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Radiological characterization of clay mixed red mud in particular as regards its leaching features

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ABSTRACT

The reuse of industrial by-products such as red mud is of great importance. In the case of the building material industry the reuse of red mud requires a cautious attitude, since the enhanced radionuclide content of red mud can have an effect on human health. The natural radionuclide content of red mud from the Ajka red mud reservoir and the clay sample from a Hungarian brick factory were determined by gamma spectrometry. It was found that maximum 27.8% red mud content can be added to fulfil the conditions of the EU-BSS. The effect of heat treatment was investigated on a red mud-clay mixture and it was found that in the case of radon and thoron exhalation the applied heat reduced remarkably the exhalation capacities. The leaching features of red mud and different mixtures were studied according to the MSZ-21470-50 Hungarian standard, the British CEN/TS 14429 standard and the Tessier sequential extraction method. The Tessier method and the MSZ-21470-50 standard are suitable for the characterization of materials; however, they do not provide enough information for waste deposition purposes. To this end, we propose using the CEN/TS 14429 method, because it is easy to use, and gives detailed information about the material's behaviour under different pH conditions, however, further measurements are necessary.

1. Introduction

There is a good potential in the reuse of NORM (Naturally Occurring Radioactive Material) containing industrial by-products, for example, in the building industry. Several studies have dealt (Kovler et al., 2005; Somlai et al., 1997, 2008; Ducman et al., 2007; Szabó et al., 2013, Sas et al., 2015a) with finding environmentally friendly materials and methods, as well as low cost materials for building purposes.

The annual 90–120 million ton red mud production in the alumina industry, with the existing store of over 2.7 billion tons, offers a good choice due to its volume (Nuccetelli et al., 2015; Ruyters et al., 2011.), and has been the target of numerous utilization efforts (Liu et al., 2012.) The traditional approach was wet or dry stockpiling or marine dumping, but due to the red mud's properties there is a risk of alkali, fluoride, heavy metal and other contaminations, causing severe environmental concerns. Better solutions are sought after; the most significant are the recovery of metals and rare earth elements, and use as construction material, with other possible alternatives utilising the high alkalinity or the heavy metal ion absorption capability (Qu and Lian, 2013; Liu et al., 2012.). Still the factors causing problems during deposition (alkalinity, heavy metal and other toxic compound content, radioactivity, etc.) remain.

Identification of environmental factors that pose a risk to human health along with understanding mechanisms leading to exposures have recently become important issues for scientists working with NORM. The production and design of new types of building materials based on NORM by-products is raising concerns among authorities, the public and scientists. It is incumbent on professional engineers and scientists to demonstrate that these materials do not pose significant risks to human health and the environment (WHO, 2009; UNSCEAR, 2008).

From a radiological point of view, three main problems can arise in the case of the NORM materials: the direct gamma dose rate, radon and thoron exhalation and leaching of radionuclides. The

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gamma dose rate has been seen asa health risk for a long time, and is covered by the RP 112 guideline.

The following activity concentration index (I) has been derived to identify whether a dose criterion is met:

$$I = \frac{C_{Ra-226}}{300\ Bq/kg} + \frac{C_{Th-232}}{200\ Bq/kg} + \frac{C_{K-40}}{3000\ Bq/kg} \quad (1)$$

where $C_{Ra\text{-}226}$, $C_{Th\text{-}232}$, $C_{K\text{-}40}$ are the Ra-226, Th-232 and K-40 activity concentrations in Bq/kg.

The activity concentration index value of 1.0 can be used as a conservative screening tool for identifying materials that during their use would cause doses exceeding the reference level laid down in Article 75(1) of the 2013/59/EURATOM council directive. The council directive allows the dilution and mixing of construction materials as long as the final building product itself (the bricks) is below the activity concentration index value of 1.0.

The radon isotopes are the major contributors to the ionizing radiation dose received by most of the population. The inhaled radon (Rn-222), thoron (Rn-220) and their progenies augment the risk of the evolution of pulmonary cancer (WHO, 2009). Radon isotopes have a significant contribution to the natural background radiation of humans, the inhalation of Rn-222's short-lived progenies is responsible for about half of the total effective dose received by humans from all natural sources of ionizing radiation. The EU Member States are to establish national reference levels for indoor radon concentrations. The reference levels for the annual average activity concentration of the indoor air in workplaces (buildings, underground workplaces, e.g. mines, caves, etc.) and residential buildings must not exceed 300 Bq m^{-3}. (Article 75(1) of 2013/59/EURATOM).

