

Natural Radioactivity Emitted from Granite and Marble Samples Collected from Sinai Area Egypt and Excess Lifetime Cancer Risk

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Abstract— Due to the widespread use of granite and marble as building and ornamental materials, marble and granite samples from Sinai Location in Egypt, 10 samples granite and 10 samples marble were collected from different places. Combining spectral analysis of gamma rays and the nuclear track detector technique to determine radon and uranium concentrations recommended. It was identified natural radioactivity levels in the samples of marble and granite. High-resolution γ -ray spectrometry and track detectors (CR-39) were used to demonstrate the radiological health hazards, terrestrial absorbed dose rate (DR), and annual effective dose. Concerning the radiological risk, the radium equivalent activity (Raeq) external/internal hazard index (Hex and Hin), activity utilization indices (I_y, I_a) caused by gamma emitting natural radionuclide and excess lifetime cancer risk (ELCR) are determined from the obtained values of ²²⁶Ra, ²³²Th and ⁴⁰K. The granite and marble samples were pulverized, sealed in plastic Marinelli beakers, and their γ -ray spectra measure in the laboratory with an accumulating time 80000 Sec each. The activity concentration ranges for granite samples were (120.02 \pm 2.81 to 184.40 \pm 7.23 Bq/kg) for ²³⁸U, (125.24 \pm 3.67 to 192.70 \pm 6.45 Bq/kg) for ²²⁶Ra, (112.11 \pm 5.21 to 191.92 \pm 7.56) Bq/kg) for ²³²Th and (317.77 \pm 45.97 to 1315.80 \pm 121.38 Bq/kg) for ⁴⁰K. The radioactivity levels determined, the γ -absorbed dose rates in the air above the ground was calculated. The radium equivalent activity Raeq for granite samples were varied from (362.12 to 553.68 Bq/kg) which exceeds the permitted value (370 Bq/kg) for all samples. Elemental concentrations mean values for granite samples were evaluated (9.64 to 14.81 ppm) for ²³⁸U, (10.06 to 15.48 ppm) for ²²⁶Ra, (28.03 to 47.98 ppm) for ²³²Th and (1.23 to 5.08) % for ⁴⁰K. The calculated values of the absorbed dose rate and the indoor annual effective dose for most granite samples and the hazard indices are higher compared with to the recommended worldwide values, while for all marble samples the hazard indices are lower compared with to the recommended worldwide values. Chemical and structural analyses by using (XRF and XRD) technique of the studied samples were also undertaken. The results of X-ray diffraction spectroscopy indicate that the major, minor and trace components vary from one model to another. In addition, physical and chemical characteristics of granite and marble samples were investigated and analyzed for any correlation between the granite characteristics and the radionuclide content. Uranium, radium concentration and radon exhalation rate in twenty granite and marble samples collected from Sinai of Egypt were measured using the sealed can technique based on the (CR-39) track detector. In granite samples, the radon concentration CR_n was found from (91.38 to 109.84 Bq/m³). The values of effective radium concentration CR_a were found to vary from (2.55 to 3.92 Bq/kg) with mean value of (3.05 Bq/kg). The values of mass exhalation rates of radon vary from (29.96 $\times 10^{-8}$ to 46.09 $\times 10^{-8}$ Bq/kg.d) with a mean value (35.81 $\times 10^{-8}$ Bq/kg.d), while the surface exhalation rate of radon varies from (19.94 $\times 10^{-6}$ to 30.68 $\times 10^{-6}$ Bq/m².d) with a mean value of (23.83 $\times 10^{-6}$ Bq/m².d). Uranium content in these samples has been found, it is varying from (9.64 to 14.81 ppm) with mean value of 11.09 ppm. It was found that the average values of radon exhalation rate, the effective concentration of radium and uranium concentration (marble only) in granite samples much lower than the recommended world values of (57.600 mBq/m².h, 370 Bq/kg and 3 ppm) respectively. Hence it can be concluded that the study area is safe from the health hazard of radium.

Index Terms— Enhance radionuclides, Radon. High-resolution γ -ray spectrometry, track detectors (CR – 39), radiological indices and the mass exhalation rate of radon; XRF.

1 INTRODUCTION

Natural radiation refers to ionizing radiation that arise either from cosmic rays and high energy that enter the Earth's atmosphere from outer space or from naturally radioactive source (NORM) present in the Earth's crust. It is characterized by radiation from artificial radiation produced by nuclear or atomic transitions of man-made. Human exposure to natural background radiation is an ongoing feature and inescapable to life on Earth. The effective dose due to ionizing radiation for these members of the public differs significantly from where they live, occupation, personal habits, diet and type of construction and the use of home

style. The radiation of higher levels is associated with volcanic rocks, such as granite, and low levels are associated with marble rock. There are exceptions, however, as some shale of granite and marble rocks have a relatively high content of radionuclides. In addition to the natural source granite and marble radioactivity is also affected by man-made activities [1].

Certain levels of environmental radiation associated with the ground geological configuration for each rocky area of separation and the content in ²³⁸U, ²³²Th and ⁴⁰K of the rock from which granite arise in each region. The naturally occurring uranium contains 99.2745 % by weight ²³⁸U, 0.7200 % ²³⁵U, and 0.0055 % ²³⁴U [2]. Uranium (U), thorium (Th) and potassium (K) are the major radioactive nuclides contained in the earth's crust [3]. Since the age of the earth around the age of ²³⁸U, was found other radioactive elements from the ²³⁸U

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series is also in the cortex. Radionuclides are carcinogen in human and a known kidney toxin. The toxic effects of chemicals from radionuclides, especially uranium as a heavy metal on public health issues were concerned, especially in areas where pollution of local granite and marble of radioactive material was made [4]. These radionuclides accumulate in various organs once in the system. Due to their long half-lives (^{232}Th : 1.4×10^{10} yrs., ^{238}U : 4.47×10^9 yrs. and ^{40}K : 1.28×10^9 yrs.) and chemical behavior they deliver radiation doses which results in alteration in the structure of chromosomes leading to the development of different types of diseases including cancers. ^{232}Th , ^{238}U and ^{40}K are radiotoxic even though a small quantity of stable potassium is nutritionally important to the human system [5]. Environmental problems associated with technological enhance radionuclides in the uranium mine sites of Sinai can be radiological hazardous if the doses are very high and are not monitored. The spread of radioactive natural source (NORM) in the environment is a way of exposure to radiation likely for members of the public special for granite and marble.

Materials derived from rocks and soil contains mainly natural radioactive elements uranium (^{226}Ra), thorium series (^{232}Th), as well as potassium (^{40}K). Marble, in particular, holds a focus to enhance this natural radionuclides element compared with the very low abundance of these elements observed in the earth's crust and the mantle. All building materials including marble and granite contain different amounts of natural radionuclides. Materials derived from rock and soil contains mainly natural radioactive elements uranium (^{226}Ra), thorium series (^{232}Th), as well as potassium (^{40}K). Igneous rocks are enriched configured marble strongly in ^{238}U and ^{232}Th (on average 5 ppm U and 15 ppm of ^{232}Th), compared with granite and basaltic rocks formation or ultramafic (<1 ppm of ^{238}U) [6-8]. ^{238}U in the series and the decay chain from radium (^{226}Ra) is radiologically the most important and therefore reference is often made for ^{226}Ra instead of the U. The worldwide average concentrations of ^{226}Ra , ^{232}Th and ^{40}K in the earth's crust are about (50, 50 and 500 Bq/kg), respectively [9, 10]. The present work is aiming to determine some metal concentrations and measure the natural radioactivity levels of ^{226}Ra , ^{232}Th , and ^{40}K in the samples of granite and marble materials collected from Sinai region, Egypt. Moreover the main objectives of the study to determine the concentrations of radon gas and exhalation rate, in order to detect any harmful rays that would affect human background levels of radioactivity in the Egyptian building materials, that can be used as reference information to assess any changes in the radioactive background level in our homes. Also to assess the radiological Hazard indicators in the air and compare this results with international levels.

