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Natural Radioactivity levels and Elemental Analysis of Cement by Gamma-Ray Spectrometer and Neutron Activation Analysis

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Abstract

Cement is considered a basic industry. For this reason, the current work involves the use of INAA for elemental analysis and Pollutant concentration in cement. The samples were collected from Saudi market. The samples were irradiated using the thermal neutrons "at the TRIGA Mainz research reactor" and at a neutron flux "of 7 x 10 ^{11}n/cms". Twenty elements were identified. The elements determined are: Na, K, Sc, Cr, Co, Ti, Mn, Fe, Ga, Sr, Sn, Ba, Cs, Ce, Sm, Yb, Lu, Hf, Th and U. The concentrations of natural radionuclides ^{232}Th, ^{226}Ra and ^{40}K were also measured. The average values for ^{226}Ra, ^{232}Th and ^{40}K are 35.60 , 43.17, 82.08 Bq·kg^{-1} for Portland cement and 28.53, 43.46, 67.38 Bq·kg^{-1} for white cement. The radiation hazard indices such as radium equivalent activities, effective dose rate, and the external hazard indices have been computed. The obtained results were compared with related studies carried out in other countries and with the UNSCEAR reports.

***Keywords*:** Elemental analysis; Natural Radioactivity; Hazard indices; Cement; INAA; EDXRF; Triga Mainz.

1. Introduction

Great attention has been paid to the determining radionuclides concentration in cement in many countries [1-4]. Various analytical techniques have been utilized in the elemental analysis of Portland cement.

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Common among them are X-ray fluorescence XRF, WDXRF, EDXRF, Atomic Absorption and INAA [5,6] . Neutron activation analysis is a sensitive analytical technique useful for performing both qualitative and quantitative multi-element analysis of major, minor and trace elements in samples from almost every conceivable field of scientific or technical interest. “For many elements and applications, the NAA offers sensitivities that are superior to that possible by other methods of the order of parts per billion or better. Also, because of its accuracy and reliability, the NAA is recognized as the reference method of choice when new procedures are being developed or when other methods yield results that do not agree” [7,8]. The aim of the present work is to analyze major, minor and trace elements in cement as well as to measure the concentration of the natural radionuclides and radiation level using NAA and a gamma spectrometer to check the quality control also to evaluate the reliability of these methods in the daily analysis of cement products [9].

2. Material and Methods

2.1 Samples preparation

Portland and white cement were collected for investigation from Saudi market. Each of the samples is Weighing about 1 kg and then dried in an oven at about 105^0c to make sure that all the moisture has been removed. For elemental analysis using instrumental neutron activation analysis: the powder samples were sieved through a set of standard sieves with diameters ranged of between 63-125 mm, and an electric shaker was used to obtain homogeneous samples.Then, the irradiation of the samples by using thermal neutrons, concerning the measurement of the natural radioactivity: Each sample was grinded, homogenized. The samples were weighed, packed-sealed in a polyethylene Marinelli beakers, of $350cm^3$ volume each and then stored for four weeks to attain secular equilibrium with the short-lived daughters of ^{232}Th and ^{226}Ra and their long-lived parent radionuclides[10. The activity concentrations of radionuclides were determined from the significant average energy lines of 609.3, 1120.3 and 1764.5 keV (^{214}Bi),352.9 keV (^{214}Pb) for .^{226}Ra , 1460.7 keV for ^{40}K and 968.9, 338.4 and 9,11.1 keV (^{228}Ac) for ^{232}Th series[11].

2.2 Instrumentation and irradiations

One hundred mg of powder cement samples was filled in Polyethylene capsules and then irradiated with a Dolerite WSE and Microgabro PMS standard reference material with thermal neutrons "at the University of Mainz Triga research reactor (100 kWth) with a flux of $7x10^{11}$ n/cm^{2}s". The concentration of the elements determined in the irradiated samples was quantitatively specified by comparison with the activities of the reference materials [7,12]. After appropriate cooling times, the data were collected to conduct different measurements[13]. The irradiation conditions for the elements determined were shown in Table 1. The measuring of activity concentration for radionuclide in studying samples was defined using gamma-ray spectrometer system with a HPGe detector with an electronic circuit. The HPGe detector has equipped with specifications as a following : energy resolution (FWHM) is 1.70 keV at 1.33 MeV ^{60}Co, Peak to Compton ratio ^{60}Co is 65.2, relative efficiency is 29.2 at 1.33 MeV ^{60}Co. The Inter-gamma Software that generated by the Inter-technique “Deutschland GmbH, Mainz, Germany [14], accomplished the analysis of results. In all measurements, the electronic dead time is less than 10 % and the Inter-Gamma software performs the correction automatically [15] .

