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POSTER SECTION

RADIONUCLIDE CONTENT OF NORM BY-PRODUCTS ORIGINATED FROM COAL FIRED POWER PLANT OF OROSZLÁNY (HUNGARY)

R. Kardos[1, 2], Z. Sas[1], J. Szántó[1], A. Shahrokhi[1], J. Somlai[1] and T. Kovács[1, *]
[1]University of Pannonia, Institute of Radiochemistry and Radioecology, 10 Egyetem str. H-8200, Veszprém, Hungary
[2]Social Organization of Radioecological Cleanliness, 10. Egyetem str. H-8200, Veszprém, Hungary

In Thermal Power Plant of Oroszlány (Hungary) huge amount of by-products were produced since 1961. In this survey coal and different by-products were examined (fly-ash, bottom-ash, fluidized bed bottom-ash, gypsum, slurry-type ash). The natural isotopes were determined using HPGe detector. It was found that the radionuclide content of coal was significantly lower (^{226}Ra = 45.3 ± 6.3; ^{232}Th = 26.3 ± 5.7; ^{40}K = 210 ± 21 Bq kg^{-1}) than in case of ashes except fluidized type. The average values of the bottom ash – deposited in the largest quantity – was 3 times higher than coals' (^{226}Ra = 144 ± 18; ^{232}Th = 84.3 ± 14; ^{40}K = 260 ± 25 Bq kg^{-1}). In case of fractionized bottom ash the radionuclide content under 0.1 mm was 45% higher than above 1.6 mm and the massic radon exhalation under 0.1 mm was approximately four times higher than above this range.

INTRODUCTION

Certain industrial residues that are produced in large quantities offer an interesting option for reuse, and can be used as additives in the cement industry, such as fly ash, bottom ash, red mud, steel slag, nonferrous slag, etc.

As a result of energy production in coal fired power plants huge amount of by-products produce. In Thermal Power Plant of Oroszlány (Hungary) different techniques have been used since 1961 to burn brown-coal with various qualities.

On the basis of previous studies it was found that several Hungarian coals have elevated natural radionuclide content[(1)].

The reuse of by-products is raising concerns among authorities, public and scientists. Nowadays more and more attention is given the survey and the limitation of the natural public exposure[(2-6)]. People spend most of their time in buildings and the material of the building may include radionuclides, therefore, the actual radiation exposure of people may be different from the measured value in outdoors. Purpose of the reduction and limited of exposure the materials must meet various radiological conditions[(7)]. In some cases components of the raw materials remaining in the by-product may cause human health and environmental risks.

In addition to the potentially toxic compounds risks from NORMs (Naturally Occurring Radioactive Materials) with elevated natural radionuclide content need to be evaluated. In case of NORMs the elevated radionuclide content can pose risk to residents.

To avoid elevated risk the screening of building materials and raw materials is necessary before building in. The new Basic Safety Standard[(7)] (BSS) recommends a limit for gamma exposure according to the I-index. The index value is calculated using the following formula:

$$I = C_{^{226}Ra}/300 + C_{^{232}Th}/200 + C_{^{40}K}/3\,000 \qquad (1)$$

Where: I = Activity index, $C_{^{226}Ra}$ $C_{^{232}Th}$ $C_{^{40}K}$ activity concentrations of the ^{226}Ra, ^{232}Th and ^{40}K [Bq kg^{-1}].

The activity concentration index value of 1.0 can be used as a conservative screening tool for identifying materials that may cause the reference level laid down in the new EU BSS to be exceeded.

Due to the elevated radium concentration in NORMs the risk of increased radon exposure in case of build-in can be significantly high[(8,9)].

The radon exhalation rate of building materials greatly depends on the internal structure conditions of the matrix. This fact provides a great opportunity for their modification and optimization (heat-treatment, production technologies and additives, etc.) to reduce the exhalation.

The radon exhalation – defined in NEN 5699:2001 EN Standard[(10)] – is the radon activity that diffuses per unit of time from a material to the air surrounding the material, in Bq s^{-1}. By dividing the radon exhalation rate by either the area of the exhaling surfaces or by the mass of the sample, the areic (radon flux Bq m^{-2} s^{-1}) and massic radon exhalation rates (Bq kg^{-1} s^{-1}) can be calculated. Of course the massic radon exhalation rate should depend on several factors, such as porosity and geometry (especially on the thickness) of the sample.

It is possible to ensure an extreme case when the thickness of the samples is very small against the diffusion length of radon. In that case only the sample characteristics (^{226}Ra content, emanation coefficient, and the amount of the sample) have influence on exhalation rate[(11)]. It means all the emanated radon can

*Corresponding author: kt@almos.uni-pannon.hu

exhale from the matrix and the massic radon exhalation rate can be determined.

