

## EXTERNAL GAMMA EXPOSURE DUE TO THE APPLICATION OF CARBONATE NIOBIUM TAILING AS SOIL AMENDMENT

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### ABSTRACT

The storage of tailing from anthropic activities like mining, which may contain radionuclides, is a problematic situation consequent from NORM industries and for which alternatives should be sought. This paper presents the preliminary results for the use of a carbonate tailing derived from niobium extraction as soil amendment from the point of view of the radiological indices, since this material is a NORM residue. The activity concentration of radionuclides <sup>226</sup>Ra, <sup>228</sup>Ra and <sup>40</sup>K were determined in six samples of carbonate by gamma spectrometry and the radiological hazard indices were calculated for the carbonate itself and simulated for soil application. The results indicated that the dilution of the carbonate in the soil do not increase the radiological hazard indices.

### 1. INTRODUCTION

Mineral extraction is an important activity for the socioeconomic development of the country, due to its importance in the production chain, from the extraction of minerals, production of industrialized products, needs of industries for transformation of raw material, besides being a technological activity. However, mining activities also has the potential to cause social and environmental problems that may differ from other anthropic activities [1], due to tailing generation, which must be properly stored to mitigate social-environmental damages.

Worldwide, various types of tailing are already used in agriculture. The bauxite mining tailing was applied as a soil conditioner in sugarcane cultivation to verify the availability of

macronutrients in the soil and leaves of the plant. As a result, the bauxite mining tailing provide the plant nutrients resulting in a lesser environmental impact [2].

Tailing of vermiculite, a mineral formed by hydration of basaltic minerals was applied as an alternative fertilizer for potassium. From the results obtained, there is the possibility of using the tailing in perennial crops that requires small but constant rates of potassium [3].

Phosphogypsum, a tailing resulting from the phosphate fertilizer manufacturing, that generally contain uranium series radionuclides, is used in agriculture as a soil conditioner due to its high solubility, improvement in the availability of nutrients to plants and reduction of soil erosion. In Brazil, phosphogypsum is the only mineral industrial tailing with specific regulation for its use [4-6].

In agriculture, the process of liming (addition of limestone or virgin lime to soil) increases the performance of cultures in acidic soils in tropical and subtropical regions due to the increase of the pH making phosphorous more available, as well as, supporting the microbial activity and either decreasing or extinguishing the phytotoxicity of other elements, such as aluminum and manganese. The liming is advantageous to enhance the ability of water absorption for the plants, as well as, the nutrients absorption [7, 8].

The use of soil conditioners may reduce the toxicity of some chemical elements, increase the availability of other chemical elements and assist in plant development. Thinking about the use of mining tailing can mitigate two environmental issues, the disposal of this tailing and the decrease in the use of fertilizers, because the composition of these fertilizers depends on the rock that originated them, which can cause an increase in the concentration of chemical elements in the environments agricultural [9].

The industrial process for metallic niobium obtention, from niobium ore, generates a carbonate tailing which is currently stored as waste. Niobium is a refractory metal that can be extracted primarily from columbite and pyrochlore ores. It is important for metal alloys production, due to its low hardness and high strength. Brazil holds about 98% of its world reserve in the states of Minas Gerais, Amazonas, Goiás, Rondônia and Paraíba, followed by Canada and Australia, and is also the world's largest exporter of ore, representing more than 90% [10].

To obtain the ore it is necessary to subject the rock to the *crushing* and *preconcentration* process by means of magnetic separation, in which the magnetic particles are considered as product and the non-magnetic particles are considered as tailing. Grinding and sorting are then carried out, followed by *sludge removal*, to remove very fine particles (<0.010 mm).

After the process, the ore pulp is directed to the *flotation of silicates*. In this flotation, the pulp has a basic character with a pH of approximately 10. The concentrates of silica are obtained from the flotation cleaning step of silicates, which, in this case, are particles from the foam [11].

After obtaining the silicates, carbonate flotation occurs, and this flotation also occurs in basic pH, approximately 10. The concentrates of carbonate are acquired from its foam. Then, the concentrates of silica and carbonate are sent to containment dams, constituting process tailing deposits [11].

The use of this carbonate in agriculture, as soil amendment, emerges as a proposal for its application. Nevertheless, such tailing concentrates a great amount of radioactive elements, mainly from the thorium series, but also from the uranium and  $^{40}\text{K}$ . This characteristic classifies the niobium industry as NORM, which are those in which natural radioactive materials are treated or separated, due to the processes of raw material transformation, resulting in an unintended concentration of the natural radionuclides [12].

