CHEMICAL ENGINEERING TRANSACTIONS

VOL. 32, 2013

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at: www.aidic.it/cet

Chief Editors: Sauro Pierucci, Jiří J. Klemeš

ISBN 978-88-95608-23-5; **ISSN** 1974-9791

DOI: 10.3303/CET1332280

Study of Natural Radioactivity of Slovak Cements

Adriana Eštoková*, Lenka Palaščáková

Technical University of Košice, Faculty of Civil Engineering, Institute of Environmental Engineering, Vysokoškolská 4, 042 00 Košice, Slovakia
adriana.estokova@tuke.sk

Building materials belongs to the sources causing direct radiation exposure, therefore the natural radionuclide content of building materials is necessary to be still discussed over the world. Cements cause direct radiation exposure because of their radium (^{226}Ra), thorium (^{232}Th) and potassium (^{40}K) content. Like other construction materials, the natural level of radioactivity in cement gives rise to external and internal indoor exposure.
This work is focused on the assessment of natural radioactivity of cements commonly used in the Slovak Republic. The cement samples of CEM I, CEM II, CEM III and CEM V types from the significant Slovak cement producers were analyzed in the experiment. The samples were tested for the radionuclides content by using gamma spectroscopic measurements. The radionuclides activity in the Portland cements ranged from 5.8 – 21.6 Bq kg^{-1}, 16.0 – 38.23 Bq kg^{-1} and 52.0 – 733.6 Bq kg^{-1} for ^{226}Ra, ^{232}Th and ^{40}K, respectively. The measured radionuclides content was compared to the specific requirements in relation to the Slovak eco-labelling process. The index of mass activity of natural radionuclides (gamma index) in cements was calculated in the range from 0.122 – 0.484.

1. Introduction

All building raw materials and products derived from rock and soil contain various amounts of mainly natural radionuclides of the uranium (^{238}U) and thorium (^{232}Th) series, and the radioactive isotope of potassium (^{40}K) (Turhan, 2008). It has long been known that some construction materials are naturally more radioactive than others. The natural level of radioactivity in construction materials, even of low-level activity, gives rise to external and internal indoor exposure (Pauliková and Kopilčáková, 2009). The external radiation exposure is caused by gamma radiation originating from members of the uranium and thorium decay chains and from 40 potassium however, the internal radiation exposure, mainly affecting the respiratory tract, is due to the short-lived daughter products of radon which are exhaled from construction materials into room air (Khan and Khan, 2001). Thus, the knowledge of radioactivity in building materials is important to estimate the radiological hazards on human health (El-Taher et al., 2010). The most important naturally occurring radionuclides present in cements are 226 radium, 232 thorium and 40 potassium as mentioned above (Damla et al., 2010).
The distribution of natural radionuclides in building materials samples under investigation is not uniform. Therefore, a common radiological index has been introduced to represent the specific radioactivity level of ^{226}Ra, ^{232}Th and ^{40}K by a common index, which takes into account the radiation hazards associated with them. This index is usually known as radium equivalent (Ra_{eq}) activity (Beretka and Mathew, 1985):

$$Ra_{eq}=A_{Ra}+1.43A_{Th}+0.077A_K \quad (1)$$

where A_{Ra}, A_{Th} and A_K are the specific activities of ^{226}Ra, ^{232}Th, and ^{40}K, respectively in Bq kg^{-1}. In the definition of Ra_{eq}, it is assumed that 10 Bq $kg^{-1}$of ^{226}Ra, 7 Bq kg^{-1} of ^{232}Th and 130 Bq kg^{-1} of ^{40}K produce equal gamma-ray dose rate (Beretka and Mathew, 1985).
In order to assess whether the safety requirements for building materials are being fulfilled, a gamma index $I\gamma$is calculated as proposed by the European Commission (EC, 1999):

