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# METALS CONCENTRATION IN PHOSPHOGYPSUM AND PHOSPHATE FERTILIZERS PRODUCED IN BRAZIL USING INAA

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## ABSTRACT

Phosphogypsum is obtained by wet reaction of the igneous phosphate rock with concentrated sulphuric acid, giving as final product phosphoric acid and dihydrated calcium sulphate ($CaSO_4.2H_2O$) as by-product. It may contain high quantities of $P_2O_5$, trace metals and radionuclides of U and Th series. Phosphogypsum worldwide production on 2006 was estimated in 170 million tons. All the countries that produce phosphate fertilizers by wet process are facing the same problem of finding solutions for the safe application of phosphogypsum, in order to minimize the impact caused by the disposal of large amounts of this by-product. Phosphogypsum can be used in agriculture as a soil amendment; however, for its safe application the concentration of the impurities present and their behaviour in the environment should be better understood. The radiological characterization has been extensively studied in the last decade, but there are few studies about the metals concentration in phosphogypsum. This work intends to determine the concentration of metals (Ba, Co, Cr, Fe, Hf, Na, Sc, Ta, Th, U, Zn e Zr) and rare earth elements (REE) present in phosphogypsum produced in Brazil and to compare the results with those found in the phosphate fertilizers commonly commercialized. The technique used for the determination of the metals was instrumental neutron activation analysis (INAA).

## 1. INTRODUCTION

The presence of natural radionuclides in mineral ores and their redistribution in industrial products and wastes has been well known.

Brazilian phosphate industries produce fertilizers by precipitation during wet sulphuric acid processing of phosphate rocks, resulting in phosphoric acid as main product and phosphogypsum (PG) as by-product. 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).

Among industrial wastes containing technologically enhanced naturally occurring radioactive materials (TENORM), excluding those generated by nuclear technology, of particular concern is phosphogypsum. Depending upon the level of radioactivity the TENORM industries are subjected to the recommendations given by Comissão Nacional de Energia Nuclear (CNEN), which include compliance with the radiological protection regulations [1, 2].

Several publications are available in the literature related with the radiological characterization of Brazilian phosphogypsum [3-7] however few publications discuss about the metals characterization in phosphogypsum.

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PG is stored at open air or discharged to the sea throughout the world and represents a serious environmental concern. All the countries that produce phosphate fertilizer by wet processing of phosphate rock are facing the same problem of finding solutions for the safe application of this residue, in order to minimize the impact caused by the disposal of large amounts of PG.

In Brazil, three main national producers, Copebras, Ultrafertil (Cubatão facilities) and Fosfertil (Uberaba facility) are responsible for the production of approximately $5.4x10^6$ tonnes of phosphogypsum waste per year [3]. Ultrafertil and Copebras use phosphate rock from Catalão - Goiás, a phoscorite, which is an igneous rock constituted by apatite, magnetite and olivine cut by abundant veins of carbonatites. Both industries are located in Cubatão – São Paulo, which is considered one of the most polluted areas of Brazil. The raw material used by Fosfertil comes from Tapira - Minas Gerais, it is constituted by carbonatite and piroxenite. PG is moved to nearby storage areas, the so-called gypsum stacks. Santos et al. (2006) performed the characterization of natural radionuclides of the U and Th series in the stockpiled PG waste in Cubatão [4]. According to ABNT NBR10004-2004 [8], PG is classified as "Classe II residue".

PG worldwide production on 2006 was estimated in 170 million tons [4]. One possibility is the use of PG in agriculture as a soil amendment. For its safe long term application it is necessary to characterize the impurities present in phosphogypsum and to study their mobility and bioavailability in the environment, specially the contamination of draining water soil and the absorption by plants. This study is important since such impurities can migrate to agricultural products and food chain.

Although there is little information about rare earth elements (REE) toxicity and mobility in the environment, its study is important because these elements are present in the phosphate rock and concentrate in phosphogypsum [5].

The main objective of this paper is to determine metals (Ba, Co, Cr, Fe, Hf, Na, Sc, Ta, Th, U, Zn and Zr) and REE (Ce, Eu, La, Lu, Nd, Sm, Tb and Yb) in PG by instrumental neutron activation analysis (INAA) and to evaluate the environmental impact of the use of PG as a soil amendment. As a complementary study, the same elements will be determined in phosphate fertilizers and their raw material – phosphate rock.

