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Rare earth elements in phosphogypsum and phosphate fertilizers in Brazil

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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 and heavy metals in PG has been extensively studied by several authors. In this paper, the concentration of rare earth elements - REE (Ce, Eu, La, Lu, Nd, Sm, Tb and Yb) present in Brazilian phosphogypsum and the most used phosphate fertilizers (single super phosphate (SSP), triple super phosphate (TSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP) were determined by instrumental neutron activation analysis - INAA. 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 0.05M (procedure established by the European Community) and the REE in the leachate were determined by INAA. REEs concentrate preferentially in PG and the fertilizers TSP and SSP. The results obtained using the methodology with mild leaching of PG with EDTA and total dissolution in water showed that the REEs are not extracted from the PG, and therefore are not available to the environment.

Keywords: rare earth elements, phosphogypsum, fertilizers

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, three main national producers, Copebras, Ultrafertil (Cubatão facilities) and Fosfertil (Uberaba facility) are responsible for the production of approximately $5.4x10^6$ tones of phosphogypsum waste 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 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 REE (Ce, Eu, La, Lu, Nd, Sm, Tb and Yb) in PG and the most used phosphate fertilizers, single super phosphate (SSP), triple super phosphate (TSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP). The technique used was the instrumental neutron activation analysis (INAA). 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 (procedure established by the European Community) and the REE in the leachate were determined by INAA.

Material and methods

The samples analyzed in this study come from the three main fertilizers producers, Copebras, Ultrafertil and Fosfertil. The REEs 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 16 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, Nd, Sm, Tb and Yb. The second count was made after 15 days of decay and allows identifying Ce, Eu and Lu. Gamma spectrometry was measured with a Ge-hyperpure 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 REEs 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. The leaching solution after filtering and the residue were used for the determination of the leaching fraction. In both cases, the REEs were determined by INNA, as already described.

Results and discussion

REE (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu) in PG and phosphate fertilizers (TSP, SSP, MAP and DAP) were determined by INAA and the results are presented in Table 1. Accuracy and precision were evaluated and the results are presented in Tables 2 and 3 for the reference materials Buffalo River Sediment (NIST-8704) and Soil-7, respectively. In general, relative standard deviation and relative error were lower than 10% proving the precision and accuracy of the INAA technique.

It can be seen that the REEs concentrate preferentially in PG and the fertilizers TSP and SSP. 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 [5] 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. In order to check the availability of the REEs two experiments were carried out: in the first, the PG was extracted with water, at a concentration of 2.4 grams of PG in one liter of water (that's corresponds to the solubility of PG in water); in the second one 5g of PG was dissolved in 50 ml of EDTA-NH_4 solution 0.05 mol L^{-1} at pH 7. The results obtained for the REEs concentration present in the leachate and in the residue for both experiments are presented in Table 4. The results of the extraction of PG in water show that, although 90% of the PG mass was dissolved in the water almost all the REEs concentration were retained in the final residue. The results of the extraction with the EDTA solution also showed that only 10% of the PG mass was dissolved in the solution and that less than 1% of the REEs were extracted. It can be concluded that the relatively high concentration of REEs present in the PG is not available to the environment.

Conclusion

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

Acknowledgments

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Table 1 Mean values of REEs concentration in phosphogypsum and phosphate fertilizers (mg kg^{-1})

