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Characterization of bauxite residue (red mud) for ^{235}U, ^{238}U, ^{232}Th and ^{40}K using neutron activation analysis and the radiation dose levels as modeled by MCNP

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ABSTRACT

This study employs thermal and epithermal neutron activation analysis (NAA) to quantitatively and specifically determine absorption dose rates to various body parts from uranium, thorium and potassium. Specifically, a case study of bauxite residue (red mud) from an industrial facility was used to demonstrate the feasibility of the NAA approach for radiological safety assessment, using small sample sizes to ascertain the activities of ^{235}U, ^{238}U, ^{232}Th and ^{40}K. This proof-of-concept was shown to produce reliable results and a similar approach could be used for quantitative assessment of other samples with possible radiological significance. ^{238}U and ^{232}Th were determined by epithermal and thermal neutron activation analysis, respectively. ^{235}U was determined based on the known isotopic ratio of ^{238}U/^{235}U. ^{40}K was also determined using epithermal neutron activation analysis to measure total potassium content and then subtracting its isotopic contribution. Furthermore, the work demonstrates the application of Monte Carlo Neutral-Particle (MCNP) simulations to estimate the radiation dose from large quantities of red mud, to assure the safety of humans and the surrounding environment. Phantoms were employed to observe the dose distribution throughout the human body demonstrating radiation effects on each individual organ.

1. Introduction

Red mud is the insoluble slurry residue generated during the digestion of bauxite ores in the alumina producing Bayer process. It contains elevated concentrations of potentially toxic elements and is often listed as a naturally occurring radioactive material (NORM). It has been estimated that more than 150 M tonnes of red mud are produced yearly with more than 3 billion (three thousand million) tons being presently stored as calculated from by Power et al. (2011) and Evans (2016). The high production of red mud has resulted in several investigations on the environmental impact of such large volumes (Akinci and Artir, 2008; Von Philipsborn and Kuhnast, 1992; Papatheodorou et al., 2005; Pontikes et al., 2006; Wang, 1992; Jobbágy et al., 2009). Since the severe Ajka, Hungary red mud reservoir accident in 2010 there have been additional studies on the environmental impact of red mud (Mayes et al., 2016; Ruyters et al., 2011; Rubinos and Barral, 2013; Gelencsèr et al., 2011; Kovàcs et al., 2012; Hegedus et al., 2013).

The radionuclides of ^{238}U, ^{235}U, ^{232}Th and their progenies (which includes ^{222}Rn) along with ^{40}K account for the vast majority of naturally occurring radiation absorbed by the public. In previous studies, we have shown the usefulness of applying neutron activation analysis for the non-destructive determination of ^{238}U, ^{235}U, ^{232}Th and ^{40}K in tobacco and various consumed nuts and their implication on radiation dose levels to the human body (Landsberger et al., 2015, 2016). These same techniques were also used for geological materials (Landsberger et al., 2013). More recently we successfully employed MCNP modeling of NORM dosimetry in the oil and gas industry for ^{226}Ra, ^{228}Ra and ^{210}Pb (Wang and Landsberger, 2016). In view of the significant amounts of red mud, its applicability for re-use in building materials (Gu et al., 2008), and the potential for severe environmental accidents, we have initiated a preliminary study to ascertain the dose levels accumulated by workers in the field, based on neutron activation analysis measurements and MCNP modeling.

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2. Neutron activation analysis

Typically the determination of ^{235}U, ^{238}U, ^{232}Th and ^{40}K require standard gamma-ray spectrometry techniques requiring large sample sizes between 0.2 and 0.5 kg of material with long counting times between 12 and 36 h. As well, gamma-ray attenuation can pose a serious problem for samples that contain high-Z materials such as minerals, scale in oil residues, smelting processes, etc. Furthermore there is always a serious spectral interference of the 186. 3 photopeak of ^{235}U on the 186.5 photopeak of ^{238}U. The goal of using neutron activation analysis (NAA) is to establish that these four radionuclides can be analyzed by using a fraction of the material (less than 0.5 g) with a much quicker time period. The clear disadvantage is that NAA cannot determine any of the long-list of radionuclides in the decay chains of ^{235}U, ^{238}U or ^{232}Th. There has been some previous work employing NAA for bauxite and red mud (Ochsenkühn et al., 1995; Obhodas et al., 2011), respectively. While uranium and thorium were determined the main focus of their papers was multielemental and rare-earth characterization of the materials without any discussion of radiation levels.

