IOP Conf. Series: Materials Science and Engineering **385** (2018) 012050 doi:10.1088/1757-899X/385/1/012050

Examination of potential radiation hazard of concrete composites with different slags as additives

E Singovszka and A Estokova

Department of Material Engineering, Technical University of Kosice, Faculty of Civil Engineering, Institute of Environmental Engineering, Kosice, Slovakia

Abstract. Present day steelmaking slags are being successfully used as a high quality mineral aggregate for the building materials. With this, it is of vital importance to be familiar with the technical significance of the secondary application of slag, because some slag might contain increased concentration of substances harmful to human health. In terms of slag impact on the environment, radionuclides are the least researched of all pollutants emitted from the metallurgical processes. The paper presents the results of the measurement the natural radioactivity levels in concrete composites with incorporated slags in various proportions. The radionuclides´ activity index, dose rate and annual effective dose were evaluated to assess the potential radiological hazard associated with composites with slag and ferromanganese slag.

1. Introduction

Most building materials of natural origin contain small amounts of naturally occurring radioactive material (NORM), mainly radionuclides from the ^{238}U and ^{232}Th decay chains and the radioactive isotope of potassium, ^{40}K. The activity concentration of the radionuclides in building materials varies considerably, depending on both the nature and the origin of the raw material compounds. Generally, natural building materials reflect the geology of their site of origin. The average activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in the Earth's crust are about 40, 40 and 400 Bq.kg^{-1} respectively [1-2]. Available literature shows typical and maximum activity concentrations in common building materials and industrial by-products used for building materials in the EU (max. values of activity for slag of ^{226}Ra is 2100 Bq.kg^{-1}, for ^{232}Th Bq.kg^{-1} is 340 and for ^{40}K is 1000 Bq.kg^{-1}). The radioactivity concentrations found in certain kinds of industrial by-products (fly ash, phosphogypsum, etc.) can often be significantly higher in comparison with most common building materials [1-3]. Metallurgical industry influences the environment directly with its by-products, i.e. various hazardous and non-hazardous technological wastes (slag, refractories, sludge, dust, mill scale, etc.) which are most commonly disposed of at their inadequate landfills. The most common technological waste inadequately disposed of in the said manner is unprocessed steel slag. Through awareness of environmental considerations and more recently, the concept of sustainable development, extensive research and development has removed slag from industrial waste into modern industrial product which is effectively and profitably used for many industrial purposes, especially as raw material in the numerous building applications [4-6]. Slags from different metallurgical processes contain many useful components (metals and oxides) used for various industrial and construction purposes. The properties of slag including mineralogical composition play important roles in determining specific applications. Steel-making processes produce significant volumes of waste, which is a problem both from the economical and environmental point of view. In order to find solutions for exploitation of steel slag, as well as due to increasingly demanding legal regulations in environment protection, physical, chemical and radiochemical properties of this material are more and more frequently subjected to systematic research. The amounts of radionuclides involved are noteworthy. US, Australian, Indian and UK coals contain up to about 4 ppm uranium, those in Germany up to 13 ppm, and those from Brazil and China range up to 20 ppm uranium. Thorium concentrations are often about three times those of uranium [7-8].

2. Experimental

2.1. Materials

Research on radioactivity of building materials was performed using 12 mixtures of cement composites with different portions of cupola furnace slag (TH) and ferromanganese slag (TO). Recipes of cement composites are given in table 1.

Table 1. Recipes of cement mortars per 1m^3.

The components of mortar mix [kg]	TH 0	TH 10	TH 20	TH 30	TO 0	TO 10	TO 20	TO 30
Cement CEM I 42.5 R [kg]	450	405	360	315	450	405	360	315
Cement replacement [wt.%]	0%	10%	20%	30%	0%	10%	20%	30%
Cupola furnace slag [kg]	0	45	90	135	-	-	-	-
Ferromanganese slag [kg]	-	-	-	-	0	45	90	135
Fine aggregate [kg]	1350							
Water [L]	225							

2.2. Radiological measurements

The mass activities of radionuclides (^{226}Ra, ^{232}Th and ^{40}K) in cement composites were measured using gamma ray spectrometry. This technique is an important tool in field of environmental radioactivity measurements due to its high resolution, large photo peak efficiency and it can measure different radionuclides in a single spectrum. Measurements were carried out using an EMS-1A SH (Empos, Prague, Czech Republic) detection system equipped with a NaI/Tl scintillation detection probe and a MC4K multichannel analyzer with optimized resolution of 818 V, 4.096 channel and with 9 cm of lead shielding and internal lining of 2 mm tinned copper.