Although the main source of indoor radon is the soil, the radon exhalation of inbuilt materials should be kept as low as possible. For thoron the main source is the building material due to its short (55.6 s) half-life. In the case of elevated thoron exhalation the exposure to thoron may be even higher than the exposure to radon (Yonehara et al., 2005).

To ensure safe inbuilt building materials the exhalation of both isotopes should be reduced during production processes. If the thickness of the investigated sample is remarkably smaller than the diffusion length of radon or thoron all the emanated radon and thoron has a chance of being exhaled, i.e. the amount of the sample determines the exhalation rate, which can be related to unit mass. In the case of thoron a former survey performed by Csige et al., 2013 proved that in the case of adobe the optimal sample thickness is 5.0 cm to measure the thoron generation rate.

Owing to that fact, the determination of the massic exhalation rate can provide a great possibility to compare exhalation features of samples in granular form (Kovler et al., 2005; Mujahid et al., 2005).

Leaching tests are a very important tool to assess the long-term environmental behaviour and environmental impact of various materials related to toxic compounds. In the EU, although there are encouraging tendencies for the standardisation of methods such as the LEAF protocols (Kosson et al., 2014), or the harmonisation of protocols for waste evaluation, there are still no commonly accepted methods for the evaluation of the leaching characteristics of NORM materials. The used methods vary greatly, ranging from sequential extraction procedures (Vandenhove et al., 2014) to column tests (Nisti et al., 2015) and single step batch extractions (Lysandrou and Pashalidis, 2008), both for scientific and regulatory purposes (Tiwari et al., 2015; Kosson et al., 2014).

2. Measurements and methods

2.1. Sampling and sample preparation

Red mud samples were collected from the Ajka red mud reservoir (1–2 m depth) and were homogenized; homogenized clay sample was gathered from a Hungarian brick factory. The samples were dried to constant mass at 105 °C, crushed in a mortar and sieved under 0.63 mm. Homogeneity was assured by representative sampling and homogenisation of the powdered samples by mixing. Before measurements the samples were stored for 30 days in 600 cm^3 radon-tight aluminium Marinelli vessels to reach the radioactive equilibrium between Ra-226 and Rn-222, their short-lived progenies. For massic exhalation measurements spherical-shaped clay-based mixture samples were prepared containing 20% red mud content and with a 0.5 cm diameter. The samples were dried and heat-treated to follow the effect of different temperatures on radon and thoron exhalation features.

2.2. Gamma spectrometry

The Ra-226 activity concentration was obtained via the radon progenies Pb-214 (295 keV) and Bi-214 (609 keV), the Th-232 content was determined from Ac-228 (911 keV) and Tl-208 (2614 keV) and the K-40 content was measured from the 1460 keV gamma line (Shakhashiroa et al., 2012) by an ORTEC GMX40-76 HPGe detector. The sample measuring time was 80 000 s. The system was calibrated with IAEA-326 soil reference material.

2.3. Radon and thoron exhalation rates

The radon and thoron exhalation rates of samples were measured using an accumulation chamber technique described in former studies (Sas et al., 2012, 2015b). To obtain the maximum thoron release rate of samples the prepared and treated spheres were put into an accumulation chamber with 5 cm thickness (Csige et al., 2013). After the accumulation time the radon and thoron content were measured together using an AlphaGUARD Pro radon monitor (SAPHYMO). After the sampling had finished the thoron decayed in the detector chamber and only the radon was inside. The AlphaGUARD radon monitor is a PIC (Pulse Ionization Chamber) detector, which cannot distinguish between radon and thoron. This is the reason why the thoron concentration was obtained from the measured activity concentration difference. To obtain accurate thoron concentration measurements using an AlphaGUARD, a RAD7 type radon-thoron monitor (Durridge Co.) was used as a reference instrument.

2.4. Leachability experiments

The leaching features of red mud, clay and clay-mixed red mud were investigated using different leaching methods, the MSZ-21470-50:2006 Hungarian standard, the British CEN/TS 14429 standard and Tessier sequential extraction. The MSZ-21470-50 Hungarian standard has been selected because it's the most common test used in environmental protection for heavy metals in soil in Hungary. It contains 4 different batch extractions, including aqua regia and $HNO_3 + H_2O_2$, which are necessary to give the total content of the material as a base of reference. It should be kept in mind while these methods are called 'total digestion methods', true total digestion would require additional reagents, such as HF and $HClO_4$. The distilled water test is for simulating availability to rainwater (very similar to other common standards such as EN 12457-2, DIN 38414-S4 or the ASTM D 3987-85), while the