Please cite this article as: Estokova A., Palascakova L., 2013, Study of natural radioactivity of slovak cements, Chemical Engineering Transactions, 32, 1675-1680 DOI: 10.3303/CET1332280

$$I\gamma = \frac{A_{Ra}}{300} + \frac{A_{Th}}{200} + \frac{A_K}{3000} \quad (2)$$

where A_{Ra}, A_{Th} and A_K are the specific activities of ^{226}Ra, ^{232}Th, and ^{40}K, respectively in Bq kg^{-1}. $I\gamma \leq 1$ corresponds to an absorbed gamma dose rate less or equal to 1 mSv y^{-1}, while $I\gamma \leq 0.5$ corresponds to a dose rate less or equal to 0.3 mSv y^{-1}.
There are many types of cements according to the chemical composition and hydraulic properties for each one. The contents of ^{226}Ra, ^{232}Th and ^{40}K in cements materials can vary considerably depending on their geological source and geochemical characteristics. This work is focused on the assessment of natural radioactivity of cements produced and commonly used in the Slovak Republic.

2. Materials and methods

The natural radioactivity was measured in 11 samples of 4 cement types (CEM I – III, CEM V) produced in the Slovak Republic. The characterisation of the assessed cement samples is presented in Table 1.
The basic chemical composition of tested cements was investigated by X-ray fluorescence analysis using SPECTRO iQ II (Ametek, Germany) with silicon drift detector SDD with resolution of 145 eV at 10,000 pulses. The primary beam was polarized by Bragg crystal and Highly Ordered Pyrolytic Graphite - HOPG target. The samples were measured during 300 s at voltage 25 kV and 50 kV respectively, at current of 0.5 and 1.0 mA under helium atmosphere by using the standardised method of fundamental parameters for cement pellets. The cement samples were prepared as pressed tablets with diameter of 32 mm by mixing of 5 g of cement and 1 g of dilution material (M-HWC) and pressed at pressure of 10 tons.
Measurement of radioactivity was carried out using a detection system EMS-1A SH (Empos) with a multichannel analyzer MC4K with optimized resolutions of 818 V, 4,096 channel and with 0.9 cm of lead shielding and internal lining of 2 mm tinned copper.
The samples in powder form having mass of 0.53 ± 0.06 kg were prepared in the Marinelli containers with size of 450 mL. Thus prepared samples in containers were sealed hermetically and stored for more than 40 days to achieve the secular equilibrium between ^{226}Ra and its short-lived daughters before gamma spectrometry measurements. The spectra were first measured with empty containers (blank sample) and then with containers filled with weighed amounts of sample.
The background of the detection system plays a vital role in the measurement of low-level activity as typically found in construction materials. The counting system must have a background as low as attainable with a minimum number of spectral lines originating from natural radionuclides which may be present in the system components and in the surrounding environment of the counting facility. In the presented study, routine measurements of the background count rates for natural radionuclides were carried out before each set of measurements, each for a counting time of 43,200 s (i.e. 12 h). The emphasis was on the determination of specific activity concentration of ^{226}Ra, ^{232}Th and ^{40}K. The radioactivity of ^{40}K was measured directly through its gamma ray energy peak at 1,460.8 keV, while activities of ^{226}Ra and ^{232}Th were calculated based on the mean value of their respective decay products. Activity of ^{226}Ra was measured using the 351.9 keV gamma rays from ^{214}Pb and the activity of ^{232}Th was measured using the 238.6 keV gamma rays of ^{212}Pb. Every sample of cement was measured for 18,000 s.

Table 1: The characteristics of tested cement samples in accordance to STN EN (2002)

Sample	Cement type		Composition
1	CEM I	Portland cement	clinker without no other single constituents
2	CEM I	Portland cement	clinker without no other single constituents
3	CEM II/A-S	Portland slag cement	from 6 to 20 % of slag
4	CEM II/B-S	Portland slag cement	from 21 to 35 % of slag
5	CEM III/A	Blastfurnace cement	from 36 to 65 % of slag
6	CEM V/A	Composite cement	more than 35 % of blastfurnace slag, puzzolana or flyash
7	CEM I	Portland cement	clinker without no other single constituents
8	CEM II/A-LL	Portland limestone cement	from 6 to 20 % of limestone
9	CEM II/B-M	Portland composite cement	contains slag and limestone
10	CEM II/B-S	Portland slag cement	from 21 to 35 % of slag
11	CEM III/A	Blastfurnace cement	from 36 to 65 % of slag

3. Results and discussions

The percentage of basic components of tested cement samples measured by XRF spectroscopy is shown in Table 2.

