Leachability of natural radionuclides and rare earth elements in Brazilian phosphate fertilizers and phosphogypsum

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Abstract. The Brazilian phosphate fertilizers are obtained by wet reaction of the igneous phosphate rock with concentrated sulphuric acid, giving as final product phosphoric acid and dehydrated calcium sulphate (phosphogypsum - PG) as by-product. The level of impurities (metals and radionuclides, among others) present in the phosphate rock used as raw material is distributed among products and by-products. In Brazil, PG has been used for many years in agriculture as a soil amendment. The characterization of natural radionuclides elements in Brazilian PG and the most used phosphate fertilizers, single super phosphate (SSP), triple super phosphate (TSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP) has been already published by the same authors. However, for a long-term safe application of these fertilizers and PG it is important to study the availability of these elements to the environment. For this purpose, the evaluation of radionuclides and rare earth elements concentration in the labile fraction is more suitable than the total concentration, since this fraction is more available for the absorption by plants and water contamination. In order to evaluate the available fraction of these elements to the environment, PG and phosphate fertilizers samples were leached with water and EDTA solution. The total and leached concentrations of radionuclides (^{226}Ra, ^{228}Ra and ^{210}Pb) were determined by using high-resolution gamma spectrometry and by measuring the gross alpha and beta counting after a radiochemical separation of the elements of interest, respectively. The concentration of rare earth elements - REEs (Ce, Eu, La, Lu, Sm, Tb and Yb), U and Th were determined by instrumental neutron activation analysis. The results obtained using the methodology with mild leaching with EDTA and with water showed that the radionuclides and REEs although present in the PG are not available to the environment.

Keywords: Leachability of radionuclides, Leachability of rare earth elements, phosphogypsum, fertilizers

1. Introduction

The presence of natural radionuclides and metals in mineral ores and their redistribution in industrial products and wastes is well known. Brazilian fertilizer industries produce phosphoric acid by reacting phosphate rocks with sulphuric acid giving as by-product phosphogypsum (PG). Phosphoric acid is the starting material for the most utilized Brazilian fertilizers: triple superphosphate (TSP), single superphosphate (SSP), mono ammonium phosphate (MAP) and diammonium phosphate (DAP).

In Brazil, the main producers of phosphate fertilizers are responsible for the production of approximately 5.4×10^6 tons of phosphogypsum per year. This PG has been used for many years in agriculture as a soil amendment. For its safe long term application, it is necessary to characterize the impurities present in PG. This study is important since such impurities can migrate to agricultural products and food chain. Several papers were published concerning the characterization of radionuclides and heavy metals in PG and phosphate fertilizers [1-3].

Although there is little information about rare earth elements toxicity and mobility in the environment, the characterization of these elements in the phosphate industry is important because these elements are present in the phosphate rock used as raw material [4].

The main objective of this paper is to determine the radionuclides (^{238}U, ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{232}Th) and REEs (Ce, Eu, La, Lu, Sm, Tb and Yb) in Brazilian PG and the most used phosphate fertilizers, single super phosphate (SSP), triple super phosphate (TSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP). In order to evaluate the availability of these elements to the soil and plants, the PG samples were extracted with water and a solution of EDTA- NH_4 0.05 mol L^{-1} at pH 7.

2. Material and methods

The samples analyzed in this study come from the three main fertilizers facilities, Copebras and Ultrafertil, located in Cubatão - São Paulo and Fosfertil, located in Uberaba - Minas Gerais.

The radionuclides ^{226}Ra, ^{228}Ra and ^{210}Pb were measured in PG and phosphate fertilizers samples using high-resolution gamma spectrometry, with a hyper-pure germanium detector, EGNC 150-190 R, from Eurisys Measures, with resolution of 1.8 keV for the 1332 keV ^{60}Co photopeak and 15% efficiency. The detector was calibrated using natural soil, rock and water spiked with radionuclides certified by Amersham. The ^{226}Ra activities were determined by taking the mean activity of its daughter nuclides: ^{214}Pb at 295 keV and 352 keV, and ^{214}Bi at 609 keV. The ^{228}Ra was determined by measuring the 911 keV and 968 keV gamma-ray peaks from ^{228}Ac. The concentration of ^{210}Pb was determined by measuring the intensity of the 46.5 keV peak. Self-absorption correction was applied to ^{210}Pb since the attenuation for low energy gamma rays is highly dependent upon sample composition. The approach used was suggested by Cutshall [5].