2 EXPERIMENT AND METHODOLOGY

2.1 Granite and marble sampling preparation

A total of twenty granite and marble samples were collected from different geographical areas of Sinai in Egypt as explained in Figure 1. Ten granite samples from different

locations and ten marble are collected. Granite and marble samples were grinding by using Boll mill and sieved at $\leq 63 \mu\text{m}$ powder. Each of the samples was packed and sealed in an airtight PVC container to allow radioactive equilibrium among the radon (^{222}Rn), thoron (^{220}Rn), and their short lived progenies. On an average 0.25 kg of soil was taken for each sample and transferred to 300 ml labeled Marinelli beakers. The samples were dried in an oven at about 383 oK for 24 hours before measurement [11]. It was packed the dry soil samples in a plastic container of 250 ml to full size with a unified bloc. These containers were tightly protected and externally to ensure that all products daughter of uranium and thorium, particularly gas, radon formed, not escape. The net weight of the sample was determined before counting. The soil samples were stored about 35 days before counting so as to ensure ^{226}Ra and its short-lived progeny to reach radioactive equilibrium [12].

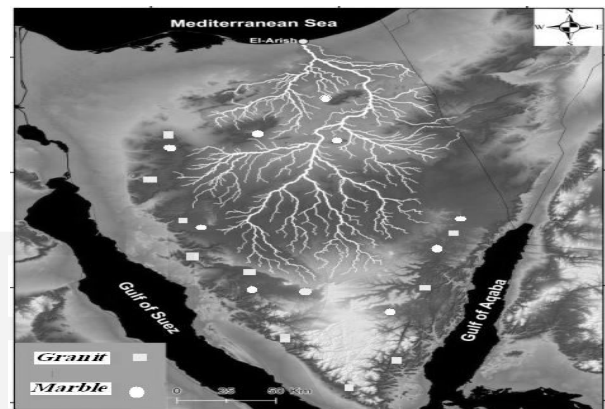


Figure 1: Map of the granite and marble samples sites in Sinai Egypt

2.2 Detector calibration

2.2.1 HPGe detector.

HPGe detector has a relative efficiency of 40% and the full width at half maximum (FWHM) of 1.89 keV in 1332 keV of the γ -rays line of ^{60}Co . Heavy lead shield about 10 cm thickness was but surrounded the detector with inside dimensions 28 cm diameter and 40.5 cm height to reduce background radiation originating from soil sample and cosmic rays. Spectrometer was calibrated using each source of uranium nitrate and potassium chloride standard sources in the same geometry as samples by using a range of high quality certified reference materials (IAEA, RG-set). The output spectrum analysis was supported with the help of Canberra Genie 2000 version 3.0 software. Activities estimation of ^{226}Ra (or activities ^{238}U samples supposed to be in the case of radiation equilibrium) were from activates of ^{214}Pb (351.9 keV), ^{214}Bi (609.3, 1764.5 keV) and ^{226}Ra (185.99 keV). It was also monitoring several ^{214}Pb peaks and ^{214}Bi . The use of gamma-ray energies of ^{212}Pb (238.6 keV) and ^{228}Ac (338.4, 911.07, 968.90 keV) to estimate the concentration of ^{232}Th . Natural abundance of ^{235}U is only 0.72% of the total uranium content, and thus is not considered in this study. Activity concentration of ^{40}K was measured directly by gamma rays (1460.8 keV) [13].

2.2.2 (CR-39) detector

By using (CR-39) detectors, the concentration of radon gas and exhalation rate can be calculated, because its ability to record tracks in different levels of sensitivity recording. It should be performed calibration of (CR-39), where the integration radon concentrations are known [14]. Detector (CR-39) used in this work was supplied by Pershore Mouldings, Ltd., UK, in the form of large sheets which were cut into 2 cm x 2cm squares. Sample is placed in a glass cylinder with a radius of 3.5 cm and a length of 10 cm. It was closed cylindrical container and (CR-39) detector was putting in the bottom of the chamber cover. Samples were stored for at least 30 days. The concentrations of alpha particles emitted from radon in soil samples were determine using nuclear track detector (CR-39) with thickness (250 μ m), and an area of about (1 \times 1cm²). By using a sealed cup technique as shown in Figure 2, the concentration of radon gas in soil samples was obtained. After the time of irradiation (45 Days), (CR-39) detector were etched in (6.25 N), and sodium hydroxide at a temperature of (⁶⁰Co) for (6 hours). Optical microscope with magnification (400 X) was used to record tracks density (ρ).

2.3. EDEX and XRD technique

(EDS or EDX) is an analytical technique used to analyze the elements or chemical properties of the sample. It is one of the variants of X-ray fluorescence spectroscopy analyzing X-rays emitted by the matter in response to being hit with charged particles, e.g. in SEM the sample is subjected to an energetic electron beam (20 keV) resulting in production of characteristic X-rays from the sample where the incident beam, expel an electron from one of the inner shells. An electron from the outer shells, which is higher energy and then engage the hole, the difference in energy can be emitted in the form of X-rays. It can measure the number and energy of X-rays emitted from the sample through the dispersive spectrometer energy. X-rays as energy is the difference in energy between the two shells attributes, and installation of atomic element that has been emitted, and this allows the elemental composition of the sample to be measured. It has been issued in the form of X-rays, the technical conditions of X-rays tube used in this investigation with filtered copper radiation $\lambda = 1.542 \text{ \AA}$, X-ray tube operated in (40 kV and 30 mA) current anodes in all parts of the measurements. Scan pattern recorded at a rate of 40 minutes. It has maintained the above process conditions during all relevant measurements. Hence, it is a plot of the intensity against the angle 2λ , where λ is the reflection angle of X-ray given in Bragg's equation.

2.4. Calculation of activity concentration

The activity concentration of the radionuclides found in the soil samples were determined using the following equation, and expressed in Bq/kg:

$$A = \left(\frac{C_{NP}}{g_{dl} \times \epsilon (E_\gamma) \times m} \right) Bq / kg \quad (1)$$

Where: C_{NP} = net peak counts for a given energy line, g_{dl} = absolute gamma decay intensity for the specific energy photo-peak, $\epsilon (E_\gamma)$ = the absolute peak efficiency of the detector's at

energy E, and the mass sample is m in kg. The measured of mean activity concentration of ²²⁶Ra and ²³²Th dependant on the decay of the shortest-lived radionuclides in ²³⁸U and ²³²Th decay chains. The related errors were associated based on the following equation (2) [17]:

$$W_{mean} = \frac{\sum_{i=1}^n \frac{a_i}{(b_i)^2}}{\sum_{i=1}^n \frac{1}{(b_i)^2}} \quad (2)$$

Where: $a_i \pm b_i$ = respective associated activities (a_i) and uncertainty (b_i) of the shorter-lived radionuclides in ²³⁸U and ²³²Th decay chains, $i = 1, 2, \dots, n$

And the propagated uncertainty in the weighted mean is:

$$\Delta W_{mean} = \left(\sqrt{\sum_{i=1}^n \frac{1}{(b_i)^2}} \right)^{-1} \quad (3)$$

The gamma-ray peaks associated with decays from ⁴⁰K at 1460.21 keV was used to determine the activity concentrations for the nuclei. The activity concentration of ²²⁶Ra present in the samples was estimated indirectly from one of the reference peaks in radium indicators. The contribution of ²²⁶Ra through its (3.59 % branching ratio) gamma ray at the energy of 186.1 keV was calculated by employing the spectral interference correction method [18] using the least spectrally disturbed peak (reference peak) at 295.2 keV from the decay of ²¹⁴Pb. The net peak area of ²²⁶Ra at the energy line of 186.1 keV was then estimated by employing the equation [19]:

$$C_{NP \text{ at } 186.1keV (^{226}Ra)} = \frac{(g_{dl})_{at 186.1keV} \epsilon_{at 186.1keV} [F_C F_S]_{at 186.1keV}}{(g_{dl})_{at 295.2keV} \epsilon_{at 295.2keV} [F_C F_S]_{at 295.2keV \text{ Ref}}} \times C_{NP \text{ at } 295.2keV (^{214}Pb)_{Ref}} \quad (4)$$

where $C_{NP \text{ at } 295.2keV (^{226}Ra)}$ are the net peak counts at 186.1 keV line for ²²⁶Ra, $C_{NP \text{ at } 295.2keV (^{214}Pb)}$ are the net peak counts at 295.2 keV line for ²¹⁴Pb (reference peak), g_{dl} are the respective gamma decay intensity for 186.1 keV and 295.2 keV lines, ϵ are the respective efficiency values for 186.1 keV and 295.2 keV lines and F_C and F_S are the correction factors of the true coincidence summing peak and self-absorption. In the current work, the effect of self-absorption and true coincidence summary peak were assumed to be minimal (= 1).

