

RARE EARTH ELEMENTS IN PHOSPHOGYPSUM AND PHOSPHATE FERTILIZERS IN BRAZIL

Barbara P. MAZZILLI, Fernanda M. LE BOURLEGAT, Catia H. R. SAUEIA, Deborah I. T. FÁVARO
 Instituto de Pesquisas Energéticas Nucleares (IPEN), BRASIL
 mazzilli@ipen.br

Phosphogypsum is a by-product of the phosphate fertilizer industry. PG has been used for many years in agriculture as a soil amendment. 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 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-NH₄ solution 0.05 mol L⁻¹ at pH 7.

The samples analyzed in this study come from the three main fertilizers producers, Copebras, Ultrafertil and Fosfertil. The REEs were determined by 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 10¹² n.cm⁻²s⁻¹, at IPEN research reactor IEA-R1.

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. 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

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 1 - Mean values of REEs concentration in phosphogypsum and phosphate fertilizers (mg/kg)

Extraction with H ₂ O		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	

Table 2 - Concentration of REEs in the residue and in the leachate (mg/kg)