



The phosphoric acid ( $H_3PO_4$ ) production currently employed is not very efficient with respect to the generation of by-products because for every tone of acid produced 4.5 ton of phosphogypsum (PG) are generated, and this product by not having direct and continuous use and also by being currently stored in landfills exposed to the weather, which becomes one of the biggest environmental problems for fertilizers producers.

The annual phosphogypsum production is around 5 million tons per year and the trend is increasing, especially in the Brazil Southeast, since the main fertilizer industries are located in Cajati and Cubatão in São Paulo State and in Uberaba in the State of Minas Gerais. Currently in Brazil there is a stock of phosphogypsum of about 150 million tons. The natural extraction of gypsum is concentrated in the Northeast. In the region of Araripe in Ceará State, there is one of the largest gypsum deposits in the world. The transport, from the Northeast region to the Southeast and South regions, is responsible for about 50% of the cost of ordinary gypsum.

The destination for the phosphogypsum is urgent, since the world agricultural demand is increasing and it is the real responsible for the emergence of this environmental problem. There are some possibilities of application of this material, such as civil construction, including cost reduction in housing construction [1], paving streets [2], agriculture [3] as remedial physical and chemical characteristics of soil [4], in wastewater treatment [5], etc. However, all these applications are invariably very difficult due to the fact that phosphogypsum is classified as TENORM (Technologically Enhanced Naturally Occurring Radioactive Material), that is, a solid waste containing naturally occurring radioactive elements from the rock matrix.

Environmental impact studies should assess the existing site and conditions and evaluate the anticipated impacts on the environment itself by the human activity. In order to access the potential environmental problems of a product it is extremely important to perform a precise characterization. The environmental problems of phosphogypsum are directly related to the rock matrix, which depends on the rock micro composition provoking distinct environmental impact.

There are several analytical methods which can be used on sample characterization. To perform the determination of chemical elements usually spectrometry techniques are used with liquid state samples. There are several strategies to digest solid samples, however, in some cases the decomposition does not occur in micro level, so the recovery of the total concentration of selected elements is not adequate [6]. To overcome this difficulty it is fundamental to do experimental tests using distinct accessories and/or reagents. After the spectrometry analysis on the digested sample, the total content of the chemical element can be obtained. Nevertheless, no information about the chemical availability is provided.

The environmental contamination is often associated with the proximity to industrial complexes, or by improper disposal of the waste or lack of awareness and oversight of this activity. The metal contamination may affect the functionality, sustainability and biodiversity of ecosystems, causing damages, sometimes irreversible on its chemical physical and biological properties [7]. The bioaccumulation of metals in organisms is correlated with the bioavailability of metal contents and not to the total content in the same source material. Thus, in order to evaluate the bioaccumulation the sequential extraction is used. The

sequential extractors, however, aim to separate the metals present in each compartment of the soil, in order to enable an even greater understanding about the dynamic mechanisms [8].

The speciation procedures in solid samples should be a method of extraction, which can be selective or sequential. An element can be present in a solid under different forms such as adsorbed species on the surface, precipitates, and co-precipitates or occluded as coordination compounds. The sequential extraction consists of an extractant progression from a weak one such as water, until a strong one, as a concentrated acid. Through the sequential extraction steps, the interchangeable elements, or elements that could be bioavailable in specific conditions are transferred to various extraction solutions. Thus, the sequential extractions are used to identify and quantify the bioavailability of chemical species [9].

To standardize the procedures of sequential extractions allowing their comparison and quality control, the institution European Community Bureau of Reference (Bureau Communautaire de Référence, BCR) developed a method for the trace metals determination in soils and sediments. Based on this protocol, a standardized procedure of extraction in four steps with three extracts [10] has also been proposed for the analysis of trace elements in sediments [11, 12] as is the case of the elements present in phosphogypsum. This protocol simulates the environmental conditions, based on the differentiation of trace elements according to their chemical nature. For comparison purposes it is necessary to perform an analysis of the sample before extraction. The BCR extraction is being done in four steps: Step 1: extraction with acetic acid in order to extract all the elements exchangeable, in acid and water soluble; Step 2: extraction with hydroxylamine chloride in order to remove the reducer elements; Step 3: extraction with hydrogen peroxide to get off the oxidizable elements; Step 4: extraction with aqua-regia to remove the remaining elements to the silica binder. In each of these steps, after shaking, separation by centrifugation is done, and then the liquid phase is analyzed and the remained solid material is submitted to the extraction next steps.

