kg^{-1}$, respectively. The calculated values of external hazard index obtained in this study ranged from 0.1 ± 0.002 to 0.58 ± 0.06 with mean value of 0.37, **Table 7**. If the maximum concentration of radium is half that of the normal acceptable limit, then H_{in} will be less than 1.0. For the safe use as a material in for the construction of dwellings, H_{in} should be less than unity. The calculated values of H_{in} for the studied gypsum samples range from 0.12 ± 0.005 (G1) to 0.79 ± 0.09 (G14). Once again, all these values are less than unity.

3) Representative Gamma Index (I_γ) and (I_α)

Number of indices dealing with the assessment of the excess gamma radiation arising from building materials such as external and internal hazard indices and gamma concentration indices have been proposed by several investigators [30-33]. In this study, the gamma index (I_γ) It was calculated as proposed by the European Commission [30]:

$$I_\gamma = C_{Ra}/150 + C_{Th}/100 + C_K/1500 \left(Bq \cdot kg^{-1}\right) \quad (10)$$

where C_{Ra}, C_{Th} and C_K are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in $Bq \cdot kg^{-1}$, respectively. $I \leq 1$ corresponds to a does creation of 1 $mSv \cdot y^{-1}$, while $I \leq 0.5$ corresponds to 0.3 $mSv \cdot y^{-1}$. The mean values of I_γ calculated from the measured activity concentration of ^{226}Ra, ^{232}Th and ^{40}K are presented in **Table 7** for different gypsum samples. The mean calculated values of I_γ for the studied samples varied in the range between 0.31 ± 0.03 – 2.3 ± 0.19 ($Bq \cdot kg^{-1}$) which were higher than the critical value of unity.

So far, several alpha indices have been proposed to assess the exposure level due to radon inhalation originating from building materials [30]. The alpha index was determined by the following formula:

$$I_\alpha = C_{Ra}/200 \left(Bq \cdot kg^{-1}\right) \quad (11)$$

where C_{Ra} ($Bq \cdot kg^{-1}$) is the activity concentration of ^{226}Ra assumed in equilibrium with ^{238}U. The recommended exemption and upper level of ^{226}Ra activity concentrations in building materials are 100 and 200 $Bq \cdot kg^{-1}$, respectively, as suggested by ICRP [30]. These considerations are reflected in the alpha index. The recommended upper limit concentration of ^{226}Ra is 200 $Bq \cdot kg^{-1}$, for

Table 7. The external and internal hazard and I_{gamma}, I_{alpha} of gypsum in Egypt.

Sample	H_{ex}	H_{in}	I_{γ}	I_{α}	eTh/eU (ppm)	eU/eRa (ppm)
G1	0.10 ± 0.002	0.12 ± 0.005	0.31 ± 0.03	0.05 ± 0.002	1.02 ± 0.07	0.70 ± 0.08
G2	0.15 ± 0.004	0.17 ± 0.007	0.46 ± 0.04	0.07 ± 0.003	1.20 ± 0.09	0.67 ± 0.07
G3	0.49 ± 0.05	0.61 ± 0.07	1.85 ± 0.17	0.60 ± 0.07	0.13 ± 0.006	0.36 ± 0.03
G4	0.31 ± 0.03	0.38 ± 0.03	1.29 ± 0.11	0.44 ± 0.04	0.38 ± 0.03	0.27 ± 0.02
G5	0.55 ± 0.06	0.68 ± 0.08	2.3 ± 0.22	0.85 ± 0.10	0.16 ± 0.007	0.28 ± 0.02
G6	0.33 ± 0.03	0.43 ± 0.04	1.17 ± 0.10	0.38 ± 0.04	0.62 ± 0.07	0.46 ± 0.05
G7	0.55 ± 0.06	0.75 ± 0.08	1.87 ± 0.17	0.68 ± 0.09	0.20 ± 0.02	0.55 ± 0.06
G8	0.41 ± 0.04	0.51 ± 0.06	1.68 ± 0.16	0.61 ± 0.08	0.15 ± 0.007	0.31 ± 0.03
G9	0.39 ± 0.04	0.45 ± 0.04	1.84 ± 0.17	0.69 ± 0.09	0.36 ± 0.03	0.16 ± 0.004
G10	0.57 ± 0.06	0.74 ± 0.08	1.78 ± 0.16	0.49 ± 0.05	0.09 ± 0.001	0.63 ± 0.07
G11	0.22 ± 0.02	0.27 ± 0.02	0.63 ± 0.07	0.12 ± 0.005	0.68 ± 0.07	0.82 ± 0.15
G12	0.48 ± 0.05	0.62 ± 0.07	1.48 ± 0.15	0.37 ± 0.04	0.38 ± 0.04	0.67 ± 0.08
G13	0.48 ± 0.05	0.65 ± 0.08	1.68 ± 0.11	0.61 ± 0.03	0.42 ± 0.05	0.51 ± 0.06
G14	0.58 ± 0.06	0.79 ± 0.09	2.06 ± 0.19	0.74 ± 0.09	0.05 ± 0.001	0.50 ± 0.06
G15	0.15 ± 0.004	0.18 ± 0.001	1.25 ± 0.14	0.66 ± 0.08	0.54 ± 0.07	0.08 ± 0.001
G16	0.28 ± 0.02	0.35 ± 0.03	1.36 ± 0.20	0.58 ± 0.06	0.27 ± 0.02	0.23 ± 0.02
G17	0.25 ± 0.02	0.32 ± 0.03	0.79 ± 0.09	0.2 ± 0.009	0.80 ± 0.09	0.65 ± 0.08
G18	0.35 ± 0.03	0.47 ± 0.05	0.84 ± 0.16	0.14 ± 0.009	0.07 ± 0.001	1.60 ± 0.11
Min	**0.1 ± 0.002**	**0.12 ± 0.005**	**0.31 ± 0.03**	**0.05 ± 0.002**	**0.05 ± 0.001**	**0.08 ± 0.003**
Max	**0.58 ± 0.06**	**0.79 ± 0.09**	**2.3 ± 0.22**	**0.74 ± 0.09**	**1.2 ± 0.09**	**1.60 ± 0.11**
Mean	**0.37 ± 0.04**	**0.47 ± 0.05**	**1.37 ± 0.16**	**0.46 ± 0.05**	**0.44 ± 0.04**	**0.54 ± 0.06**

