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Radon exhalation study of manganese clay residue and usability in brick production

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ABSTRACT

The reuse of by-products and residue streams is an important topic due to environmental and financial aspects. Manganese clay is a residue of manganese ore processing and is generated in huge amounts. This residue may contain some radionuclides with elevated concentrations. In this study, the radon emanation features and the massic exhalation rate of the heat-treated manganese clay were determined with regard to brick production. From the manganese mud depository, 20 samples were collected and after homogenization radon exhalation characteristics were determined as a function of firing temperatures from 100 to 750 °C. The major naturally occurring radionuclides ^{40}K, ^{226}Ra and ^{232}Th concentrations were 607 ± 34, 52 ± 6 and 40 ± 5 Bq kg^{-1}, respectively, comparable with normal clay samples. Similar to our previous studies a strong correlation was found between the internal structure and the radon emanation. The radon emanation coefficient decreased by ~96% from 0.23 at 100 °C to 0.01 at 750 °C. The massic radon exhalation rate of samples fired at 750 °C reduced by 3% compared to samples fired at 100 °C. In light of the results, reusing of manganese clay as a brick additive is possible without any constraints.

1. Introduction

The importance of the utilization of by-products and residue streams has grown over recent decades due to the concern about sustainability of the human environment; of course, the use of residues sometimes provides better financial solutions. The building industry seems to be an appropriate solution as certain residues and waste materials have long been used in the construction industry (Adam, 1994). The use of certain mining by-products such as waste rock also has a past (Hooke, 2000). The use of other wastes, i.e. coal slag and fly-ash has become frequent after the development of cement production (Blezard, 2004). However, the use of these by-products has to be restricted in several cases as, on the one hand, waste impairs the structural properties of the end-product (Ducman and Kopar, 2007), on the other hand, different contaminants dissolved and entered the environment causing harm to the environment or to human health (Uhde and Salthammer, 2007).

The quantity and quality of additives usable in building materials has long been set out by strict regulations. The radioactivity of materials usable in building materials is regulated explicitly by the standards of only relatively few countries. However, some have been established for many years: Hungary the regulation setting out the radioactivity limit of building materials has been in effect since 1960 (no. 26/1960 Directive of Hungarian Ministry of Construction).

Over recent years more and more studies have been published on the harmfulness of NORM materials, and there has been no unified recommendation (regulation) on the restriction of their use until recently, yet the newest EU-BSS (Council directive 2013/59/EURATOM, European Basic Safety Standards) emphasizes the restrictions related to these materials. The reference level applying to indoor external exposure to gamma radiation emitted by building materials, in addition to outdoor external exposure, shall be 1 mSv per year.

In this study the potential usage of the residue of manganese ore mining in the building industry, i.e. manganese clay, was investigated from a radiological point of view. Manganese clay is the residue of manganese mining, it is not classified as a by-product as it is listed as a secondary raw material (Farkas and Vigh, 2004; Vigh, 2005). The underground manganese ore mine in Úrkút, Hungary is

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one of the biggest European manganese mines (Polgari et al., 2000).

Over recent decades 2.8 million tons of manganese clay has been deposited on the land surrounding the mine covering a territory of 20 ha (Szabo, 2006; Vigh, 2005). The recent study of Vigh et al., 2013 investigated the radioactivity of a manganese clay. That study showed that the activity concentrations of the primordial radioisotopes (^{238}U, ^{226}Ra, ^{40}K) of different black shales (manganese clay) do not exceed average soil activity concentrations. In the other study Kavasi et al., 2012, and Sas et al., 2015a investigated its utilization as a building material, however, this study only considered the gamma dose and did not include radon exhalation measurements. However, as several of our previous surveys have proved the measurement of gamma dose or even that of ^{226}Ra alone is not suitable for the estimation of building material radiation dose as the majority of radiation dose is provided by radon and its progenies (Somlai et al., 1997, 2006). The amount of radon emitted greatly depends on the inner structure of the used building material (Somlai et al., 2008; Sas et al., 2012, 2015b). Therefore, measuring radionuclide concentration is insufficient for an accurate dose estimation and it is necessary to take into account the processing used in the building industry to derive useful radon exhalation data.

According to NEN (Netherlands Standardization Institute) 5699:2001 EN standard entitled Radioactivity measurement - Determination method of the rate of the radon exhalation of dense building materials the exhalation rate (radon activity that diffuses per unit of time from a material into the air surrounding the material, in Bq s^{-1}) can be divided either the area of the exhaling surfaces or by the mass, the areic (radon flux Bq m^{-2} s^{-1}) and massic radon exhalation rates (Bq kg^{-1} s^{-1}). It is important to clarify that the areic exhalation can be a characteristic parameter of investigated materials only if the sample thickness is greater than the diffusion length of the radon belongs to investigated matrix. In case of massic exhalation the sample thickness has to be very small against the diffusion length of radon to estimate the radon exhalation without significant loss as a result of its decay inside the matrix. This assumption can be used for comparison (Kovler et al., 2005) if the sample thickness of porous material is less than 5 cm (López-Coto et al., 2009). Under this circumstance all the radon has a chance to exhale and the massic radon exhalation rate can be determined (Sas et al., 2015b).

