Natural γ-ray-emitting radionuclides in Egyptian cement

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Abstract Samples of cement manufactured in Egypt and the raw materials have been analyzed using gamma-spectroscopy, in order to determine the concentration of natural radionuclides and associated radiological hazard. The mean of specific activity due to radionuclides of ^{226}Ra, ^{232}Th and ^{40}K was found to be (20±4), (11± 2), (320±18) (gypsum), (41±8), (27±5), (410±27) (clay), (58±11), (18±3), (321±20) (iron ore) and (37.6±6), (11.8±3), (178.6±15) Bq•kg^{-1} (Portland cement), respectively. ^{40}K concentration could not be detected in slag, limestone, sulphate resistant cement (S.R.C.), clinker and white cement, while the mean specific activities of ^{226}Ra and ^{232}Th are (239±16), (48.7±7); (31.5±5), (10±2); (47±7), (20±5); (23±5), (10.4±3) and (23±5), (11±3) Bq•kg^{-1}, respectively. The activities (concentrations) are in the same range as the data released in other countries. The calculated radiation hazard parameters for all the samples are still lower than the acceptable values in Egypt and other countries.

Key words Gamma ray, Natural radionuclides, Cement, Radiation hazard

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1 Introduction

Radionuclides occurring naturally in building materials are sources of external and internal radiation exposure in dwellings. The most important naturally occurring radionuclides present in soil and rocks are ^{226}Ra, ^{232}Th and ^{40}K. Since these radionuclides are not uniformly distributed, the knowledge of their distributions in soil and rocks plays an important role in radiation protection and measurement.[1,2] In the forthcoming years lower regulatory limits are likely to become obligatory. Precautionary measures and restrictions in order to protect workers in the factories and on the farm-yards may become compulsory.

Cement is commonly used in building materials, which is considered as one of the basic industries playing an important role in national economy of developing countries.[3,4] There are many types of cement according to chemical composition and hydraulic properties. The process of cement manufacturing consists of grinding the raw materials (limestone and clay) and mixing them intimately in certain proportions. Chemical analysis must be done before the mixing process for the clay, limestone or any other added materials such as sand, iron ore, gypsum and slag. The mixture is heated in large rotary kiln at approximately 1450℃ when the material sinters and partially fuses into balls known as “clinker”, which is left to cool by air and water, and ground with raw gypsum (4%-6%) used as regulator of the cement setting.

The concentrations of radioelements in the building materials and its components are important in the assessment of population exposures, as most individuals spend 80% of their time indoors. Like other construction materials, the natural level of radioactivity in cement gives rise to external and internal indoor exposure. The external radiation exposure is caused by γ-rays from members of the uranium and thorium decay chains and from potassium-40, and the internal radiation exposure, mainly affecting the respiratory tract, is due to short-lived daughter products of radon, which are exhaled into room air from construction materials.[5,6]

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The contents of ^{226}Ra, ^{232}Th and ^{40}K in raw and processed materials can vary considerably according to the geological locations and geo-chemical characteristics of the materials. Knowledge on occurrence and concentration of the natural radioactivity of the materials is essential for checking its quality in general and knowing its effect on environment surrounding the cement producing factories in particular and also for estimation of radiological hazards to human health.

In the present study, cement manufactured in Egypt, as well as the raw materials have been analyzed using γ-spectroscopy in order to determine concentrations of natural radionuclides and associated radiological hazard.

2 Experimental

One hundred and six samples of local cement and its raw materials were collected from different cement factories of Egypt and prepared for measuring the radioactivity due to ^{226}Ra, ^{232}Th and ^{40}K using low level NaI(Tl) detector coupled to a 1024-channel pulse height analyzer.

Samples with large grain size were crashed into small pieces using mechanical crusher. They were dried at 105℃ and ground into powder of fine grain size. The powder samples were filled in a ϕ55mm×13mm polyethylene disc, whose inner diameter equals to diameter of the detector in face-to-face geometry. Every sample was stored for four weeks to reach the equilibrium state between ^{226}Ra and its decay products. The spectrometer was calibrated using standard point sources (^{133}Ba, ^{60}Co and ^{137}Cs). The efficiency dependence on γ-ray energy was determined at 0.0 mm sample-detector distance. To minimize γ-ray background, the detector and sample were housed within a 5 cm thick lead castle. The measurements were carried out by daily calibrations, repeating each sample measurements.

