

# PHYSICO-CHEMICAL AND RADIOACTIVE CHARACTERIZATION OF MATERIALS ASSOCIATED TO THE PHOSPHORIC ACID PRODUCTION

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## ABSTRACT

The industry devoted to the production of phosphoric acid by using as raw material sedimentary phosphate rock is considered as a NORM (Naturally Occurring Radioactive Materials) industry due to the high levels in U-series radionuclides contained in this ore, which are around 1-2 Bq g<sup>-1</sup> (two orders of magnitude higher than typical unperturbed soils) for the majority of the mines of this ore. This fact allowed us to study the different materials involved in this NORM industry.

The present work has been focused to characterize the raw materials, wastes, and several intermediate and final products from a typical phosphoric acid industry, in relation to their elemental composition (major, minor and trace elements), radioactive contents, granulometry, mineralogy and physical composition. This characterization aims to obtain information for possible applications of materials and waste in future commercial uses.

The physicochemical and radioactive characterization of these materials has enabled to know the behaviour of different elements, and to quantify the fractionation of the different elements (and radio-elements) into the materials involved in the process of phosphoric acid production. Additionally, this knowledge permits through the measuring of the possible variations in the physicochemical composition of the raw materials along the time to control its influence in the characteristics of the obtained co-products. The highest radionuclide activity concentrations have been found in “scales” (internal incrustations), coming from the pipes which conduce phosphoric acid, containing <sup>226</sup>Ra and <sup>40</sup>K concentrations up to 9 and 5 Bq g<sup>-1</sup>, respectively. The sludge thickener has a high concentration in most of the analyzed trace elements Cd, Cr, Ni, Sr, Y, V, Zn, Th and U. The gypsum sample obtained after washing, just before the pump to the rafts, shows a concentration of activity of thorium and uranium isotopes less than that measured in the sample of phosphogypsum obtained directly from the rafts, while the concentrations of <sup>226</sup>Ra and <sup>210</sup>Po are similar in both samples.

## 1. Introduction

For over 30 years there is a clear awareness in the scientific community to carry out the evaluation of the occupational and environmental radiological impact caused by the activities of non-nuclear industries, called NORM industries (Naturally Occurring Radioactive Material). These factories are characterized either by using in their production processes raw materials containing significant levels of natural radionuclides; the processing of these materials can expose workers to radiation levels well above the natural background. On the other hand, some commercial products, by-products or wastes can be enriched in natural radionuclides.

In our case, we have performed the study in an NORM industry devoted to the production phosphoric by the wet process, where the phosphate rock is dissolved by adding diluted sulphuric acid (70%), and then is produced a solid waste called phosphogypsum (PG) and phosphoric acid (dissolution of about 27% in P<sub>2</sub>O<sub>5</sub>). These plants were closed at the end 2010, but they have been until this date the major producers of phosphoric acid in the European Union by wet method, and annually processed more than two million metric tons of phosphate rock (PR). At present only produces fertilizer from phosphoric acid supplied by other companies.

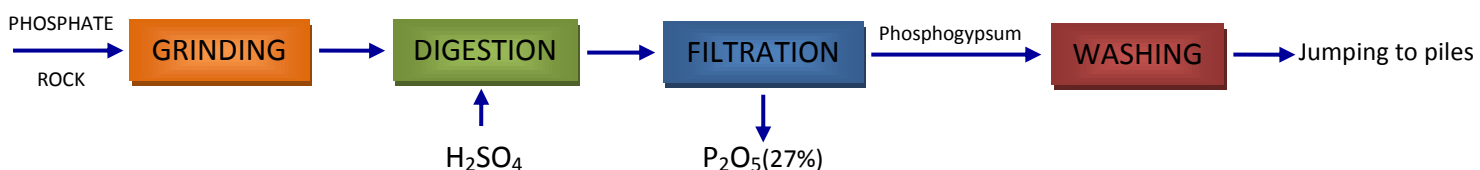
This industry mainly has used Moroccan sedimentary phosphate rock containing <sup>238</sup>U-series radionuclides with activity concentrations in order of 1300-1500 Bq·kg<sup>-1</sup>. However, they also sometimes treat phosphate ores from other geographical areas as, for example, Kola Peninsula, containing <sup>238</sup>U-series activity concentration dropping low 100 Bq·kg<sup>-1</sup>, and with similar activity concentrations for <sup>232</sup>Th-series isotopes [1]. The main difference among both types of rocks is based in their respective origins: Morocco ore is sedimentary rock (phosphorite, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>), while Kola ore is igneous rock (3Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>CaF<sub>2</sub>). The differences in geological origins lead to very different radionuclide contents [2].

Moreover, is important to note that in the production process, according to the previous study based on the use of Moroccan phosphate rock [2], the radioactive content originally present in phosphate rock undergoes a selective fractionation. In this sense, most of the radionuclides contained in the raw material are dissolved in the process, which are largely distributed between phosphoric acid (final product) and phosphogypsum (waste) produced. Thus, over 80% of the uranium originally contained in the raw material remains in the acid while, in contrast, more than 90% of <sup>226</sup>Ra, <sup>210</sup>Pb and <sup>210</sup>Po originally present in the phosphate rock will finish associated to the phosphogypsum [3,4]. Average concentrations of <sup>226</sup>Ra, <sup>210</sup>Pb and <sup>210</sup>Po around 500-700 Bq kg<sup>-1</sup> are found in the PG generated of the studied factories [5], but with a wide variability.

The phosphoric production process is based on the dissolution of the phosphate ore by leaching with sulphuric acid (60%), reaction that give rise to phosphoric acid, and as waste, a called phosphogypsum solid, composed primarily of calcium sulfate dihydrate (CaSO<sub>4</sub> · 2H<sub>2</sub>O). The chemical reaction with phosphate rock is as follows [6]:



To summarize, this process consists of four main stages: (1) grinding, (2) digestion, (3) filtration, and (4) washing (Figure 1).



*Fig. 1. Outline of the manufacturing process of phosphoric acid by wet*

The process starts with a grinded phosphate rock continuing with a digestion process where a blend of raw material is mixed with diluted sulphuric acid (60%). In the digestion process, a "pulp" containing phosphoric acid in dissolution and a solid fraction of waste (phosphogypsum), are formed. The generated pulp pass then to a filtration step, and the "production phosphoric acid" (liquid phase containing of about 27%  $P_2O_5$ ) and "phosphogypsum" (solid phase) are separated by filtration of the "pulp" coming from the attack step. For every ton of pure  $P_2O_5$  generated of about five tons of phosphogypsum are generated. After that, the filtered PG is subjected to three washing steps to extract the  $P_2O_5$  not recovered in the previous filtration stage. Nevertheless, the final phosphogypsum has a minimum content of both soluble  $P_2O_5$  (< 0.5 %) and structural  $P_2O_5$  (< 0.5 %).

Finally, the produced acid is stored in big tanks (decanters), with the aim that the most of the suspended solids are precipitated and removed from the acid dissolution, obtaining a phosphoric acid with a concentration in salts as low as possible which is used for the manufacture of fertilizers, or commercialization.

The main objective of the present study has been to carry out a physicochemical and radioactive characterization of the several materials involved in the production of phosphoric acid by the wet process in order to understand the mechanisms by which the different elements and radionuclides contained in the ore remain on the intermediate and final solid materials involved in this industrial process.

## **2. Materials and methods**

### **2.1 Materials and sampling**

After an exhaustive study of the production steps of phosphoric acid plants, the most significant samples were selected among the set of sampling trying to be the most representative of all industrial activity, depending on the objectives raised. We can characterize all the industrial process and also others that we consider priori "hot spots" for up locations in which, by its specific characteristics, could accumulate certain radioelements. The selected samples are shown in table 1.

For the selection of the samples considered two areas: **a) Zone 1:** Phosphoric acid production plant; **b) Zone 2:** Stacking active phosphogypsum.

Each sample was dried at 95 °C to avoid the loose of hydration water in the cristaline materials until constant weight, and late they were grinded. Samples [PU], [DS] and [TS] where it could not be dried at this temperature due to they did not loosen all the water, so it was necessary their calcinations up to 350 °C.