Therefore, the objective of this study was to evaluate the radiological hazard indices due to the use of a niobium carbonate tailing as soil amendment for agricultural purpose. In this sense, the activity concentration of  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  and  $^{40}\text{K}$  were determined by high resolution gamma spectrometry. The carbonate of interest in this work comes from the Nb mining located in Catalão - Goiás, Brazil. It is important to note that for this tailing there is no regulation for its application.

## **2. MATERIALS AND METHODS**

### **2.1. Samples**

The carbonate samples, collected in November 2012 (sample “A”) and December 2016 (sample “B”, “C”, “D”, “E” and “F”), were supplied by the NORM industry, CMOC INTERNATIONAL BRASIL.

### **2.2. Gamma Spectrometry**

Activity concentrations of  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  and  $^{40}\text{K}$  were measured by gamma spectrometry with a high purity germanium detector (HPGe). This technique has been highlighted due to the low detection limits, for being a non-destructive technique and the capability of determining several radionuclides simultaneously. For the measurements, samples were placed in  $40\text{ cm}^3$

polyethylene flasks, sealed in order to avoid radon escape and set apart for about four weeks prior the measurements, to ensure reaching out the radioactive equilibrium between  $^{226}\text{Ra}$  and its short-living decay products. The counting time was 80.000 seconds. The  $^{40}\text{K}$  activity was determined directly through at 1460 keV peak. The  $^{226}\text{Ra}$  activities were determined by taking the mean activity of three separate photopeaks of its daughter nuclides:  $^{214}\text{Pb}$  at 352 keV and  $^{214}\text{Bi}$  at 609 keV and 1120 keV. The  $^{228}\text{Ra}$  content in the samples was determined by measuring the intensities of the 338 keV and 911 keV gamma-ray peaks from  $^{228}\text{Ac}$ .

### 2.3. Radiological Hazard Index

The analysis of radiation hazard index due to the natural radioactivity was estimated by different approaches: *absorbed dose rate* (D), *excess lifetime cancer risk* (ELCR), *annual gonadal dose equivalent* (AGDE) and the *annual effective dose rate* (AEDR) and compared with the international recommended values or global average. The application of the following equations for the radiological hazard indices determination supposes equilibrium in the  $^{238}\text{U}$  series with  $^{226}\text{Ra}$  and equilibrium of the  $^{228}\text{Ra}$  with  $^{232}\text{Th}$  decay series, according to IAEA [13].

The absorbed *dose rate* (D) is related to the risk from the amount of radiation deposited on a body per unit time that comes from terrestrial gamma emitters. The absorbed dose rate (nGy  $\text{h}^{-1}$ ) may be derived from the measured activity concentrations and UNSCEAR factors and shown in equation 1 [14]:

$$D = 0.462 \cdot A_{226\text{Ra}} + 0.604 \cdot A_{232\text{Th}} + 0.0417 \cdot A_{40\text{K}} \quad (1)$$

The annual effective dose equivalent (AEDE) is a measure of the adsorbed dose rate and also the time spent in contact with the radioactive source – occupancy factor, for outdoor exposition, according to the equation 2 [14].

$$\text{AEDE} [(\mu\text{Sv})/\text{y}] = D [\text{nGy}/\text{h}] \cdot 8760\text{h} \cdot 0.2 \cdot 0.7 \text{ Sv/Gy} \cdot 10^{-3} \quad (2)$$

Excess lifetime cancer risk (ELCR) was calculated according to equation 3.

$$\text{ELCR} = \text{AEDE} \cdot DL \cdot RF \quad (3)$$

where, *DL* is lifetime (70 years) taking into consideration *AEDE* and a risk factor (*RF* in  $\text{Sv}^{-1}$ ) established as 0.05 by the ICRP 60 for stochastic effects for the public [14].

The annual gonadal dose equivalent (AGDE) is a measure of the genetic significance of the dose equivalent received by the population's reproductive organs per year, according to [14]. The UNSCEAR considers some organs being of particular interest and includes values for

spinal cord activity and bone surface cells, for example. To determine the AGDE index, it was used the equation 4 [14, 15]:

$$\text{AGDE } [(\mu\text{Sv})/\text{y}] = 3,09 \cdot A_{226\text{Ra}} + 4,18 \cdot A_{232\text{Th}} + 0,314 \cdot A_{40\text{K}} \quad (4)$$

To calculate the annual effective dose rate (AEDR) index for external exposure, the equation 5 was used [16].

$$\text{AEDR } [\text{mSv}/\text{y}] = D \text{ [nGy/h]} \cdot 8760\text{h}/\text{y} \cdot 0.2 \cdot 0.7[\text{Sv}/\text{Gy}] \cdot 10^{-6} \quad (5)$$

where the value of 0.7 ( $\text{Sv Gy}^{-1}$ ) gives the effective dose absorbed dose conversion coefficient and 0.2 is the outdoor occupancy factor, both proposed by [16].

