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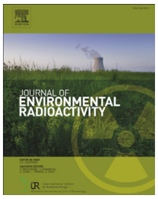

Influencing effect of heat-treatment on radon emanation and exhalation characteristic of red mud

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ABSTRACT

The reuse of industrial by-products is important for members of numerous industrial sectors. However, though the benefits of reuse are evident from an economical point of view, some compounds in these materials can have a negative effect on users' health.

In this study, the radon emanation and exhalation features of red mud were surveyed using heat-treatment (100–1200 °C). As a result of the 1200°C-treated samples, massic radon exhalation capacity reduced from 75 ± 10 mBq kg^{-1} h^{-1} to 7 ± 4 mBq kg^{-1} h^{-1}, approximately 10% of the initial exhalation rate.

To find an explanation for internal structural changes, the porosity features of the heat-treated samples were also investigated. It was found that the cumulative pore volume reduced significantly in less than 100 nm, which can explain the reduced massic exhalation capacity in the high temperature treated range mentioned above.

SEM snapshots were taken of the surfaces of the samples as visual evidence for superficial morphological changes. It was found that the surface of the high temperature treated samples had changed, proving the decrement of open pores on the surface.

1. Introduction

The inherent compounds of building materials can have a negative effect on human health. Today, the reuse of red mud in the building material industry has developed into both a public discussion and a debate among scientists and the industrial sector. To avoid the contingent negative effects caused by the reuse of this material and its inherent properties, different possibilities from a range of perspectives have to be considered.

Recently, several studies have addressed the reuse possibilities of industrial by-products reasons that are disposed in waste reservoirs. As a result of the depletion of raw materials, the reuse of these materials has become the focal point of interest. On the one hand, reuse could reduce the environmental impact of deposited by-products, while the health risks of doing so can be prevented by the dusting of reservoirs in the vicinity of inhabited areas (Kovács et al., 2012; Karangelos et al., 2004).

The integration of by-products into other industries as secondary raw materials can be beneficial for companies from an economical perspective. However, the reuse of new types of synthetic materials has raised concerns among authorities, the public and researchers (Gelencsér et al., 2011; Winkler, 2014). In some cases, certain components of raw materials can remain in the by-product and pose an elevated risk to humans. During the applied Bayer-process, for example, the aluminium industry produces large amount of alkali red mud, wherein a significant amount of natural radionuclide content of bauxite remains.

The natural radionuclide content of manufactured building material products (e.g. Szabó et al., 2013; Trevisi et al., 2012; Cosma et al., 2013) contributes to natural background radiation in two ways. On the one hand, the gamma radiation of the primordial radionuclides (K-40 and daughter elements of U-238, Th-232) increases the external gamma dose rate. On the other hand, the inhaled Rn-222, Rn-220 and their progenies augment the risk of the evolution of lung cancer (UNSCEAR, 2010; WHO, 2009). Radon is a radioactive noble gas that originates from Ra-226 content with a relatively long half-life (3.82 d). This time can be enough to get out

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of the matrix into the pore space and into the air as well, depending on the condition of the containing matrix.

While the alpha particle ejected from the Ra-226 isotope as a result of alpha decay, the daughter element (Rn-222) is recoiled and can be released into the pore space or embedded in adjacent particles, owing to its kinetic energy (86 keV) remaining as the result of energy from alpha decay (Ishimori et al., 2013).

The emanation coefficient or emanation power is defined as the quantitative rate of the released radon from the crystal structure into the open pore space to the total amount of the generated in the matrix. Thus, many factors determine the amount of the emanated radon such as the variation of the radium concentration of particles, density, homogeneity in radium distribution, grain size, volume of pore space and moisture content (Ishimori et al., 2013).

Only the emanated radon has a chance to exhale from the open pores of the matrix into the air depending on the several influencing parameters such as, porosity, temperature, moisture content, pressure conditions and thickness, amongst others.

The determination of radon exhalation has not standardized in international level due to difficulties of “ideal” conditions of measurement circumstances (Kovler, 2011).