The ^{226}Ra concentration was determined by measuring the 295.1 (19.2%) and 352 (37.1%) keV γ-rays from ^{214}Pb and the 609.3 (46.1%) and 1120.3 (15%) keV γ-rays from ^{214}Bi. The ^{226}Ra concentration was calculated by averaging over the measured concentrations for ^{214}Pb and ^{214}Bi. The ^{232}Th activity was determined from the γ-peaks of 238.6 (43.6%) keV from ^{212}Pb and 338.4 (12%), 911.2 (29%) and 969 (17%) keV from ^{228}Ac and 583.0 (86%) keV γ-rays from ^{208}Tl. The ^{40}K activity was measured from its 1460 (10.7%) keV γ-line. The counting time was about 10 hours and sometimes a longer counting time was needed to obtain energy spectra with good resolution. Based on counting statistics, the errors of ^{226}Ra, ^{232}Th and ^{40}K were determined. Chemical compositions of the samples were determined by X-ray fluorescence (XRF-Model JSX-3222) technique.

3 Results and discussion

Portland cement, an essential binding agent in concrete, is the most widely used construction material worldwide due to its advantages of lower cost (relative to steel, aluminum or polymers), durability and other properties. More than 95 wt.% of ordinary Portland cement consists mainly of CaO, SiO_2, Al_2O_3 and Fe_2O_3. Average values of the uranium and thorium contents were studied with the major oxides in cement and raw material samples. Three samples from each kind were chosen for chemical analysis using X-ray florescence (XRF) at the Material Testing Laboratory in South Valley University, and chemical compositions of the samples are given in Table 1.

Table1 The chemical composition (molar fraction) of the cement and raw material samples %

Sample type	SiO_2	MgO	CaO	Al_2O_3	Fe_2O_3	SO_3	Na_2O
Limestone	1.0 ±0.15	0.8 ± 0.05	98 ± 10	--	0.1±0.001	0.2 ±0.03	--
Clay	50.5± 7.1	5.2 ± 2.3	23.5 ± 4.9	8.5 ±2.5	7.8 ±2.8	1.6 ±0.3	--
Raw gypsum	5.8 ±2.4	4.0 ±1.5	63.5 ±8	0.5 ±0.05	0.5 ±0.05	25.5 ±5	0.1 ±0.01
Iron ore	5.2± 2.3	--	9.9 ±3.1	1.5 ±0.65	83.3 ±9.1	--	--
Slag	31.7 ±5.6	5.7 ±2.4	43.2 ±6.2	5.1 ±2.3	0.6 ±0.05	3.1 ±1	--
S.R.C	14.3±3.8	1.1 ±0.4	77.4 ±8.7	1.4 ±0.4	2.7 ±0.9	2.4 ±0.8	0.5 ±0.05
Clinker	15.3 ±3.9	1.6 ±0.5	78.1 ±8.7	1.2 ±0.3	2.6 ±0.9	0.7 ±0.05	--
White cement	14.2 ±3.7	0.3 ±0.02	80.4 ±8.9	1.7 ±0.6	0.1 ±0.01	3.1 ±1	--
Portland cement	15.4 ±3.9	1.8 ±0.4	75 ±8.7	1.8 ±0.7	1.7 ±0.6	3.1 ±1	0.15 ±0.01

The gamma spectrometric analyses of the samples from three different locations (eastern desert, Egypt) indicate that the main radioisotopes were ^{226}Ra, ^{232}Th and sometimes ^{40}K. The mean values of specific activity in the samples are listed in Table 2.

