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RADIONUCLIDES IN BAYER PROCESS RESIDUES: PREVIOUS ANALYSIS FOR RADIOLOGICAL PROTECTION

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ABSTRACT

Natural occurring radionuclides are present in many natural resources. Human activities may enhance concentrations of radionuclides and/or enhance potential of exposure to naturally occurring radioactive material (NORM). The industrial residues containing radionuclides have been receiving a considerable global attention, because of the large amounts of NORM containing wastes and the potential long term risks of long-lived radionuclides. Included in this global concern, this work focuses on the characterization of radioactivity in the main residues of Bayer process for alumina production: red mud and sand samples. Usually, the residues of Bayer process are named red mud, in their totality. However, in the industry where the samples were collected, there is an additional residues separation: sand and red mud. The analytical techniques used were gamma spectrometry (HPGe detector) and Neutron Activation Analysis. The concentrations of radionuclides are higher in the red mud than in the sand. These solid residues present activities concentrations enhanced, when compared to bauxite. Further uses for the residues as building material must be more evaluated from the radiological point of view, due to its potencial of radiological exposal enhancement, specially caused by radon emission.

1. INTRODUCTION

Natural occurring radionuclides are present in many natural resources. Human activities may enhance concentrations of radionuclides and/or enhance potential of exposure to naturally occurring radioactive material (NORM). The industrial residues containing radionuclides have been receiving considerable global attention, because of the large amounts of NORM containing wastes and the potential long term risks of long-lived radionuclides [1].

Researchers start to be concerned with the exposure that NORM can represent. Even though the specific activities are usually low, the large amounts handled by a group of workers may turn it to a potential problem.

Bayer process is the process to refine bauxite and produce alumina. It consists in the bauxite digestion in caustic soda at a high temperature and pressure, separation and washing of the

residues (called red mud), crystallization of hydrated alumina and calcination to produce anhydrous alumina.

Von Philipsborn & Kühnast investigated bauxites from Australia, Guinea and Sierra Leone. Their activities were about four times the geogenic level. The radionuclides concentration in the red mud from their processing to obtain alumina (Bayer) was twice the values for bauxite [2]. According to Cooper, the bauxite radioactivity can range 10-9000 $Bq.kg^{-1}$ for ^{238}U and 35-1400 $Bq.kg^{-1}$ for ^{232}Th, depending on the source of the bauxite ore. The content of radionuclides in red mud can increase threefold compared to the original bauxite [3].

Righi *et al* [4] investigated natural radioactivity bauxite and found activity concentrations in bauxites up to 500–600 Bq. kg^{-1} of ^{238}U and 400–450 Bq. kg^{-1} of ^{232}Th, confirming findings in literature of significant quantities of NORM in this raw material.

The possible end uses for red mud, like bricks production, need a better understanding of the radioactivity associated to this residue.

The elements of concern are the long-lived radionuclides and radio, due to their potential risks. Radio decays to radon, increasing the occupational risk. The long-lived radionuclides last in the environment, what is considered a risk along the years, depending on their concentrations. These elements may contaminate superficial and ground water, being a possible way of direct or indirect ingestion (by animals and plants contaminated). Dusts from the residues generated in land disposals or during the process are a source of inhalation and incorporation of radionuclides.

Included in this global concern, this paper focuses on the characterization of radioactivity in samples of Bayer process for alumina production, especially the main residues: red mud and sand. The analytical techniques used were gamma spectrometry for the gamma emitters isotopes and Instrumental Neutron Activation Analysis (INAA) for U and Th. This paper intends to present the first results of studies on the radioactivity in a Brazilian bauxite and during Bayer process, associated to a previous analysis for radiological protection.

2. MATERIALS AND METHODS

The samples were collected at an alumina industry in the north region of Brazil. The bauxite is mined in a near area. The industrial process is shown in Figure 1, as well as the samples collected.