In this work, phosphogypsum sample was chemical analyzed by plasma mass spectrometry (ICP-MS). First, some tests on the decomposition of the phosphogypsum sample were done. Each solubilization test was analyzed by the ICP-MS procedure. BCR protocol was also done on the extracted solutions, after a mass optimization.

## **2. EXPERIMENTAL PROCEDURE**

### **2.1. Materials and Methods**

The phosphogypsum sample studied was provided by the Brazilian Fosfertil Industry. The chemical reagents used are analytical grade (P. A.). The acids were used as concentrated solution unless it is indicated. The ICP-MS equipment used is an Perkin Elmer Elan 6100. The multi-element reference solutions used for the spectrometer calibrations were obtained through the dilution of the individual Merck certified reference solution. The microwave-assisted system used is a Provecto Analítica DGT-100 PLUS. The water used in all analytical steps was purified (18.2 MOhm.cm) in a Gehaka Master System, in this system the water is first distilled, then deionized and then the remaining microorganisms are eliminated by a UV irradiation.

## 2.2. Sample Digestion

To perform the phosphogypsum decomposition it was necessary to make a series of tests with different combinations of acids. In Table 1, different combinations of PG mass and acids are presented. All tests were done on a closed microwave system. It was used the microwave-assisted digestion since the contamination risks with this system is minimal and the combination of heating and pressure is ideal for solubilization of the refractory materials. It is important to mention the blank samples were done simultaneously to each digestion test.

**Table 1. Decomposition Tests on Phosphogypsum.**

Test	Phosphogypsum mass (g)	Acid Solution
1	0.1570 ± 0.0001	5 mL HNO <sub>3</sub>
2	0.1576 ± 0.0001	5 mL HClO <sub>4</sub>
3	0.1660 ± 0.0001	5 mL de HNO <sub>3</sub> + 1.5 mL de HF
4	0.1613 ± 0.0001	3 mL de HF
5	0.0555 ± 0.0001	5 mL H <sub>3</sub> PO <sub>4</sub>
6	0.0511 ± 0.0001	4 mL de H <sub>3</sub> PO <sub>4</sub> + 4 mL de HClO <sub>4</sub>
7	0.0638 ± 0.0001	4 mL de H <sub>3</sub> PO <sub>4</sub> + 4 mL de HNO <sub>3</sub>
8	0.0622 ± 0.0001	5 mL HNO <sub>3</sub>
9	0.0650 ± 0.0001	1 mL de H <sub>3</sub> PO <sub>4</sub> + 4 mL de HClO <sub>4</sub>
10	0.0473 ± 0.0001	1 mL de HF + 4 mL de HClO <sub>4</sub>
11	0.0666 ± 0.0001	2 mL de HNO <sub>3</sub> + 4 mL de HClO <sub>4</sub>
12	0.0430 ± 0.0001	1 mL de HF + 4 mL de HClO <sub>4</sub>
13	0.0645 ± 0.0001	1mL de HNO <sub>3</sub> + 2 mL de HClO <sub>4</sub>
14	0.0674 ± 0.0001	1 mL de H <sub>3</sub> PO <sub>4</sub> + 4 mL de HClO <sub>4</sub>

A second solubility test was performed using a hot plate to verify if it was necessary to use a microwave digester system. About 0.5 g of phosphogypsum, 40mL HCl (2mol/L) and 150mL of distilled water were added in a beaker. This solution was boiled in a hot plate for 10 minutes with a watch glass capping the beaker and then the cover was removed and the solution was evaporated reaching a final volume of about 100mL.