Generally, the diffusion length in case of porous materials is higher than 40 cm(12,13) (e.g. porous soil 40 cm, gypsum 110 cm, sand 200 cm). Owing to that fact, this assumption can be used if the sample thickness of porous material is less than 5 cm.

However, in OECD countries the average radon level is 39 Bq m^{-3}. Geogenic radon sources e.g. granite, shale rocks, as well as industrial by-products (bottom ash, coal ash), can significantly increase the indoor radon levels(14). In view of the latest scientific data, WHO proposes a reference level of 100 Bq m^{-3} (the ERR, excess relative risk, of pulmonary cancer per 100 Bq m^{-3} increase in long-term radon concentration at 16%) to minimize health hazards due to indoor radon exposure(15, 16).

Description of sampling site

The investigated materials come from the vicinity of Oroszlány. Initially, the coal-fired power plant was 4 x 50 MW, by the summer of 1990 it was reconstructed. The capacity of the power plant is 240 MW of electricity and further 84 MW of thermal power. Hungarian carbon stocks are depleted. The Hungarian brown coal contains many pollutants, by the burning generated many ash and sulphur dioxide.

In this power plant there was energy shift, and fluidized bed combustion are used. The fuel for combustion is fed airflow loosened and suspended state, previously preheated at 600-700 °C, refractory granular bed, where the fuel ignites. The temperature of the bed increases, at 800-900 °C stabilize with heat removal. The combustion is perfect, with low excess air, the system is insensitive to the coal quality. Occurs during burning of coal coarse slag, which falls into the bottom of the boiler, and fine ash which leaving the boiler with the flue gas, and accumulates in a container of the dust.

MATERIALS AND METHODS

Sample preparation

In this survey coal and different deposited by-products were examined (fly-ash, bottom-ash, fluidized bed bottom-ash, gypsum, and slurry-type ash). The samples were dried in a drying oven for 24 hours to constant weight at 105 °C to remove moisture. The samples were homogenized, grinded and sieved under 0.63 mm. In case of bottom ash 5 kg was fractionized to survey the radionuclide distribution and massic radon exhalation rate in function of the grain size.

Gamma spectrometry

The natural radionuclide content was determined by semiconductor HPGe detector (ORTEC GMX40-76, efficiency of 40 %). The data and spectra were recorded by ORTEC DSPEC LF 8196 MCA. The ^{226}Ra and the ^{232}Th content were determined via their progenies (295 keV of ^{214}Pb and 609 keV of ^{214}Bi, ^{232}Th were obtained via 911 keV of ^{228}Ac and 2614 keV of ^{208}Tl). The activity of ^{40}K was measured by the 1461 keV.

Determination of radon exhalation

After gamma spectrometry the samples were enclosed in a glass accumulation chamber covered by a metal cap. The chambers were aerated with radon-free N_2 gas prior to the accumulation to reduce the initial radon concentration to zero. Following the accumulation period, the chamber was connected to a closed loop system (Figure 1.), wherein the radon increment was measured by a SARAD RTM2100 radon/thoron monitor.

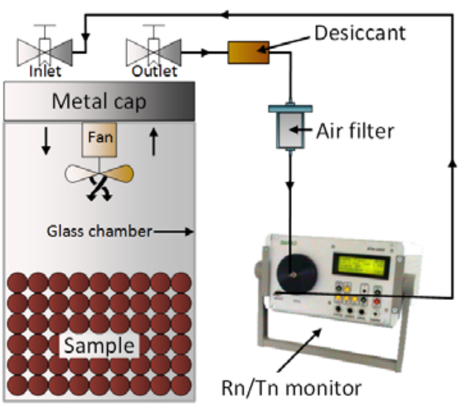

Figure 1. Closed loop exhalation sampling system

The accumulated radon concentration was obtained after the 60 minutes measurement period.

Calculation of massic exhalation rate and emanation factor

The massic radon exhalation rate can be calculated using the following formula(5):

$$E_{mass} = \frac{C_{\infty} \cdot \lambda \cdot V}{m} \tag{2}$$

Where: C_∞ = saturated radon concentration [Bq m^{-3}], E_{mass} = massic exhalation rate [mBq kg^{-1} h^{-1}], V = volume of the accumulation kit [m^3], m = mass of the sample [kg], λ = decay constant of radon [h^{-1}]

The emanation factor (ε) is the ratio between the calculated activity of saturated radon (C_∞) and the ^{226}Ra activity of the sample[5] determined by gamma spectrometry.

RESULTS AND DISCUSSION

Gamma spectrometry

The ^{226}Ra, ^{232}Th, ^{40}K contents and I-index of the samples (fly-ash, bottom-ash, fractionised bottom-ash, fluidized bed bottom-ash, gypsum, and slurry-type ash) can be seen in Table 1.