Table 2: The basic chemical composition of studied cements

Oxides	Sample										
(%)	1	2	3	4	5	6	7	8	9	10	11
MgO	2.14	3.82	4.23	5.87	6.23	3.75	1.54	2.05	2.18	2.81	4.95
Al_2O_3	3.91	4.39	4.31	5.57	5.44	9.57	4.06	4.77	4.54	4.51	5.58
SiO_2	19.8	19.7	20.9	26.4	28.8	37.9	17.8	19.2	18.9	20.6	27.1
SO3	3.13	3.17	3.08	2.85	2.72	2.58	3.25	3.17	3.19	3.10	2.86
K_2O	0.49	0.58	0.53	0.55	0.53	1.00	1.15	1.09	1.04	0.94	0.80
CaO	63.6	58.2	55.9	53.1	48.4	40.1	54.2	58.2	52.8	51.9	50.0
TiO_2	0.23	0.21	0.22	0.26	0.24	0.32	0.21	0.22	0.22	0.22	0.24
MnO	0.33	0.35	0.36	0.38	0.38	0.35	0.33	0.33	0.33	0.33	0.34
Fe_2O_3	2.73	3.25	2.64	2.50	1.71	5.21	2.63	2.70	2.40	2.21	1.75

The chemical composition of the investigated cement samples correlate to the standard chemical composition of particular cement types (Lam et al., 2010). The percentage of the oxides depends on both raw materials and constituents.

The specific activity values due to ^{40}K, ^{226}Ra and ^{232}Th and their sum for measured samples of cement have been summarised in Table 3. The table shows that the specific activity due to ^{40}K is the largest contributor to the total activity for all the cement samples.

The average concentrations of the radionuclides measured in the cements were 269.24, 12.59 and 25.03 Bq kg^{-1} for ^{40}K, ^{226}Ra and ^{232}Th, respectively. Analysing the results, the lowest radionuclide activity of ^{40}K was measured in sample 1 of CEM I Portland cement (51.982 Bq kg^{-1}), while the highest value for the same radionuclide reached 733.66 Bq kg^{-1} measured in sample 6 (CEM V/A – Composite cement). ^{226}Ra lowest value was 5.795 Bq kg^{-1} measured in sample 1 (CEM I – Portland cement) and the highest value was 21.57 Bq kg^{-1} in sample 11 (CEM III/A – Blastfurnace cement).The highest activity value for ^{232}Th (38.23 Bq kg^{-1}) was found in sample 6 (CEM V/A – Composite cement) and the lowest radionuclide activity (15.98 Bq kg^{-1}) in sample 9 (CEM II/B-M – Portland composite cement). The average concentrations for all three radionuclides in Portland cements were 149.9 Bq kg^{-1}, 9.39 Bq kg^{-1} and 18.3 Bq kg^{-1} for ^{40}K, ^{226}Ra and ^{232}Th, respectively. The contents of ^{40}K, ^{226}Ra and ^{232}Th in tested cements depend on the raw materials and probably vary considerably in relation to the various geological source and geochemical characteristics.

The specific activity of ^{40}K, ^{226}Ra and ^{232}Th determined in the presented study for Portland cements has also been compared with the values reported for Portland cements in other countries (Table 4). The measured activities due to all three radionuclides in Portland cements in Slovakia have been found to be comparable with those reported abroad.