*Table 1. Summary description of the selected samples.*

| CLASSIFICATION        | CODE       | SAMPLE           | DESCRIPTION   |
|-----------------------|------------|------------------|---|
| RAW MATERIALS         | <b>KO</b>  | Kola             | Phosphate rock from Kola Peninsula (igneous origin, deposit of Oblast, northern Russia) |
|                       | <b>TO</b>  | Togo             | Phosphate rock from Togolese Republic (sedimentary origin).                             |
|                       | <b>PR</b>  | Phosphate Rock   | Phosphate rock from Morocco (sedimentary origin). Unmilled fraction stored in silos     |
| INTERMEDIATE PRODUCTS | <b>PU</b>  | Pulp             | Solid fraction obtained by filtration of the pulp obtained in the acid attack step.     |
|                       | <b>DS</b>  | Decanter Sludge  | Solid fraction coming from clarifier or decanter  |
|                       | <b>TS</b>  | Thickener Sludge | Solid fraction coming from thickener  |
|                       | <b>SC</b>  | Scale            | Inlay from inside of the phosphoric acid production pipe                                |
|                       | <b>ES</b>  | Ext. Scale       | External scales from the phosphogypsum deposit where this is pumped into the PG piles.  |
| WASTE                 | <b>PG1</b> | Phosphogypsum    | Fresh phosphogypsum taken just before it is pumped to the piles.                        |
|                       | <b>PG2</b> | Phosphogypsum    | Deep phosphogypsum taken from the stacks (1 m below surface)                            |

## 2.2 Methods for physical and chemical characterization

### 2.2.1 Techniques based on X-ray

#### 2.2.1.1 X-Ray Diffraction (XRD)

The mineralogical studies were carried out by applying the X-ray diffraction technique (XRD). In particular, they have been carried out by applying the disoriented dust method in a Bruker laser diffraction instrument using K<sub>α</sub> radiation of Cu filtered by a Ni film and excited by 30 mA of intensity and 40 kV of tension. The mineralogical quantification of samples has been carried out using Bruker's EVA software with internal standard. We point out that this technique is only valid for detecting crystalline compounds.

#### 2.2.1.2 X-ray Fluorescence (XRF)

On the other hand, major elements have been measured for X-ray fluorescence (XRF) with a Bruker S4 Pioneer system which has the following characteristics: 4 kW, front window and anode of Rh; five analyzing crystals; LIF200, Ge, PET, OVO55 y OVOC, and two X-ray detectors. This technique requires that the samples to be analyzed should be as homogeneous as possible. There are two ways to prepare the samples, as pearls, or as pressed pills. In our case have all been prepared as pressed pills, taking 6 g of dry sample with 2.4 cm<sup>3</sup> agglutinative Elvacite ® dissolved in acetone. The mixture is homogenized in agate mortar and is introduced in the press. Then maintained a pressure of 150 bars for 10 seconds and be remove the pill.

### 2.2.2 Chemical analysis

Trace elements have been determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). When solid samples by acid digestion are adequate. Sample was treated with hydrofluoric acid, nitric and perchloric acid. Hydrofluoric acid is used to remove silica and release chemicals such as ions. Nitric acid is an oxidant that prevents the volatilization of certain elements and perchloric acid is responsible for removing the remains

of hydrofluoric acid that may have precipitated as fluoride. He took care of putting the right amount of perchloric acid, if you put too much potassium perchlorate may form highly insoluble and can thus mask the metallic elements. The nitric acid amounts used were 7 mL, 8 mL of hydrofluoric acid, perchloric acid and 7 mL. All samples were evaporated on a hot plate. After the digestion, the final tax rate is adapted to a 2% solution in nitric Milli-Q water for analysis by ICP-OES.

### *2.2.3 Laser granulometry measurements*

Granulometry analyses are achieved by using the Mastersize 2000 APA 2000 model (©Malvern Instruments Ltd). For a precise granulometric measurement, a representative amount of each sample is placed in water for 24 hours to achieve a high level of disintegration of the original matrix. For a correct homogenization of the matrix, each sample is then introduced into a magnetic separator at a constant speed of 700 rotations per minute, and from here aliquots are collected by the Mastersize 2000 system for their analysis.

### *2.2.4 Alpha and gamma Spectrometry*

The radioactive characterization of the samples has been performed by applying two independent techniques; both gamma-ray and alpha-particle spectrometry. Gamma measurements were carried out by using a gamma spectrometry system equipped with a XtRa coaxial germanium detector (Canberra), which has 38% relative efficiency, and FWHM of 0.95 keV at the 122 keV line of  $^{57}\text{Co}$  and 1.9 keV at the 1333 keV line of  $^{60}\text{Co}$ . The whole procedure of calibration of this gamma spectrometry system is described elsewhere [7].

Th- and U-isotopes activity concentrations were determined by alpha-particle spectrometry in aliquots of the homogenized samples. For the determination of these isotopes, a sequential well-established radiochemical method was applied [8] in order to put the radio-elements in dissolution, and later they are isolated and electrodeposited onto stainless steel discs to obtain very thick radioactive sources. The discs were counted by using an EG&G Ortec alpha spectrometry system equipped with ion-implanted silicon detectors.

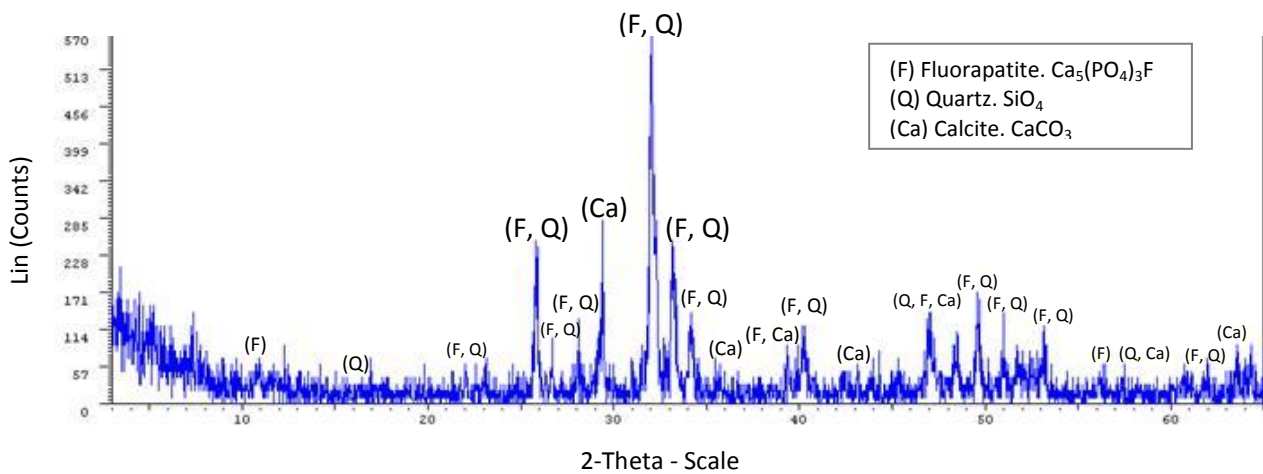
## **3. Results and discussion**

### **3.1 Mineral composition**

The diffractogram shown in Figure 2 demonstrate that fluorapatite,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ , is the main mineral component present in the rock phosphate,. Similar results have been found by other authors [6]. The phosphate rock and Togo, have a higher content of carbonates, fluorides and metals such as iron and aluminum, and often contain organic compounds because their origin is associated with the material derived from living things [9].

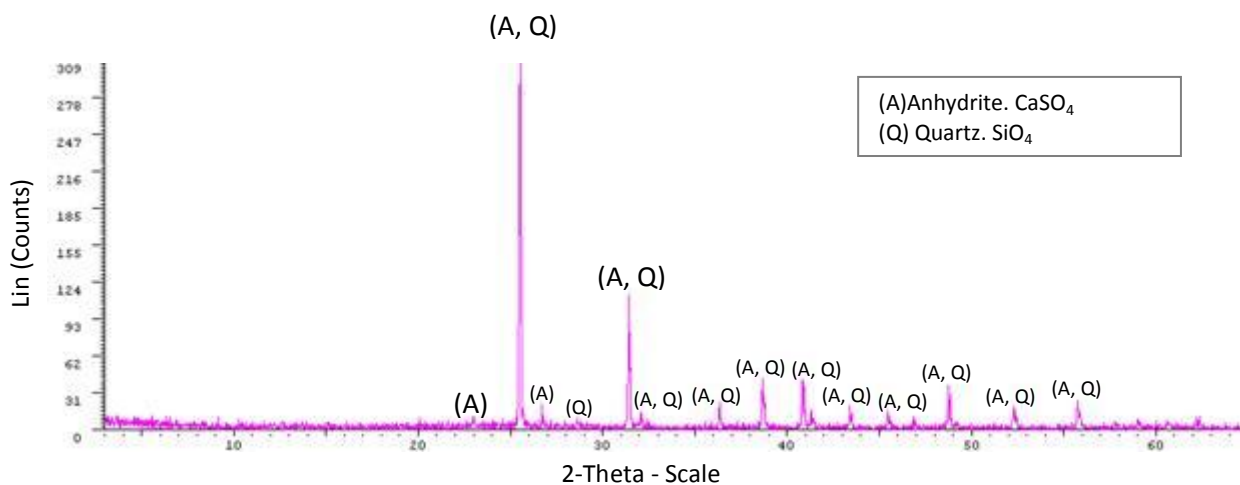
The marine sedimentary phosphate, sample [PR], is used mainly in many factories in Spain and Morocco. The ore used for the manufacturing of phosphoric acid answers to the generic formula  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ , because of it has been formed by precipitation of calcium phosphate within the seawater when deep cold waters very enriched in phosphates reach the Atlantic Ocean surface and they increase their temperature [10-12]. So, according to our results, the

following species were observed: fluorapatite,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ , calcite ( $\text{CaCO}_3$ ), and quartz ( $\text{SiO}_2$ ) (Figure 2). This composition is agree with those published by other authors [6,15]