Table 1: Irradiation cycles and determined elements

Irradiation time	Cooling time	Measuring time	Determined elements
1 m	5m	4m	Ti
5 m	1h	15m	Mn, Sr
6 h	2d	1h	Mn, K, Ga, Sm, U
6 h	14d	8h	Sc, Cr, Fe, Co, Zn, Sn, Ba, Cs, Ce, Yb, Lu, Hf, Th

2.3 Estimation of radiological dose and hazard indices

2.3.1 Radium equivalent activity(Ra_{eq})

The radium equivalent activity (Ra_{eq}) values in Bq/kg were obtained by using the following equation:

$$Ra_{eq} = C_{Ra} + C_{Th} \times 1.43 + C_K \times 0.077 \qquad (1)$$

Where, C_k, C_{Th} and C_{Ra} are the activity concentrations of ^{40}K, ^{232}Th and ^{226}Ra in samples, respectively. The definition is based on the supposition that 130 Bq/kg of ^{40}K, 7 Bq/kg of ^{232}Th and 10 Bq/kg of ^{226}Ra are created the same gamma radiation exposure dose[16].

2.3.2 Absorbed dose rate (D)

The absorbed dose rate in the air due to radionuclides at 1 m above the ground surface for the uniform distribution of (^{226}Ra, ^{232}Th, and ^{40}K) was calculated according to the guidelines supplied from [17]

$$D = C_{Ra} \times 0.462 + C_{Th} \times 0.604 + C_K \times 0.0417 \qquad (2)$$

Where, 0.462, 0.0417 and 0.604 nGy h^{-1} per Bq/kg were the conversion factors corresponding to ^{226}Ra (^{238}U-series), ^{40}K and ^{232}Th [17.

2.3.3 External hazard index (H_{ex})

The recommended value of absorbed is 1.5 mSv y^{-1} [18]. To limit the radiation dose value to this rate, by the conventional model suggest based on infinitely thick walls, without doors and windows to serve as a standard for the computation of index defined as external hazard index H_{ex} from the following relation [19] :

$$Hex = CRa / 740 + CTh / 520 + CK/9620 \leq 1 \qquad (3)$$

4. Results and Discussion

The average concentration values of the elements determined in cement samples in four irradiation cycles are shown in Table 2. Twenty elements were identified: Na, K, Sc, Cr, Co, Ti, Mn, Fe, Ga, Sr, Sn, Ba, Cs, Ce, Sm, Yb, Lu, Hf, Th and U . The concentrations of all elements were expressed in μg/g except for Na, Mn, Fe, Ti and K were given in g/kg. The concentration of determining elements was specified using multiple activities produced by (nγ) reactions, since, some of the radionuclides committed to exhibit more than one obvious and distinct gamma line. In all other situations, the elements were measured by their most distinctive peaks, with lowest statistical errors, free of interference, with lowest statistical errors, and free of interference. The measurement accuracy has been estimated using the PMS and WSE analysis, for the standard reference materials. From the obtained results, we can say that INAA is an effective and successful mean to supply valuable data for cement samples with a satisfying precision. The accuracy for most elements in present results are in the range of 10 % of the reference values, and a good precision has been shown in most results [14]. The rare earth elements determined are Ce, Sm, Yb and Lu. The selection of photopeaks for the analysis is briefly discussed below for each element. For cerium, the photopeak of ^{141}Ce at 145 keV was used. For samarium, the isotope ^{153}Sm is used. Ytterbium can be determined using the 198 keV peak of ^{169}Yb. The 396 keV peak cannot be resolved from nearby peaks of ^{152}Eu 383 keV and ^{233}Pa 381 keV. For lutetium, the high abundance peak at 208 keV of ^{177m}Lu was used. The elemental concentration of uranium via ^{238}U and thorium via ^{232}Th in clay samples. The activation converts ^{238}U and ^{232}Th into ^{239}Np and ^{233}Pa, respectively, by neutron capture and successive β-decay [20].

$$^{238}U\,(n,\gamma)\;^{239}U \;\text{------}\xrightarrow{\beta-}\;^{239}Np \qquad E^{\gamma} = 106\ keV$$

$$^{232}Th\,(n,\gamma)\;^{233}Th \;\text{-----}\xrightarrow{\beta-}\;^{233}Pa \qquad E^{\gamma} = 312\ keV$$

The results of natural radionuclides concentration in Portland and white cement are presented in Table 3. The average values for ^{226}Ra, ^{232}Th and ^{40}K are 35.60 , 43.17, 82.08 Bq·kg^{-1} for Portland cement and 28.53, 43.46, 67.38 Bq·kg^{-1} for white cement. The obtained results show that the radionuclide concentrations in the Portland and white cement are below the world averages for building materials which are 50, 50 and 500 (Bq.kg^{-1}) for ^{226}Ra, ^{232}Th and ^{40}K, respectively [17]. Table 4, shows a comparison between the average concentration values from the present study with similar studies performed in other countries. From Table 4, the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K for Portland and white cement were comparable with the results of similar studies undertaken in other countries. The activity concentration in Portland cement changes from one country to another with consideration of various materials used in cement production. The contents of ^{226}Ra, ^{232}Th and ^{40}K in cement materials depend on their chemical composition that related to geological source and geochemical characteristics. "It is important to point out that these values are not representative values of the countries mentioned but are specific to the regions from where the samples were collected.