From the aspect of building industry usage this parameter provides tangible information. From the aspect of brick manufacturers, the maximum amount of by product that can be added is important, and this may be driven by the amount of radon emitted. It is not easy to comply with both requirements, the amount of radon emitted is simulated using complex models in most cases (Risica et al., 2001). However, for modelling it is rather important to identify the radon potential of materials. As already mentioned above radon emission is considerably influenced by the inner structure of the building material (Sas et al., 2012, 2015b) or materials (Jobbagy et al., 2009) and for red mud it has been shown that specific surface area and porosity greatly influence radon emission. However, both specific surface area and porosity can be affected by thermal treatment of the material (Vigh, 2005; Sas et al., 2015b).

Due to other major components of manganese clay (Seil and Heiligman, 1928) it is potentially useful in brick productions. Thermal treatment (firing) is the basic treatment method of brickmaking and this has implications on the amount of radon emitted.

In this study the radon emanation characteristics of manganese clay were measured at different temperatures identifying the optimum firing temperature in order to minimize radon exhalation and provide useful data for later modelling and also for construction companies, and information for authorities on the maximum amounts of additives.

2. Materials and methods

2.1. Sampling and sample preparation

The manganese mining is based on a sedimentary manganese deposit containing a very fine grained, laminated ore of Jurassic age and the main ore minerals of rhodochrosite and kutnahorite. Samples were taken from a waste depository site of Úrkút manganese mine located near the village of Úrkút in the Balaton Upland region of Hungary (Fig. 1).

In total 20 grab clay samples (about 10 kilograms) were taken from the difference part of the depository site, the depository site is marked for environmental monitoring, after removing the 70 cm thick upper layer (from 0 to 40 cm deep) and then each samples were dried at room temperature then crushed and homogenized. For gamma spectrometry, samples were crushed to under 0.63 mm in grain size and then dried in an oven at 105 °C for 24 h to remove any moisture and to achieve mass constancy. The prepared samples were weighed, sealed in aluminium Marinelli vessels of 600 cm^3 in volume and stored for at least 27 days in order to reach the radioactive equilibrium between ^{226}Ra and its decay products prior to counting using gamma spectrometry (Somlai et al., 2008).

Kovler et al., 2005 was found that the massic exhalation cannot be considered as characteristic values of the tested materials, but can be used rather for comparison because the massic exhalation rate should depend on some more factors, such as degree of compaction and geometry (thickness of the layer, mainly) of the powder/granular sample. If the sample thickness is much lower against diffusion length all emanated radon has a chance to exhale from the matrix. In that case the massic exhalation can be a characteristic value. This phenomena was examined by Sas et al., 2012 and it was found that the required sample thickness should be thinner than 1 cm in the case of humid clayish materials to avoid the diffusion inhibition effect of the sample thickness on radon exhalation. To evaluate the effects of heat-treatment on morphological attributes, radon emanation and the exhalation rate, about 1 kilogram of mixed homogenized manganese clay was moulded into small spheres of 1–2 mm in diameter to ensure the required condition to measure the massic exhalation rate. In case of massic exhalation the sample thickness has to be very small against the diffusion length of radon to ensure the radon exhalation without significant loss as a result of its decay inside the matrix (Sas et al., 2015b; López-Coto et al., 2009). Then prepared samples were fired each of 100, 250, 350, 450, 550, 650 and 750 °C for 24 h (150 g

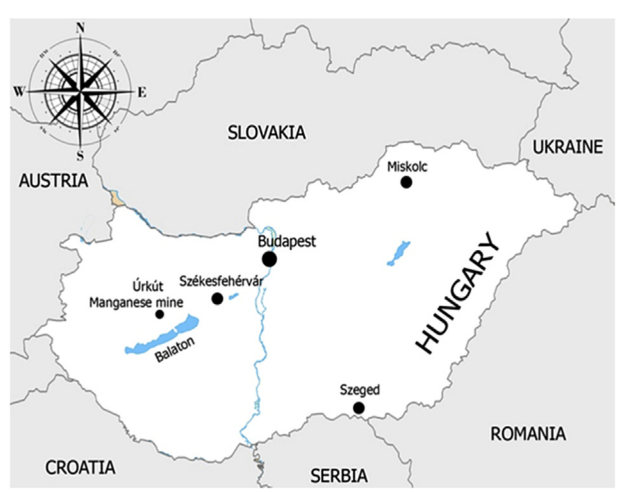

Fig. 1. Location of the Úrkút manganese mine.

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