Table 3: The average activity concentration of ^{40}K, ^{226}Ra and ^{232}Th for the assessed samples

Sample	^{40}K (Bq kg^{-1})	^{226}Ra (Bq kg^{-1})	^{232}Th (Bq kg^{-1})	Total (Bq kg^{-1})
1	51.982	5.795	16.98	74.757
2	169.32	13.08	19.84	202.24
3	314.56	10.83	32.80	358.19
4	460.33	12.38	34.23	506.94
5	417.08	16.68	37.47	471.23
6	733.66	14.61	38.23	786.50
7	228.32	9.286	18.15	255.76
8	178.89	8.186	18.65	205.73
9	145.95	12.12	15.98	174.05
10	150.24	13.95	20.08	184.27
11	111.29	21.57	22.94	155.80

Table 4: Comparison the radionuclides activity of Portland cements

Country	^{40}K (Bq kg^{-1})	^{226}Ra (Bq kg^{-1})	^{232}Th (Bq kg^{-1})	Reference
Australia	114.7	51.8	48.1	Beretka and Mathew (1985)
Austria	210.0	26.7	14.2	Sorantin and Steger (1984)
Bangladesh	1133	61.0	80.0	Roy et al. (2005)
Brazil	564.0	61.7	58.5	Malanca et al. (1993)
China	173.0	57.0	37.0	Xinwei (2005)
Egypt	93.00	35.0	19.0	El-Bahi (2004)
Finland	251.0	40.2	19.9	Mustonen (1984)
Greece	310.0	92.0	31.0	Stoulos et al. (2003)
Italy	316.0	46.0	42.0	Sciocchetti et al. (1984)
Japan	139.0	36.0	21.0	Suzuki et al. (2000)
Malaysia	203.5	81.4	59.2	Chong and Ahmed (1982)
Netherlands	230.0	27.0	19.0	Ackers et al. (1985)
Norway	259.0	29.6	18.5	Stranden and Berteiz (1980)
Pakistan	272.9	26.1	28.7	Khan and Khan (2001)
Turkey	267.0	41.0	26.0	Turhan (2008)
Slovakia	149.9	9.39	18.3	Presented study

The range of radium equivalent activities Ra_{eq} was calculated for all assessed samples from 34.05 – 125.66 Bq kg^{-1}. From the results it can be noticed that the lowest value of Ra_{eq} (34.05 Bq kg^{-1}) was calculated for sample 1 (CEM I – Portland cement), while the highest value of 125.66 Bq kg^{-1} was calculated for sample 6 (CEM V/A – Composite cement).

The high Ra_{eq} values calculated for sample 5 (CEM III/A – Blastfurnace cement) and sample 6 (CEM V/A – Composite cement) can be rendered to the high concentration of the three radionuclides ^{40}K, ^{226}Ra and ^{232}Th in these materials as shown in Table 3. Comparing the results, it is evident that there are considerable variations in the Ra_{eq} of the different cement types and also within the same type of cement originating from different areas. This fact is important from the point of view of selecting suitable cement for use in building and construction especially concerning those which have large variations in their activities. Large variation in radium equivalent activities may suggest that it is advisable to monitor the radioactivity levels of cements from a new source before adopting it for use as a building material. The maximum value of Ra_{eq} in building raw materials and products must be less than 370 Bq kg^{-1} for safe use, i.e., to keep the external dose below 1.5 mSv y^{-1} (UNSCEAR, 2000). Radium equivalent activities calculated for all assessed samples were less than 370 Bq kg^{-1} that means safe using these cements as building material. Radium equivalent activities calculated for the assessed cement samples are illustrated in Figure 1.