2.5. Calculation of radiological risk indices

The measured activity of ²³⁸U, ²³²Th and ⁴⁰K were converted into doses by applying the factors 0.461, 0.604 and 0.0417 for uranium, thorium and potassium respectively as:

$$D_R = (0.461A_R + 0.604A_{Th} + 0.0417A_K) nGy / h \quad (5)$$

Where: D_R is the gamma dose rate in the outdoor air at 1m above the ground and A_R , A_{Th} and A_K are the activity concentrations (Bq/kg) of radium, thorium and potassium,

respectively in the samples. The conversion factors mentioned above, it is assumed that all products decay of ^{226}Ra and ^{232}Th are in the radiation equilibrium [20]. The published maximal admissible (permissible) dose rate is (51 nGy/h) [21]. It must be taking into account the conversion coefficient from absorbed dose in air to the effective dose received by an adult to estimate the annual effective dose rate in air. This value is (0.7 Sv/Gy) for environmental exposure to gamma rays of moderate energy published in UNSCEAR. The outdoor and indoor occupancy factors are 0.2 and 0.8 respectively. The annual effective dose equivalent is given by [22]:

$$AEDE_{outdoor} = (D_R \times DCF \times 0.2 \times T) \text{ mSv/yr} \quad (6)$$

$$AEDE_{indoor} = (D_R \times DCF \times 0.8 \times T) \text{ mSv/yr}$$

Where: DCF = dose conversion factor (0.7 Sv/Gy) and T = time (8760 H/yr). The world average of outdoor annual effective dose equivalent (AEDE) of terrestrial gamma ray is (0.046 mSv/yr). The annual effective dose external is given by the equation (7) [22, 23]:

$$AEDE_{EX} = (\sum AEDE_{outdoor} + AEDE_{indoor}) \text{ mSv/yr} \quad (7)$$

Excess lifetime cancer risk (ELCR) was calculated by using equation (8):

$$ELCR = AEDE_{outdoor} \times E_{LD} \times C_{RF} \quad (8)$$

Where: E_{LD} = Expected lifetime duration (70 yrs.) and C_{RF} = fatal cancer risk factor (for stochastic effects, [22] uses a value of 0.05 for the general public). The world average annual effective dose equivalent (AEDE) from outdoor terrestrial gamma radiation is (0.046 mSv/yr).

Radium equivalent activity (Ra_{eq}) is used to assess the hazards associated with materials that contain ^{226}Ra , ^{232}Th and ^{40}K in Bq/kg, which is, calculated on the assumption that 370 Bq/kg of ^{226}Ra or 260 Bq/kg of ^{232}Th or 4810 Bq/kg of ^{40}K produce the same gamma dose rate. The Ra_{eq} of the sample in Bq/kg can be achieved using the equation [23-25]:

$$Ra_{eq} = [(A_{Th} \times 1.43) + (A_K \times 0.077) + (A_U)] \text{ Bq/Kg} \quad (9)$$

The radium equivalent is the most useful guideline for regulating safety standards on radiation protection for the general public and as published, the maximal admissible (permissible) Ra_{eq} is 370 Bq/kg.

In order to evaluate the external hazard index (H_{ex}), a model proposed by Beretka and Mathew [24] was used. This index actually evaluates the hazard of the natural gamma radiation. However, the mean purpose of this index is to reduce the dose of radiation to be somewhat equivalent the allowed dose of 1mSv/yr [26, 27]. The equation used in evaluating H_{ex} :

$$H_{ex} = (A_U / 370) + (A_{Th} / 259) + (A_K / 4810) \leq 1 \quad (10)$$

The standard model criterion take into consideration that the external hazard of the gamma rays corresponds to the maximum radium equivalent active of 370 Bq/kg for this article [24, 28].

$$H_{in} = (A_U / 185) + (A_{Th} / 259) + (A_K / 4810) \leq 1 \quad (11)$$

Where: A_{Ra} , A_{Th} and A_K are the activity concentrations of ^{238}U , ^{232}Th and ^{40}K in Bq/kg, respectively. If the maximum concentration of radium is half that of the normal acceptable limit then H_{in} will be ≤ 1 .

A number of indices dealing with the assessment of the external and internal radiations originating from building materials and gamma concentration indices have been proposed by several investigators [25, 26]. As proposed by the European Commission [29], the gamma index was evaluated in the present work.

$$I_\gamma = A_{Ra} / 150 + A_{Th} / 100 + A_K / 1500 \quad (12)$$

A_{Ra} , A_{Th} and A_K are the activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K in Bq/kg, respectively. Values of index $I_\gamma \leq 1$ corresponds to a dose rate criterion of (0.3 mSv/yr) while $I_\gamma \leq 3$ correspond to (1 mSv/yr). Thus, the activity concentration index should be used only as a screening tool to identify materials that may be a source of concern for use cover materials. According to this standard dose and materials with $I_\gamma > 3$ should avoid use as building material [27-31].

So far, several alpha indices have been proposed to assess the exposure level due to radon inhalation originating from soil materials. While the values of I_α for critical value are unity ($I_\alpha = 1$). The recommended exemption and upper level of ^{226}Ra activity concentrations in soil are 100 and 200 Bq/kg, respectively, as suggested by [32] ($I_\alpha = 1$). These respects are reflected in the alpha index. The recommended upper limit concentration of ^{226}Ra is 200 Bq/kg, for which ($I_\alpha = 1$). The alpha index was determined using the following formula:

$$I_\alpha = A_{Ra} / 200 (\text{Bq / kg}) \quad (13)$$

Where A_{Ra} is the specify activity concentration of ^{226}Ra assumed in equilibrium with ^{238}U

2.7. Evaluation of ^{222}Rn

In order to evaluate the radon risk in a given atmosphere, it is necessary to check the relation between the activity concentrations of uranium and radon for the samples under investigations. The concentrations of alpha particles emitted from radon in soil samples and the exhalation rate measurements were determined by using nuclear track detector (CR-39). According to the following equation (14), the density of the tracks (ρ) in the samples was calculated.

$$\text{track} \cdot \text{density} (\rho) = \frac{\text{Average} \cdot \text{number} \cdot \text{of} \cdot \text{total} \cdot \text{pits} (\text{tracks})}{\text{Area} \cdot \text{of} \cdot \text{field} \cdot \text{view}} \quad (14)$$

The radon gas concentrations in the samples were obtained by the comparison between track densities registered on the detectors of the samples and that of the standard soil samples. Radon concentrations (C_{Rn}) were calculated by the equation (15) [33-36]:

$$C_{Rn} = \frac{N_0 t_0 \rho}{\rho_0 t} (\text{Bq / m}^3) \quad (15)$$

Where:

N_0 = activity concentration for a record source (^{226}Ra),

t_0 = exposure time record for the source (^{226}Ra),

ρ_0 = track density for a record source (^{226}Ra), (track/cm²),

ρ = track density for the sample (track/cm²), and

t = exposure time of the sample. The effective radium content of the solid sample can be calculated by the formula [37-39]:

$$C_{Ra} = \left(\frac{\rho}{kT_e} \right) \left(\frac{hA}{M} \right) (Bq / kg) \quad (16)$$

Where: M is the mass of sample in kg, A is the cross-section of the cylindrical space can in m² and h is the distance between the detectors and the highest of the sample in m. ρ is the track density counted, k is the track detector (CR-39) calibration factor and T_e denotes the effective exposure time. The exhalation rate was calculated using the following equation (17) [33-35, 36]:

$$E_x = \frac{CV\lambda}{A(T + \frac{e^{-\lambda T} - 1}{\lambda})} \quad (17)$$

Where: E_x is the radon exhalation rate (Bq/kg.d), C is the measured radon concentration by the (CR-39) detector (Bq/m³.d), λ is the decay constant of radon gas (d⁻¹), T is the exposure time (d), V is the volume of the radon chamber (m³) and A is the area covered by the can (m²). The radon exhalation rate in terms of mass can be calculated by using the following expression [34, 36]:

$$E_x(M) = C_{Ra} [(\lambda_{Ra} / \lambda_{Rn})] (1/T_e) (Bq / kg.d) \quad (18)$$

Where λ_{Ra} and λ_{Rn} are the decay constant of ^{226}Ra and radon ^{222}Rn respectively. They are related with half-life period in the following way:

$$\lambda_{Ra} = \log_e 2 / T_{1/2} \quad (T_{1/2} = 1622 \text{ years}) \quad \text{and} \quad \lambda_{Rn} = \log_e 2 / T_{1/2} \quad (T_{1/2} = 3.8 \text{ days})$$

Similarly the radon exhalation rate in terms of area can be calculated by using the following expression:

$$E_x(S) = [E_x(M)] (M / A) (Bq / m^2.d) \quad (19)$$

The annual effective dose (H_E) in the present work was calculated from the following formula according [10, 25, 38]:

$$H_E = C \times F \times T \times D (mSv / yr) \quad (20)$$

Where: C is the radon concentration in Bq/m, F is the ^{222}Rn indoor equilibrium factor (0.4), T is time (8760 h/yr), and D for dose conversion factor (9×10^{-6} mSv/yr (Bq/m³)⁻¹).

