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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 $607 \pm 34$, $52 \pm 6$ and $40 \pm 5$ 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.

Keywords

Manganese clay, Heat-treatment, Radiation hazard, Radon, Emanation, Exhalation, Building material
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 et al., 2007), on the other hand, different contaminants dissolved and entered the environment causing harm to the environment or to human health (Uhde et al., 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 et al., 2004; Vigh, 2005). The underground
manganese ore mine in Úrkút, Hungary is 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 hectares (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 et al., 1928) it is potentially useful in brick productions. Thermal treatment (firing) is the basic treatment method of brick-making 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.

**Materials and methods**

**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 (Figure 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 cm³ 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 hours (150 gram of prepared spherical samples for each temperature) (Sas et al., 2012). Owing to occurred loss of mass uniformly 140 grams of each fired sample was weighed and placed into glass emanation tubes, which were sealed and stored for 30 days to achieve an equilibrium radon concentration (Jobbagy et al., 2009).

**Internal structure related measurements**

The relative densities were measured using Density Kit and the reference liquid (White Spirit 150/200) with a density of 0.775 g cm⁻³ at 15 °C. A graduated glass body of defined reference liquid volume \( V_i \) was weighed in air and marked as \( M_i \); the samples were dipped into the holder and placed on an ultrasound wave shaker for 30 minutes and then the new volume and weight were recorded as \( V_2 \) and \( M_2 \). Then their density was calculated by dividing \( \Delta M \) by the reference displacement volume (Speight, 2015).

The porosity features and specific surface area were calculated by changing the absorbed component of samples in a nitrogen gas tube under specific conditions (Jobbagy et al., 2009). Total pore volumes from 1 nanometre to 15 micrometres were determined by combining results from ASAP 2000 gas absorption (Micromeritics, U.S.A) and mercury penetration (Micromeritics, U.S.A) methods.

**Gamma spectrometry**

A high resolution gamma ray spectrometer, using an ORTEC GMX40-76 HPGe semiconductor detector with efficiency of 40 %, and an energy resolution of 1.95 keV at
1332.5 keV was used to determine the concentrations of $^{40}$K, $^{226}$Ra and $^{232}$Th present in the samples. The activity concentration of $^{40}$K was determined by the 1461 keV gamma peaks, and for $^{232}$Th by the 911 keV gamma peaks of $^{228}$Ac, and the 2614 keV gamma peaks of $^{208}$Tl. The $^{226}$Ra concentrations were determined by measuring the activities of its decay product $^{214}$Pb using 352 keV gamma peaks (IAEA, 2007; Somlai et al., 2008).

**Radon emanation and exhalation**

For calibration and determining the efficiency of a Lucas cell, a certified Genitron EV 03209 calibration chamber, a RN2000A solid $^{226}$Ra source with an activity of 104 ± 0.4 kBq (Pylon Electronics Inc., Canada) and an AlphaGUARD PQ2000Pro radon monitor (Saphymo GmbH, Germany) as a reference were used.

The grab sampling method using Lucas scintillation cells (1 dm$^3$ Lucas covered by ZnS(Ag), MÉV Ltd., Hungary) and an EMI photomultiplier were used to determine the radon concentrations.

The sample container (sealed glass tube) was broken inside a special breaker and radon-free N$_2$ gas transferred the evaluated radon gas to the Lucas cell. After transferring the Lucas cells were stored for 3 hours to reach secular equilibrium between $^{222}$Rn and its decay products. Each cell was measured for 3 × 2000 s. The calculated MDA was determined by the Currie method (Currie, 1968). Radon concentration activity can be calculated using Eq. (2) (Kovacs et al., 2003):

$$A_{Rn-222} = \frac{N}{(V \times E \times S \times F \times t \times 3)}$$  \hspace{1cm} (2)

where $A_{Rn-222}$ is the activity of the $^{222}$Rn concentration (Bq m$^{-3}$), $N$ is the net count, $V$ is the volume of the scintillation cell in litres, $E$ is the counting efficiency of the cell (cpm/dpm), $S$ is the decay correction factor for the time interval between sampling and measuring, $F$ is the transfer efficiency (0.95), $t$ is the measurement time and 3 is the number of alpha emitters under equilibrium conditions which are reached after 3 hours.

The radon exhalation rate in terms of mass was calculated using Eq. (3) (Sas et al., 2015b):
\[ E_{\text{Mass}} = \frac{C \cdot V}{m \cdot t} \cdot \frac{\lambda \cdot t}{1 - e^{-\lambda t}} \]  

(1)

where:
- \( C \) = accumulated radon concentration [Bq m\(^{-3}\)]
- \( E_{\text{Mass}} \) = massic exhalation rate [mBq kg\(^{-1}\) h\(^{-1}\)]
- \( t \) = accumulation time [h]
- \( V \) = volume of the accumulation kit [m\(^{-3}\)]
- \( m \) = mass of the sample [kg]
- \( \lambda \) = decay constant of radon [h\(^{-1}\)]

The emanation coefficient of each investigated sample was calculated from obtained massic exhalation results. (Kovler et al., 2005).