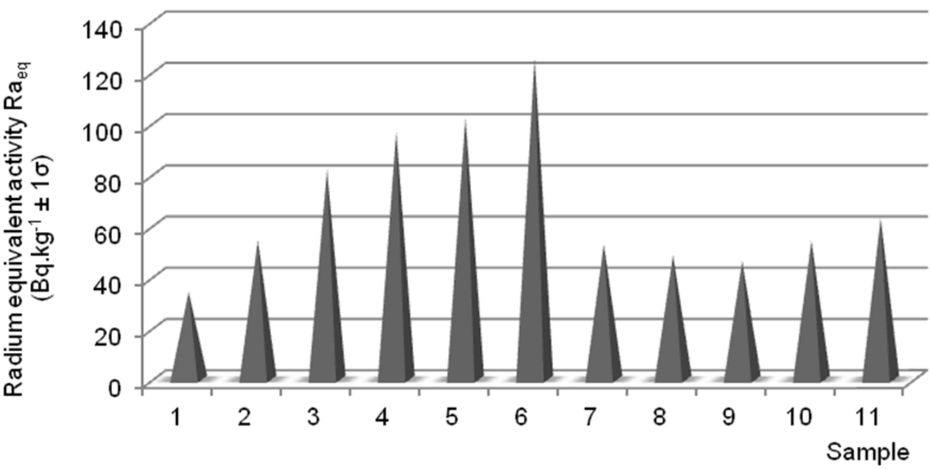

Figure 1: Radium equivalent activity Ra_{eq} in (Bq kg^{-1} ± 1σ) for the tested cement samples

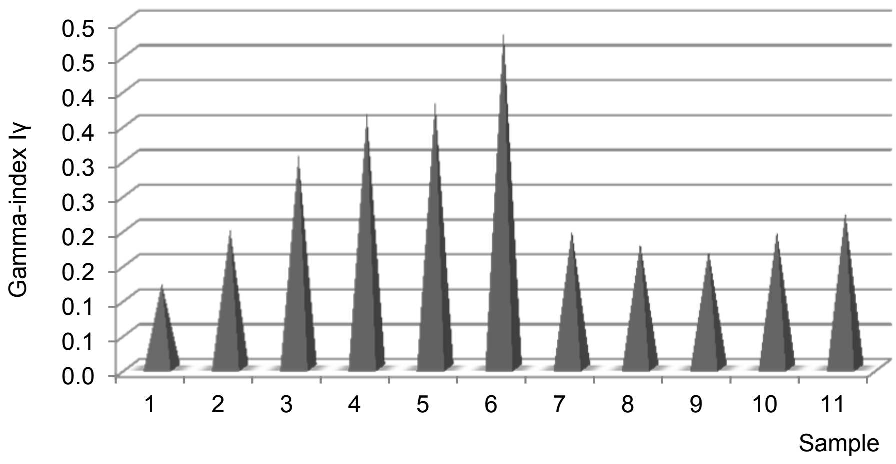

Figure 2: Gamma-index $I\gamma$ in assessed samples

The mean values of index of natural radionuclides mass activity (gamma index) $I\gamma$ calculated from the measured activity concentration of ^{226}Ra, ^{232}Th and ^{40}K are presented in Figure 2 for different cement types. The mean calculated values of $I\gamma$ for the studied samples values varied in the range between 0.122 – 0.484. The lowest value of $I\gamma$ was 0.122 calculated for sample 1 (CEM I – Portland cement) and the highest one was 0.484 calculated for sample 6 (CEM V/A – Composite cement). The gamma index should also take into account typical ways and amounts in which the material is used in a building. The limit values depend on the dose criteria, the way and amount of the material and the manner in which it was used in a building and construction. For material used in bulk amounts $I\gamma \leq 1$ corresponds to an absorbed gamma dose rate of 1 mSv y^{-1} (EC, 1999). The gamma index calculated for all assessed samples was less than gamma index limit.

4. Conclusion

The specific activity of ^{40}K, ^{226}Ra and ^{232}Th, the radium equivalent activity and gamma index were evaluated in cement samples to assess the potential radiological hazard associated with the building materials. Such data are of value in determining the radioactivity content of the buildings and the possible radiological risks associated with these structures. The variations and the large spread in the data measured are a reflection of the different geological origins of the raw materials.

The results of the presented study showed the activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in all samples are in the range of limit values. The average Ra_{eq} values of the studied samples range from 34.05 – 125.66 Bq kg^{-1}, which are below the internationally accepted values (370 Bq kg^{-1}). The calculated total annual effective dose of all cement samples was lower than 1 mSv y^{-1}. The study shows the analysed cements do not pose any significant source of radiation hazard and are safe for use in the construction of dwellings.