3. Result and Discussions

Detailed information on specific activities of ^{238}U , ^{226}Ra , ^{232}Th and ^{40}K in samples of granite and marble in Sinai, Egypt is not available in the literature to some extent. The measurement of the specific activity of ^{238}U , ^{232}Th and ^{40}K in the granite and marble samples using gamma-ray spectrometric technique and estimation of the gamma dose rate of these radionuclides

has been done. Also, the radiological parameters such as indices of radium equivalent activity, external hazard index, and outdoor absorbed gamma dose rate were calculated to estimate the exposure risk in granite and marble samples, Sinai Egypt.

3.1 Activity concentration

It has been identified specific activities of natural radionuclides from ^{238}U , ^{226}Ra , ^{232}Th and ^{40}K using gamma-ray spectroscopy in different types of granite and marble that have been collected from the Sinai region of Egypt. Table 1 Shows average activity concentrations together with their associated uncertainties reported at standard deviation. The concentrations of certain activity in the granite samples investigated were found to vary from (120.02 ± 2.81 to 184.40 ± 7.23 Bq/kg) for ^{238}U (125.24 ± 3.67 to 192.70 ± 6.45 Bq/kg) for ^{226}Ra , (112.11 ± 5.21 to 191.92 ± 7.56 Bq/kg) for ^{232}Th and from (317.77 ± 45.97 to 1315.80 ± 121.38 Bq/kg) for ^{40}K , respectively. Although the lowest activity concentration of ^{226}Ra was observed in G9 sample, the highest value was in G1 sample. For ^{232}Th the lowest activity value was observed in G3 sample and the highest value was obtained in granite sample referred as G1. It is known that potassium is present high in almost all geological granite samples. In case of ^{40}K , granite sample (G4) showed the highest activity value. The specific activity of ^{238}U , ^{226}Ra , ^{232}Th and ^{40}K values specified in the granite samples vary from one sample to another. These differences activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K in the samples may depend to investigate the content of uranium, thorium and potassium under the earth's crust from where the granite samples were obtained.

The radioactivity concentration values in the selected marble samples ranged from (40.08 ± 4.75 to 78.40 ± 7.90 Bq/kg) for ^{238}U , (35.36 ± 7.88 to 85.99 ± 11.36 Bq/kg) for ^{226}Ra , (35.23 ± 4.59 to 67.04 ± 5.90 Bq/kg) for ^{232}Th , and (284.11 ± 14.47 to 323.81 ± 26.18 Bq/kg) for ^{40}K . All samples have ^{40}K activity concentrations lower than the regular soil values. Moreover samples M3, M4 and M8 have ^{226}Ra and ^{232}Th activity concentrations higher more than the regular soil concentrations. It is clear that the mean activity concentrations of ^{238}U , ^{232}Th and ^{40}K in marble samples are within the permissible levels 50, 50 and 500 Bq/kg [10], while that in granite samples are higher than the permissible levels.

3.2. Outdoor terrestrial gamma dose rates DR, the annual effective dose (AEDE) and Excess Lifetime Cancer Risk (ELCR).

Table 1 shows the absorbed dose rate DR (nGy/h) and the annual effective dose AEDE (mSv/yr) estimated for the granite and marble samples examined. The annual effective dose limit was considered to be 1 mSv/yr. Outdoor gamma dose rates were determined in 20 sampling geographical locations as described in Figure 1. As observed in Table 1, the outdoor gamma dose rates measured in granite samples were from (163.91 nGy/h to 255.07 nGy/h) and with mean (198.71 nGy/h). The mean outdoor absorbed dose rate from all granite samples is about three times higher than the world average (populated-weighted). The absorbed dose rate for

Granite Samples	A_U (Bq/Kg)	A_{Ra} (Bq/Kg)	A_{Th} (Bq/Kg)	A_K (Bq/Kg)
G1	184.40±7.23	192.70±6.45	191.92±7.56	1123.78±58.02
G2	126.38±1.82	162.48±1.92	155.32±1.70	1129.32±59.85
G3	120.02±2.81	135.75±2.09	112.11±5.21	1125.14±58.47
G4	138.93±0.14	175.28±3.84	139.11±0.89	1315.80±121.38
G5	121.32±2.61	135.00±2.21	128.49±2.59	1054.84±35.27
G6	124.6±2.10	129.74±3.00	143.49±0.19	750.74±65.09
G7	168.14±4.70	163.06±2.00	171.16±4.24	1030.18±27.13
G8	139.02±0.15	145.26±0.67	134.54±1.62	317.77±207.97
G9	132.83±0.81	125.24±3.67	141.74±0.47	1077.77±42.83
G10	124.62±2.09	132.61±2.57	131.68±2.08	554.33±129.90
Mean	138.03±21.56	149.71±22.52	144.96±22.81	947.97±70.49
Max	184.40±7.23	192.70±6.45	191.92±7.56	1315.8±121.38
Min	120.02±2.81	125.24±3.67	112.11±5.21	317.77±45.97
Marble Samples	A_U (Bq/Kg)	A_{Ra} (Bq/Kg)	A_{Th} (Bq/Kg)	A_K (Bq/Kg)
M1	48.56±1.95	35.36±7.88	46.72±0.80	294.24±17.46
M2	48.96±1.82	48.18±3.01	44.69±1.47	284.11±14.47
M3	78.4±7.90	85.75±11.27	64.26±4.99	291.31±16.60
M4	70.94±5.44	85.99±11.36	67.04±5.90	306.38±21.04
M5	45.07±3.10	50.65±2.07	36.29±4.24	310.61±22.29
M6	40.08±4.75	45.12±4.17	35.23±4.59	291.79±16.74
M7	43.42±3.64	51.64±1.69	36.62±4.13	302.54±19.91
M8	60.3±1.93	51.19±1.87	54.28±1.69	297.98±18.56
M9	51.94±0.83	45.31±4.10	57.16±2.64	318.82±24.71
M10	56.88±0.80	61.79±2.16	49.24±0.03	323.81±26.18
Mean	54.46±18.15	56.10±21.51	49.15±16.27	302.16±89.21
Max	78.40±7.90	85.99±11.36	67.04±5.90	323.81±26.18
Min	40.08±4.75	35.36±7.88	35.23±4.59	284.11±14.47

Table 1a: Activity concentration of ²³⁸U, ²²⁶Ra, ²³²Th and ⁴⁰K, absorbed dose rate (DR), annual effective dose rate (AEDE), and Excess Lifetime Cancer Risk for different Egyptian granite and marble samples

marble samples under investigation varied from 54.89 to 94.14 with mean value 69.04 nGy/h, as presented in Table 1. It is clear that these values were high compared to the recommended value of (55.00 nGy/h) by [10] for all granite and marble samples except marble sample M6.

The calculated annual outdoor effective dose equivalent with mean due to activity of natural radionuclides in granite and marble samples, vary from (0.20 mSv/yr to 0.31 mSv/yr) and from (0.07 mSv/yr to 0.12 mSv/yr) with an average of (0.24 mSv/yr and 0.08 mSv/y) respectively Table 1. The estimated results for indoor annual effective dose equivalent in granite and marble samples are given in Table 1. The indoor annual effective dose equivalent ranged from (0.80 to 1.25 mSv/yr) from (0.27 to 0.46 mSv/yr) with a mean of (0.97 and 0.34 mSv/yr) respectively. It is noted that the indoor annual effective dose equivalent (AEDE) exceeds the dose criterion of (1 mSv/yr) (EC, 1999; ICRP, 1991) for four granite samples as follows: G1,G2,G4,G7.This means that the general population of people living in area used granite or marble has the burden of total annual average effective dose equivalent (AEDE)ex