The specific activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K were determined in Bq.kg−1 using the count spectra. The ^{40}K radionuclide was measured directly through its gamma ray energy peak at 1461 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. The same counting time of 86,400 s (24 h) was used for all measured samples.

2.3.Methods for radiological analysis

Gamma index Iγ

Within the European Union effective doses exceeding 1 mSv.y^{-1} should be taken into account from the radiation protection point of view. Since several radionuclides contribute to the overall dose, in order to assess whether the dose criterion is met, an activity concentration index Iγ have been established. Radionuclides´ activity index, or shortly gamma index, Iγ was defined according to the following equation (1):

$$I_\gamma = \frac{A_{Ra}}{300} + \frac{A_{Th}}{200} + \frac{A_K}{3000} \quad (1)$$

where A_{Ra}, A_{Th}, A_K are the radium, thorium and potassium, activity concentration (Bq.kg^{-1}) in the building materials. The gamma index is derived to identify whether a dose criterion is met. The gamma index of materials used in building should not exceed limit values depending on the dose criterion ($I_\gamma \leq 1$) [9,10]. The gamma index should be used only as a screening tool for identifying materials which might be of concern.

Dose rate and annual effective dose
The absorbed dose rates in air in a room can be calculated by using the specific dose rates given in [9-10]. The specific dose rates for radionuclides are given for different screening tool of identifying materials which might be of concern. Indoor dose rates for a model room (dimension of 4m x 5m x 2.8 m, thickness of 20 cm, density of 2,35 g/cm^3, and the background of 50 nGy.h^{-1}) are calculated with different structures in a building causing the irradiation as follows:
All structures:

$$D = 0.92.A_{Ra} + 1.1.A_{Th} + 0.08A_K \quad (2)$$

Floor and walls:

$$D = 0.67.A_{Ra} + 0.78.A_{Th} + 0.057A_K \quad (3)$$

Floor only:

$$D = 0.24.A_{Ra} + 0.28.A_{Th} + 0.02A_K \quad (4)$$

The annual effective dose D_E (mSv), due to gamma radiation from building materials with the annual exposure time of 7000 h [9,10] was calculated by next equation:

$$D_E = 0.7\ (Sv.Gy^{-1})x7000\ (h)x10^{-6}\ xD(nGy.h^{-1}) \quad (5)$$

3. Results and discussion

Table 2 presents the measured radionuclides´ mass concentrations in input materials and studied cement composites with slag additives as well as the calculated gamma indexes.

Table 2. The mass activities of radionuclides and gamma indexes in input materials and composites samples.

Sample	Mass activity [Bq.kg^{-1}] ^{226}Ra	^{232}Th	^{40}K	Gamma index Iγ [-]
TH 0	5.72	20.74	80.45	0.149
TH10	3.17	8.54	5.78	0.055
TH20	3.54	7.53	3.74	0.049
TH30	4.06	8.013	22.31	0.053
TO 0	5.72	20.74	80.45	0.149
TO10	3.36	6.66	14.37	0.044
TO20	2.96	6.08	4.987	0.040
TO30	4.07	8.26	4.794	0.055
Cupola furnace slag	16.95	48.95	97.04	0.345
Ferromanganese slag	14.82	48.93	155.28	0.333
Cement	3.03	11.63	57.27	0,09
Fine aggregates	4.11	4.86	33.23	0.06

