The dependence of radon emanation from red mud on heat treatment

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Abstract. The radionuclide concentration in red mud was examined from the aspect of its availability for use in the building industry. It turned out from the preliminary examination that the concentration of natural origin radionuclides is higher in red mud than in the bauxite raw material. ^{226}Ra and ^{232}Th activity concentrations about 10 times higher were measured in these red mud samples compared with the radionuclide concentration in common soils. It was found that red mud is not suitable for direct use as a building material according to the European Union classification concerning building materials, but using the following mixing ratio: maximum 20% red mud, minimum 80% clay, these requirements are met. The radon emanation experiments were also conducted. The aim was to examine the dependence of emanation factor on different parameters (e.g. firing temperature). This procedure was carried out in two different ways: first without any additional material and then adding a known amount of sawdust (5–35 wt%) and firing at a given temperature (400–1000^{o}C). During the examination of emanation factors it appeared that a significant decrease can be obtained through control of the firing temperature. The average emanation factor of the untreated dry red mud was 20%; it decreased by about 5% during the heat treatment. Lower values were found when using a reducing atmosphere. In order to find the reason for the decreased emanation, measurements of specific surface and pore volume were carried out. A correlation was determined between these factors.

1. Introduction

Interest has recently been focused on the elimination of the environmental damage caused by industrial by-products containing elevated NORM concentrations, and the utilization of such materials instead. One example is red mud, which originates from bauxite processing. Naturally occurring radioactive material (NORM) generally contains radionuclides found in nature, i.e. thorium, uranium, and their progeny. Once this NORM becomes concentrated through human activity such as mineral extraction, it may become a radioactive contamination hazard.

The use of industrial by-products (e.g. slag, fly-ash and red mud) is widespread in building industry, and they are primarily used as additives to concrete [1–4]. In buildings where materials with a high ^{226}Ra concentration are used, the gamma dose rate increases due to radium and its daughter elements, which cause a higher external radiation dose [5–6]. Radon-222 possibly emanates from red mud and accumulates in closed rooms; therefore, the increase of internal radiation dose must be taken into account with the inhalation of ^{222}Rn and its decay products [7–8]. Several authors [9–14] have pointed out that the emanation coefficient can be significantly influenced by many parameters. Consequently the following parameters are of interest: pore size, specific surface, grain size distribution, density of the grains, homogeneity of ^{226}Ra within the grain, humidity etc. For this purpose it is necessary to examine the role of these parameters.

The main goal of the work was to find out the possibilities for utilization of bauxite wastes in the building industry taking radiological factors into account. The European Union index classification concerning building materials was applied [15]. The activity concentrations of ^{226}Ra, ^{40}K and ^{232}Th and the radon emanation coefficient of red mud were determined under different conditions.

If red mud is applied as a component of building material, not only the gamma dose but also the radon emanation may have radiological consequences. That is the reason for firing the ‘pure’ red mud samples and the red mud mixed with sawdust, in the hope of obtaining a decreased emanation coefficient. The thermal dependence of the emanation coefficient was determined to be in the range 300–1000^{o}C in the case of ‘pure’ red mud samples and also in presence of additional material (sawdust) in some cases.

2. Materials and methods

2.1. Sampling

Red mud samples were collected from the deposition ponds of two alumina plants in Hungary, located as shown in Fig.1 (the Almásfüzitő plant was closed several years ago, but the Ajka plant is still working). Samples were dried at a temperature of 105 ± 0.5°C to a constant weight and then the fractions were sieved according to grain size using an Edmund Bühler KS 15-B type shaker. These samples were measured by gamma-ray spectroscopy by radon emanation method.

FIG. 1. Origins of red mud samples (1. Almásfüzitő, 2. Ajka)

2.2. Determination of ^{226}Ra and ^{232}Th

The dried bauxite and the red mud samples were stored for 30 d in air-tight aluminium Marinelli beakers with a volume of 600 cm^3 in order to attain radioactive equilibrium of ^{226}Ra with its progeny. The concentrations of naturally occurring radionuclides were determined by high resolution gamma-ray spectrometry, using a Eurisys EGNC 20-190-R n-type HPGe detector with an efficiency of 20% and with an energy resolution of 1.8 keV at the energy peak of 1333 keV of the ^{60}Co isotope. The gamma spectra were recorded by a Tennelec PCA-MR 8192 multichannel analyser. The data collection time was in the range 15 000–40 000 s. The system was calibrated using an etalon certified by the Hungarian National Authority of Measures. The ^{226}Ra concentrations were determined by measuring the activities of its decay products ^{214}Pb (295 and 352 keV) and ^{214}Bi (609 and 1120 keV) that were in secular equilibrium with ^{226}Ra following the 30 d storage. The activity of ^{40}K was measured by the 1461 keV gamma ray, and that of ^{232}Th by the 911 keV gamma ray of ^{228}Ac and the 2614 keV gamma ray of ^{208}Tl [16].