## 2.3. Sequential Extraction

As previously mentioned, for each step of the BCR protocol it is necessary to use a different reagent. The solutions used in the extraction were: a) acetic acid solution 0.11mol/L (Step 1),

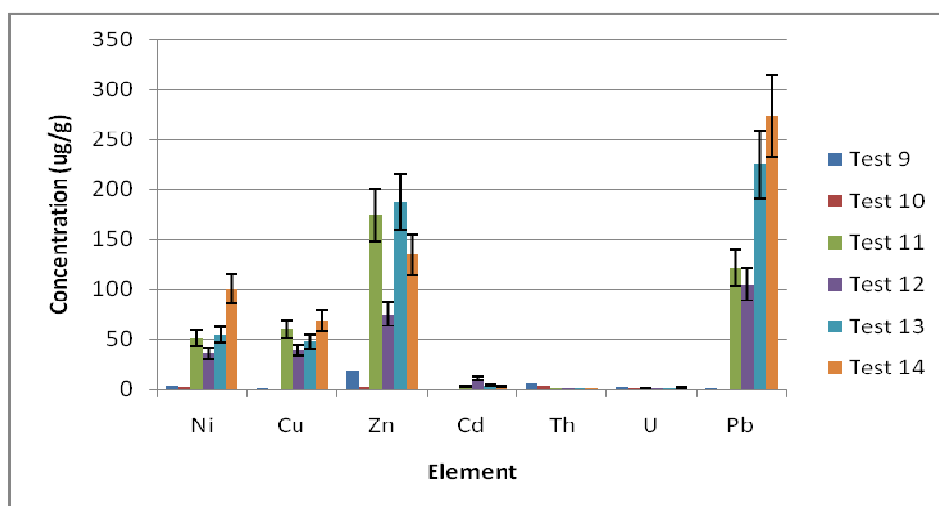
b) hydroxylamine chloride solution 0.5mol/L (Step 2), c) hydrogen peroxide solution 8.8mol/L (Step3), and d) aqua-regia (Step 4). All reagents should be prepared immediately before performing the extraction.

The first BCR extraction performed used the solutions above mentioned and about 500mg of phosphogypsum. Due to the high PG solubility almost no solid sample remained after the first step. Additional BCR extractions were done using 0.75, 1.00 and 1.25g of phosphogypsum.

### 3. RESULTS AND DISCUSSION

Tests 1 to 8, described on Table 1, did not promote the complete solubilization, because there was still solid material in the solution, so these test solutions were discarded. The tests 9 to 14 were successful on the complete PG digestion, so the obtained solutions were transferred to volumetric flasks and the volume was completed to 50mL with purified water. These digested samples were analyzed by ICP-MS.

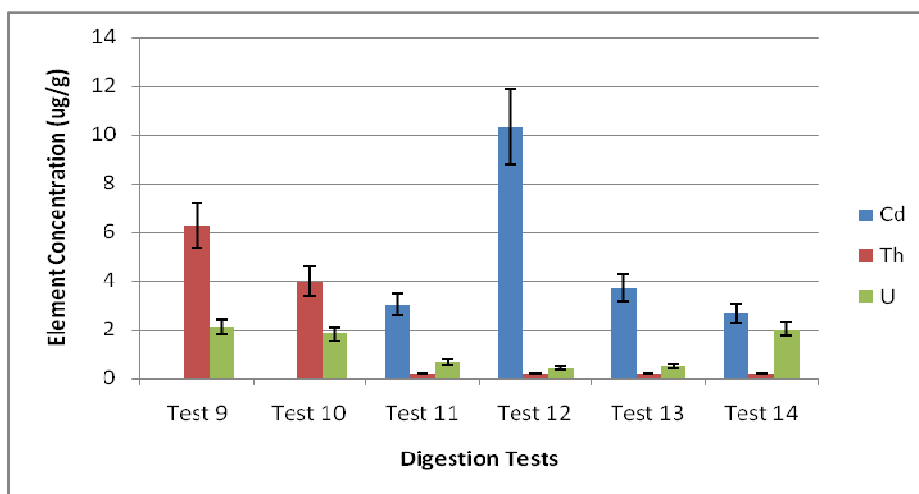
The ICP-MS equipment allows performing semi-quantitative and quantitative analysis. In order to compare the digestion solutions, the samples were analyzed in the semi-quantitative mode, since the matrices of the digestion tests are quite different. This analysis strategy is less affected by spectral and chemical interferences; however, this mode has higher determination limits when compared to the quantitative mode. Only some elements could be determined and the obtained results are presented in Figure 1. Since the concentration levels of the analites are different Cd, Th and U concentration are presented in Figure 2. In Figure 3 results for Ni, Cu and Zn are shown.