Table 2: The elemental content of cement using INAA.

Element	Isotope	Eγ, keV	T1/2	Portland Cement	White cement
Na%	Na-24	1368.6	14.96 h	10.04	0.7
K %	K-42	1524	12.4 h	1.17	---
Sc ppm	Sc-46	1120	83.8 d	---	2.35
Cr ppm	Cr-51	320	27.7 d	2.3	34.8
Ti %	Ti-51	320	3.75 m	0.45	0.45
Mn %	Mn-56	847	2.59 h	0.019	0.001
Fe %	Fe-59	1099	44.5 d	----	0.008
Co ppm	Co-60	1332&1173	5.27 y	---	0.02
Ga ppm	Ga-72	834	14.1 d	----	5.63
Sr ppm	Sr-87	388	2.81h	179	247
Sn ppm	Sn-117	159	13.6 d	0.90	1.63
Ba ppm	Ba-131	496	11.5 d	---	103
Cs ppm	Cs-134	605	2 y	0.014	---
Ce ppm	Ce-141	145	32.5 d	1.30	8.17
Sm ppm	Sm-153	103	46.2	0.3	0.84
Yb ppm	Yb-169	198	32d	---	0.71
Lu ppm	Lu-177	208	161d	----	0.10
Hf ppm	Hf-182	482	42.39d	0.18	3.73
Th ppm	Pa-233	312	27d	0.13	2.48
U ppm	Np-239	106	2.35d	0.69	---

Radium, thorium, and potassium are not uniformly distributed in soil or rocks, from which building materials are derived, but the radioactivity varies, often greatly, over a distance of some meters."[20] . The average activity concentrations of ^{232}U, ^{232}Th and ^{40}K in the cement samples under study are given in Figure 1. Table 5, gives the estimated radium equivalent activity, dose rate, external hazard index and representative level index due to natural gamma emitters as measured in Portland and white cement under study. From this Table, for all samples, we can indicate the following: - The Raeq values varying from 90.50 to 145.13 Bq kg^{-1}with a mean value of 99.24 Bqkg^{-1}. These values are lower than the maximum permissible value of 370 Bq kg-1. The absorbed dose rate varying from 49.02 to 63.73 nGy /h with a mean value of 51.87 nGy /h. These values are lower than the maximum permissible value of 55 nGyh^{-1}[17]. The calculated external hazard values for cement samples varies from 0.17 to 0.29 with a mean value of 0.23. All the cement samples have values lower than unity. Based on the obtained results of radium equivalent activity, representative level index and external hazard indices, one can conclude that there is no health hazard from the using of this cement in construction. Figure 2 showed the radium equivalent and absorbed dose of the present cement samples.

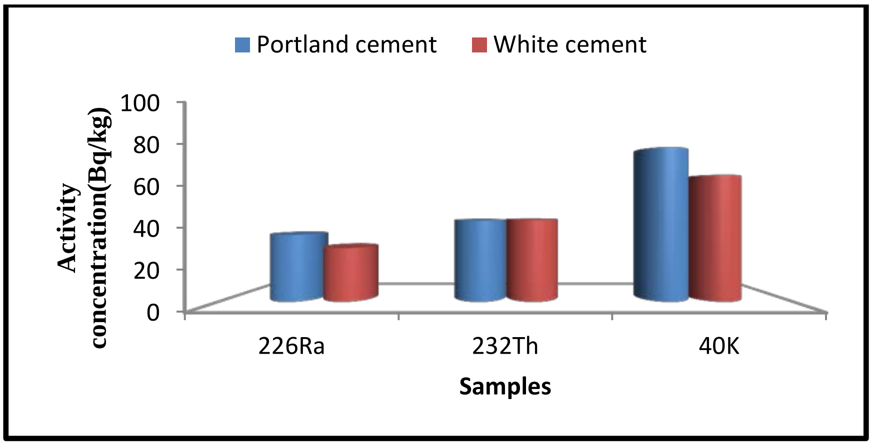

Figure 1: Comparison between the average activities of ^{226}Ra, ^{232}Th and ^{40}K of Portland and white cement samples under investigation.