Table 2 Mean specific activity ($Bq{\bullet}kg^{-1}$) for cement and raw material samples

Sample type	Number of samples	Radioactivity ($Bq.kg^{-1}$)			Ra/Th
		^{226}Ra	^{232}Th	^{40}K	
Limestone	13	31.5 ± 5	10± 2	--	3.2
Clay	15	41± 8	27± 5	410 ± 27	1.5
Raw gypsum	10	20 ± 4	11± 2	320 ± 18	1.8
Iron ore	10	58 ±11	18± 3	321 ± 20	3.2
Slag	5	239 ±15.5	48.7± 7	--	4.9
S.R.C	5	47.2 ± 6.9	20± 4.5	--	2.4
Clinker	5	22.7 ± 4.8	10.4± 3.2	--	2.2
White cement	14	23 ± 5	11± 3	--	2.1
Portland cement	29	37.6 ± 6	11.8± 3	178.6±15	3.2

The analysis shows that both U and Th increase with content of SiO_2, $A1_2O_3$, Fe_2O_3 and MgO, a less correlation is observed in $A1_2O_3$ and Fe_2O_3. From another point of view, the U and Th concentrations decrease with the percentage of CaO and SO_3. The U content increases apparently with the Fe_2O_3, $A1_2O_3$ and SiO_2 contents, due to the fact that these constituents are acting as effective adsorbing agents for uranium.

The results indicate that ^{226}Ra exhibits the highest activity value compared with ^{232}Th, which may be due to higher mobility of radium with respect to thorium, resulting in an excess of ^{226}Ra coming from other areas. The lowest value of ^{226}Ra activity was found in the raw gypsum samples, while the highest was found in the slag samples. The limestone samples have the lowest value of ^{232}Th while the highest was found in the slag samples. The high activity values of ^{226}Ra and ^{232}Th in slag samples can be attributed to the composition of these waste products of iron fabrication process by melting different raw materials (iron ore, fly ash, limestone, etc). Slag will be precipitated in the bottom as residual parts associated with ^{226}Ra and ^{232}Th because of the high density of these radionuclides. For ^{40}K the lower values were found in the Portland cement samples and the higher in the clay samples. The activity of ^{40}K in the slag, limestone, S.R.C., clinker, and white cement samples, and some ordinary Portland cement samples, could not be detected because the counting rate was less than the lower limit of detection.

For S.R.C. manufacture, a known percent of iron oxide is added to the raw materials to decrease tricalcium aluminate ($3CaO{\bullet}Al_2O_3$) and increase tetracalcium aluminoferrite ($4CaO{\bullet}Fe_2O_3$). Quality of the S.R.C. increases with decreasing $3CaO{\bullet}Al_2O_3$ content, which should not exceed 3.5%. In the S.R.C samples, the ^{226}Ra activity was ranging from (35.2±5.9) to (69.3±8.3) $Bq{\bullet}kg^{-1}$, whereas the ^{232}Th activity was in the range of (10.1±2.2) to (26.6±5.2) $Bq{\bullet}kg^{-1}$. The average value of Ra/Th ratio in all samples is 2.4.

The corresponding values in the clinker samples varied from (11.4±2.4) to (32.6±5.7) $Bq{\bullet}kg^{-1}$ with an average of (22.7±4.8) $Bq{\bullet}kg^{-1}$, and (4.8±1.2) to (14.7±2.8) $Bq{\bullet}kg^{-1}$ with an average value of (10.4±3.2) $Bq{\bullet}kg^{-1}$. The average value of Ra/Th ratio is 2.2.

White cement is made with raw materials free from iron and colored oxides, such as clay, limestone, white sand and gypsum. The limestone is from Minia (the Samalut Mountain) and clay from Aswan (Kalabsha) or Sinai, etc. The pure gypsum is from the Red Sea beach. Natural gas is used for white cement production so as to be free from lead and colored materials. The mean values of ^{226}Ra and ^{232}Th in the samples from white cement are (23±5) and (11±3) $Bq{\bullet}kg^{-1}$, respectively.

Results of the Portland cement samples show that ^{226}Ra activity varies from (13.9±2.7) to (50.5±7.1) with an average value of (37.6±6) Bq•kg^{-1}, while ^{232}Th is from (2.4±1.6) to (13.1±2.6) with an average value of (11.8±3) Bq•kg^{-1}. ^{40}K is from (80.8±9) to (243±16) with an average value of (178.6±15) Bq•kg^{-1}. Average value of Ra/Th ratio in all the Portland cement samples is 3.2.