Table 1. ^{226}Ra, ^{232}Th and ^{40}K activity concentration of the samples

Sample	^{226}Ra [Bq kg^{-1}]	^{232}Th [Bq kg^{-1}]	^{40}K [Bq kg^{-1}]	I-index
Gypsum	22 ± 3	<LD	13 ± 3	0.08
Fly-ash	178 ± 31	55 ± 19	387 ± 48	1.00
Slurry-ash	175 ± 19	70 ± 10	327 ± 27	1.04
Coal	45 ± 6	26 ± 6	210 ± 21	0.35
Fluidized ash	49 ± 7	30 ± 6	211 ± 21	0.38
Bottom ash	144 ± 19	84 ± 14	260 ± 25	0.99
< 0,1 mm	171 ± 22	90 ± 14	296 ± 28	1.12
0,1-0,25 mm	158 ± 19	90 ± 14	267 ± 24	1.06
0,25-0,5 mm	145 ± 17	80 ± 13	259 ± 23	0.98
0,5-1,0 mm	117 ± 13	75 ± 11	170 ± 16	0.82
1,0-1,6 mm	115 ± 11	67 ± 9	253 ± 19	0.80
>1,6 mm	118 ± 12	60 ± 8	260 ± 20	0.78

The gypsum originated from the desulphurization process had very low natural radionuclide content (^{226}Ra = 22 ± 3 Bq kg^{-1}, ^{232}Th = <LD, ^{40}K = 13 ± 3 Bq kg^{-1}). The calculated I-index was only 0.08.

In the case of coal the measured activity concentrations were almost 4 times lower than in case of originated ashes except the fluidized type where the measured activity concentrations were similar. This anomaly can be explained with various quality and origin of burned coal.

The average radionuclide content of the bottom ash was approximately 3 times higher than examined coal sample (^{226}Ra = 144 ± 18 Bq kg^{-1}, ^{232}Th = 84 ± 14 Bq kg^{-1}, ^{40}K = 260 ± 25 Bq kg^{-1}). The calculated I-index was 0.99 which barely reached the recommended 1.0 index value.

In case of the fractionized samples it was found that the radionuclide content (^{226}Ra, ^{232}Th and ^{40}K) under 0.1 mm was 45 % higher than above 1.6 mm grain size. The calculated I-index varied between 0.78–1.12. Due to that fact it can be stated that the rate of radioisotope enrichment in the case of bottom ash was significant under 0.5 mm grain size. However, the average I-index of examined bottom ash was barely under 1.0 I-index value in case of grain size under 0.25 mm the obtained index values (between 0,1-0,25 mm and under 0.1mm were 1.06 and 1.12) were higher than the recommended value.

Owing to this after fractionation the higher grain size above 0.5 mm can be reused with lower gamma dose rate compared with the original bottom ash or higher amount of mixing can be applicable in case of building material production to ensure 1.0 I-index of final product.

Radon exhalation and emanation features

The obtained massic exhalation rates are illustrated in Fig 2.

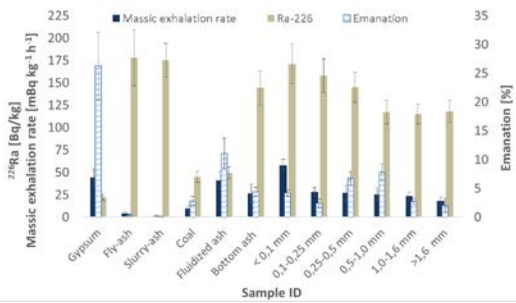

Figure 2. ^{226}Ra content, radon exhalation and emanation features of examined samples

It was found that not only the ^{226}Ra content was responsible for elevated massic exhalation rates. The emanation factor had also cardinal role on exhalation. In case of gypsum the highest emanation factor was found. Despite of relatively low ^{226}Ra content the massic exhalation rate of the gypsum was the second among the investigated by-products.

In case of fly-ashes and slurry ash the measured exhalation rates were almost zero. It can be caused because of the applied high burning temperature used in thermal power plant. In the case of the fractionated bottom ash – as it was expected – the massic exhalation rate was the highest in the low range of grain size. It means that the radon exhalation has inverse relationship with grain size.

The massic radon exhalation rate from fly-ash, bottom-ash, fluidized bed bottom-ash, gypsum, and slurry-type ash are of prime importance for the estimation of radiation risk when we use this materials as additive during building materials production.

CONCLUSION

In recent years fly-ash, bottom-ash, fluidized bed bottom-ash, gypsum, slurry-type ash have found diversified applications in construction materials, so it is important the screening of by-products according to BSS and gather information about the radon exhalation rates. However, in case of building materials the exhalation rate of certain products greatly depends on the geometry and the internal structure parameters the survey of massic radon exhalation rate of porous materials (raw, additive materials, industrial by-products) can be used rather for comparison and characterization of them. Owing to this method fast information can be obtained also about emanation coefficient, which has strong correlation with internal structure features.