**Results and discussion**

The relative detection efficiencies and minimum detectable activities of gamma spectrometry for \(^{40}\)K, \(^{226}\)Ra and \(^{232}\)Th were calculated as 1.2\%, 2.4\% and 1.4\% and the MDAs as 46, 1.3 and 2.3 Bq kg\(^{-1}\), respectively.

The concentration of \(^{40}\)K, \(^{226}\)Ra and \(^{232}\)Th in the manganese clay were determined in Bq kg\(^{-1}\) as 607±34, 52±6 and 40±5, respectively. The concentrations of \(^{40}\)K and \(^{226}\)Ra with the exception of \(^{232}\)Th were higher than the world average mean radionuclide concentration of soils reported in UNSCEAR 2008 Annex B (\(^{226}\)Ra: 32 Bq kg\(^{-1}\), \(^{232}\)Th: 45 Bq kg\(^{-1}\), \(^{40}\)K: 412 Bq kg\(^{-1}\)) and RP112 (\(^{226}\)Ra: 40 Bq kg\(^{-1}\), \(^{232}\)Th: 40 Bq kg\(^{-1}\), \(^{40}\)K: 400 Bq kg\(^{-1}\)).

The morphological attributes of the clay are related to the firing temperature with the exception of pore volume. The effects of firing on the samples in terms of different temperatures show in Table (1).

| Table 1- The modification of morphological attributes as a function of firing temperature |
Increasing the firing temperature resulted in gradual decreases of specific surface area and density decreased except at 550 °C (Fig. 2.).

Fig. 2 Morphological modifications as a function of temperature

The efficiency and MDA of scintillation cells were calculated to be between 60 and 70 % and 32 to 41 Bq m⁻³, respectively. A significant difference among firing temperatures was observed for ²²²Rn exhalation and emanation rates and temperature (Table 2).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>100</th>
<th>250</th>
<th>350</th>
<th>450</th>
<th>550</th>
<th>650</th>
<th>750</th>
</tr>
</thead>
<tbody>
<tr>
<td>Massic exhalation (Bq kg⁻¹ h⁻¹)</td>
<td>76</td>
<td>67</td>
<td>74</td>
<td>30</td>
<td>51</td>
<td>46</td>
<td>3</td>
</tr>
<tr>
<td>Emanation factor</td>
<td>0.25</td>
<td>0.22</td>
<td>0.24</td>
<td>0.11</td>
<td>0.17</td>
<td>0.16</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Table 2 – Radon concentration, exhalation rates and emanation factors for manganese clay in terms of firing temperatures

In Fig. 3, the relationship between cumulative pore volume and exhalation rate and the emanation factor are shown.

Fig. 3 The relationship between pore volume and radon concentration, exhalation rate and the emanation factor

Fig. 4 shows Cumulative pore volume distribution of fired manganese clay. The obtained results clearly proved that in the case of high temperature range the pore size distribution significantly shifted towards bigger pore diameter compared with at low temperatures. As a result, it can be stated that low emanation and exhalation rates at high temperatures can be caused by the modified porosity features. Furthermore, it can be concluded that by firing, the radon emanation and exhalation features can be significantly reduced, which can ensure safer building material production from manganese clay in terms of a radiological point of view.
In the light of the obtained results it can be stated that similar behaviour was found between presented results of manganese clay, previously studied red mud (Sas et al., 2015b) and clay (Sas et al., 2012). In the case of red mud and clay study the exhalation characteristic of heat-treated samples was obtained with accumulation chamber technique, whilst in the case of currently presented study the radon exhalation results were obtained with sealed glass tube technique. Despite of different methods the radon emanation and exhalation decrement was observed in all cases around the high temperature range. In the case of cumulative pore volume distribution of red mud also similarity was found. The porosity changes of clay material were not investigated. The cumulative pore volume of red mud and manganese clay has decreasing tendency in the function of increasing firing temperature in both cases. Generally, the applied heat in the case of brick production is around 800 °C, which means technological modification would not be required if these material will be used for brick production.

Conclusions
This study characterized manganese clay in terms of major naturally occurring radioactive materials, internal morphological modifications, and radon emanation and exhalation rates as a function of firing temperature. The concentration of $^{226}$Ra and $^{40}$K presented in clay were higher than the global average values, while the $^{232}$Th concentration was lower than the global average. Results show a link between firing temperatures and changes in morphological nature, and subsequently the radon emanation and exhalation rates. The density, specific surface area and total pore volumes decreased as temperature increased. The radon exhalation rate reduced by 97% from 75.7 to 2.4 mBq kg$^{-1}$h$^{-1}$. To change properties of manganese mine slag waste as a by-product and reduce the radon exhalation rate to eliminate health hazards for usage in the building and ceramic industries, firing at 750 °C is recommended. All in all, it can be stated that the high temperature treatment has beneficial effect on internal structure of all type of investigated clayish materials, which is favourable from building material production point. However, the application of by-products (manganese clay and red mud) on its own can arise concerns from mechanical point of view. On the basis of presented results, the possibility of the application of manganese clay and also red mud as additive material is considerable, which justifies further experiments of their clay-based mixtures focusing on mechanical and radiological properties.

**Acknowledgements**

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https://www.nen.nl/pdfpreview/preview_113701.pdf


No. 26/1960 Directive of Hungarian Ministry of Construction


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