Granite Samples	D_R (nGy/yr)	(AEDE) outdoor (mSv/yr)	(AEDE) indoor (mSv/yr)	ELCR $\times 10^{-3}$
G1	255.07	0.31	1.25	1.09
G2	218.61	0.27	1.07	0.94
G3	179.26	0.22	0.88	0.77
G4	222.24	0.27	1.09	0.95
G5	186.15	0.23	0.91	0.80
G6	180.35	0.22	0.88	0.77
G7	224.58	0.28	1.10	0.96
G8	163.91	0.20	0.80	0.70
G9	190.82	0.23	0.94	0.82
G10	166.15	0.20	0.82	0.71
Mean	198.71	0.24	0.97	0.85
Max	255.07	0.31	1.25	1.09
Min	163.91	0.20	0.80	0.70
Marble Samples	D_R (nGy/yr)	(AEDE) outdoor (mSv/yr)	(AEDE) indoor (mSv/yr)	ELCR $\times 10^{-3}$
M1	57.62	0.07	0.28	0.25
M2	61.86	0.08	0.30	0.27
M3	91.67	0.11	0.45	0.39
M4	94.14	0.12	0.46	0.40
M5	58.89	0.07	0.29	0.25
M6	54.89	0.07	0.27	0.24
M7	59.21	0.07	0.29	0.25
M8	69.78	0.09	0.34	0.30
M9	69.72	0.09	0.34	0.30
M10	72.63	0.09	0.36	0.31
Mean	69.04	0.08	0.34	0.30
Max	94.14	0.12	0.46	0.40
Min	54.89	0.07	0.27	0.24

Table 1b: Activity concentration of ²³⁸U, ²²⁶Ra, ²³²Th and ⁴⁰K, absorbed dose rate (DR), annual effective dose rate (AEDE), and Excess Lifetime Cancer Risk for different Egyptian granite and marble samples

from both indoor and outdoor exposure of 1.21 mSv/yr and 0.46 mSv/yr which are higher than the maximum permissible dose of 1 mSv/yr, for granite samples, while less than the maximum permissible dose, recommended for the public by [23] for marble samples.

By using equation (8), the ELCR was calculated and results are shown in Table 1. The evaluated ELCR in almost all marble samples were comparatively low making reference to the world average value of (0.29×10^{-3}) [22]. On the other hand, in granite samples, the calculated ELCR were averagely high. In some specific locations like G1 the calculated (ELCR) were 1.09 times higher than the world's average recommended value. It should be noted that the ELCR as a health parameter cannot be translated to a probability that an adverse health effects will occur, and is unlikely to be proportional to the risk of any fatal event [22].

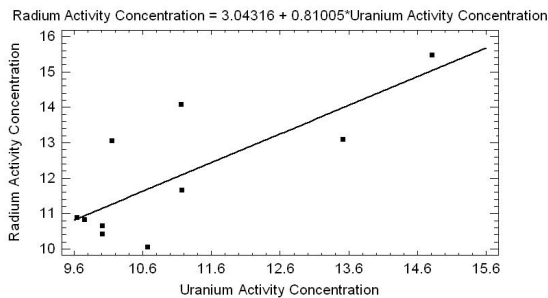


Figure 2, a: Correlation between ^{238}U and ^{226}Ra for Egyptian granite samples.

3.3. Radium equivalent (Ra_{eq}), external hazard index (H_{ex}) and internal hazard index (H_{in}):

The distribution of ^{226}Ra , ^{232}Th and ^{40}K in the studied granite and marble samples were not uniform. In this study, it was observed the non uniformity of natural radionuclide in the samples, Ra_{eq} was calculated to compare the specific activity of the studied samples and the results are summarized in

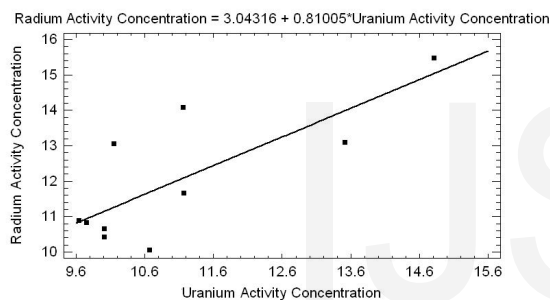


Figure 2, a: Correlation between ^{238}U and ^{226}Ra for Egyptian granite samples.

Table 2. The calculated radium equivalent for marble samples ranged between (117.97 and 205.45 Bq/kg). The obtained values of Ra_{eq} in the studied marble samples are lower than the recommended amount of 370 Bq/kg maximum value [22], which corresponds to an annual effective dose of 1 mSv. Thus, these marble samples are within the recommended safety limit when used as building raw materials and products.

The results obtained for the radium equivalent activity index Ra_{eq} of all granite samples are varied from (362.12 to 553.68 Bq/kg) as listed in Table 2. It is observed that the values of radium equivalent index of granite samples (G8 and G10) are lower than the recommended value 370 Bq/kg [22] while the other granite samples are higher than the recommended value. The high Ra_{eq} values calculated in most granite samples may be attributed to the high concentration of the radionuclides ^{238}U , ^{232}Th and ^{40}K in these materials as shown in Table 2. From the results it is clear that there are significant differences in Ra_{eq} of different materials. This fact is important to select the appropriate materials for use in building and construction, especially with regard to those that have significant differences in their activities. A large variation in the radium equivalent activity indicates that it is advisable

to monitor radioactivity levels of the material from a new source before adopting it for use as a building material.

The average external radiation hazard index (H_{ex}) for the granite and marble samples were 1.47 and 0.40 respectively. These values were low compared to the maximum value of unity in some samples and higher in samples from G1 to G7 and G9, which corresponds to the maximum activity of radium 370 Bq/kg for all terrestrial materials. This value must be less than the index unit to the risk of radiation would be minimal [40]. For the maximum value of H_{ex} to be less than unity, the maximum value of Ra_{eq} must be less than 370 Bq/kg. According to the calculated equation of H_{ex} [24, 40] the values of H_{ex} for the studied marble samples ranged from 0.31 (M6) to 0.52 (M3), values which indeed are less than unity. While the values of H_{ex} for the studied granite samples are higher than unity except for (G3, G8 and G10). The calculated values of H_{in} for the studied marble samples range from 0.41 (M6) to 0.73 (M3). Once again, all these values are less than unity. The calculated values of H_{in} for all the studied granite samples are higher than unity, which ranged from 1.3 to 1.97 with mean value 1.5.

Granite Samples	Ra_{eq} (Bq/Kg)	IGamma	I Alpha	Hex	Hin
G1	553.68	3.95	0.96	1.47	1.97
G2	471.55	3.39	0.81	1.18	1.52
G3	382.70	2.78	0.68	0.99	1.32
G4	475.52	3.44	0.88	1.19	1.56
G5	399.96	2.89	0.67	1.04	1.37
G6	392.74	2.80	0.65	1.05	1.38
G7	487.14	3.49	0.82	1.33	1.78
G8	362.12	2.53	0.73	0.96	1.34
G9	410.92	2.97	0.63	1.13	1.49
G10	363.60	2.57	0.66	0.96	1.30
Mean	429.99	3.08	0.75	1.13	1.50
Max	553.68	3.95	0.96	1.47	1.97
Min	362.12	2.53	0.63	0.96	1.30
Marble Samples	Ra_{eq} (Bq/Kg)	IGamma	I Alpha	Hex	Hin
M1	124.83	0.90	0.18	0.37	0.50
M2	133.96	0.96	0.24	0.36	0.50
M3	200.07	1.41	0.43	0.52	0.73
M4	205.45	1.45	0.43	0.51	0.71
M5	126.46	0.91	0.25	0.33	0.45
M6	117.97	0.85	0.23	0.31	0.41
M7	127.30	0.91	0.26	0.32	0.44
M8	151.75	1.08	0.26	0.43	0.60
M9	151.60	1.09	0.23	0.43	0.57
M10	157.14	1.12	0.31	0.41	0.56
Mean	149.65	1.07	0.28	0.40	0.55
Max	205.45	1.45	0.43	0.52	0.73
Min	117.97	0.85	0.18	0.31	0.41

Table 2: Radium equivalent (Ra_{eq}), I Gamma, I Alpha and external and internal hazard index (Hex, Hin) for different Egyptian granite and marble samples

3.4. Activity Indices Gamma-index (I_γ) and Alpha Index (I_α):

Displays the average I_γ values calculated from the measured activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K for various all samples and all areas in terms of collected in Table 2. The radiation level index I_γ of marble and granite samples are varied from 0.85 to 1.45 and from 2.53 to 3.95, respectively which is found to be less than unity for most marble samples except (M3,M4,M8,M9 and M10), and higher than unity for all granite samples, as listed in Table 2. The index I_γ is correlated with the annual dose due to the excess external gamma radiation caused by superficial material. Values of index $I_\gamma \leq 1$ correspond to (0.3 mSv/yr), while $I_\gamma \leq 3$ correspond to (1 mSv/yr). Thus, the focus of activity index should be used only as a screening tool to identify materials that may be a source of concern for use cover materials. According to this standard dose, granite materials with $I_\gamma \geq 3$ (G1,G2,G4 and G7) should be avoided, since these values correspond to dose rates higher than 1.mSv/yr [23], which is the highest value of dose rate in air recommended for population [10,22]. The mean computed I_α values for the studied samples are given in Table 2 for the different granite types and the regions where they were collected. The values of I_α ranged from (0.63 to 0.96), with the mean value of 0.75. For the safe use of a material in the construction of dwellings, I_α should be less than unity. The mean computed I_α values for the studied marble samples are less than unity with value 0.28.

