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Research Article

The Technological Enhancement of Normally Occurring Radioactive Materials in Red Mud due to the Production of Alumina

Maurice O. Miller[1] and Dionne A. Miller[2]

[1] *The University of the West Indies, Mona Campus, Kingston 6, Jamaica*
[2] *LaGuardia Community College, 31-10 Thomson Avenue, Long Island City, NY 11101, USA*

Correspondence should be addressed to Maurice O. Miller; moneilmiller@gmail.com

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This study investigates the level of technological enhancement of normally occurring radioactive materials (TENORM) in the red mud waste due to the production of alumina in Jamaica. Technological enhancements factors (TEF) were determined for the uranium, thorium, actinium series, their progenies, and the nonseries potassium-40 using gamma spectrometry. The study concluded that bauxite production technologically enhances the uranium progenies Th-234, Pb-214, Bi-214, and Pa-234 and the thorium-232 progenies Ac-228, Pb-212, and Bi-212 in red mud. The actinium series was technologically enhanced, but K-40 and the thorium daughter, Tl-208, were reduced. The spectrometric comparison of Tl-208 (at 510 keV) was unexpected since its other photopeaks at 583 keV, 934 keV, and 968 keV were markedly different. An explanation for this anomaly is discussed. An explanation regarding the process of accumulation and fractionation of organically derived phosphate deposits and potassium-feldspar is offered to explain the spectrometric differences between the alumina product and its waste material, red mud.

1. Overview

Bauxite is the geological result of plate tectonics and climatic conditions occurring over a period of approximately 500 million years [1]. The impact and radioecological significance of bauxite in the environment have been studied [2–8]. Other studies have examined the mineralogy of bauxite deposits in Jamaica and in Nigeria. The NORM and dose assessment in the bauxite industry has been analyzed [9, 10]. In China, analysis of the levels of radioactivity in the red mud and red mud cement and its dose rate for local residents demonstrate the level of interest in this area [11]. Gibbsitic bauxite with a mineralogical composition $Al(OH)_3$ is the most predominant and geologically youngest type of bauxite. It is found in tropical or subtropical regions such as Jamaica and located very close to the ground surface. Jamaican bauxite is about 80% gibbsitic (α-$Al_2O_3 \cdot 3H_2O$) but some amount of boehmite, α-$Al_2O_3 \cdot H_2O$ (up to 20% in some instances), is also present (α = 90) [9, 12]. The most abundant minerals associated with the deposits are iron oxide, kaolinite $Al_2Si_2O_5(OH)_4$, and quartz. Results (from X-ray diffraction, differential thermal analysis, electron, and optical microscope) indicate that the White Limestone is the source of the Jamaican ore. In this study the main constituents were determined to be Al_2O_3 (45–52%), Fe_2O_3 (15–25%), SiO_2 (0.1–10%), TiO_2 (2.0–2.6%), P_2O_5 (0.1–5.0%), and water (18.0–25.0%) [9]. In Jamaica, approximately ten million tons of bauxite and alumina has been mined each year since 2011. At the height of its production, over 14 million tons per year was produced between 2005 and 2008 [13]. It is estimated that 4 million tons of bauxite waste per year is produced locally and 70 million tons per year worldwide [14]. In Jamaica, this red mud waste is distributed over six locations covering a total of 650 hectares (Ha). Bauxite ore is processed by mixing dried bauxite with hot caustic solutions to dissolve the alumina from the bauxite. The chemical composition of red mud varies but in general is comprised as follows: Al_2O_3 (10–25%), Na_2O (2–10%), SiO_2 (3–50%), Fe_2O_3 (30–60%), TiO_2 (1–10%), and CaO (1–8%) [15]. Bauxite refineries produce alumina (Al_2O_3) which is used primarily as a feedstock for the aluminum production

industry. The bauxite residue, called "red mud," is removed in settling tanks and placed in a tailings impoundment near the plant. In some plants, red mud is further processed to produce aluminum oxides. The waste product from this process is called "brown mud." The refinery muds (both red and brown mud) dry to a solid with very fine particle size (about 1 μm) and contain significant amounts of iron, aluminum, calcium, and sodium. They may also contain trace amounts of TENORM and various elements, such as barium, boron, cadmium, chromium, cobalt, gallium, lead, scandium, and vanadium. The types and concentrations of minerals present in the muds depend on the composition of the ore and processing conditions [16]. NORM wastes are the radioactive residues from anthropogenic mining sources such as uranium, fertilizer, copper, gold, silver, rare earth metals, titanium, zircon, and aluminum. These products and their waste may contain varying elevated concentrations of primordial radionuclides depending on the activity and the materials being processed. It is estimated that each year hundreds of millions of metric tons of NORM waste is generated from a wide variety of processes, ranging from uranium and phosphate mining to municipal drinking water treatment [16].