## 2. EXPERIMENTAL PROCEDURES

INAA is based on the reaction between neutrons and a target nucleus. The neutron is captured by the nucleus and produces a radioactive nucleus. This excited nucleus decays according its half-life time and emits gamma-radiation which can be detected by spectrometry with a hyper-pure germanium detector from Eurisys Measures, with resolution of 1.8 keV for the 1332 keV $^{60}Co$ photopeak and 15% efficiency.

The determination of the elements was carried out by irradiation of approximately 150mg of each sample, 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, Na, Sm, Tb, U and Yb. The second count was made after 15 days of decay and allows identifying Ba,

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Ce, Co, Cr, Eu, Fe, Hf, Lu, Sc, Ta, Th, Zn and Zr. The spectra analyses were made by WinnerGamma program on InterWinner 1998.

The concentration of the metals is obtained by comparing irradiated standard and sample peak areas in the gamma-spectra by the expression:

$$C_a^i = \frac{(A_a^i \cdot m_p \cdot C_p^i) \cdot e^{\lambda(ta-tp)}}{A_p^i \cdot m_a} \quad (1)$$

where: $C_a^i$ = i-element concentration in the sample (µg $g^{-1}$ or %)
$C_p^i$ = i-element concentration in the standards (µg $g^{-1}$ or %)
$A_a^i$ = i-element peak area in the sample (cps)
$A_p^i$ = i-element peak area in the standard (cps)
$m_a$ e $m_p$ = standard and sample weight, respectively (g)
$\lambda$ = radioisotope decay constant ($t^{-1}$)
$t_a$ - $t_p$ = Difference between sample count time and standard respectively (min)

The standard reference materials Buffalo River Sediment (NIST-8704) and Soil-7 (IAEA) were used to analyse the raw materials, fertilizers and PG samples.

## 3. RESULTS AND DISCUSSION

REE (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu) and metals (Ba, Co, Cr, Fe, Hf, Na, Sc, Ta, Th, U, Zn and Zr) in PG, phosphate rock and phosphate fertilizers (TSP, SSP, MAP and DAP) were determined by INAA and the results are presented in Tables 1 and 2. Accuracy and precision were evaluated and the results are presented in Tables 3 and 4 for the reference materials analyses by INAA. In general, relative standard deviation and relative error were lower than 10% proving the precision and accuracy of the INAA technique.

In São Paulo state, the agency responsible for the regulation and control of the environmental quality is Companhia de Tecnologia de Saneamento Ambiental (CETESB). In the CETESB report "Relatório de Valores Orientadores Para Solos e Águas Subterrâneas no Estado de São Paulo" [9], the limits for metals concentration in soils and groundwater are established as well as the quality values (a reference for a clean soil) and intervention values (above it there is potential direct or indirect danger for human health) [9].

CETESB restricts several metals for agriculture soil. Table 5 presents CETESB quality values and intervention levels for agriculture soil and the mean values of metals concentrations in PG obtained in this study, for Ba, Co, Cr, Fe and Zn.

Although there are no limits available for the other analyzed metals, their chemical characterization in phosphate fertilizers and PG is relevant since they complete a database for future applications of PG.

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**Table 1. REE mean concentration in phosphate rock (PR), phosphate fertilizers (SSP, TSP, MAP and DAP) and phosphogypsum (PG) samples (μg $g^{-1}$) and standard deviation**

