Characterization and obtention of phosphate rock concentrates of Turmequé, Boyacá

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Abstract. The work focuses on the use and exploitation of the mineral concentrates from phosphate rock (PR) coming from mines with a low percentage of phosphorus. The procedure was based on the collection of a source of phosphate rock from the department of Boyacá (municipality of Turmequé), using a randomized design with three replications. The samples were initially milled and sifted using meshes between 140 and 200 US standard, homogenizing them and improving the process of solubility of the phosphorus in the soil. We conducted Z-potential tests, which show that by performing a prior wash on the mineral and maintaining certain concentrations and pH defined, better results are achieved in terms of the buoyancy of the particles in the flotation process. The results obtained from the microflotation tests; both direct and inverse, and the results of chemical composition, with X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD), before and after the microflotation process, were carried out to obtain commercial laws grade phosphate rock concentrate, confirm that the protocol used increases by 9% the value of total phosphorus in the collected sample. These concentrates from phosphate rock, could be used in the future for the attainment of simple superphosphate (SSP), with the help of sulphuric acid and ammonium thiosulphate mixtures.

1. Introduction
Fertility problems limit the production of crops in many acid soils around the world, especially in the tropics. These soils generally have a low content of phosphorus (P), available to the plants [1]. Phosphorus used in agriculture comes from non-renewable sources, mainly from phosphate rock [2], which is insoluble in water and cannot be used directly in agriculture, in neutral or basic soils. In acid soils, finely ground phosphate rock is often applied, phosphorus pentoxide (P₂O₅) slowly enters the solution, throughout months or years, according to the pH of the soil [3]. However, for the most part, before phosphate rock can be used as a fertilizer, it is essential to treat it in some way in order to turn phosphorus into a soluble form [4]. The classic method used is acidulation, in order to produce normal superphosphate.

Colombia which has a significant agricultural potential of around four million arable hectares, imports virtually all of its phosphorus needs, despite having significant deposits of phosphate rock (PR) in the departments of Boyacá, Huila and Santander [5]. Some of these deposits were partially explored by “Ingeominas” in the early 1960s. According to this entity, the thickness of the mineralized levels varies between 0.5 to 5.4 meters and the tenors of P₂O₅ range between 10 and 37% [6]. In Boyacá, mines with a high percentage of phosphorus are being exploited, ignoring those with a low tenor. This study intends to harness and leverage the areas that have a low percentage of this element, as is the case of the ores located in the municipality of “Turmequé, Boyacá”, exploiting the mineral and turning it into raw material for the attainment of phosphate rock concentrates and their subsequent use in the production of...
simple superphosphate type (SSP) type fertilizers [7], with the help of sulphuric acid and ammonium thiosulphate mixtures [8].

2. Experimental methodology

The samples of PR were homogenized, cracked and sieved successively until smaller samples were obtained, a part of them was wet grinded and dried in the oven at 60°C. for 24h. and sieved. For each treatment, approximately 3g was weighed and the respective flotation in the hallimond tube was performed, and then reproduced on a larger scale to obtain the phosphate rock concentrate, which will be the raw material for the production of simple superphosphates (SSP) [9].

2.1. Materials and methods

2.1.1. Sources of phosphorus. Phosphoric rock from the municipality of “Turmequé”, Rosales sidewalk, was used; with a pH of 5.6 and a total phosphorus content of 16%.

2.1.2. Sample size. After carrying out the granulometric classification of the sample and were realized several tests of micro-buoyancy of the ore, it was found that the ideal size to find a greater performance in the phosphorus concentration was between 140 and 200 US standard mesh.

2.1.3. Experimental procedure. The phosphoric rock samples were homogenized, cracked and sieved successively until granulometric smaller samples were obtained, some of them were wet grinded and dried in the oven at 60°C. for 24h, then sifted. For each treatment, 3g of sample was weighed and the respective microflotation process in hallimond tube; to obtain the phosphate rock concentrate, for further analysis.