Usually, the residues of Bayer process are named red mud, in their totality. However, in the industry where the samples were collected, there is an additional residues separation: sand and red mud. They were analyzed separately in this work, in order to verify the contribution of each residue in the final disposal, even though they are generally disposed together.

The samples were transferred to Marinelli beakers (500mL). Each recipient was sealed for at least four weeks to reach secular equilibrium between ^{226}Ra and ^{224}Ra and their respective immediate progeny [5,6].

The measurements of natural radioactivity were performed by gamma-ray spectrometry: a system from *CANBERRA*, consisting of a hyper-pure germanium detector (HPGe), coaxial geometry, 15% efficiency, with data acquired and treated with *Genie 2000* software.

All the gamma emitters nuclides from natural series of U and Th were determined by Gamma Spectrometry. U and Th were determined also by Instrumental Neutron Activation Analysis (INAA). ^{226}Ra (^{238}U chain) and ^{224}Ra (^{232}Th chain) were determined by measuring the areas of ^{214}Bi and ^{212}Pb, respectively, because the ageing time of at least thirty days after sealing the Marinelli beakers, which assures the secular equilibrium between these elements and their progeny [7]. This period of time is also enough to restore the equilibrium in ^{232}Th chain, between ^{228}Ac and ^{228}Ra. Due to the low natural abundance of ^{235}U, its chain was not considered in this study.

The laboratories at CDTN/CNEN, where the analyses were carried out, participate in a National Intercomparison Program coordinated by IRD/CNEN (Institute of Radiation Protection and Dosimetry), in Brazil, and by the IAEA (International Atomic Energy Agency). The isotopes ^{60}Co, ^{65}Zn, ^{106}Ru, ^{133}Ba, ^{134}Cs, ^{137}Cs, ^{226}Ra, Th and U are analyzed in the intercomparison programs.