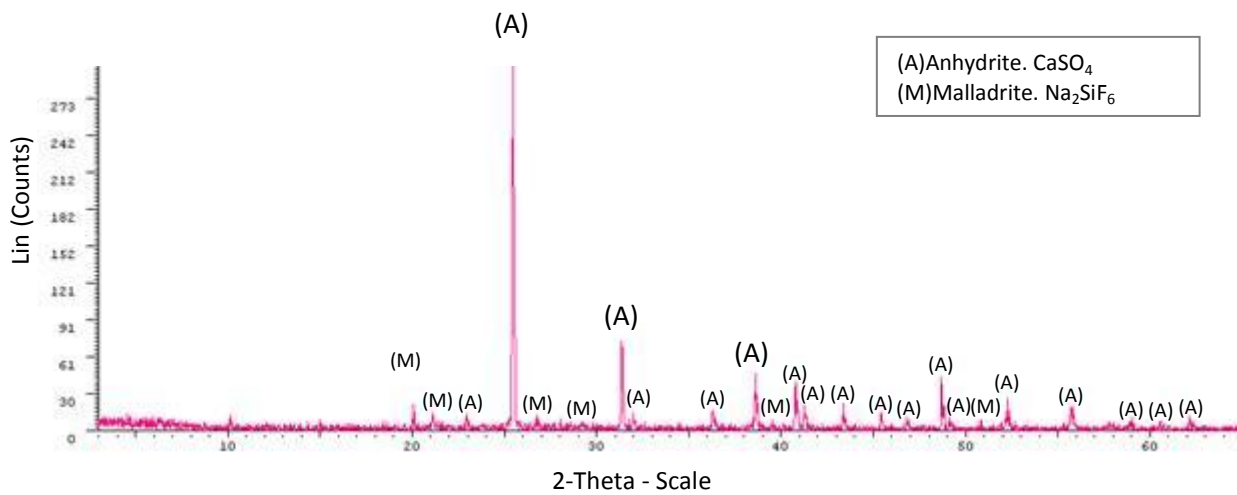
**Fig.2** Diffraction pattern of the sample Phosphate Rock [PR]

In the relation to the intermediate products, Figure 3 shows the diffractogram for [PU] sample and almost all the crystalline phase corresponds to the anhydrite ( $\text{CaSO}_4$ ), because of this one was calcined at 350 °C losing the water of it crystalline structure.

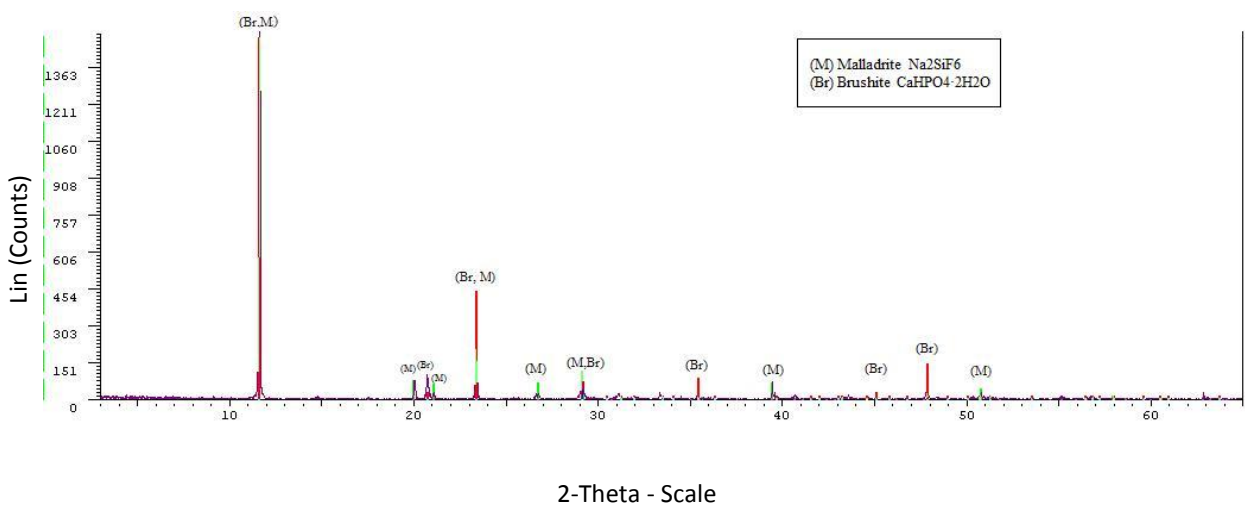


**Fig.3** Diffraction pattern of the sample Pulp [PU]

The sludge taken from the acid decanter, [DS], is formed by material decanted in this tank from very fine suspended solids (salts) that passed throughout the filter used in the separation acid-PG, or by suspended particles formed by co-precipitation during the time that phosphoric acid is stored in these tanks. The crystalline phase of this sludge (Figure 4), corresponds to the very fine particles of anhydrite ( $\text{CaSO}_4$ ), as we will see on the granulometry analysis (Figure 7), and very insoluble alkaline fluorosilicates as malladrite ( $\text{Na}_2\text{SiF}_6$ ). The external scales of the tank of phosphogypsum + water from plants 1 and 2, where the gypsum is pumped toward the rafts, are basically phosphate calcium dehydrate, brushite ( $\text{Ca}(\text{HPO}_4)\cdot 2\text{H}_2\text{O}$ ) and alkaline fluorosilicates as malladrite ( $\text{Na}_2\text{SiF}_6$ ) (Figure 5).

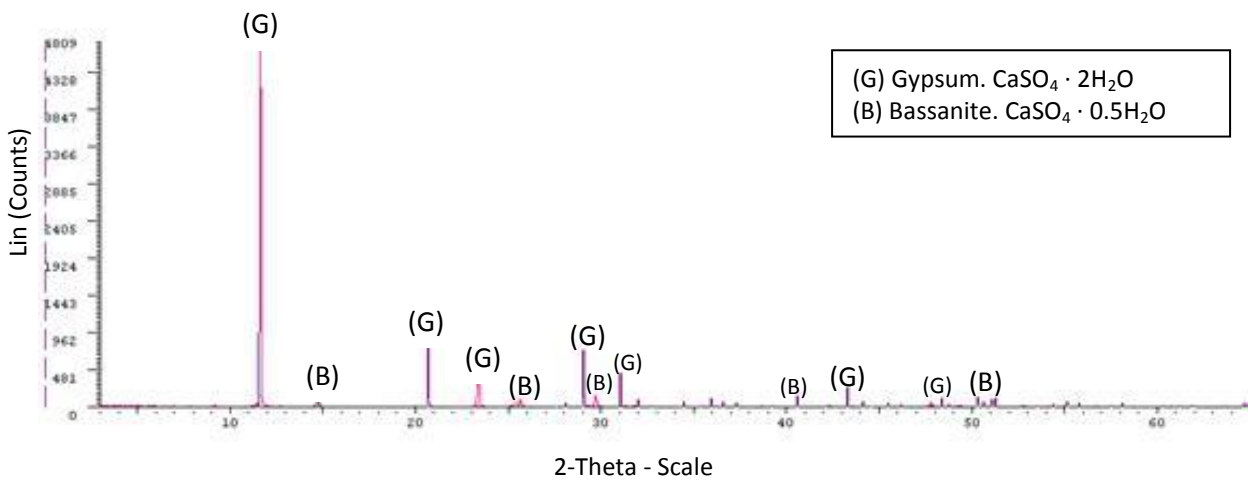


**Fig.4** Diffraction pattern of the sample Decanter Sludge [DS]



**Fig.5** Diffraction pattern of the sample External Scales [ES]

Finally, both phosphogypsum samples analyzed [PG1] and [PG2], are in agreement with the expected results, being gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) the main mineral in their composition. Other weaker peaks are attributed to the presence of crystal phases in trace amounts.