The variations and large spread in the data are a reflection of different geological regions of the raw materials. However, except for the slag and iron ore samples, the natural radionuclide concentrations in all the raw material and cement samples were lower than the world averages for building materials, i.e. 50, 50 and 500 Bq•kg^{-1} for ^{226}Ra, ^{232}Th and ^{40}K, respectively.[7,8] So these materials do not pose a significant radiological hazard when used for construction of buildings.

Average specific activities in the samples under investigation compared with values in different countries are listed in Table 3. The radioactivity in cement and raw materials varies from one country to another, even within the same type of materials. From the obtained data, it is evident that, the mean value of ^{40}K in all the samples was higher when compared with ^{226}Ra and ^{232}Th. The mean specific activity of ^{226}Ra, ^{232}Th and ^{40}K in all cement samples under test are lower than the most published data.

Table 3 Comparison of average specific activities in various raw materials and cement in the present study with corresponding values reported in other countries

Countries	Sample type	Activity (Bq•kg^{-1})			Reference
		^{226}Ra	^{232}Th	^{40}K	
Egypt	Limestone	31.5	10	--	Present work
Italy		11	2	22	[9]
Brazil		24.3	7.0	205	[10]
India		73.9	--	64.6	[11]
Egypt	Clay	41	27	410	Present work
Austria		38.3	44.7	635	[12]
Brazil		51.7	65.3	747	[10]
Pakistan		43.2	53.7	631	[13]
Egypt	Gypsum	20	11	320	Present work
India		8.3	--	26.7	[11]
Cyprus		3.8	2.8	20.9	[14]
Italy		6	2	32	[9]
Egypt	Cement	37.6	11.8	177	Present work
Egypt		25.0	12.0	498	[6]
Brazil		61.7	58.5	564	[10]
Pakistan		31.3	26.8	212	[13]

It is important to point out that these values were not the representative values for the countries mentioned but for the regions from where the samples were collected. Large variations in radioactivity may suggest that it is advisable to monitor the radioactivity levels of raw materials from a new source, before adopting it for using as a cement raw material.

It is important to assess the γ-ray hazards from the ^{226}Ra, ^{232}Th and ^{40}K nuclides. The most widely used radiation hazard index is Ra_{eq}, the radium equivalent activity, which is a weighted sum of activities of the three radionuclides based on the assumption that 370 Bq•kg^{-1}of ^{226}Ra, 259 Bq•kg^{-1} of ^{232}Th and 4810 Bq•kg^{-1} of ^{40}K produce the same γ-ray dose rate.[15-17]

$$Ra_{eq} = (A_{Th}\times 1.43) + A_{Ra} + (A_K \times 0.077)$$

where A_{Ra}, A_{Th} and A_K are activities of ^{226}Ra, ^{232}Th and ^{40}K respectively in Bq•kg^{-1}.

For all samples under investigation, the radium equivalent values are lower than the acceptable value 370 Bq•kg^{-1}[17] which is in a good agreement with other published results and also less than the other parameters of cement samples in other different countries. An appreciable increase could be noticed in slag samples because the high content of ^{226}Ra and ^{232}Th activities in these samples.

From the calculation of radiation hazard index, it is clear that this will not give high exposure either for the inhabitants or workers dealing with transportation of cement and it has a good safety index in all building materials. Since the levels of radiation hazard parameter of some raw materials are slightly higher, it may be recommended utilizing them in other building applications.

4 Conclusions

The mean value of ^{40}K in all measured samples was found to be higher when compared with ^{226}Ra and ^{232}Th. The mean specific activity of ^{226}Ra, ^{232}Th and ^{40}K in all cement samples under test are lower than the most published data. The radioactivity in raw materials varies from one country to another for different materials and also within the same type of materials. The results may be important from the point of view of selecting suitable materials for use in cement manufacture.

The average radiation hazard parameters for all samples under investigation are still lower than the acceptable value[17] and also less than the other parameters of cement samples in other different countries. From the calculation of dose rate and external hazard index, it is clear that this will not give high exposure either for the inhabitants or workers dealing with transportation of cement and it has a good safety index in all building materials except in a very few cases.

The consequences for the manufacturing of cement would then be maintained within acceptable values and the mean resulting additional dose equivalents would remain within the variations of natural radiation exposure. Some raw materials, such as the slag, have higher values of specific radioactivity. It may be recommended utilizing the material consignment in other building application, such as road or underground construction.

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