The highest values of individual ^{226}Ra, ^{40}K and ^{332}Th mass activities were found for cupola furnace slag followed by ferromanganese slag. Measured activities of radionuclides in cement were lower than measured previously [11]. In [11], the radionuclide activities in CEM I cements ranged from 3.69 – 36.8 Bq·kg^{-1}, 11.8 – 24.9 Bq·kg^{-1} and 36.98 – 331.4 Bq·kg^{-1} for ^{226}Ra, ^{232}Th and ^{40}K, respectively. The analyzed mass activities in aggregates were also low. According to Terpakova [12], the aggregates radioactivity strongly depends on the geological sources and ranges from 21.5 to 29.9 Bq·kg^{-1} for ^{226}Ra, 5.0 to 11.4 Bq·kg^{-1} for ^{232}Th and 106.5 to 270.6 Bq·kg^{-1} for ^{40}K.

Surprisingly, the highest gamma radiation was observed in cement composites without any slag additions. Cabanekova [13] presents a very wide range of radionuclides activities regarding concretes. In spite of the highest radiation in slags themselves, no increasing trend was observed with the increasing portion of slag in composites. The calculated gamma indexes for input materials have been also extremely low when compared to Vietnamese and Indian study [10,14] where for example the Iγ of cement was four times higher. On the other hand, the results are similar to the Egyptian ones, as reported in [15].

The gamma index ranged from 0.04 (TO 20) – 0.35 (slag). The limit value of gamma index ($I_\gamma \leq 1$) was not exceed in any sample. Surprisingly, the highest values of gamma index have been calculated for the composites without any additives (TH0, TO0). In descending, the gamma index of 12 samples are of the sequence: Cupola furnace slag >ferromanganese slag> TH0=TO0 > cement >fine aggregates>TH10=TO30>TH30 >TH20>TO0>TO20. In particular, the I_γ values of cupola furnace slag and ferromanganese slag are significant to be considered in the assessment of radiological risk linking to standards and regulators on natural radioactivity in composites.

The values of dose rates depended on the structures in building causing the irradiation in samples are compared in figure 1.

The annual effective dose, calculated in accordance with equation (5), is given in table 3.

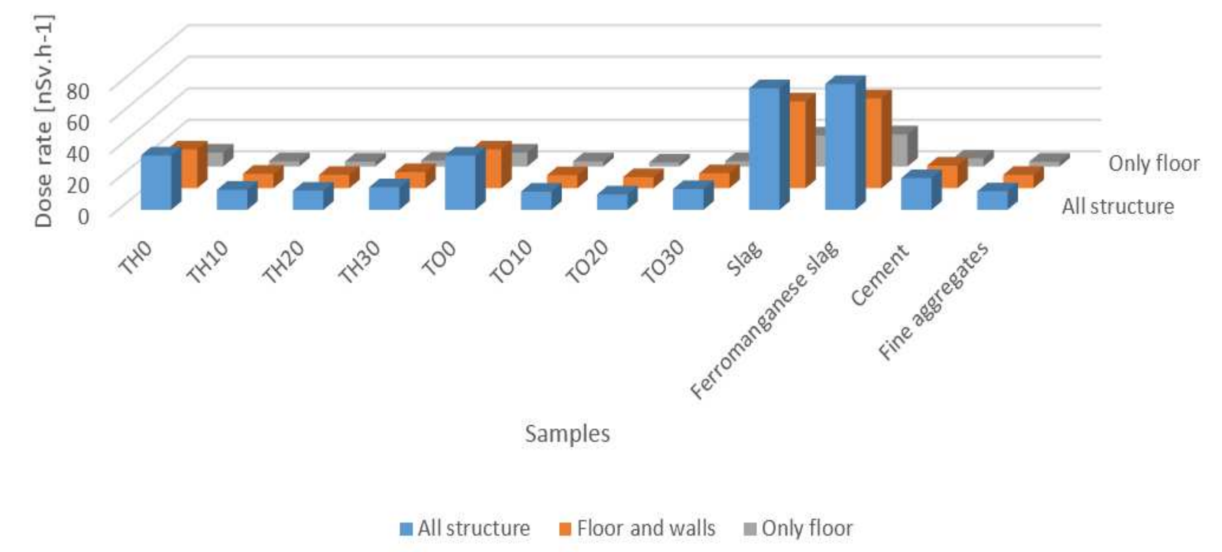

Figure 1. The dose rates of analyzed samples in nSv.h^{-1}.