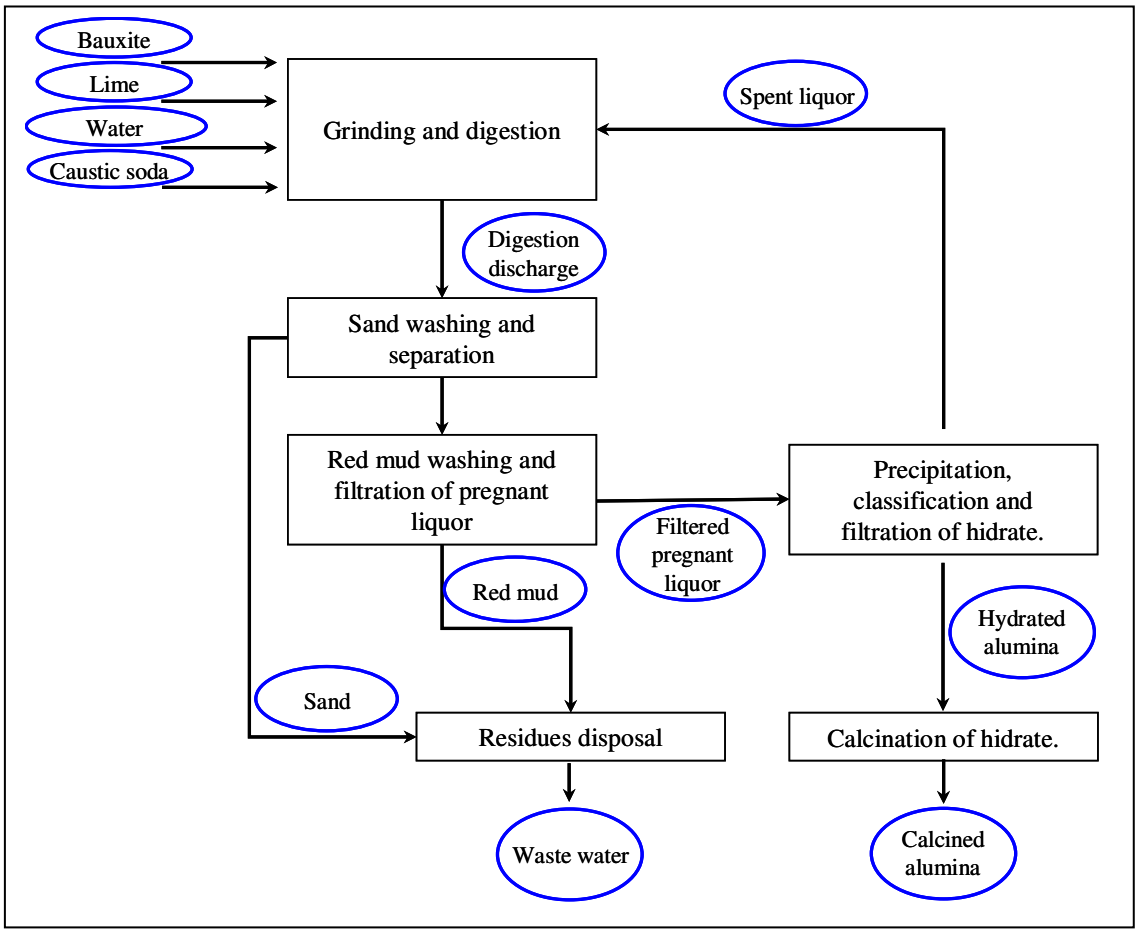

Figure 1. Simplified fluxogram of Bayer process, including samples collected in each phase.

If the samples were in secular equilibrium, the activities of uranium and thorium decay series could be determined by measuring the areas of some members' peaks located downstream of the radionuclides (^{214}Bi for ^{238}U chain and ^{228}Ac for ^{232}Th chain). However, in these samples, the equilibrium was disturbed by Bayer process. Then, the activity of uranium was determined by using the TRIGA MARK I IPR-R1 Reactor, by Delayed Neutrons Analysis (DNA), a kind of Instrumental Neutron Activation Analysis (INAA). The samples were homogenized, weighed and irradiated in the pneumatic system, specially designed for this type of analysis. Thorium was analyzed by INAA, counting the gamma line of ^{233}Pa. The technique used for each radionuclide, the specific gamma line used and the detection limits are showed in Table 1.

Table 1. Radionuclides, respective analytical technique used and detection limits

Radionuclide	Technique	Used gamma lines [energy (keV) - emission probability]	Detection limit ($Bq.kg^{-1}$)
^{40}K	GSA[a]	1460.8 (10.7%)	1.0
^{238}U	INAA[b]	Counting of Delayed Neutrons	12[d]
^{214}Bi (^{226}Ra)[c]	GSA[a]	609.3 (46.3%)	0.4
^{232}Th	INAA[b]	^{233}Pa – 312 (100%)	4.0[d]
^{228}Ac	GSA[a]	338.3 (11.4%); 911.6 (27.7%); 968.2 (16.6%)	0.4
^{212}Pb (^{224}Ra)[c]	GSA[a]	238.6 (44.6%)	0.4

[a] GSA – Gamma Spectrometry Analysis
[b] INAA – Instrumental Neutron Activation Analysis
[c] The gamma lines represent ^{214}Bi and ^{212}Pb. ^{226}Ra and ^{224}Ra were determined indirectly.
[d] Detection limit of 1μg.g^{-1}, corresponding to about 12Bq.kg^{-1} for ^{238}U and 4,0Bq.kg^{-1} for ^{232}Th.

3. RESULTS

The specific activities of individual nuclides determined in each sample are presented in Table 2. The shown results are the mean values of three measurements and the standard deviation.

Table 2. Activities of samples during Bayer process.