2.1. Uranium

The activity of ^{238}U can readily be determined by epithermal neutron activation analysis using the ^{238}U(n,γ)^{239}U reaction ($t_{1/2}$ = 25 min) with the 74.5 keV gamma-ray. The use of epithermal neutrons, as opposed to typical thermal NAA, allows for better counting statistics at low uranium concentrations. This is due to both the large epithermal absorption cross-section of ^{238}U and the low epithermal absorption cross-sections of ^{37}Cl, ^{23}Na and ^{56}Mn. The ^{23}Na(n,γ)^{24}Na, ^{37}Cl(n,γ)^{38}Cl and ^{55}Mn(n,γ)^{56}Mn reactions typically increase the Compton continuum of irradiated environmental or biological samples, and reduce the ability to detect other short-lived radionuclides at low-level concentrations. Through the equation $A = \lambda N$ where A is the activity, λ is the decay constant and N is the number of atoms, the amount activity of ^{238}U can be calculated as 1 μg = 1.2×10^{-2} Bq. The ratio of ^{238}U/^{235}U is 137.88 and only in rare circumstances does this vary in nature. The activity of terrestrial radiation due to the decay of ^{235}U is more difficult to quantify when limiting our scope of analysis to neutron activation. ^{235}U which accounts for only 0.72 at% of natural uranium cannot be determined by NAA, since the (n,γ) product has a half-life of 2.5×10^7 years and is a pure alpha emitter. However, we can determine its activity using the prescribed isotopic ratio of ^{238}U/^{235}U. Therefore the contribution of ^{235}U can be similarly calculated as 5.6×10^{-4} Bq. If one can assume secular equilibrium in the front end of the ^{238}U decay chain (^{238}U → ^{234}Th → ^{234m}Pa → ^{234}U), then the activity of 1 μg of ^{234}U is equal to 1.2×10^{-2} Bq. Thus the total activity of 1 μg of uranium is the sum of ^{238}U, ^{235}U, and ^{234}U which equals 2.45 Bq × 10^{-2} Bq, with the ^{235}U being a very small fraction of ~4.7% of the total amount.

2.2. Thorium

Thorium can be easily determined using thermal neutrons and the ^{232}Th(n, γ)^{233}Th ($t_{1/2}$ = 23.4 min) → ^{233}Pa ($t_{1/2}$ = 27.7 d) reaction using the 312.0 keV gamma-ray. Similarly using $A = \lambda N$ the activity of 1 μg of ^{232}Th is equal to 4.1×10^{-3} Bq.

2.3. Potassium

Geological and biological materials are typically analyzed for activity levels of ^{40}K using gamma-ray spectrometry by utilizing its 1.46 MeV photopeak due to electron capture decay. However, due to the long half-life of ^{40}K, ($t_{1/2} = 1.3 \times 10^9$ years), this technique often requires considerable sample sizes and lengthy count times in a well-shielded detector system. Therefore, it would not be feasible to determine the activity due to ^{40}K, which accounts for only 0.0117 at% of natural potassium, while maintaining a fast analysis time and small sample volumes. In order to quantify the activity due to ^{40}K in these red mud samples, this work sought to determine the concentration of the more abundant nuclide, ^{41}K utilizing the ^{41}K(n,γ)^{42}K neutron capture reaction. Then, using isotopic ratios, the activity due to ^{40}K was found by the determined concentrations of ^{41}K in the bulk material, without extended counting times and with small sample sizes. Total potassium was determined using epithermal neutrons and the ^{41}K(n,γ)^{42}K reaction ($t_{1/2}$ = 12.8 h) using the 1524.3 keV gamma-ray. It has been shown previously that ^{40}K can be easily calculated if one knows the total potassium concentration (Sanchez et al., 2006). Again using $A = \lambda N$ the activity of every 1 μg of potassium is equal to 3.23×10^{-5} Bq.

3. Experimental

Approximately one-half a kg of three red mud samples each from an undisclosed European facility arrived in the laboratory. Approximately 100 g of each material was dried for 24 h at 105° C and then pass through a 250 μm sieve. Triplicate samples of three red mud residues weighing ~0.3 g were placed into 1 cm^3 polyethylene vials. Uranium as ^{238}U and potassium were determined using epithermal neutrons with a neutron flux of ~2.25×10^{11} n cm^2 s^{-1}. Each sample was irradiated for 5 min at 500 KW of the TRIGA research reactor. For uranium decay times of 8–15 min and counting times of 5–8 min were used while for potassium decay times of 8–16 h and counting times of 6 h were used. For thorium the samples were irradiated using thermal neutrons with a neutron flux of ~4.5×10^{12} n cm^2 s^{-1} for 1 h with a decay of 2 weeks and a counting time of 2 h. An overview of the analytical procedures is shown in Table 1.

A Canberra high-purity germanium detector (HPGe) with a full width half maximum resolution of 2.1 of the 1332.4 keV gamma ray of ^{60}Co and efficiency of 35% was used for the analysis. A Compton suppression system used for the determination of uranium and potassium is described elsewhere (Michenaud-Rague et al., 2012). All dead-times were kept at or below 10%. Calibration was performed using NIST traceable liquid standards for uranium and thorium analyses. For potassium, NIST 1515 Apple Leaves was used for calibration. Quality control for the determination of uranium, potassium and thorium was implemented by analyzing NIST biological and geological reference materials 1570a Spinach Leaves, 1573 Tomato Leaves, Coal 1632d, Coal Fly Ash 1663a and Coal Fly Ash 1633b. Results for uranium, potassium and thorium agreed within ±10% of the certified NIST values.

4. Results

The results for three replicate samples for the three different samples of the red mud (nine values in all) are shown in Table 2. Compared to data in the literature on ^{232}Th and ^{40}K, these values are within the range of previous studies (Nuccetelli et al., 2015 and

Table 1
Irradiation conditions for neutron activation analysis.

Element	Neutron energy	Irradiation time	Decay time	Counting time
Uranium	Epithermal	5 min	8-15 min	5-8 min
Potassium	Epithermal	5 min	8-16 h	6 h
Thorium	Thermal	1 h	2 w	2 h

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