| | *Rare Earth Elements* | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **La** | **Ce** | **Nd** | **Sm** | **Eu** | **Tb** | **Yb** | **Lu** |
| **Copebras – Cubatão** | | | | | | | | |
| PR (n=3) | 1717±170 | 4217± 661 | 1752± 543 | 224±23 | 58±7 | 12±7 | 13±4 | 0.62± 0.11 |
| SSP (n=4) | 1037±396 | 2197±602 | 1237±615 | 116±28 | 30±7 | 7±3 | 6±2 | 0.38±0.16 |
| TSP (n=2) | 751±38 | 1759±178 | 751±13 | 107±4 | 26±1 | 5±1 | 7.4±0.4 | 0.73±0.05 |
| PG (n=4) | 1136±330 | 2579±756 | 1401±545 | 137±43 | 36±10 | 6±1 | 5±2 | 0.23±0.04 |
| **Fosfertil – Uberaba** | | | | | | | | |
| PR (n=3) | 1222±251 | 2176±194 | 1820±60 | 157±38 | 41±8 | 7.4±1.0 | 12±2 | 0.98±0.23 |
| MAP(n=3) | 271±74 | 509±163 | 405±208 | 48±14 | 14±3 | 3.9±0.9 | 12±4 | 1.08±0.13 |
| TSP (n=3) | 607±129 | 1369±243 | 599±154 | 82±17 | 27±4 | 9±4 | 12±2 | 1.14±0.13 |
| PG (n=2) | 823±237 | 1621±174 | 622±342 | 98±28 | 28±5 | 8±5 | 5.6±0.8 | 0.36±0.01 |
| **Ultrafertil – Cubatão** | | | | | | | | |
| PR (n=3) | 2319±718 | 5468±1537 | 1720±560 | 245±61 | 67±15 | 12±6 | 13±3 | 0.65±0.19 |
| MAP (n=3) | 332±18 | 788±43 | 409±115 | 63±8 | 18±1 | 5.1±0.3 | 9±1 | 0.75±0.04 |
| DAP (n=3) | 418±151 | 807±179 | 335±26 | 81±14 | 20±2 | 4.4±0.6 | 9±2 | 0.70±0.01 |
| PG (n=2) | 1485±282 | 3015±54 | 970±358 | 150±3 | 37±1 | 6±2 | 6±1 | 0.17±0.07 |

**n=number of samples analyzed**

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**Table 2. Metal mean concentration in phosphate rock (PR), phosphate fertilizers (SSP, TSP, MAP and DAP) and phosphogypsum (PG) samples ($\mu g\ g^{-1}$) and standard deviation**

| | *Metals* | | | | | |
|---|---|---|---|---|---|---|
| | **Ba** | **Co** | **Cr** | **% Fe** | **Hf** | **Na** |
| **Copebras – Cubatão** | | | | | | |
| PR (n=5) | 2379±638 | 14±5 | 76±9 | 1.4±0.26 | 17±6 | 2121±123 |
| SSP (n=4) | 1439±566 | 9±3 | 39±10 | 0.77±0.02 | 11±5 | 1087±716 |
| TSP (n=2) | 2517±572 | 23±5 | 53±22 | 1.68±0.27 | 13±1 | 879±76 |
| PG (n=4) | 1376±408 | 1.2±0.35 | 40±8 | 0.19±0.06 | 7±3 | 1733±1495 |
| **Fosfertil – Uberaba** | | | | | | |
| PR (n=3) | 867±223 | 5.7±0.5 | 34±10 | 1.0±0.4 | 6±1 | 1749±826 |
| MAP (n=3) | 300±153 | 13±4 | 59±69 | 2.2±1.1 | 6±2 | 581±102 |
| TSP (n=3) | 718±226 | 11±2 | 24±4 | 1.6±0.4 | 6±1 | 773±392 |
| PG (n=2) | 1244±722 | 1.6±0.1 | 25±7 | 0.31±0.07 | 5±2 | 797 |
| **Ultrafertil – Cubatão** | | | | | | |
| PR (n=4) | 9856±2833 | 12±5 | 84±29 | 1.9±0.5 | 17±5 | 1276±126 |
| MAP (n=3) | 543±98 | 14±1 | 43±3 | 1.9±0.5 | 7.6±0.4 | 1305±255 |
| DAP (n=3) | 561±100 | 14±1 | 35±12 | 1.80±0.03 | 9±2 | 993±283 |
| **PG (n=2)** | 2516±239 | 2.0±0.4 | 48±13 | 0.3± 0.1 | 4.8±0.7 | 428±366 |

