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BIOAVAILABILITY OF RADIONUCLIDES ^{226}Ra, ^{228}Ra AND ^{210}Pb PRESENT IN BRAZILIAN PHOSPHOGYPSUM AND PHOSPHATE FERTILIZERS

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ABSTRACT

Phosphogypsum (PG) is a by-product of phosphate fertilizers industries. The USEPA classified PG as a "Technologically Enhanced Naturally Occurring Radioactive Material" (TENORM). Its worldwide production on 2006 was estimated in 150 million tons. Annually the three main phosphate industries in Brazil are responsible for $5.5x10^6$ tons of phosphogypsum, which is stored in stacks. The level of radionuclides present in phosphogypsum is well-known and makes its disposal or reutilization an environmental concern. Part of this by-product can be reused, for example, to improve fertility of agricultural soils. To assess the long term environmental impact of radioactive contamination of ecosystems, information on source term including radionuclide speciation, mobility and biological uptakes have high importance.
This paper intends to evaluate the bioavailability of the radionuclides ^{226}Ra, ^{228}Ra and ^{210}Pb to the environment by following a procedure established by the EC (European Community), which includes a single EDTA-NH_4 0.05M extraction at pH 7.0 prior to the analyses. These results is compared with the total activity concentration of these radionuclides in Brazilian PG and the most used phosphate fertilizers (SSP, TSP, MAP and DAP). This procedure intends to represent on a more realistic way the leaching of radionuclides from PG and fertilizers to soil and agricultural products.

1. INTRODUCTION

The natural series of radionuclides from U and Th are present in numerous natural resources. High concentrations of these elements are often found in geological materials such as igneous rocks and minerals. Human activities that exploit these resources can cause a significant increase in concentration of these elements, commonly defined as TENORM "Technologically Enhanced Naturally occurring Radioactive Material" and an increased potential for exposure to natural radiation in products, by-products and waste generated. Such activities can also lead to significant changes in the concentration of natural radionuclides in the various compartments of the ecosystem.

One important example of this is the phosphate fertilizer industry in Brazil, which uses the phosphate rock as raw material, called apatite. The apatite presents in its composition traces of radionuclides of the U and Th decay series. As this ore has low phosphate content, it is subjected to a physical chemical treatment that increases the concentration of P_2O_5, called rock concentrate.

The Brazilian phosphate industries occupies the eighth place among world producers of rock concentrate, being used in the production of phosphoric acid, fertilizers and other inputs [1].

The phosphate fertilizer is obtained by wet reaction of the igneous phosphate rock with concentrated sulphuric acid, giving as final product, phosphoric acid, and dehydrated calcium sulphate (phosphogypsum) as by-product, as shown in the following equation [2]:

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \rightarrow 6H_3PO_4 + 10CaSO_4.2H_2O + 2HF$$

Phosphoric acid is the starting material for the most utilized Brazilian fertilizers: triple superphosphate (TSP), single superphosphate (SSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP).

For each ton of phosphoric acid produced, 5 tons of phosphogypsum are generated. The annual world production of gypsum can be estimated at 150 million tons. The main Brazilian phosphate fertilizer industries are located in Cubatão (São Paulo state) and Uberaba (Minas Gerais state), which together are responsible for generating about 5.5 million tons of phosphogypsum per year, which is stored in open waste piles, next to production facilities.

This waste concentrates radionuclides of the natural series of U and Th and metals present in the phosphate rock used as raw material. During the chemical attack of the concentrate rock, all the chemical species are redistributed between the phosphoric acid and gypsum produced. The separation of both radionuclides and stable elements is given by their solubility and chemical characteristics. Studies show that radionuclides (^{226}Ra, ^{228}Ra, ^{232}Th, ^{210}Pb and ^{210}Po) migrate to the phosphogypsum while uranium migrates to the phosphoric acid [3].

Research aiming at developing the uses of phosphogypsum becomes important both from an economic standpoint, as technological and environmental, as this can be considered as a waste abundant, inexpensive and which use would avoid the environmental commitment of large areas, where it is stored. Moreover, its reuse would contribute to the preservation of natural gypsum reserves.