2.3. Measurements of ^{222}Rn emanation

A precise weight of dried red mud sample (about 10 g) was put into a 50 cm^3 glass ampoule and was dried in a vacuum dryer chamber for 3 h at 60°C before sealing. After a 30 d storage period, the ampoule was broken in a special metal receptacle. The radon gas was pressed through a filter by N_2 into a 1 L Lucas cell. The method was repeated with another Lucas cell, so the efficiency of transport was higher than 99.7 %. After 3 h — in order to have time to reach the equilibrium of radon with its progeny having short half life [17] — measurements were performed twice with an EMI photomultiplier for 1000 s. The Lucas cells were calibrated by a PYLON RN 2000A type passive radon source, with an activity of 105.7 ±0.4% kBq in a Genitron EV 03209 calibration chamber of volume 210.5 L. The emanation coefficient (ε) was determined as a quotient of the activity of the radon sucked from the ampoule and the activity of ^{226}Ra of red mud in the ampoule. The overall relative standard uncertainty was less than 12%.

2.4. Specific surface, pore volume measurements

A Micrometics ASAP 2000 device was used to measure the pores smaller than 100 nm. Samples of mass 1-2 g of different granulation were put into a vacuum (pressure <100 Pa) at 100^{o}C to remove gases linked to the surface. Then adsorption and desorption isotherms for nitrogen gas were measured at the temperature of liquid nitrogen. The specific surface was calculated according to the BET theory. Pores larger than 100 nm were measured by an SMH6 type mercury poremeter device. Samples of mass 1-5 g were put into a vacuum (pressure <0.1 mm Hg) at room temperature, after which the measuring receptacle was filled with mercury and the change of Hg level in the capillary versus pressure (0–1000 bar) was recorded. The distribution of pore volume was calculated by using the above mentioned results.

3. Characterization of samples for use as construction materials

Two major problems arise in the course of utilization of red mud in the building industry. The first is the internal gamma dose, and the other is the radon problem due to the relatively high ^{226}Ra and ^{232}Th activity concentrations. The estimation of potential risk associated with ^{222}Rn is based on the activity concentration of ^{226}Ra and the emanation power.

The radiological testing of construction materials is based on the ^{226}Ra, ^{232}Th and ^{40}K concentrations. The value recommended for the maximum allowable activity concentration index by the European Union (and some individual countries such as Finland and Norway) [15] is:

$$I = \frac{C_{Ra}}{300\ Bq/kg} + \frac{C_{Th}}{200\ Bq/kg} + \frac{C_K}{3000\ Bq/kg}$$

where:

I is the activity concentration index
C_x is the measured activity concentration of the radioisotope x (Bq/kg).

The values recommended by the EU were taken into account in the course of the qualification (see Table 1).

TABLE 1. THE ACTIVITY CONCENTRATION INDEX

	Activity concentration index for two dose criteria	
	0.3 mSv/a	1 mSv/a
Materials used in bulk amounts, e.g. concrete	≤ 0.5	≤ 1
Superficial and other materials with restricted use, e.g. tiles, boards	≤ 2	≤ 6

4. Results

The activity concentrations of different isotopes in the samples are shown in Table 2. It can be clearly seen that the measured activities in the samples are higher than the world average ^{226}Ra and ^{232}Th activity concentrations of building materials. The activity-concentrations of these samples (e.g. ^{226}Ra: 105–700 Bq/kg) are between 2–14 times higher than the world average radionuclide concentration of clays (^{226}Ra: 50 Bq/kg, ^{226}Th: 50 Bq/kg, ^{40}K: 670 Bq/kg) [5]. The activity index was calculated from the above mentioned values and shown in Table 3.

TABLE 2. ACTIVITY CONCENTRATIONS IN THE SAMPLES [18]

	Average radionuclide concentrations, range in parentheses (Bq/kg)		
	^{40}K	^{232}Th	^{226}Ra
Sample from Ajka	48 (5–101)	292 (285–380)	360 (150–700)
Sample from Almásfüzitő	102 (50–207)	232 (92–545)	298 (105–498)
World average for clay	670	50	50

TABLE 3. ACTIVITY CONCENTRATION INDEX OF THE SAMPLES

	Activity concentration index		
	Average	Minimum	Maximum
Ajka (100%)	2.58	2.09	3.85
Almásfüzitő (100%)	2.08	1.06	4.42
Ajka (20%)	1.04	0.75	1.27
Almásfüzitő (20%)	0.89	0.68	1.35

On the basis of the activity concentration index, samples of red mud of different origin could be used with restrictions, for example as an additional material in maximum mixing ratio of 20%.

The radon emanation coefficient (ε) was determined in some cases and was found to be in the range 6–22%, with an average value of about 10–20%, as shown in Table 4. The emanation coefficient depends on the material, grain size, moisture and origin of sample.

TABLE 4. AVERAGE EMANATION COEFFICIENT OF THE SAMPLES

	Average emanation coefficient, range in parentheses (%)
Sample from Ajka	18.5 (12–22)
Sample from Almásfüzitő	12 (6–14)

In most manufacturing processes, additional materials — sawdust, polypropylene pellets —are used in various mixing ratios (5–40%) to improve the quality (porosity, strength, thermal insulation) of bricks. Therefore, red mud samples were mixed with sawdust in different ratios and fired in the temperature range 300–1000°C. The variation of emanation coefficient as a function of additional material and burning temperature is shown in Fig. 2.