**n=number of samples analyzed**

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**Cont. Table 2**

| | *Metals* | | | | | |
|---|---|---|---|---|---|---|
| | **Sc** | **Ta** | **Th** | **U** | **Zn** | **Zr** |
| **Copebras – Cubatão** | | | | | | |
| PR (n=5) | 25±6 | 24±13 | 98±23 | 74±38 | 1290±968 | 2629±987 |
| SSP (n=4) | 15±5 | 15±7 | 47±17 | 64±16 | 380±285 | 1691±509 |
| TSP (n=2) | 37±3 | 29±1 | 50±3 | 174±1 | 162±100 | 2689±1070 |
| PG (n=4) | 2.1±0.6 | 6±2 | 57±16 | 1.4±0.1 | 27±1 | 1663±545 |
| **Fosfertil – Uberaba** | | | | | | |
| PR (n=3) | 14±2 | 4.1±0.4 | 80±10 | 20±6 | 978± 1210 | 2065±1002 |
| MAP (n=3) | 33±10 | 3.6±0.6 | 109±22 | 36±10 | 205±13 | 862±234 |
| TSP (n=3) | 21.7±0.3 | 4.3± 1.3 | 102±21 | 18±3 | 163±47 | 985±349 |
| PG (n=2) | 2.0±0.2 | 3.7±1.9 | 22±5 | 8 | 22 | 1091±843 |
| **Ultrafertil – Cubatão** | | | | | | |
| PR (n=4) | 28±8 | 15±4 | 96±24 | 39±14 | 164±41 | 2193±1938 |
| MAP (n=3) | 33±7 | 12±3 | 28±5 | 51±10 | 159±31 | 850±116 |
| DAP (n=3) | 31±3 | 14±2 | 37±7 | 56±9 | 151±28 | 596±53 |
| PG (n=2) | 2.51 ± 0.01 | 3.2±0.3 | 52±10 | 0.9 | 121±1 | 427±96 |

**n=number of samples analyzed**

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**Table 3. Concentration values for Soil-7 (IAEA) reference material (μg $g^{-1}$).**

| *Element* | *Certified values* | *Calculated values* | *RSD* | *RE (%)* |
|---|---|---|---|---|
| **Ba** | 159 | 182±38 | 20 | - |
| **Ce** | 61±7 | 60±2 | 3.3 | 1.6 |
| **Co** | 8.9±0.9 | 8.8±0.3 | 3.3 | 1.1 |
| **Cr** | 60±13 | 65±7 | 10 | 8.3 |
| **Eu** | 1±0.2 | 1.1±0.1 | 9.0 | 10 |
| **Fe (%)** | 2.57 | 2.6±0.2 | 7.6 | 1.1 |
| **Hf** | 5.1±0.4 | 5.3±0.6 | 11 | 3.9 |
| **La** | 28±1 | 27±1 | 3.7 | 3.5 |
| **Lu** | 0.3 | 0.33±0.03 | 9.0 | 10 |
| **Na** | 2400 | 2368±254 | 10 | 1.3 |
| **Sc** | 8.3±0.1 | 8.4±0.2 | 2.3 | 1.2 |
| **Sm** | 5.1±0.3 | 5.3±0.1 | 1.8 | 3.9 |
| **Tb** | 0.6±0.2 | 0.53±0.02 | 3.7 | 11 |
| **Th** | 8.2±1.1 | 8.4±0.4 | 4.7 | 2.4 |
| **U** | 2.6±0.5 | 2.57±0.4 | 15 | 1.1 |
| **Yb** | 2.4±0.4 | 2.0±0.3 | 15 | 16 |
| **Zr** | 185±11 | 215±20 | 9.3 | 16 |