**Fig.6** Diffraction pattern of the sample fresh phosphogypsum taken just before it is pumped to the piles [PG1]

The presence of bassanite ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ) is explained by water loss through evaporation at  $95^\circ$  [13,14]. This was observed when samples of phosphogypsum, having been previously dried in an oven at  $95^\circ\text{C}$  for 24 h (as in our case) were analyzed using XRD. In fact, the crystalline composition showed a significant change, indicating that calcium sulfate hemihydrate and calcium sulfate dihydrate can coexist [15].

### 3.2 X-Ray Fluorescence

In Table 3, we can see the concentrations of major elements determined by XRF, in the samples studied. The raw materials have a similar concentration of F, about 4%, and significant amounts of  $\text{P}_2\text{O}_5$ , about 27%, and CaO 52% and remarkable of  $\text{SiO}_2$ , as expected with the mineral phases found in the section 3.1. Concentrations in non-negligible amounts of Na, Al, K and Fe, are also observed. The sedimentary origin of the phosphate rock [PR] is confirmed by studying the concentrations of main major elements and impurities [16]. Thus, typical levels of calcium oxide and fluorine for the sample of Kola [KO], igneous origin, are slightly lower than those found in the sample [PR], 50% versus 54% and 3.9 versus to 5.1%, respectively. In addition, the sample [PR] contains smaller amounts of iron oxide, 0.3 compared to 0.42% and potassium oxide, 0.09 compared to 0.14% [16].

In relation to intermediate products, the pulp [PU] is associated to a significant percentage of  $\text{P}_2\text{O}_5$  (15%) since it is a mixture of PG+PR since in this step it has not been yet dissolved the all the added phosphate rock. The mineralogy supports this conclusion since the majority phase found is anhydrite ( $\text{CaSO}_4$ ), with  $\text{SO}_3$  and CaO values of 31 and 34%, respectively, and a remnant of quartz (0.4 %  $\text{SiO}_2$ ).

**Table 3.** Concentration (%) of the major elements determined by XRF. The total iron is expressed as  $\text{Fe}_2\text{O}_3$ . N.D not detected. (\*) Samples calcined at  $350^\circ\text{C}$ . (Limit of Detection (LOD) about  $<0.01\%$  ppm).

|               | F     | $\text{Na}_2\text{O}$ | MgO  | $\text{Al}_2\text{O}_3$ | $\text{SiO}_2$ | $\text{P}_2\text{O}_5$ | $\text{SO}_3$ | $\text{K}_2\text{O}$ | CaO  | $\text{Fe}_2\text{O}_3$ |
|---------------|-------|-----------------------|------|-------------------------|----------------|------------------------|---------------|----------------------|------|-------------------------|
| <b>KO</b>     | 3.92  | 0.41                  | 0.07 | 0.46                    | 1.37           | 28.7                   | 0.50          | 0.14                 | 50.1 | 0.42                    |
| <b>TO</b>     | 4.66  | 0.19                  | 0.09 | 1.16                    | 2.5            | 27.7                   | 0.55          | 0.03                 | 51.1 | 1.65                    |
| <b>PR</b>     | 5.13  | 0.7                   | 0.4  | 0.8                     | 3.1            | 25                     | 2.0           | 0.09                 | 54.9 | 0.3                     |
| <b>PU (*)</b> | N.D   | 0.79                  | 0.17 | 0.30                    | 0.40           | 15.4                   | 30.8          | 0.06                 | 33.7 | 0.16                    |
| <b>DS (*)</b> | N.D   | 3.3                   | 0.16 | 0.33                    | 0.50           | 15.5                   | 30.2          | 1.11                 | 32.0 | 0.14                    |
| <b>TS (*)</b> | N.D   | 5.8                   | 1.03 | 1.69                    | 0.07           | 27.5                   | 20.4          | 0.26                 | 21.0 | 0.36                    |
| <b>SC</b>     | 56.53 | 16.5                  | 0.05 | 0.21                    | 24             | 3.87                   | 2.45          | 16.3                 | 2.05 | 0.03                    |
| <b>ES</b>     | 26.3  | 5.9                   | 0.03 | 0.18                    | 9.98           | 1.37                   | 41.2          | 0.03                 | 25.3 | 0.46                    |
| <b>PG1</b>    | 2.22  | 0.26                  | 0.03 | 0.13                    | 0.92           | 1.32                   | 56.7          | 0.01                 | 39.9 | 0.03                    |
| <b>PG2</b>    | 1.9   | 0.18                  | 0.02 | 0.21                    | 0.94           | 0.46                   | 50.8          | $<0.01$              | 38.2 | 0.07                    |

Both, decanter sludge [DS] and thickener sludge [TS], contain high values in phosphorus (15.5 and 27.5% of  $\text{P}_2\text{O}_5$ , respectively), indicating that a significant fraction of them is probably formed by the phosphate rock remaining without dissolve and particulate matter co-precipitated during the storage of phosphoric acid inside these storing tanks. We can also observe significant amounts of sulfur as  $\text{SO}_3$ , (30.2 and 20.4%, respectively), and CaO (31.9 and 21%, respectively), ratifying that a significant fraction of these sludge are formed by very



fine particles of phosphogypsum. And finally, the high Na concentrations of these materials confirm the presence of malladrita ( $\text{Na}_2\text{SiF}_6$ ) observed in the DRX analysis (3.2% and 5.8% of  $\text{Na}_2\text{O}$  for the samples [DS] and [TS]).

Moreover, these samples show a peculiarity in relation to the fluorine. The XRD technique revealed the presence of aluminum fluorosilicate, while in the analysis carried out by XRF was not found any concentration of this element. This fact could be explained if it is taken in consideration that all samples were dried at 95 °C for 24 hours, excepting these three samples ([PU], [DS] and [TS]) since they remained after drying with a high degree of humidity. Therefore, were calcined at 350 °C. So, it is expected that fluorine and other elements have been volatilized and they will not be found in XRF analysis.

Scales samples ([SC] and [ES]), present high contents in Fluor (56.5 and 26.3 %, respectively), which probably could come from precipitated salts found in the phosphoric acid, since the alkali fluorosilicate are very insoluble, potassium and sodium fluorosilicate, for example. In this sense, high concentrations of  $\text{SiO}_2$  (24 and 9.9%, respectively),  $\text{Na}_2\text{O}$  (16.5 and 5.8%, respectively), and  $\text{K}_2\text{O}$  are found in these samples. Sample SC present the highest concentrations of both Na and K, but very low values for Ca and  $\text{SO}_3$ , indicating this fact that this scale is mainly formed by very insoluble salts of alkali fluorosilicates. On the contrary, the [ES] sample presents significant values of  $\text{SO}_3$  (41%) and CaO (25%) due to the presence of calcium sulfate in its mineral composition. It is important to remember that this sample was taken from the outer surface of the tank where the phosphogypsum is pumped into the ponds.

Finally, the contents of  $\text{SO}_3$  and CaO in the phosphogypsum samples ([PG1] and [PG2]) indicate that more than 90% in these samples is calcium sulphate. Moreover, important impurities for  $\text{P}_2\text{O}_5$  (~ 1 %),  $\text{Al}_2\text{O}_3$  (~ 0.2 %),  $\text{Na}_2\text{O}$  (~ 0.2 %),  $\text{SiO}_2$  (~ 1 %) and F (~ 2 %) were found in the PG2 (see table 3). The very low pH of PG2 stored in the piles (< 2) due to the presence of  $\text{P}_2\text{O}_5$  could leach both these ones and other pollutants into their surrounding environment. Moreover, the  $\text{SiO}_2$  can be found as quartz, and together with  $\text{Al}_2\text{O}_3$  and  $\text{Na}_2\text{O}$  and/or  $\text{K}_2\text{O}$ , could indicate the presence of clay minerals ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$ ) [17]. It is also expected to find higher concentrations of  $\text{P}_2\text{O}_5$  in the fresh phosphogypsum ([PG1]), since the older phosphogypsum stored for long periods have been subjected to longer leaching processes [PG2].