The total concentration of the radionuclides ^{226}Ra, ^{228}Ra and ^{210}Pb in the leaching solution was determined by the measurement of the gross alpha and beta counting after a radiochemical separation of the elements of interest. 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.

The REEs, U and Th were determined by instrumental neutron activation analysis (INAA). The determination was carried out by irradiation of approximately 150mg of each sample and 150 mg of reference materials, during 8 hours at a neutron flux of 10^{12} n.cm^{-2}s^{-1}, at Instituto de Pesquisas Energéticas e Nucleares (IPEN) research reactor IEA-R1. The first count was made after 5 to 10 days of decay and allows identifying La, Sm and U. The second count was made after 15 days of decay and allows identifying Ce, Eu, Lu Tb, Yb and Th. Gamma spectrometry was measured with a Gehyperpure detector, Intertechnique, with 2.1 keV resolution for the 1332 keV ^{60}Co photo peak. The accuracy and precision was performed by measuring the reference materials Buffalo River Sediment (NIST-8704) and Soil-7 (IAEA). The accuracy ranged from 0.4% to 8.8% and the precision from 1.3% to 8.3%.

The extraction with water was obtained by dissolving 2.4 g of PG in 1L of water. This extraction was made in order to check the amount of radionuclides that are dissolved when the solubility product constant of PG (0.24 g/100mL at 20°C) is achieved. The mild extraction was obtained by stirring 5g of PG in 50 mL of EDTA-NH_4 solution 0.05 mol L^{-1} at pH 7, procedure established by [6] Certification of the contents (mass fraction) of Cd, Cr, Cu, Ni, Pb and Zn in an organic-rich soil following harmonized EDTA and acetic acid extraction procedures BCR 700- Information Reference Materials.

3. Results and discussion

Concentrations of ^{238}U, ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{232}Th in the PG and phosphate fertilizers and in the leachate are presents in Table 1 and Table 2, respectively. The results obtained for the total concentration of ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{232}Th show that these radionuclides are present in higher concentrations only in the PG and fertilizers SSP and TSP. The production of phosphoric acid can be described by the following reaction:

$$Ca_{10}F_2(PO_4)_6 + 10H_2SO_4 + nH_2O \rightarrow 10CaSO_4nH_2O + 6H_3PO_4 + 2HF$$

Since Ra isotopes and Pb form insoluble compounds with sulphates, they will concentrate in the final product of the reaction: calcium sulphate (PG).

During the chemical attack of the phosphate rock, different compounds can be formed, depending upon the experimental conditions and the stoichiometry of the reaction. Single superphosphate (SSP) is formed by reacting sulphuric acid with phosphate rock, according to the reaction:

$$Ca_{10}(PO_4)_6F_2 + 7H_2SO_4 + 6.5\ H_2O \rightarrow 3\ Ca(H_2PO_4)_2.H_2O + 7\ CaSO_4.\ ½H_2O + 2\ HF$$

In the production of triple superphosphate (TSP), phosphoric acid reacts with apatite, according to the reaction:

$$Ca_{10}(PO_4)_6F_2 + 14\ H_3PO_4 + 10\ H_2O \rightarrow 10\ Ca(H_2PO_4)_2.H_2O + 2\ HF$$

In both cases, most of Ra and Pb will be present in the SSP and TSP.

The concentration of ^{226}Ra, ^{228}Ra and ^{210}Pb found in the labile fractions, on the other hand, are less than 10% of the total available content of these radionuclides in PG, in spite of the high dissolution of PG in water (more than 90%). A possible explanation for such behavior is that the radium and Pb in the PG precipitate with barium sulfate instead of calcium sulfate in the chemical reaction, forming insoluble compounds. Similar behavior was observed by Santos [7], who performed a sequential extraction of Brazilian PG and found that most of the radium and lead are located in water insoluble (non-$CaSO_4$) fraction. In the case of the fertilizers SSP and TSP, the concentration found for the radionuclides in the labile fraction presented slightly higher values, indicating that in these samples the radionuclides are more available to the environment. The concentration of ^{226}Ra, ^{228}Ra and ^{210}Pb found in the labile fraction of the fertilizers MAP and DAP is negligible.