According to the United States Environmental Protection Agency, technologically enhanced naturally occurring radioactive material (TENORM) is produced from anthropological sources such as uranium mining or sewage sludge treatment. These activities concentrate or expose radioactive materials that occur naturally in ores, soils, water, or other natural materials. Naturally occurring radioactive material (NORM) consists primarily of material containing potassium-40 and isotopes belonging to the primordial series. The most environmentally important primordial radionuclides are the radioactive isotopes uranium-238 (uranium series), uranium-235 (actinium series), and thorium-232 (thorium series). All three series have very long half-lives and numerous radionuclides in their decay chains before reaching a stable end point, lead (Pb). Along with K-40, these three series are important because at background concentrations, they contribute about half of the natural background external radiation. They also account for over 80 percent of the background including radon, to which all humans are continuously exposed.

This study examines and quantifies the technological enhancement in the progenies of the thorium, actinium, and uranium series, and the nonseries potassium-40 in red mud due to alumina production in Jamaica. The rationale for the results is also discussed.

2. Methods and Materials

The detector used in this research was a Canberra 3825 HPGe detector (absolute efficiency = 27.61 percent, measured, and 28.15 percent, ISOCS value). This detector has an active area of 38 cm^2 and active diameter of 71 mm and was cryogenically cooled by liquid nitrogen in a vertical dipstick type 7500SL 30 litres Dewar throughout the measurement process. The detector and samples were enclosed in a Canberra Model 747E lead shield. The 10 cm thick shield weighted 950 kg and was graded with 1 mm tin and 1.6 mm copper liner to reduce interference from lead X-rays, cosmic and background radiation. This construction reduced counting time and improved the lower levels of detection during photopeak counting [17]. Canberra's Genie 2000 Gamma Acquisition and Analysis software (Ver 3.2.1) was used in the spectra capturing process. All spectra were energy corrected using the program Energy Correction (ENERCOR). The overlapping photopeaks at 185 keV (Ra-226 and U-235) and 241 keV (Ra-224 and Pb-212) were resolved using a program called SPLIT. Summing corrections were made using a software for correcting summing effect called $RSUMUP. The data to which the summing corrections were applied was provided by a software called Efficiency Transfer (EFTRAN). EFTRAN, an efficiency transfer correction utility for environmental gamma-ray spectrometry, was provided by Tim Vidmar of the Belgian Nuclear Research Centre. All spectra were analyzed using a gamma spectrum analytical software called SPECTRW. The spectrometric results and reports were produced with gamma utilities named ANALYSIS (for data analysis) and ISO-REPT (a utility for producing the analytical reports), respectively. SPECTRW, $RSUMUP, ISO-REPT, SPLIT, and ENERCOR were developed by Costas Kalfas, Demokritos, Greece. The spectrometric data were converted to Bq/kg, and all data were reported with their corresponding errors to at least 3 significant figures.

3. Results and Discussion

Figure 1 shows combined spectra for alumina and its red mud waste over the energy range up to 2 MeV. The spectrum in red is for red mud and the blue one is for alumina. The diagram shows well-defined photopeaks due to the high resolution of the detector used in this study. For the alumina spectrum, the full width half maximum (FWHM) of the photopeaks ranged from 0.62 to 2.36 keV. Similarly high resolutions were recorded in the red mud waste (0.67 to 2.67) where 42 photopeaks were identified. Generally, errors in the net count of the photopeaks were as low as 0.9% for peaks with high net counts (up to 20,994) and 8.3% for peaks with low net counts (<500). The activity of uranium series was deduced from the activities of U-238 progenies Ra-226, Pb-214, Th-234, Pa-234, and Bi-214. For the thorium series, the activity was determined from the activities of the Th-232 progenies Tl-208, Ac-228, Pb-212, and Bi-212. The actinium series was determined from the analysis of U-235 keV5 at 185.71 keV following its resolution from the spectral interfering Ra-226 photopeak.