### 3.3 Trace elements

Table 4 shows the obtained results for trace elements in intermediate products and waste generated in the process, which are compared with the raw materials used in the process and the global average concentration of contaminated soils [19].

Igneous phosphate rock ([KO]) is very enriched in Ba and rare earth elements as La compared to sedimentary ores ([TO] and [PR]) [16,20]. For example the concentration of Ba in [KO] is 633 mg/kg being significantly higher than those obtained in the [PR] (97 mg/kg) and [TO] (47 mg/kg). Furthermore, the concentrations of heavy metals in the igneous sample given by Da Conceicao [16] (Cd, 4 ppm; Cr, 70 ppm. Ci. 96 ppm; Ni, 117 ppm; Pb, 44ppm; Zn, 326 ppm) are higher than those found in this work. On the other hand, Martín et al. [18] and Pérez-

López et al. [21] also published concentrations of heavy metals in samples of sedimentary rock phosphate from Morocco, which were similar to the sample [PR] in this study.

In the intermediate products, the sample [TS] shows a high concentration in most of the analyzed trace elements Cd, Cr, Ni, Sr, Y, V, Zn, Th and U, respect to the other ones. Also relevant is the concentration of Y, 1370 mg/kg and La, 702 mg/kg. This fact can be explained by the origin of sludge, complex salts and very small particles of PG, which are formed in concentrated phosphoric acid and they are going accumulating and eliminating into the thickeners.

In phosphogypsum samples, most trace element have values similar or lower than those reported by other authors in phosphogypsum derived from sedimentary rock phosphate. However, the values of Ni, Zn, V and U are higher that our phosphogypsum samples studied [15] (Ni, <1 ppm; Zn, 8 ppm; V, 4.75 ppm and U, 8.3 ppm). Potential contaminants such as cadmium, have found high concentrations, reaching a factor 20 compared to a typical soil. Finally, in the table 4 has been observed a similar trace element concentration for both phosphogypsum samples, this can be explained by the fact that trace elements tend to placed in the matrix of phosphogypsum already settled.

**Table 4.** Concentrations (mg/kg) of some selected trace elements. (\*) Typical concentrations of not polluted soils. (CF) Concentration factor in relation to a not polluted soil

| Elementos | KO    | CF   | TO   | CF   | PR   | CF   | PU   | CF   | DS   | CF   | TS          | CF   | SC   | CF    | ES   | CF   | PG1  | CF    | PG2  | CF   | (*)  |
|-----------|-------|------|------|------|------|------|------|------|------|------|-------------|------|------|-------|------|------|------|-------|------|------|------|
| Ba        | 633   | 1    | 47   | 0.1  | 97   | 0.2  | 51   | 0.1  | 132  | 0.2  | 11          | 0.02 | 249  | 0.4   | 34   | 0.1  | 62   | 0.1   | 64   | 0.1  | 628  |
| Cd        | 0.3   | 3    | 51.2 | 569  | 16.6 | 184  | 9.2  | 102  | 7.1  | 79   | <b>83.7</b> | 930  | 1.5  | 17    | 1.8  | 20   | 2    | 22    | 1.6  | 18   | 0.09 |
| Cr        | 16.8  | 0.2  | 112  | 1    | 253  | 2.8  | 165  | 1.8  | 141  | 1.5  | 226         | 2.5  | 15.8 | 0.2   | 59.6 | 0.7  | 9.1  | 0.1   | 9.3  | 0.1  | 92   |
| Ga        | < 1   | 0.1  | 1.4  | 0.1  | 1.5  | 0.01 | 1.5  | 0.1  | 1.1  | 0.06 | 1.6         | 0.1  | < 1  | 0.1   | < 1  | 0.1  | < 1  | 0.05  | < 1  | 0.05 | 17.5 |
| La        | 2350  | 76   | 164  | 5    | 103  | 3    | 14.9 | 5    | 17.5 | 0.6  | <b>702</b>  | 23   | 24.4 | 0.8   | 18.1 | 0.6  | 37.7 | 1     | 34.7 | 1    | 31   |
| Ni        | 29.4  | 0.6  | 47.9 | 1    | 48.3 | 1    | 33.4 | 0.8  | 29.6 | 0.6  | 40.8        | 0.9  | 3.5  | 0.1   | 24.6 | 0.5  | 8.5  | 0.2   | 4.7  | 0.1  | 47   |
| Pb        | 3.2   | 0.2  | 9.2  | 0.5  | 4    | 0.3  | 13.5 | 0.8  | 10.3 | 0.6  | 21.4        | 1    | 0.7  | 0.04  | 25.2 | 1.5  | 2.6  | 0.2   | 3.6  | 0.2  | 17   |
| Cu        | 21.3  | 0.8  | 43.2 | 1.5  | 36.9 | 1    | 31.7 | 1.1  | 26.5 | 1    | 42.7        | 1.5  | 5.3  | 0.2   | 207  | 7.4  | 3.9  | 0.1   | 12   | 0.4  | 28   |
| Sr        | 23034 | 72   | 4313 | 13.5 | 980  | 3    | 593  | 1.9  | 643  | 2    | <b>2234</b> | 7    | 109  | 0.3   | 642  | 2    | 668  | 2     | 634  | 2    | 320  |
| Zr        | 5     | 0.03 | 6    | 0.03 | 6    | 0.03 | 4    | 0.02 | 7    | 0.04 | 16          | 0.1  | < 1  | 0.005 | 10   | 0.1  | 2    | 0.01  | 5    | 0.03 | 193  |
| Y         | 331   | 16   | 269  | 13   | 263  | 13   | 68.5 | 3.3  | 70.3 | 3    | <b>1370</b> | 65   | 123  | 6     | 28.2 | 1    | 43.5 | 2     | 38   | 2    | 21   |
| V         | 104   | 1.1  | 56   | 0.6  | 195  | 2    | 131  | 1.4  | 99   | 1    | 177         | 1.8  | 17   | 0.2   | 19   | 0.2  | 14   | 0.1   | 3    | 0.03 | 97   |
| Zn        | 16.9  | 0.3  | 269  | 4    | 260  | 4    | 229  | 3.4  | 167  | 2.5  | 285         | 4    | 21.2 | 0.3   | 30.5 | 0.5  | 10.4 | 0.2   | 13.4 | 0.2  | 67   |
| Mn        | 195   | 0.3  | 155  | 0.2  | 14   | 0.02 | 107  | 0.1  | 23   | 0.03 | 30          | 0.04 | 14   | 0.02  | 28   | 0.04 | 1    | 0.001 | 21   | 0.03 | 774  |
| As        | 4.7   | 1    | 17.8 | 4    | 20   | 4.2  | 9.2  | 2    | 6.3  | 1    | 5.7         | 1    | 3.3  | 0.7   | 19.9 | 4    | 2.7  | 0.6   | 2.6  | 0.5  | 4.8  |
| Co        | 1.4   | 0.1  | 6.4  | 0.4  | < 1  | 0.05 | 2.5  | 0.2  | < 1  | 0.05 | < 1         | 0.05 | < 1  | 0.05  | < 1  | 0.05 | < 1  | 0.05  | < 1  | 0.05 | 17   |
| Th        | 23.4  | 2    | 16.7 | 1.5  | 3.3  | 0.3  | 2.9  | 0.3  | 2.2  | 0.2  | <b>7.4</b>  | 0.7  | 3.4  | 0.3   | 1.2  | 0.1  | 2    | 0.2   | 1.3  | 0.1  | 11   |
| U         | 5.6   | 2.1  | 103  | 38   | 144  | 53   | 87.5 | 0.9  | 48.8 | 18   | <b>154</b>  | 57   | 21.2 | 8     | 14.9 | 5.5  | 4.5  | 1.7   | 9.2  | 3    | 2.7  |

### 3.5. Granulometry

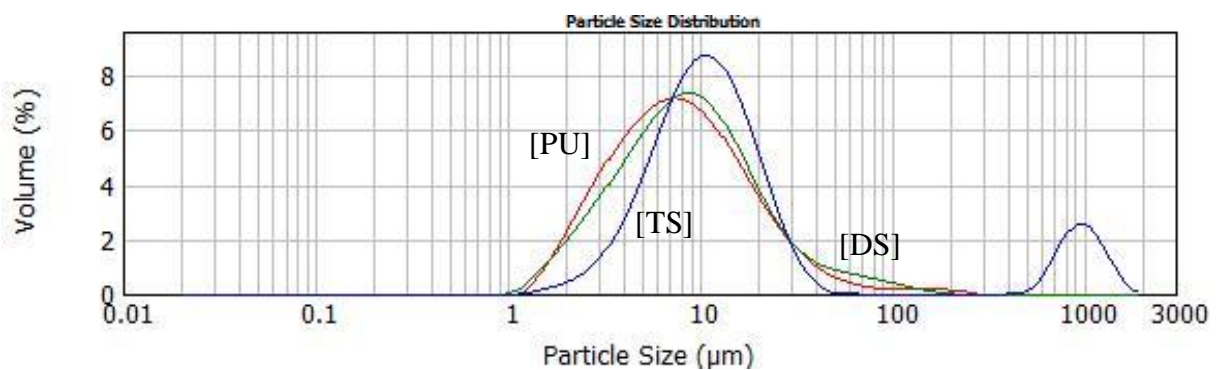
An important aspect when commercial applications are being investigated for a waste it is the granulometry spectrum of them, since the most physical and chemical properties will depend on the specific surface of material grains. The size distribution in the different studied raw materials is very heterogeneous, with a high concentration of coarse sand (65%) in [PR] and 51 and 64% silt in [TO] and [KO], respectively (table 5).