which $I_{\alpha} = 1$. The mean computed I_{α} values for the studied gypsum samples are given in **Table 7** for the different gypsum samples. The values of I_{α} of gypsum samples are values varied in the range between 0.05 ± 0.002 to 0.74 ± 0.09 ($Bq \cdot kg^{-1}$) with mean 0.46 ($Bq \cdot kg^{-1}$). For the safe use of a material in the construction of dwellings, I_{α} should be less than unity. The mean calculated values were less than unity.

4) eTh/eU, eU/eRa Elemental Ratio

The eTh/eU ratio has also proven to be useful in the recognition of "geochemical facies". Based on their analyses of numerous rock samples, Adams and Weaver [34], in a classic paper, demonstrated the usefulness of the thoriumto-uranium ratio as an indication of relatively oxidizing or reducing conditions. Uranium has an insoluble tetravalent state that is fixed under reducing conditions, but is transformed to the soluble hexavalent state which may be mobilized into solution. In contrast, thorium has a single insoluble tetravalent state which is geochemically associated with uranium and, therefore, is a useful standard for comparison purposes [35,36]. Adams and Weaver [34] further suggested that ratios <2 were highly suggestive of relative uranium enrichment, and implicates reducing conditions, as contrasted with ratios >7, which indicate preferential removal of uranium, possibly by leaching.

A study of the Th/U, K/U and K/Th elemental ratios may provide an indication whether relative depletion or enrichment of radioisotopes had occurred. The theoretically expected Th/U elemental ratio for normal continental crust is about 3.0, while the corresponding values obtained for this (min, max, mean) eTh/eU ratio are 0.05 ± 0.001, 1.2 ± 0.09 and 0.44 for gypsum samples respectively, which are more less than the expected value.

The equilibrium factor, which was defined by Hussein [37] as P-factor and expressed in the ratio between radiometrically measured equivalent uranium and equivalent radium (eU/eRa) was calculated in all rock and soil samples. This factor is more or less than unity indicating a state of disequilibrium, while P-equal unity indicated the state of equilibrium. From the estimated values, **Table 7** we note that the gypsum samples (G1, G2, G7, G10, G11,

G12, G13, G14, G17 and G18) are in the equilibrium state within experimental error. Furthermore, the average of the radioactivity hazard indices and radium equivalent values are little more than restricted levels to the public. So, some precautions and recommendations should be followed and consider for the public uses these materials while there are disequilibrium between ^{226}Ra and ^{238}U (eU/eRa) in some gypsum samples (G3, G4, G5, G6, G8, G9, G15 and G16).

4. CONCLUSIONS

Exploitation of high-resolution γ-ray spectroscopy provides a sensitive experimental tool in studying natural radioactivity and determining elemental concentrations and dose rates for various rock types. Eighteen kinds of gypsum were collected from natural and manufactured building materials used in Egypt, considered as the most popular ones, and were measured for their natural radioactivity in order to assess the radiological impact when they are used as building materials. The activities of ^{238}U, ^{226}Ra, ^{232}Th and ^{40}K of most the gypsum samples exceed the average level of these radionuclides in regular soil 35 Bq·kg^{-1}, 35 Bq·kg^{-1}, 30 Bq·kg^{-1} and 400 Bq·kg^{-1}, respectively. The corresponding absorbed dose rate from all those radionuclides also exceeds significantly the average value of 55 nGy·h^{-1} from these terrestrial radionuclides in regular soil, and the annual effective dose is based on the standard room model, less than the dose limit of 1 mSv·y^{-1} for all samples under studies.

In addition, according to the dose criteria recommended by the European Union (EC, 1999), two of the samples meet the exemption dose limit of 0.3 mSv·y^{-1}, "G1, G2", three of them—"G11, G17 and G18" meet the upper dose limit of 1 mSv·y^{-1}, and 13 samples clearly exceed this limit.

The extracted values are, in general, comparable to the corresponding ones obtained from other studies in Egypt, and they all fall within the average worldwide ranges. The results can be considered as basic values for distribution of natural radionuclides in the area and will be used as reference information for determining any future changes.

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