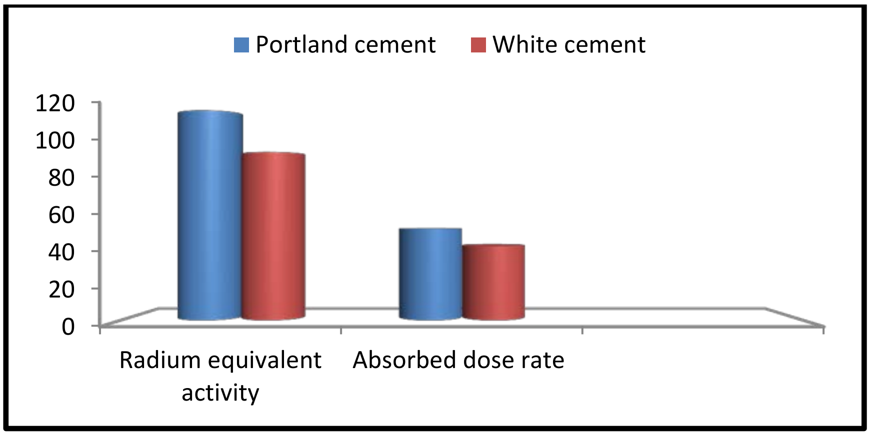

Figure 2: Average absorbed dose rate (nGy/h) and Radium equivalent (Bq/Kg) for Portland and white cement samples

Table 3: The activities of ^{226}Ra, ^{232}Th and ^{40}K (Bq Kg^{-1}) of cement

Sample number	Sample Name	^{226}Ra	^{232}Th	^{40}K
1	Portland	18.09±3.81	8.24±0.49	76.86±3.84
2		41.89±5.11	47.55±2.39	89.14±4.45
3		36.22±5.06	45.94±2.30	86.64±4.33
4		37.10±3.98	71.65±3.58	79.32±3.96
5		44.71±4.08	42.45±2.12	78.42±3.92
Average		**35.60±4.41**	**43.17±2.18**	**82.08±4.10**

6	White	34.57±4.51	43.15±2.16	74.17±3.70
7		25.14±3.33	44.25±2.22	56.63±2.83
8		31.04±3.96	44.72±2.24	71.42±3.57
9		27.29±3.32	42.45±2.13	66.613±3.33
10		24.61±3.63	42.74±2.14	68.05±3.40
Average		**28.53±3.75**	**43.46±2.18**	**67.38±3.36**

Table 4: Comparison the activities of ^{226}Ra, ^{232}Th, ^{40}K and $(Ra)_{eq}$ in cement from worldwide

Sample number	Types of cement	Ra_{eq} (Bq/kg)	D, (nGy/h)	H_{ex}
1	Portland	115.27	46.54	0.24
2		116.13	51.79	0.20
3		107.99	48.09	0.19
4		145.13	63.73	0.29
5		110.91	49.57	0.18
Average		**119.09**	**51.94**	**0.22**
1	White	101.47	45.12	0.18
2		92.40	40.71	0.18
3		99.99	44.33	0.18
4		92.66	41.03	0.17
5		90.50	40.02	0.17
Average		**95.40**	**42.24**	**0.18**

Table 5: The radiation hazard parameters of cement

Material	Country	Activity concentration			$Ra_{\mathbf{eq}}$	Références
		^{226}Ra	^{23}2Th	^{40}K		
Portland cement	Turkey	12.5	2.7	1141.9	104.2	[1]
	Pakistan	37	28	200	92.0	[2]
	Egypt	33.8	61.8	89.0	129	[3]

	India	19	35	406	60.8-121	[4]
	China	118.7	36.1	444.5	154.4	[21]
	Tanzania	46	28	228	103.60	[22]
	Nigeria	30.2	24.6	251.3	84.7	[23]
	Malaysia	34.7	32.9	190.6	96.42	[24]
	Saudi Arabia	**35.60**	**43.17**	**82.08**	**103.09**	**Present work**
White cement	Turkey	35.60	43.17	82.08	103.09	[1]
	Egypt	12.5	2.7	1141.9	104.2	[3]
	Nigeria	40.7	65.5	77.9	140.3	[23]
	Iraq	41.9	30.1	340.2	111.1	[25]
	Saudi Arabia	**28.53**	**43.46**	**67.38**	**95.40**	**Present work**

5. Conclusion

Twenty elements were quantitatively determined in cement samples collected from the local market in Saudi Arabia. The elements determined are: Na, K, Sc, Cr, Co, Ti, Mn, Fe, Ga, Sr, Sn, Ba, Cs, Ce, Sm, Yb, Lu, Hf, Th and U. From the obtained findings, we can say that INAA is an effective and useful tool to provide a good data for cement samples. The average values for ^{226}Ra, ^{232}Th and ^{40}K are 35.60, 43.17, 82.08 Bq·kg^{-1} for Portland cement and 28.53, 43.46, 67.38 Bq·kg^{-1} for white cement and were less than the recommended levels of UNSCEAR data.

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