**Table 5.** Average composition (% V) of grain size in samples of raw materials Kola [KO], Togo [TO] and phosphate rock [PR]

| Size ( $\mu\text{m}$ ) | Type | KO             |            | TO             |                | PR             |                |
|------------------------|------|----------------|------------|----------------|----------------|----------------|----------------|
|                        |      | Average        | Total      | Average        | Total          | Average        | Total          |
| < 4                    | Clay | $14 \pm 4$     | $14 \pm 4$ | $6.2 \pm 0.9$  | $6.2 \pm 0.9$  | $3.8 \pm 0.6$  | $3.8 \pm 0.6$  |
| [4-8)                  |      | $11.8 \pm 1.0$ |            | $13.5 \pm 1.7$ |                | $11.3 \pm 1.7$ |                |
| [8-16)                 | Silt | $12.8 \pm 2.0$ | $64 \pm 3$ | $10.3 \pm 0.7$ | $51.2 \pm 0.3$ | $6.6 \pm 1.0$  | $31.7 \pm 2.4$ |
| [16-32)                |      | $19.3 \pm 1.7$ |            | $11.5 \pm 1.2$ |                | $5.5 \pm 0.9$  |                |
| [32-63)                |      | $19.8 \pm 1.7$ |            | $16.9 \pm 2.1$ |                | $8.3 \pm 1.2$  |                |
| [63-125)               |      | $9.8 \pm 0.9$  |            | $18.4 \pm 2.2$ |                | $9.2 \pm 1.5$  |                |
| [125-250)              |      | $1.9 \pm 0.8$  |            | $7.6 \pm 1.2$  |                | $13.4 \pm 1.8$ |                |
| [250-500)              | Sand | $4 \pm 4$      | $23 \pm 8$ | $8 \pm 4$      | $28 \pm 1$     | $25 \pm 4$     | $64.5 \pm 7.1$ |
| [500-1000)             |      | $7 \pm 7$      |            | $7 \pm 4$      |                | $15 \pm 5$     |                |
| [1000-2000)            |      | $0.7 \pm 0.7$  |            | $0.3 \pm 0.2$  |                | $2.4 \pm 2.3$  |                |

The sample of phosphate rock has a low percentage of silt, 7% versus 64% of the Kola. This is because unlike the Kola phosphate rock sample is not ground.

On the other hand, the grain size for intermediate products (figure 7 and 8) depends of the origin of each material: 1°) Pulp of coarse silt of the direct reaction the mineral with the acid; 2°) Coarse sludges of the direct decantation and of the thickener; 3°) Scales caused by accumulation of different materials with similars granulometry between coarse silt and sandy.



**Fig. 7.** Distribution (% V) of grain size in samples of co-products [PU], [DS] and [TS]

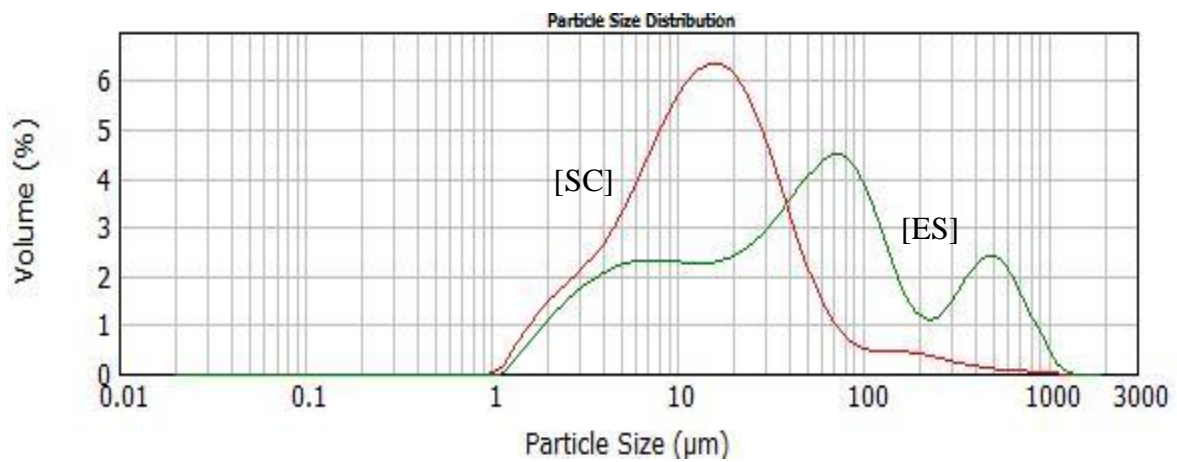


Fig. 8. Distribution (% V) of grain size in samples of co-products [SC] and [ES]

Finally, figure 9 shows the grain size distribution of phosphogypsum samples, where it is possible to obtain that about 80 and 50 % is silt for [PG1] and [PG2], respectively. But the maximum percentage is produced for the phosphogypsum 2 [PG2] at 40 microns (38%), while for [PG1] (taken just before it is pumped to the piles) the maximum is given around 70 microns and in the same proportion (40%).

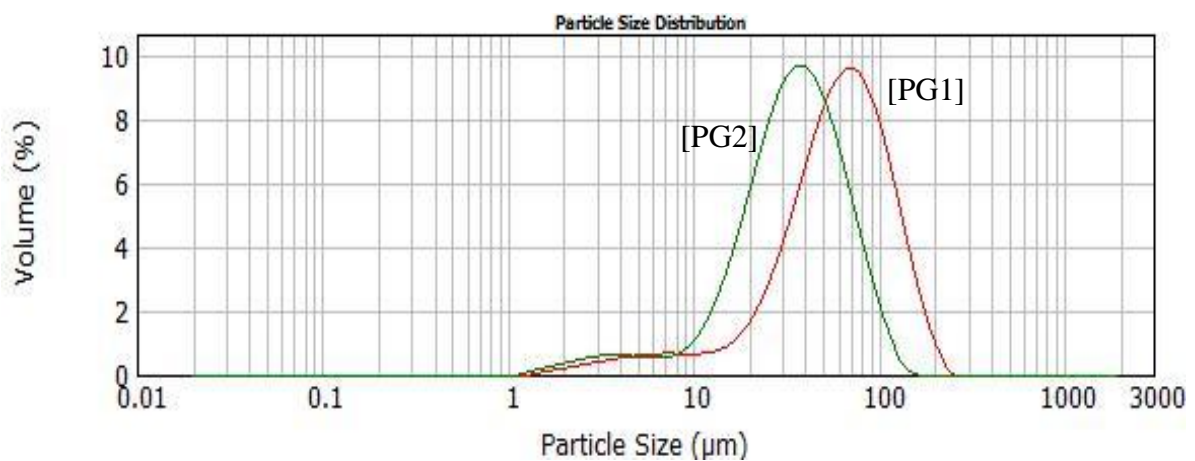


Fig. 9. Distribution (% V) of grain size in samples of waste [PG1] and [PG2]

### 3.6. Radiological concentrations

The average values and standard deviations (SD) of the specific activity obtained in this work for different natural radionuclides of long half-life (higher than several months), are presented in Table 6. From this table it follows that in the raw materials, the activity concentration of  $^{238}\text{U}$  is very variable, being between 70 Bq/kg in the [KO] sample and 1200-1600 Bq/kg of the raw materials with sedimentary origin, thereby corroborating the fact that phosphates from sedimentary origins ([TO] and [PR]) show a higher U content than levels observed in igneous phosphate ([KO]) [6,22,23]. In relation to the concentration of  $^{232}\text{Th}$ , we can see that is similar in samples [KO] and [TO], about 80 Bq/kg, while decreasing by a factor 4 in the [PR] (20 Bq/kg), which is similar to the undisturbed soil ones [24].