### 3. RESULTS AND DISCUSSION

#### 3.1. Gamma Spectrometry

In order to evaluate the activity concentrations in the samples, the results presented are the mean of triplicated measurements made for each sample. Sample A refers to the sampling performed in November of 2012 and samples B, C, D, E e F refers to samples collect from the same batch of carbonate produced in December of 2016. Table 1 presents the results obtained for the activity concentration of  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  and  $^{40}\text{K}$  determined in the carbonate samples and for comparison, the averages of world activity concentration in soil [16].

The activity concentration in the samples ranged from 250 to 305  $\text{Bq kg}^{-1}$  for  $^{226}\text{Ra}$ , with mean value and standard deviation of  $264 \pm 21 \text{ Bq kg}^{-1}$ . For  $^{228}\text{Ra}$ , the variation ranged from 1690 to 2400  $\text{Bq kg}^{-1}$ , with the mean value and standard deviation of  $2055 \pm 301 \text{ Bq kg}^{-1}$ , while  $^{40}\text{K}$ , ranged from 320 to 574  $\text{Bq kg}^{-1}$  with mean value and standard deviation of  $471 \pm 91 \text{ Bq kg}^{-1}$ . It can be observed that the distribution of the determined radionuclides activity concentrations is relatively well homogeneous in the samples with coefficient of variation of 8%, 15%, and 19%, for  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ , and  $^{40}\text{K}$ , respectively. This homogeneity is relevant considering the possible application of the carbonate as an agricultural input in the soil, so that it would not be expected a material with a higher concentration than the expected.

**Table 1: Activity Concentration Carbonate of  $^{226}\text{Ra}$  ( $^{238}\text{U}$  series),  $^{228}\text{Ra}$  ( $^{232}\text{Th}$  series) and  $^{40}\text{K}$ .**

| Sample                        | $^{226}\text{Ra}$<br>(Bq kg <sup>-1</sup> ) | $^{228}\text{Ra}$<br>(Bq kg <sup>-1</sup> ) | $^{40}\text{K}$<br>(Bq kg <sup>-1</sup> ) |
|-------------------------------|---|---|---|
| A                             | 259   | 2130  | 574                                       |
| B                             | 254   | 2330  | 527                                       |
| C                             | 250   | 1690  | 453                                       |
| D                             | 305   | 2070  | 429                                       |
| E                             | 265   | 1710  | 320                                       |
| F                             | 251   | 2400  | 522                                       |
| <b>UNSCEAR</b><br><b>[16]</b> | <b>45</b>                                   | <b>30</b>                                   | <b>400</b>                                |

It is noticed that the values obtained for the average activity concentration in the samples analyzed in this study are higher than the world references. Calculating the ratio between averages,  $R = \text{experimental reference}^{-1}$ , it is obtained values higher than the world reference of 12.4 for  $^{226}\text{Ra}$ , 86.9 for  $^{228}\text{Ra}$  and 1.29 for  $^{40}\text{K}$ , confirming the enrichment in Th series radionuclides of the samples.

As there are no regulation for the use of carbonate tailings as soil amendment, the obtained values were compared with the ones applied for phosphogypsum. According to CNEN standard 179/14 which states as dispense-for-use in agriculture the limit value of 1,000 Bq kg<sup>-1</sup> for  $^{226}\text{Ra}$  and for  $^{228}\text{Ra}$ . Considering these values, the activity concentration observed for  $^{226}\text{Ra}$  is in accordance with the limit,  $^{228}\text{Ra}$ , on the other hand surpass in about 2 times the recommended value.

### 3.2. Radiological Hazard Index

The possible use of a mining tailing from a NORM industry may be an alternative to lower environmental impact. Nevertheless, studies are necessary to be carried out in order to verify if the use of this material may cause any damage to human health due to the increment of radiation exposition. The results of the radiological hazard index calculated from the results obtained by gamma spectrometry for considering just the carbonate samples are presented in the Table 2. In can be observed that the values obtained for the absorbed dose (D) are much higher than that found globally for soil worldwide, that varies from 28 to 120 (nGy h<sup>-1</sup>) [15]. The values of AGDE correspond to the possible effects on descendants or sterility of the subjected person, resulting from the radiation of the gonads cells. These values depend on the

rate of dose absorption. According to CNEN [17], the values for radiation dose in gonads of 0.4 Sv, may cause temporary sterility and 2 Sv, permanent one, in protracted or fractionated exposures for many years. The for AGDE found for the pure carbonate exposure are below these values, nevertheless they are much higher the average values for soil of  $300 \mu\text{Sv y}^{-1}$  [18]. Similarly, the obtained values for ELCR are much higher than world's average value  $2.8 \times 10^{-3}$  and the AEDR surpass the increment of dose recommended of  $1 \text{ mSv y}^{-1}$ .