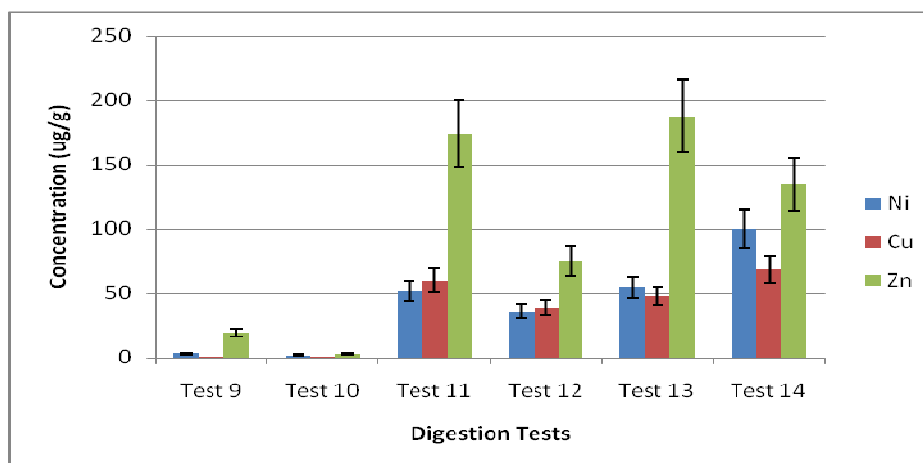
**Figure 1. ICP-MS Analysis of PG Digestion Solutions**

Analyzing the results it is possible to observe there is a direct correlation between the digestion procedure and the analite concentration.

Analyzing the results shown in Figures 1-3 it is possible to observe Th behavior is different from the other elements, decreasing its concentration different procedure tests. Tests 9, 10 and 14 seemed to be more adequate for U determination. The Cd results indicate probably interference has occurred when the acid mixture of test 12 was used. Cu and Ni concentration were not so affected by the acid combination. For Zn instead, it is clear that when HNO<sub>3</sub> is used Zn concentration are higher. Test 13 and 14 promotes higher concentrations for Pb. However, all concentration values measured are only indicative and, in further studies, recovery tests and quantitative analysis will be performed, in order to be feasible a more precise analites determination.



**Figure 2. Cd, Th and U Determination on PG Digestion Solutions**

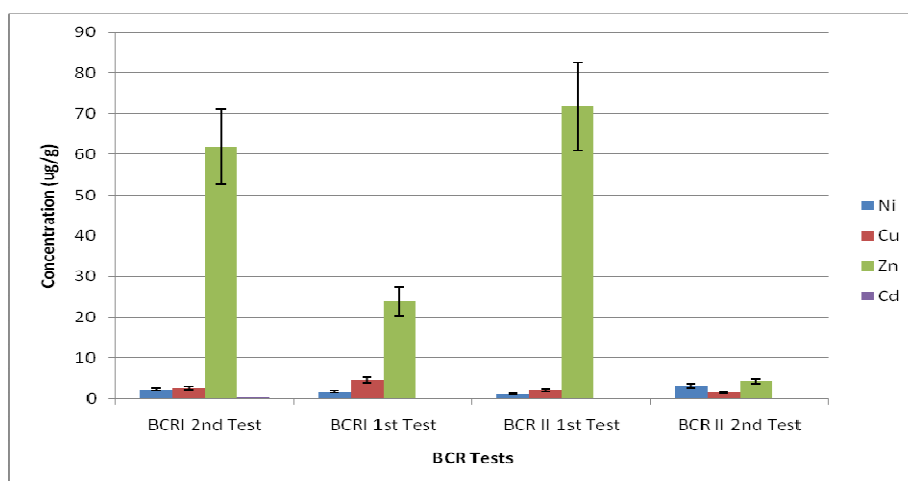


**Figure 3. Ni, Cu and Zn Determination on PG Digestion Solutions**

Despite a complete sample solubilization on the hot plate, ICP-MS analysis was not possible due to a strong physical interference which overlapped the element signals.

In Figure 4 the results obtained after two steps of BCR sequential extractions are shown. Two BCR tests were done; to compare two strategies on performing the sequential extraction. The difference between these two experiments is only the accessories used for shaking and separation. In the first test, it was used a vibratory plate and the solutions were separated with centrifugation. In the second test, the sample was mixed with the extracting solution using a mechanical shaker and the solid material was separated from the solutions through filtration.