Closer spectral comparison for various energy ranges is shown in Figures 2–6. It is observed that all the major progenies in the uranium, thorium, and actinium series are technologically enhanced in the red mud waste (Figures 2–4 and 6). The opposite is noted with potassium-40, where its value decreases in the red mud (Figure 5). From the calculated specific activities, actinium-228 (Ac-228), protactinium-234 (Pa-234), lead-212 (Pb-212), and bismuth-212 were determined to be below the MDA in the Jamaican alumina sample.

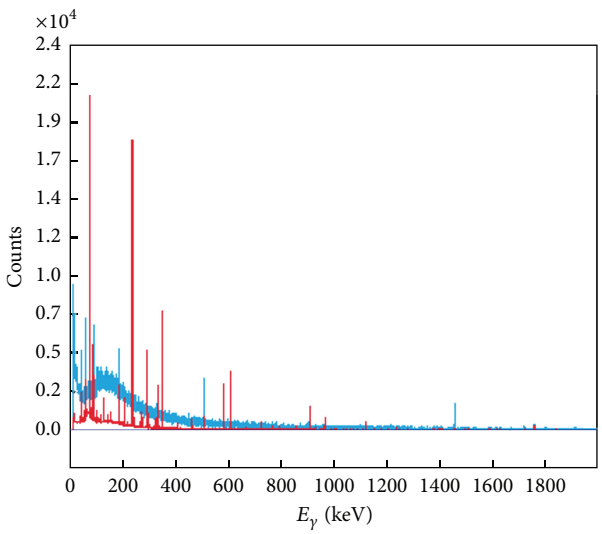

Figure 1: Spectral comparison in the gamma energy range up to 2 MeV showing the photopeaks in red mud (red spectrum) and alumina (blue spectrum) after the background was subtracted. All samples were counted for 24 hours. Counts on the vertical axis are in 10^4.

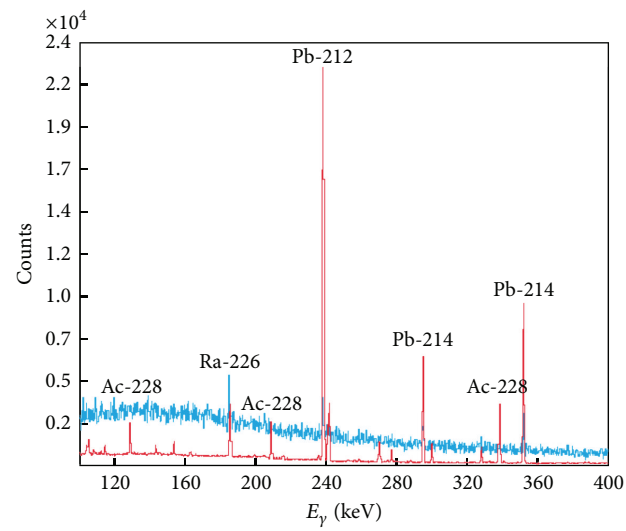

Figure 2: Comparison in the gamma energy range 120 to 380 keV showing the photopeaks for Ac-228 (128.7 keV), composite U-235 and Ra-226 (185.71 keV and 186.21 keV), Ac-228 (209.39 keV), composite Ra-224 and Pb-212 (241 keV and 241.91 keV), Pb-214 (295.17 keV), Ac-228 (338.42 keV), and Pb-214 (351.9 keV) in red mud (red spectrum) and alumina (blue spectrum). Counts on vertical axis are in 10^4.

Although the thorium series was technologically enhanced in red mud, the photopeak for its progeny, Tl-208 at 510.77 keV, was higher in alumina (1298.5 ± 29.0) Bq/kg than in its red mud waste (289.07 ± 5.67) Bq/kg by a factor of 5. Its other photopeaks at 583 keV (Figure 3) and 964 keV (Figure 4) have reverse comparative values. It should be noted however that spectral interference due to the gamma pair production process occurs in the vicinity of 510 keV and may therefore account for this anomalous result. For this reason, this photopeak is generally disregarded in gamma spectrometry.

Although U-238 was technologically enhanced by a factor of 3.86 in alumina (Table 1), the enhancement of its progeny Bi-214 at 1764 keV (Figure 6) was less significant. The comparative specific activities at this energy were 239.84 ± 8.13 Bq/kg and 350.50 ± 10.76 Bq/kg for alumina and red mud, respectively, a TEF of 1.46. The study concludes that the lower energy peaks of the U-238 progenies (<1200 keV) have a greater impact in the technological enhancement data.