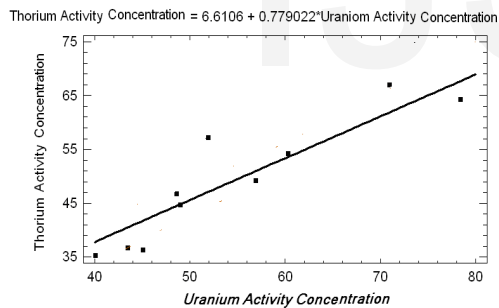


Figure 3, a: Correlation between ^{238}U and ^{226}Ra for Egyptian granite samples.

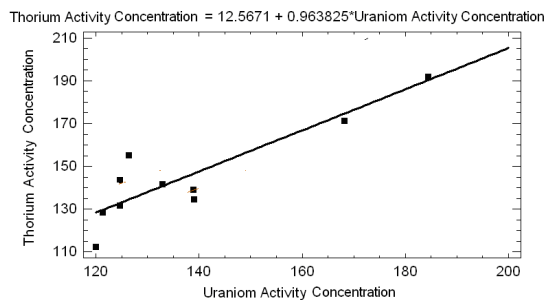


Figure 3, b: Correlation between ^{238}U and ^{232}Th for Egyptian marble samples

3.5 Radioactive inspections

The measured activity concentrations of ^{238}U , ^{232}Th and ^{40}K can be converted into total elemental concentrations of U, Th (in ppm) and of K (in percent), respectively. The specific activity of a sample containing 1.0 ppm, by weight, of ^{238}U is 12.35 Bq/kg, 1.0 ppm of ^{226}Ra is (11.1 Bq/kg), 1 ppm of ^{232}Th is (4.06 Bq/kg) and 1% of ^{40}K is (313 Bq/kg), [41]. From the data given in the analyzed 20 granite and marble samples

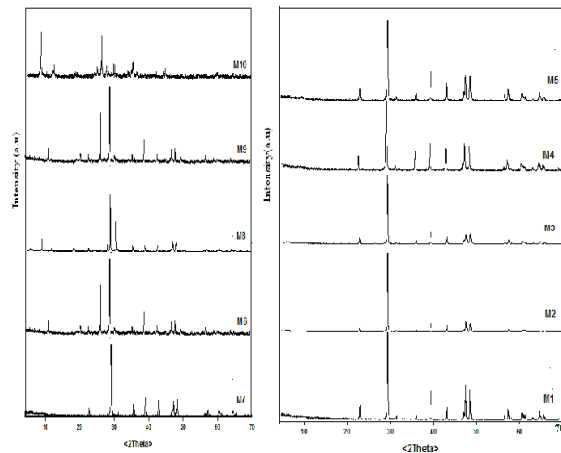


Figure 4, b: X- Ray Diffraction pattern for different Egyptian marble samples

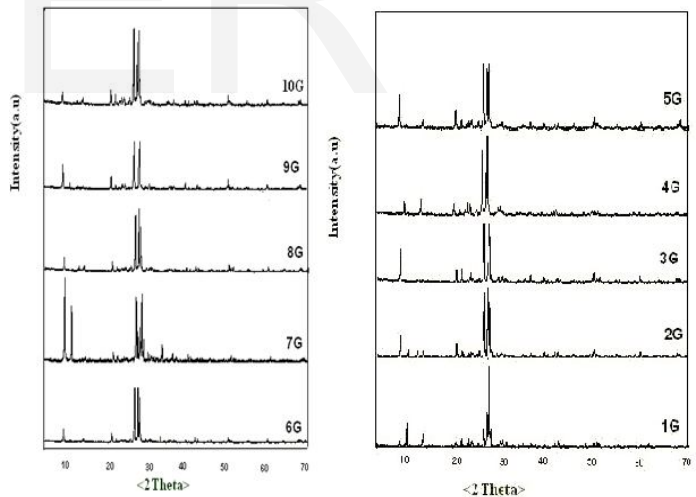


Figure 4, b: X- Ray Diffraction pattern for different Egyptian marble samples

Table 3, it is clear that for granite samples, ^{238}U content ranges from (9.64 to 14.81 ppm) with an average of (11.09 ppm). ^{232}Th content ranges from (28.03 to 47.98 ppm) with an average of (36.24 ppm). ^{226}Ra (A_{Ra}) increases with increasing U content. Generally, its average concentration is (12.03 ppm). K% content ranges from (1.23 % to 5.08 %) with an average value 3.66 %. $A_{\text{Th}}/A_{\text{U}}$ ratio were ranges from (2.91 to 3.82 Bq/kg) and with (3.28 Bq/kg) as an average. The theoretical expected $A_{\text{Th}}/A_{\text{U}}$ ratio of the normal continental crust is about

(4 Bq/kg) [42, 43]. This indicates granite and marble slightly had been undergoing alteration, weathering and metasomatic processes. [44].

Table 3 presents also the activity concentration of ^{238}U and ^{232}Th in (ppm) as well as ^{40}K in % for marble samples, showing that they range from (3.22 to 6.30 ppm), from (8.81 to 16.76 ppm), and from (1.10 to 1.25 %) respectively. Permissible concentrations of Th and U in the building materials should not exceed the internationally accepted levels of 20 and 10 mg/kg, respectively [45]. The mean obtained values for U are not within the international accepted values in general. It is also clear that the ratio $^{232}\text{Th}/^{238}\text{U}$ for granite samples (3.28 Bq/kg) is agreement with (3.5 Clark's value), and less than Clark's value for marble samples (2.81 Bq/kg), which denotes enrichment of uranium in the area under investigation.

Granite Samples	AU (ppm)	ARa (ppm)	ATh (ppm)	AK (%)	AU/ARa	ATh/AU
G1	14.81	15.48	47.98	4.34	0.96	3.24
G2	10.15	13.05	38.83	4.36	0.78	3.82
G3	9.64	10.90	28.03	4.35	0.88	2.91
G4	11.16	14.08	34.78	5.08	0.79	3.12
G5	9.75	10.84	32.12	4.07	0.90	3.30
G6	10.01	10.42	35.87	2.90	0.96	3.58
G7	13.51	13.10	42.79	3.98	1.03	3.17
G8	11.17	11.67	33.64	1.23	0.96	3.01
G9	10.67	10.06	35.44	4.16	1.06	3.32
G10	10.01	10.65	32.92	2.14	0.94	3.29
Mean	11.09	12.03	36.24	3.66	0.93	3.28
Max	14.81	15.48	47.98	5.08	1.06	3.82
Min	9.64	10.06	28.03	1.23	0.78	2.91
Marble Samples	AU (ppm)	ARa (ppm)	ATh (ppm)	AK (%)	AU/ARa	ATh/AU
M1	3.90	2.84	11.68	1.14	1.37	2.99
M2	3.93	3.87	11.17	1.10	1.02	2.84
M3	6.30	6.89	16.07	1.13	0.91	2.55
M4	5.70	6.91	16.76	1.18	0.82	2.94
M5	3.62	4.07	9.07	1.20	0.89	2.51
M6	3.22	3.62	8.81	1.13	0.89	2.74
M7	3.49	4.15	9.16	1.17	0.84	2.62
M8	4.84	4.11	13.57	1.15	1.18	2.80
M9	4.17	3.64	14.29	1.23	1.15	3.42
M10	4.57	4.96	12.31	1.25	0.92	2.69
Mean	4.37	4.51	12.29	1.17	1.00	2.81
Max	6.30	6.91	16.76	1.25	1.37	3.42
Min	3.22	2.84	8.81	1.10	0.82	2.51

Table 3: Activity Concentration for (U and Th)in (ppm), (K) in (%),Ratio of U/Ra Ratio of Th/U.for different Egyptian granite and marble samples

3.6 Radioactive equilibrium

In order to find the extent of the presence of these radioactive nuclides together in a certain place, correlation studies were performed among groups of radioactive elements such as ^{226}Ra , ^{238}U , ^{232}Th and ^{40}K . In fact know the terms of the secular balance are essential in order to make the correct assumptions to assess the dose [46].