Depending on the level of radioactivity present, the mining and industrial facilities with associated uranium and thorium are subjected to CNEN control, regarding compliance with its standards. According to CNEN "Requisitos de Segurança e Proteção Radiológica para Instalações Minero-Industriais" - NN - 4.01, the industrial complex of phosphate can be classified as Category III, with specific activity of solid natural radioactive substances or concentrated below 10 Bq g^{-1}.

The CNEN regulation "Diretrizes Básicas de Radioproteção" CNEN - NN - 3.01 establishes a system of dose limitation, in which the normal exposure of individuals should be restricted so that neither the dose nor the effective dose equivalent to organs or tissues of interest caused by the possible combination of exposures arising from authorized practices, exceeds the dose limit specified which is 1 mSv.

The potential problem, from the radiological point of view, of the phosphate industry is the generation of phosphogypsum waste, which is stored and can impact the environment.

Studies about radiological characterization of Brazilian phosphogypsum and the environmental impact of its disposal can be found in the literature [4-7], as well as, researches dealing with its use in agriculture and construction [3; 8-14].

The gypsum can be used as soil conditioner due to many factors such as high solubility, which allows it to penetrate into the soil profile, providing high calcium in depth, reducing

aluminum saturation, deepening the root system and encouraging the absorption of water and nutrients [15]. The solubility of gypsum in water is 150 times greater than the limestone [16], giving the largest gypsum solubility and mobility, justifying its best effects in soils.

The Brazilian agricultural soils are considered acid, pH between 4.3 and 6.2, low in calcium and magnesium, with high levels of aluminum and low phosphorus availability to plants [17].

Speciation of radionuclides in Brazilian phosphogypsum has not been explored from the bioavailability point of view. This parameter is relevant, since a better understanding of the set of phenomena that control the mobility of contaminants in soils and also its retention by the plants is necessary for a correct evaluation of health and environmental risks.

The use of the total concentration of the elements for the evaluation of its environmental impact is not strictly correct. In fact, it is important to determine the fraction of the element, which is dissolved and released into the environment. The sequential extraction is the methodology usually used to know the distribution of the element in soil or sediment. In this procedure, the sample is dissolved sequentially, with different chemical aggressiveness, ranging from mild to drastic action, which represent the following phases: soluble, exchangeable, bound to carbonates, Fe and Mn oxides, organic and residual [18].

Therefore, an acid digestion applied to soil samples, to phosphogypsum or a mixture containing soil fertilized with phosphogypsum, represents the potential bioavailability of radionuclides to plants, whereas, a mild digestion with EDTA solution, for example, may represent the labile fraction, which is more representative of the phenomena of nature [19].

The solution of EDTA has been used for understanding the extraction of elements from soil and consequent absorption of metals by plants [20]. Furthermore, the EDTA solution extracts more elements than other salts diluted.

Taking into account the presence of natural radionuclides in phosphogypsum and its use as soil amendment, it is important to study the mobility of radioactive elements in soil and plant uptake. Also, there are few studies in the literature that deal with the accumulation of radionuclides in the soil.

Therefore, this paper aims to study the availability of radionuclides (^{226}Ra, ^{228}Ra and ^{210}Pb) present in phosphogypsum and phosphate fertilizers, following a procedure established by the EC (European Community), which includes a single EDTA extraction prior to the analyses. The activity concentration of ^{226}Ra, ^{228}Ra and ^{210}Pb were determined in the phosphogypsum and phosphate fertilizers samples and in the leachate solution.

2. METHODOLOGY

2.1. Determination of ^{226}Ra, ^{228}Ra and ^{210}Pb by gamma spectrometry

The phosphogypsum samples were collected from the three main producers of phosphoric acid in Brazil named A (Copebras located in Cubatão-SP), B (Fosfertil located in Uberaba-MG) and C (Ultrafertil located in Cubatão-SP).

The total concentrations of ^{226}Ra, ^{228}Ra and ^{210}Pb were measured in samples in duplicate by gamma-spectrometry with a hyper-pure germanium detector, EGNC 15-190-R, from Eurisys. The detector was calibrated using natural soil spiked with radionuclides certified by Amersham. Samples were packed in 100 cm^3 cans and sealed for four weeks prior in order to ensure that equilibrium had been reached between ^{226}Ra and its decay products. The ^{226}Ra activity was determined by taking the mean activity of three separate photopeaks of its daughter nuclides: ^{214}Pb at 295 and 352 keV, and ^{214}Bi at 609 keV. The ^{228}Ra content of the samples was determined by measuring the intensities of the 911 and 968 keV gamma-ray peaks from ^{228}Ac. The concentration of ^{210}Pb was determined by measuring the activity of its low-energy peak 46.5 keV. Self-absorption correction was applied since the attenuation for low-energy gamma-rays is highly dependent upon sample composition. The approach used was modified from that suggested by Cutshall [21].