2.1.4. Analytical determinations. The total and assimilable phosphorus in ammonium citrate, are determined for the washed “Turmequé” phosphoric rock sample. (See Table 1), with the spectrophotometric method of the phosphor-molybdovanadate under the Colombian Technical Norm NTC 234.

| Table 1. Phosphorus results of the initial sample. |
|-----------------------------------------------|
| Sample | P total (%) | P assimilable (%) |
| Turmequé | 16 | 2.15 |

3. Results and discussion

3.1. Characterization

3.1.1. XRF analysis. The sieve analysis of washed and unwashed samples was carried out in order to know the elemental semiquantitative percentage retained in each mesh, besides selecting the appropriate size for the microflotation process. (See Figure 1 and Table 2). This analysis was determined by x-ray fluorescence, In the equipment Scattered Energy Fluorescence Spectrometer (Brand: PANalytical. Model: MiniPal 2). Located in the laboratory of the Institute for Research and Innovation in Materials Science and Technology (INCITEMA) of the “Universidad Pedagógica y Tecnológica de Colombia (UPTC).”

The previous Figure shown signals correspond to elements found in the phosphoric rock after having been subjected to previous washing in a ball mill.
The advantage of washing the samples is the reduction of the clay content, which will lead to an increase in the recovery of the ore of interest in the microflotation process. This is observed in the reduction of silica and aluminium content [10]. After performing the grading of the samples and conducting several tests of mineral buoyancy, it was found that the ideal size to find a higher concentration of the sample was between 140 and 200 US standard mesh.

3.1.2. XRD analysis. These analyses were performed on X-ray diffraction equipment. (Brand: PANalytical. Model: XPert-PRO), Located in the laboratory of the INCITEMA, UPTC, with the objective of knowing the mineralogical phases present in the sample. (See Figure 2 and Table 3).
Table 3. Mineralogical species of interest.

| Sample                  | Fluorapatite (%) | Quartz (%) |
|-------------------------|------------------|------------|
| Washed in the mill      | 55.4             | 44.6       |
| Washed in tray          | 52.5             | 57.5       |

3.1.3. Potential zeta. These tests were carried out on the potential equipment Z, Zetasizer, located in the Institute of minerals CIMEX, belonging to the faculty of mines of the “Universidad Nacional de Colombia, Medellín” (See Table 4).

Table 4. Potential results Z.

| Reference of the analysis sample | PZ (mV) | Average |
|----------------------------------|--------|---------|
| Turmequé, washed. pH 10          | -44.3  |         |
|                                  | -45.7  | -45.13  |
|                                  | -45.4  |         |
|                                  | -19.8  |         |
| Turmequé, without washing. pH 5,8| -20.3  | -20.26  |
|                                  | -20.7  |         |

The efficiency of this process depends on the degree of adsorption between the collector and the mineral [11]. When applying the collectors, it is observed that the zeta potential of the unwashed ore tends to values close to zero, which causes the mineral to maintain an area of instability and enable depression in the process of rock flotation. Moreover, there is no selective flotation. As a general rule, if there is to be repulsion between particles, the zeta potential value should be greater than +30mV or below -30mV [12], which suggests that washing is necessary when the flotation reagents are applied.

3.1.4. Direct floating. The following results were found for the Turmequé sample, after the direct flotation in hallimond tube (See Figure 3 and Table 5).

Figure 3. Flotation in hallimond tube.
Table 5. Results obtained with the spectrophotometer.

| Fractions | P₂O₅ Total (ppm) | P₂O₅ Total (%) |
|-----------|------------------|----------------|
| Concentrates | 13.31 | 25.0 |
| Tailings   | 7.69  | 15.3 |

The data obtained with the direct microflotation process indicate that a good part of phosphorus is recovered from the PR, making it viable for later production on a larger scale in Denver cells. It is expected to continue with reverse flotation, to clear the excess silica from the concentrate obtained.

4. Conclusions
The ideal size to find a greater performance in the phosphorus concentration was between 140 and 200 US standard mesh. Furthermore, if the samples are washed previously, either in a ball mill or in tray, the silica and aluminium content is reduced, thus contributing to a selective flotation of the mineral when applying the appropriate reagents in the process of mineral concentration.

After conducting flotation processes on phosphate rock, the total phosphorus was increased by up to 9%, from 16% to 25%. These results are attractive for future exploitation of mines with a low concentration of phosphorus, as in the case of “Turmequé, Boyacá”.

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