Figure 7 shows the specific activity (Bq/kg) of the non-series potassium-40, actinium, uranium, and thorium series in red mud and alumina in Jamaica. The levels of technological enhancements in the red mud waste compared to the alumina are shown in Table 1.

With the exception of potassium-40 (K-40), the specific activities in all the primordial series (actinium, thorium, and uranium) were all enhanced in the red mud lakes. The results suggest that the accumulation of K-40 in alumina is dominant in the Bayer process, while uranium, actinium, and thorium accumulates in the red mud. The Bayer process is the industrial means of refining bauxite to produce alumina (aluminum oxide). The potassium is likely found in potassium-feldspar, as there is no other evidence for other potassium salts/compounds in Jamaican bauxite [9]. The higher levels of K-40 in alumina indicate that the potassium-feldspar

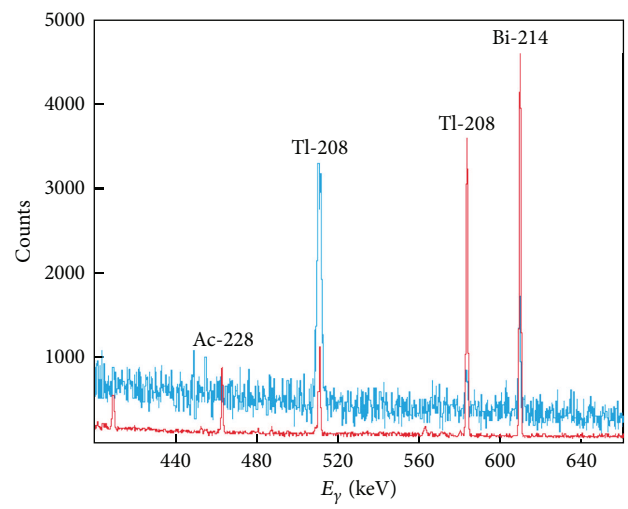

Figure 3: Comparison in the gamma energy range 480 to 640 keV showing the photopeaks for Ac-228 (463.1 keV), Tl-208 (510.77 keV), Tl-208 (583.19 keV), and Bi-214 (609.32 keV) in red mud (red spectrum) and alumina (blue spectrum).

($KAlSi_3O_8$) in the soil is more strongly bounded to alumina than the other mineral elements in the red mud. Another likely explanation is that K-feldspar (containing K-40 among other isotopes) is also soluble in the caustic solution used to dissolve alumina and coprecipitates with the alumina. In Jamaica, the high levels of U-238 are associated with concentrations in organically derived phosphate deposits. The higher concentration of this radionuclide in the red mud suggests an increased concentration following the removal of alumina from the bauxite ore. It is quite probable that the calcination

Table 1: Technological enhancement factor (TEF) in red mud. The TEF in red mud in this study is determined by the ratio of the specific activity (Bq/kg) of the primordial in red mud to the specific activity in alumina. MDA refers to the "minimum detectable activity" of the detector used in this study.

Primordial/specific activity	Alumina (Bq/kg)	Red mud (Bq/kg)	Technological enhancement factor (TEF) in red mud
K-40	1130.9 ± 27.6	79.200 ± 3.336	0.07 (reduction)
U-238	69.46 ± 3.10	268.31 ± 4.71	3.86
Th-232	Below MDA	326.08 ± 5.33	High and undefined
U-235	10.075 ± 0.405	16.153 ± 1.006	1.60

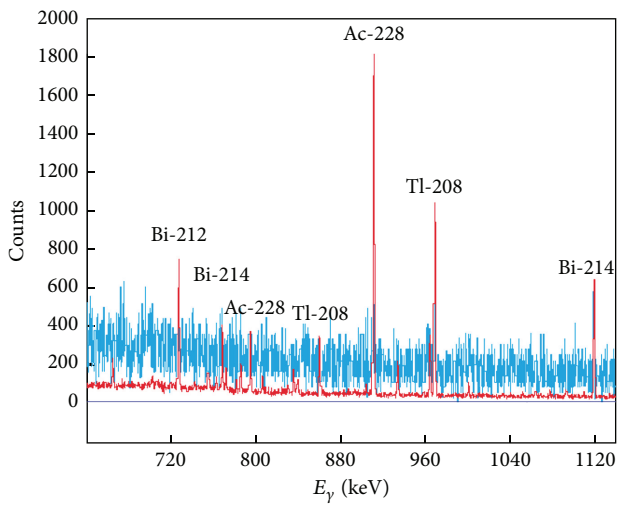

Figure 4: Comparison in the gamma energy range 640 to 1120 keV showing the photopeaks for Bi-212 (727.33 keV), Bi-214 (768.36), Ac-228 (794.79 keV), Tl-208 (860.56 keV), Ac-228 (911.16 keV), Ac-228 (964.64 kev and 968.97 keV), and Bi-214 (1120.27 keV) in red mud (red spectrum) and alumina (blue spectrum).