Sample	Specific Activity ($Bq.kg^{-1}$)					
		Uranium series		*Thorium series*		
	^{40}K	^{238}U	^{214}Bi (^{226}Ra)	^{232}Th	^{228}Ac	^{212}Pb (^{224}Ra)
Bauxite	9.4±0.2	37±12	64±1	154±16	225±2	237.4±0.7
Water	1.4±0.4	<DL	1.4±0.1	<DL	1.6±0.2	0.9±0.1
Lime	4.8±0.6	<DL	3.4±0.2	<DL	<DL	1.1±0.1
Caustic soda	14±1	<DL	0.8±0.1	<DL	<DL	0.59±0.04
Digestion discharge	23±1	<DL	5.5±0.1	16±4	21.7±0.2	18.3±0.05
Filtered pregnant liquor	31±1	<DL	83.8±0.1	<DL	<DL	0.631 ± 0.003
Spent liquor	28±1	<DL	0.6±0.1	<DL	<DL	0.51±0.04
Hydrated alumina	<DL	<DL	0.79±0.02	<DL	<DL	0.775 ± 0.003
Calcined alumina	7.4±0.5	<DL	1.45±0.01	<DL	1.6±0.2	0.84±0.01
Sand	14±1	36±12	51.2±0.5	264±24	314±2	259±1
Red mud	45±1.9	100±10	139.2±0.8	350±19	553±3	544±1
Waste water	3.3±0.6	3.8±0.1	1.1±0.1	3.8±0.1	3.8±0.1	1.0±0.1

Usually, the residues of Bayer process are named red mud, in their totality. However, in the industry where the samples were collected, there is an additional residues separation: sand and red mud. They were analyzed separately in this work, in order to verify the contribution of each residue in the final disposal, even though they are generally disposed together.

According to the equilibrium conditions previously exposed, ^{226}Ra and ^{222}Rn have the same activity as ^{214}Bi, as well as their immediate progeny. ^{224}Ra and ^{220}Rn are equal to ^{212}Pb and their progeny. ^{228}Ra has the same activity as ^{228}Ac.

To represent the activity levels of ^{226}Ra, ^{232}Th and ^{40}K by a single quantity, which takes into account the radiation hazards associated with them, a common radiological index has been introduced. This index is called radium equivalent (Ra-eq) activity and is mathematically defined by equation (1), where A represents the activity level of ^{226}Ra, ^{232}Th and ^{40}K. In the above relation, it has been assumed that 10 Bq kg^{-1} of ^{226}Ra, 7Bq kg^{-1} of ^{232}Th and 130 Bq kg^{-1} of ^{40}K produce equal γ-dose. [8, 9, 10, 11]

$$Ra-eq(Bq.kg^{-1}) = A(^{226}Ra) + 1{,}43A(^{232}Th) + 0{,}077A(^{40}K) \quad (1)$$

The maximum dose Ra-eq in building materials must be less than 370 Bq kg^{-1} for safe use, i.e., to keep the external dose below 1.5mGy.yr^{-1}. [8, 9, 10] The results of Ra-eq for the samples and the comparison to these limits are shown in Figure 2.

