STUDY OF REUSABILITY OF RED MUD IN CLAY BASED BUILDING MATERIALS, ON RADIOLOGICAL POINT OF VIEW (GAMMA DOSE, EXHALATION, LEACHABILITY)

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Abstract

Components of the NORMs (Naturally Occurring Radioactive Materials) remaining in by-products (e.g. ash, red mud, slag etc.) may cause health and environmental risks. In our Institute an overall NORM investigation protocol was established. Gamma spectrometry revealed that red mud has significantly higher radionuclide concentration than the world average of soils (5-10 times higher) under inhomogeneous conditions. Despite of the elevated isotope content the mixing of red mud with clays provide possibility to reuse in building material production industry (12-39 %) depending on their isotope content. Heat-treatment and mixing with clay also had beneficial effects on radon exhalation properties (90 % and above) and also on leaching characteristics (for U -10 %).

Introduction

There is a good potential in the reuse[1,2,3] of NORM containing industrial by-products, for example in the building industry, however this practice is raising concerns among authorities, public and scientists. Protocols covering these additives are usually concerned with only the physical properties connected to the construction industry, and do not cover the radiological or any toxic compound related aspects. Nowadays several studies[1,2,3] deal with finding environmental friendly materials and methods, as well as low cost materials for building purposes. Reusing of by-products or residues as building materials appear to be a possible solution.[1,2] From radiological point of view three problems can arise in the case of the NORM materials: direct gamma dose rate,[2] radon[2] and thoron exhalation and leaching of radionuclides.[4] Gamma dose rate has been viewed as a health risk for a long time, and is covered by the RP 112 guideline.[5] Radon exhalation is also a very important, the inhalation of the ^{222}Rn's short-lived progenies are responsible for about half of the total effective dose received by humans from all natural sources of ionising radiation according to UNSCEAR 2008. Leaching tests are a very important tool to assess the long-term environmental behaviour and the 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[4] protocols, or the harmonisation of protocols for waste evaluation there are still no commonly accepted methods for evaluation of the leaching characteristics of NORM materials. At PE-RRI (Institute of Radiochemistry and Radioecology, University of Pannonia, Veszprém, Hungary) an overall NORM investigation protocol was established, which is composed by defined case studies. This study introduces the NORM policy of PE-RRI on the example of bauxite, red mud, and their reuse possibilities.

Measurements and Methods

Sampling

68 red mud samples were collected from 1 and 2 meter depths from the cassettes of the Ajka red mud reservoir and 27 clay samples were gathered from various brick factories. The samples were dried to constant mass at 105 ^{0}C, were crushed in mortar and sieved under 0.63 mm. Homogeneity was assured by representative sampling and homogenisation of the powdered samples by mixing.

Gamma spectrometry

Before measurement samples were stored for 30 days in 600 cm^3 radon-tight aluminium Marinelli-beakers to reach the secular equilibrium between ^{226}Ra and their progenies. The ^{226}Ra activity concentration was obtained via the radon progenies ^{214}Pb (295 keV) and ^{214}Bi (609 keV), the ^{232}Th content was determined from ^{228}Ac (911 keV) and ^{208}Tl (2 614 keV) and the ^{40}K was measured trough the 1 460 keV gamma line by an ORTEC GMX40-76 HPGe detector[1]. The sample measuring time was 80.000 s. The data was given with the confidence interval of 95%.The I-index was calculated according to RP 112 guideline[5] and EU BSS[6] to identify whether a dose criterion is met:

$$I = \frac{C_{226_{Ra}}}{300\,\mathrm{Bq/kg}} + \frac{C_{232_{Th}}}{200\,\mathrm{Bq/kg}} + \frac{C_{40_{K}}}{3{,}000\,\mathrm{Bq/kg}}$$

Where: $C_{226_{Ra}}$, $C_{232_{Th}}$, $C_{40_{K}}$ are the Ra-226, Th-232 and K-40 activity concentrations (Bq/kg) in the building material.

Radon exhalation rate determination

The radon exhalation of samples was measured with accumulation chamber technique describe in former study.[7] 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 thickness. The radon concentration was obtained with the help of accumulation chamber technique described in former article.[8]

Leachability experiments

MSZ-21470-50, which is the Hungarian standard for the measurement of toxic elements, heavy metals and Chrome(IV) in soil consisting of 4 separate single-step batch processes:

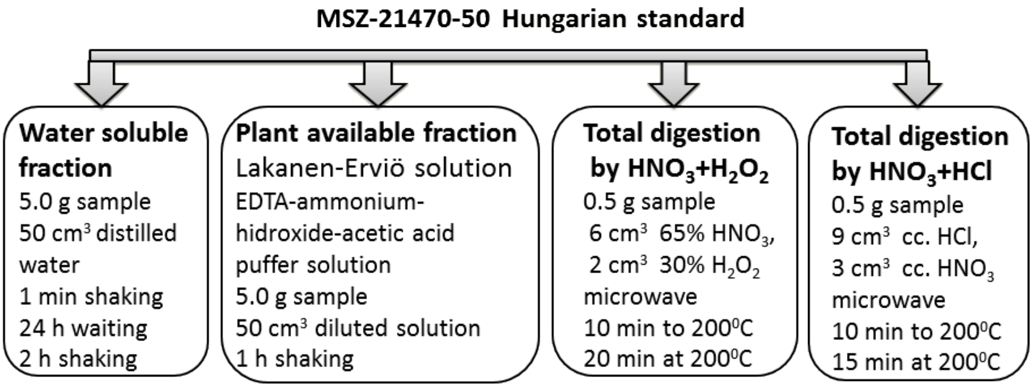

Figure 1: Flowchart of MSZ-21470-50

The **Tessier sequential extraction** is a 5 step process. The referred method describes the procedure for 1 g, but for the measurement of natural radionuclides 5 g was necessary because of the small concentrations.

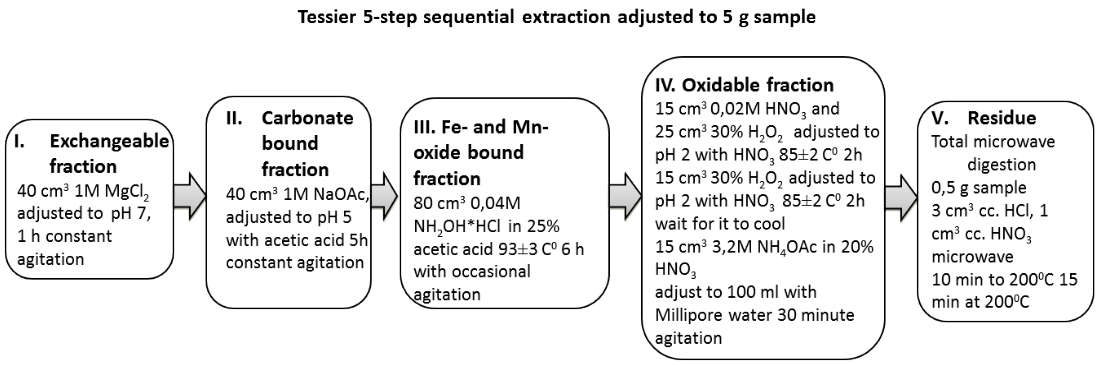

Figure 2: Flowchart of the Tessier 5-step sequential extraction

Results and Discussion

Determination of the gamma dose surplus (I-index)

The Hungarian clays are comparable (Table 1) with world average mean radionuclide concentration of soils reported in UNSCEAR2008 Annex B (^{226}Ra: 32 Bq/kg, ^{232}Th: 45 Bq/kg, ^{40}K: 412 Bq/kg) and RP112 (^{226}Ra: 40 Bq/kg, ^{232}Th: 40 Bq/kg, ^{40}K: 400 Bq/kg). The calculated I-index of the examined clay samples, obtained from building material factories, was lower than 1.0 value (average 0.59).

Table 1: Measured activity concentrations of clay and red mud samples

	^{226}Ra Bq/kg	^{232}Th Bq/kg	^{40}K Bq/kg
	Mean (Min-Max)	Mean (Min-Max)	Mean (Min-Max)
Clay (27 samples)	37 ± 7 (16 ± 3- 105 ± 17)	40 ± 9 (31 ± 7- 49 ± 11)	803 ± 98 (534 ± 16- 1 127 ± 105)
Red mud (68 samples)	289 ± 31 (152 ± 15-435 ± 24)	255 ± 25 (129 ± 12 – 314 ± 26)	110 ± 12 (17 ± 29 – 360 ± 40)

The natural radionuclide content of the deposited red mud by-product varied in great range, which requires frequent sampling and homogenising before reuse. The calculated I-indexes ranged from 1.3 to 3.0. The inhomogeneity can be caused by the condition of the processed bauxite residue and deposition factors such as particle size and particle density within the reservoirs. The maximum permissible amount of red mud to be mixed in building materials for bulk use according to I-index was between 12 and 39 %, which means constant monitoring or homogenisation is necessary.

Radon exhalation

The exhalation rate dependency was plotted as a function of the applied heat-treatment in the case of selected clay, red mud and their mixture (Figure 3).