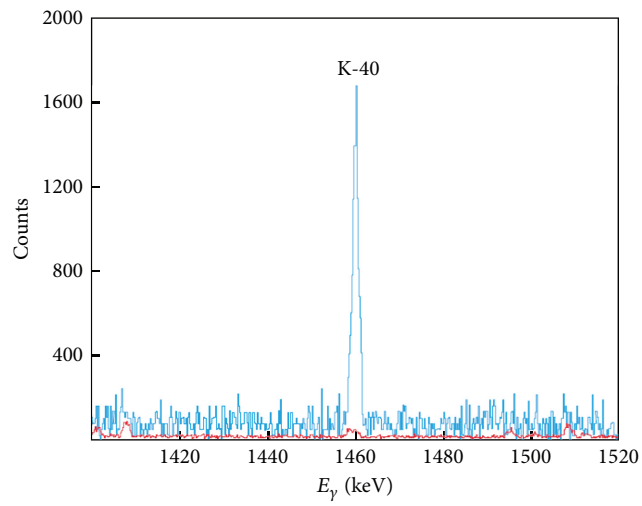

Figure 5: Comparison showing the reduction of K-40 photopeak (1460.83 keV) in alumina (blue spectrum) compared to red mud (red spectrum).

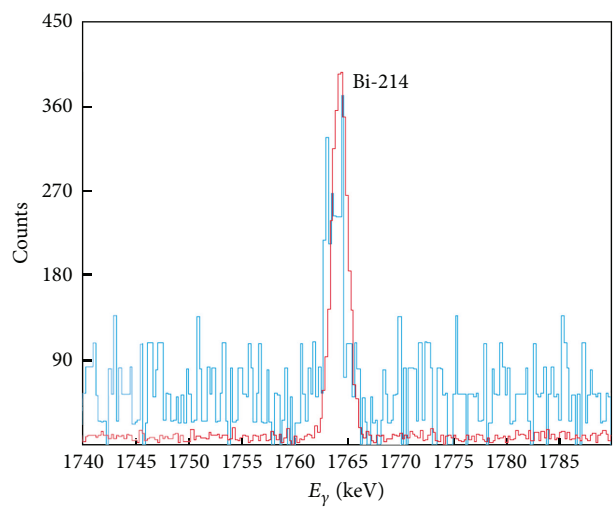

Figure 6: Comparison showing the photopeaks for Bi-214 (1764 keV) in red mud (red spectrum) and alumina (blue spectrum).

process where gibbsitic bauxite is heated to approximately 1100°C to remove chemically combined water (to produce alumina) concentrates the phosphate deposits in the red mud. Another heat-related process is the digestion process which relies on the solubility of amphoteric aluminum oxides to form a solution of aluminate ions. This chemical process occurs at between 135 and 150°C for the predominant bauxite gibbsite found in Jamaica:

$$Al_2O_3 \cdot 3H_2O + 2NaOH \longrightarrow 2NaAlO_2 + 4H_2O \quad (135\text{–}150^\circ C) \quad (1)$$

This process would also impact water-soluble radionuclides.

The accumulations noted in the red mud are problematic from the perspective of exposure to humans. The fractionation process in potassium-40 is also problematic. Miller and Voutchkov and other researchers have noted that Cs-137 and K-40 are negatively correlated in the soil environment [18]. This is demonstrated in this study, where Cs-137 with an activity of 328.92 ± 20.18 Bq/kg was detected in the red mud, but not in its alumina product. Figure 8 and Table 2 show the detailed comparisons of the major progenies of the uranium, thorium, and the actinium series investigated in this study.

From the technological enhancement factor (TEF) in Table 2, the study concludes that the bauxite production technologically significantly enhances the uranium progenies Th-234 and Pa-234 and the thorium-232 progenies Ac-228 and Bi-212 in red mud, while reducing K-40 and Tl-208.