**RSD:** relative standard deviation and **RE:** relative error

**Table 4. Concentration values for Buffalo River Sediment (NIST-8704) reference material (μg $g^{-1}$).**

| *Element* | *Certified values* | *Calculated values* | *RSD* | *RE (%)* |
|---|---|---|---|---|
| **Ba** | 414±12 | 408±75 | 18 | 1.5 |
| **Ce** | 66.5±2 | 68±2 | 2.9 | 2.3 |
| **Co** | 13.6±0.43 | 15±1 | 6.7 | 10 |
| **Cr** | 121.9±3.8 | 119±19 | 16 | 2.3 |
| **Eu** | 1.31±0.03 | 1.2±0.1 | 8.3 | 8.3 |
| **Fe (%)** | 3.97±0.1 | 3.98±0.09 | 2.2 | 0.25 |
| **Hf** | 8.4±1.5 | 8.7±0.4 | 4.5 | 3.5 |
| **La** | 29 | 29±1 | 3.4 | - |
| **Lu** | 0.6 | 0.55±0.03 | 5.4 | - |
| **Na** | 5530±150 | 5489±396 | 7.2 | 0.74 |
| **Sc** | 11.3±0.19 | 11.1±0.2 | 1.8 | 1.4 |
| **Sm** | 6.7 | 5.8±0.2 | 3.4 | - |
| **Th** | 90.7±0.16 | 89±0.3 | 0.33 | 1.9 |
| **U** | 3.09±0.13 | 3.3±0.4 | 12 | 6.7 |
| **Yb** | 2.8 | 3.0±0.6 | 20 | - |
| **Zn** | 408±15 | 348±19 | 5.4 | 15 |
| **Zr** | 300 | 318±25 | 7.8 | - |

**RSD:** relative standard deviation
**RE:** relative error

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**Table 5. CETESB quality values and intervention levels for agriculture soil and mean values of metals concentrations in PG (mg kg$^{-1}$)**

| | CETESB Quality values | CETESB Intervention values - Agriculture area | PG Copebras – Cubatão | PG Fosfertil – Uberaba | PG Ultrafertil – Cubatão |
|---|---|---|---|---|---|
| **Ba** | **75** | **300** | 1376 ± 408 | 1244 ± 722 | 2516 ± 239 |
| **Co** | **13** | **35** | 1,2 ± 0,35 | 1,6 ± 0,1 | 2,0 ± 0,4 |
| **Cr** | **40** | **150** | 40 ± 8 | 25 ± 7 | 48 ± 13 |
| **Fe%** | **-** | **-** | 0,19% ± 0,06 | 0,31% ± 0,07 | 0,3 ± 0,1 |
| **Zn** | **60** | **450** | 27 ± 1 | 22 | 121± 1 |

All metals concentration present in PG, except for Ba, were below the CETESB intervention values for agriculture area. Therefore they do not contribute to an increase in the concentration of these elements in soil, at least if only one application is considered.

Santos et al. (2006) evaluated the bioavailability of radionuclides and metals in PG, by applying the sequential extraction based on Tessier method. They observed that Ba is present in the last fraction of the sequential extraction, defined as the residual phase, forming insoluble sulphates and silicates or insoluble rock [5]. Thus, although Ba in PG was found in concentrations above the CETESB limits, its mobility in environmental conditions is much reduced and it poses little risk for the environment.

In the literature, several papers are concerned with the impact of the metals present in commonly commercialized fertilizers on soils. Their conclusion suggest that the transfer of metals to soil is almost negligible [10-13]; since the metals concentration in PG is of the same order of magnitude, one single application should not cause any environmental impact. However, it should be important to evaluate a long term scenario.

REE are present in the phosphate rock and concentrate in the phosphate fertilizers and PG.. There is little information about their toxicity and mobility in the environment, therefore the results obtained in this study will complete a database for future applications of PG.

## 4. CONCLUSIONS

This work presented the concentration of metals (Ba, Co, Cr, Fe, Hf, Na, Sc, Ta, Th, U, Zn e Zr) and REEs present in PG produced in Brazil. Comparing the PG results with those found for the phosphate fertilizers commonly commercialized, it can be concluded that the metals migrate preferentially from phosphate rock to the fertilizers and PG.

The metals concentrations found in the PG are of the same order of magnitude of the results observed in the phosphate fertilizers and therefore it can be used as soil amendment without additional risk.

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The long term contribution of metals concentration to agricultural lands is not easily quantified, since the quantity of metals spread along with fertilizers and PG in the agricultural fields depends upon the quantity of fertilizers and PG used, the type of crop and soil and the number of applications per year. Therefore, the data presented here can be used for studies of different scenarios of the application of Brazilian phosphate fertilizers and PG in agriculture.

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