The radon exhalation is the radon activity that diffuses per unit of time from a material to the air surrounding the material, in Bq s^{-1} defined in NEN 5699:2001 (EN standard Netherlands Standardization Institute (NEN), 2001). 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. The exhalation rate related to mass 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 (Ra-226 content, emanation coefficient, and the amount of the sample) have influence on exhalation rate (López-Coto et al., 2009). It means all the emanated radon can 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 (Keller et al., 2001; Mujahid et al., 2005) (e.g. porous soil and brick 40 cm, gypsum 110 cm, sand 200 cm). Owing to that fact, this assumption can be used for comparison (Kovler et al., 2005) if the sample thickness of porous material is less than 5 cm.

The above-mentioned circumstances had a significant effect on the final exhalation capacity of the materials. For this reason, the determination of Ra-226 content is not sufficient for characterizing the raw material, since radon emanation and the exhalation greatly depends on internal structure changes occurring as a result of the applied processing technique (Kovács et al., 2012; López-Coto et al., 2009; Tuccimei and Moroni, 2006; Prasad et al., 2012; Cosma et al., 2001; Sas et al., 2012). Several studies have dealt with the usability of red mud in the building material industry in terms of thermal behaviour (Zhang et al., 2011; Sglavo et al., 2000a, 2000b; Pontikes et al., 2007, 2009; Yao et al., 2013).

1.1. The aims of this study

- Determination of the emanation- and massic exhalation-modifying effects of heat treatment on red mud samples as a result of applied heat-treatment.
- Determination of the main internal structural changes of the heat-treated samples (pore space, specific surface, superficial morphology determination with SEM)
- Comparison of the heat-treated red mud massic exhalation characteristics and the obtained internal structural changes

2. Material and methods

2.1. Sampling and sample preparation

The investigated red mud sample was collected from a 1–2 m depth of red mud reservoirs in Ajka (Hungary). The samples were heated to a constant mass at a temperature of 105 ± 3 °C, grinded under 0.63 mm and homogenized. In order to obtain Ra-226 activity concentration of the sample the powdered red mud was put into aluminium Marinelli vessel, weighted, sealed and stored during 27 days to reach the secular equilibrium between Rn-222 and its progenies.

For massic exhalation measurement spherical-shaped red mud samples were prepared. The size of the samples was 0.5 cm diameter to ensure exhalation condition which was not dependent from sample.

This is the reason why the effect diffusion length can be neglected under presented measurement conditions. Of course the inhomogeneity of the samples also can have effect but because of the low sample thickness and the continuous and slow warm up program of the kiln the balanced internal structure changes of the samples was ensured. Furthermore glazing material was not used which could cardinally change the surface of treated samples. This is the reason why all the emanated radon can exhale from the prepared matrix.

To ensure the representative conditions, parallel procedures were carried out. The total amount of prepared sample was divided into two equal parts (sample “A” and sample “B”). In the case of the heat-treatments, samples A and B were treated in a pre-programmed kiln (one hour heating, three hours constant heat); following on, cooled down to room temperature by itself. Following treatment in certain temperatures, the massic radon exhalation features of the samples were measured. Thereafter, the samples were again treated at a higher temperature. Altogether, seven different temperatures were used ranging from 100 to 1200 °C (100, 200, 400, 600, 800, 1000 and 1200 °C). All the massic exhalation measurements were performed in room temperature after heat-treatments.

2.2. Gamma spectrometry

The Ra-226 activity concentration was determined via its progenies (295 keV of Pb-214 and 609 keV of Bi-214) reached the secular equilibrium by gamma spectrometry used a semiconductor HPGe detector (ORTEC GMX40-76, efficiency of 40%). The data and spectra were recorded by ORTEC DSPEC LF 8196 MCA. The system was calibrated with IAEA soil reference material.

2.3. Determination of exhalation rate and emanation factor

The prepared and heat-treated samples were surveyed from the massic exhalation point of view. After sample preparation, 0.5–0.5 kg of red mud spheres was enclosed in a glass accumulation chamber covered by a metal cap. The homogeneity of the inner air was ensured by a small size 12 V DC ventilator, which was placed inside the chamber. The chamber volume was more than ten times higher than the sample volume to avoid the back diffusion of radon into the sample pores (Tuccimei and Moroni, 2006; Prasad et al., 2012; Cosma et al., 2001).

The radon leakage features of the accumulation chambers were surveyed with the help of a PYLON RN 2000A-type passive radon source. All the accumulation chambers were filled with Rn-222 gas. The radon activity concentration in the chambers were measured with AlphaGUARD 2000 portable radon monitor under close loop circulation. After measurement the valves of the chamber were