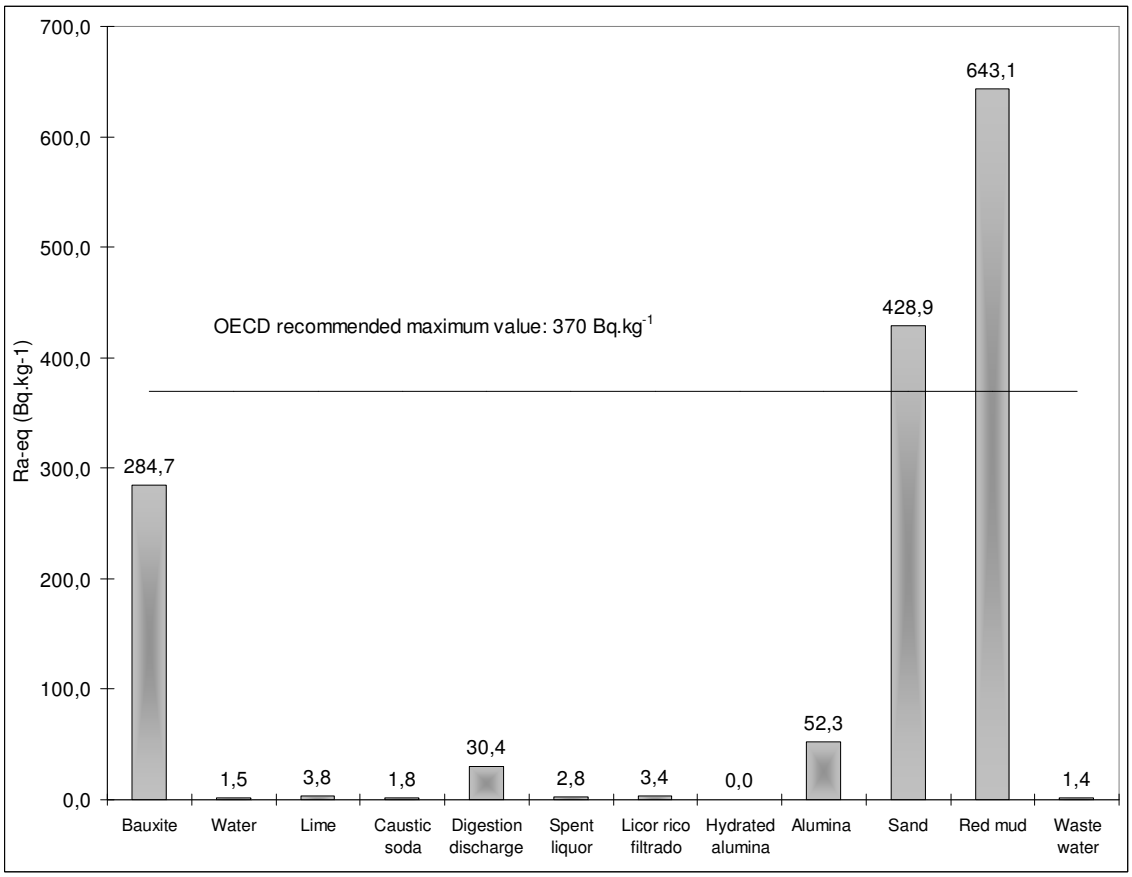

Figure 2. Ra-eq for each sample compared to OECD limit for building materials.

4. DISCUSSION

As expected, the results show the disequilibrium in both uranium and thorium series due to the chemical differences between the chain's elements. Bauxite is the only sample in which the secular equilibrium could be expected. However, its equilibrium may have been disturbed because the ore has been washed before it arrives at the industry.

The bauxite has a concentration of activities higher than the digestion discharge sample, due to the addition, to bauxite, of lime, caustic soda and spent liquor, which do not add significant radioactivity to the process. Then, the radioactivity in this industrial process is mainly originated from bauxite. Other minor sources of radioactivity are the caustic soda (specially for ^{40}K), lime and water.

The end products, hydrated and calcined alumina, do not carry significant activities. The radionuclides concentration is threefold higher in the residues than in bauxite, which classifies the residues as TENORM (Technologically Enhanced Naturally Occurring Radioactive Material)[1]. Sand and red mud have different contributions of activities in residual disposal. In this case, the concentration of ^{226}Ra is about twofold higher in the red mud than in the sand. Information about both the residues has not been found in the specialized literature yet, probably due to the fact that they are disposed together and named red mud.

The activity due to ^{40}K is about threefold in red mud than in sand, probably because of the caustic liquor that remains in the mud after washing it. ^{40}K is more present in the liquors and digestion discharge. These concentrations may be caused by the addition of caustic soda to the process, which comes associated to potassium and introduces most part of this element in the process.