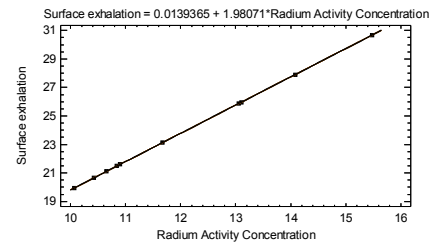


Figure 5,a.: The variation of surface radon exhalation rate with activity concentration of radium (ppm) in Egyptian granite samples.

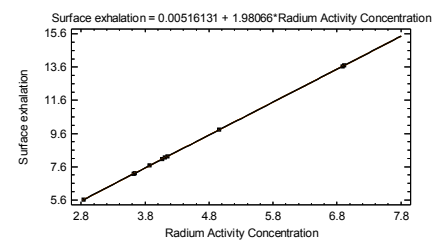


Figure 5,b.: The variation of surface radon exhalation rate with activity concentration of radium (ppm) in Egyptian marble samples.

Correlation studies were performed between the combinations of radionuclides like ^{238}U and ^{226}Ra as well as ^{238}U and ^{232}Th activity concentrations. Figure 2 (a, b) shows the moderate correlation between uranium and radium in granite samples under investigation (correlation coefficient = 0.78) which indicate the secular disequilibrium between ^{238}U and ^{226}Ra . The R-Squared statistic indicates that the model as fitted explains (60.07 %) of the variability in Activity Concentration of ^{226}Ra . For marble samples the correlation coefficient equals (0.89), indicating a relatively strong relationship between the variables ($R^2 = 79.41\%$). While Figure 3 (a, b) similarly, moderate correlation were also observed between (^{238}U and ^{232}Th) with ($R^2 = 78.39\%$, $N = 10$ and correlation coefficient = 0.89) for marble samples and with ($R^2 = 84.86\%$, $N = 10$ and correlation coefficient = 0.92) for granite samples due to the high activity concentration of ^{238}U than ^{232}Th .

3.8. Elemental analysis's of materials

EDAX DA-90 analyzer is used for the qualitative analysis in all samples from different upgrading stages. Chemical compositions of samples are shows in Tables 4, 5 which forgets by using analysis (EDAX). The marble and granites (M, G) samples were arrangement by increase the (Ca, Si) element respectively. Major element composition of the marble and granites(M, G) Tables 4,5 are quite similar, but Calc alkaline granite samples are slightly richer in Fe, Mg and Na. Calcium and Silicon (Ca, Si) are the major components of this region

and other elements such as Al, Mg, Na, S, Ti, Zn, Cu, K, Cl and Fe are also present. The chemical composition data of marble samples are presented in Table 4. It can be observed that in all of them, Ca is the predominant, followed by Na, Mg. The (M5, M6, M8, M10) samples are characterized by appearing Ti and (M5, M5, M8, M 10) appear K meanwhile disappear in other samples. It can be observed that in all of the granite samples Table 5, Si is the predominant, followed by Al, Mn with a significant amount of iron. The significant amount of iron is responsible for a darker colouring of the sintered samples. From the results of XRF it can be seen that granite samples have higher content of K_2O , this reflect the higher activity of ^{40}K in these samples. The marble and granite reject is formed basically by SiO_2 , Al_2O_3 and CaO , with small amounts of TiO_2 , MgO , Fe_2O_3 , K_2O and Na_2O [47]. The radioactivity was due mainly to the high presence of uranium bearing minerals such as apatite, sphene, zircon, allanite, as well as iron oxides.

Element	Na	Mg	Al	Si	S	Cl	Ca	Ti	Fe	Cu	K	Zn
M1	5.56	2.29	0.29	1.31	0.054	0.03	83.36	--	0.13	0.75	-	0.87
M2	7.23	4.83	0.12	0.15	0.054	0.01	84.76	--	0.12	0.21	-	0.30
M3	4.14	2.96	0.56	0.23	1.135	0.03	78.34	--	0.22	0.15	-	0.13
M4	7.23	4.13	0.42	1.29	1.108	0.08	86.52	1.18	0.31	0.32	-	0.04
M5	6.49	3.27	0.27	2.49	0.045	0.04	79.54	2.45	0.14	0.67	3.57	0.56
M6	7.81	3.33	0.12	2.85	0.054	0.07	93.49	--	0.24	0.22	-	0.23
M7	10.42	3.91	1.71	0.23	0.072	0.1	79.84	--	0.32	0.16	2.92	0.54
M8	6.21	2.26	0.42	0.92	0.144	0.18	87.53	6.11	0.32	0.34	3.83	0.21
M9	3.24	3.52	0.61	2.30	0.054	0.1	82.67	--	0.45	0.43	-	0.35
M10	9.11	9.28	0.27	0.95	0.207	0.05	78.93	3.33	0.21	0.87	3.17	0.42

Table 4: Chemical composition of Egyptian marble samples

Element	Na	Al	Si	S	Cl	K	Ca	Mn	Fe	Cu	Zn
G1	2.34	9.80	79.77	0.32	0.18	3.47	0.18	4.82	1.40	1.76	2.34
G2	4.22	10.42	67.91	0.33	0.27	5.48	0.01	2.58	1.28	1.34	4.22
G3	1.35	9.47	67.23	0.27	0.28	9.27	0.09	4.08	1.14	1.16	1.56
G4	3.64	9.62	66.35	0.23	0.32	8.60	0.05	3.08	1.06	0.98	3.64
G5	2.63	9.82	66.12	0.28	0.50	7.97	0.16	6.25	1.18	0.79	2.63
G6	1.66	10.37	65.09	0.26	0.57	8.19	0.22	6.17	1.29	1.62	2.55
G7	2.78	10.12	64.86	0.22	0.12	7.48	0.07	4.18	1.16	0.81	2.78
G8	8.49	12.89	59.40	0.20	0.27	8.70	0.20	6.49	0.22	0.02	8.49
G9	2.67	9.96	58.68	0.21	0.22	5.46	0.34	14.21	0.70	0.42	3.29
G10	6.69	14.29	65.86	0.07	0.23	10.84	0.22	2.94	0.85	0.95	6.69

Table 5: Chemical composition of Egyptian granite samples

3.9. Results of X- Ray Diffraction

X- ray diffraction technique has been used to investigate the structure and characteristics of the prepared samples. The obtained X- ray diffraction patterns of the investigated powder samples are shown in Figure 4 (a, b). The XRD analysis showed three main peaks characteristic of calcium carbonate ($CaCO_3$) and silicate oxide (SiO_2) minerals, while attributed to other stages of secondary mineral impurities. In the present

study, the XRD results indicate that the main constituents (major) of these samples are Albite ($NaAlSi_3O_8$), Microcline ($KAlSi_3O_8$), Quartz (SiO_2) in granite samples and Dolomite ($CaMg(CO_3)_2$) in marble samples. Small amount (Minor) and (Trace) minerals are presented as well [48]. Figure 4 (a, b) shows metal components of the 20 samples were analyzed by XRF spectrometer in Figure 4 (a, b).

3.10. Radon exhalation ^{222}Rn

The present investigation based on the study of 20 samples from different kind's granite and marble samples collected from Sinai region Egypt, using (CR-39) detectors. The values of radon concentration C_{Rn} (Bq/m³), Effective radium content C_{Ra} (Bq/kg) Surface exhalation E_x (S) (Bq/m² day), Mass exhalation E_x (M) (Bq/kg day) and Annual effective dose H_E (mSv/yr) of the granite and marble samples are given in Table 6.