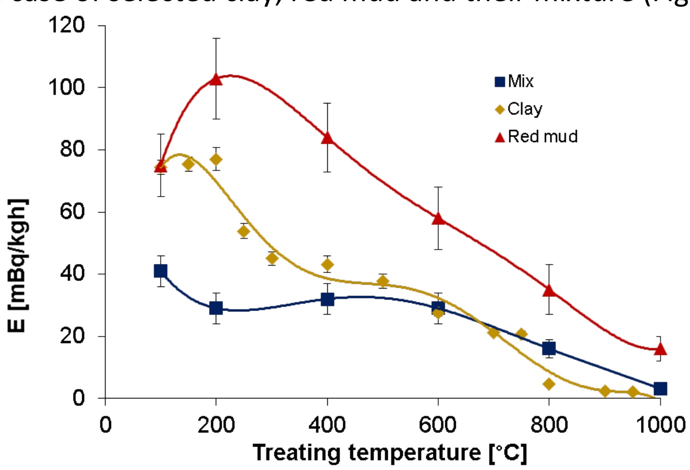

Figure 3: Effects of heat treatment on radon exhalation characteristics

It was found that the heat-treatment has beneficial effect on radon exhalation characteristic on red mud, clay and even in case of the mixture as well. Above 800 °C the measured exhalation rate was significantly lower than in case of the non-treated materials. Owing to that fact the mixing of red mud with clays can be solution to produce building materials with reduced radon exhalation features. Furthermore, the heat-treatment does not require any changes in e.g. brick production since the applied heat in case of used kilns is between 800-1000 °C.

Leachability experiments

The results of leachability experiments are presented in Figure 4. With total microwave digestion by nitro-hydrochloric acid 262 ± 19 Bq/kg U-238 was measured, while the leached amount was HNO_3+H_2O_2 digestion ~75%, Lakanen-Erviö solution ~26%, distilled water ~4.5 %; for Tessier: step I. ~1 %, step II. ~1 %, step III. ~30 %, step IV. ~7 %, step V. ~61 %. In case of the bricks compared to the total amount (23.25 ± 3.94 Bq/kg) the leached U-238 was Tessier: step I. ~6 %, step II. ~9 %, step III. ~9 %, step IV. ~4 %, step V. ~73 %.

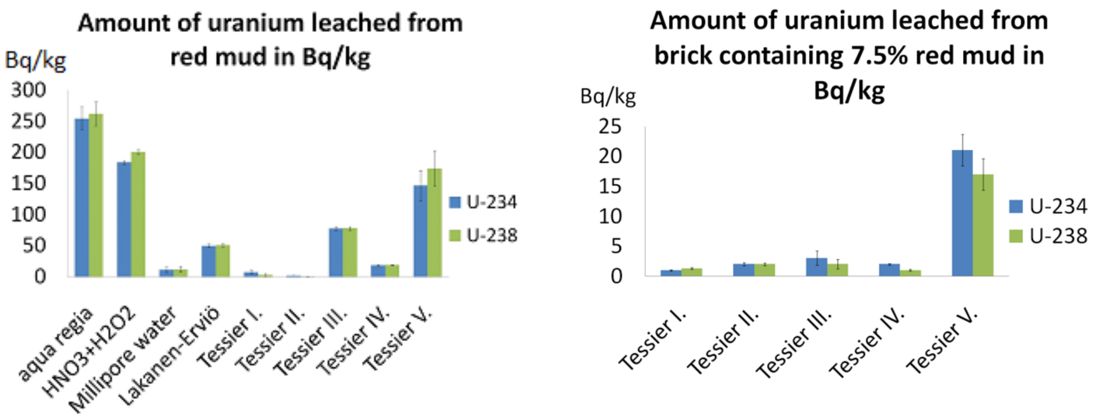

Figure 4: The measured activity concentrations of leaching tests performed on red mud and bricks with 7.5 % red mud content

The parallel single steps were faster and simpler than the Tessier method, which is more detailed. The results indicate that while the directly water soluble fraction is relatively small, with the changing of conditions a considerable amount of the red mud's uranium content becomes available for leaching. In case of red mud the Tessier-method showed that the majority of the leachable uranium is bound to the iron- and manganese-oxide bound fraction. The Hungarian standard revealed that 26 % of the uranium content in red mud is available for plants, so it can get into the food-chain. In case of model bricks less uranium becomes available, but earlier.

Conclusions

The following protocol is suggested for the evaluation of NORM materials based on the case studies: Sampling has to be representative, the samples have to be dried and homogenised before any measurement can take place. First the activity concentrations of natural radionuclides have to be determined by gamma-spectrometry and the I-index has to be calculated. This is also the base of further emanation or leaching tests. Second the radon exhalation rate of the material has to be measured. Third leaching experiments have to be performed to predict the end of life consequences and safe deposition conditions. The two described methods are suitable for characterisation of materials, however do not provide enough information for waste deposition purposes. To this end, we propose using the EN/TS 15364:2006 method, because it is easy to use, gives detailed information of the materials behaviour under different conditions, however further measurements are necessary.

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Recovery
of
Minor Elements and REE