Table 3. The annual effective dose for composite samples.

Sample	Annual effective dose DE [mSv]
TH 0	0.17
TH10	0.06
TH20	0.06
TH30	0.07
TO 0	0.17
TO10	0.06
TO20	0.05
TO30	0.06

The obtained data show that there are many samples with annual effective doses not exceeding the criterion of 1mSv. The highest values of rate dose calculated for slag-free composites were significantly lower than recommended dose criterion of 84 nSv.h^{-1}. The calculated values for dose rate for input materials have been lower when compared to Turkish study [16] where for example the D of cement was twice higher. This was the case for all three applications of composites: in floors, in floors and walls, and even in all structures.

4. Conclusion

The natural radioactivity of composites with slag additives was investigated to estimate the potential radiological hazard of the waste-based materials. The results showed that the mass activities of radionuclides or gamma indexes of the composites did not exceed the limit values recommended by UNSECAR. In addition, the values of the annual effective dose have been found within the safe limit. Addition of slag materials has not proved any significant positive or negative effect.

Another concern was to study the correlation between the amount of the slags and radioactivity´s increasing. However, no correlation was observed in this study. The present study will be helpful to understand radiation level in the research of cement composites with additives for further studies.

Acknowledgments
This work has been supported by the Slovak Grant Agency for Science (Grant No. 1/0648/17).

References

[1] Radiological Protection Principles concerning the natural radioactivity of building mateials, Radiation Protection 112, European Commision, Directorate Geeneral, Environment, Nuclear Safety and Civil Protection, 1999 11 p 16
[2] Mustonen R Pennanen M Annanmaki M Oksanen E 1999 *Enhanced radioactivity of building materials. Final Report of the Contract No 96-ET-003 for the European Commission*, Radiation and Nuclear Safety Authority, STUK: Finland p 16
[3] Soflic T Barisic D Sofilic U 2011 *Arch. Metall. Mater* **56** 627-634
[4] Huang Y Bird RN Heidrich O 2007 *Resour. Conserv. Recycl.* **52** 58-79
[5] Ducman V and Mirti B 2009 *Waste Manage*. **29** 2361-2368
[6] Svyazhin AG Shakhpazov E KH Romanovich DA 1998 *Metallurg* **42** 25-27
[7] Naturally-occuring radioactive materilas (NORM), Avaliable on internet: http://www.world-nuclear.org/information-library/safety-and-security/radiation-and-health/naturally-occurring-radioactive-materials-norm.aspx (Access: 18.12.2017)
[8] Liu H et al. 2013 Characteristics and disposal categorization of solid radioactive waste from the front end of the uranium fuel cycle. *In Naturally occuring radioactive material (NORM VII) Proceedings of an International Symposium Beijing China*
[9] EC (European Commission) 2000 Radiological Protection Principles Concerning the Natural Radioactivity of Building Materials. Directorate-General Environment, Nuclear Safety and Civil Protection; Luxembourg, Belgium: (Radiation Protection 112)
[10] Sieu LN et al. 2011 Natural radioactivity in commonly building materials used in Vietnam In *37th Annual Radioactive Waste Management Symposium* pp 1–9
[11] Estokova A and Palascakova L 2013 *Int J Env Res Pub He* **10** 7165–7179
[12] Terpakova E 2000 *Zeszyty naukowe Politechniki Rzeszowskiej* **32** 555-562
[13] Cabanekova H 1996 *J Radioanal Nucl Ch* **209** 301–306
[14] Raghu Y 2017 *J. Taibah Uni. Sci* **11** pp 223-233
[15] El-Taher A 2010 *Radiat Prot Dosim* **138** 158–165
[16] Mehmet A et al 2017 *J Radioanal Nucl Ch* vol **314** 941-948