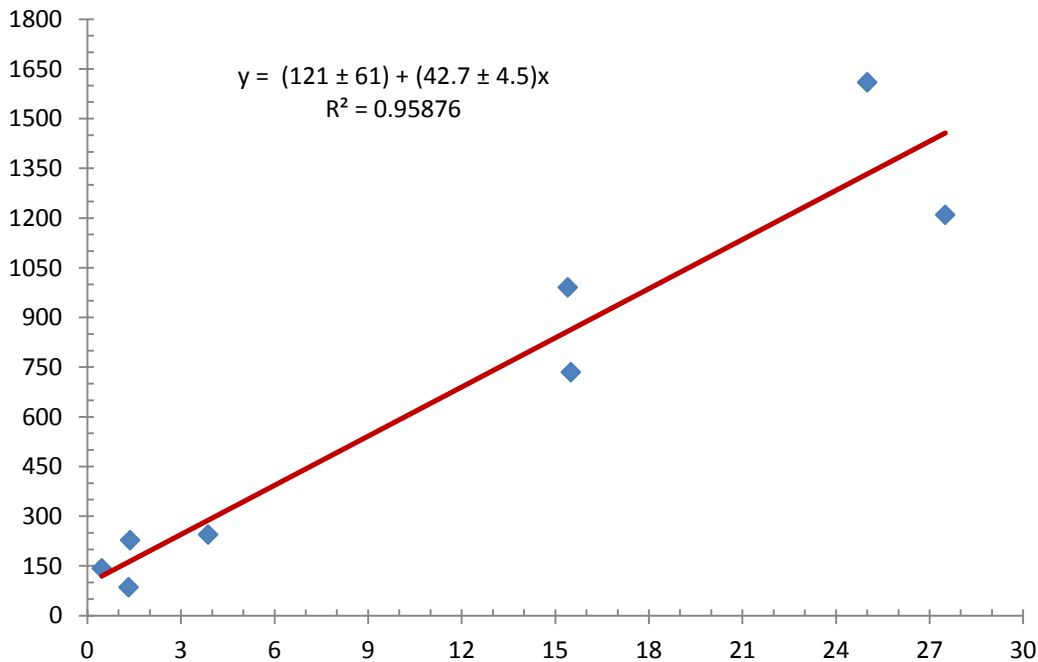
Finally, the levels of  $^{40}\text{K}$  are very low, around 40 Bq/kg, about 16 times lower than the average concentration of a typical soil of Spain (around 600 Bq/kg) [24].

**Table 6.** Activity concentration (Bq/kg) for radioelements of interest in the samples taken. The uncertainty is given by the standard deviation of the mean.

|       | $^{230}\text{Th}$ | $^{232}\text{Th}$ | $^{234}\text{U}$ | $^{238}\text{U}$ | $^{210}\text{Po}$ | $^{226}\text{Ra}$ | $^{228}\text{Th}$ | $^{228}\text{Ra}$ | $^{40}\text{K}$ |
|-------|-------------------|-------------------|------------------|------------------|-------------------|-------------------|-------------------|-------------------|-----------------|
| [KO]  | $70 \pm 5$        | $88 \pm 5$        | $70.6 \pm 2.3$   | $69.7 \pm 2.3$   | $97 \pm 4$        | $76 \pm 5$        | $105 \pm 7$       | $104 \pm 7$       | $54 \pm 6$      |
| [TO]  | $1100 \pm 60$     | $80 \pm 7$        | $1205 \pm 34$    | $1200 \pm 30$    | $1240 \pm 30$     | $1373 \pm 80$     | $82 \pm 5$        | $90 \pm 6$        | $< 48$          |
| [PR]  | $1600 \pm 70$     | $20 \pm 2$        | $1612 \pm 30$    | $1610 \pm 30$    | $1520 \pm 40$     | $1770 \pm 70$     | $< 7$             | $< 16$            | $36 \pm 7$      |
| [PU]  | $780 \pm 40$      | $8 \pm 2$         | $991 \pm 22$     | $991 \pm 22$     | $879 \pm 30$      | $700 \pm 40$      | $< 5$             | $13.4 \pm 1.5$    | $< 34$          |
| [DS]  | $880 \pm 60$      | $16 \pm 3$        | $742 \pm 18$     | $735 \pm 17$     | $1780 \pm 40$     | $2300 \pm 140$    | $< 13$            | $< 27$            | $322 \pm 26$    |
| [TS]  | $2640 \pm 90$     | $30 \pm 2$        | $1199 \pm 4$     | $1210 \pm 40$    | $3350 \pm 90$     | $1140 \pm 30$     | $24 \pm 5$        | $13 \pm 6$        | $96 \pm 19$     |
| [SC]  | $1800 \pm 50$     | $19 \pm 2$        | $265 \pm 17$     | $245 \pm 16$     | $550 \pm 15$      | $9000 \pm 530$    | $29.5 \pm 1.9$    | $85 \pm 5$        | $4992 \pm 292$  |
| [ES]  | $120 \pm 6$       | $3 \pm 1$         | $217 \pm 9$      | $228 \pm 9$      | $2810 \pm 90$     | $1533 \pm 90$     | $< 9$             | $15.8 \pm 1.9$    | $200 \pm 16$    |
| [PG1] | $75 \pm 15$       | $10.7 \pm 4.2$    | $83 \pm 4$       | $86 \pm 5$       | $1150 \pm 40$     | $1124 \pm 66$     | $28.3 \pm 2.3$    | $53 \pm 4$        | $25 \pm 5$      |
| [PG2] | $510 \pm 40$      | $17 \pm 4$        | $144 \pm 4$      | $143 \pm 3$      | $775 \pm 28$      | $946 \pm 55$      | $< 4$             | $7.4 \pm 0.8$     | $< 23$          |

With regard to intermediate products, uranium concentration tends to increase with the  $\text{P}_2\text{O}_5$  concentrations, fact found by other authors [15]. In fact, in figure 10 it is observed a linear relation between the both elements concentrations, so uranium travel along the production process bound to the phosphoric acid (soluble fraction), and being the equation:

$$^{238}\text{U} (\text{Bq kg}^{-1}) = (121 \pm 61) + (42.7 \pm 4.5) \text{P}_2\text{O}_5 \quad [\text{Eq. 2}]$$



**Fig. 10.** Linear relation between the  $^{238}\text{U}$  and  $\text{P}_2\text{O}_5$

The previous fitting has a determination coefficient ( $R^2$ ) of 0.958, and the constant is not statistically significant but the slope it is as could be obtained from their standard uncertainties.

The ratio of  $^{232}\text{Th}/^{230}\text{Th}$  in the [PR] is similar in all samples analyzed ( $\approx 80$ ). And the low values of  $^{232}\text{Th}$  in all products confirm that the [PR] of Morocco is usually used.

With respect to  $^{230}\text{Th}$ , in the samples of intermediate products this radionuclide is distributed very similar to uranium. Relatively new results, since most studies indicate that the  $^{230}\text{Th}$  has a greater tendency to bind with the solid fraction or phosphogypsum. In the sludge, for example, the concentration of  $^{230}\text{Th}$  is similar to that of  $^{238}\text{U}$ . This indicates that thorium is also very soluble in phosphoric acid and that the thorium fraction linked to acid varies depending on its concentration.

The thickener sludge [TS] has a concentration around 1210 Bq/kg of  $^{238}\text{U}$ , similar to phosphoric acid production, 1300 Bq/kg [6], compared to 1000, 735, 245 and 228 Bq/kg of pulp [PU], decanter sludge [DS] and both scale [SC] and [ES] respectively, which indicates us that is formed by phosphoric acid highest concentration.

On the other hand, the highest concentrations of  $^{226}\text{Ra}$  have been found in sludge, [DS] and [TS], 1140 and 2300 Bq/kg, respectively, in the [SC] around 9000 Bq/kg, and in the [ES], 1500 Bq/kg. These results indicate that the highest enrichments of radium are associated with fine textured material that flow in suspension in the liquid fraction, or to be formed when the concentrated acid is produced.