Concentrations of REEs in the PG and in the leachate are presented in Table 3. It can be seen that the REEs concentrate preferentially in PG. Although there are no limits available for the concentration of REEs in phosphate fertilizers and PG, such characterization is relevant since they complete a database for the safe application of PG. Elevated concentrations of REEs, like most heavy metals in solution, above those which plants are accustomed to, may cause toxic reactions and negative effects on plants. Tyler [8] reported that the transfer of REEs from soil to plants is generally low and that the uptakes are correlated with the soil acidity and the solubility of the REEs, therefore only a small part of the total concentration is available to the environment. The results of the extraction with the EDTA solution showed that only 10% of the PG mass was dissolved in the solution and that less than 1% of the REEs were extracted. The results of the extraction with water showed that, although the high dissolution of PG (~90%), only a small amount of REEs was extracted. It can be concluded that the relatively high concentration of REEs present in the PG is not available to the environment.

4. Conclusion

In general, the total concentration obtained for the radionuclides and REEs were higher in the PG samples. The results obtained using the methodology with mild leaching of PG with EDTA and total dissolution in water showed that these elements are not available to the environment, giving evidence that the application of PG and phosphate fertilizers in agriculture is safe as far as contamination by such elements.

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Table I. Radionuclides concentration in phosphogypsum (Bq kg^{-1}) and in the labile fraction (Bq L^{-1})

		U-238	Ra-226	Pb-210	Th-232	Ra-228	Solubility%
PG Copebras	Total conc	<2	744±138	1061±132	232±35	242±23	
	Leached H_2O	<2	105±6	35±4	ND	3.5±0.2	96
	Leached EDTA	ND	16±0.7	26±1	<3	45±4	10
PG Fosfertil	Total conc	<2	186±46	182±46	90±20	151±27	
	Leached H_2O	ND	17±1	8.1±0.6	ND	10±1	93
	Leached EDTA	<2	1.5±0.2	12±1	<3	22±4	9
PG Ultrafertil	Total conc	<2	344±65	347±44	212±41	219±40	
	Leached H_2O	<2	15±1	6.1±0.4	ND	3.1±0.3	90
	Leached EDTA	ND	4.2±0.2	17±1	<3	16±2	15

Table II. Radionuclides concentration in phosphate fertilizers (Bq kg^{-1}) and in the labile fraction (Bq L^{-1})

			Ra-226	Pb-210	Ra-228	Solubility%
Copebras	SSP	Total conc	720±96	1084±106	196±33	43
		Leached EDTA	11.0±0.4	75±2	9.2±0.1	
	TSP	Total conc	546±10	904±60	157±24	76
		Leached EDTA	100±3	316±4	72±6	
Fosfétil	MAP	Total conc	10±4	<19	293±74	86
		Leached EDTA	1.0±0.2	2.0±1	25±4	
	TSP	Total conc	105±28	175±54	189±28	65
		Leached EDTA	2.6±0.2	29±1	24±3	
Ultrafértil	MAP	Total conc	9±1	40±2	126±11	85
		Leached H_2O	2.7±0.2	5±1	20±2	
	DAP	Total conc	5±1	<19	48±5	81
		Leached EDTA	3.7±0.2	7±1	17±1	

Table III. Concentration of REEs concentration in phosphogypsum (Bq kg^{-1}) and in the labile fraction (Bq L^{-1}) (mg kg^{-1})

		La	Ce	Sm	Eu	Tb	Yb	Lu	Solubility%
PG Copebras	Total conc	1178 ± 18	2480 ± 102	139± 5	33 ±2	6.4 ± 0.6	7.2 ± 0.9	0.16 ± 0.05	
	Leached H_2O	<0.9	<2.5	<0.05	<0.06	ND	ND	ND	96
	Leached EDTA	0.94±0.02	2.7±0.2	0.42±0.02	0.07±0.01	<0.26	<0.36	ND	10
PG Fosfertil	Total conc	1017 ± 16	956 ± 55	123 ± 4	26.3 ± 2.0	7.3 ± 0.7	10 ± 2	0.4 ± 0.1	
	Leached H_2O	<0.9	<2.5	<0.05	ND	ND	ND	ND	88
	Leached EDTA	5.4±0.1	11±1	1.32±0.04	0.22±0.03	<0.26	<0.36	ND	9
PG Ultrafertil	Total conc	1349 ± 17	2977 ± 123	154 ± 4	34 ± 2	6.9 ± 0.6	7.2 ± 0.9	ND	
	Leached H_2O	<0.9	<2.5	<0.05	<0.06	ND	ND	ND	90
	Leached EDTA	5.3±0.1	12±1	1.23±0.04	0.18±0.03	<0.26	<0.36	ND	15