Table 2: The technological enhancement in the specific activity (bq/kg) of the progenies of the primordial radionuclides series in red mud due to the production of alumina in Jamaica.

Progenies and K-40 (primordial series)	Alumina (Bq/kg) Bq/kg	Red mud (Bq/kg) Bq/kg	Technological enhancement factor (TEF) in red mud
K-40	1130.9 ± 27.6	79.200 ± 3.336	0.07
Th-234	316.21 ± 8.01	345.54 ± 10.24	1.09
Pa-234	Below MDA	341.10 ± 6.90	Positive and undetermined
Ra-226	218.04 ± 8.73	341.10 ± 6.90	1.56
Pb-214	48.060 ± 1.503	293.43 ± 13.29	6.10
Bi-214	111.49 ± 3.38	292.73 ± 13.50	2.62
Pa-234	Below MDA	156.92 ± 6.62	Positive and undetermined
Ac-228	Below MDA	326.84 ± 5.46	Positive and undetermined
Pb-212	Below MDA	353.16 ± 5.14	Positive and undetermined
Bi-212	Below MDA	363.04 ± 19.15	Positive and undetermined
Tl-208	1298.5 ± 29.0	289.07 ± 5.67	0.22
U-235	10.075 ± 0.405	16.153 ± 1.006	1.60

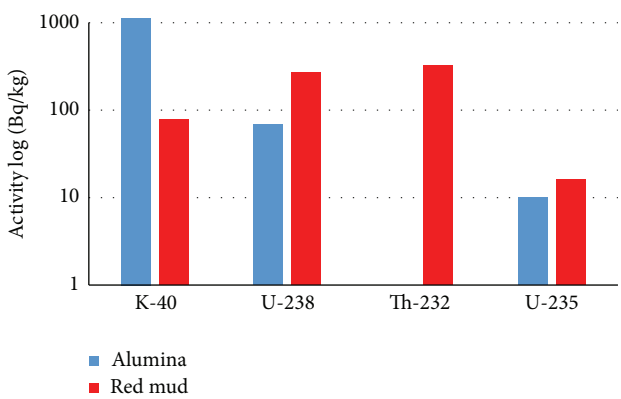

Figure 7: The figure shows the specific activity (Bq/kg) of the nonseries potassium-40, actinium, uranium, and thorium series in red mud and alumina in Jamaica. The levels of technological enhancements in the red mud waste compared to the alumina are shown in Table 1.

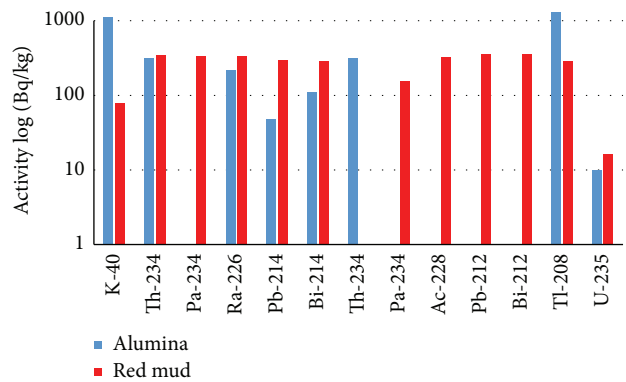

Figure 8: Logarithmic graph showing the specific activity (bq/kg) of the progenies of the primordial radionuclides series in red mud and alumina due to the production of alumina in Jamaica.

4. Conclusion

This study confirms and quantifies technologically enhanced normally occurring radioactive material (TENORM) process in the production of alumina from bauxite mining in Jamaica. The data suggest that significant accumulation of K-40 occurs in alumina by the production process, resulting in very low levels of the radionuclide in the red mud waste product. The specific activity of K-40 in alumina (1234 Bq/kg) is higher by a factor of six (6) than the mean soil value (M = 200.76 ± 21.50, SD = 177.33) reported by Miller and Voutchkov [18]. The spectrometric comparison of Tl-208 (at 510 keV) is unexpected since its other photopeaks at 583 keV (Figure 3), 934 keV, and 968 keV (Figure 4) are markedly different. A possible explanation for this anomaly is that spectral interference, due to the pair production process, was more significant in alumina than in red mud. Due to the elevation of U-238 and Th-232, and the reduction of K-40, the study disagrees with a recommendation from the United States Environmental Protection Agency (US EPA) that this waste can be used in land reclamation [19].

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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