In general, the  $^{210}\text{Po}$  tends to "travel" throughout the industrial process adhered to the solid phases, but their concentrations are lower than those of  $^{226}\text{Ra}$ . This is possibly due to that the polonium tends to co-precipitate with the gypsum less than the radium. The explanation may lie in the fact that polonium is a little more soluble than the radium, and therefore, something remains in the  $\text{P}_2\text{O}_5$  that still containing the gypsum (3000 Bq/kg of  $^{210}\text{Po}$  [TS] compared to 800-1200 Bq/kg measured in samples of phosphogypsum).

The concentrations of  $^{40}\text{K}$ , in general, are also low, as expected. However, are seen high concentrations in the [SC] (about 5000 Bq/kg, compatible with the  $\text{K}_2\text{O}$  concentration obtained by XRF) and in the [DS] (with more 300 Bq/kg). Factor 140 and 9 respectively, relative to that in the [PR]. Is possible that this result is related to the "special" mineralogy to those scales [SC, fluorosilicates alkali], whose material has two origins: solid material formed from dissolved material in the digesters, or insoluble minerals circulating throughout the process.

On the other hand, during the phosphoric acid process, the radioactive equilibrium is broken, and every radionuclide is distributed differently depending on its solubility. Thus, the uranium mainly remains in phosphoric acid (under oxidizing conditions, up to 90%), while most of the radium is transferred into phosphogypsum [6,25,30]

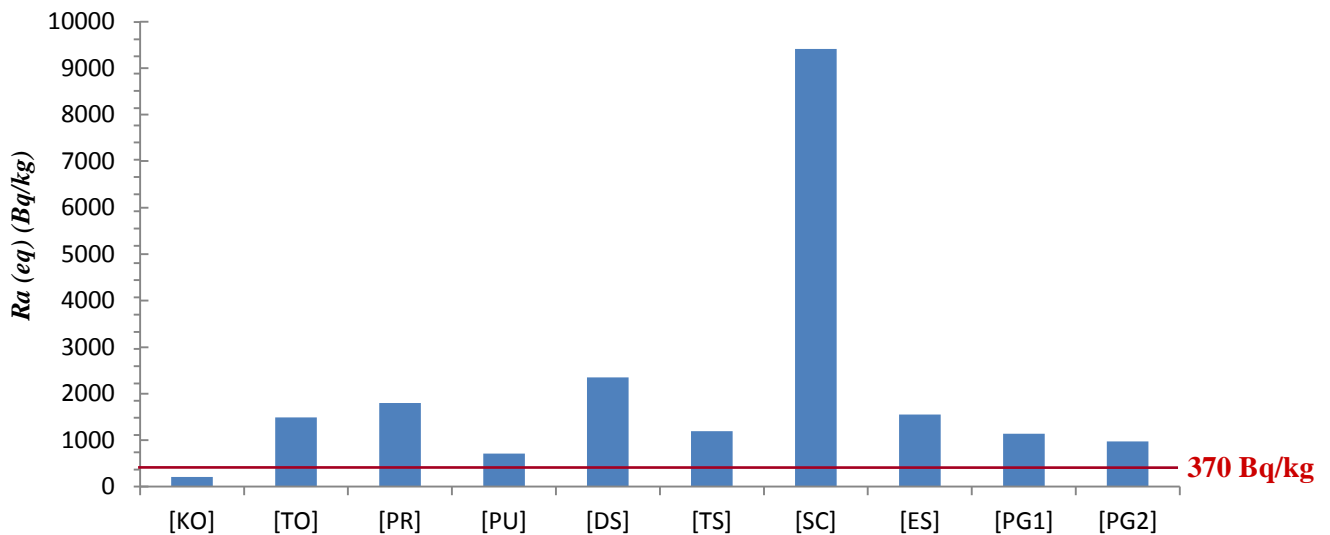
Our results are in agreement with this behavior. Thus, the activity concentration of  $^{226}\text{Ra}$  and  $^{210}\text{Po}$  are higher than the activity concentration of  $^{238}\text{U}$  in both phosphogypsum. Moreover, the

three radioisotopes show similar concentrations to those previously reported by other authors [25-29].

The equivalent of radio activity,  $Ra_{eq}$ , is used to compare the specific activity of materials containing different amounts of  $^{40}\text{K}$ ,  $^{226}\text{Ra}$  and  $^{232}\text{Th}$ .  $Ra_{eq}$  has been calculated in Bq/kg, from the following relation [31]:

$$Ra_{eq} = (A_{Th} \times 1.43) + A_{Ra} + (A_K \times 0.077) \quad [\text{Eq. 3}]$$

where  $A_{Th}$ ,  $A_{Ra}$  and  $A_K$  the activities concentrations of  $^{232}\text{Th}$ ,  $^{226}\text{Ra}$  and  $^{40}\text{K}$ , respectively, measured in Bq/kg. values of the constants in the equation is based on the estimation that 370 Bq/kg for  $^{226}\text{Ra}$ , 259 Bq/kg of  $^{232}\text{Th}$  and 4810 Bq/kg dose produced the same  $^{40}\text{K}$ . Applying Equation 3, yields a radius equivalent activities Bq/kg for the different samples (Figure 11)



*Fig. 11. Equivalent of radio activity of the different samples*

On the other hand, assuming a radius equivalent activity 370 Bq/kg in building materials produce an exposure of about 1.5 mGy/year in the population [32], which is considered by the International Commission on Radiological Protection (ICRP) [33] as the maximum limit allowable.

Therefore, the values obtained in the various samples are well above the maximum limit recommended, for example in [SC] with a factor 26. Except to the [KO] with an equivalent activity of 206 radio Bq/kg

#### 4. CONCLUSIONS

The present study has been focused in the characterization of several raw materials, co-products and waste involved in the production process of phosphoric acid by wet sulfate, aiming to study their elemental composition (major, minor and trace elements), granulometry, mineralogy, microscopic morphology and physical composition. The main objective has been to increase our knowledge about these industrial materials, in order to evaluate the degree of



fractionation of different elements and compounds analyzed in the stages of the industrial process.

In more detail, our results indicate that the main raw material in the industrial process, in relation to the study by XRD, shows the expected response to the bibliography, fluorapatite, calcite and quartz. On the other hand, we highlight in sludge samples [DS] and [ES], new mineral phases previously undetected as malladrita (alkaline fluosilicate) coming from the precipitation of salts present at the phosphoric acid obtained. Moreover, in the waste sample (PG) gypsum mineral phase ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) have been obtained with a significant percentage of calcium sulfate hemihydrate ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ), product of the high temperature (95 °C), for proceed to dry out the sample, that causes you to lose the water of crystal structures.

Secondly, the levels of major elements, in raw materials are correlated with the origin of the materials used, with high concentrations of F,  $\text{P}_2\text{O}_5$  and CaO. On the other hand, in the decanter samples [DS] and sludge thickener [TS], are observed high values in  $\text{P}_2\text{O}_5$  and significant amounts of  $\text{SO}_3$ , and CaO. Finally, the major elements in both phosphogypsum samples indicate that the mass of  $\text{SO}_3$  and CaO is more than 90% from total weight.

In relation with the concentration of trace elements in co-products (pulp, both sludge and scales), have different concentrations associated with their training process. The thickener sludge has a high concentration in most of the analyzed trace elements Cd, Cr, Ni, Sr, Y, V, Zn, Th and U. This fact can be explained by the characteristics of origin of the sludge, they are just suspended solids, where complex salts are formed on the phosphoric acid, being accumulated in the thickeners.

On the other hand, in the granulometric analysis has been observed that in the raw material milled, Kola and Togo, the majority of the particles have a size less than 63 microns (optimums size for digestion). Moreover, the granulometry of intermediates products, we have seen as practically 90% of the particles are below 63 microns in the samples of pulp sludge (decanted and thickened), as well as inner scales. Finally, have seen as external scales present a grain size greater other, with 40% in the sandy area. In both phsphogypsum samples we have obtained two different distributions, one of them around 40 microns and the other around 70 microns.

Lastly, radioactive results indicate that the raw material used until 2010 in the manufacturing process, phosphate rock from Morocco, is a NORM material because it contains significant concentrations of radionuclides of  $^{238}\text{U}$  serie, around 50 times the concentration in undisturbed soil. For the sludge, has been observed as the activity concentrations of different radionuclides are higher in the sludge thickener than in the decanter, except for the  $^{40}\text{K}$ , (clearly higher in a factor 3), and  $^{226}\text{Ra}$  (a factor of 2). With regard to the phosphogypsum, we have observed as are enriched in several radionuclides from the uranium series,  $^{226}\text{Ra}$  and  $^{210}\text{Po}$  with activity concentration around 1000 Bk/kg.

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