The index Ra-eq for sand, red mud and digestion discharge is higher than 370 $Bq.kg^{-1}$, the OECD recommended maximum value. These results show that specific studies must be carried out for a better comprehension of radiological implications of the residues utilization as building material, especially in enclosed spaces due to radon exhalation.

During the operation of the landfill, the access to the area is restricted and the radioactivity of the residues should not be a concern. In the other hand, the decommissioning of the landfills must be evaluated from the radiological point of view, considering that the area may be used for many activities afterwards, even agriculture and houses construction.

It is important to observe that the results for landfill waste water suggests that no significant radionuclides leaching took place from the sand and red mud to groundwater, due to the low concentrations obtained.

5. CONCLUSIONS

As expected, bauxite is the major contributor to radioactivity in Bayer process. It has activities of 37 ± 12 $Bq.kg^{-1}$ for ^{238}U and 154 ± 16 $Bq.kg^{-1}$ for ^{232}Th. The entry of radionuclides is mainly from this ore, with no relevant contribution from lime (added for better process control), water and caustic soda. However, caustic soda is the major contributor for ^{40}K.

The end products do not carry significant activity, desirable characteristic from the health physics point of view.

The residues, sand and red mud, carry most part of the radionuclides. Thus, these solid residues present activities concentrations threefold enhanced when compared to bauxite. In the evaluated process, the concentration of ^{226}Ra is twofold higher in the red mud than in the sand.

Specific studies must be carried out for a better comprehension of radiological implications of the landfills liberation and the residues utilization as building material especially in enclosed spaces due to radon exhalation.

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REFERENCES

1. IAEA – International Atomic Energy Agency. *Technical Reports Series no. 419: Extent of environmental contamination by naturally occurring radioactive material (NORM) and technological options for mitigation*. Vienna, 2003.
2. H. Von Philipsborn; E. Kühnast, "Gamma spectrometric characterisation of industrially used African and Australian bauxites and their red mud tailings." *Radiation Protection Dosimetry.* **Vol. 45**, n 1/4 (1992).
3. M. B. Cooper, *Natural occurring radioactive materials (NORM) in Australian industries – Review of current inventories and future generation*, http://www.arpansa.gov.au/pubs/rhsac/norm_report.pdf, (2003).
4. Righi, S et al. "Natural radioactivity in refractory manufacturing plants and exposure of workers to ionising radiation." *Journal of Environmental Radioactivity*. **Vol. 100**, pp. 540-546 (2009).
5. A. Nada, "Evaluation of natural radionuclides at Um-Greifat area, eastern desert of Egypt", *Applied Radiation and Isotopes*. **Vol. 58**, pp. 275-280 (2003).
6. L. Bruzzi *et al*. "Radioactivity in raw materials and end products in the Italian ceramics industry." *Journal of Environmental Radioactivity*. **Vol. 47**, pp. 171-181 (2000).
7. M. Authier-Martin *et al*. "The Mineralogy of Bauxite for Producing Smelter-Grade Alumina", *JOM* (2001).
8. E.M. El-Afifi *et al*. Evaluation of U, Th, K and emanated radon in some NORM and TENORM samples. *Radiation Measurements*. **Vol. 41**, pp. 627-633 (2006).
9. M.H. El Mamoney; A.E.M Khater,. Environmental characterization and radio-ecological impacts of non-nuclear industries on the Red Sea coast. *Journal of Environmental Radioactivity*. **Vol. 73**, pp. 151–168 (2004).
10. J. Beretka; P.J.Mathew. "Natural radioactivity of Australian building materials, industrial wastes and by-products." Health Physics. **Vol. 48**, no. 1, pp. 87-95. (1985).
11. N. W. El-Dine *et al*. Measurement of radioactivity and radon exhalation rate in different kinds of marbles and granites. *Applied Radiation and Isotopes*. **Vol. 55**, pp. 853-860. (2001).