**Table 2: Hazards hazard indices estimated for the carbonate samples**

| Sample | D<br>[nGy/ h] | ELCR<br>[ $10^{-6}$ ] | AGDE<br>[ $\mu\text{Sv/y}$ ] | AEDR<br>[mSv/y] | AEDE<br>[mSv/y] |
|--------|---------------|-----------------------|------------------------------|-----------------|-----------------|
| A      | 1430          | 6139                  | 9884                         | 1.75            | 1754            |
| B      | 1547          | 6639                  | 10690                        | 1.9             | 1897            |
| C      | 1155          | 4958                  | 7979                         | 1.42            | 1417            |
| D      | 1409          | 6048                  | 9730                         | 1.73            | 1728            |
| E      | 1169          | 5016                  | 8067                         | 1.43            | 1433            |
| F      | 1587          | 6813                  | 10972                        | 1.95            | 1947            |

To verify the effect of adding the carbonate to the soil it was simulated the application of this tailing in same proportion of regular limestone allowed as a soil corrective (3 kg of limestone per  $1 \text{ m}^3$  of soil). As soil activity concentrations it was used the average values reported by UNSCEAR [16]. To perform this correction, a density of  $1.25 \text{ g cm}^{-3}$  was considered, in accordance with [19]. The activity concentration that should be obtained after this dilution is presented in Table 3 and values for the radiological hazard indices was then calculated for the amended soil. The results are showed in Table 4.

The dose values (D) obtained showed results for soil and carbonate mixture very similar to each other, with low variation (between  $53.61$  and  $54.65 \text{ nGy h}^{-1}$ ) and in accordance with the average dose values ( $28$  to  $120 \text{ nGy h}^{-1}$ ). The obtained results for the AGDE considering the dilution proportion of carbonate in soil did not indicate damage to tissues, given that the obtained values are well below the allowed limits. The values of ELCR found for the dilute carbonate in soil presented mean value of  $0.93$ , therefore, lower than the global average. The AEDR values obtained in this case presented a constant value of  $0.07 \text{ mSv y}^{-1}$ .

**Table 3: Activity concentration of  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ , and  $^{40}\text{K}$ , in  $\text{Bq kg}^{-1}$ , for the soil carbonate mixture**

| Sample | $^{226}\text{Ra}$<br>( $\text{Bq kg}^{-1}$ ) | $^{228}\text{Ra}$<br>( $\text{Bq kg}^{-1}$ ) | $^{40}\text{K}$<br>$\text{Bq kg}^{-1}$ |
|--------|--|--|--|
| A      | 35.54  | 35.03  | 400.42                                 |
| B      | 35.52  | 35.51  | 400.30                                 |
| C      | 35.51  | 33.97  | 400.13                                 |
| D      | 35.65  | 34.88  | 400.07                                 |
| E      | 35.55  | 34.02  | 399.81                                 |
| F      | 35.52  | 35.67  | 400.29                                 |

**Table 4: Radiological hazard indices estimated for the carbonate diluted in soil**

| Sample | D<br>[nGy/h] | ELCR<br>[ $10^{-6}$ ] | AGDE<br>[ $\mu\text{Sv/y}$ ] | AEDR<br>[mSv/y] | AEDE<br>[mSv/y] |
|--------|--------------|-----------------------|------------------------------|-----------------|-----------------|
| A      | 54           | 932                   | 382                          | 0.07            | 67              |
| B      | 55           | 937                   | 384                          | 0.07            | 67              |
| C      | 54           | 921                   | 377                          | 0.07            | 66              |
| D      | 54           | 931                   | 382                          | 0.07            | 66              |
| E      | 54           | 921                   | 378                          | 0.07            | 66              |
| F      | 55           | 938                   | 385                          | 0.07            | 67              |

#### 4. CONCLUSION

The use of tailing in agriculture to mitigate environmental problems, such as tailing disposal, requires compliance with standards, as well as studies regarding the treatment of this tailing, its chemical characterization, health implications, in order not to endanger society.

The results obtained showed that the carbonate resulting from the niobium production present a  $^{226}\text{Ra}$  and  $^{40}\text{K}$  activity concentrations, although higher than the global average, that is not a threat for the environment and health, from the radiological hazard indices point of view. Nevertheless, activity concentration of  $^{228}\text{Ra}$  are well above the global values being responsible for approximately 80% of the absorbed dose observed. On the other hand, the addition of the carbonate to the soil as amendment resulted in no increase in the exposure to radiation, indicating that, from the radiological perspective, its use is unlikely to pose a health concern. However, specific studies must be carried out for a better comprehension of radiological implications concerning the availability of the radionuclides present for plant and human consume.

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