Sample/ Provenance	**La**	**Ce**	**Nd**	**Sm**	**Eu**	**Tb**	**Yb**	**Lu**
PG Copebras	1178 ± 18	2480 ± 102	944 ± 96	139± 5	33 ±2	6.4 ± 0,6	7.2 ± 0.9	0.16 ± 0.05
PG Fosfertil	1017 ± 16	956 ± 55	765 ± 78	123 ± 4	26.3 ± 2.0	7.3 ± 0.7	10 ± 2	0.4 ± 0.1
PG Ultrafertil	1349 ± 17	2977 ± 123	1077 ± 69	154 ± 4	34 ± 2	6.9 ± 0.6	7.2 ± 0.9	ND
MAP Fosfertil	262 ± 4	479 ± 20	155 ± 16	42 ± 1	9.2 ± 0.7	4.7 ± 0.6	9.5 ± 1.2	1.0 ± 0.3
MAP Ultrafertil	313 ± 3	987 ± 42	574 ± 44	85 ± 2	21 ± 1	6.6 ± 0.9	7.2 ± 0.7	0.7 ± 0.1
TSP Copebras	791 ± 8	1898 ± 79	753 ± 54	113 ± 2	ND	6.4 ± 0.6	5 ±1	0.13 ±0.06
TSP Fosfertil	709 ± 11	1294 ± 78	567 ± 57	93 ± 3	26 ± 3	7±2	10 ± 2	1.0 ± 0.3
SSP Copebras	950 ± 13	2173 ± 128	1014 ± 87	137 ± 4	31 ± 3	6±1	ND	ND
DAP Ultrafertil	333 ± 4	794 ± 38	293 ± 25	66±2	11.2 ± 0.8	4.4 ± 0.5	3.1 ±0.8	0.6 ± 0.1

Table 2 Concentration values for Soil-7 (IAEA) reference material (mg kg^{-1})

Element	Certified values	Calculated values	RSD	RE (%)
La	28±1	27±1	3.7	3.5
Ce	61±7	60±2	3.3	1.6
Sm	5.1±0.3	5.3±0.1	1.8	3.9
Eu	1±0.2	1.1±0.1	9.0	10
Tb	0.6±0.2	0.53±0.02	3.7	11
Yb	2.4±0.4	2.0±0.3	15	16
Lu	0.3	0.33±0.03	9.0	10

RSD: relative standard deviation and RE: relative error

Table 3 Concentration values for Buffalo River Sediment (NIST-8704) reference material (mg kg^{-1})

Element	Certified values	Calculated values	RSD	RE (%)
La	29	29±1	3.4	-
Ce	66.5±2	68±2	2.9	2.3
Sm	6.7	5.8±0.2	3.4	13
Eu	1.31±0.03	1.2±0.1	8.3	8.3
Yb	2.8	3.0±0.6	20	7.1
Lu	0.6	0.55±0.03	5.4	8.3

RSD: relative standard deviation   RE: relative error

Table 4 Concentration of REEs in the residue and in the leachate (mg kg^{-1})

Extraction with H_2O		La	Ce	Sm	Eu	Tb	Yb	Lu	Solubility%
PG Copebras	Leached	<0.9	<2.5	<0.05	<0.06	ND	ND	ND	96
	Residue	1287±158	2579±756	137±43	36±9	6±1	5±2	0.23±0.04	
PG Fosfertil	Leached	<0.9	<2.5	<0.05	ND	ND	ND	ND	88
	Residue	823±237	1621±174	98±28	28±5	8±2	5.6±0.8	0.36±0.01	
PG Ultrafertil	Leached	<0.9	<2.5	<0.05	<0.06	ND	ND	ND	90
	Residue	1485±282	3015±54	150±30	37±1	6±2	6±1	0.17±0.07	
Extraction with EDTA		**La**	**Ce**	**Sm**	**Eu**	**Tb**	**Yb**	**Lu**	**Solubility%**
PG Copebras	Leached	0.94±0.02	2.7±0.2	0.42±0.02	0.07±0.01	<0.26	<0.36	ND	10
	Residue	922±27	2370±170	102±4	35±5	8±1	4.4±0.4	<0.15	
PG Fosfertil	Leached	5.4±0.1	11±1	1.32±0.04	0.22±0.03	<0.26	<0.36	ND	9
	Residue	895±27	1885±140	82±3	32±4	8±1	7±1	0.38±0.07	
PG Ultrafertil	Leached	5.3±0.1	12±1	1.23±0.04	0.18±0.03	<0.26	<0.36	ND	15
	Residue	1460±44	3550±260	145±6	39±4	9±1	4.5±0.5	<0.15	