2.2. Radiochemical determination of ^{226}Ra, ^{228}Ra and ^{210}Pb

The activity concentration in the leached solution was determined by a radiochemical procedure that consists in a precipitation of Ra and Pb and measurement of the total alpha and beta gross counting. For the determination of ^{226}Ra, ^{228}Ra and ^{210}Pb in the leaching solution, 5g of fertilizers and PG were dissolved in 50 mL of EDTA-NH_4 0.05M solution at pH 7 and the final solution was filtered for the determination of the leached fraction.

In each sample 1 mL of Pb^{2+} and Ba^{2+} carrier were added to the solution. The precipitation of $Ba(Ra)SO_4$ was performed by the addition of H_2SO_4 3M and ammonium sulphate. The Pb was determined by the addition of EDTA solution and 30% sodium chromate for precipitation of $^{210}PbCrO_4$.

The ^{226}Ra and ^{228}Ra concentrations were determined by measuring the gross alpha and beta activity of the precipitate $Ba(Ra)SO_4$ and the concentration of ^{210}Pb was determined through its decay product ^{210}Bi, by measuring the gross beta activity of the precipitate of $^{210}PbCrO_4$. Both radionuclides were measured in a low background gas flow proportional detector for 200 minutes. The activity concentration of ^{226}Ra and ^{228}Ra were measured after 21 days of the radium precipitation and the concentration of ^{210}Pb after 10 days of the precipitation of Pb as chromate. The accuracy and precision was performed by measuring the reference materials IAEA 326- Radionuclides in soil and IAEA-300 Baltic Sea Sediment, and ranged from 2.7 to 7.9% and from 2.2 to 7.6%, respectively.

3. RESULTS AND DISCUSSION

The results obtained for the total activity concentration and activity concentration in the leaching solution for ^{226}Ra, ^{228}Ra and ^{210}Pb are presented in Table 1. In the same Table 1 are also presented the weight loss in percentage of the samples in the extraction with EDTA. It can be observed that the fertilizers SSP, TSP and MAP are more soluble in the EDTA solution than the PG samples. This behavior is reflected in the radionuclides extraction by EDTA: the fertilizers presented higher percentages of the radionuclides extraction compared with PG. The solubility of the PG samples in the EDTA solution is low and varied from 10 to 16%, as a consequence the extraction of the radionuclides were generally lower than 10%.

Table 1 Activity concentration of ^{226}Ra, ^{228}Ra and ^{210}Pb in PG and fertilizers samples and in the leachate (Bq kg^{-1})

	Total concentration			Leachate concentration			Solubility (%)[1]	Extraction (%)[2]		
	^{226}Ra	^{228}Ra	^{210}Pb	^{226}Ra	^{228}Ra	^{210}Pb		^{226}Ra	^{228}Ra	^{210}Pb
SSPA	720±96	196±33	1084±106	11	9	75	43	2	5	7
TSPA	546±10	157±24	904±60	100	72	316	76	18	46	35
FGA	744±138	242±23	1061±132	16	45	26	10	2	19	2
MAPB	10±4	293±74	<19	1	25	2	86	9	9	10
TSPB	105±28	189±13	175±54	3	24	29	65	2	13	17
FGB	186±46	151±27	182±46	1	22	12	11	1	15	7
MAPC	9±1	126±11	40±2	3	20	5	85	30	16	12
DAPC	5±1	48±5	<19	4	17	7	81	75	36	35
FGC	344±65	219±40	347±44	4	16	17	16	1	7	5

1 - Solubility in percentage of the samples in the extraction with EDTA
2 – Extraction percentage of the radionuclides in the EDTA solution

4 CONCLUSIONS

It can be concluded that the radionuclides ^{226}Ra, ^{228}Ra and ^{210}Pb, although present in the PG samples are not leached with the EDTA solution and therefore are not available to soil and agricultural products.

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