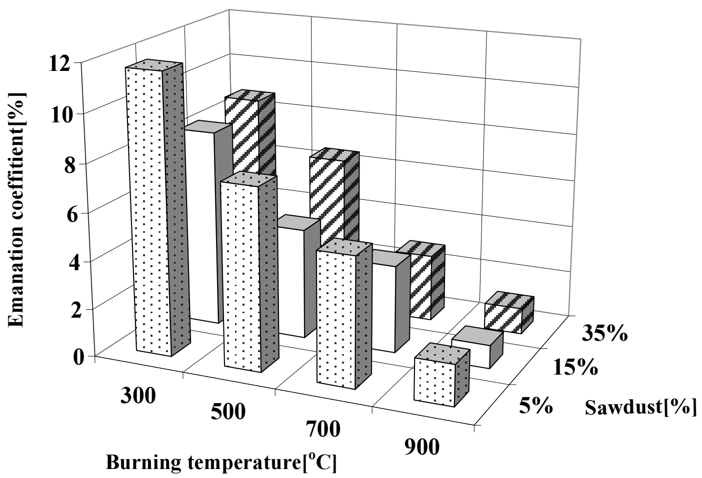

FIG. 2. Variation of emanation coefficient at different firing temperatures and mixing ratios

Temperature can be seen to have an effect on the emanation coefficient. The effects of changing pore volume and specific surface on emanation coefficient were examined. The results are shown in Figs. 3–5. Raising the amount of sawdust and the firing temperature decreases the emanation coefficient. The specific surface is inversely proportional to the firing temperature. The pore volume changes proportionally with the amount of additional material and the emanation coefficient changes in accordance with this tendency. It is evident that a change of pore volume and specific surface may have a considerable effect on the emanation coefficient. It can be very important from the point of view of radiation protection in case of future applications.

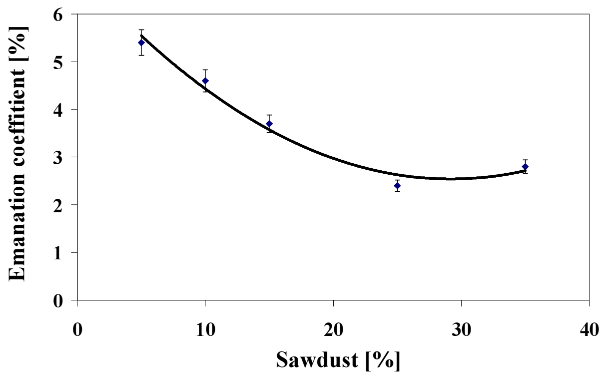

FIG. 3. Correlation between emanation coefficient and amount of sawdust (700°C)

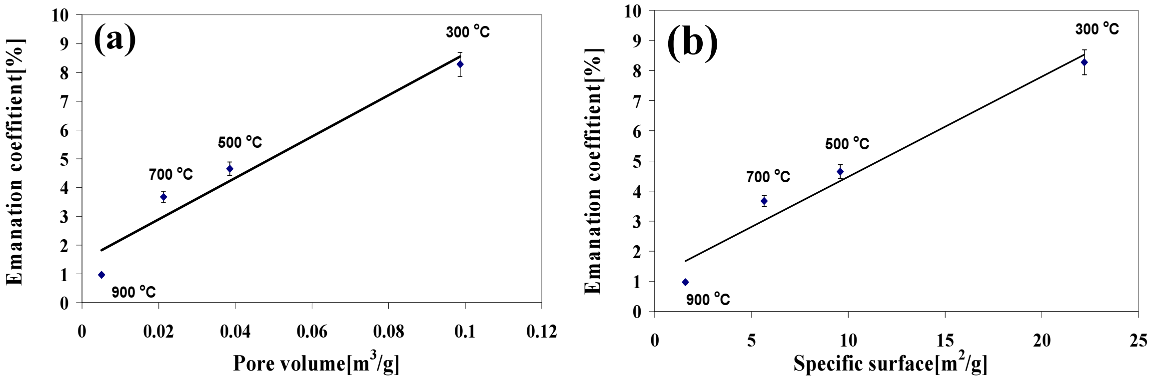

FIG. 4. Dependence of emanation coefficient on (a) pore volume, (b) specific surface (15% sawdust)

5. Conclusion

In the samples investigated, the activity concentrations of radionuclides of natural origin are higher than the world average values for rocks. Hungarian red mud is suitable for use with restrictions as an additive (maximum 20 wt%) according to EU recommendations. However, on the basis of emanation measurements, increased radiation exposure could be expected in dwellings. Examining the emanation factors, it has been found that:

a) The emanation coefficient of red mud can be decreased significantly (perhaps by up to 80%) by:

— Increasing the firing temperature to above 800°C;

— Optimizing the use of additional materials (e.g. sawdust at 15–25 wt%).

b) The emanation coefficient decreases linearly with specific surface and pore volume.

c) Radiological factors must be taken into account when constructing buildings using red mud.

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