The third and the fourth steps were not performed, because the remaining solid material, after the steps 1 and 2 was minimal. It became clear a definition of a PG adequate mass is fundamental.

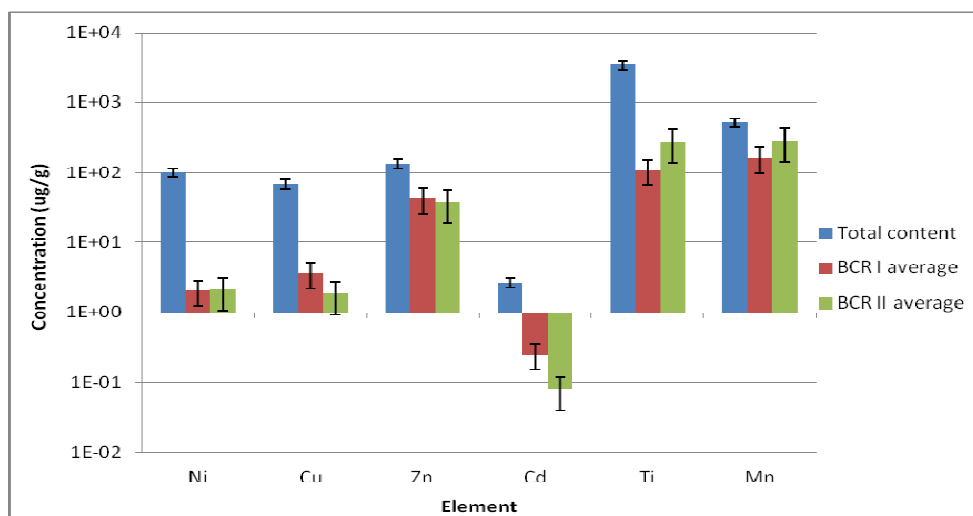


**Figure 4. Ni, Cu, Cd, Zn Concentration on PG BCR Solutions**

U and Th concentrations were below the determination limit, so they are not presented in the figure 4. All concentration results presented on Figure 4 are lower than the ones showed on Figure 1. This is probably an indication the remaining concentrations are probably in the remaining solid material, adsorbed as refractory material for instance.

As pointed on Figure 4 all operational conditions have influence on the sequential extraction performance, mainly in the elements presented in higher concentration. This fact was also observed on Ti and Mn determination.

On Figure 5 a comparison between the total concentration values obtained, after Test 14, and the two BCR steps performed on PG sample is presented. The results for BCR I (1<sup>st</sup> Step) presented are the average of the values presented on Figure 4. The results for BCR II (2<sup>nd</sup> Step) presented are the average of the values presented on Figure 4. Once the elements are presented in distinct magnitude orders, the concentration is presented in logarithmic scale.



**Figure 5. Comparison of Element Content Extracted by BCR Steps I and II**

Analyzing the data presented on Figure 5, together with the experimental observation, very little phosphogypsum mass has left after the second BCR step, it became clear the Test 14 results are in fact seriously affected by physical interference. After all, if it was not the case, the amount of the elements extracted would be higher, once almost no sample has left after the first two steps of the BCR extraction.

#### 4. CONCLUSIONS

Several methods for sample digestion were evaluated and, even with a blank subtraction, the concentration results are strongly dependent on the decomposition method, indicating a special care should be taken when concentration results are compared.

There are some sequential extraction procedures and despite having a BCR protocol which provides guidelines for the extractions, this protocol is not adequate for sequential extractions of phosphogypsum, so further studies on the adequate proportions of sample mass and extracting solution volume are needed.

With the results of both series of experiments, digestion and extraction, it became easily to identify the results of the digestion test 13 and 14 were probably affected by the matrix, once these tests had provided element concentrations higher than the ones obtained by BCR. It is also possible the BCR extracting solutions are also causing some matrix interferences on ICP-MS analysis.

Due to the differences found in the digestions tests and also in the BCR experiments, a standard addition recovery test is needed. These two aspects will be the focus of the next studies. A validation of the ICP-MS analysis in order to achieve a robust method will be also done in order to overcome all matrix effects.



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