Acknowledgements

The research has been carried out within the project no. 1/0481/13 Study of selected environmental impacts of building materials.

References

Ackers J.G., Den-Boer J.F., De-Jong P., Wolschrijn R.A., 1985, Radioactivity and exhalation rates of building materials in the Netherlands, Sci. Total Environ. 45, 151-156.

Beretka J., Mathew P.J., 1985 Natural radioactivity of Australian building materials, Industrial wastes and by-products, Health Phys. 48, 87-95.

Chong C.S., Ahmed G.U., 1982, Gamma activity in some building materials in West Malaysia, Health Phys. 43, 272-273.

Damla D., Cevik U., Kobya A.I., Celik A., Celik N., Van Grieken R., 2010, Radiation dose estimation and mass attenuation coefficients of cement samples used in Turkey, Journal of Hazardous Materials 176, 644-649.

EC (European Commission), 1999. Radiation protection 112. Radiological protection principles concerning the natural radioactivity of building materials. Directorate-General Environment, Nuclear Safety and Civil Protection.

El-Bahi S.M., 2004, Assessment of radioactivity and radon exhalation rate in Egyptian cement, Health Phys. 86, 517-522.

El-Taher A., Makhluf S., Nossair A., Abdel Halim A.S., 2010, Assessment of natural radioactivity levels and radiation hazards due to cement industry, Applied Radiation and Isotopes 68, 169-174.

Khan K., Khan, H.M., 2001, Natural gamma-emiting radionuclides in Pakistani Portland cement, Applied Radiation and Isotopes 54, 861-865.

Lam H.K., Barford J.P., McKay G., 2010, Utilization of incineration waste ash residues as Portland cement clinker, Chemical Engineering Transactions 21, 757-762 DOI: 10.3303/CET1021127

Malanca A., Pessina V., Dallara G., 1993, Radionuclide content of building materials and gamma-ray dose rates in dwellings of Rio-Grande Do-Norte Brazil, Radiat.Prot. Dosim. 48, 199-203.

Mustonen R., 1984, Natural radioactivity and radon exhalation rate from Finnish building materials, Health Phys. 46, 1195-1203.

Pauliková A., Kopilčáková L., 2009, Indoor Environmental Managament, Pollution Engineering 40, 28-30.

Roy S., Alam M.S., Begum M., Alam B., 2005, Radioactivity in building materials used in and around Dhaka city, Radiat. Prot. Dosim. 114, 527-532.

Sciocchetti G., Scacco F., Baldassini P.G., 1984, Indoor measurement of airborne natural radioactivity in Italy, Radiat. Prot. Dosim. 7, 347-351.

Sorantin P., Steger F., 1984, Natural radioactivity of building materials in Austria, Radiat. Prot. Dosim. 7, 59-61.

STN EN, 2002, STN EN 197-1: Cement Part 1: Composition, specifications and conformity criteria for common cements, Slovak Standard Institute, Bratislava, Slovak Republic (in Slovak).

Stoulos S., Manolopoulou M., Papastefanou C., 2003, Assessment of natural radiation exposure and radon exhalation from building materials in Greece, J. Environ. Radiact 69, 225-240.

Stranden E., Berteiz L., 1980, Radon in dwellings and influencing factors, Health Phys. 39, 275-284.

Suzuki A., Lida T., Moriizumi J., Sakuma, Y., 2000, The effects of different types of concrete on population doses, Radiat. Prot. Dosim. 90, 437-443.

Turhan Ş., 2008, Assessment of the natural radioactivity and radiological hazards in Turkish cement and its raw materials, Journal of Environmental Radioactivity 99, 404-414.

UNSCEAR, 2000. Sources and Effects of Ionizing Radiation. United Nations Scientific Committee on the Effects of Atomic Radiation, United Nations Publication, New York, USA.

Xinwei L., 2005, Radioactive analysis of cement and its products collected from Shaanxi, China, Health Phys. 88, 84-86.