Granite Samples	A_{Ra} (ppm)	Radon concentration C_{Rn} (Bq/m ³)	Effective radium content C_{Ra} (Bq/kg)	Surface exhalation E_x (S) (Bq/m ² day) $\times 10^{-6}$	Mass exhalation E_x (M) (Bq/kg day) $\times 10^{-8}$	Annual effective dose H_E (mSv y ⁻¹)
G1	15.48	109.84	3.92	30.68	46.09	3.53
G2	13.05	92.61	3.31	25.86	38.86	2.99
G3	10.90	91.38	2.76	21.61	32.47	2.95
G4	14.08	113.39	3.57	27.90	41.92	3.64
G5	10.84	104.73	2.75	21.49	32.29	3.37
G6	10.42	116.96	2.64	20.65	31.03	3.76
G7	13.10	139.51	3.32	25.96	39.00	4.47
G8	11.67	109.66	2.96	23.12	34.74	3.53
G9	10.06	115.53	2.55	19.94	29.96	3.71
G10	10.65	107.33	2.70	21.11	31.72	3.45
Mean	12.03	110.10	3.05	23.83	35.81	3.54
Max	15.48	139.51	3.92	30.68	46.09	4.47
Min	10.06	91.38	2.55	19.94	29.96	2.99
Marble Samples	A_{Ra} (ppm)	Radon concentration C_{Rn} (Bq/m ³)	Effective radium content C_{Ra} (Bq/kg)	Surface exhalation E_x (S) (Bq/m ² day) $\times 10^{-6}$	Mass exhalation E_x (M) (Bq/kg day) $\times 10^{-8}$	Annual effective dose H_E (mSv y ⁻¹)
M1	2.84	20.16	0.72	5.63	8.46	0.70
M2	3.87	27.46	0.98	7.67	11.52	0.93
M3	6.89	52.38	1.74	13.65	20.51	1.72
M4	6.91	54.64	1.75	13.69	20.57	1.79
M5	4.07	29.58	1.03	8.06	12.11	1.00
M6	3.62	28.72	0.92	7.18	10.79	0.97
M7	4.15	29.85	1.05	8.22	12.35	1.01
M8	4.11	44.24	1.04	8.15	12.24	1.46
M9	3.64	46.59	0.92	7.21	10.84	1.54
M10	4.96	40.14	1.26	9.84	14.78	1.33
Mean	4.51	37.38	1.10	8.90	13.40	1.25
Max	6.91	54.64	1.75	13.69	20.57	1.79
Min	2.84	20.16	0.72	5.63	8.46	0.70

Table 6 : Radon concentrations, Effective radium content, (surface and mass) exhalation rates and annual effective dose for different Egyptian granite and marble samples.

The values of radon concentrations in granite samples are ranged from 91.38 to 139.51 Bq/m³ and 20.16 to 54.64 Bq/m³ for marble samples. The values of radon concentrations in the granite samples (M1, M4, M5, M6, M7, M8 and M9) has a high value but all marble samples has low value. These values are below the radon reference level which ranges from 200–600 Bq/m³ as recommended by ICRP, IAEA. The radon surface exhalation rates in terms of area from the granite samples varied from 19.94 to 30.68 (Bq/m² day), with a mean of 23.83 (Bq/m² day), whereas the surface exhalation rates from the marble samples varied from 5.63 to 13.96, with a mean of 8.90 (Bq/m² day). The radon exhalation rate in terms of mass varied from 29.96 to 46.09 with a mean of 35.81 (Bq/kg day) for the granite samples. The values of exhalation rates of studied are vary from one material to another. The difference may have arisen because of the difference in the nature of the samples, and the radium content of samples for radium presence of varying levels in all parts of the world.

The Effective radium content in granite samples of the study area is found to vary from (2.55 to 3.92 Bq/kg) with a mean value of (3.05 Bq/kg), where as in the marble samples this parameter were small. Thus, the effective radium content in the study materials are less than the permissible value (370 Bq/kg), which is acceptable a safe limit recommended by Organization for Economic Cooperation and Development (OECD) [49]. The comparison between the average annual effective doses for measuring samples values, we find that the average annual effective dose rate of granite samples have a high values and marble samples have a low values Table 6. The correlation relation between radium activity concentration (ppm) measured by HPGe spectrometry and surface exhalation rate measured by the passive technique showed a strong linear correlation (correlation coefficient = 0.99, R² = 99.99 %) for both granite and marble samples Figure 5 (a, b). Hence, the result shows that this studied material is safe as far as the health hazards of radium are concerned. It means that the material samples under investigation from these locations cannot produce dangerous levels of indoor radon when used as building materials.

4. Conclusion

It is important to determine the background radiation level in order to evaluate the health hazards. Environmental monitoring should be carried out for marbles and granites used as building materials in Egypt where people might be exposed to radioactivity. It has been using a combination of gamma rays spectral analysis and nuclear track detector to determine radon and uranium concentrations. This study determined the average activity concentrations of granite and marble samples which collected from different sit of Sinai Egypt and compared results with the world average values. The activity concentrations of ²³⁸U, ²³²Th and ⁴⁰K in different granite and marble samples as well as radiological doses and risks were established. Activities of ²³⁸U, ²²⁶Ra, ²³²Th and ⁴⁰K of all granite samples and some samples of marble (M4, M8, M9 and M10) exceeds the average level of these radionuclides in normal soil (35 Bq/kg, 35 Bq/kg, 30 Bq/kg and 400 Bq/kg) respectively. Significantly, the related

absorbed dose rate from all those radionuclides also exceeds the wormed average value of (55 nGy/h) from these terrestrial radionuclides in regular soil. Consequently the annual effective dose based on the standard model room, exceeds the dose limit of (1 mSv/yr) for all types granite and marble.

Annual effective gamma doses and the lifetime risks of cancer were higher than the world's average across the entire granite samples collected from Sinai Egypt. Moreover, lifetime risks of cancer in the granite samples was higher for must location with mean value (0.85 x 10⁻³) comparing with the world average, although the ELCR values are generally lower for marble sample. From the results it is clear that there are significant differences in Raeq of different materials. This fact is important to select the appropriate materials for use in building and construction. A large variation in the activity of radium equivalent indicates that it is advisable to monitor radioactivity levels of the material from a new source before adopting it for use as a building material. The index I_y is correlated with the annual dose due to the excess external gamma radiation caused by superficial material. Values of index I_y ≤ 1 correspond to (0.3 mSv/yr), while I_y ≤ 3 correspond to 1 mSv/yr. Thus, the activity concentration index should be used only as a screening tool for identifying materials which might be of concern to be used as covering material. According to this dose criterion, granite materials with I_y ≥ 3 (G1, G2, G4 and G7) should be avoided, since these values correspond to dose rates higher than 1mSv/yr [23], which is the highest value of dose rate in air recommended for population [10,22]. Correlation studies were performed between the combinations of radionuclides like ²²⁶Ra, ²³⁸U, ²³²Th, and ⁴⁰K, in order to find the extent the existence of these radioactive nuclides together at a particular place, The mean obtained values for U are not within the international accepted values in general. It is also clear that the ratio ²³²Th/²³⁸U for granite samples (3.28) is agreement with 3.5 (Clark's value), and less than Clark's value for marble samples (2.81), which demonstrates the enrichment of uranium in the area under investigation. In the present study, the XRD results indicate that the main constituents (major) of these samples are Albite (NaAlSi₃O₈), Microcline (KAlSi₃O₈), Quartz (SiO₂) in granite samples and Dolomite Ca Mg (CO₃)₂ in marble samples. Small amount (Minor) and (Trace) minerals are presented. The high level of natural radioactivity of the inspected granite samples was associated with the existence of both the K-rich Minerals (Kefeldspars, biotite), accessories (monazite, zircon, apatite, Titanite, allanite and hematite), which are mainly found in granitic rocks.

(CR-39) detectors are widely for radon exhalation rate, radium content and uranium concentration measurements in study samples under different conditions. The study showed that radon in all tested samples had radon exhalation rate much lower than the average world value of 57.600 mBq/m² h (0.016 Bq/m².s). Thus our values for effective radium content in study materials are less than the permissible value (370 Bq/kg), which is acceptable as a safe limit recommended by Organization for Economic Cooperation and Development [49]. The comparison between the average values of annual

effective dose for the measured samples, we find that the average annual effective dose rate of granite samples have a high values and marble samples have a low values Table 6. Hence, the result shows that these studied materials are safe as far as the health hazards of radium are concerned. It means that the material samples under investigation from these locations cannot produce dangerous levels of indoor radon when used as building materials. This study can be used as reference information to assess any changes in the radioactive background level in our homes and to disclose any harmful rays that would affect human. From the obtained results we find that granite samples have high concentration of radon than the marble materials. The variations in the values of radon concentrations due to the difference in the chemical composition and the geological form the samples. A measurement of radon exhalation rate is a good indicator of the concentrations of radon found in samples. The obtained results showed that the radon surface exhalation rate varies linearly with activity concentration of radium (ppm) which measured by HPGe detector. Most of the interior radon gas values evaluated in the range of action levels from (200-600 Bqm-3) recommended by the International Commission on Radiological Protection [ICRP] for all the samples under investigation.

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