The obtained results clearly proves that in case of low grain size (<0.5 mm) the accumulation of investigated radionuclides were more significant than in case of higher grain size. The calculated I-index of the surveyed samples proved that under <0.5 mm the I-indexes were higher than the BSS recommended 1.0 limit. In case of reuse the fractionation can be a useful possibility to reduce the risk originated from radiation exposure.

Thus, the concentration of natural radionuclides in fly-ash, bottom-ash, fluidized bed bottom-ash, gypsum, and slurry-type ash used as additives in building materials should be monitored carefully as well to avoid elevated radiological risk.

Due to the obtained results it can be stated that the I-index is not enough to characterize the building materials because the risk originated from exhaled radon can be significantly higher despite of relatively low Ra-226 content of porous materials.

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REFERENCES

1. Somlai, K., Jobbágy, V., Kovács, J., Somlai, J., Németh, Cs. and Kovács, T. *Connection between radon emanation and some structural properties of coal slags as building material*, Radiat Meas **43**, 72-76 (2007).
2. Cosma, C., Cucoş-Dinu, A., Papp, B., Begy, R. and Sainz, C. *Soil and building material as main sources of indoor radon in Băiţa-Ştei radon prone area (Romania)*, J Environ Radioact **116**,174-179 (2013).
3. Szabó, Zs., Völgyesi, P., Nagy, H.É., Szabó, Cs., Kis, Z. and Csorba, O. *Radioactivity of natural and artificial building materials – a comparative study*. J Environ Radioact **118**, 64-74 (2013).
4. Stals, M., Verhoeven, S., Bruggeman, M., Pellens, V., Schroeyers, W. and Schreurs S. *The use of portable equipment for the activity concentration index determination of building materials: method validation and survey of building materials on the Belgian market.* J Environ Radioact **127**, 56-63 (2014).
5. Kovler K., Perevalov, A., Steiner, V. and Metzger, L.A. *Radon exhalation of cementitious materials made with coal fly ash: Part 1 – scientific background and testing of the cement and fly ash emanation* J Environ Radioact 82, 321-334 (2005).
6. Nuccetelli, C. *In situ gamma spectroscopy in environmental research and monitoring*. Appl Radiat Isot **66,** 1615-1618 (2008).
7. European Basic Safety Standards (BSS) for protection against ionizing radiation. Official Journal of the European Union, Council directive 2013/59/EURATOM, (2014).
8. Szeiler, G., Somlai, J., Ishikawa, T., Omori, Y., Mishra, R., Sapra, B.K., Mayya, Y.S., Tokonami, S., Csordás, A. and Kovács, *T. Preliminary results from an indoor radon thoron survey in Hungary*. Radiat Prot Dosimetry **52**, 243-246 (2012).
9. Műllerova, M., Kozak, K., Kovács, T., Csordás, A., Grzadziel, D., Holy, K., Mazur, J., Moravcsík, A., Neznal, M. and Smetanová I. *Preliminary results of indoor radon survey in V4 countries*. Radiat Prot Dosimetry **160**, 210-213 (2014)
10. Netherlands Standardization Institute (NEN) *Radioactivity measurement - Determination method of the rate of the radon exhalation of dense building materials,* NEN 5699:2001 EN (2001)
11. López-Coto, I., Mas, J.L., Bolivar, J.P. and García-Tenorio R. A short-time method to measure the radon potential of porous materials Appl Radiat Isot 6, 133-138 (2009)
12. Keller, G., Hoffmann, B. and Feigenspan, T. *Radon permeability and radon exhalation of building materials*. Sci Tot Environ 272, 85-89 (2001)
13. Mujahid, S.A., Hussain, S., Dogar, A.H. and Karim, S. *Determination of porosity of different materials by radon diffusion.* Radiat Meas 40, 106-109 82005).
14. Prasad, G., Ishikawa, T., Hosoda, M., Sahoo, S.K., Kavasi, N., Sorimachi, A., Tokonami, S. and Uchida, S. *Measurement of radon/thoron exhalation rates and gamma-ray dose rate in granite areas in Japan*. Radiat Prot Dosimetry **152,** 130-134 (2012).
15. WHO Handbook on Indoor Radon. World Health Organization, (2009).
16. Darby, S., Hill, D., Auvinen, A., Barros-Dios, J.M., Baysson, H., Bochicchio, F., Deo, H., Falk, R., Forastiere, F. et al. *Radon in homes and risk of lung cancer: collaborative analysis of individual data from 13 European case-control studies*, BMJ **330** (2005).